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Solution-Processed Photonics for Light and Heat Management

A thesis by

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Declaration of Originality

I, Stefan Bachevillier, declare that this thesis, 'Solution-Processed Photonics for Light and Heat Management' under the supervision of Professor Natalie Stingelin, Professor Paul N. Stavrinou and Doctor Andreas Hafner, and the work presented in it are my own. I confirm that:

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Abstract

Printed photonic devices have drawn increasing interest during the last decade thanks to the prospect of low-cost, high-throughput and large-area manufacturing. However, the realisation of novel solution-processed technologies requires the development of new advanced and functional materials that combine the often-superior properties of inorganics with the straightforward, low-cost fabrication features of organics. This thesis is based on a printable molecular hybrid composed of titanium oxide hydrates and the commodity polymer poly(vinyl alcohol) exhibiting high refractive index, low optical losses, pristine film quality and ease of production.

After confirmation of the structural organisation leading to these properties by optical and material characterisations, thermal patterning of the refractive index within a thin-film was found possible. This was thanks to the short time required to anneal the material, measured by time-resolved optical spectroscopy. The local change in refractive index and the versatile tunability of the hybrid allowed the straightforward fabrication of multiple coplanar refractive indices and large gradients by thermal stamping. Furthermore, a novel microcontact photo-annealing method enabled sharper patterns, crucial for advanced planar photonic structures such as light-guides for solar concentration.

The high index and excellent quality of hybrid films were then applied in multilayer photonic structures. Combined for the first time with the commodity polymer poly(methyl methacrylate), distributed Bragg reflectors were produced in close agreement with optical modellings using a transfer-matrix method. Large-area (100 cm^2) devices as well as cylindrical dielectric mirrors were fabricated through dip-coating methods.

Finally, broadband reflectors were modelled and produced by geometrical chirping of the multilayer structure. Extended reflection band of $\sim 400\text{ nm}$ was enabled across the whole visible range while still transparent to infrared. Similarly, a 81-layer chirped design was used to reflect the solar near-infrared responsible for heating within buildings. This metal-free omnidirectional heat reflector was shown to be equivalent to commercial silver-based window glazings. A brief energy analysis confirms its suitability for low-solar heat gain by blocking most of the solar radiation, both in UV and infrared, while being transparent to visible light. This, to the best knowledge of the author, is the first demonstration of a solution-processed dielectric mirror for low-solar heat gain window glazing.

Contents

List of Figures	10
List of Tables	13
List of Abbreviations	14
1 Motivation	15
1.1 References	20
2 Underlying Concepts	22
2.1 Light-Matter Interactions	22
2.1.1 Propagation of light in a medium	22
2.1.2 Light at an interface between two media	23
2.1.3 Optical interferences in thin-films	26
2.2 Solution-processable high refractive index materials	29
2.2.1 Optical properties of polymers	30
2.2.2 Polymer hybrid nanocomposites	31
2.2.3 PVAI/titanium oxide hydrate hybrid	33
2.3 Solution-processed photonic devices	38
2.3.1 Planar modulation of refractive index	39
2.3.2 Antireflection coating	41
2.3.3 Dielectric mirror	42
2.4 References	45
3 Experimental Techniques	50
3.1 PVAI/Titanium oxide hydrate hybrid synthesis	50
3.1.1 Poly(vinyl alcohol)	50
3.1.2 Titanium oxide hydrates	51
3.1.3 Hybrid formulation	53
3.1.4 Hybrid solution procedure	54

3.2	Film deposition methods	55
3.2.1	Substrates	55
3.2.2	Spin-coating	55
3.2.3	Dip-coating	56
3.2.4	Multilayer fabrication processes	58
3.3	Optical characterisation	60
3.3.1	UV-visible spectrometry	60
3.3.2	Time-resolved <i>in situ</i> UV-Visible spectrometry	62
3.3.3	Transfer-matrix method	64
3.3.4	Modelling of DBRs: effect of experimental errors	67
3.4	Structural characterisation techniques	72
3.4.1	Scanning electron microscopy	72
3.4.2	Transmission electron microscopy	72
3.4.3	Atomic Force Microscopy	74
3.5	References	75
4	Poly(vinyl alcohol)/titanium oxide hydrate hybrid	77
4.1	Nanostructural characterisation of the hybrid	77
4.1.1	A closer look inside a molecular hybrid	77
4.1.2	The nanoparticle case	84
4.2	Optical characterisation	88
4.2.1	Refractive index	88
4.2.2	A low loss material	90
4.3	A thermo-responsive material	92
4.3.1	Post-deposition tuning by annealing	93
4.3.2	Thickness / refractive index relation	95
4.4	Conclusion and Outlook	98
4.5	References	99
5	Fast thermal patterning of refractive indices	101

5.1	Background	101
5.2	Results and Discussion	103
5.2.1	<i>In situ</i> annealing of hybrid	103
5.2.2	Thermal stamping	106
5.2.3	Multiple coplanar refractive indices	108
5.2.4	Patterning by microcontact photothermal-annealing	111
5.3	Conclusions and Outlook	114
5.4	References	115
6	Solution-processed photonic reflectors	119
6.1	Background	119
6.2	Results and Discussion	121
6.2.1	A quest for low index materials	121
6.2.2	Solution-processed DBRs	124
6.2.3	Broadband metal-like reflectors	127
6.2.4	Dip-coating of photonic mirrors	131
6.2.5	Upscaling	134
6.2.6	Circular substrates	135
6.3	Conclusion and Outlook	140
6.4	References	141
7	Solar radiation management for sustainable buildings	149
7.1	Background	150
7.2	Results and Discussion	154
7.2.1	Near-IR DBRs	154
7.2.2	Design of chirped photonic coating at specific angle	156
7.2.3	Solar-control coating with low-emissivity	161
7.2.4	Solar radiation glazing factors	164
7.2.5	Energy efficiency analysis	168
7.3	Conclusion and Outlook	174

7.4	References	175
8	Summary and Outlook	177
8.1	Summary	177
8.2	Overall Outlook	179
	Appendices	182
A	Hybrid formulation details	182
B	Optical and experimental design of broadband visible reflectors	184
C	Low-emissivity NSG TECTM 15	188
D	Experimental design of broadband solar-control coating	189
E	Tables for calculations of solar radiation glazing factors	191
E.1	References	193
F	Angular transmittance of glazing	194
F.1	References	196
	Publications, Prizes, Talks & Posters	198

List of Figures

1.1	Structural colouration from thin-film interferences	17
1.2	Schematic of solar-control window glazing	19
2.1	Angular reflectance at air/glass interface for polarised light	24
2.2	Illustration of the multiple light paths in a coherent thin-film structure	27
2.3	Effect of thickness, refractive index and optical loss on transmittance spectra	28
2.4	Photographs of the structural colour of films with increasing thickness	29
2.5	Suggested chemical organisation of the PVAI/TiO _x H hybrid	36
2.6	Step-index and graded-index planar waveguide configurations	39
2.7	Examples of planar graded index structures with local index patterning	40
2.8	The phase change principles behind ARCs	42
2.9	Schematic of a DBR showing the phase changes on reflection	43
2.10	Transmittance of DBR versus number of periods	44
3.1	Chemical structures of PVAc and PVAI	51
3.2	Experimental setup of titanium oxide hydrates synthesis	52
3.3	Description of spin-coating method	56
3.4	Description of dip-coating method	57
3.5	Drying of dip-coated DBRs	59
3.6	Schematic of the integrating sphere configuration in a UV-Visible spectrometer	62
3.7	Schematic of time-resolved <i>in situ</i> spectrometry setup	63
3.8	Coherent multilayer structure and incoherent substrate for optical modelling.	65
3.9	Effect of DBR detuning on λ_0 and T_{min}	69
3.10	Optical simulation of non-ideal DBR stacks	70
3.11	Optical simulation of DBR stacks with roughness	71
4.1	Schematic of multilayer sample with a range of concentrations for TEM study	78
4.2	HRSEM cross-section of multilayer sample	79

4.3	HRTEM cross-section of hybrid films with various concentrations	81
4.4	EDS analysis of multilayer sample with various hybrid concentrations	82
4.5	Atomic fractions of Ti, O, C and Cl in hybrid films	83
4.6	EDS mapping of a range of hybrid concentrations	85
4.7	TEM micrograph of 80 vol% hybrid film and particle size analysis	86
4.8	Electron diffraction of 80 vol% hybrid particle	87
4.9	Transmittance spectra of hybrid thin-films with different concentrations	89
4.10	Wavelength-dependent refractive index curves of hybrids at room temperature	89
4.11	Roughness of a 60 vol% hybrid thin-film by AFM before and after annealing	91
4.12	Absorbance of titanium oxide hydrate, PVAI and hybrid 60 vol% solutions	92
4.13	Schematic of contraction during drying, ageing, vacuum treatment or annealing.	93
4.14	Transmittance spectra of 60 vol% hybrid before and after annealing	94
4.15	Full refractive index range accessible with the hybrid material.	95
4.16	Change in optical path length as a function of temperature	96
4.17	Absorptance study of the hybrid with temperature	97
5.1	Finite-element modelling of planar waveguide	102
5.2	Continuous change of hybrid at 20 °C min ⁻¹	105
5.3	Time-resolved hybrid change under fast heating	106
5.4	Linear patterning of hybrid by thermal stamping	107
5.5	Successive thermal stamping of a thin-film	108
5.6	Chemical structures of PVAc and PVAI	109
5.7	Fabrication of a planar waveguide with an additional coupling structure	110
5.8	Transmittance spectra and fits taken during mapping	110
5.9	μCPA process for thermal patterning	112
5.10	Refractive index patterning by μCPA	113
6.1	Chemical structures of low index polymers	122
6.2	80 vol% hybrid and CA 4.5-period DBR	123
6.3	Spin-coated green 41-layer DBR	126

6.4	Design of metal-like superlattices	128
6.5	Chirping of 1-D photonic structures	129
6.6	Reflectance of metal-like chirped reflectors	130
6.7	Dip-coated 7.5-period DBRs	132
6.8	Cross-sectional TEM of hybrid/PMMA multilayer	134
6.9	Upscaling of 10.5-period dip-coating DBRs (100 cm ²)	136
6.10	Dip-coated ARC on glass tube	137
6.11	Dip-coated broadband dielectric mirror on glass tube	139
7.1	Main spectra involved in window technologies	151
7.2	Dip-coated near-IR DBR	155
7.3	Upscaling of dip-coated near-IR DBRs	156
7.4	Structure of near-IR superlattice at 50°	159
7.5	Calculated reflectance of NIR chirped mirror at normal incidence, 25° and 50° .	160
7.6	Calculated angular reflectance of the NIR chirped mirror	161
7.7	Measured broadband near-IR superlattice reflector	162
7.8	Angular solar radiation glazing factors	167
7.9	Solar incident angle on South windows	169
7.10	Daily solar control factors for high-SHG glazings	171
7.11	Daily solar control factors for low-SHG glazings	171
7.12	Solar irradiance in London during summer solstice	173
B.1	Calculated spectra of chirped metal-like reflectors	185
B.2	Spin-coating calibration	185
C.1	T , R and SEM images of NSG TEC TM 15	188
D.1	Spin-coating calibration	189
F.1	Angular transmittance of BK7	194
F.2	Angular transmittance of high-SHG windows	195
F.3	Angular transmittance of low-SHG windows	196

List of Tables

3.1	PVAI/titanium oxide hydrate hybrid formulations	54
3.2	Design parameters of DBR at $\lambda_0 = 700$ nm	68
4.1	Cauchy parameters and Abbe's number of hybrids	90
4.2	Cauchy parameters of hybrids with annealing	94
6.1	Designed and measured parameters of spin-coated DBR at $\lambda_0 = 550$ nm	125
6.2	Designed and measured parameters of dip-coated DBR at $\lambda_0 = 525$ nm	133
6.3	Designed and measured parameters of dip-coated DBR at $\lambda_0 = 700$ nm	133
7.1	Design and measured parameters of dip-coated DBR at $\lambda_0 = 1100$ nm	155
7.2	Design parameters for solar-control chirped dielectric mirror at 50°	158
7.3	Solar radiation glazing factors of window coatings	166
B.1	Design parameters for metal-like chirped reflectors	184
B.2	Parameters used for the fabrication of silver-like reflector.	186
B.3	Parameters used for the fabrication of gold-like reflector.	187
D.1	Experimental parameters used for NIR reflector	190
E.1	Spectral distribution of solar radiation for T_{solar}	191
E.2	Spectral distribution of solar radiation for T_{UV}	192
E.3	Spectral distribution of solar radiation for $T_{visible}$	192
E.4	Spectral distribution of solar radiation for $T_{sol\ IR}$	193

List of Abbreviations

ARC	Antireflection coating
AFM	Atomic Force Microscopy
DBR	Distributed Bragg Reflector
EDS	Energy Dispersive X-ray Spectroscopy
FTO	Fluorine-doped Tin Oxide
GI	Graded Index
HAADF	High Angle Annular Dark Field
IR	Infrared
Low-e	Low-emissivity
PDMS	Poly(dimethylsiloxane)
PFP	Poly[4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole-co-tetrafluoroethylene]
PMMA	Poly(methyl methacrylate)
PVAc	Poly(vinyl acetate)
PVAI	Poly(vinyl alcohol)
SCR	Solar Control Factor
SAED	Selected Area Electron Diffraction
(HR)SEM	(High Resolution) Scanning Electron Microscopy
SHG	Solar Heat Gain
TCO	Transparent Conductive Oxide
(HRS)TEM	(High Resolution Scanning) Transmission Electron Microscopy
TiO _x H	Titanium Oxide Hydrates
TMM	Transfer-Matrix Method
TOC	Thermo-Optic Coefficient
UV	Ultraviolet
μCP	MicroContact printing
μCPA	MicroContact photothermal-annealing

1 | Motivation

Thin-films optical devices are becoming increasingly important for present day challenges. Photonics, defined as the science and technology of light ('photon') generation, transmission and manipulation, enables applications ranging from antireflection coatings (ARCs), optical filters, solar concentrators, solar cells, sensors and lasers.^{1,2} With most of them operating in the visible and near-infrared (IR) ranges, the effective management of light is possible by precise control of the media properties at a scale similar to the wavelength, *i.e.* from tenths of nanometres to a few microns. Consequently, the following aspects are essential to enable efficient light engineering:

1. **Materials:** the complex refractive index, the overall cost, the versatility and the processability of the materials are probably the most critical parameters to consider here. With large-area and high-throughput manufacturing as the underlying motive of this thesis, solution-processing is expected. Low-optical losses and a high index of refraction are also required.³⁻⁷
2. **Optical design:** to manipulate light effectively, advanced structures must be designed adequately. For example, by tuning the optical path length of the layers, multilayer coatings could become either antireflective or highly reflective. Furthermore, thin-films made of the same materials can be tailored and arranged in specific ways to satisfy the needs of a wide range of applications.^{3,5,8}
3. **Fabrication:** the quality of the coatings is fundamental for efficient devices. It encompasses the properties of the materials and structural aspects after deposition such as thickness and roughness. Since photonic structures are extremely sensitive to defects down to the nanometre size, high precision processing must be utilised.^{3,5,8}

The high-quality fabrication and exceptional range of properties given by inorganics are the primary reasons for their use in photonics. Nevertheless, the field can greatly benefit from the recent advances in novel organic and hybrid materials, and thus, avoid the typical drawbacks associated with inorganics. For instance, they can be efficiently processed at low-temperature and without vacuum while their counterparts generally require energy and capital intensive deposition techniques. Nanocomposites are particularly interesting since they can merge unique optical properties with the strong chemical and mechanical resistance associated with their inorganic moieties to the tunability, flexibility, chemical functionalisation and low-cost that organics have to offer.^{3,5-7,9-11} The key enabling technology in this thesis is a high refractive index molecular hybrid composed of titanium oxide hydrates (TiOxH) and the bulk commodity polymer poly(vinyl alcohol) (PVAI).^{12,13} The simplicity of the formulations, allied with the versatility of its properties (discussed in Chapters 3 and 4), make it likely scalable and widely applicable to large-area coatings.

In this regards, confinement and guiding, accessed by total internal reflection between different media, *e.g.* core and cladding components in optical fibres, could drive considerable advances in several fields such as solar concentrators and lighting. Also leading to planar optical integrated circuits and holographic data storage. More specifically, the local change of high refraction index in thin-films is strongly desired to create planar waveguides.¹⁴⁻¹⁶ Typically challenging, the development of more accessible and straightforward material systems and fabrication techniques will undoubtedly benefit the research community. Therefore, it is believed that the tunability of inorganic/organic hybrids, like the one mentioned above, can offer suitable solutions. Chapter 5 builds on the work described in the master thesis by S. Bachevillier.¹⁷

Another relevant research field of photonics lies in the study of *Photonic Crystals* where materials with different refractive indices are assembled in highly ordered structures following a specific periodicity. When the characteristic dimensions of the architecture are similar to the wavelength, the behaviour of light starts to be dominated by interference effects. Commonly observed with the iridescent appearance of soap bubbles and oil puddles, interferences have the ability to modulate the light propagation and, therefore, the physical aspect of objects (Figure 1.1.a). For instance, when two waves of equal amplitude interfere, they can add-up or cancel each others depending on whether they are in or out-of-phase, respectively.⁸

THIN-FILM STRUCTURAL COLOURATION

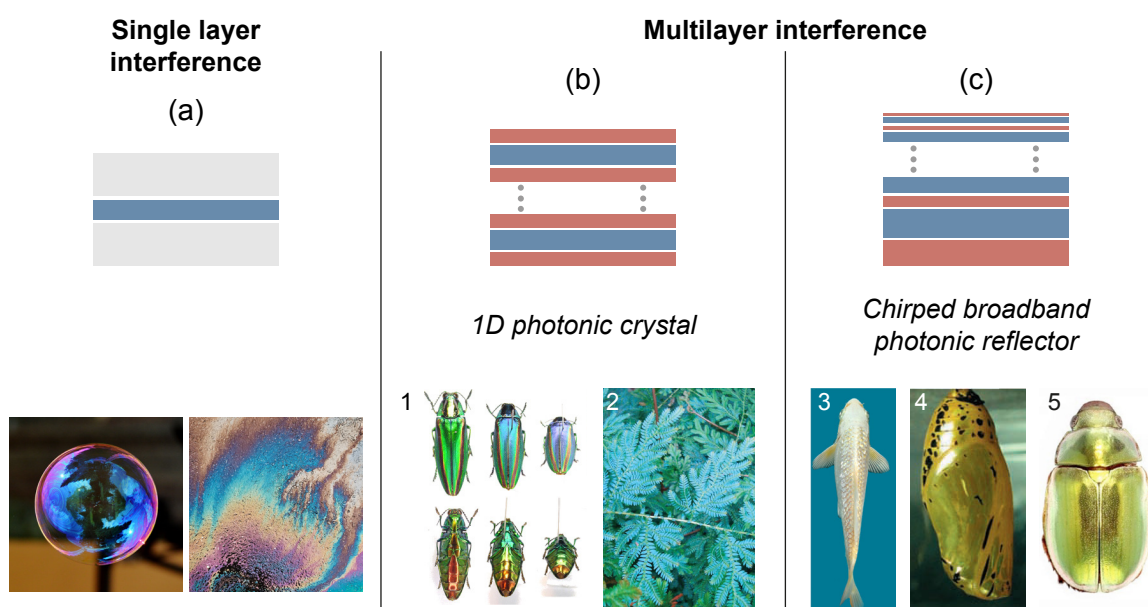


Figure 1.1: Structural colouration from thin-film interferences. (a) Single layer interference are commonly observed in soap bubbles and oil puddles. (b) Regular one-dimensional photonic crystals occur in Nature resulting in bright colours as shown in b.1 and b.2. (c) Chirping of the layer thicknesses creates broadband reflection giving silver and gold appearances. Few examples are shown in c.3, c.4 and c.5. 1 - Dorsal and ventral views of the Japanese jewel beetle, *Chrysochroa fulgidissima*, at various viewing angles. Reprinted with permission from Kinoshita et al.¹⁸ Copyright 2005 John Wiley and Sons. 2 - Photograph of tropical blue iridescence plant *S. willdenowii*. Adapted with permission from Thomas et al.¹⁹ Copyright 2010 The Royal Society. 3 - The Japanese *Gin Rin Platinum Ogon Koi* fish. Adapted with permission from Gur et al.²⁰ Copyright 2014 American Chemical Society. 4 - Pupa of a tree nymph, *Idea leuconoe*. Reprinted with permission from Kinoshita et al.¹⁸ Copyright 2005 John Wiley and Sons. 5 - The golden beetle *Plusiotis resplendens*. Reprinted with permission from Karthaus et al.²¹ Copyright 2012 Taylor & Francis.

Optical multilayer structures often occur in Nature, as reported by Hooke in his 1665 book *Micrographia*.²² In the specific case of an one-dimensional photonic crystal, also called dielectric mirror, distributed Bragg reflector (DBR) or dichroic mirror, multiple thin-films of alternating high and low refractive indices are stacked (Figure 1.1.b). The optical path length of each layer is designed to produce destructive interferences in transmission, *i.e.* constructive interferences in reflection, within a delimited wavelength regime, referred to as a photonic band-gap.^{23,24}

The structural colouration from dielectric mirrors is usually more intense than dyeing as shown in Figure 1.1.b. The reflection is wavelength-specific, can be tuned, and close to 100 % with minimal loss, making them essential in lasers for example. Respectively, printable DBRs have a significant role to play for many applications such as semi-transparent solar cells, flexible organic lasers along with chemical, biological and thermal sensors. Nevertheless, common obstacles include the limited choice of materials and the quality of fabrication, impacting the optical response and hindering the progress in advanced structural designs. Once again, polymer/inorganic hybrids appear as strong candidates thanks to their high refractive index and good processability. As a result, dielectric mirrors based on PVAI/TiO_xH hybrids are explored in Chapter 6.

Advanced optical designs would also strongly benefit from solution-processability. In particular, chirped architectures are known for broadband and omnidirectional reflectance, as it can be observed in Figure 1.1.c. Although attractive for many other uses, the control of infrared radiation is one possible application often mentioned. With the potential low-cost and scalable manufacturing, these complex structures could be applied on windows to limit solar heating. Considering the significant environmental impact of building thermal efficiency and that 50 % of solar radiation energy is emitted in the near-IR, Chapter 7 investigates the design, fabrication and energy impact of advanced photonic coatings for window glazings, as shown in Figure 1.2.

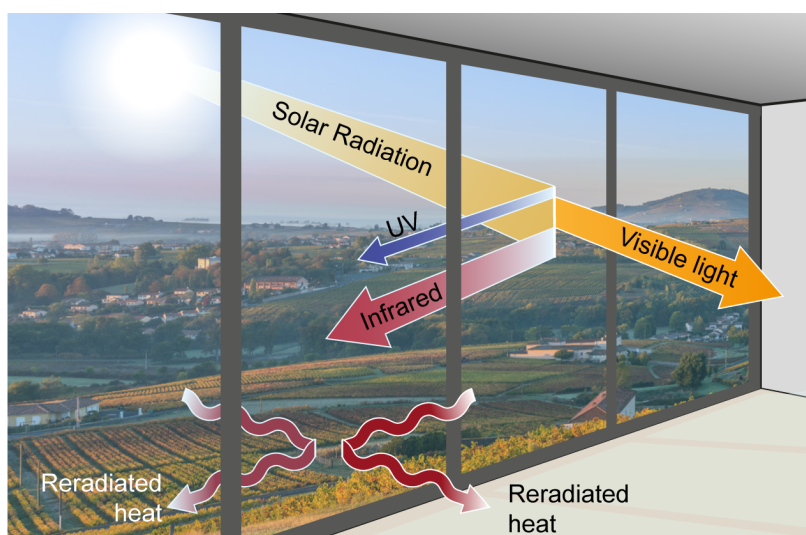


Figure 1.2: Schematic of solar-control window glazing where UV and solar near-IR radiations are reflected outside and visible light transmitted inside the room. This could potentially be achieved using broadband IR chirped dielectric mirrors. The coating should also be opaque to longer infrared radiation for better thermal insulation.

1.1 References

1. Soref, R. The Past, Present, and Future of Silicon Photonics. *IEEE Journal of Selected Topics in Quantum Electronics* **12**, 1678–1687 (2006).
2. Saleh, B. E., Teich, M. C. & Saleh, B. E. *Fundamentals of Photonics* (Wiley New York, 1991).
3. Lü, C. & Yang, B. High Refractive Index Organic–Inorganic Nanocomposites: Design, Synthesis and Application. *Journal of Materials Chemistry* **19**, 2884 (2009).
4. Biron, M. High Refractive Index Polymers. *Popular Plastics & Packaging* **55**, 49–53 (2010).
5. Cheng, Y., Lu, C. & Yang, B. A Review on High Refractive Index Nanocomposites for Optical Applications. *Recent Patents on Materials Science* **4**, 15–27 (2011).
6. Bettotti, P. Hybrid Materials for Integrated Photonics. *Advances in Optics* **2014**, 891395 (2014).
7. Zvonkina, I. & Soucek, M. Inorganic–Organic Hybrid Coatings: Common and New Approaches. *Current Opinion in Chemical Engineering. Biological Engineering / Material Engineering* **11**, 123–127 (2016).
8. Macleod, H. A. *Thin-Film Optical Filters, Third Edition* 682 pp. (CRC Press, 2001).
9. Hanemann, T. & Szabó, D. V. Polymer-Nanoparticle Composites: From Synthesis to Modern Applications. *Materials* **3**, 3468–3517 (2010).
10. Judeinstein, P. & Sanchez, C. Hybrid Organic–Inorganic Materials: A Land of Multidisciplinarity. *Journal of Materials Chemistry* **6**, 511–525 (1996).
11. Caseri, W. R. Nanocomposites of Polymers and Inorganic Particles: Preparation, Structure and Properties. *Materials Science and Technology* **22**, 807–817 (2006).
12. Russo, M., Rigby, S. E. J., Caseri, W. & Stingelin, N. Versatile Chromism of Titanium Oxide Hydrate/Poly(Vinyl Alcohol) Hybrid Systems. *Advanced Materials* **24**, 3015–3019 (2012).
13. Russo, M., Campoy-Quiles, M., Lacharmoise, P., Ferenczi, T. A. M., Garriga, M., Caseri, W. R. & Stingelin, N. One-Pot Synthesis of Polymer/Inorganic Hybrids: Toward Readily Accessible, Low-Loss, and Highly Tunable Refractive Index Materials and Patterns. *Journal of Polymer Science Part B: Polymer Physics* **50**, 65–74 (2012).
14. Salameh, H. A. B. & Irshid, M. I. Wavelength-Division Demultiplexing Using Graded-Index Planar Structures. *Journal of Lightwave Technology* **24**, 2401–2408 (2006).

15. Del Monte, F., Martínez, O., Rodrigo, J. A., Calvo, M. L. & Cheben, P. A Volume Holographic Sol-Gel Material with Large Enhancement of Dynamic Range by Incorporation of High Refractive Index Species. *Advanced Materials* **18**, 2014–2017 (2006).
16. Mao, X., Lin, S.-C. S., Lapsley, M. I., Shi, J., Juluri, B. K. & Huang, T. J. Tunable Liquid Gradient Refractive Index Lens with Two Degrees of Freedom. *Lab on a Chip* **9**, 2050–2058 (2009).
17. Bachevillier, S. *Tunable High Refractive Index Hybrid for Solution-Processed Light Management Devices: Time-Resolved Annealing Study by in Situ Spectroscopy* M.Res (Imperial College London, 2015).
18. Kinoshita, S. & Yoshioka, S. Structural Colors in Nature: The Role of Regularity and Irregularity in the Structure. *ChemPhysChem* **6**, 1442–1459 (2005).
19. Thomas, K. R., Kolle, M., Whitney, H. M., Glover, B. J. & Steiner, U. Function of Blue Iridescence in Tropical Understorey Plants. *Journal of The Royal Society Interface* **7**, 1699–1707 (2010).
20. Gur, D., Leshem, B., Oron, D., Weiner, S. & Addadi, L. The Structural Basis for Enhanced Silver Reflectance in Koi Fish Scale and Skin. *Journal of the American Chemical Society* **136**, 17236–17242 (2014).
21. Karthaus, O. *Biomimetics in Photonics* 277 pp. (CRC Press, 2012).
22. Hooke, R. *Micrographia* (Allestry, 1965).
23. Krauss, T. F. & De La Rue, R. M. Photonic Crystals in the Optical Regime — Past, Present and Future. *Progress in Quantum Electronics* **23**, 51–96 (1999).
24. Yablonovitch, E. Inhibited Spontaneous Emission in Solid-State Physics and Electronics. *Physical Review Letters* **58**, 2059–2062 (1987).

2 | Underlying Concepts

The study of integrated optics from solution-processed hybrid systems requires the understanding of light-matter interactions but also the materials science of printed high refractive index structures. Therefore, both fields are discussed in this chapter, followed by the concepts behind the relevant devices of this thesis such as planar waveguides and multilayer photonic crystals.

2.1 Light-Matter Interactions

2.1.1 Propagation of light in a medium

Light can be described either as a stream of particles so-called photons or as an electromagnetic wave widely studied by James Clerk Maxwell (1831-1879). The second definition is particularly appropriate for the scope of this thesis. In this case, the propagation of the electric field can be expressed as:¹

$$\mathbf{E} = \mathcal{E} \exp^{i[\omega t - (2\pi N/\lambda)x]} \quad (2.1)$$

where $\mathcal{E}$ is the vector amplitude of a wave propagating along the x -axis with a wavelength λ and the angular frequency ω . N is defined as the complex refractive index and can be written:

$$N = n - ik \quad (2.2)$$

The real part n is often simply called the refractive index while the imaginary part k is the extinction coefficient. n is also defined with the speed of light in a dielectric medium such as $n = c/v$ where c and v are speeds of propagation in vacuum and the medium, respectively. On the other hand, k is a measure of absorption in the medium. The amplitude of the wave falls to

$1/e$ of its initial value after propagating for a distance of $\lambda/(2\pi k)$. This distance is also known as the absorption coefficient α (in cm^{-1}).

Therefore, Equation 2.1 can be restated as:

$$E = \mathcal{E} \exp^{-\alpha x} \exp^{i[\omega t - (2\pi n/\lambda)x]} \quad (2.3)$$

where amplitude $\mathcal{E} = |\mathcal{E}|$.

The second exponent of Equation 2.3 is representative of the change in phase of the wave having travelled a distance x in the medium. In interference-based structures as discussed later, the phase is generally the most meaningful parameter to consider, hence, the critical control over the refractive index for the study of photonic structure.

2.1.2 Light at an interface between two media

Dielectric media having different chemical compositions or morphologies result in two distinct refractive indices. When both materials are in contact, this difference plays a significant role in the behaviour of light, especially for optical components and thin-film optics where boundaries are often dominant. A plane wave which reaches a medium discontinuity is partly transmitted and partly reflected. Both transmission and reflection can either be specular, diffuse or a combination of both, depending on the roughness of the surface. Furthermore, the intensity of the transmitted and reflected waves depends on the polarisation of the incoming light when at oblique incidence, the electric field being parallel to the plane of incidence for the s -polarisation (indexed $\parallel$) or perpendicular to the plane of incidence for the p -polarisation (indexed $\perp$).

Equations 2.4 and 2.5 present the reflection and transmission coefficients, so-called Fresnel equations, as a function of refractive indices n and angles of light θ in each medium:²

$$r_{\perp} = \frac{n_i \cos \theta_i - n_t \cos \theta_t}{n_i \cos \theta_i + n_t \cos \theta_t} \quad r_{\parallel} = \frac{n_i \cos \theta_t - n_t \cos \theta_i}{n_i \cos \theta_t + n_t \cos \theta_i} \quad (2.4)$$

$$t_{\perp} = \frac{2n_i \cos \theta_i}{n_i \cos \theta_i + n_t \cos \theta_t} \quad t_{\parallel} = \frac{2n_i \cos \theta_i}{n_i \cos \theta_t + n_t \cos \theta_i} \quad (2.5)$$

Reflectance R , the ratio of reflected power to the incident power, and the transmittance T , the ratio of transmitted power to the incident power, can be calculated from the Fresnel's coefficients using the following equations where t and r could be for either polarisations:

$$R = r^2 \quad T = \frac{n_t \cos \theta_t}{n_i \cos \theta_i} t^2 \quad (2.6)$$

From these equations, the reflectance and transmittance at interfaces can be calculated as a function of the incident angle for s - and p -polarisations at the air/glass interface, as shown in Figure 2.1. The Brewster's angle displayed by the dotted line corresponds to the specific angle at which the light is not reflected for the p -polarisation.

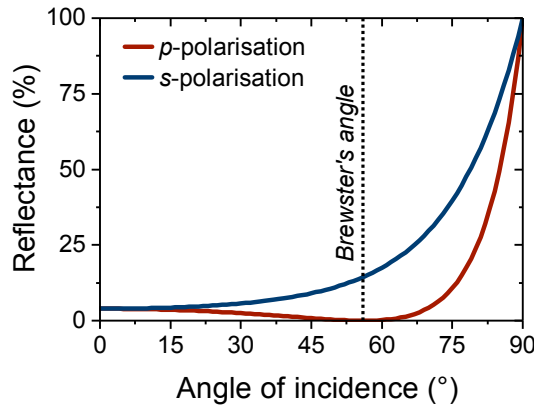


Figure 2.1: Calculated angular reflectance at the air/glass interface for polarised light. Black dotted line represents the Brewster's angle where p -polarisation reflectance is minimum.

In the particular case of normal incidence, reflectance and transmittance are independent of the polarisation. Equations reduce to:

$$R = \left(\frac{n_i - n_t}{n_i + n_t} \right)^2 \quad T = \frac{4n_i n_t}{(n_i + n_t)^2} \quad (2.7)$$

It is noteworthy to mention that there is no phase change between the incident and transmitted waves. The same happens for reflection when $n_i > n_t$, however, if $n_i < n_t$ a phase change of π occurs.²

Using Equations 2.7, in agreement with the law of conservation of energy we have:

$$T = 1 - R \quad (2.8)$$

While extinction coefficient k and the absorption coefficient α have been discussed above, it is essential to precisely defined the often confusing and misused terms *absorptance* and *absorbance*. Similarly to transmittance and reflectance, absorptance is a ratio of the absorbed irradiance to the incident irradiance, *i.e.* a fraction of intensities. Thus, similarly to Equation 2.8, Equation 2.9 can be written when optical losses must be considered.

$$1 = T + R + A \quad (2.9)$$

where A is the absorptance.

On the other hand, the absorbance is calculated from the transmittance only using the Beer-Lambert-Bouguer law (Equation 2.10). To account for the solvent or the substrate absorbance, it is common to replace the transmittance by the ratio of the reference to the sample transmittance.

$$Absorbance = -\log_{10} T \quad (2.10)$$

The main drawback of this relation is that it does not measure the real absorption (the physical mechanism of absorbing photon) but only the light attenuation. In this case, there is no differentiation between losses by absorption, reflection or scattering amongst other things. This is particularly inappropriate for the characterisation of optical thin-films where reflectance can be high due to interferences as explained in the next part. As a result, mainly absorptance will be used in this thesis.

2.1.3 Optical interferences in thin-films

The discussion in the previous part allows the prediction of optical response from a substrate thanks to the Fresnel equations. When the optical thickness of the medium is much larger than the coherence length of the light source, the variation in phase prevents waves to interfere. Moreover, the thickness variation of a substrate, for example, are most likely too large to induce coherent interference effect. This is referred to as an incoherent medium. However, when the film thickness is in a similar range as the wavelength, it is considered as the coherent regime and interferences should be weighed.

Figure 2.2 shows a system with two boundaries creating a coherent layer of refractive index n_1 and thickness d . The phase shift δ of a wave travelling through this thin-film is expressed by:

$$\delta = 2\pi n_1 d \cos\theta / \lambda \quad (2.11)$$

where θ is the angle of incidence of the wave, thus, $\cos\theta = 1$ at normal incidence.

Incident light bouncing in the thin-film results in multiple transmitted and reflected waves at each interface. For a given optical thickness, transmitted waves are out-of-phase while reflected waves are in-phase at particular wavelengths and *vice versa*. Therefore, the transmitted and reflected intensities are oscillating between these specific wavelengths; they are called Fabry-Pérot oscillations. In the particular case where reflected waves are out-of-phase, they do not carry energy, and so, in the absence of absorption, all the energy is transmitted. The film does not affect light any more resulting in an overall transmittance equal to the one of the substrate alone, given by Equation 2.7. This is observable in Figure 2.3.

The effect of a thin-film on the transmittance and reflectance is relatively easy to measure by UV-vis spectroscopy (part 3.3) and carries several characteristics such as index of refraction, thickness and optical losses. On the top panel of Figure 2.3, transmittance spectra of two films with indices of $n = 1.8$ and $n = 2$ are plotted. The depth of the oscillations is directly related to these indices, independently of the thickness.

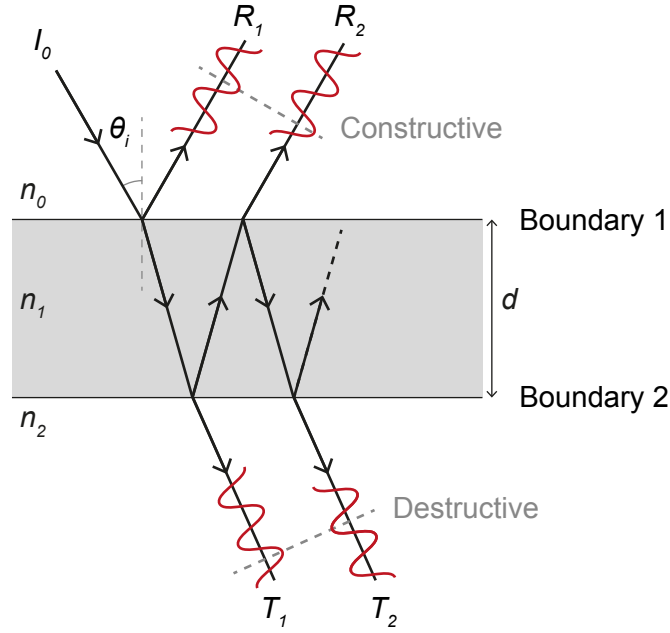


Figure 2.2: Illustration of the multiple light paths in a coherent thin-film structure ($d \approx \lambda$). In this particular case, reflected waves are in-phase and transmitted waves are out-of-phase, maximising the reflectance. Each side is, in reality, an infinite sum of waves.

The free spectral range is the spacing between two successive transmittance (or reflectance) maxima. For a single material (same n), it will only vary with the thickness. The thicker the film, the smaller the free spectral range and the more oscillations are visible within a given wavelength range (Figure 2.3, middle panel).

Finally, Fabry-Pérot oscillations also give an indication of the optical loss of the film. A measurement of a non-uniform layer would average signals from regions with different optical thicknesses, flattening oscillations as well as displacing maxima away from the substrate transmittance. Similarly, since scattering would shift the oscillations down, the optical quality of the material and interfaces can be followed.

The optical effect from coherent structures is often observed in Nature with for example the colour of soap bubbles, oil stains on the floor or when two flat pieces of glass are against each other (see Figure 1.1). This phenomenon is commonly referred to as iridescence and structural colour. Colouration can indeed be observed even from entirely transparent material thin-films

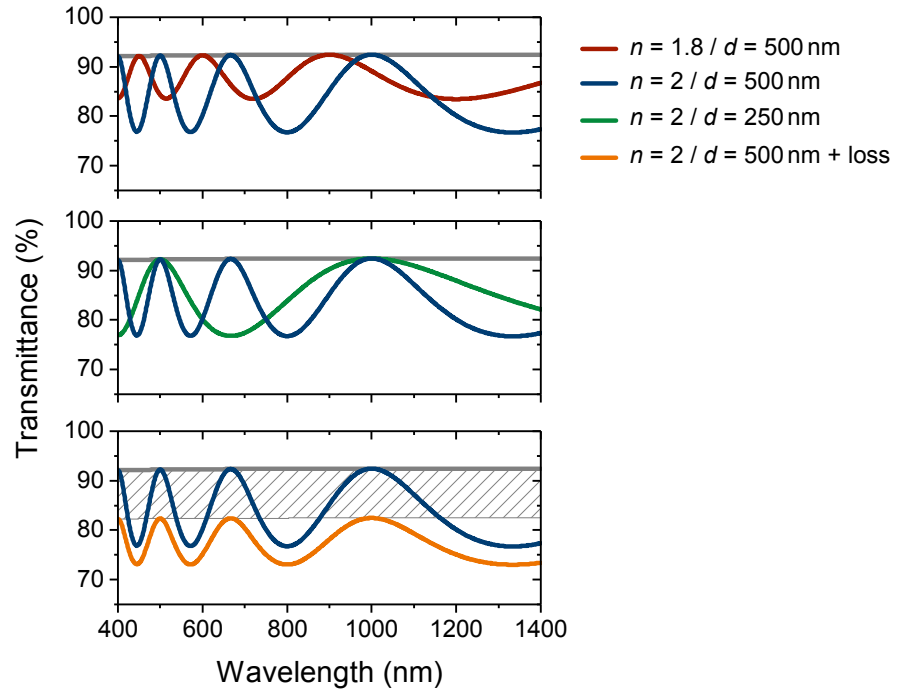


Figure 2.3: Effect of thickness, refractive index and optical loss on transmittance spectra of thin-films on glass calculated by TMM. Top panel compares a material of refractive index $n = 2$ with one of $n = 1.8$ with the same thicknesses, resulting in different Fabry-Pérot oscillation depths. In the middle panel, the free spectral range changes with the thickness of the films when they have similar index of refraction. Fabry-Pérot oscillations also give an insight on the optical losses when maxima are displaced from the substrate transmittance and flattened (bottom panel).

due to the oscillatory nature of transmittance and reflectance. An example is shown in Figure 2.4 where the hybrid material, discussed later on, was dip-coated at different speeds, producing a gradient of thickness and therefore a continuous change in colour.

Fabry-Pérot oscillations constitute the basis of the optical characterisation throughout this thesis. Total transmittance and reflectance can be calculated by combining Fresnel Equations 2.7 for incoherent substrate and transfer-matrix method (TMM) for coherent thin-films (described in part 3.3.3). In the case of non-absorbing and non-scattering coating, refractive index and thickness can be extracted by fitting measured spectrum by modelled one. This method will be extensively used in the following chapters.

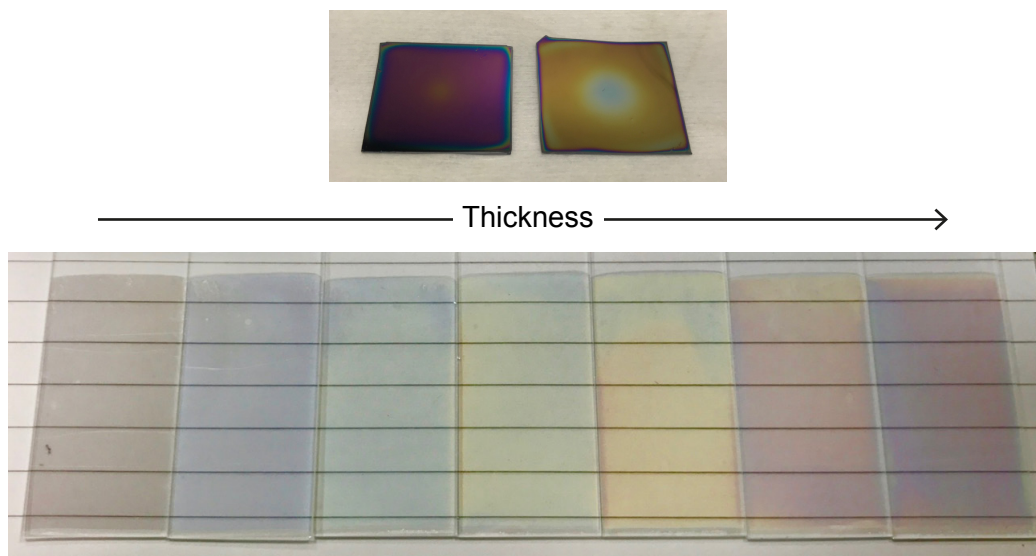


Figure 2.4: Photographs of PVAI/titanium oxide hydrate hybrid films with increasing thickness and continuous change in colour. Top images are spin-coated films on silicon substrates. Bottom images are dip-coated hybrid films with speeds increasing by 5 mm min^{-1} between each sample, producing thicker and thicker films.

2.2 Solution-processable high refractive index materials

Optical materials can interact with electromagnetic waves in various ways such as refract, diffract, reflect, transmit, polarise and diffuse light. They are used in all type of optical components and are usually compatible for a specific range of wavelengths. For interference-based applications, distinctive features for good optical materials are low absorption and scattering. In addition, the index of refraction alters the propagation of light through a medium, modulating the optical length. Therefore, its manipulation is crucial for the development of advanced optical structures and has motivated an important research field.

Several applications would directly benefit from solution-processed materials in order to simplify the fabrication process, target large-area manufacturing, potentially reduce cost and enable the use of flexible plastic substrate. In the following section, concepts behind the control of refractive index in printable materials will be discussed.

2.2.1 Optical properties of polymers

Both low and high refractive indices are required for optical applications, and much effort has been put to push both limits using solution-processed materials. It is essential to understand the basis of light interactions with matter at an atomic scale to enable the tuning of the refractive index. Electronic clouds of atoms act as scatterers for electromagnetic radiations resulting in a redistribution of the energy. Waves interfere constructively only in the forward direction called wavefront. This results in a change of the propagation direction, also known as refraction phenomenon. Moreover, atoms reduce the propagation velocity of light in the medium, responsible for the refractive index n . This is the reason why it directly depends on the chemical composition of the medium.

The introduction of highly polarisable bonds and denser molecular packing slows down the electromagnetic waves, *i.e.* increases the index.^{1,3} The Lorentz-Lorenz Equation 2.12 was developed to predict the refractive index as a function of the chemical composition:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\Gamma}{M} \times \frac{M}{V} = \frac{R_M}{V_M} \quad (2.12)$$

$$n = \sqrt{\frac{1 + 2(R_M/V_M)}{1 - (R_M/V_M)}} \quad (2.13)$$

where Γ the molecular refraction, M the molecular weight and V the volume of the polymer repeating unit. It can also be expressed as a function of molar refraction R_M and molar volume V_M . R_M can be calculated from the molar refraction of each substructure. According to Equation 2.13, the refractive index increases with the introduction of high molar refraction constituents in the repeating unit.⁴ As a consequence, the primary strategy in high index polymer chemistry is to combine the best chemical groups to achieve the higher indices with low absorption and excellent processability.^{3,5-8}

Besides refractive index, Abbe's number is another important characteristic of optical materials. Also called ν -number, it outlines the optical dispersion, in other words, the wavelength dependence of the refractive index $n(\lambda)$. It is defined as:⁹

$$\nu_D = \frac{n_D - 1}{n_F - n_C} \quad (2.14)$$

where n_D , n_F and n_C are the refractive indices of the material at the wavelengths of the Fraunhofer spectral lines D- (589.3 nm), F- (486.1 nm) and C- (656.3 nm).

A large Abbe's number demonstrates a low dispersion medium, the trend-off being that higher index implies lower ν_D .⁴ In general, optical polymers have values between 30 and 60. Only a few sulphur-containing polymers managed to combine both so far with $1.5 < n < 1.7$ and $\nu_D > 35$.⁸

Nevertheless, highly transparent and high refractive index polymers are still limited to $n < 1.8$.¹⁰ Along with significant optical dispersion, they often suffer from absorption which restrains their application. Moreover, highly refractive constituents can sometimes complicate the processability of the polymer.

2.2.2 Polymer hybrid nanocomposites

To overcome the limitation in refractive index, another strategy emerged by combining inorganic and organic phases. Hybrid coatings have seen increasing interest from the 1980s with the development of ormocers, mainly organosilanes. They are part of the ceramer group, which was defined by 'ceramic' and 'polymer' and are based on sol-gel chemistry.^{11,12} Another category of hybrid materials is based on the direct use of polymers. These materials have the advantage of polymers such as low weight, flexibility, impact resistance and superior processability with the high refractive index, thermal stability and chemical resistance of inorganics.¹³ The exceptional physical and chemical properties of polymer composites have recently grown

interest in many research fields such as optics, magnetism, microelectronics, sensors, batteries, organic solar cells and biomedical science.¹⁴

The nanoscience and the soft inorganic chemistry processes are active research topics which help the improvement of these optical hybrids.⁵ Especially, the interactions taking place at the interface between each constituent are crucial. They can be either weak or physical bonds like Van-der-Waals, ionic and hydrogen bonds or strong covalent bonds.¹⁵ The stabilisation and good spatial dispersion of the inorganic species are important for low optical losses. Moreover, the index mismatch between inorganic domains and the organic matrix reduces the transparency of nanocomposites. Consequently, the transparency loss (T_{loss}) is a function of the particle radius (r), inorganic particle volume fraction (Φ_p), the refractive index of particles n_p and polymer matrix n_m in the Rayleigh scattering formula (Equation 2.15) for free-standing film and without taking into account interference effect:

$$T_{loss}(\lambda) = \frac{I}{I_0} = \exp \left(-\frac{32\Phi_p x \pi^4 r^3 n_m^4}{\lambda^4} \left[\frac{(n_p/n_m)^2 - 1}{(n_p/n_m)^2 + 2} \right]^2 \right) \quad (2.15)$$

where I and I_0 are the intensity of incident and transmitted light, x the optical path length and λ the wavelength of light.

Furthermore, the change in refractive index in hybrid materials depends on the amount of filler introduced into the matrix as well as the refractive index of each component. It seems to be linearly related on the volume content of inorganics in most of the cases, except for semiconductors with which the Bohr radius has to be considered.^{16–18} Consequently, many efforts have been put in high content nanocomposites. In this situation, the only way to reduce scattering is to have either no particles or of minimal diameter. Nanoparticles create optical loss when inorganic domains are larger the one-tenth of the visible wavelength (< 40 nm). Aggregation of nanoparticles must be imperatively avoided because even a tiny amount of large inorganic domains can be responsible for severe scattering. Thus, their initial size is usually limited to 10 nm.¹⁹ Finally, loss of processability can be another problem induced by high concentration in inorganic compounds.

Metal oxides such as TiO_2 , ZrO_2 , CeO_2 , ZnO , etc. have been widely used as building blocks.^{20–22} Ultra high index metal sulfides and semiconducting nanoparticles (ZnS , PbS) were also introduced in polymers reaching outstanding refractive indices up to 3.9.^{23,24} However, they often suffer from absorption in the visible or poor interactions at the organic-inorganic interface. Extensive reviews of high refractive index nanocomposites and hybrids can be found in the literature.^{12,13,18,19,25,26}

Among them, TiO_2 is particularly attractive thanks to its simple preparation.^{21,27–29} It exists in three different crystal forms: rutile, anatase and brookite. The first one is the thermodynamically stable polymorph while the others are kinetic products. They require heat treatment around 700 - 900 °C to convert to rutile phase.³⁰ Thanks to a denser structure, rutile also exhibits a higher refractive index around 2.7 compared to 2.55 for anatase.^{31,32}

The synthesis of hybrid materials has been performed by various methods. The formation of nanoparticles can be done before or after being blended with a polymer, corresponding to the *ex situ* and *in situ* techniques, respectively. The four principal categories being: i) the sol-gel method where both inorganic and organic polymers are formed at the same time *in situ*, ii) the *in situ* formation of particles in a polymer matrix, iii) the blending technique where particles are formed *ex situ* then added to a polymer and iv) the blending method where pre-formed particles are, this time, mixed with monomers followed by an *in situ* polymerisation of the matrix. Each route has its advantages and drawbacks, however, the two first ones seem more suitable for excellent control over the inorganic domain size and spatial dispersion.

2.2.3 PVAI/titanium oxide hydrate hybrid

The introduction of inorganic precursors inside a polymer solution has been one of the most successful methods to control the size of the high refractive index domains. Specific polymers can directly interact with the precursors and play a role of stabiliser. For example, Russo et al. reported on the blocking effect of hydroxyl groups of glycerol on hydrolysed titanium species.³³ High refractive index poly(vinyl alcohol)/titanium oxide hydrate (PVAI/ TiOxH) hybrids (Fig-

ure 2.5) have emerged from that study and will be discussed in details here.^{34,35} Along with outstanding material properties, the synthesis is relatively simple leading to high reproducibility. Experimental details will be described in the following chapter.

A sol-gel approach

As mentioned previously, sol-gel chemistry is a conventional method for the production of solution-processed materials which could be either oxide or hybrid systems. The two main steps are the hydrolysis of a metallic precursor, typically metal alkoxides, and the condensation in oxide. During the hydrolysis, side groups are replaced by hydroxyl groups forming the metal hydroxide solution. The condensation consists in the formation of metal-oxygen-metal bridges with the release of water or alcohol molecules. Sol-gel process can be performed under various pH leading to different material properties. Basic environment favours a rapid condensation ideal for the production of nanoparticles while acidic solutions slow down the gelation which is more suitable for extended networks.³⁶ The use of metal halides tremendously increases the speed of reaction, hence chemical additive are commonly used to stabilise precursors. Often the hydrolysis, condensation and drying happen at the same time making difficult the control of the nanoparticle morphology. The sol-gel method is always followed by a drying step to remove the remaining solvent during when a substantial shrinkage and densification usually occur. Finally, a thermal treatment is also required to improved mechanical properties by inducing further condensation reactions.^{37,38}

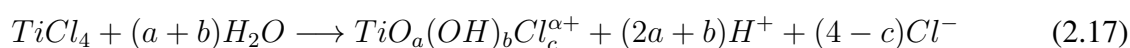
Hydrolysis of $TiCl_4$

In the case of the PVAI/TiOxH hybrid, titanium tetrachloride $TiCl_4$ is used as a precursor. Because of its halide nature, the hydrolysis is extremely fast and exothermic producing hydrochloric acid HCl as a by-product:



The solution is previously cooled down around 0 °C and kept at this temperature during the slow addition of $TiCl_4$. More experimental details can be found in part 3.1. Due to the release

of HCl, the solution exhibits a $\text{pH} < 0.5$.³³ In this acidic environment, the hydrolysis leads to mononuclear complexes described in Equation 2.17 which do not condense in oligomers and polymeric species as long as the temperature is kept low.³⁹ The description of so-called titanium oxide hydrates is complicated and often led to many different formulae.³³ Nevertheless, Nussbaumer et al. reported a more realistic hydrolysis equation than Equation 2.16:³⁹



with $\alpha = 4 - 2a - b - c$.

This process seems to be irreversible which confirms that most of the chlorine atoms are hydrolysed. Thus, titanium oxide hydrates are also referred by $(\text{Ti}_n\text{O}_x(\text{OH})_y)$ formulae. These species contain water molecules which coordinate with titanium ions. Such molecules are usually released upon ageing during the condensation step for the formation of titanium oxide.

Stabilisation by PVAI

The hybrid proposed by Russo et al. used in this thesis is based on functional interactions between the inorganics TiOxH and its organic counterpart PVAI. The incorporation of the titanium hydrated precursors to a water-based polymer solution is a similar approach to the *in situ* formation of nanoparticles in a polymer matrix mentioned above for nanocomposites. The difference here is that the alcohol groups of the polymer can directly interact with the mononuclear TiOxH species by hydrogen bonds. This step is critical by stabilising the inorganic complexes apart and avoiding condensation reactions during water removal. Therefore, the hybrid does not entirely follow the sol-gel method and results in complete inhibition of the titanium oxide formation.

Drying, ageing and annealing

A total absence of particles was achievable in previous studies.^{34,35,40} Further investigations of the molecular dispersion are discussed in Chapter 4 where very high titanium contents for nanocomposite hybrids are formulated. A suggested new chemical schematic of the hybrid after drying and annealing is shown in Figure 2.5. Hydrogen interactions between alcohol groups and

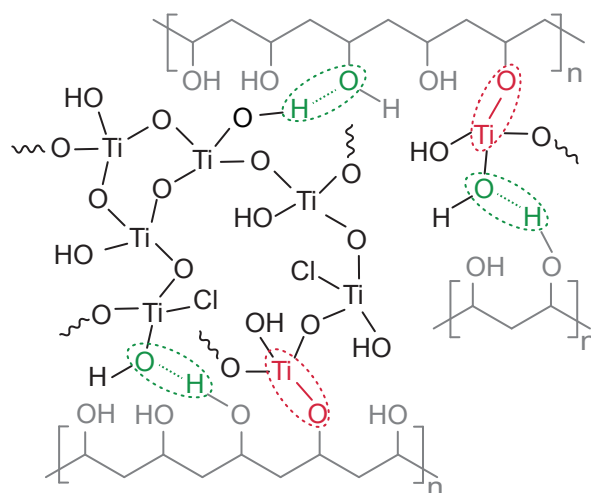


Figure 2.5: Suggested chemical organisation of the PVAI/TiOxH hybrid. Both mono (right side) and polynuclear (left side) titanium species are represented. Hydrogen bondings (in green) and covalent bondings (in red) indicate the excellent functional interactions between inorganics and polymer chains.

titanium species are shown in green while some covalent bonds are drawn in red. The complete loss in water solubility after drying confirms strong physical and chemical interactions in the hybrid.

For high inorganics volume percentage, polynuclear species are believed to form during the drying of the film since not enough organic polymer is present in the system. However, they do not result in large nanoparticles, except for the extremely high concentration of 80 vol% where organics becomes too rare (see part 4.1). During ageing and annealing, coordinated water molecules leave the structure, and a significant shrinkage, as well as densification, are observed.⁴¹ They are released by a combination of condensation reactions in polynuclear titanium hydrates and potentially between the polymer and the titanium hydroxides, resulting in the formation of covalent bonds.

An outstanding optical molecular hybrid

The PVAI/TiOxH hybrid has been proven to be an excellent optical material. Due to the absence of particles, scattering is near zero while the incredibly high inorganics amount achievable allows an essential increase in refractive index, close to 2.^{34,42} Moreover, the further condensation possible by annealing generates even higher indices. Very smooth films can be printed

by various methods such as drop-casting, spin-coating, blade-coating and dip-coating. Finally, the strong compatibility between inorganics and organics creates a densely cross-linked material completely insoluble, enabling solution-processed multilayer devices. The extensive range of possible applications for this versatile hybrid will be further explored during the following chapters.

An underexplored synthesis method

Surprisingly, the method described above is still relatively underexplored in the community. Reported methods differ from different processing steps and require many extra steps and annealing procedures. For example, in the *in situ* sol-gel method, titanium precursors (titanium butoxide $\text{Ti}(\text{OBu})_4$ or titanium isopropoxide $\text{Ti}(\text{OPr})_4$) are hydrolysed first and then added to polymers functionalised with alkoxysilanes playing the role of stabilisers instead of hydrogen bonds. Long and high curing temperatures are used to condensate the network.^{27,43,44} Another similar method consist in mixing non-hydrolysed precursors directly with the organic phase first, followed later by the slow adding of water to induce hydrolysis and condensation at the same time.^{45,46}

Curiously, studies based on hydrogen stabilisation instead of siloxane bonds tend to follow the same procedure consisting in mixing both inorganics and organics before any hydrolysis. For all, water and usually hydrochloric acid are added only after the mixing, creating some complexity in the hybrid process. Indeed, the simultaneous hydrolysis and interaction/condensation reaction make the control over the particle formation somehow uncontrollable. $\text{Ti}(\text{OBu})_4$ is always used as precursor while organic matrices are often polyimides functionalised with hydroxyl or carboxylic acid groups.^{47–52} Some other studies focused on the used of cross-linkable resins also functionalised with hydroxy or carboxy groups.^{53,54}

Only recently, Liu et al. produced a titanium oxide-based xerogel after hydrolysis and drying of $\text{Ti}(\text{OBu})_4$. The xerogel was then redissolved in water along with PVAI. However, it seems that the neutral pH and the autoclave heating step are prompt to form oxide nanoparticles in the material.⁵⁴ Maybe the closest reported material until now has been based on a different tungsten/phosphorus oxide hydrates by Matsumoto et al. They directly incorporated a commercially

available acidic hydrate called tungstophosphoric acid in an aqueous PVAI solution to form a hybrid material without an annealing step. Due to the lower index of this inorganic materials compared to titanium oxide, they achieved refractive indices up to 1.7 with an inorganic content of 90 vol%. The tailored interactions between the inorganic and organic phases seemed to create a highly amorphous system, resulting in high transparency for tungstophosphoric acid content as high as 90 vol%.⁵⁵

From the literature review detailed above and to the best of our knowledge, it seems that the one-pot PVAI/TiO_xH hybrid is still one of the only reported material allowing at the same time a relatively simple synthesis, high transparency and high refractive index thanks to the large amount of inorganic which can be incorporated. However, due to the plasticiser role of water in film, the production of thick films (> 5 µm) stays a challenge. The long drying in highly concentrated films allows the migration and formation of titanium domains often a source of scattering. Nevertheless, titanium content as high as 60 vol% can be used to form thin-films with a total absence of nanoparticles as shown in Chapter 4.

2.3 Solution-processed photonic devices

Printable photonics is an active area of research due to the demand for low cost, high throughput optoelectronic devices. When designing a photonic structure, materials with well defined refractive index over a wide range and minimal losses are sought. The range of refractive indices was the principal reason for the use of inorganics. The fact that their use requires expensive and challenging processing methods, and that they often absorb in the visible, was accepted for lack of viable alternatives. With the recent development of new optical hybrid materials, many applications could benefit from lower manufacturing cost but also from new properties which were not possible with inorganics. In this Section, the concepts behind the devices explored in this study will be explained.

2.3.1 Planar modulation of refractive index

The spatial modulation of high refractive index materials can drive a considerable development of novel and complex optoelectronic and optical devices. So-called graded index (GI) profile can be engineered to manipulate light including guiding, coupling, diffracting, focusing and defocusing. In term of device integration, in-plane structures are particularly attractive for compatibility with on-chip optical components.

Planar waveguides are made of a higher refractive index core where light is confined by total internal reflection or mode guiding depending on the dimension and the wavelength (Figure 2.6.a). A thin-film with an index higher than the substrate is required to induce guiding. Rectangular waveguides first achieved the lateral confinement in 1964 by Schlosser. The field started to get more attention when Miller used the term "integrated optics" for the first time in 1969 and surveyed the vast potential of planar optical waveguides.³

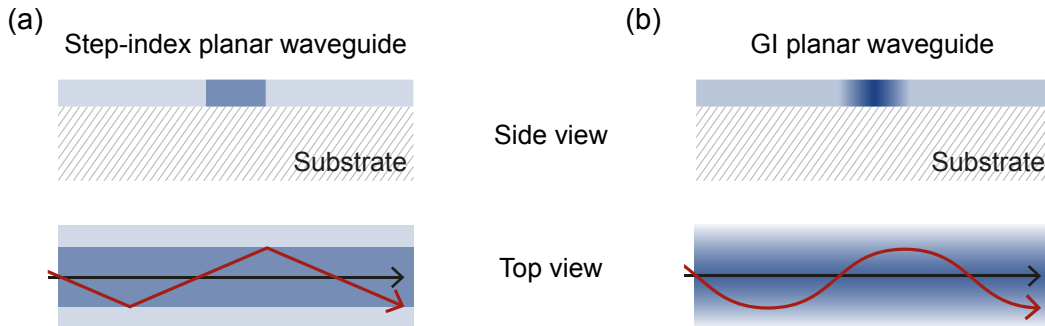


Figure 2.6: Step-index and graded-index planar waveguide configurations.

The geometrical structure of planar waveguides can be separated into two categories: step-index and GI arrangement, as shown in Figure 2.6. The first one is more often used for single-mode fibres while the second one has greater advantages for multimode light guides. Paths of different length due to rays travelling at different angles result in a modal dispersion. Considering that the speed of light is slower in larger refractive index media, it is simpler to see in Figure 2.6.b that the ray with an angle travels a longer distance but faster since the index is gradually less

high. As a result, GI waveguides have less modal dispersion allowing a broader bandwidth for data transmission.⁵⁶

Other potential applications of local patterning are displayed in Figure 2.7. It shows examples of GI lenses focusing light at a different focal distances depending on the index contrast (a,b) or defocusing light (c).⁵⁷ GI profiles have also been studied for index matching and demultiplexing multiple wavelength signals to cope with the enormous bandwidth of today's communication systems (d). In these cases, a continuous gradient of the index is needed.⁵⁸ Finally, Figure 2.7.e represents an index modulation attractive for holographic data storage. It is believed that this technology could revolutionise the field thanks to much higher capacity. While magnetic-disk technology seems to have reached its maximum potential, the local change in refractive index could help to deal with the constantly increasing amount of data.^{59–61}

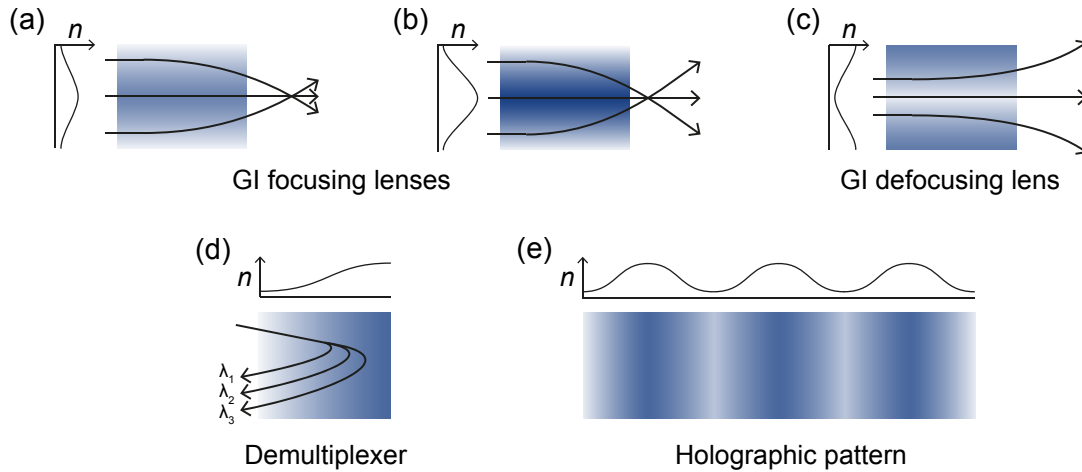


Figure 2.7: Examples of planar graded index structures where local index patterning is required. All those schematics are drawn from a top view with the darker area being more refractive than lighter ones. (a,b,c) are representations of lenses focusing light at different focal distances or defocusing light.⁵⁷ (d) is a continuous GI attractive for index matching structures and demultiplexers.⁵⁸ Holographic data storage also relies on refractive index modulation (e).⁶⁰

2.3.2 Antireflection coating

The correct manipulation of interferences is essential for many practical applications such as antireflective coatings (ARCs) and high reflectance coatings also called distributed Bragg reflectors (DBRs). ARCs have been widely applied to all kind of optical products around us to eliminate reflection automatically generated by any change in refractive index between two media. For example, the most common glass (crown glass) ($n_g = 1.52$) has a reflectance between 9 and 10 %; thus, it is clear that the reflectance would escalate in a device with multiple components. ARCs are also used in conventional silicon solar cells since its high refractive index of $n_{Si} = 3.5$ induces a reflection up to 31 %.²

The simplest ARC is based on a single quarter-wave layer as displayed in Figure 2.8.a. Considering the phase shift during propagation (Equation 2.11), an optical path of $\lambda/4$ creates destructive interferences in reflection. Besides, to reach the lowest reflected intensity the wave amplitudes need to be equal which would require a refractive index of $n = \sqrt{n_{substrate}}$. Thus, for crown glass, it means that the refractive index of the film has to be equal 1.2 which is very low for common solid materials, even if some highly porous silica thin-films with a refractive as low as 1.03 have recently been demonstrated.⁶²

As shown in Figure 2.8.b, a bi-layer structure can also result in multiple destructive interferences. In this case, a high-index layer with a half-wave condition $n_H d_H = \lambda_0/2$ is first deposited followed by a low-index thin-film with a quarter-wave condition $n_L d_L = \lambda_0/4$. This is only one of the many possible design of ARCs, however, it is noteworthy that, industrially, ARC with more than two layers are usually processed to extend the low reflectivity wavelength range or achieve lower reflection.

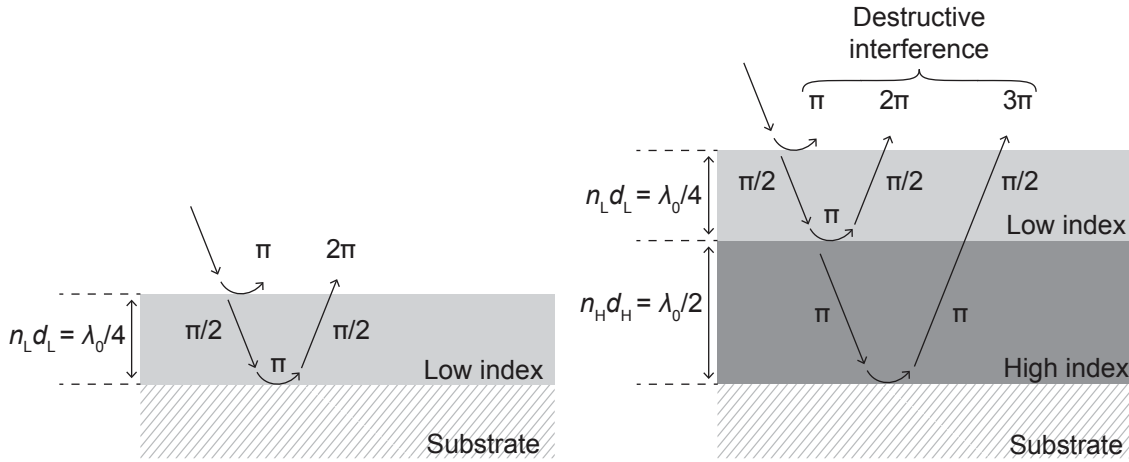


Figure 2.8: The phase change on reflection from a single quarter-wave ARC (left) and a half-wave/quarter-wave bi-layer ARC (right). The first is effective only at a given wavelength when the bi-layer leads to low reflectance for a broader spectral region. Adapted from Strang with permission.⁴²

2.3.3 Dielectric mirror

Another type of passive structures based on optical interferences are the distributed Bragg reflector (DBRs), also called dielectric mirrors. The high reflectance is a result of a repeating structure, one-dimensional photonic crystal, sometimes observed in Nature such as in butterfly's wings, beetles, etc.^{63–65} Compared to universal metallic mirrors, DBRs do not absorb light since they are supposed to be made of fully transparent materials, 100 % reflectivity is therefore enabled. However, due to its physical principle, structures are tuned only for a specific optical path length, thus only a small range of wavelengths. In order to achieve a larger reflectance band, a chirping of the stack must be done, as discussed in Chapters 6 and 7.

A dielectric mirror is a succession of alternating low and high refractive index layers (Figure 2.9). For each layer, the quarter-wave condition $n_H d_H = n_L d_L = \lambda_0/4$ must be respected, resulting in a phase change of $\pi/2$ in each layer (see Equation 2.11). Furthermore, as explained in part 2.1, a phase shift of π occurs during the reflection of a wave against a medium of a higher refractive index. From the phase description of Figure 2.9, we can see that all reflected waves combine constructively, so the reflected intensity increases.²

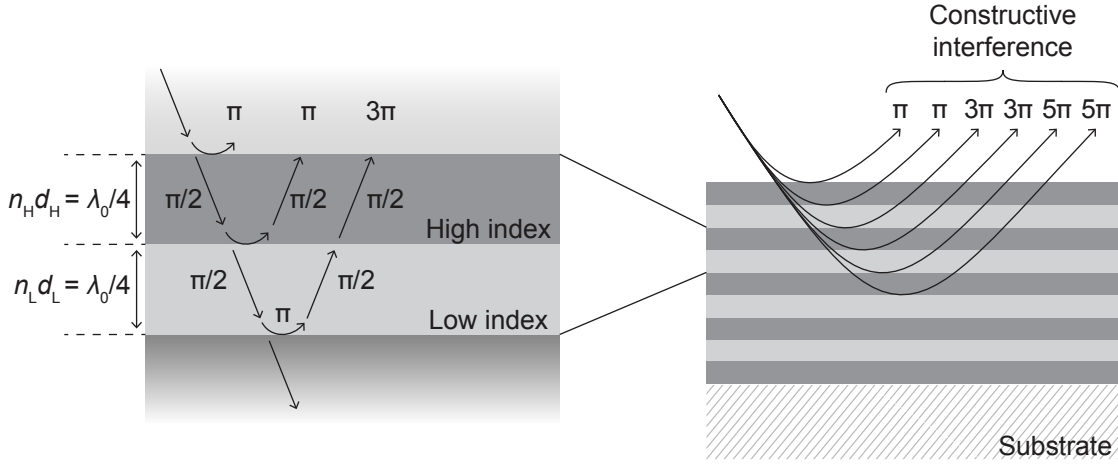


Figure 2.9: Schematic of a DBR showing the phase changes. All reflected waves combine constructively when each layer follow the quarter-wave condition. Adapted from Strang with permission.⁴²

The reflectance at normal incidence around the Bragg wavelength λ_0 can be expressed as a function of the refractive indices for a structure of $2N+1$ layers (the high index material being used for both first and last layer):²

$$R(\lambda_0) = \left(\frac{1 - (n_H/n_L)^{2N} (n_H^2/n_s)}{1 + (n_H/n_L)^{2N} (n_H^2/n_s)} \right)^2 \quad (2.18)$$

and for a structure of $2N$ layers:⁶⁶

$$R(\lambda_0) = \left(\frac{1 - (1/n_s) (n_H/n_L)^{2N}}{1 + (1/n_s) (n_H/n_L)^{2N}} \right)^2 \quad (2.19)$$

where n_s the refractive index of the substrate.

As a consequence, for any refractive index combination, the reflectance can reach 100 % if the number of bi-layers (defined as one high and one low-index layer) is large enough. It must be specified that an odd number of layers leads to higher reflectance, *i.e.* $2N-1$ will be better than $2N$ even if there is one less layer. Additionally, for a specific number of layers N , a mirror becomes more reflective when the refractive index contrast is more substantial. Similarly, the width of the stopband increases with the index contrast only.²

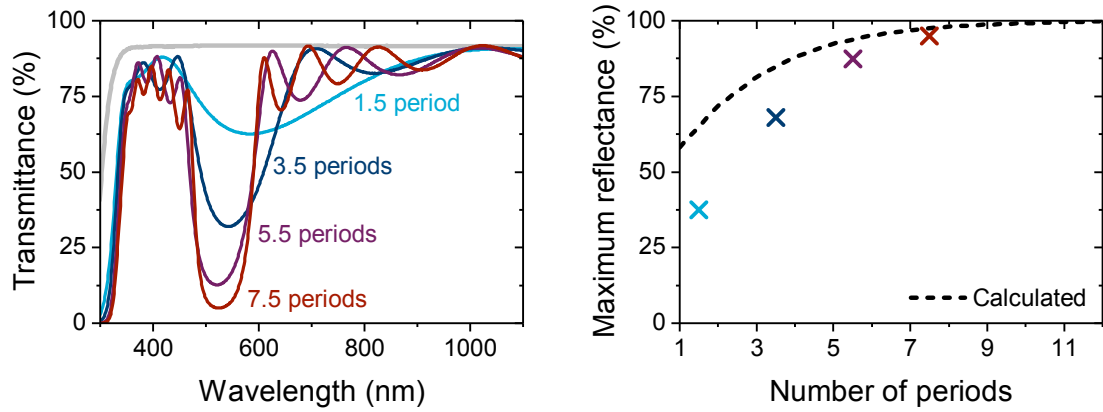


Figure 2.10: An increasing number of layers induces stronger optical interferences, resulting in lower transmittance around the Bragg wavelength. (a) shows the transmittance spectra of dip-coated PMMA / 80 vol% hybrid reflectors. As reported in (b), the corresponding reflectance increased with the number of periods (hybrid/PMMA). Values were lower than the one given by Equation 2.18 for low number of periods (dotted line) but reached 95 % after 7.5 periods.

In Figure 2.10.a, transmittance spectra are plotted for different stacks of dip-coated PMMA / 80 vol% hybrid. As expected, the two direct effects are the lower transmittance around λ_0 and the optical stopband becoming more square. Figure 2.10.b compares the calculated reflectance using Equation 2.18 with the measured values. Both reached similar reflectance of 95 % after only 15 layers (7.5 periods). Since the model is only valid for large number of layers, it is expected to have lower experimental data at the start.

From the above overview, it has been clear that control of light for specific needs is challenging. For instance, spatial modulation of the refractive index can be appropriate for many applications; however, it is not straightforward to find functional materials able to satisfy the needs. Solution-processed hybrids have opened the way to high index printable coatings, but often suffer from optical losses. This work will explore the characterisation and use of a PVAI/TiO_xH hybrid with high refractive index and low-optical losses for light and heat management applications based on the structures described above.

2.4 References

1. Hecht, E. *Optics* 698 pp. (Addison-Wesley, 2002).
2. Macleod, H. A. *Thin-Film Optical Filters, Third Edition* 682 pp. (CRC Press, 2001).
3. Ma, H., Jen, A.-Y. & Dalton, L. Polymer-Based Optical Waveguides: Materials, Processing, and Devices. *Advanced Materials* **14**, 1339–1365 (2002).
4. Yang, C.-J. & Jenekhe, S. A. Group Contribution to Molar Refraction and Refractive Index of Conjugated Polymers. *Chemistry of Materials* **7**, 1276–1285 (1995).
5. Liu, J.-g. & Ueda, M. High Refractive Index Polymers: Fundamental Research and Practical Applications. *Journal of Materials Chemistry* **19**, 8907 (2009).
6. Biron, M. High Refractive Index Polymers. *Popular Plastics & Packaging* **55**, 49–53 (2010).
7. Jha, G. S., Seshadri, G., Mohan, A. & Khandal, R. K. Development of High Refractive Index Plastics. *e-Polymers* **7**, 1384–1408 (2007).
8. Higashihara, T. & Ueda, M. Recent Progress in High Refractive Index Polymers. *Macromolecules* **48**, 1915–1929 (2015).
9. Sultanova, N., Kasarova, S. & Nikolov, I. Dispersion Proper Ties of Optical Polymers. *Acta Physica Polonica-Series A General Physics* **116**, 585 (2009).
10. Macdonald, E. K. & Shaver, M. P. Intrinsic High Refractive Index Polymers. *Polymer International* **64**, 6–14 (2014).
11. Novak, B. M. Hybrid Nanocomposite Materials - between Inorganic Glasses and Organic Polymers. *Advanced Materials* **5**, 422–433 (1993).
12. Zvonkina, I. & Soucek, M. Inorganic–Organic Hybrid Coatings: Common and New Approaches. *Current Opinion in Chemical Engineering. Biological Engineering / Material Engineering* **11**, 123–127 (2016).
13. Lü, C. & Yang, B. High Refractive Index Organic–Inorganic Nanocomposites: Design, Synthesis and Application. *Journal of Materials Chemistry* **19**, 2884 (2009).
14. Hanemann, T. & Szabó, D. V. Polymer-Nanoparticle Composites: From Synthesis to Modern Applications. *Materials* **3**, 3468–3517 (2010).
15. Judeinstein, P. & Sanchez, C. Hybrid Organic–Inorganic Materials: A Land of Multidisciplinarity. *Journal of Materials Chemistry* **6**, 511–525 (1996).

16. Boyd, R. W., Gehr, R. J., Fischer, G. L. & Sipe, J. E. Nonlinear Optical Properties of Nanocomposite Materials. *Pure and Applied Optics: Journal of the European Optical Society Part A* **5**, 505 (1996).
17. Zimmermann, L., Weibel, M., Caseri, W., Suter, U. W. & Walther, P. Polymer Nanocomposites with “Ultralow” Refractive Index. *Polymers for Advanced Technologies* **4**, 1–7 (1993).
18. Caseri, W. R. Nanocomposites of Polymers and Inorganic Particles: Preparation, Structure and Properties. *Materials Science and Technology* **22**, 807–817 (2006).
19. Cheng, Y., Lu, C. & Yang, B. A Review on High Refractive Index Nanocomposites for Optical Applications. *Recent Patents on Materials Science* **4**, 15–27 (2011).
20. Krogman, K. C., Druffel, T. & Sunkara, M. K. Anti-Reflective Optical Coatings Incorporating Nanoparticles. *Nanotechnology* **16**, S338 (2005).
21. Nussbaumer, R. J., Caseri, W. R., Smith, P. & Tervoort, T. Polymer-TiO₂ Nanocomposites: A Route Towards Visually Transparent Broadband UV Filters and High Refractive Index Materials. *Macromolecular Materials and Engineering* **288**, 44–49 (2003).
22. Demir, M. M., Koynov, K., Akbey, Ü., Bubeck, C., Park, I., Lieberwirth, I. & Wegner, G. Optical Properties of Composites of PMMA and Surface-Modified Zincite Nanoparticles. *Macromolecules* **40**, 1089–1100 (2007).
23. Kyprianidou-Leodidou, T., Caseri, W. & Suter, U. W. Size Variation of PbS Particles in High-Refractive-Index Nanocomposites. *The Journal of Physical Chemistry* **98**, 8992–8997 (1994).
24. Lü, C., Cui, Z., Li, Z., Yang, B. & Shen, J. High Refractive Index Thin Films of ZnS/Polythiourethane Nanocomposites. *Journal of Materials Chemistry* **13**, 526–530 (2003).
25. Caseri, W. Nanocomposites of Polymers and Metals or Semiconductors: Historical Background and Optical Properties. *Macromolecular Rapid Communications* **21**, 705–722 (2000).
26. Jeon, I.-Y. & Baek, J.-B. Nanocomposites Derived from Polymers and Inorganic Nanoparticles. *Materials* **3**, 3654–3674 (2010).
27. Lü, C., Cui, Z., Guan, C., Guan, J., Yang, B. & Shen, J. Research on Preparation, Structure and Properties of TiO₂/Polythiourethane Hybrid Optical Films with High Refractive Index. *Macromolecular Materials and Engineering* **288**, 717–723 (2003).
28. Nakayama, N. & Hayashi, T. Preparation and Characterization of TiO₂ and Polymer Nanocomposite Films with High Refractive Index. *Journal of Applied Polymer Science* **105**, 3662–3672 (2007).

29. Liu, J.-g., Nakamura, Y., Ogura, T., Shibasaki, Y., Ando, S. & Ueda, M. Optically Transparent Sulfur-Containing Polyimide-TiO₂ Nanocomposite Films with High Refractive Index and Negative Pattern Formation from Poly(amic Acid)-TiO₂ Nanocomposite Film. *Chemistry of Materials* **20**, 273–281 (2007).
30. Ovenstone, J. & Yanagisawa, K. Effect of Hydrothermal Treatment of Amorphous Titania on the Phase Change from Anatase to Rutile during Calcination. *Chemistry of Materials* **11**, 2770–2774 (1999).
31. Grant, F. A. Properties of Rutile. *Reviews of Modern Physics* **31**, 646–674 (1959).
32. Diebold, U. The Surface Science of Titanium Dioxide. *Surface Science Reports* **48**, 53–229 (2003).
33. Russo, M., Rigby, S. E. J., Caseri, W. & Stingelin, N. Pronounced Photochromism of Titanium Oxide Hydrates (Hydrous TiO₂). *Journal of Materials Chemistry* **20**, 1348–1356 (2010).
34. Russo, M., Campoy-Quiles, M., Lacharmoise, P., Ferenczi, T. A. M., Garriga, M., Caseri, W. R. & Stingelin, N. One-Pot Synthesis of Polymer/Inorganic Hybrids: Toward Readily Accessible, Low-Loss, and Highly Tunable Refractive Index Materials and Patterns. *Journal of Polymer Science Part B: Polymer Physics* **50**, 65–74 (2012).
35. Russo, M., Rigby, S. E. J., Caseri, W. & Stingelin, N. Versatile Chromism of Titanium Oxide Hydrate/Poly(Vinyl Alcohol) Hybrid Systems. *Advanced Materials* **24**, 3015–3019 (2012).
36. Wright, J. D. & Sommerdijk, N. A. *Sol-Gel Materials: Chemistry and Applications* (CRC press, 2014).
37. Brinker, C. J. & Scherer, G. W. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing* 925 pp. (Academic Press, 2013).
38. Hench, L. L. & West, J. K. The Sol-Gel Process. *Chemical Reviews* **90**, 33–72 (1990).
39. Nussbaumer, R. J., Smith, P. & Caseri, W. Transparent, Anatase-Free TiO₂ Nanoparticle Dispersions. *Journal of Nanoscience and Nanotechnology* **7**, 2422–2432 (2007).
40. Russo, M. *Titanium Oxide Hydrates: Optical Properties and Applications* Ph.D. (Queen Mary University of London, 2010).
41. Votta, I. *Titanium-Oxide-Hydrates Based Organic/Inorganic Molecular Hybrids Produced via Sol-Gel Processing* Ph.D. (Imperial College London, 2017).
42. Strang, A. *Organic/Inorganic Hybrid Materials for Solution-Processed Photonic Applications* Ph.D. (Imperial College London, 2015).

43. Lee, L.-H. & Chen, W.-C. High-Refractive-Index Thin Films Prepared from Trialkoxysilane-Capped Poly(Methyl Methacrylate)-Titania Materials. *Chemistry of Materials* **13**, 1137–1142 (2001).
44. Wang, B., Wilkes, G. L., Hedrick, J. C., Liptak, S. C. & McGrath, J. E. New High-Refractive-Index Organic/Inorganic Hybrid Materials from Sol-Gel Processing. *Macromolecules* **24**, 3449–3450 (1991).
45. Chang, C.-C. & Chen, W.-C. High-Refractive-Index Thin Films Prepared from Aminoalkoxysilane-Capped Pyromellitic Dianhydride–Titania Hybrid Materials. *Journal of Polymer Science Part A: Polymer Chemistry* **39**, 3419–3427 (2001).
46. Chen, W.-C., Liu, W.-C., Wu, P.-T. & Chen, P.-F. Synthesis and Characterization of Oligomeric Phenylsilsesquioxane-Titania Hybrid Optical Thin Films. *Materials Chemistry and Physics* **83**, 71–77 (2004).
47. Liou, G.-S., Lin, P.-H., Yen, H.-J., Yu, Y.-Y., Tsai, T.-W. & Chen, W.-C. Highly Flexible and Optical Transparent 6F-PI/TiO₂ Optical Hybrid Films with Tunable Refractive Index and Excellent Thermal Stability. *Journal of Materials Chemistry* **20**, 531–536 (2009).
48. Yen, H.-J., Tsai, C.-L., Wang, P.-H., Lin, J.-J. & Liou, G.-S. Flexible, Optically Transparent, High Refractive, and Thermally Stable Polyimide–TiO₂ Hybrids for Anti-Reflection Coating. *RSC Advances* **3**, 17048–17056 (2013).
49. Tsai, C.-L., Yen, H.-J., Chen, W.-C. & Liou, G.-S. Novel Solution-Processable Optically Isotropic Colorless Polyimidothioethers–TiO₂ Hybrids with Tunable Refractive Index. *Journal of Materials Chemistry* **22**, 17236–17244 (2012).
50. Park, S. K., Kang, B.-K., Shin, J.-W., Joo, C. W., Moon, J., Cho, D.-H., Yu, B., Chu, H. Y. & Lee, J.-I. Triethylene Glycol–Titanium Oxide Hydrate Hybrid Films with High Refractive Index and Surface Evenness. *Journal of Materials Chemistry C* **2**, 4468–4475 (2014).
51. Su, H.-W. & Chen, W.-C. High Refractive Index Polyimide–Nanocrystalline-Titania Hybrid Optical Materials. *Journal of Materials Chemistry* **18**, 1139–1145 (2008).
52. Yu, Y.-Y., Chien, W.-C., Lin, J. M. & Yu, H.-H. High Transparent Polyimide/Titania Multi-Layer Anti-Reflective Hybrid Films. *Thin Solid Films. 5th International Conference on Technological Advances of Thin Films & Coatings* **519**, 4731–4736 (2011).
53. An, Y. C. & Konishi, G.-i. Preparation of High-Refractive-Index Trimethoxybenzene Novolac-Titania Hybrid. *Macromolecular Research* **19**, 1217–1219 (2011).

54. Dan, S., Gu, H., Tan, J., Zhang, B. & Zhang, Q. Transparent Epoxy/TiO₂ Optical Hybrid Films with Tunable Refractive Index Prepared via a Simple and Efficient Way. *Progress in Organic Coatings* **120**, 252–259 (2018).
55. Matsumoto, S., Ishii, T., Wada, M., Kuwahara, Y., Ogata, T., Nagaoka, S., Takafuji, M. & Ihara, H. Facile Preparation of High Refractive Index Polymer Films Compositing with a Tungstophosphoric Acid. *Materials Letters* **190**, 236–239 (2017).
56. Koike, Y. & Koike, K. Progress in Low-Loss and High-Bandwidth Plastic Optical Fibers. *Journal of Polymer Science Part B: Polymer Physics* **49**, 2–17 (2011).
57. Mao, X., Lin, S.-C. S., Lapsley, M. I., Shi, J., Juluri, B. K. & Huang, T. J. Tunable Liquid Gradient Refractive Index Lens with Two Degrees of Freedom. *Lab on a Chip* **9**, 2050–2058 (2009).
58. Salameh, H. A. B. & Irshid, M. I. Wavelength-Division Demultiplexing Using Graded-Index Planar Structures. *Journal of Lightwave Technology* **24**, 2401–2408 (2006).
59. Haw, M. *Holographic Data Storage: The Light Fantastic* <https://www.nature.com/articles/422556a> (2018).
60. Del Monte, F., Martínez, O., Rodrigo, J. A., Calvo, M. L. & Cheben, P. A Volume Holographic Sol-Gel Material with Large Enhancement of Dynamic Range by Incorporation of High Refractive Index Species. *Advanced Materials* **18**, 2014–2017 (2006).
61. Zilker, S. J. Holographic Data Storage—The Materials Challenge. *ChemPhysChem* **3**, 333–334 (2002).
62. Chi, F., Yan, L., Yan, H., Jiang, B., Lv, H. & Yuan, X. Ultralow-Refractive-Index Optical Thin Films through Nanoscale Etching of Ordered Mesoporous Silica Films. *Optics Letters* **37**, 1406 (2012).
63. Parker, A. R., McKenzie, D. R. & Large, M. C. J. Multilayer Reflectors in Animals Using Green and Gold Beetles as Contrasting Examples. *Journal of Experimental Biology* **201**, 1307–1313 (1998).
64. Vignolini, S., Rudall, P. J., Rowland, A. V., Reed, A., Moyroud, E., Faden, R. B., Baumberg, J. J., Glover, B. J. & Steiner, U. Pointillist Structural Color in Pollia Fruit. *Proceedings of the National Academy of Sciences* **109**, 15712–15715 (2012).
65. Parker, A. R. 515 Million Years of Structural Colour. *Journal of Optics A: Pure and Applied Optics* **2**, R15 (2000).
66. Born, M. & Wolf, E. *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light* 996 pp. (CUP Archive, 2000).

3 | Experimental Techniques

3.1 PVAI/Titanium oxide hydrate hybrid synthesis

The inorganic-organic hybrid described in part 2.2.3 has been reported for the first time by Russo et al.^{1,2} Other recent works can be found on the similar material.^{3,4} The formulation starts with two distinct solutions: poly(vinyl alcohol) (PVAI) in water and an aqueous solution of titanium oxide hydrates (TiOxH). The concentration of each solution can be changed resulting in different viscosity of the hybrid solution. For example, solutions will be different for thicknesses around a micrometre or a hundred of nanometres. Similarly, thin hybrid solutions are usually better for dip-coating and stable for a longer time while thick solutions are preferably used with spin-coating. Finally, the ratio of the polymer with titanium species is critical since it impacts the same characteristics of the solution but also the final properties of the film, optically and mechanically.

3.1.1 Poly(vinyl alcohol)

The polymer matrix is essential for the stabilisation of the inorganic species. All hydroxyl groups of PVAI can interact with the hydrolysed titanium. PVAI is produced from the hydrolysis of polyvinyl acetate, both shown in Figure 3.1. Different grades can result from this step depending on the number of acetate side groups left along the carbon backbone. The annual worldwide production is over 1 million tonnes.⁵ For the hybrid discussed in this thesis, a grade of 88 % and a molecular weight of $130\,000\text{ g mol}^{-1}$ are used. It is sold under the trademark name of Mowiol 18-88®.

The correct mass of PVAI powder is slowly added to deionised water under stirring. The solution is heated around 80 °C until complete dissolution. In this work, concentrations between 20 and 40 g L⁻¹ are used. Those solutions are favourable to mould growth, thus, must be kept in the fridge where they are stable months.

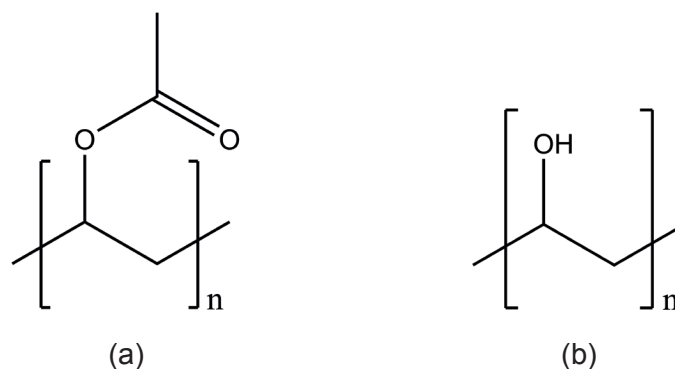


Figure 3.1: (a) Chemical structures of poly(vinyl acetate) (PVAc). (b) Chemical structures of poly(vinyl alcohol) (PVAI) produced from hydrolysis of PVAc.

3.1.2 Titanium oxide hydrates

The inorganic part of the hybrid is hydrolysed titanium, also called *hydrous titania*. The general formula of titanium oxide hydrates can be expressed as $Ti_nO_x(OH)_y$ (see Section 2.2.3). This compound, often referred to as a titanium sol-gel precursor, is surprisingly not well studied but widely used for the production of titanium oxide particles.

The hydrolysis of titanium can be performed from various precursors, however, the use of titanium tetrachloride $TiCl_4$ shows direct advantages compared to the others. Firstly, the reactivity is very high and does not require any additional chemicals. Secondly, during hydrolysis, chlorine is released and the pH of the solution decreases. TiO_xH are stabilised by the acidic environment preventing the formation of titanium oxide. The reactant used, Titanium(IV) chloride, ReagentPlus[®], 99.9 % trace metals basis, is bought from Sigma-Aldrich. The complete reaction is described by Equations 2.16 and 2.17.

The hydrolysis of TiCl_4 is extremely reactive and must be performed with care. It is added drop by drop using a separatory funnel to a stirred volume of water in an erlenmeyer flask. To avoid oxide formation and considering the extremely exothermic nature of the reaction, the temperature of the solution is kept around 0°C with an ice bath. Vapours of hydrochloric acid (HCl) are released during the process. The use of open glassware allows HCl to leave which reduces the amount of chlorine in the solution, even if traces can still be found in films, as discussed in part 4.1.1. It was noticed that when using a closed flask, the TiOxH solution appeared more yellow due to the higher residual chlorine. The setup is shown in Figure 3.2.

To prepare 100 mL of 1 mol L^{-1} and 2 mol L^{-1} solutions of TiOxH , 10.96 mL and 21.93 mL of TiCl_4 are respectively added to water. The final volumes are then adjusted to 100 mL. Clear solutions can be kept several months around -15°C .

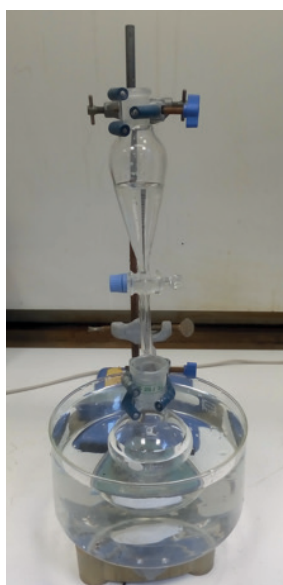


Figure 3.2: Experimental setup for the hydrolysis of titanium tetrachloride TiCl_4 in water leading to the formation of titanium oxide hydrates. TiCl_4 is dropped from a separatory funnel on the top to water contained in an erlenmeyer flask under stirring and kept at a temperature around 0°C in an ice bath.

3.1.3 Hybrid formulation

Inorganic/organic composites can be tuned thanks to the ratio of both components. Optically, the higher the inorganic content, the higher the refractive index. The most straightforward unit to qualify the hybrid concentration is the number of titanium atoms per gram of polymer, expressed as *mol Ti/g PVAI*. From the optical characterisation discussed in the following chapter, it has been proven that the amount of titanium in films matches with formulations and none of the titanium species leaves the films during annealing. Therefore, we can assume that the ratio titanium/polymer is kept all along the use of the material.

The volume fraction of inorganic species is another unit system also used in this thesis. Based on studies from Russo et al., a density of 1.95 g cm^{-3} and a molecular weight of 90 g mol^{-1} were measured for the titanium species in the hybrid.¹ The volume fraction of titanium species in the solid state of the hybrid can then be calculated and expressed as:

$$\%vol Ti = 100 \times \frac{V_{Ti \text{ species}}}{V_{Ti \text{ species}} + V_{PVAI}} = 100 \times \frac{n_{Ti} \cdot (M_{Ti \text{ species}} / \rho_{Ti \text{ species}})}{n_{Ti} \cdot (M_{Ti \text{ species}} / \rho_{Ti \text{ species}}) + V_{PVAI}} \quad (3.1)$$

$$\%vol Ti = 100 \times \frac{C_{Ti} \cdot 46.2}{C_{Ti} \cdot 46.2 + 0.794} \quad (3.2)$$

where C_{Ti} is the concentration in *mol Ti/g PVAI*, thus considering 1 g of PVAI.

The hybrid concentrations employed during this work are shown in Table 3.1 with both unit systems. Corresponding formulations are also included for 10 mL of solution using PVAI stock solution of 40 g mol^{-1} and TiOxH stock solution of 2 mol L^{-1} as an example. Calculation details for the formulation can be found in Appendix A.

Table 3.1: Usual concentrations of PVAI/TiOxH hybrids used in this thesis expressed with both unit systems. On the right hand side, the corresponding formulations for a volume of 10 mL of solution using PVAI stock solution of 40 g mol⁻¹ and TiOxH stock solution of 2 mol L⁻¹ are shown.

Concentration <i>mmol Ti/g PVAI</i>	Concentration <i>%vol Ti</i>	Volume of PVAI <i>mL</i>	Volume of Titanium oxide hydrate <i>mL</i>
0.9	5	9.82	0.18
4.3	20	9.21	0.79
11.5	40	8.13	1.87
25.8	60	6.60	3.40
68.8	80	4.21	5.79

3.1.4 Hybrid solution procedure

The exceptional properties of the PVAI/TiOxH hybrid rely on the good interactions between the inorganic and organic moieties, in this case, hydrogen bondings. The absence of particles is also a result of the fine mixing between the two phases. To achieve a similar organisation in the solid phase, initial hybrid solutions must be alike. During the preparation, the correct amount of PVAI solution is first filtered using syringes and Acrodisc[®] filters with pore size of 0.2 or 0.45 μm depending on the viscosity. Then, the adjusted volume of TiOxH is slowly added to the PVAI solution under stirring, operating through 0.2 μm Acrodisc[®] filters. Proper mixing of the two phases must result in a single phase. It happens that bubbles are present in the solution after mixing which would induce defects during dip-coating deposition. Therefore, before processing, it can be useful to sonicate the solution and/or soak the bubbles laying at the surface with Pasteur pipettes.

Despite the solution being unstable by principle, usual formulations in this work could usually last up to 24 hours in ambient conditions. The main problem is the formation of titanium aggregates in the solution when left for a long time at room temperature. For example, for DBRs reported here, solutions of 60 and 80 vol% with low viscosity were used which considerably slowed down the phenomenon. On the other hand, the solution may start to gel. However, this occurs only for a low concentration of titanium such as 5 vol% and below. In this case, substantial dilution is also required.

3.2 Film deposition methods

Throughout this thesis, two deposition methods are mainly used. It is essential to consider the scalability of the technique considering the scope of the large-area applications. For example, spin-coating is an ubiquitous approach to produce thin-films thanks to its versatility and ease but is often limited to laboratory scale. Conversely, dip-coating is an industrial solution-based process with a relatively simple scale-up.

3.2.1 Substrates

The glass substrates were purchased from VWR. They are 1 mm thick and exhibit Cauchy coefficients (Equation 3.13) of $n_a = 1.499$ and $n_b = 0.003$, measured by transfer-matrix method (TMM) (part 3.3.3). Large glass substrates (10 cm $\times$ 10 cm $\times$ 2 mm) were purchased from Schott and have indices of $n_a = 1.478$ and $n_b = 0.002$, measured by TMM. Circular fused silica (10 mm $\times$ 1.2 mm) were bought from UQC with refractive indices of $n_a = 1.445$ and $n_b = 0.004$, measured by TMM. Before each deposition, substrates were cleaned by sonication in acetone then isopropyl alcohol for 5 minutes. Once dried, UV-ozone activation treatment could be performed depending on the type of substrate and ink.

3.2.2 Spin-coating

Spin-coating is perfectly adapted when small area layer are needed. It is simple to carry out and the thickness is simply controllable with the spin-speed. The faster the speed, the larger the centrifuge force on the ink, therefore, the thinner the film. Furthermore, a more viscous solution would induce a thicker film. The process is shown in Figure 3.3. Due to the low evaporation rate of water, composite films with thicknesses larger than a micron take longer to dry which would leave more time for the titanium species to migrate and aggregate. The fast rotation

of this technique allows the freezing of the mixed phases and enables the generation of thick films. Nevertheless, spin-coating is not suitable for large-areas due to its lack of scalability. This technique is indeed limited to batch processing. Moreover, most of the solution initially spread on the substrate is lost, a major drawback for expensive materials (Figure 3.3.a).

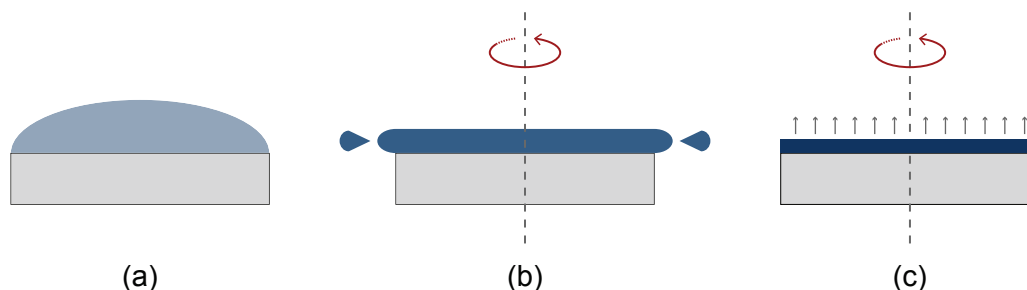


Figure 3.3: Schematics describing the spin-coating method. The solution is first deposited on the surface of the substrate held on a rotating platform (a). The sample is spun at speeds between 500 and 10 000 rpm with a specific acceleration and time. Most of the ink is ejected off the substrate during the first seconds (b). During rotation, the solvent evaporates and only the solid phase stays on the surface forming a thin-film (c). Drying often continues after spinning when using a solvent with low evaporation rates such as water.

3.2.3 Dip-coating

Perfect control of the thickness all across the sample is crucial for thin-film photonic devices. Dip-coating is particularly attractive for its ease of scalability, as opposed to spin-coating. It has been used at an industrial scale since the 1950s by Schott and the large-scale production of oxide-based automotive rear-view mirrors. Antireflection coatings and sunshield windows were also produced from 1964 and 1969 using this method.⁶ Furthermore, Schott dip-coated very large panes (about 3 m × 4 m) thanks to automated processes.⁷ The large amount of solution usually required by this technique could also be greatly minimised by the use of bi-phasic liquids.⁸

Dip-coating is a technique which enables a precise deposition thanks to the low withdrawing speeds.^{9–12} After dipping, the substrate is slowly pulled out of the solution. A thin layer stays

on the surface by capillarity and starts to dry by evaporation of the solvent. A viscous-drag plays an opposite effect by pulling down the liquid as shown in Figure 3.4.b. Thus, a faster withdrawing speed would limit the impact of the downward force and results in thicker films. Unfortunately, when the speed is too fast, a substantial thickness gradient can be observed from top to bottom. One can compensate by using a more viscous solution to produce thicker films. Another beneficial aspect is the simultaneous formation of films on each side of the substrate. This is particularly advantageous for the multilayer reflectors discussed in part 2.3.3.

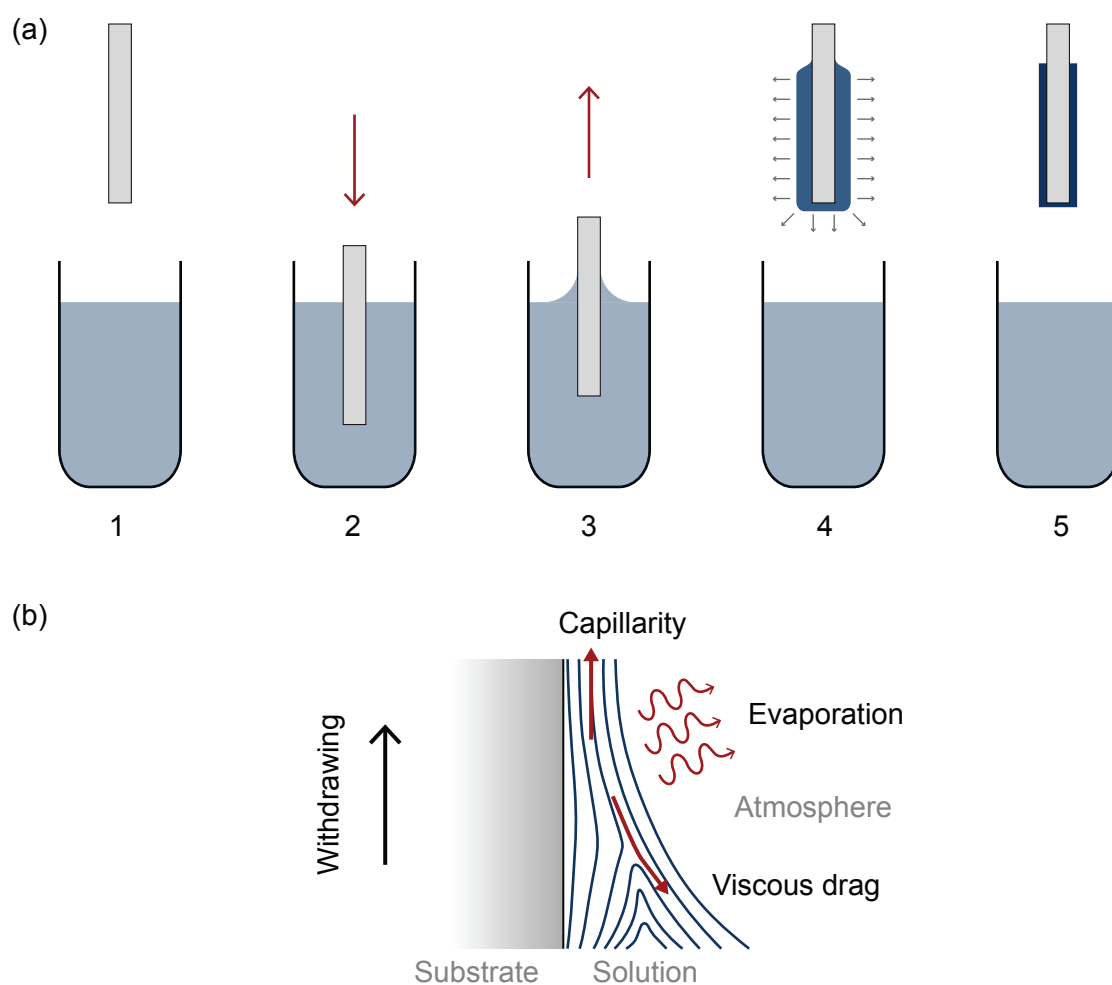


Figure 3.4: (a) Schematics describing the dip-coating method. The substrate is dipped in the solution and withdrawn at slow speeds usually between 5 and 50 mm min^{-1} (1, 2 and 3). Evaporation of the solvent starts as soon as the top of the film comes out of the solution (4). A homogeneous thin-film is formed after a few minutes of drying (5). Schematic (b) shows the main parameters involved in the film formation: the capillarity on the top, the viscous drag on the bottom and the evaporation on the side.

3.2.4 Multilayer fabrication processes

For the fabrication of multilayer structures, the first and crucial step is the calibration of the thicknesses versus spin-speeds or withdrawal speeds. The final temperature of the device must be taken into account since it would often induce shrinkage. Moreover, the previously deposited layer can play a considerable role due to the possible difference in surface energy, thus, resulting in a slight change in thickness.

In Chapters 6 and 7, a few spin-coated PMMA/hybrid multilayer samples are discussed. The fabrication is relatively simple and fast compared to dip-coated devices. After spinning and drying using a higher spin-speed for 10 seconds, an annealing step at 100 °C is performed after each coating in order to remove the remaining solvent and harden all layers.

Dip-coated mirrors are also reported to demonstrate the scalability of the solution-processed DBRs. Wrinkling of the stack was generally observed after dipping in the hybrid solution (see Figure 6.2). This phenomenon usually happened after 5 layers and further. Unlike with cellulose acetate, this instability issue could be stopped with the PMMA/hybrid combination by avoiding the intermediate annealing step. The hypothesis behind this unexpected behaviour is that PMMA swells slightly during the time spent in the hybrid solution. With the curing, a harder skin on top of PMMA formed and wrinkled when the underneath bulk PMMA started to swell. Surprisingly, a simple 20-minute drying step at room temperature appeared to be an adequate solution to the problem. A final annealing of the whole stack was performed only once the last layer was deposited to reach optimum conditions such as higher refractive indices.

Furthermore, dip-coating is much more sensitive to the drying phase. As reported recently by Bindini et al, the atmosphere is crucial for the control of the final thickness.¹³ The volatility of the solvent, the shape of the solution tank and the height of the solution in the tank can considerably alter the coating, which is one of the reason why a new calibration was performed before each device fabrication. It was also noticed that the air draft around the sample must be limited. Figure 3.5.b shows a dip-coated DBR fabricated in a fume hood. The different drying rate on the front and the back of the glass slide resulted in different thicknesses, thus shifted

the photonic stopbands. After removing the back or front layers, the sample looked green or red, respectively, while the appearance was yellow when both sides of the sample were kept. By adding a sealed box around the dip-coater, drying rate became constant and a single optical stopband was measured (Figure 3.5.c and 3.5.d). The close environment also limits the amount of dust and defects on the samples.

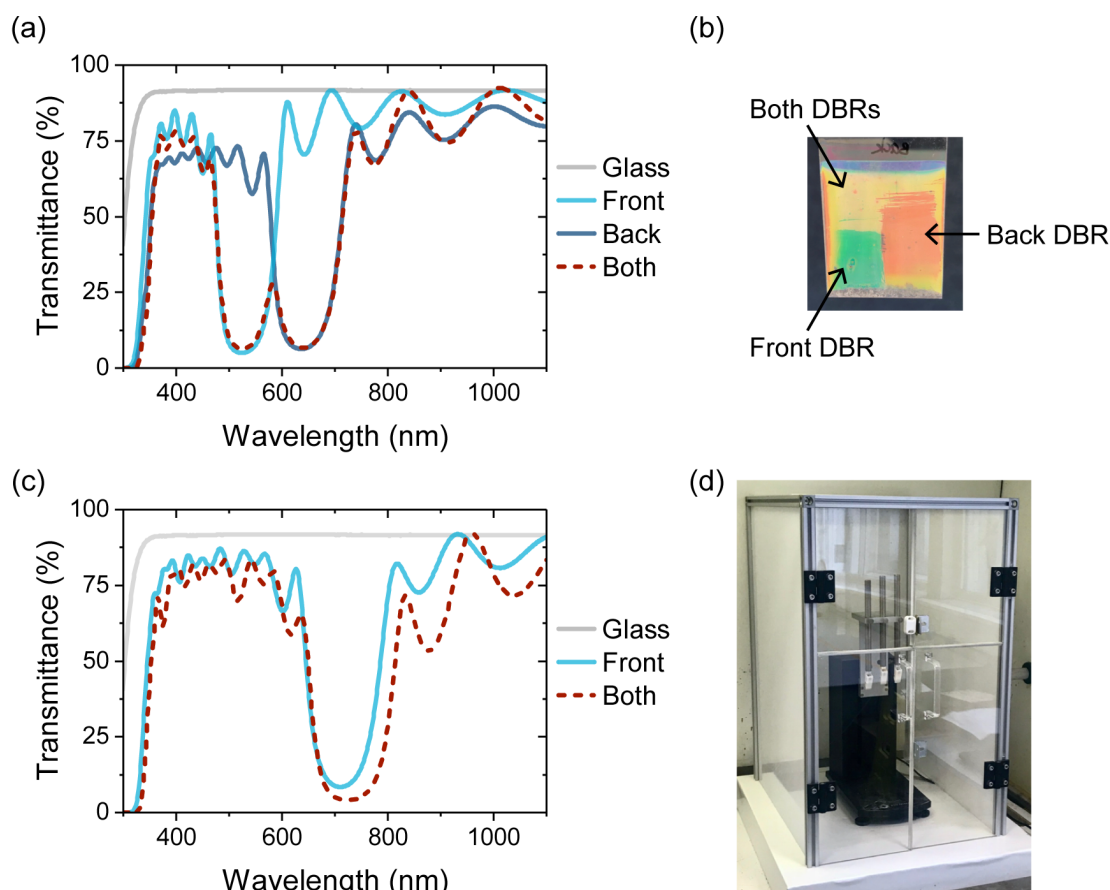


Figure 3.5: Comparison of dip-coated 7.5 bi-layer DBRs produced from 80 vol% hybrid and PMMA with different processing conditions. (a) displays the transmittance spectra of the sample shown in (b), fabricated in a fume hood. The front mirror (green area/light blue line) and the back mirror (red area/dark blue line) appears differently because of uncontrolled drying rates. However, a close environment around the dip-coater (d) limits the air movement and enables the deposition of similar coatings on both sides of the substrate.

3.3 Optical characterisation

Characterisation via UV-vis-NIR spectrometer can give valuable insights about optical materials such as their refractive index, transmission and optical losses based on the concepts explained in part 2.1. This technique was used in various ways throughout this thesis on the hybrid.

3.3.1 UV-visible spectrometry

The operating principle of UV-vis spectroscopy is rather simple considering the variety of information accessible with it. A grating diffracts a white light source in order to produce monochromatic beams. After passing through a 5 nm slit to select the wavelength, the beam is split in two for the reference and the sample analysis, represented by dashed grey and solid red arrows in Figure 3.6, respectively. Intensities at each wavelength are directly compared to quantify the effect of the material on light, which also removes any possible small fluctuation of the light intensity in contrast with a single beam configuration.

The baseline of the measurement is a crucial step, yet, often misunderstood. For example, a bare substrate is sometimes used as the reference which could lead to a transmittance higher than 100 % in some instances *e.g.* antireflection coatings. In transmission, it is always better to perform the baseline with air since we can consider its absorption as essentially zero with the distances involved here. The transmittance of glass is directly related to its refractive index and the Fresnel coefficients, as discussed in part 2.1.2. Experimentally, it is calculated by:

$$T(\%) = 100 \times \frac{I}{I_0} \quad (3.3)$$

where I and I_0 are the intensities with and without the sample in place, respectively.

The baseline is not as straightforward for reflectance measurements. In the ideal scenario, a perfect broadband reflector should be used, however, this is not easy to find. Polished aluminium

is often considered, however, reflectance is not exactly 100 %, in particular around 815 nm.¹⁴ Consequently, a less reflective but well-known low-absorbing material was utilised in this thesis: fused silica. Its relative transmittance can be measured as explained previously and following the low-loss assumption, the absolute intensity calculated by:

$$R_{fused\ silica} = 1 - T_{fused\ silica} \quad (3.4)$$

Using fused silica as a baseline, the absolute reflectance of the thin-film is calculated back using the following equation:

$$R(\%) = 100 \times R_{fused\ silica} \times \frac{I}{I_{fused\ silica}} \quad (3.5)$$

where I and $I_{fused\ silica}$ are the intensities of the reflection from the sample and the fused silica substrate, respectively.

Most of the UV-vis spectra reported in this thesis were measured using a Shimadzu UV-2600 spectrophotometer with an integrating sphere, a slit width of 5 nm and a spectral range of 220 - 1400 nm. The area covered by the light beam is around 2 mm × 3 mm. This add-on allows the measurement of total, specular and diffuse signals for both transmission and reflection. This is particularly important when non-uniform materials are used such as nanocomposites which could display important scattering. The different configurations are shown in Figure 3.6. Diffuse transmittance can be probed by removing the BaSO₄ reflector from the specular transmitted beam. Another specificity for the total reflectance is that the sample is set at an angle of 8° with respect to the incoming beam. Only in this position, the specular reflected signal is integrated by the sphere (Figure 3.6.b).

A similar instrument, Cary 5000 UV-Vis-NIR with integrating sphere from Agilent, was used in Chapter 7 to access a larger spectral range of 200 - 2500 nm.

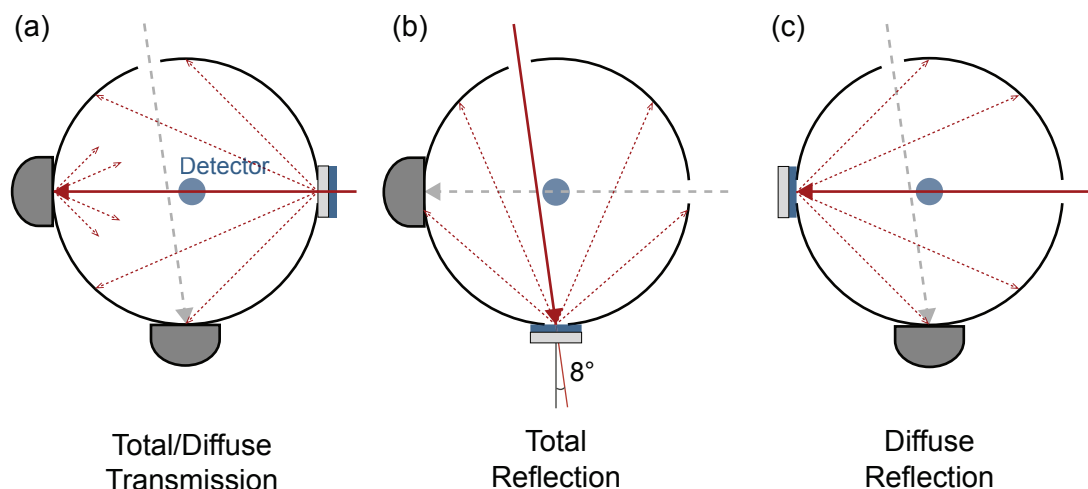


Figure 3.6: Schematic of the integrating sphere configuration in a UV-visible spectrometer for transmittance and reflectance measurements. The grey dotted line represents the reference beam while the solid red arrow refers to the sample beam. (a) shows both the total and diffuse transmission, however, for diffuse measurement, the perfect BaSO_4 reflector on the left (dark grey) is removed from the specular transmission pathway. In this configuration, only the dotted red lines are collected by the detector. Total reflection is performed at a 8° angle (b). In schematic (c), the specular reflection leaves the integrating sphere and only the diffuse light is probed.

3.3.2 Time-resolved *in situ* UV-Visible spectrometry

The UV-vis spectrometer described above allows high-quality measurement thanks to the monochromatic configuration. Nevertheless, a scan lasts several minutes limiting the characterisation to steady conditions at room temperatures. Conversely, it was demonstrated that the use of white light and analysed only after it has experienced the sample, allowed the capture of a spectrum every 30 ms.¹⁵ Unfortunately, this is only possible at the cost of a narrower wavelength range and a lower signal-to-noise ratio.

A schematic of the setup is shown in Figure 3.7 with four main parts. An optical microscope (Zeiss AX10 Imager.Z1m) is used with a tungsten bulb to send a focused light beam on the sample and collect the transmitted or reflected signal through the objective. Then, a light-pipe transports the light towards a spectrometer (ORIEL instrument 77400) and a camera (Andor Technology DV420A-OE), while a computer records spectra. Simultaneously, the temperature

of the sample can be controlled by a hot-plate (Linkam LTS420). Magnification must be limited to 20x to reduce the diversion of rays. Built-in apertures are adjusted to control the spot size allowing the analysis of smaller sample than in a classic UV-vis spectrometer. Consequently, time-resolved analysis is enabled with the recording of spectra between 500 and 750 nm every 30 ms. Unfortunately, the spectrometer only comes with a slit width of $25\text{ }\mu\text{m}$ which is much larger than the slit width of the UV-Vis spectrometer used otherwise (5 nm). It provides more light to the camera, yet, it is less effective in resolving sharp features in a spectrum. For instance, extrema of squeezed Fabry-Pérot oscillations might be cut off, resulting in a lower estimation of the refractive index after fitting by the transfer-matrix method discussed later.

Another advantage of this setup is that it enables a fine two-dimensional mapping of the sample with a small spot size and a translating stage like discussed in Section 5.2.2. A longer integration time with a higher signal-to-noise ratio can be set up when a steady-state measurement is wanted. Simultaneous non-destructive characterisation of a sample refractive index and thickness can be performed as a function of position when combined with the transfer-matrix method described in the following part.

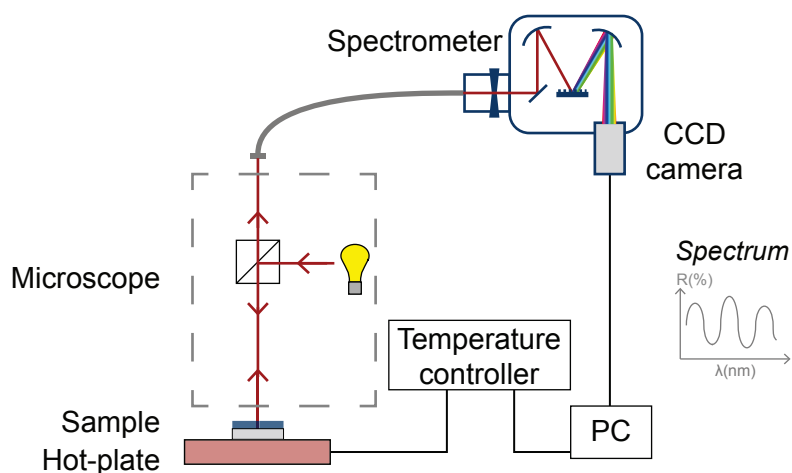


Figure 3.7: Schematic of time-resolved *in situ* spectrometry setup. It is built around an optical microscope allowing the focus of white light beam on the sample and the collection of the transmitted or reflected light depending on the configuration. After collection, a spectrometer diffracts the polychromatic light which is then analysed by a camera. The resulting spectrum is recorded by a computer. At the same time, the temperature of the sample can be controlled by a microscope hot-stage.

3.3.3 Transfer-matrix method

As discussed in part 2.1.3, the optical effect of thin-films can be relatively complex. The Fresnel's equations describe transmission and reflection at interfaces of incoherent slabs while the presence of multiple interfaces of coherent layers induces constructive and destructive interferences.¹⁶

The transfer-matrix method is a powerful analytical technique to predict the effect of optical thin-films. It is based on the continuity of the electric field at interfaces according to Maxwell's equations. Each layer can be described by a matrix of amplitudes of electric and magnetic fields. By knowing the fields at one interface, the refractive index and the thickness of the layer, the electromagnetic fields at the next interface can be calculated by a simple matrix multiplication (Equation 3.6):^{17,18}

$$\begin{bmatrix} E_1 \\ H_1 \end{bmatrix} = [\Omega_1] \begin{bmatrix} E_2 \\ H_2 \end{bmatrix} \quad (3.6)$$

where E_i and H_i are amplitudes of $\mathbf{E}$ and $\mathbf{H}$ at boundary i . Ω_1 is the characteristic matrix of the layer.

TMM is particularly valuable when multilayer samples are studied. Each layer is represented by a matrix and their multiplication enables the modelling of the overall optical response (Figure 3.8 and Equation 3.7):

$$\begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} E_1/E_n \\ H_1/E_n \end{bmatrix} = [\Omega_1] [\Omega_2] [\Omega_3] \dots [\Omega_n] \begin{bmatrix} 1 \\ n_s \end{bmatrix} \quad (3.7)$$

with Ω_n being the characteristic field matrix of the n^{th} thin-film and n_s the complex refractive index of the emergent medium, likely to be the substrate.

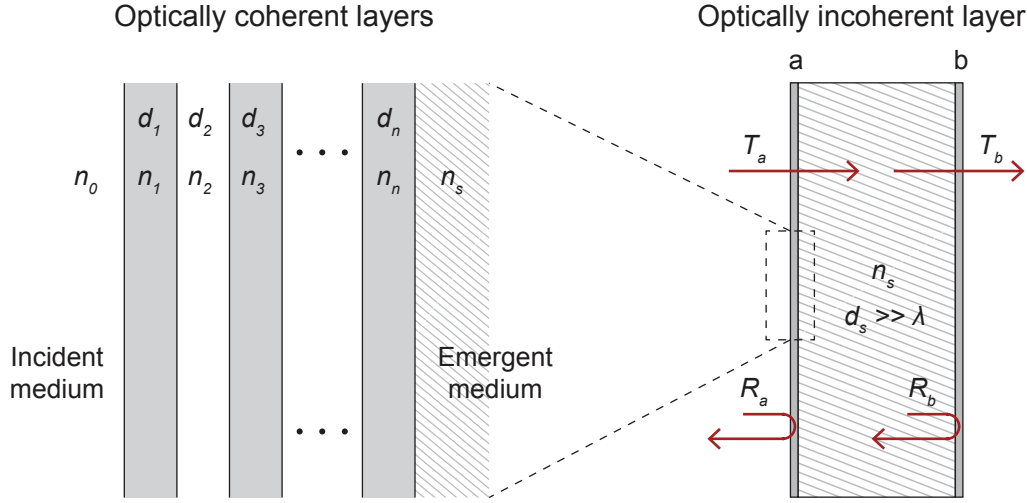


Figure 3.8: (Left) schematic of a coherent multilayer structure for TMM calculation. Each layer can be modelled as a 2×2 matrix using refractive index and thickness and multiply as described in Equation 3.7. (Right) Layer representing the incoherent case when the thickness is much larger than the wavelength of the light. In this situation, optical response of coherent films at each interfaces are first modelled with TMM and then included in Equations 3.11 and 3.12.

Finally, the transmittance and reflectance of the thin-films can be extracted from the field matrix, leading to equations:

$$T = \frac{4n_0 \text{Re}(n_s)}{(n_0 X + Y)(n_0 X + Y)^*} \quad (3.8)$$

$$R = \left(\frac{n_0 X - Y}{n_0 X + Y} \right) \left(\frac{n_0 X - Y}{n_0 X + Y} \right)^* \quad (3.9)$$

Considering that $A = 1 - T - R$, absorptance can be defined as:

$$A = \frac{4n_0 \text{Re}(XY^* - n_s)}{(n_0 X + Y)(n_0 X + Y)^*} \quad (3.10)$$

where n_0 and n_s are the complex refractive indices of air and the substrate, respectively.

TMM can calculate optical behaviour for thin-films with thicknesses in the same range of the wavelength of the light (coherent films) but does not work when some part of the structure is

much thicker like substrates, so-called incoherent part. Therefore, another method is adopted to predict the optical response. Considering that the transmitted intensity for an incoherent layer is the infinite sum of each wave, transmittance can be expressed as a function of transmittances through the first and the second interfaces, as shown in Figure 3.8. Each interface can include a coherent structure such as a dip-coated thin-film or a DBR which is taken into account in the calculation by using TMM. Similarly, total reflectance can be calculated from the reflectances at each interface, as stated:

$$T = \left(\frac{1}{T_a} + \frac{1}{T_b} - 1 \right)^{-1} \quad (3.11)$$

$$R = \frac{R_a + R_b - 2R_a R_b}{1 - R_a R_b} \quad (3.12)$$

Thanks to its flexibility and reliability, TMM was used throughout this thesis for the modelling of optical thin-films and devices. Refractive index and thickness can also be extracted by fitting experimental and modelled spectra. Furthermore, it has been shown previously that the Cauchy formula is suitable to express the wavelength dependence of the refractive index of the hybrid.³ The Cauchy dispersion model can be stated as:

$$n(\lambda) = n_a + n_b/\lambda^2 \quad (3.13)$$

where n_a is wavelength-independent and n_b is the index dispersion term (in μm^{-2}).

An algorithm was therefore developed by Kevin (Hua-Kang) Yuan to reach satisfying fit by adjusting thickness and refractive index Cauchy's coefficients.¹⁹ This optical characterisation process is sometimes referred as *spectra reflectance method* and commercialised by the company Filmetrics, Inc. for thickness measurement which rely on their refractive index database.

3.3.4 Modelling of DBRs: effect of experimental errors

In the literature, TMM is often applied to analyse dielectric mirrors. It allows the direct juxtaposition between experimental data and original design. It can also be used to gain insight into the parameters of the fabricated devices such as refractive indices and thicknesses. The effect of several crucial parameters on the optical behaviour of multilayer structures will be discussed here such as defect layers, lack of control over coating repeatability and layer roughness. It is essential to understand their role in order to establish the assumptions behind a spectral comparison.

Effect on the optical stopband

In order to quantify the impact of non-ideal stacks, the minimum transmittance (T_{min}) and the wavelength at which it occurs (λ_{min}) were calculated for a 7.5 period DBR as a function of thickness errors Δd (similar Δd for all the layers made of the same materials). The details of the modelled structure are given in Table 3.2. In practice, a constant error in the layers could correspond to an imperfect calibration or an incorrect annealing temperature which impact all the layers in a similar fashion. Plotted in Figure 3.9.a, the position of T_{min} is relatively sensitive to the thickness errors. For example, errors of $\Delta d_L = \Delta d_H = -10$ nm blue-shift T_{min} by ~ 60 nm. Nevertheless, λ_{min} is curiously constant when errors have opposite signs ($\Delta d_L = -\Delta d_H$). When analysing the graph as a function of the quarter-wave condition $n.d/\lambda = 0.25$ (top-x and right-y axes), a stopband centred at $\lambda_{min} = 700$ nm could also be obtained with detuned values of $n_H.d_H/\lambda_0 = 0.30$ and $n_L.d_L/\lambda_0 = 0.22$.

The change in the minimum transmittance for the same stack is reported in Figure 3.9.b against the errors in thicknesses or the quarter-wave conditions. The first observation is the slightly higher transmittance as soon as one of the materials has layers thicker than expected. The lower reflectance (higher transmittance) achieved for negative errors on all layers is primarily caused by the increase in refractive indices at shorter wavelengths, thus resulting in higher reflectance (Equation 2.18). On the other hand, a large detuning does not have a significant impact on

the minimum transmittance value neither. For instance, T_{min} is only higher by $\sim 3\%$ when $\Delta d_L = +25\text{ nm}$ ($+21\%$) and $\Delta d_H = -25\text{ nm}$ (-26%).

From those two graphs, it is understandable that the fitting of the multilayers structures is particularly challenging with all the parameters involved. Especially, errors of $\pm 5\text{ nm}$ do not significantly affect the optical stopband.

Table 3.2: Design parameters for a DBR centred at $\lambda_0 = 700\text{ nm}$ and annealed at 100°C using PMMA and 80 vol% hybrid.

<i>Design $\lambda_0 = 700\text{ nm}$</i>	<i>$n_{700\text{nm}}$</i>	<i>d</i>	<i>nd/λ_0</i>
PMMA	1.50 ($n_a=1.49 / n_b=0.003$)	117 nm	0.25
80 vol% hybrid (100°C)	1.80 ($n_a=1.75 / n_b=0.025$)	97 nm	0.25

Effect on the side interference fringes

Conversely to the photonic bandgap, side interferences are severely modified by experimental defects. In a perfect alternative structure, side fringes are regular with a smooth envelope (solid black line in Figure 3.10). In general, experimental spectra of printed DBRs do not exhibit perfect side interferences partly due to a lack of control over the film formation compared to evaporated devices. This is for example the case for the data shown by the grey line in Figure 3.10.

In order to find the possible causes, several cases are modelled using TMM. Firstly, spectrum 2 of Figure 3.10 displays the side interferences of a nearly perfect DBR with a single defect layer ($+10\text{ nm}$ in the 4th hybrid layer). This example which represents only one of the infinite possibilities demonstrates the substantial effect on the transmittance spectrum and could be at the origin of the measured phenomenon.

Several groups recently explored the effect of non-perfect thicknesses and layer roughness on DBR stacks.^{20–22} Following their methods, a DBR was modelled by introducing a random error in each thickness around the perfect quarter-wave conditions given in Table 3.2. The modulation

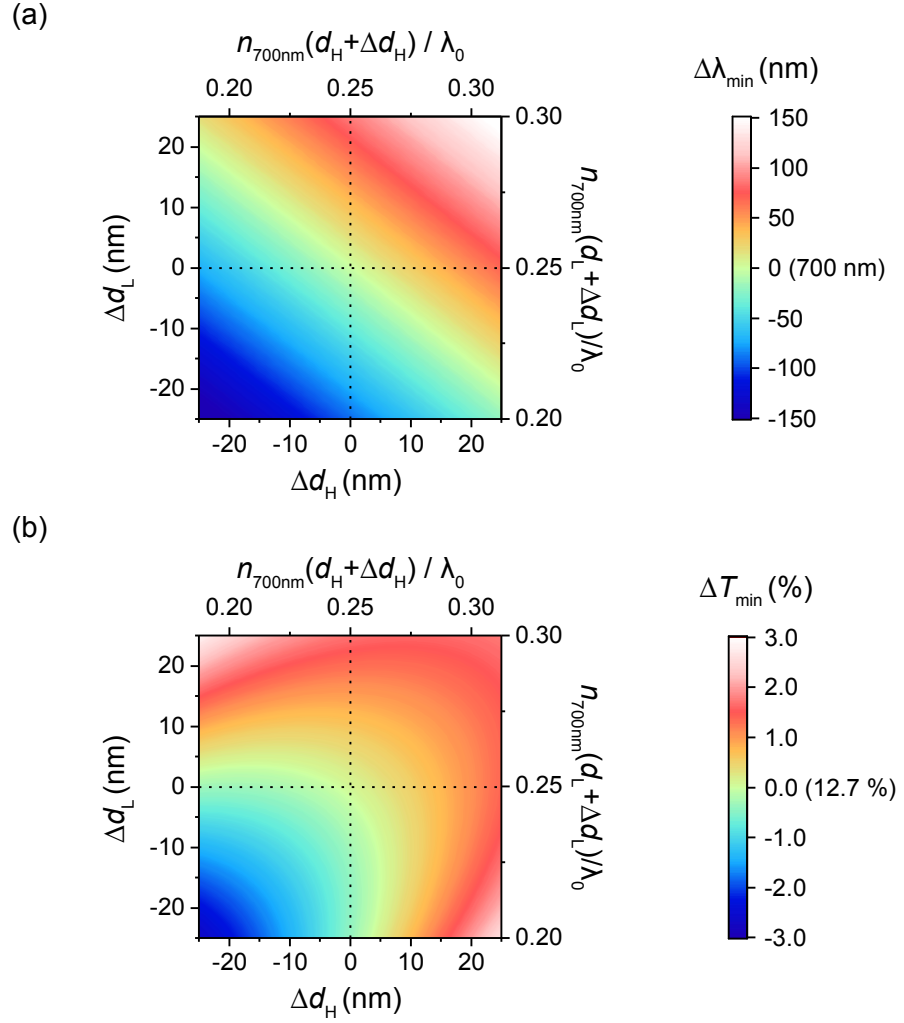


Figure 3.9: Optical stopband analysis of a 7.5 period DBR centred at $\lambda_0 = 700$ nm based on PMMA and 80 vol% hybrid (100 °C). The relative changes in the central wavelength $\Delta \lambda_{\min}$ and the minimum transmittance $\Delta T_{\min}$ are followed as a function errors in thickness in the hybrid layers (bottom x-axes) and the PMMA layers (left y-axes) using TMM. Corresponding quarter-wave conditions ($n_{\lambda_0} \cdot d / \lambda_0$) are shown on the top x-axes and right y-axes.

was given by a normal distribution around the mean value:

$$f(x, \mu, \sigma) = \exp\left(-\frac{(x - \mu)^2}{2\sigma^2}\right) \quad (3.14)$$

where μ is the mean (thickness for the quarter-wave condition) and σ the variance.

Spectrum 3 of Figure 3.10 shows one example of a stack with random thickness errors using variances of 5 nm. Interestingly, the resulting transmittance is not much disordered than the one layer defect situation. Therefore, it is also extremely challenging to know the exact structure of the sample by looking at the side fringes.

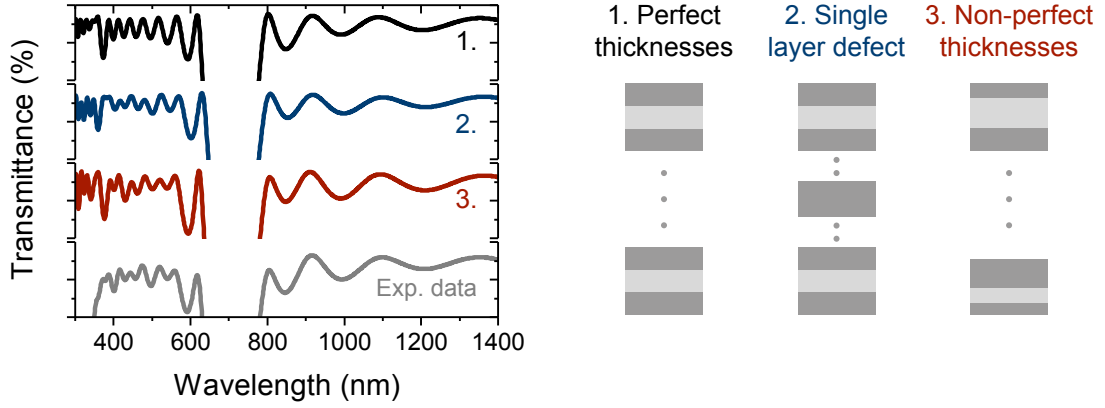


Figure 3.10: Transmittance spectra of 7.5 period DBRs centred at $\lambda_0 = 700$ nm based on PMMA and 80 vol% hybrid (100 °C). The modelled ideal case (Spectrum 1) is compared with the experimental data (grey line) and calculated spectra of non-ideal stacks. Single-layer defect results in Spectrum 2 while non-perfect thicknesses all across the DBR produces Spectrum 3. A variance of 5 nm was used to generate the distribution of thicknesses in situation 3. All spectra are plotted between 60 % and 100 %.

Based on the procedure from Bronnbauer et al., rough layers were introduced in the stack. For this, a sample area is thought as a juxtaposition of 500 slightly different stacks with "non-perfect thicknesses". Individual transmittance spectra are calculated for DBRs using normal distributions around the mean thicknesses (Equation 3.14). An arithmetical average is then performed with all the spectra. Figure 3.11 displays transmittance for increasing variance values and three distinct situations: roughness in hybrid layers only (a), roughness in PMMA layers only (b) and roughness in all the layers (c). In all cases, side oscillations are flattened, and the overall transmittance is lowered when σ is increased. Furthermore, introducing roughness in hybrid layers seems to have a larger impact than with the PMMA. Changes of the stopband are again relatively minor, except when both materials exhibit large roughness (Figure 3.11.c). Finally, smoothness does not alter the shape of the oscillation envelop, conversely to defect layers.

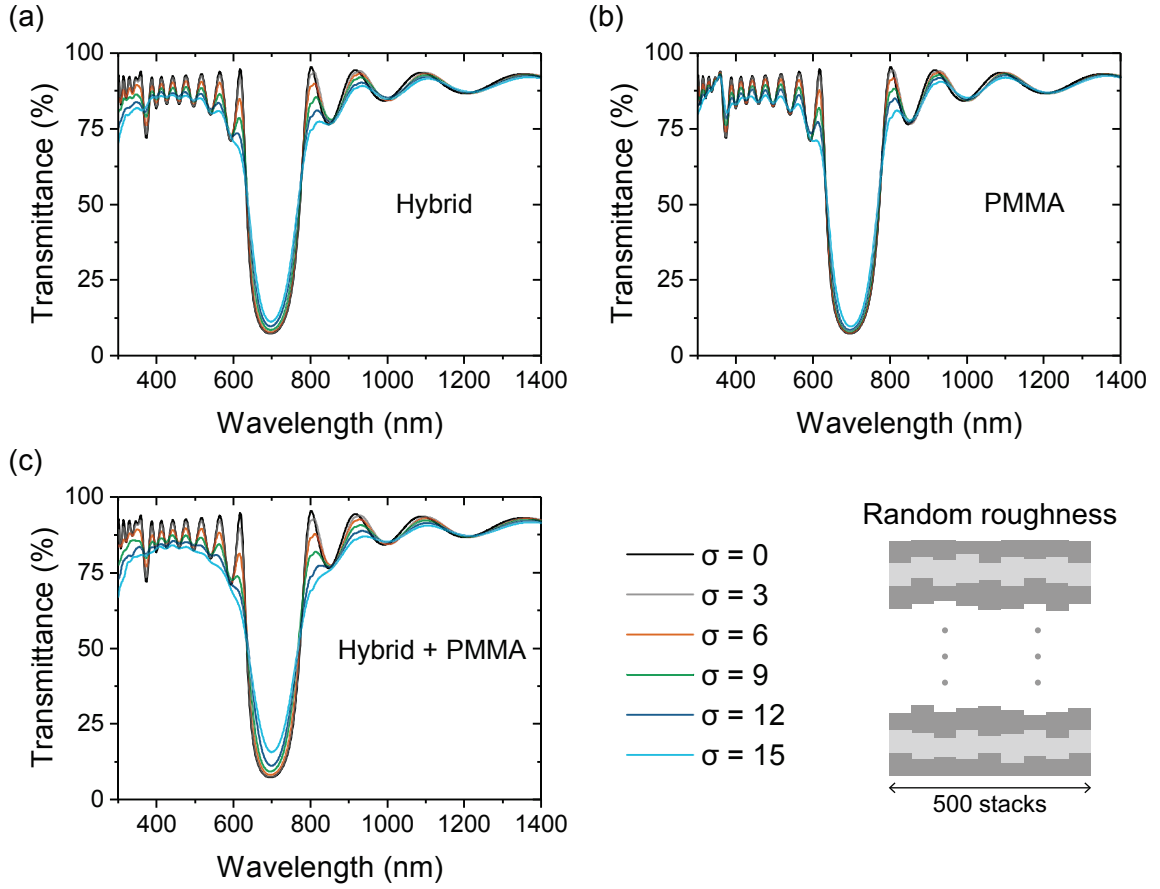


Figure 3.11: Transmittance spectra of 7.5 period DBRs centred at $\lambda_0 = 700$ nm based on PMMA and 80 vol% hybrid (100 °C). Roughness in layers is introduced using normal distribution in thicknesses of variance σ around the mean. Each spectra is an average of 500 stacks.

To conclude, the number of possible experimental errors during the printing of DBRs can have a significant impact on the transmittance spectra. Many unknown are involved which induce different responses. While the minimum transmittance is barely affected by any of the parameters, the position of T_{min} can be quite sensitive to systematic errors in thicknesses. On the other hand, side interference fringes are sensitive to layer roughness (flattened and lowered) and random defect thicknesses (disturbed envelop of the oscillations). As a consequence, it is virtually impossible to fit multilayer devices perfectly. In the following sections, only comparisons between experimental data and calculated spectra will be performed, assuming the absence of roughness and a perfect repeatability in thicknesses for each material.

3.4 Structural characterisation techniques

Structural organisation of nanocomposite hybrids are directly responsible for their optical properties. Nanoparticles larger than 10 nm will start to scatter short wavelength light. Similarly, significant surface roughness would induce diffusion. Recently, structural characterisation techniques have remarkably improved and allow direct observation of nanoscale organisation.

3.4.1 Scanning electron microscopy

Scanning electron microscopy (SEM) is based on a beam of electrons rastering the surface of a sample. An image is constructed from the signal analysed at each point. Electrons interact with the matter in various ways. For instance, secondary electrons, produced at ~ 100 nm under the surface by inelastic scattering, can be detected to probe the topography of the sample. The brightness given by the in-lens detector corresponds to the number of secondary electron received.

Additionally, material composition is sensitively analysed using an energy and angle selective backscattered electron detector (EsB). Backscattered electrons originate from deeper in the film ($\sim 1 \mu\text{m}$) and carry composition information. Heavier elements are stronger scatterers, resulting in brighter areas on the image.*

3.4.2 Transmission electron microscopy

SEM is used to study the surface or near surface of a sample, whereas transmission electron microscopy (TEM) can provide substantial insights on the internal structure of a thin layer of material.²³ In this configuration, an electron beam is used to image material by passing through

*Thank you to Artem Levisky and Prof Gitti Frey, Department of Materials Science and Engineering, Technion, Israel Institute of Technology, for assistance with these measurements.

it. Similarly to SEM, scanning transmission electron microscopy (STEM) operates by rastering a finely focused beam and collecting signal at each pixel. The main difference is that extremely thin samples (< 100 nm) must be prepared to allow electrons to travel through the material. This can be done using a TEM copper grid with holey carbon film where the material is floating above or by cutting a thin vertical section of a sample. The last one, performed for cross-sectional STEM, results in a lengthy preparation process using a focussed ion beam microscope.

In standard bright field microscopy, the brightness of the image diminishes when the material scatters more light away from the optical axis. Therefore, both atomic mass and thickness of the sample would influence the brightness. On the other hand, a dark field detector (sometimes named high angle annular dark field (HAADF)) collects only scattered electron creating better image contrast. In this mode, higher atomic mass elements appear brighter thanks to their strong scattering effect.

High-resolution STEM (HRSTEM) usually refers to phase contrast electron microscopy. This mode is highly sensitive to lattices, particularly relevant for the study of crystalline particles. The phase of each electron waves interfere and create an image. Diffraction contrast after Bragg scattering appears as fringes and cannot be interpreted as thickness or mass contrast.

TEM can also directly performed crystallographic analysis using selected area electron diffraction (SEAD). The beam can be sent on a small area of the sample, probing only this specific region. It can generate either a 2-dimensional diffraction pattern of dots for single crystals or a set of concentric rings for polycrystalline materials. Interpretation of the spacing gives access to the crystal plane spacing.

Finally, inelastic scattering of electrons produces secondary electrons which induce the relaxation of electrons from higher energy shells of the atom. X-ray photons with a wavelength characteristic of the atom are released and collected. Hence, energy dispersive X-ray spectroscopy (EDS) combined with STEM enables the elementary mapping of a sample.[†]

[†]Thank you to Dr. Claire Burgess, Department of Materials, Imperial College London, Artem Levisky and Prof Gitti Frey, Department of Materials Science and Engineering, Technion, Israel Institute of Technology, for assistance with these measurements.

3.4.3 Atomic Force Microscopy

Atomic force microscopy (AFM) is a type of scanning probe microscopy mainly used for topography imaging of a surface at high resolution. It became widely used thanks to its relatively simple application at ambient conditions and on all type of materials like isolating polymers and nanocomposites. However, only the surface of the material is characterised. Piezoelectric actuators control a pointed tip to record the height of the surface while a platform moves the position of the sample in a raster pattern. The deflection of the cantilever is followed using a laser beam focused at the end of the probe and reflected on a photodiode.^{24,25}

AFM for topography generally operates in two modes: contact or tapping. In the first one, the deflection of the cantilever is kept constant by changing the height of the sample, with a higher risk of breaking the tip against a sharp feature. In tapping mode, the tip vertically oscillates at the cantilever frequency without physically touching the surface. When the tip is very close to the surface, the interaction changes the frequency. Consequently, the height is resolved by changing the height of the sample in order to stay at a constant frequency.²⁶

An Oxford Instruments MFD 3D AFM was used in tapping mode in Chapter 4. A lateral increment of 4 nm with a tip profile width of ~ 10 nm. It is, however, challenging to measure the real height and to know both lateral and vertical resolutions precisely. In this study, AFM is only used as a surface characterisation method to complement optical measurement of the film smoothness.[‡]

[‡]Thank you to Jonathan Ngiam, Department of Materials, Imperial College London, for assistance with these measurements.

3.5 References

1. Russo, M. *Titanium Oxide Hydrates: Optical Properties and Applications* Ph.D. (Queen Mary University of London, 2010).
2. Russo, M., Campoy-Quiles, M., Lacharmoise, P., Ferenczi, T. A. M., Garriga, M., Caseri, W. R. & Stingelin, N. One-Pot Synthesis of Polymer/Inorganic Hybrids: Toward Readily Accessible, Low-Loss, and Highly Tunable Refractive Index Materials and Patterns. *Journal of Polymer Science Part B: Polymer Physics* **50**, 65–74 (2012).
3. Strang, A. *Organic/Inorganic Hybrid Materials for Solution-Processed Photonic Applications* Ph.D. (Imperial College London, 2015).
4. Votta, I. *Titanium-Oxide-Hydrates Based Organic/Inorganic Molecular Hybrids Produced via Sol-Gel Processing* Ph.D. (Imperial College London, 2017).
5. Hallensleben, M. L., Fuss, R. & Mummy, F. in *Ullmann's Encyclopedia of Industrial Chemistry* 1–23 (American Cancer Society, 2015).
6. Dislich, H. & Hinz, P. History and Principles of the Sol-Gel Process, and Some New Multicomponent Oxide Coatings. *Journal of Non-Crystalline Solids. Proceedings of the International Workshop on Glasses and Glass Ceramics from Gels* **48**, 11–16 (1982).
7. Dislich, H. & Hussmann, E. Amorphous and Crystalline Dip Coatings Obtained from Organometallic Solutions: Procedures, Chemical Processes and Products. *Thin Solid Films* **77**, 129–140 (1981).
8. Ceratti, D. R., Louis, B., Paquez, X., Faustini, M. & Grosso, D. A New Dip Coating Method to Obtain Large-Surface Coatings with a Minimum of Solution. *Advanced Materials* **27**, 4958–4962 (2015).
9. Brinker, C. J., Frye, G. C., Hurd, A. J. & Ashley, C. S. Fundamentals of Sol-Gel Dip Coating. *Thin Solid Films* **201**, 97–108 (1991).
10. Brinker, C. J., Hurd, A. J., Schunk, P. R., Frye, G. C. & Ashley, C. S. Review of Sol-Gel Thin Film Formation. *Journal of Non-Crystalline Solids. Advanced Materials from Gels* **147-148**, 424–436 (1992).
11. Faustini, M., Louis, B., Albouy, P. A., Kuemmel, M. & Grosso, D. Preparation of Sol-Gel Films by Dip-Coating in Extreme Conditions. *The Journal of Physical Chemistry C* **114**, 7637–7645 (2010).

12. Grosso, D. How to Exploit the Full Potential of the Dip-Coating Process to Better Control Film Formation. *Journal of Materials Chemistry* **21**, 17033–17038 (2011).
13. Bindini, E., Naudin, G., Faustini, M., Grosso, D. & Boissière, C. Critical Role of the Atmosphere in Dip-Coating Process. *The Journal of Physical Chemistry C* **121**, 14572–14580 (2017).
14. Hass, G., Schroeder, H. H. & Turner, A. F. Mirror Coatings for Low Visible and High Infrared Reflectance. *JOSA* **46**, 31–35 (1956).
15. Bachevillier, S. *Tunable High Refractive Index Hybrid for Solution-Processed Light Management Devices: Time-Resolved Annealing Study by in Situ Spectroscopy* M.Res (Imperial College London, 2015).
16. Hecht, E. *Optics* 698 pp. (Addison-Wesley, 2002).
17. Macleod, H. A. *Thin-Film Optical Filters, Third Edition* 682 pp. (CRC Press, 2001).
18. Orfanidis, S. J. *Electromagnetic Waves and Antennas* (Rutgers University, Piscataway, NJ, 2014).
19. Yuan, H.-K. *Solution-Processed Waveguides/Dielectric Mirrors, Materials Synthesis and Processing* M.Res (Imperial College London, 2015).
20. Jordan, T. M., Partridge, J. C. & Roberts, N. W. Disordered Animal Multilayer Reflectors and the Localization of Light. *Journal of The Royal Society Interface* **11**, 20140948 (2014).
21. Bronnbauer, C., Hornich, J., Gasparini, N., Guo, F., Hartmeier, B., Luechinger, N. A., Pflaum, C., Brabec, C. J. & Forberich, K. Printable Dielectric Mirrors with Easily Adjustable and Well-Defined Reflection Maxima for Semitransparent Organic Solar Cells. *Advanced Optical Materials* **3**, 1424–1430 (2015).
22. Bronnbauer, C., Riecke, A., Adler, M., Hornich, J., Schunk, G., Brabec, C. J. & Forberich, K. Printing of Large-Scale, Flexible, Long-Term Stable Dielectric Mirrors with Suppressed Side Interferences. *Advanced Optical Materials* **6**, 1700518 (2017).
23. Goodhew, P. J., Humphreys, J. & Beanland, R. *Electron Microscopy and Analysis* (CRC Press, 2014).
24. Binnig, G., Quate, C. F. & Gerber, C. Atomic Force Microscope. *Physical Review Letters* **56**, 930–933 (1986).
25. Wang, D. & Russell, T. P. Advances in Atomic Force Microscopy for Probing Polymer Structure and Properties. *Macromolecules* **51**, 3–24 (2018).
26. García, R. & Pérez, R. Dynamic Atomic Force Microscopy Methods. *Surface Science Reports* **47**, 197–301 (2002).

4 | Poly(vinyl alcohol)/titanium oxide hydrate hybrid

The molecular organisation of the PVAI/TiOxH hybrids underpins the unique properties over most of the other polymer nanocomposites reported in the literature (see part 2.2.2). The optical characteristics observed by Russo et al., such as high refractive index with very low optical losses, already imply an excellent dispersion of the inorganic phase.¹ Moreover, it has been shown that the hybrid can change upon heat.^{2,3} Nevertheless, a better understanding of the material structure, in particular at high concentrations, and its direct relation with the optical properties before and after annealing is still needed for further development.

4.1 Nanostructural characterisation of the hybrid

4.1.1 A closer look inside a molecular hybrid

Superior optical properties require exceptional mixing of the inorganic and organic phases. High titanium content increases the index of refraction but can also results in scattering from particles with sizes larger than one-tenth of the wavelength, known as Rayleigh scattering. Besides, electron microscopy is a powerful tool to probe materials at the micro and nanoscale. As explained in Section 3.4, the topography of a material can be analysed by AFM and SEM while TEM allows the observation of the internal morphological structure. Cross-sectional TEM is also carried out to characterise interfaces of multilayer structures. Furthermore, other methods are now integrated into these high-end instruments such as energy-dispersive x-ray spectroscopy (EDS) and selected-area electron diffraction (SAED) allowing the elemental and

crystalline analysis of the materials.* Those techniques bring new insights to understand the micro and nano-structure of the PVAI/TiOxH hybrid. In particular, a comparative study of a range of concentrations might be able to clarify the hybrid organisation.

High-resolution scanning electron microscopy (HRSEM)

SEM does not require complicated sample preparation compared to TEM and gives now access to high magnification imaging. In this study, we decided to make a multilayer sample with all usual hybrid concentrations to limit the number of samples, with the time-consuming cross-sectional HRTEM discussed later in mind. At the same time, this sample, showed in Figure 4.1, allowed a direct comparison of all the different formulations. PMMA layers were deposited as interlayers. Fabrication was performed using dip-coating. Two layers of 80 vol% were coated to assure consistency in the sample (hybrid on top of PMMA) and because PMMA adhesion is relatively weak on silicon. To avoid outgassing in ultra-high vacuum chambers, samples were annealed at 100 °C for 30 seconds.

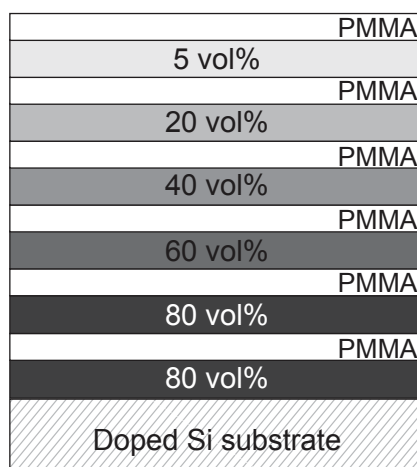


Figure 4.1: Schematic of multilayer sample containing all usual hybrid concentrations (80, 60, 40, 20 and 5 vol%) with interlayers of PMMA. It allows the direct comparison of the concentrations in similar condition by cross-section electron microscopy. The sample was fabricated by dip-coating and annealed at 100 °C.

*Thank you to Artem Levisky and Prof Gitti Frey, Department of Materials Science and Engineering, Technion, Israel Institute of Technology, for assistance with the measurements discussed in part 4.1.1.

A HRSEM cross-section was first carried out to confirm the sample quality, as displayed in Figure 4.2. Secondary electron images (4.2.a and b) are sensitive to the topography of the surface while backscattered electron images (BSE) probe the materials composition (4.2.c and d). Large titanium atoms are strong scatterers of electrons, thus the hybrid appears brighter than fully-organic PMMA. In Figure 4.2.d, we can already notice that the hybrid layers became darker and darker from bottom to top when the titanium concentration was decreasing. The 5 vol% hybrid was almost not distinguishable from the PMMA layers due to the low amount of titanium. It is also worth noticing the neat interfaces between PMMA and hybrid layers, an essential characteristic required by the dielectric mirrors studied in Section 6.

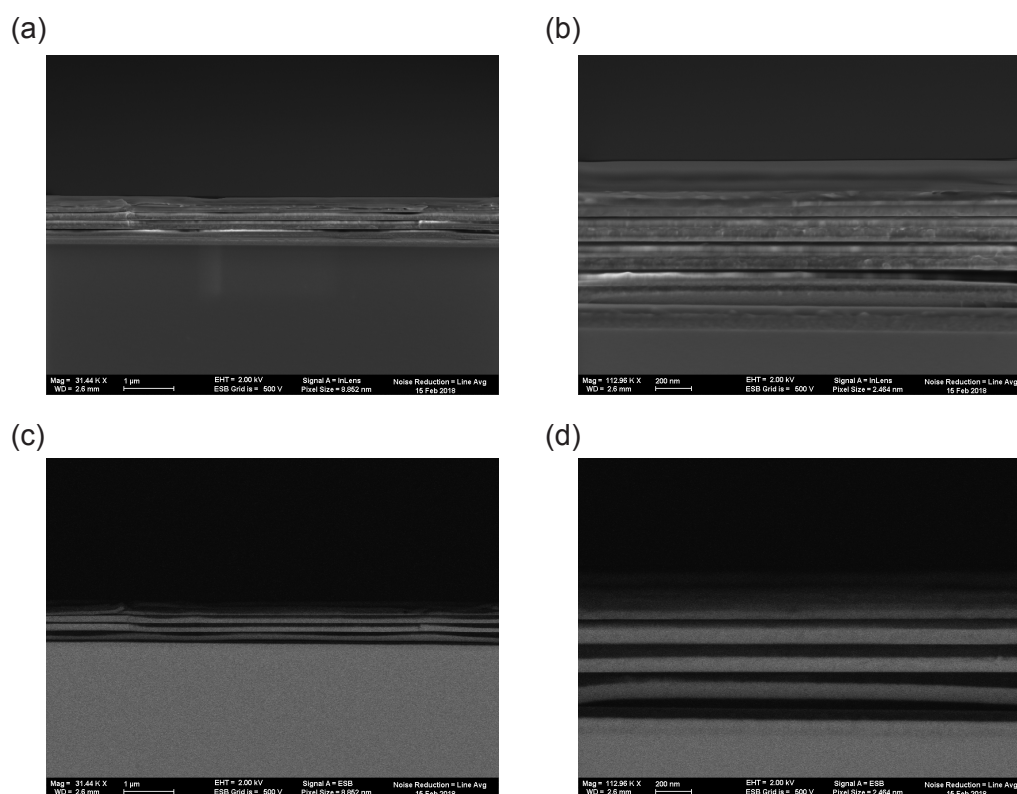


Figure 4.2: Cross-section HRSEM images of the multilayer sample shown in Figure 4.1. (a) and (b) are in-lens images from secondary electrons for topography measurements while (c) and (d) are the corresponding backscattered electron analysis related to the material composition. Those last one clearly show the difference in concentration of heavy atoms such as titanium. The lower the concentration (toward the top of the sample), the lower the intensity.

High-resolution transmitted electron microscopy (HRTEM)

In SEM, secondary electrons are created only at the very near surface. On the other hand, HRTEM can achieve very high-resolution and probe the inside of a thin sample which unlocks other types of information such as diffraction pattern and fine mapping of the chemical composition. The first aim of this study was to inspect the uniformity of the material and the presence or not of nanoparticles. From previous reports, the hybrid was considered fully amorphous, however, imaging techniques were not as precise and studied concentrations were usually quite low.⁴

A straightforward way of making a sample for TEM is to deposit a thin layer of material on top of a copper grid and holey carbon film. Unfortunately, the presence of holes induced different drying rates, especially around the edges. After observation of the peculiar formation of large aggregates in that region only, we deduced that holes created an outward flow of solution where titanium species could migrate and aggregate. Consequently, we decided to switch to cross-sectional HRTEM analysis. Unfortunately, the sample fabrication is complicated and tedious as explained in Section 3.4.2. Consequently, the multilayer sample described previously (Figure 4.1.b) was fabricated to reduce the preparation time and facilitate direct comparison.

Figure 4.3 displays images of each hybrid concentration at high magnification using HRTEM. Firstly, the highly amorphous state and uniformity of the material is observed for most of the films confirming previous investigations. Even at extremely high titanium concentration, coatings looked fairly homogeneous, despite the presence of small crystalline particles with diameters smaller than 5 nm. We can confirm that the pathway used to make the hybrid provides the extraordinary means to stop crystalline particles formation up to a concentration around 80 vol%. Furthermore, depending on the surface it was applied onto, the same solution behaved quite differently. Based on the TEM image discussed later in Figure 4.7.a, we treated 4.3.a as an outlier, probably due to the different surface energy of the pre-treated silicon substrate.

At this point, the total absence or the small crystalline particles present in the material after annealing at 100 °C and under ultra-high vacuum already confirms the suitability of the highly

concentrated hybrid for optical applications. Along with the sleek layer interfaces, low optical losses by scattering in the visible are forecast.

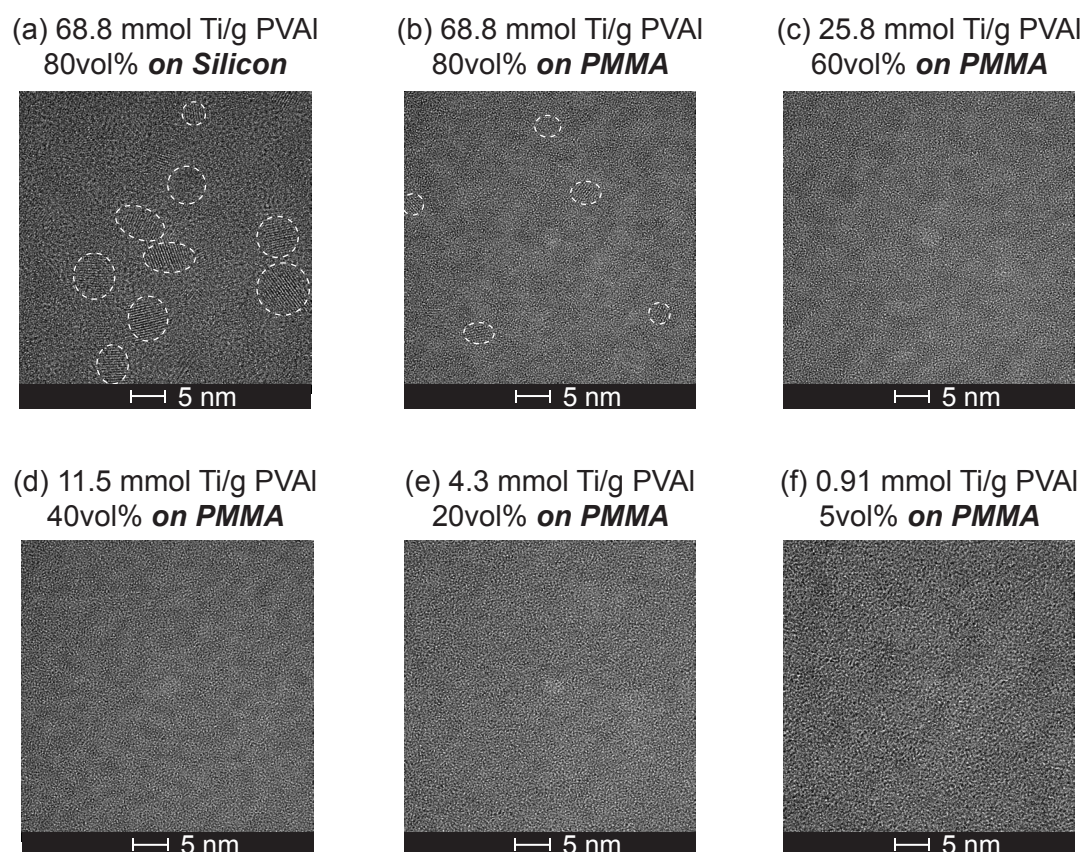


Figure 4.3: HRTEM cross-section images of hybrid films with different concentrations. Only the 80 vol% hybrid shows crystalline particles whereas all other layers (≤ 60 vol%) are remarkably uniform and amorphous. Particles were larger when the 80 vol% hybrid was processed on treated silicon than in the film onto PMMA.

Energy-dispersive x-ray spectroscopy (EDS)

From the study above, the absence of crystalline particles of TiOxH was assessed in most of the cases. By performing a mapping of the chemical elements by EDS, we could also have a look at the titanium dispersion and the possibility of amorphous aggregates. A cross-section was first done as shown in Figure 4.4.a. Atomic fractions (mol/mol) of each element found in the structure are plotted in Figure 4.4.b allowing the direct comparison of the different hybrid formulations. As expected, mainly titanium, oxygen, carbon and chlorine were observed in the

materials, silicon being the substrate. It can also be noticed, from Figure 4.4.b and EDS images intensities, that concentrations in titanium, oxygen and chlorine EDS images decreased when less TiOxH was used in the formulation. Conversely, carbon concentration increased when more polymer was added.

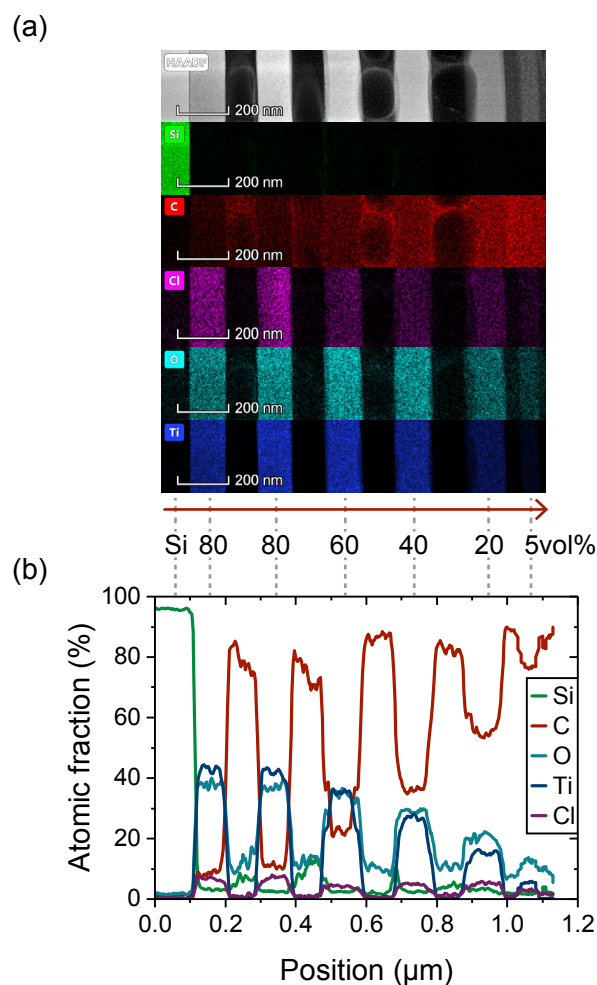


Figure 4.4: Energy-dispersive X-ray spectroscopy of different the multilayer film. The scan showed in (a) allows the direct comparison of the main chemical elements present in the films. Hybrid films are starting from high to low concentrations from left to right. The top image is a dark field STEM while other are images in EDS mode. The elemental analysis plotted in (b) demonstrates the decrease of titanium and chlorine in the films. Oxygen also becomes less and less present but the decrease happens at a lower rate since oxygen is also contained in the PVAI matrix. Conversely, carbon from the polymer only increases when the concentration in titanium species decreases.

Figure 4.5 reports the atomic fraction of each element from Figure 4.4.b as a function of the hybrid concentration. Trends were even clearer with steep decrease in titanium and increase in carbon. As a direct consequence of the formulation, oxygen decreased at a slower rate than titanium since more PVAL, which also contained oxygen atoms, were used.

On the other hand, considering the chemistry from the titanium precursor TiCl_4 and the low pH of the initial TiOxH solution, we expected a certain amount of residual chlorine in films. However, the significant quantity analysed here was relatively large. It was previously believed that most of it was leaving during hydrolysis and with the solvent during processing and drying. Moreover, the sample was annealed at 100°C and measurements performed under ultra-high vacuum which most likely extracted any other volatile species remaining in the films. Chlorine content was found to be around 5 % slightly decreasing with the titanium concentration because less and less TiOxH was added in the formulation (Table 3.1).

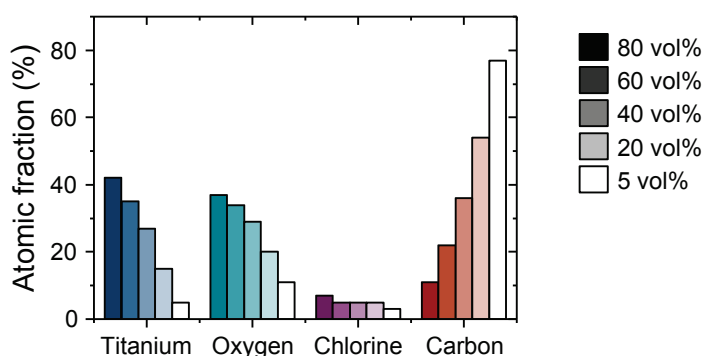


Figure 4.5: Bar graph reporting the atomic fraction of titanium, oxygen, carbon and chlorine in hybrid films. Hybrid concentrations of 80, 60, 40, 20 and 5 vol% are compared going from darker to lighter colour bar.

Higher magnification mappings are shown in Figure 4.6 corresponding to images (a), (b), (c) and (d) of Figure 4.3. The left-hand side column is showing the distribution of titanium within the four films. The good uniformity of the micrographs confirmed the absence of amorphous aggregates, except for Figure 4.6.a. In this layer (80 vol% hybrid on silicon), titanium and oxygen-rich regions are nicely correlated confirming the composition of the titanium oxide

particles. More importantly, carbon and chlorine mappings are darker in these areas, meaning a depletion of chlorine in the crystalline nanoparticles.

This study also allowed us to have a direct look at the organisation of the inorganic/polymer mix within a thin-film. No phase segregation was observed and elemental dispersions were highly uniform even with extremely low amount of polymer matrix. This uniformity confirmed the excellent optical fitting of hybrid films using the transfer-matrix method which considers only perfectly uniform layer with a single refractive index. Holes in the polymer layers visible in the carbon mapping are artefacts of the sample preparation.

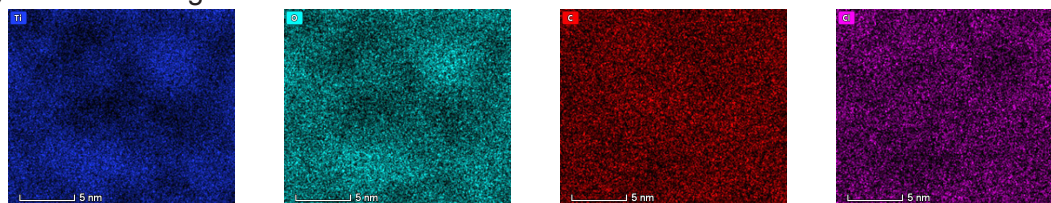
4.1.2 The nanoparticle case

It has been seen previously that very high concentration in titanium species could favour the formation of crystalline nanoparticles. In the scope of this thesis, it is always attractive to have a high concentration in titanium in order to increase the index of refraction. Nevertheless, the size of the particles is particularly crucial since they can result in optical scattering and therefore limit the application of the material. Based on the Rayleigh scattering Equation 2.15, it has been demonstrated that nanoparticles smaller than a tenth of the wavelength (< 40 nm) prevent optical losses. It was also shown that only a few large aggregates larger than 100 nm could induce relatively strong scattering. Therefore, it is better to limit the size down to 10 nm in nanocomposites to avoid any large cluster.⁵⁻⁷

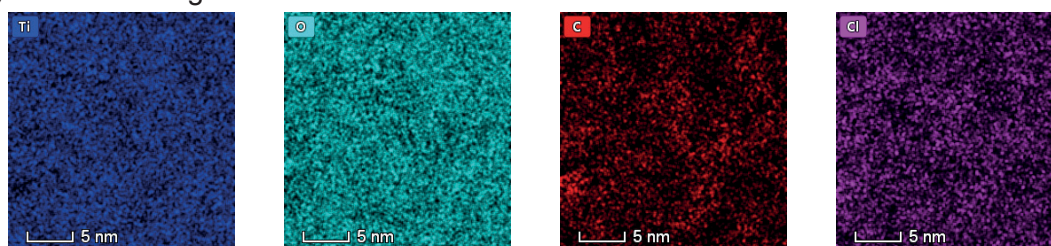
From the HRTEM cross-section discussed in Figure 4.3, the particle size seemed to be smaller than 5 nm. A simpler TEM measurement on a copper grid/holey carbon film was performed to have a better idea of the nanoparticle size dispersion, despite the known issues of the sample preparation on this type of substrate as discussed in part 4.1.1. TEM micrograph of the 80 vol% hybrid is displayed along with the particle size analysis in Figure 4.7.[†] The presence of small particles was confirmed along with the good dispersion and the absence of large aggregate.

[†]Thank you to Dr Claire Burgess, Department of Materials, Imperial College London for assistance with the measurements discussed in part 4.1.2.

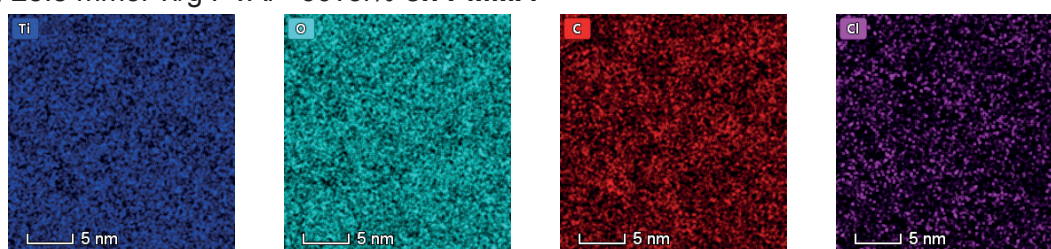
(a) 68.8 mmol Ti/g PVAI - 80vol% **on Silicon**



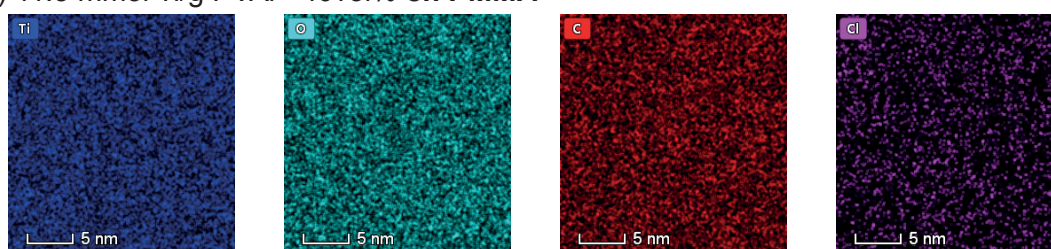
(b) 68.8 mmol Ti/g PVAI - 80vol% **on PMMA**



(c) 25.8 mmol Ti/g PVAI - 60vol% **on PMMA**



(d) 11.5 mmol Ti/g PVAI - 40vol% **on PMMA**



Titanium

Oxygen

Carbon

Chlorine

Figure 4.6: Energy-dispersive X-ray spectroscopy of different hybrid films during TEM analysis. Titanium, oxygen, carbon and chlorine are the four different elements shown. (b), (c) and (d), 80, 60 and 40 vol% respectively, are very homogeneous over the analysed area. However, 80 vol% deposited directly onto silicon (a) shows regions with larger amount of titanium and oxygen, in direct agreement with the crystalline titanium oxide particles observed in the TEM cross-section images in Figure 4.3. This EDS analysis is a direct confirmation of the extremely fine dispersion of the titanium species within the polymer matrix.

The particle diameter was centred around 1.5 nm with a maximal size of 2.5 nm confirming the absence of Rayleigh optical loss of the hybrid even at high concentrations.

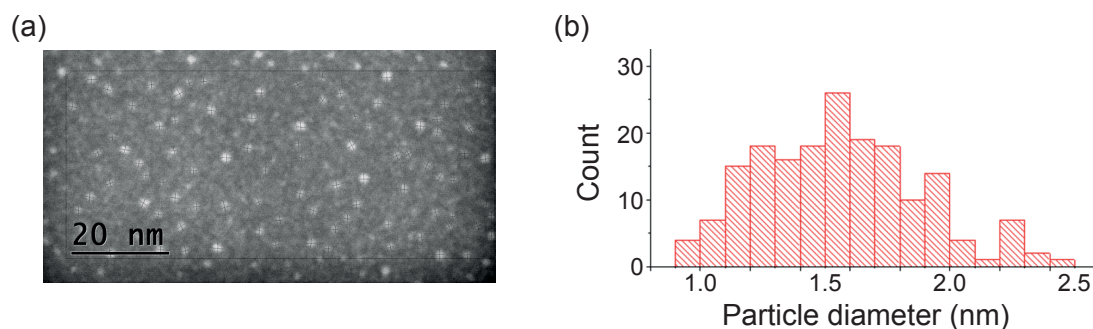


Figure 4.7: (a) TEM analysis of 80 vol% hybrid film on a copper grid/holey carbon film. As expected from previous measurements, nanoparticles can be observed. (b) represents the number of particles as a function of their diameters, extracted from the image (a). Even in this particularly unfavourable case, the particle diameter is limited to 1.5 nm on average. This is acceptable for any optical application in the visible range and above.

Selected-area electron diffraction (SAED)

Several crystal polymorphs of titanium oxide can be found in nature, resulting in different optical properties. For example, the higher packing density of rutile compared to anatase is a direct cause of its higher refractive index (2.7 vs. 2.55).⁸ Knowing the nature of the crystal phase in the hybrid material can give access to the maximum index of refraction achievable from this synthesis route. SAED, displayed in Figure 4.8, was carried out on 80 vol% hybrid film particles during cross-sectional TEM. A diffraction circle was observed on top of the silicon substrate dotted pattern. The Ewald sphere was measured at a distance of 0.350 nm^{-1} corresponding to TiO_2 anatase 101 crystal plane spacing.⁹ The crystal structure was also confirmed by fast-Fourier transform of the fringes observed in Figure 4.3 created by interferences of the electron waves through the crystal structure.

Rutile polymorph is the thermodynamically stable polymorph of TiO_2 , while anatase and brookite are kinetic polymorphs products. Yet, it appears challenging to produce rutile particles directly at room temperature. In most synthesis route, the transformation from anatase or brookite to rutile happens at curing temperatures between 600 and 1100 °C.¹⁰ Considering the relatively low temperatures used with this materials ($< 150 \text{ °C}$), it seems reasonable to favour the form-

ation of anatase crystal phase. Furthermore, the strong interactions between the polymer hydroxyl groups and the titanium species are most likely to stabilise the anatase phase even more. It is noteworthy that a PVAI/TiO₂ nanocomposite with 2.5 nm rutile particles can be found in the literature. To enable the other crystalline phase, they used an extra heating step of the titanium oxide hydrate solution to produce rutile particles. Those were only added to the polymer once synthesised *ex situ*.¹¹

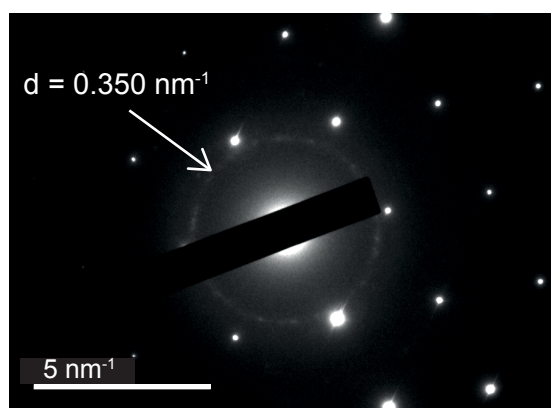


Figure 4.8: An electron diffraction pattern was taken from 80 vol% hybrid sample on silicon using SEAD. A diffraction circle (Ewald sphere) is observed at a distance of 0.350 nm^{-1} which corresponds to the TiO₂ anatase 101 crystal plane spacing. Bright dots are the silicon diffraction in K-space.

4.2 Optical characterisation

From previous studies, the PVAI/TiOxH hybrid shows remarkably low optical losses from scattering and absorption.^{1,2} Moreover, as discussed in Section 2.2, the higher the fraction of inorganic species, the higher the index of refraction, following the linear relation with the volume fraction of each constituent (Bruggeman effective medium theory).^{12,13} Low losses and high index are both crucial for the fabrication of advanced photonic structures, yet, precise calibration is required.

4.2.1 Refractive index

In this part, optical interferences and their fitting with a transfer-matrix method, described in Section 3.3.3, are used to characterise the refractive index of the materials. The depth of the oscillations is indeed governed by the refractive index of the thin-film, as shown in Figure 2.3. After coating films with a similar optical path length for simpler comparison, transmittances were captured by UV-vis spectroscopy and plotted in Figure 4.9. As expected, the depth of the oscillations is reducing with decreasing the titanium content, down to the point where interferences are barely observable with PVAI since it exhibits a refractive index very close to the glass substrate one.

Cauchy coefficients (see Section 3.3) extracted after fitting of hybrid thin-films of various concentrations and corresponding refractive index values are reported in Table 4.1. Cauchy curves are also plotted in Figure 4.10 where the increase in refractive index is confirmed along with a larger dispersion for higher concentrations. As shown later in Figure 4.15, the index of refraction follows a linear behaviour against the vol% concentration agreeing with Bruggeman theory.

The significant UV absorption of the titanium species in this materials generates a large optical dispersion. This is due to the natural frequency of the titanium species being around $\lambda = 230$ nm

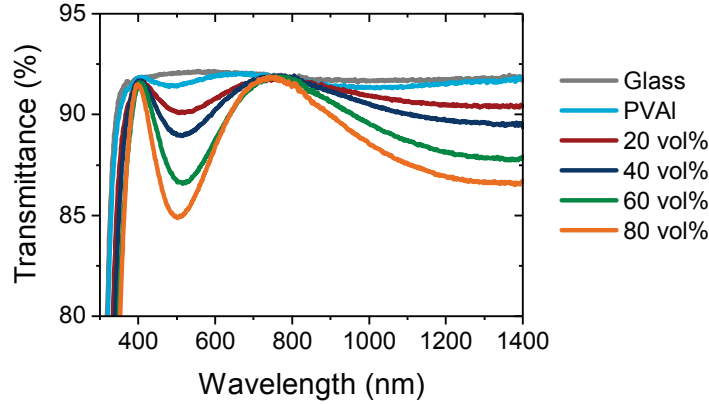


Figure 4.9: Transmittance spectra of PVAI/TiO_xH hybrid thin-films on glass. The depth of the Fabry-Pérot oscillations is proportional to the refractive index of the medium, indicating its increase with titanium content. All films have a similar optical path length (nd) resulting in oscillations appearing at similar wavelengths. Films were aged at room temperature.

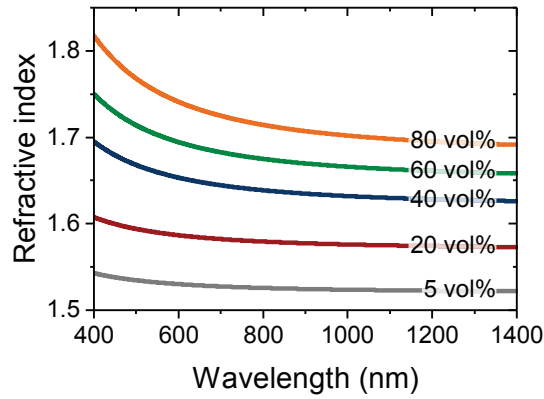


Figure 4.10: Wavelength-dependent refractive index curves for different hybrid concentrations. These Cauchy curves are calculated from parameters extracted using TMM on the Fabry-Pérot oscillations of thin-films processed at room temperature. Films were aged at room temperature. Values are reported in Table 4.1.

(Figure 4.12). Classically, the electron-oscillators in the dielectric material vibrate at the frequency of the incident wave. When the frequency of light is very different, the effect on the refractive index is small and dispersion negligible. However, when the frequency of light approaches it, the electrical polarisation of the dielectric material increases which induces a larger index of refraction. Consequently, the more absorbing the material (higher titanium content),

Table 4.1: Cauchy parameters for wavelength dependent refractive index and Abbe's number ν_D of hybrids with different concentrations at room temperature.

Concentration Ti vol%	n_a	n_b μm^{-2}	n (550nm)	ν_D
PVAI	1.52			
5	1.52	0.004	1.53	76
20	1.57	0.006	1.59	51
40	1.62	0.012	1.66	29
60	1.65	0.016	1.70	23
80	1.68	0.022	1.75	18

the stronger the effect on the wavelength dispersion.¹⁴ Mathematically, this is often referred to the Kramers-Kronig relation.¹⁵

Nevertheless, the hybrid system is still considered as a rather low dispersive medium, considering the relatively magnified scale of the graph. Material's dispersion are commonly classified using the Abbe's number (Equation 2.14), or ν_D . The higher ν_D , the less dispersive the material. Crown glasses usually have ν_D up to 65 while for the slightly more dispersive flint glass, it is lower than 55, comparable with 5 and 20 vol% hybrids. The commodity optical polymer PMMA exhibits a high $\nu_D \approx 60$, but the commodity polymers like polycarbonate and polystyrene have lower values around 30.¹⁶ For example, 40 and 60 vol% hybrids have ν_D laying between 20 and 30 which is close to the previously mentioned polymers but with considerably higher refractive indices. ν_D are also reported in Table 4.1.

4.2.2 A low loss material

The hybrid material exhibits relatively low scattering even at high titanium content.^{1,2} It was confirmed with the transmittance spectra displayed in Figures 4.9 and 4.14 where Fabry-Pérot oscillations are reaching the substrate transmittance at the constructive interference wavelengths, independently on their position.

Scattering in nanocomposites materials is often caused by the presence of large particles, something which has been ruled out previously. Besides, surface roughness is another possible source of scattering and often a problem in thin-film optics and integrated optics.¹⁷ Cross-sectional HRSEM and HRTEM already showed promising results on the interfaces between PMMA and hybrid coatings. Yet, AFM is a technique enabling the surface characterisation for valuable insight on the roughness; even if one always has to be cautious when comparing measurements between different studies with this method.¹⁸ Figure 4.11 shows 1 x 1 μm scans on a 60 vol% hybrid before and after annealing. A root mean square roughness R_q (also called RMS) of 2.2 $\text{\AA}$ was measured, a value which seems relatively similar to bare glass.¹⁹ Moreover, the hybrid becomes smoother after annealing by reaching $R_q = 1.6 \text{ \AA}$.[‡] These low values are an important parameter to minimise the surface scattering but also to achieve good interfaces in multilayer devices.

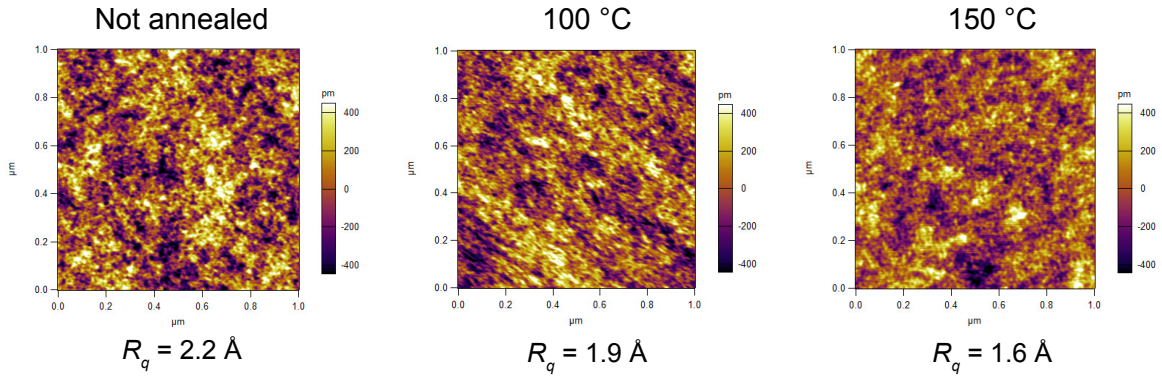


Figure 4.11: Roughness of a 60 vol% hybrid thin-film by AFM before and after annealing at 100 °C and 150 °C. Low R_q values were measured for all temperatures. This confirms the low losses by surface scattering and the hybrid suitability for integrated optics and DBRs.

Absorption is another crucial material parameter for optical materials. It certainly depends on the type of applications and their wavelength domain. In particular, for the structures discussed in the following chapters, the hybrid must be transparent in the visible and near-IR range. First, solution absorbance was measured by UV-vis spectroscopy and using Equation 2.10 for PVAI, TiOxH and 60 vol% hybrid solutions (Figure 4.12). The two first absorb only from wavelength

[‡]Thank you to Jonathan Ngiam, Department of Materials, Imperial College London, for assistance with these measurements.

shorter than 350 nm and 240 nm, respectively. As expected, the absorbance of the hybrid solution is directly linked to its components. Later discussed in Section 4.3.2, the absorbance of hybrid thin-films was also measured (Figure 4.17). It is maximal at the wavelength $\lambda = 230$ nm making it an excellent visibly transparent UV absorber, attractive for protective coatings.¹¹ This is not surprising considering that titanium oxide is the main compound used in sun creams.

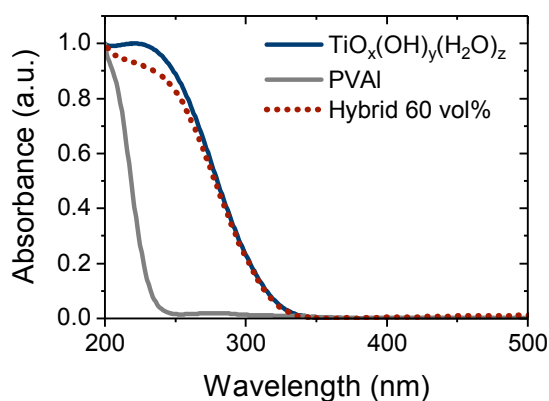


Figure 4.12: Absorbance of titanium oxide hydrates, PVAI and 60 vol% hybrid solutions in water by UV-vis spectroscopy using Equation 2.10.

4.3 A thermo-responsive material

Post-deposition annealing of the hybrid also induces an increase in refractive index. It suggests a densification of titanium species, which is one of the expected mechanism behind the index increase (Figure 4.13). TiOxH refers to hydrolysed titanium species containing Ti-OH groups which would eventually convert to titanium oxide TiO₂ upon ageing. In fact, the high Ti_nO_x(OH)_y loading is only possible thanks to the good interactions between alcohol groups of PVAI and hydroxyl groups of the inorganic phase by both hydrogen and covalent bonds, shown in Figure 2.5. This phenomenon is directly related to the contraction of the hybrid with temperature.

As discussed in Chapter 2, the hybrid can be seen as a type of sol-gel chemistry where initial fully hydrolysed inorganic precursors are employed. However, surrounding polymer chains interact with the hydrolysed species blocking the condensation reaction like a stabiliser. Initial TiOxH become stable within the organic matrix giving rise to another parameter compared to conventional sol-gel materials in which full condensation thermodynamically occurs leading systematically to pure oxide phase. It is believed that post-processing annealing favours further condensation of the TiOxH, replacing hydrogen bonds in covalent bonds. Consequently, films become denser, tougher,³ and more refractive without creating more particles thanks to the polymer matrix blocking any migration of inorganic species. Water molecules are also expected to leave during the process.

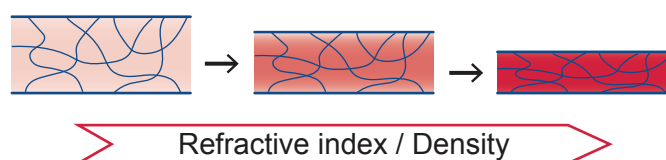


Figure 4.13: Schematic showing the contraction of hybrid films during ageing, vacuum treatment or annealing. It results in denser films with higher refractive indices than their as-cast counterpart. This phenomena can be tuned and stopped at any intermediate state, still leading to stable materials. Thanks to the polymer matrix, no cracking is observed neither lateral contraction.

4.3.1 Post-deposition tuning by annealing

Similarly to Figure 4.9, interference oscillations from transmittance spectra were measured and fitted for each hybrid formulation as a function of the annealing temperature. The curing time was approximatively 30 seconds which was shown to be sufficient for a complete and plateaued conversion (latter discussed in part 5.2.1). An example of the optical response is displayed in Figure 4.14 for a 60 vol% hybrid before and after annealing at 100 °C and 150 °C. Qualitatively, the blue shift and deeper oscillations demonstrate the change in optical thickness, *i.e.* the sim-

ultaneous shrinkage and increase in refractive index in this case. Cauchy coefficients for 20, 40, 60 and 80 vol% hybrids were calculated using TMM and reported in Table 4.2.

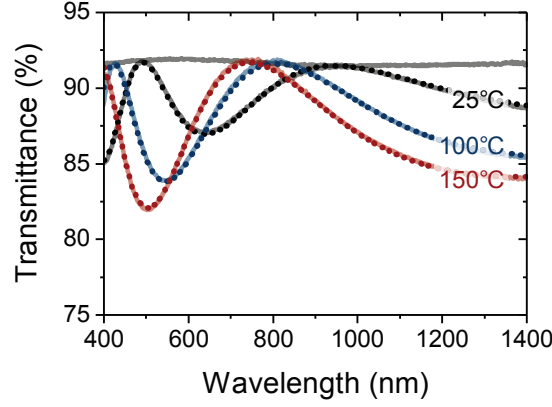


Figure 4.14: Transmittance spectra of 60 vol% hybrid before and after annealing at 100 °C and 150 °C. The increase in Fabry-Pérot oscillations depth confirms the higher refractive indices while the blue shift shows the reduction in optical thickness nd . Transmittance curves were fitted using TMM and plotted in dotted lines.

Table 4.2: Cauchy parameters for wavelength-dependent refractive indices of hybrid films with various concentrations and after annealing for 30 seconds. n_a relates to the non-dispersive part whereas n_b (in μm^{-2}) introduces the dispersion. The higher the concentration and the annealing temperature, the higher the index of refraction and the optical dispersion. Values were extracted after fitting the optical interferences measured by UV-vis spectroscopy with TMM.

Temperature	20 vol%	40 vol%	60 vol%	80 vol%
25 °C	$n_a = 1.57$	$n_a = 1.62$	$n_a = 1.65$	$n_a = 1.68$
	$n_b = 0.006$	$n_b = 0.012$	$n_b = 0.016$	$n_b = 0.022$
100 °C	$n_a = 1.58$	$n_a = 1.66$	$n_a = 1.72$	$n_a = 1.75$
	$n_b = 0.009$	$n_b = 0.013$	$n_b = 0.025$	$n_b = 0.025$
150 °C	$n_a = 1.59$	$n_a = 1.68$	$n_a = 1.75$	$n_a = 1.82$
	$n_b = 0.010$	$n_b = 0.014$	$n_b = 0.029$	$n_b = 0.032$

Refractive indices at $\lambda = 550$ nm of thin-films aged at room temperature and after maximum annealing at 150 °C both linearly increase with titanium species volume percentage. In both cases, the Bruggeman effective medium theory is respected. It means that indices can be roughly

guessed at any intermediate temperature up to 150 °C by linear extrapolation by studying only one film at the needed temperature. Furthermore, Figure 4.15 also shows the whole accessible range of refractive indices with the hybrid material, demonstrating its outstanding versatility.

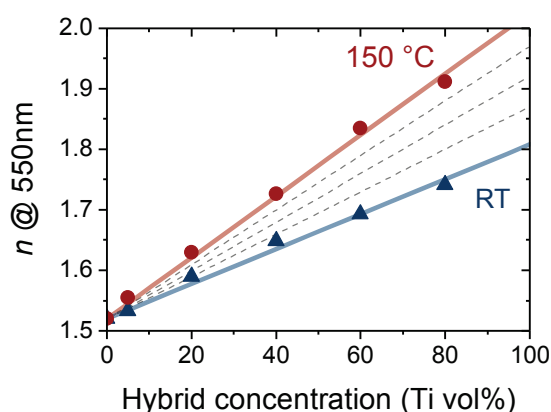


Figure 4.15: Refractive index range accessible with the hybrid material from using different concentrations and annealing temperatures. The linear relationship is in direct agreement with the Bruggeman effective medium theory for both as-cast and 150 °C anneal hybrids and enables the prediction of the refractive index for any concentration and annealing temperature and *vice versa*. Data were extracted using TMM on thin-films.

4.3.2 Thickness / refractive index relation

As already discussed, the hybrid index increase is directly linked to its contraction. Since the optical path length nd is generally the most relevant parameter in optical coatings (part 2.3), it is important to know if the decrease in thickness directly compensates the increase in the index of refraction. It is even more relevant when multilayer devices must be fabricated at room temperature and only annealed afterwards since an optical thickness change would completely alter its behaviour.² Figure 4.16 displays the change in the discussed parameters (n , d and nd) as a function of annealing temperature for a 60 vol% hybrid film. It is clear from this graph that the optical path length is not constant and, therefore, both thickness and index changes must be fully predicted before fabrication.

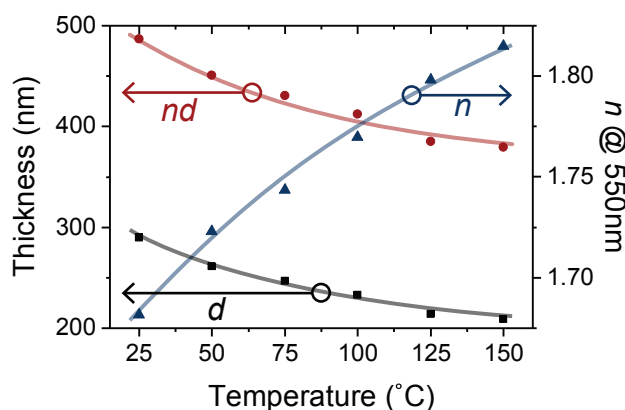


Figure 4.16: Change in optical path length as a function of temperature for a 60 vol% hybrid 300nm thick film. Both thickness and refractive index were extracted from transmittance spectra using TMM. Optical path length is defined as nd .

In all likelihood, the increase in refractive index is a combination of several phenomena. The first is the densification of the material, as measured by Votta, which certainly induces a reduction of the free volume in the film.³ Kim et al. demonstrated for example that there is a gain in refraction and a lessening in porosity and thickness of sol-gel films during curing.²⁰ Secondly, the polarisability of the material has to be discussed in regard to the Lorentz-Lorenz formula (Equation 2.13). As mentioned previously, hydroxyl groups are likely replaced by oxide bonds during annealing, which exhibit higher molecular refraction. As a consequence, atoms with low atomic polarisability, like hydrogen and oxygen, are removed from the material. Both phenomena will mathematically increase the averaged material polarisability. Nevertheless, this is correct exclusively under the condition that titanium atoms are not leaving the hybrid during heating.

Thus, absorbance measurements on various concentrations were carried out as a function of temperature to confirm this hypothesis. Absorbance is calculated after measuring transmittance and reflectance, based on the conservation of energy following Equation 2.9. Absorbance curves and extracted values at $\lambda = 230$ nm are displayed in Figure 4.17.a and 4.17.b, respectively.

Since the titanium oxide hydrates and PVAI absorb only in the UV, any breakdown of the polymer or loss of inorganic species would primarily impact this part of the spectrum. It is clear here that the absorbance is constant with annealing temperature for each hybrid composition. Since absorbance is a measurement dependent on the volume, or thickness, it always probes total material content. It should stay constant when the species are unchanged. However, any significant loss of titanium or polymer degradation would cause variations. From Figure 4.17.b, it confirms that, despite the change in thickness, the absorbing components of the material are still equally present and no degradation occurs from the absence of extra absorption bands elsewhere in the spectra.

It is important to note that this study would be difficult from a thickness independent property, such as absorption, since this last one is expected to increase with refractive index, as stated by the Kramers-Kronig relations. As shown previously, the index of refraction varies with temperature, therefore, making the analysis complicated by this way.

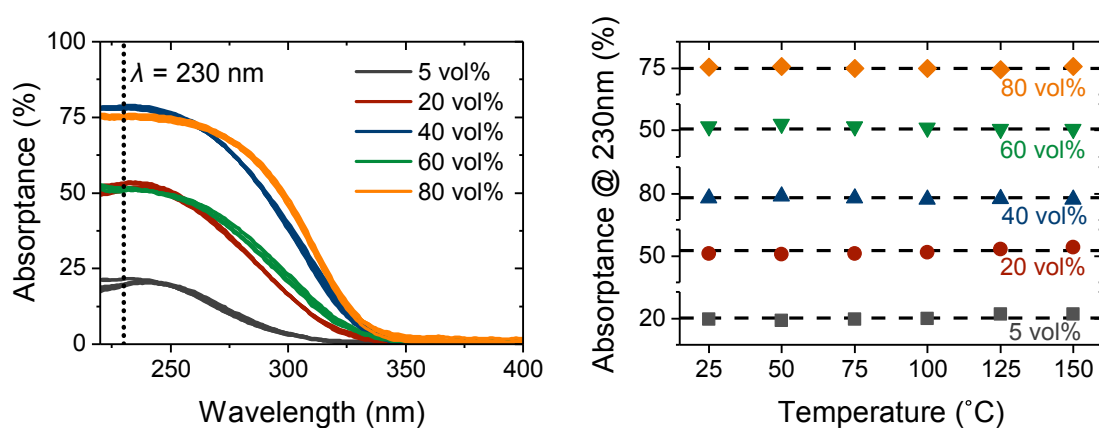


Figure 4.17: Absorbance of hybrid thin-films on fused silica as a function of annealing temperature. (a) shows all superposed curves for each hybrid formulation. (b) reports the absorbance at $\lambda = 230$ nm. All concentrations absorb in UV due to TiOxH and PVAI. Despite the change in thickness, absorbance is constant, confirming that none of the major components change with heating.

4.4 Conclusion and Outlook

To summarise, these results demonstrate the superior quality of the PVAI/TiOxH hybrid made via the one-pot synthesis. The absence of particles, crystalline or amorphous, was confirmed thanks to ultra-high resolution electron microscopy for all concentrations but the 80 vol% hybrid. Nevertheless, even in this case of extremely high titanium content, the diameter of the anatase particles is constrained under 5 nm thanks to the chemical and physical interactions with the polymer matrix. Moreover, elemental mappings established the remarkable uniformity of the dispersion in the materials but also across a thin-film cross-section.

This unique molecular hybrid allows high inorganic contents while leading to high refractive indices and excellent transparency. The refraction of the material is tunable by both the formulation and the annealing temperature, giving access to a valuable range from 1.5 to more than 2. Post-deposition curing indeed increases the refractive index by pushing toward more condensation of hydrolysed species and a denser film. On the other hand, the low optical losses are made possible by the perfect molecular dispersion, the low absorption and the extremely smooth surface and interfaces.

In regards to the materials reported in the literature so far and to the best of our knowledge, this hybrid exhibits properties significantly superior to most of the polymer hybrids, as discussed in part 2.2.2. Adding the relatively simple synthesis and its intrinsic cross-linking after drying, the PVAI/TiOxH hybrid is a perfect candidate for integrated optics. With the aim of environmentally appealing, printable, low-cost, light-weight and flexible devices, a few solution-processed optical applications will be demonstrated with this materials in the following chapters.

4.5 References

1. Russo, M., Campoy-Quiles, M., Lacharmoise, P., Ferenczi, T. A. M., Garriga, M., Caseri, W. R. & Stingelin, N. One-Pot Synthesis of Polymer/Inorganic Hybrids: Toward Readily Accessible, Low-Loss, and Highly Tunable Refractive Index Materials and Patterns. *Journal of Polymer Science Part B: Polymer Physics* **50**, 65–74 (2012).
2. Strang, A. *Organic/Inorganic Hybrid Materials for Solution-Processed Photonic Applications* Ph.D. (Imperial College London, 2015).
3. Votta, I. *Titanium-Oxide-Hydrates Based Organic/Inorganic Molecular Hybrids Produced via Sol-Gel Processing* Ph.D. (Imperial College London, 2017).
4. Russo, M. *Titanium Oxide Hydrates: Optical Properties and Applications* Ph.D. (Queen Mary University of London, 2010).
5. Caseri, W. Nanocomposites of Polymers and Metals or Semiconductors: Historical Background and Optical Properties. *Macromolecular Rapid Communications* **21**, 705–722 (2000).
6. Caseri, W. R. Nanocomposites of Polymers and Inorganic Particles: Preparation, Structure and Properties. *Materials Science and Technology* **22**, 807–817 (2006).
7. Lü, C. & Yang, B. High Refractive Index Organic–Inorganic Nanocomposites: Design, Synthesis and Application. *Journal of Materials Chemistry* **19**, 2884 (2009).
8. Diebold, U. The Surface Science of Titanium Dioxide. *Surface Science Reports* **48**, 53–229 (2003).
9. Rehan, M., Lai, X. & M. Kale, G. Hydrothermal Synthesis of Titanium Dioxide Nanoparticles Studied Employing in Situ Energy Dispersive X-Ray Diffraction. *CrystEngComm* **13**, 3725–3732 (2011).
10. Ovenstone, J. & Yanagisawa, K. Effect of Hydrothermal Treatment of Amorphous Titania on the Phase Change from Anatase to Rutile during Calcination. *Chemistry of Materials* **11**, 2770–2774 (1999).
11. Nussbaumer, R. J., Caseri, W. R., Smith, P. & Tervoort, T. Polymer-TiO₂ Nanocomposites: A Route Towards Visually Transparent Broadband UV Filters and High Refractive Index Materials. *Macromolecular Materials and Engineering* **288**, 44–49 (2003).

12. Boyd, R. W., Gehr, R. J., Fischer, G. L. & Sipe, J. E. Nonlinear Optical Properties of Nanocomposite Materials. *Pure and Applied Optics: Journal of the European Optical Society Part A* **5**, 505 (1996).
13. Choy, T. C. *Effective Medium Theory: Principles and Applications* 257 pp. (Oxford University Press, 2015).
14. Hecht, E. *Optics* 698 pp. (Addison-Wesley, 2002).
15. Lucarini, V., Saarinen, J. J., Peiponen, K.-E. & Vartiainen, E. M. *Kramers-Kronig Relations in Optical Materials Research* (Springer-Verlag, Berlin Heidelberg, 2005).
16. Sultanova, N., Kasarova, S. & Nikolov, I. Dispersion Properties of Optical Polymers. *Acta Physica Polonica-Series A General Physics* **116**, 585 (2009).
17. Tien, P. K. Light Waves in Thin Films and Integrated Optics. *Applied Optics* **10**, 2395–2413 (1971).
18. Duparré, A., Ferre-Borrull, J., Gliech, S., Notni, G., Steinert, J. & Bennett, J. M. Surface Characterization Techniques for Determining the Root-Mean-Square Roughness and Power Spectral Densities of Optical Components. *Applied Optics* **41**, 154–171 (2002).
19. Webb, H. K., Truong, V. K., Hasan, J., Fluke, C., Crawford, R. J. & Ivanova, E. P. Roughness Parameters for Standard Description of Surface Nanoarchitecture. *Scanning* **34**, 257–263 (2012).
20. Kim, D. J., Hahn, S. H., Oh, S. H. & Kim, E. J. Influence of Calcination Temperature on Structural and Optical Properties of TiO₂ Thin Films Prepared by Sol–Gel Dip Coating. *Materials Letters* **57**, 355–360 (2002).

5 | Fast thermal patterning of refractive indices

Although printed integrated optics have seen increasing interest thanks to the development of optical polymers and polymer hybrids, they often require complex processing or exhibit limited refractive index and versatility.¹⁻⁷ As discussed in Section 2.3.1, spatial modulation of the optical properties can lead to advanced applications such as planar waveguides, lenses, demultiplexers or holographic data storage.⁸⁻¹⁰ This chapter builds on the work carried out during the Master of Research by S. Bachevillier to further explore the potential of the PVAI/titanium oxide hydrate hybrid for local refractive index patterning.¹¹

5.1 Background

The lack of functional materials generally limits the development of refractive index patterning. Planar lenses are often based on liquid gradient index^{10,12} while ion beam implantation appears to be the main technique to produce planar waveguides.¹³⁻¹⁵ Another way to have good control on spatial refractive modulation is the use of graded photonic crystals to bend light.¹⁶⁻¹⁸ However, having access to an extended range of refractive indices which can be precisely modulated is extremely challenging for the materials research community. Solution-processed materials are particularly attractive to reduce cost and adapt integrated optics on flexible substrates, yet, their post-deposition tuning is quite restricted. Some polymers can show thermo-optic coefficients (TOCs) between -1×10^{-4} to $-3 \times 10^{-4} \text{ K}^{-1}$ but this does not allow neither permanent spatial patterning, nor a large change in optical properties.^{19,20} Photobleaching of dye-doped polymers with lasers or UV light has also been reported for polymer films.²¹⁻²³ Nevertheless,

refractive indices can be switched only between two distinct values, within a narrow range and toward lower index.

The possibility to locally pattern the refractive index of the PVAI/TiO_xH hybrid was previously demonstrated by Russo et al.²⁴ Moreover, a time-resolved annealing study was later performed to show that the hybrid was able to respond to thermal stress and stabilise only after 5 to 10 seconds, independently of the concentration or the applied temperature.¹¹ This could allow the fabrication of planar optical waveguides with different index contrasts. As shown by the finite-element modelling of the zero order modes in Figure 5.1, a more substantial refractive index contrast improves the localisation of light within the core. In this case, index tunability not only controls the number of modes and modal field profiles, but also permits wavelength specific design.*

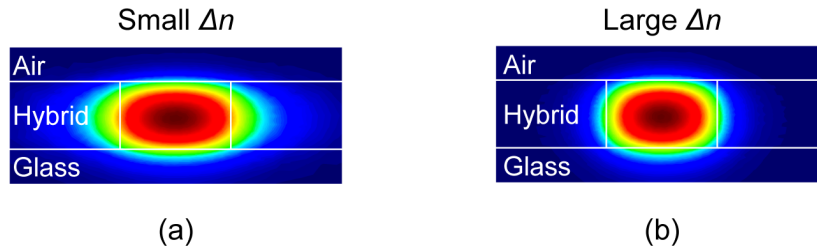


Figure 5.1: Finite-element modellings of patterned planar waveguides show improvement of energy localisation offered by higher refractive index contrast (b). The central section was modelled with an index difference of +0.05 for the small Δn case and +0.1 for the large Δn modelling. Calculations performed by H.K. Yuan.

*Thank you to Kevin (Hua-Kang) Yuan, Department of Physics, Imperial College London, for the finite-element method calculations.

5.2 Results and Discussion

As shown in Figure 5.1, the refractive index patterning of the hybrid can allow a direct control of the light flow. In this chapter, the concentration used was 60 vol% formulated with 2 M TiOxH solution and 40 g L⁻¹ PVAI solution in water. Films of a few hundreds of nanometres were spin-coated and aged in a vacuum chamber for about 5 days for good stabilisation.²⁵ The aim here is to characterise the thermal response of the hybrid versus time and demonstrate the potential planar devices.

5.2.1 *In situ* annealing of hybrid

In previous works related with the PVAI/TiOxH hybrid, annealing time of 15 minutes, sometimes in humid environment, were done to alter its optical properties.^{24–26} The two main drawbacks of this method were the potential degradation when the material was exposed to 150 °C for more than 10 minutes and the impossibility to locally apply the heat. Furthermore, the optical characterisation was carried out by standard UV-vis spectroscopy, limiting the tracking of the material change during external stress. As a result, an *in situ* spectroscopy, described in part 3.3.2, was set up. It enabled the capture and analysis of transmittance or reflectance spectra as frequently as 30 ms. In order to produce complex structures, further experiments were ran using this technique.

As discussed in the previous Chapter 4, the change in refractive index is related to a contraction of the thin-film. To quantify the shrinkage independently of the initial thickness, a fractional contraction is introduced. The term one-dimensional is also used here to indicate the absence of lateral contraction and cracking of the film. Mechanical strains involved after a change larger than 30 % are believed to be absorbed by the plasticity of the polymer matrix, preventing the film from fracturing. Lateral contraction is also avoided thanks to good interactions between

glass substrate and hybrid via hydroxyl groups. It is defined as:

$$1D \text{ contraction}(\%) = 100 \times (d_0 - d)/d_0 \quad (5.1)$$

where d_0 and d are thicknesses of the film before and after annealing, respectively.

For the time-resolved measurements, a double optical cavity made of a silicon substrate with 1 μm of silicon oxide and the film on top was used. It increased the number of interference oscillations within the restricted wavelength range of the instrument. It also improved the thermal conduction between the hotplate and the coating and intensified the reflectivity reducing the signal-to-noise ratio. The measured response time was shown to be independent on the thickness of the oxide or the coating.¹¹

Firstly, a continuous calibration of the hybrid state as a function of temperature was required. A heating rate of 20 $^{\circ}\text{C min}^{-1}$ was applied and both one-dimensional contraction and refractive index were extracted from the reflectance measurements after fitting. Curves are plotted in Figure 5.2 and show shallower reaction before 40 $^{\circ}\text{C}$ and a slower change toward 150 $^{\circ}\text{C}$ as expected. In this thesis, no temperature higher than 150 $^{\circ}\text{C}$ were applied to the hybrid. After comparing with values in Section 4.3.1, indices at 150 $^{\circ}\text{C}$ are slightly lower than expected. The difference could be due to an inaccurate calibration of the microscope hotplate used in this study. Nevertheless, this does not impact the linear relationship between the change in index of refraction and the fractional contraction shown in the inset. This direct correlation is particularly interesting to back-calculate the refractive index when the thickness change is known or *vice versa*. It was put into practice in the following part 5.2.4.

A modulation as large as $\Delta n = +0.11$ over a 125 $^{\circ}\text{C}$ range was measured, almost 3 times larger than the best thermo-optic polymers exhibiting changes of $\Delta n = -0.0375$ within the same range of temperature. As a comparison, a photobleached dye-doped polymer reported by Wolfe et al. showed an exclusively binary change of $\Delta n = -0.025$ and required a 90 seconds treatment.²³ Moreover, the PVAI/TiOxH hybrid exhibits an unusual positive modulation.

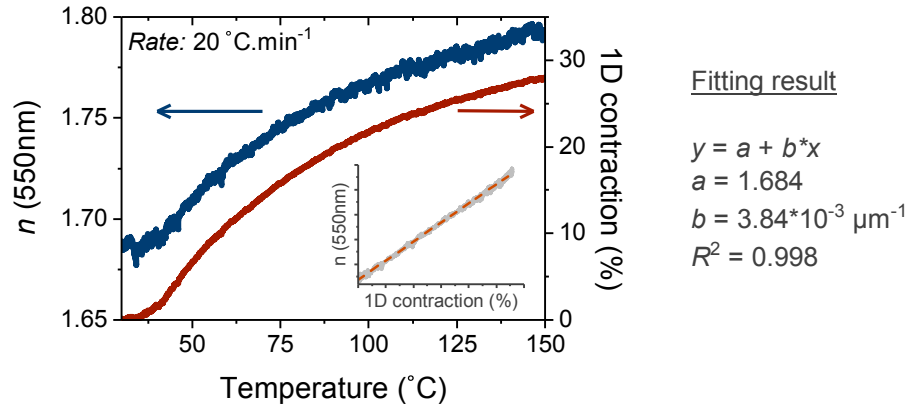


Figure 5.2: Refractive index and one-dimensional contraction as a function of temperature measured by continuous heating at 20 °C min⁻¹. The inset show the linear relation between both hybrid properties. The dashed orange line shows the good fit ($R^2 = 0.998$).

Unlike other materials used for refractive index patterning, the hybrid proved to be able to stabilise at any intermediate temperature and in an additive way. Once again, the time required to alter the properties is crucial for local patterning: the longer it is, the further the heat will spread, blurring any local patterning. The fact that the index and thickness change could follow a temperature gradient of 20 °C min⁻¹ was already a fair indication of its fast response time. To have a more precise idea of the optimum time to use for local heating, a hybrid film was quickly put on top of a hot-plate previously heated up and below the microscope objective while recording the reflectance. Like the time-resolved technique discussed above, Fabry-Pérot oscillations were captured and fitted using TMM. Refractive index and contraction as a function of time for three successive but distinct annealing temperatures (50, 100 and finally 150 °C) are shown in Figure 5.3.

Interestingly, both film properties plateaued after 5 seconds only, independently of the initial state and the temperature applied. Each time, it led to a different and irreversible equilibrium state which can only be “erased” with a higher temperature. The annealing procedure is therefore additive and can be applied for the fabrication of refractive index gradient. Since the initial values correspond precisely to the final ones of the previous measurement, it also confirms that the hybrid is stable in his final state, even after cooling. Unfortunately, indices here were

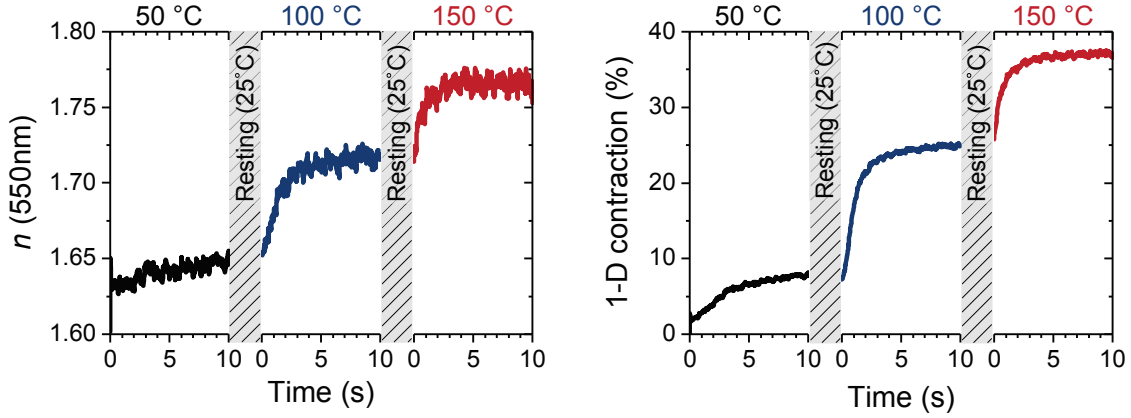


Figure 5.3: Time-resolved measurements of refractive index and thickness change for 3 different temperatures. The sample was briefly put on top of pre-heated microscope hot-plate. The time required by the coating to equilibrate at the new temperature appears to be around 5 ms. In-between each annealing, the sample was passively cooled down at room temperature. Values were extracted using TMM fitting.

slightly off-set with the steady-state measurements. Nevertheless, this does not impact the response time, which was the aim of this study. Furthermore, the required time underpinned during this experiment seems to be an over-estimation of the real one. The final part of this chapter indeed suggests that the phenomena might lie into a much shorter time when heat is applied directly to the film. In conclusion, the high-speed response allows index patterning with limitation of the lateral spread of heat.

5.2.2 Thermal stamping

The local patterning of refractive index of a solution-processed thin-film facilitates the single step fabrication of complex optical structures. Direct thermal printing has been developed in the seventies and is now widely used for receipt printing on thermochromic paper. It has the advantage of being relatively fast and economical. It consists of a thermal print head which changes the colour of the paper in the areas which are heated. A similar process could be adapted to other functional materials for the production of planar integrated optics such as waveguides and holographic storage.

First, a hybrid film was coated on a glass substrate and initially mapped using the same setup as the one used for the *in situ* study (see experimental Section 3.3.2). Figure 5.4 shows the good uniformity of the layer. A 2 mm wide stainless steel blade heated at 150 °C was put against the coating for 10 seconds on two areas. The sample was then quickly transferred to a cold metal plate to limit the spread of heat. A second top-view mapping was performed by taking a spectrum every millimetre. The annealed pattern is clearly observable with both the refractive index increase and the thickness decrease. Between the two lines, the properties of the layer were not impacted by the patterning. Thus, this simple pattern paves the way toward planar waveguides and holographic storage (see Section 2.3).

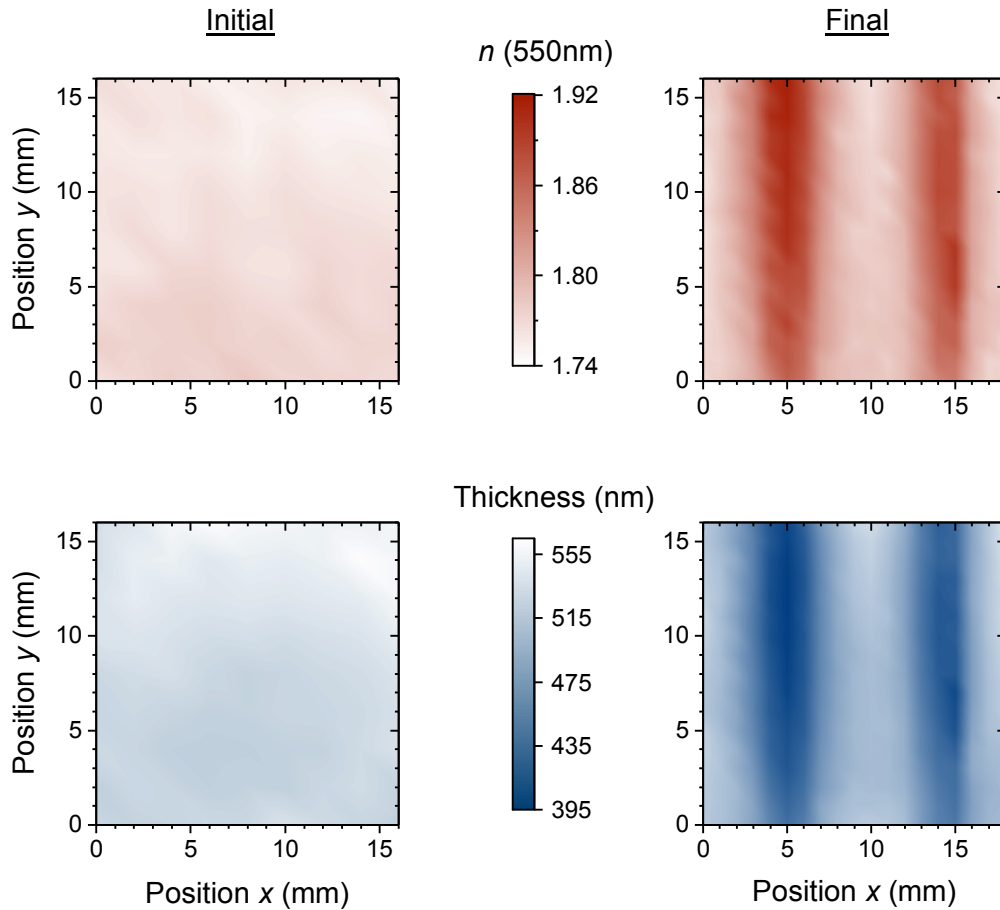


Figure 5.4: Patterning of hybrid coating with a single temperature (150 °C). A hot 2 mm wide stainless steel was put against the coating for 10 seconds. The local increase in refractive index (top panels) can be applied for planar waveguides and holographic storage. Mapping was performed at every millimetre before and after the thermal stamping. Values were extracted using TMM.

5.2.3 Multiple coplanar refractive indices

As established previously, the PVAI/TiO_xH hybrid gives an unique access to any indices within a range. If multiple states can be produced on a single film at the same time, it would also add another degree of freedom for the design of advanced optics. Figure 5.5 shows a succession of thermal stamping at different temperatures on different areas. Moreover, each time one quarter was 'erased' by the following thermal treatment, proving the cumulative aspect. The stamp was left in contact with the coating for about 5 seconds each time. Figure 5.6 displays a top view mapping of the 4-time annealed hybrid film. Four areas with different refractive indices can be observed. At the same time, a linear graded index of with $\Delta n = 0.05$ was created and plotted in Figure 5.6.b, corresponding to the grey dashed line in Figure 5.6.a.

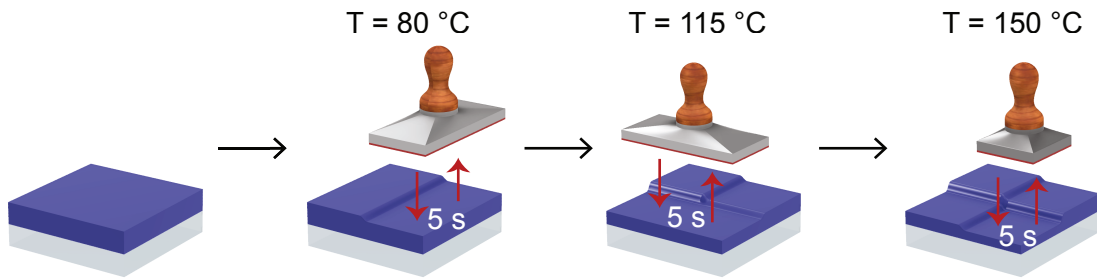


Figure 5.5: Successive thermal stamping of a thin-film.

As a result, combining thermal stamping with the polymer hybrid allows the fabrication of spatial GI which is generally problematic. Furthermore, to the best of our knowledge, this is the first demonstration of the production of multiple coplanar indices without using dopant vacuum evaporation.¹⁵ It demonstrates a straightforward and high-speed control over the refractive index contrast of the pattern, which is interesting for several applications as previously shown (see Figure 2.7 and 5.1).

This feature also gives the possibility to choose at which minimum temperature the materials can be used in a device. For example, it could be required to have a device stable at any temperature below 100 °C, thus, an initial treatment would be applied at this particular temperature before making the patterning.

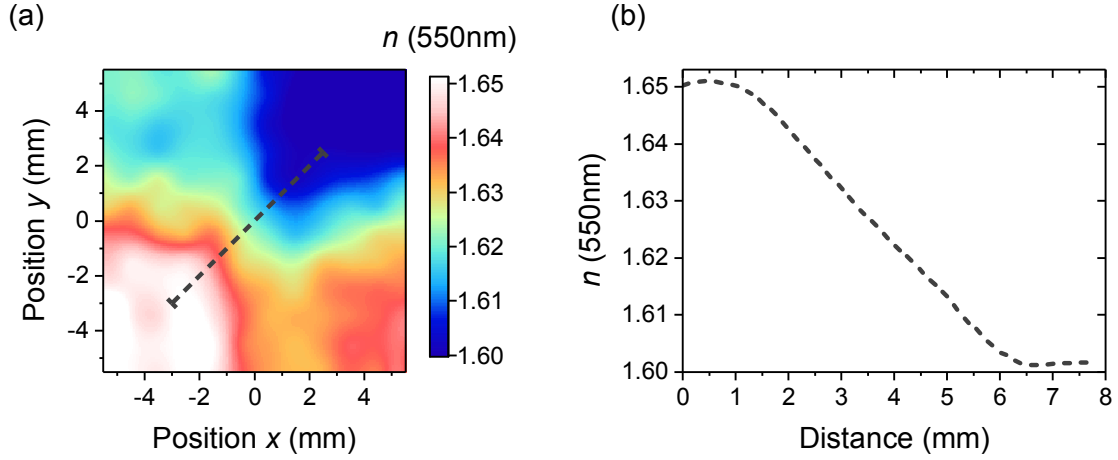


Figure 5.6: Four areas of an hybrid film were thermally stamped at different temperatures, resulting in 4 distinct refractive indices (a). The process is displayed in Figure 5.5. A cut (grey dashed line) shows the possibility to create refractive index gradient thanks to hot stamping. The corresponding data is shown in (b). Mapping was performed at every millimetre and analysed by TMM.

Following the demonstration of waveguides (Figure 5.4) and multiple coplanar refractive indices (Figure 5.6), a more complex structure was fabricated. First, a rectangular area was stamped with a 5 mm wide metal block at 100°C . Consecutively, a fine 2 mm blade heated at 150°C was applied on top. Initial, intermediate and final top view mappings are shown in Figure 5.7. The final structure can be thought as a focusing funnel (yellow region) for a planar waveguide (red line) where the light is coupled-in from the side of the film.

Figure 5.8.a is an example of spectra captured during the mapping of the final structure at 3 different positions, shown in Figure 5.8.b. Each spectrum corresponds to a region annealed at a different temperature. As expected from the optical interferences, oscillations shift to the shorter wavelengths and become deeper with increasing the temperature. Figure 5.8.b also displays the measurement positions of the spectra during the mapping of the sample.

To conclude, refractive index patterning was demonstrated in a few situations with one or multiple temperatures. It enables the fabrication of advanced planar structures which could be appealing for adequate compatibility with on-chip optical devices. Moreover, a large and linear GI was fabricated with the straightforward thermal stamping, opening the way for the use of the PVAI/TiOxH hybrid in many optical components.

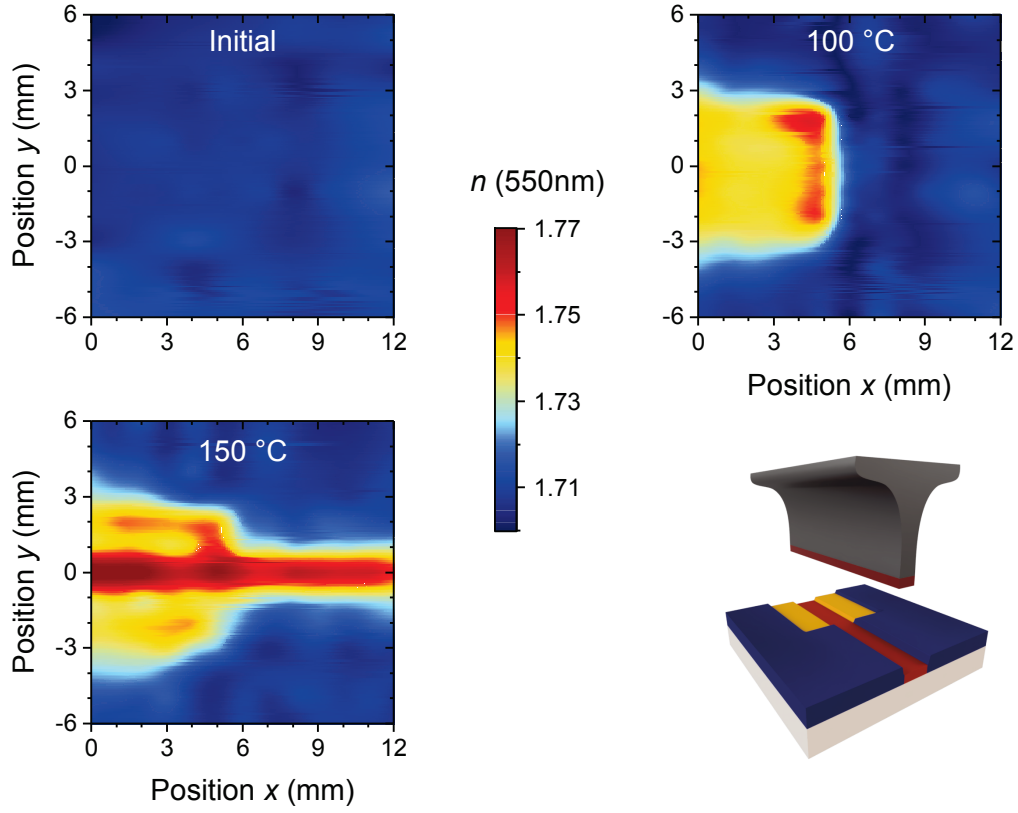


Figure 5.7: Fabrication of a planar waveguide with an additional coupling structure using thermal stamping. Mappings show initial, intermediate (100 °C) and final (150 °C) patternings. The highest refractive index in the core of the waveguide is observed in red. Spectra were measured every millimetres and fitted by TMM.

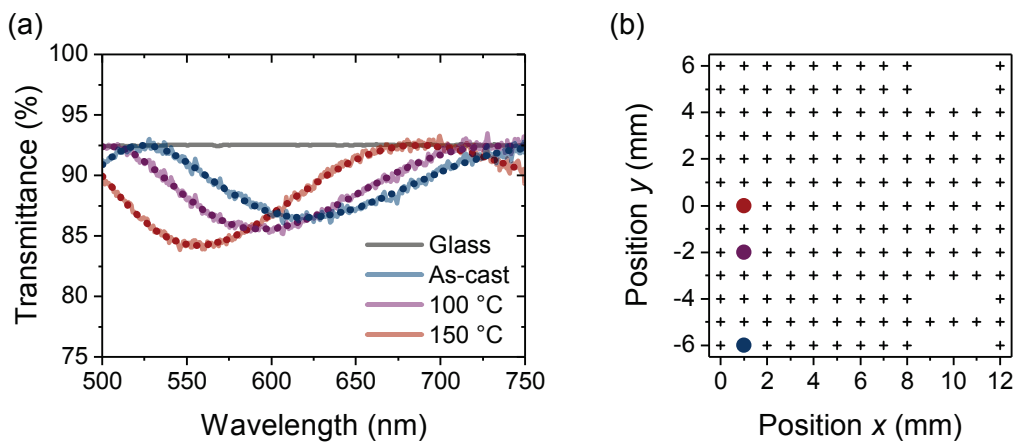


Figure 5.8: (a) Transmittance spectra (solid lines) measured by the microscope embedded setup and fitted by TMM (dotted lines). Those measurements were taken at the positions shown in (b) by the coloured dots. Crosses correspond to all the recorded and analysed spectra for the mapping.

5.2.4 Patterning by microcontact photothermal-annealing

The major drawback of temperature-based processing is the inherent spread of heat, limiting the sharpness of the features. Moreover, the uniform contact between the metallic stamps and the coating is delicate and can induce scratches.

Looking at the literature, there has been some recent research on techniques to efficiently annealed materials using very short times. For example, sol-gel metal oxides, particularly attractive for optoelectronic applications, require long and high annealing temperatures. Therefore, considerable effort has focused on alternative thermal method such as scanning thermal lithography,²⁷ direct light exposure through mask,^{28–30} laser annealing^{31,32} or high power xenon flash lamps.^{33–36} However, these techniques often suffer from slow processing, the direct use of deep-UV light which could degrade materials or the restricted need of an absorbing layer in order to generate heat. Considering the optical context of this thesis, having an absorbing material in contact with the hybrid was not satisfying.

Consequently, a new process called microcontact photothermal-annealing (μ CPA) was developed based on pulsed white light and metal-coated poly(dimethylsiloxane) (PDMS) stamp. This type of mould, inspired by the microcontact printing (μ CP) technique,³⁷ has been used before to create local heating by a quick transfer of a pre-heated PDMS structure (similarly to the thermal stamping method) or by applying an electrical current through the metal.^{23,38} Conversely, the use of a highly pulsed light to heat-up the stamp would significantly accelerate and simplify these processes, making it more attractive for inexpensive manufacturing and thermally sensitive substrate materials.³⁶

In this experiment, a 100 nm aluminium film was deposited on a 2 mm thick PDMS structure and brought into contact with the coating, in a similar way as μ CP. The softness of the PDMS allowed uniform contact with the sample without scratching. The system was then flashed with a high power white light using a 4803CX LV power supply and 105 CC Light Unit, 2 Cable from Speedotrom. Photons were absorbed by the metal and converted into heat which was instantaneously conducted to the hybrid film only where direct contact was possible. When

not in direct contact (like on the glass slide support), thermal radiation from the aluminium film was not strong enough to anneal the material. However, the presence of the metal all over the reusable stamp blocked the strong UV radiation of the pulsed light and protected the hybrid coating from degradation. The whole process is shown in Figure 5.9. To demonstrate the potential of this technique a channel was fabricated by using 10 flashes of 1 ms with a bulb recharging time of about 10 s.

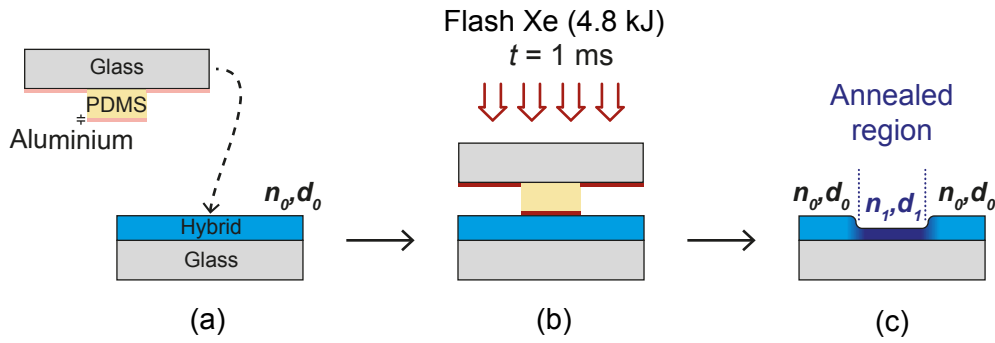


Figure 5.9: μ -contact photothermal-annealing (μ CPA) of a hybrid thin-film using a aluminium-coated PDMS stamp and a highly pulsed xenon white light. (a) The aluminium film is brought into contact with the coating. (b) The stamp is flashed with a power of 4.8 kJ and a pulse length of 1 ms. The metal absorbs light, converted to heat and conducted to the hybrid. (c) The stamp is removed and leaves the treated area with a higher refractive index and local contraction.

The optical characterisation of a thin-film exhibiting a large change in refractive index over a small area is challenging and would often result in the averaging of the output signal. Therefore, the analysis was performed on the correlated one-dimensional contraction which is simpler to probe. The edge of channel (inset, Figure 5.10) was scanned by a surface profilometre (model Dektak 3) and a thickness change of about 15 % over 100 μm was measured (top panel of Figure 5.10). Using the linear relationship between the refractive index and the contraction discussed previously (see Figure 5.2, inset), it was possible to back-calculate the optical property of the hybrid. Thus, a change from 1.675 to 1.730 ($\Delta n = +0.055$) was deduced. As a result, it seems that the hybrid experienced a temperature of about 70 $^{\circ}\text{C}$.

The sharper and smaller features achievable with this method could be used to produce even more complex photonic structures such as planar photonic crystal or holographic diffraction gratings based on index change only. μ CPA is a versatile technique where different parameters

can be easily tuned, such as the shape of the PDMS mould, the number of flashes, the thickness of the metallic layer or the use of other metals with a different light absorption spectrum. This indirect high-speed annealing, with the high adaptability of PDMS structures, shows great potential for rapid and scalable manufacturing not only for refractive index patterning but also for the fabrication of metal-oxide-based devices requiring high and rapid local heating.

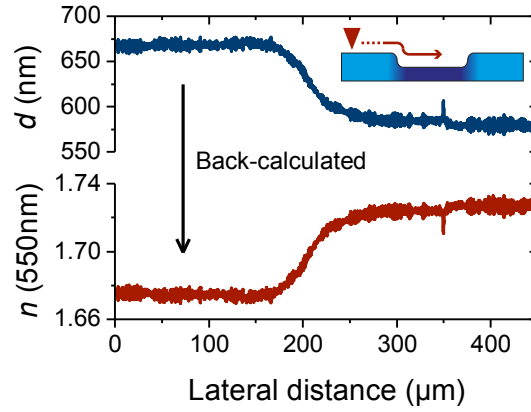


Figure 5.10: Patterning by μ CPA of a hybrid thin-film after 10 flashes. Thickness was measured by surface profilometry and used to back-calculate the spatial refractive index via the relationship between the two. The parameter of the equation applied here can be found in Figure 5.2. A sharp Δn of +0.055 over only 100 μm was calculated.

5.3 Conclusions and Outlook

To conclude, we presented the straightforward production of multiple coplanar refractive indices and large gradient on a single thin-film. After the time-resolved study of the thermal response of a PVAI/TiO_xH hybrid, it was shown that only 5 seconds was enough to pattern its refractive index independently of the temperature or the initial state. Each temperature led to different equilibrium states allowing an additive and grey-scale index patterning. This was put into practice with the production of complex multilevel patterns by thermal stamping. The low-cost and solution processability added to the simple fabrication shows great promise for the fabrication of integrated optics on-chip. The readily access to high and tunable refractive index contrasts could lead to the development of more complex structures. Moreover, sharp micro-patterning, crucial in many fields such as photonics, electronics and advanced microstructures, was demonstrated with the use of a novel μ CPA. The sub-second time required is ideal for fast manufacturing and thermally sensitive substrates such as plastic.

5.4 References

1. Lü, C. & Yang, B. High Refractive Index Organic–Inorganic Nanocomposites: Design, Synthesis and Application. *Journal of Materials Chemistry* **19**, 2884 (2009).
2. Biron, M. High Refractive Index Polymers. *Popular Plastics & Packaging* **55**, 49–53 (2010).
3. Hanemann, T. & Szabó, D. V. Polymer-Nanoparticle Composites: From Synthesis to Modern Applications. *Materials* **3**, 3468–3517 (2010).
4. Cheng, Y., Lu, C. & Yang, B. A Review on High Refractive Index Nanocomposites for Optical Applications. *Recent Patents on Materials Science* **4**, 15–27 (2011).
5. Bettotti, P. Hybrid Materials for Integrated Photonics. *Advances in Optics* **2014**, 891395 (2014).
6. Higashihara, T. & Ueda, M. Recent Progress in High Refractive Index Polymers. *Macromolecules* **48**, 1915–1929 (2015).
7. Badur, T., Dams, C. & Hampp, N. High Refractive Index Polymers by Design. *Macromolecules* **51**, 4220–4228 (2018).
8. Salameh, H. A. B. & Irshid, M. I. Wavelength-Division Demultiplexing Using Graded-Index Planar Structures. *Journal of Lightwave Technology* **24**, 2401–2408 (2006).
9. Del Monte, F., Martínez, O., Rodrigo, J. A., Calvo, M. L. & Cheben, P. A Volume Holographic Sol-Gel Material with Large Enhancement of Dynamic Range by Incorporation of High Refractive Index Species. *Advanced Materials* **18**, 2014–2017 (2006).
10. Mao, X., Lin, S.-C. S., Lapsley, M. I., Shi, J., Juluri, B. K. & Huang, T. J. Tunable Liquid Gradient Refractive Index Lens with Two Degrees of Freedom. *Lab on a Chip* **9**, 2050–2058 (2009).
11. Bachevillier, S. *Tunable High Refractive Index Hybrid for Solution-Processed Light Management Devices: Time-Resolved Annealing Study by in Situ Spectroscopy* M.Res (Imperial College London, 2015).
12. Huang, H., Mao, X., Lin, S.-C. S., Kiraly, B., Huang, Y. & Huang, T. J. Tunable Two-Dimensional Liquid Gradient Refractive Index (L-GRIN) Lens for Variable Light Focusing. *Lab on a Chip* **10**, 2387–2393 (2010).
13. Hong, W., Woo, H.-J., Choi, H.-W., Kim, Y.-S. & Kim, G.-d. Optical Property Modification of PMMA by Ion-Beam Implantation. *Applied Surface Science* **169-170**, 428–432 (2001).

14. Zakery, A. & Elliott, S. R. Optical Properties and Applications of Chalcogenide Glasses: A Review. *Journal of Non-Crystalline Solids* **330**, 1–12 (2003).
15. Tervonen, A., Honkanen, S. K. & West, B. R. Ion-Exchanged Glass Waveguide Technology: A Review. *Optical Engineering* **50**, 071107 (2011).
16. Joannopoulos, J. D., Johnson, S. G., Winn, J. N. & Meade, R. D. *Photonic Crystals: Molding the Flow of Light, Second Edition* 305 pp. (Princeton University Press, 2011).
17. Centeno, E., Cassagne, D. & Albert, J.-P. Mirage and Superbending Effect in Two-Dimensional Graded Photonic Crystals. *Physical Review B* **73**, 235119 (2006).
18. Kurt, H. & Citrin, D. S. Graded Index Photonic Crystals. *Optics Express* **15**, 1240–1253 (2007).
19. Oh, M.-C., Chu, W.-S., Shin, J.-S., Kim, J.-W., Kim, K.-J., Seo, J.-K., Lee, H.-K., Noh, Y.-O. & Lee, H.-J. Polymeric Optical Waveguide Devices Exploiting Special Properties of Polymer Materials. *Optics Communications. Polymer Photonics and Its Applications* **362**, 3–12 (2016).
20. Zhang, Z. & Keil, N. Thermo-Optic Devices on Polymer Platform. *Optics Communications. Polymer Photonics and Its Applications* **362**, 101–114 (2016).
21. Nakanishi, M., Sugihara, O., Okamoto, N. & Hirota, K. Ultraviolet Photobleaching Process of Azo Dye Doped Polymer and Silica Films for Fabrication of Nonlinear Optical Waveguides. *Applied Optics* **37**, 1068 (1998).
22. Shibata, S., Sugihara, O., Che, Y., Fujimura, H., Egami, C. & Okamoto, N. Formation of Channel Waveguide with Grating in Polymer Films Based on Simultaneous Photobleaching and Embossing. *Optical Materials* **21**, 495–498 (2003).
23. Wolfe, D. B., Love, J. C., Gates, B. D., Whitesides, G. M., Conroy, R. S. & Prentiss, M. Fabrication of Planar Optical Waveguides by Electrical Microcontact Printing. *Applied Physics Letters* **84**, 1623–1625 (2004).
24. Russo, M., Campoy-Quiles, M., Lacharmoise, P., Ferenczi, T. A. M., Garriga, M., Caseri, W. R. & Stingelin, N. One-Pot Synthesis of Polymer/Inorganic Hybrids: Toward Readily Accessible, Low-Loss, and Highly Tunable Refractive Index Materials and Patterns. *Journal of Polymer Science Part B: Polymer Physics* **50**, 65–74 (2012).
25. Strang, A. *Organic/Inorganic Hybrid Materials for Solution-Processed Photonic Applications* Ph.D. (Imperial College London, 2015).
26. Votta, I. *Titanium-Oxide-Hydrates Based Organic/Inorganic Molecular Hybrids Produced via Sol-Gel Processing* Ph.D. (Imperial College London, 2017).

27. Shaw, J. E., Stavrinou, P. N. & Anthopoulos, T. D. On-Demand Patterning of Nanostructured Pentacene Transistors by Scanning Thermal Lithography. *Advanced Materials* **25**, 552–558 (2013).
28. Kang, D. J., Kim, W.-S., Bae, B.-S., Park, H. K. & Jung, B. H. Direct Photofabrication of Refractive-Index-Modulated Multimode Optical Waveguide Using Photosensitive Sol-Gel Hybrid Materials. *Applied Physics Letters* **87**, 221106 (2005).
29. Valouch, S., Sieber, H., Kettlitz, S., Eschenbaum, C., Hollenbach, U. & Lemmer, U. Direct Fabrication of PDMS Waveguides via Low-Cost DUV Irradiation for Optical Sensing. *Optics Express* **20**, 28855–28861 (2012).
30. Kim, Y.-H., Heo, J.-S., Kim, T.-H., Park, S., Yoon, M.-H., Kim, J., Oh, M. S., Yi, G.-R., Noh, Y.-Y. & Park, S. K. Flexible Metal-Oxide Devices Made by Room-Temperature Photochemical Activation of Sol–Gel Films. *Nature* **489**, 128–132 (2012).
31. Dellis, S., Isakov, I., Kalfagiannis, N., Tetzner, K., Anthopoulos, T. D. & Koutsogeorgis, D. C. Rapid Laser-Induced Photochemical Conversion of Sol–Gel Precursors to In₂O₃ Layers and Their Application in Thin-Film Transistors. *Journal of Materials Chemistry C* **5**, 3673–3677 (2017).
32. Kalfagiannis, N., Siozios, A., Bellas, D. V., Toliopoulos, D., Bowen, L., Pliatsikas, N., Cranton, W. M., Kosmidis, C., Koutsogeorgis, D. C., Lidorikis, E. & Patsalas, P. Selective Modification of Nanoparticle Arrays by Laser-Induced Self Assembly (MONA-LISA): Putting Control into Bottom-up Plasmonic Nanostructuring. *Nanoscale* **8**, 8236–8244 (2016).
33. Yoo, T.-H., Kwon, S.-J., Kim, H.-S., Hong, J.-M., Lim, J. A. & Song, Y.-W. Sub-Second Photo-Annealing of Solution-Processed Metal Oxide Thin-Film Transistors via Irradiation of Intensely Pulsed White Light. *RSC Advances* **4**, 19375–19379 (2014).
34. Lee, W. H., Lee, S. J., Lim, J. A. & Cho, J. H. Printed In-Ga-Zn-O Drop-Based Thin-Film Transistors Sintered Using Intensely Pulsed White Light. *RSC Advances* **5**, 78655–78659 (2015).
35. Kang, C., Kim, H., Oh, Y. W., Baek, K. H. & Do, L. M. High-Performance, Solution-Processed Indium-Oxide TFTs Using Rapid Flash Lamp Annealing. *IEEE Electron Device Letters* **37**, 595–598 (2016).
36. Tetzner, K., Lin, Y.-H., Regoutz, A., Seithkan, A., J. Payne, D. & D. Anthopoulos, T. Sub-Second Photonic Processing of Solution-Deposited Single Layer and Heterojunction Metal Oxide Thin-Film Transistors Using a High-Power Xenon Flash Lamp. *Journal of Materials Chemistry C* **5**, 11724–11732 (2017).

37. Xia, Y. & Whitesides, G. M. Soft Lithography. *Annual Review of Materials Science* **28**, 153–184 (1998).
38. Zhao, D., Duan, L., Xue, M., Ni, W. & Cao, T. Patterning of Electrostatic Charge on Electrets Using Hot Microcontact Printing. *Angewandte Chemie International Edition* **48**, 6699–6703 (2009).

6 | Solution-processed photonic reflectors

Thanks to their low absorption and their wavelength selectivity, DBRs have been applied in many applications. As explained in Section 2.3.3, perfect control over the thickness, refractive index and homogeneity is primordial to obtain high-quality devices. Therefore, the use of inorganics has been favoured for a long time. However, a new interest in soft materials photonic structures emerged thanks to their ease of production, potential low-cost and large-area manufacturing along with possible stimuli-responsive properties. Furthermore, this field has been fascinatingly influenced and inspired by physical colouration in natural structures.^{1–7} This study aims to develop a new material combination leading to printable, low-loss and highly reflective dielectrics mirrors taking advantage of the exceptional properties of the PVAI/TiOxH hybrid.

6.1 Background

Organic and hybrid dielectric mirrors can be applied for different purposes such as radiation control,^{8–10} higher efficiency in semi-transparent photovoltaics,^{11–14} organic lasers,^{15–17} and chemical, biological and thermal sensors.^{18–21} Polymer-based DBRs were reported in the late sixties by coextrusion of polystyrene and PMMA. However, 200 layers were required due to low refractive index contrast and the thickness control was challenging.^{22,23} This work was followed by Weber et al. in 2000, where a high-quality chirped free-standing mirror was extruded for the first time. High and broad reflectivity were achieved but again, due to the minor refractive index contrast, over 400 layers were needed.²⁴

The first solution-based DBR based on transparent oxides was demonstrated by using dip-coating of sol-gel solutions,⁸ yet, lower processing temperatures would be beneficial. In recent years, many academic groups reported spin-coated polymer-based mirrors^{15,16,25–31} or complex self-assembled block-copolymers which are generally more responsive to environmental stress,

thus, attractive for sensors.^{18,19,32–36} Inorganic/organic hybrids have also been recently more and more investigated since they can combine solution-processing and advantageous optical properties. In 2008, Druffel et al. managed to produce the first polymer-nanocomposite DBR. After spin-coating 15 layers, reflectance reached 95 % at $\lambda = 1060$ nm.³⁷ Since then, a few groups have been publishing one-dimensional photonic crystals based on hybrid materials with few layers and high reflectivity thanks to the large refractive index range available. Nevertheless, they often suffer from optical losses (scattering of particles and rough interfaces), poor control of the thicknesses or the need for long UV or temperature curing steps.^{21,37–44}

When selecting materials for multilayer photonic structures, the main characteristics are transparency, refractive index, ease of processing, cost, mechanical properties, solubility (solvent orthogonality or cross-linking) and safety. In this regards, the cross-linked PVAI/TiO_xH hybrid is perfectly adapted. It has been demonstrated that high-quality and strongly reflective mirrors can be produced when combined with the low-index fluorinated polymer poly[4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole-co-tetrafluoroethylene] (PFP) (Figure 6.1.a). This derivative of Teflon exhibits a remarkably low index of refraction ($n = 1.29$), however, its processability is extremely challenging, especially when combined with the water-based hybrid solution.^{39,45}

6.2 Results and Discussion

The first part of this chapter investigates the replacement of the low index layer for a simpler and more scalable fabrication of DBRs with the hybrid. Later, the outstanding versatility of the devices will be discussed.

6.2.1 A quest for low index materials

Many optical low refractive index materials are available, yet, the compatibility with the high-index solution usually limits the choice to only a few. Since a more substantial refractive index contrast leads to wider optical stopband and higher reflectance, the lowest index possible is expected. However, a compromise with the processing characteristics must be found. For example, the superhydrophobicity of the PFP made it highly sensitive to any dust or particles in the solution, thus, a clean room environment was needed for the fabrication. Moreover, it did not allow the use of titanium concentration higher than 60 vol%.⁴⁵ Finally, this polymer and the solvent used were relatively costly. Replacing this material by another one with a lower contact angle with water could considerably facilitate the coating. For a multilayer device, this material must also be highly transparent, insoluble in water and resistant to acid since hybrid solutions have $pH < 1$.

In this type of structure, optical thin-films must be remarkably uniform and smooth. As it happens, dip-coating offers excellent control over the thickness and allows the production of very smooth layers thanks to the slow speeds involved (see Chapter 3). Moreover, it is compatible with large-scale processing and limits the waste of materials, unlike spin-coating. Finally, it allows the simultaneous coating of both sides of the substrate which, in our case, increases the reflectivity of the sample by making two mirrors at a time.^{46–48}

Nevertheless, a consequent amount of preliminary work should be performed to obtain suitable conditions. When choosing the solvent, there is a compromise to find between low evaporation

rate leading to more homogeneous films and the longer drying time which can hugely increase the workflow. The evaporation rate, directly related to the vapour pressure, is primordial for good coating. For example, the use of a highly volatile solvent like tetrahydrofuran led to severely non-uniform films. Furthermore, the shape and the filling percentage of the solution tank play a considerable role by keeping more solvent vapour at the surface of the liquid phase when the tank is not filled up to the top for example. This strongly impacts the evaporation rate, thus the film properties. Bindini et al. have recently investigated these experimental details.⁴⁹

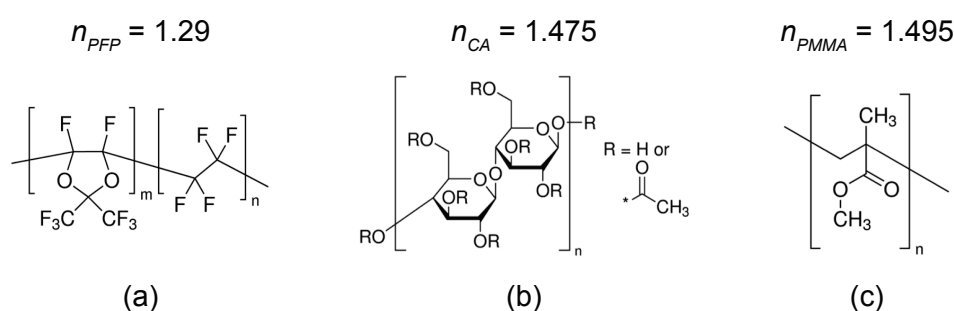


Figure 6.1: Chemical structures of low index PFP (a), CA (b) and PMMA (c). Refractive indices are reported for a wavelength of 600 nm.

Cellulose acetate

Cellulose acetate (CA), shown in Figure 6.1.b, is, for instance, an excellent optical material with a relatively low refractive index. The loss in index contrast compared to the use of PFP can be compensated by the remarkable wetting of the hybrid which allows the coating of more layers and the use of a higher titanium content (80 vol%). Many DBRs based on CA have been demonstrated in the literature.^{16,27,50–52} Other aspects of CA are perfectly relevant such as the relatively high glass transition temperature ($T_g \approx 180^\circ\text{C}$)⁵³ and its chemical resistivity, especially against acids as it is often used for drug enteric-resistive coatings.⁵⁴

CA (40 wt% acetyl - $M_n \approx 30\,000\text{ g mol}^{-1}$) and high boiling point 4-hydroxy-4-methylpentan-2-one (diacetone alcohol) were purchased from Sigma-Aldrich ($b_p = 166^\circ\text{C}$). Thin-films were deposited with a solution of 20 mg mL^{-1} and dipping speed between 5 and 20 mm min^{-1} . High-quality optical coatings were obtained and a dielectric mirror successfully produced with a high titanium content hybrid (80 vol%), as shown in Figure 6.2.a. A 150 nm wide stopband with a

reflectance as high as 90 % around $\lambda \approx 550$ nm was obtained after only 9 dips (two back-to-back 4.5-period DBRs). A 150 °C annealing step was performed after the deposition of the whole stack to increase the refractive index of the hybrid.

Despite the good optical response around the Bragg wavelength, there was a noticeable shift between the measured and modelled spectra (Figure 6.2.a). The primary cause was scattering from wrinkled surfaces in some areas of the sample, as observable in Figure 6.2.b. It happens that CA is not soluble in water but it is often used as membrane support which can swell when exposed to ionic liquid.⁵⁴ Several processing conditions were unsuccessfully tried to harden the CA layers like intermediate curing steps or vacuum annealing.

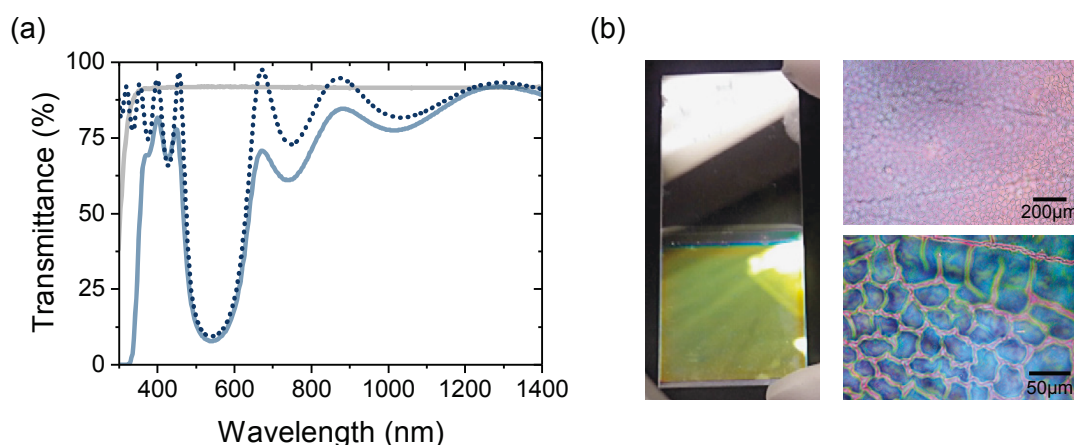


Figure 6.2: Dielectric mirror around $\lambda \approx 550$ nm produced from 80 vol% hybrid and CA. Thanks to the dip-coating method, two back-to-back 4.5-period DBRs were simultaneously fabricated. (a) shows the measured (solid line) and calculated (dotted line) transmittance spectra. (b) The sample looks high quality, however, significant wrinkling of layers was observed by optical microscopy, resulting in optical scattering.

Poly(methyl methacrylate)

PMMA (Figure 6.1.c) was identified as another alternative to replace PFP. It is already widely used in polymer optical fibres thanks to its excellent optical properties.⁵⁵ Moreover, it is insoluble in water and has a low contact angle with water (68°).⁵⁶ Good resistance against acids has also been reported.⁵⁷ Unfortunately, its refractive index ($n_{PMMA} = 1.50$) is considerably higher than the one of PFP. As mentioned previously, this can be compensated by better compatibility with a more concentrated hybrid and easier manufacturing for more layers or engineered

structures like chirping. The main drawback with PMMA is its relatively low glass transition temperature around $T_g \approx 100^\circ\text{C}$ which limits the annealing temperature of the device, capping the refractive index of the hybrid (see Chapter 4).⁵⁷

A low molecular weight PMMA ($M_n \approx 35\,000\text{ g mol}^{-1}$) was synthesised by Dean Carroll at the Department of Materials, Imperial College London by the easy to scale-up group transfer polymerisation which does not require any purification steps.^{58*} 40 and 60 mg mL⁻¹ solutions were prepared in butyl acetate purchased from Sigma-Aldrich which is a relatively high boiling point solvent ($b_p = 126^\circ\text{C}$) leading to uniform coatings.

The production of high-quality dielectric mirrors was possible using either spin-coating or dip-coating as discussed in the following sections. Low losses were achieved thanks to the absence of particles in the hybrid (see Chapter 4) and the highly transparent PMMA but also thanks to the exceptionally smooth interfaces between each layer.

6.2.2 Solution-processed DBRs

The material combination developed above has been thought for the possibility of using several processing methods: spin-coating and dip-coating of multilayers. They require drastically distinct film properties such as good wetting for the first one and good chemical resistance for the second one due to the long time spend in solution while dipping. Spin-coating is attractive for the fast fabrication of devices, however, dip-coating is more relevant for large-scale manufacturing.⁸

In the following studies, transmittance spectra are mainly used to analyse DBRs. The principal reason is that this method allows for simple normal incidence measurements and the spot size is considerably smaller than when reflectance measurements are taken (see Section 3.3.1). With the assumption that $A = 0$ for $\lambda > 400\text{ nm}$, the reflectance can be easily calculated using $R = 1 - T$ (Equation 2.8). In particular, it is worth noting that the TMM for multilayers does not include

*Thank you to Dean Carroll, Department of Materials, Imperial College London, for synthesising the PMMA.

an absorbance band in the UV which results in an apparent divergence between experimental and calculated spectra. Furthermore, in the calculated spectra plotted below, layers from one material are always assumed perfectly regular and without roughness. The impact of these defects were discussed more in depth in the experimental Section 3.3.4.

Figure 6.3 shows a green mirror produced by spin-coating. The 41 layers formed a square optical stopband in the transmittance spectrum, proof of high quality. The very sharp side oscillations are hardly measurable by UV-Vis spectroscopy due to the spectral broadening.⁵⁹ As a result, the modelled spectrum, like the one plotted in dotted line, does not match exactly with the device one. Nevertheless, it confirms the exceptional control over the thicknesses and the limited optical scattering from the materials and the interfaces. Table 6.1 reports the comparison between the initial device design and the calculated values after matching of the experimental data with TMM. Parameters are exceptionally close, confirming the refractive index and thickness calibrations and repeatability.

Table 6.1: Design parameters for a DBR centred at $\lambda_0 = 550$ nm and annealed at 100 °C using PMMA and 60 vol% hybrid. Measured parameters from a spin-coated device shown in Figure 6.3 are reported after TMM modelling of the transmittance spectrum.

<i>Design</i> $\lambda_0 = 550$ nm	n_{550nm}	d	nd/λ_0	
PMMA	1.50 ($n_a=1.49$ / $n_b=0.003$)	91.7 nm	0.25	
60 vol% hybrid (100 °C)	1.80 ($n_a=1.72$ / $n_b=0.025$)	76.3 nm	0.25	
<i>Fitting</i> $\lambda_0 = 554$ nm	n_{554nm}	d	nd/λ_0	<i>Speed</i>
PMMA	1.50 ($n_a=1.49$ / $n_b=0.003$)	92.3 nm	0.25	6000 rpm
60 vol% hybrid (100 °C)	1.80 ($n_a=1.72$ / $n_b=0.025$)	76.9 nm	0.25	4300 rpm

Figure 6.3.b displays the experimental spectrum against a logarithmic scale. The high number of periods used in this device resulted in a minimum transmittance lower than 1 %. It demonstrates the advantage of dielectric mirrors over metallic coatings which are broadband reflectors but with lower efficiency. For example, silver, which is often considered as the best metallic reflector, reflects only 96 % at 550 nm (see Figure 6.6). The sample is shown in inset against a white and a dark background. The reflectance appears fully green (bottom photograph) while

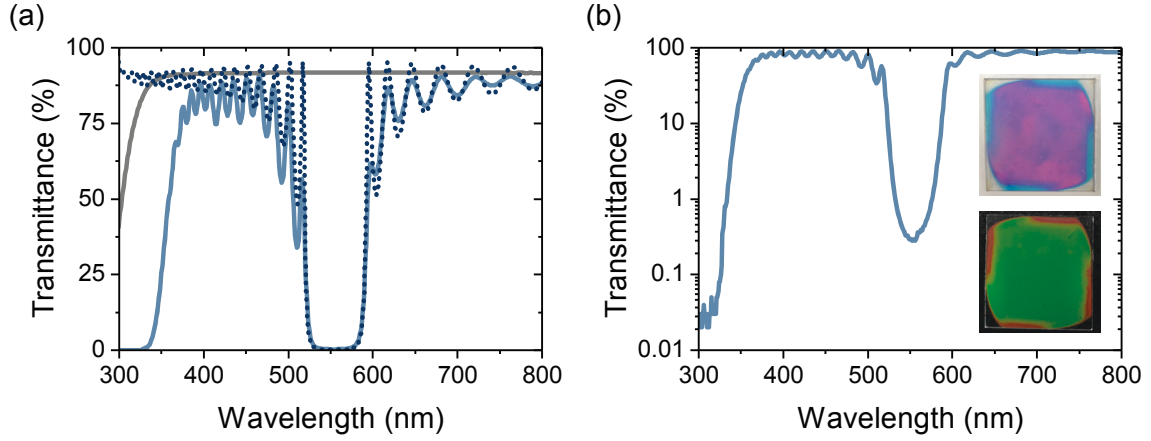


Figure 6.3: Spin-coated 41-layer DBR centred at $\lambda_0 = 550$ nm. 60 vol% hybrid and PMMA were combined and annealed at 100 °C. Calculated spectrum is plotted in blue dotted line over the experimental data which exhibits a transmittance as low as 0.3 % when plotted against a logarithmic scale (b). Photographs in inset show the visual appearance with white and dark backgrounds, confirming the green reflection and the complementary colours blue and red in transmission.

the transmitted colours, only blue and red, results in a purple appearance (top photograph). The homogeneity of the sample is also remarkable.

The high-quality DBR reported here confirms the compatibility of PMMA with the PVAI/TiOxH hybrid material. The adequate wetting allowed an easy spin-coating of the solutions and the deposition of a large number of layers, conversely to the use of fluorinated polymers. As expected the loss in refractive index contrast could be compensated by the deposition of a large number of layers. Furthermore, the interfaces between these materials are exceptionally smooth as discussed latter, reducing the potential effect of surface scattering (see Section 3.3.4).

6.2.3 Broadband metal-like reflectors

A quarter-wave stack enables high reflectance over a limited range which can sometimes limit the applications. For example, broadband reflectors are attractive for rear-view mirrors in the visible or heat-management in the infrared. Metallic coatings are the most popular options for full optical reflectance. Thanks to their continuous band of allowed energies, all incident radiation can be absorbed and immediately re-emitted with the same energy. This phenomenon causes the high reflection of metals for all energies below their plasma cut-off frequency.⁶⁰ Some metals such as gold, copper and silver, have unique electronic band structures which increase their absorption in specific parts of the spectrum. For example, gold absorbs some blue and green photons and appears yellow while copper absorption is even more shifted toward the green, thus reflects mainly orange and red light. As for silver, the energy at which the absorption occurs is in UV only, therefore keeping the metallic reflection.

Nevertheless, metallic coatings often suffer from the formation of oxides, poor adhesion and significant absorption compared to photonic structures as seen in the previous part. Dielectric reflectors are adequate candidates to achieve extended high-reflectance zone without some of the drawbacks of metals. Notably, they can be transparent to other wavelengths facilitating multifunctionalities like integrated infrared sensors for instance. The three main methods to broaden an optical band-gap are the staggering of quarter-wave stacks, the continuous chirping of the whole multilayer structure or the use of chaotic superlattices.^{61,62} The two last strategies are widely found in Nature to produce vibrant colours and reflections like some chrysalis, beetles and fishes.^{1,5,7,61,63–69}

As shown in the previous part, the replacement of PFP by PMMA greatly simplified the production of one-dimensional photonic crystals. The straightforward thickness control using spin-coating is also advantageous to make complex structures. Two different broadband mirrors were therefore designed; a silver-like and a gold-like which reflect all the visible spectrum and only from 500 nm, respectively. Each layer was tuned on a different Bragg wavelength λ_0 following a geometrical increase. The fabrication started with the thinnest layers (smallest λ_0) and required

71 and 51 layers for the silver and gold reflectors, respectively. All thicknesses are shown as a function of the layer number but also the Bragg wavelength λ_0 on the top axis in Figure 6.4. Details on the design and the fabrication can be found in Appendix B and Section 3.2.4.

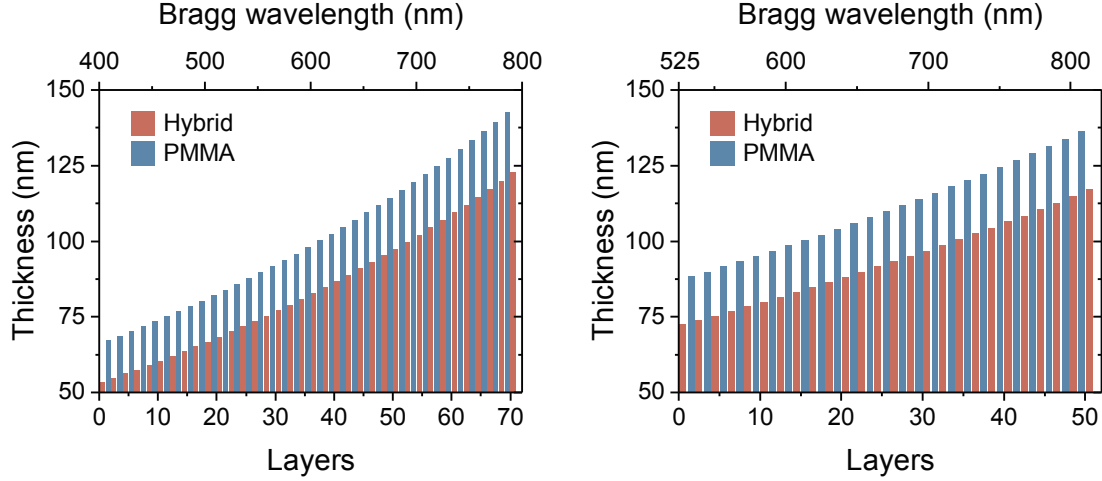


Figure 6.4: Structure of superlattices of the broadband metal-like reflectors based on the parameters given in Tables B.2 and B.3. The thicknesses of each layer along the stack and as a function of the Bragg wavelength λ_0 (top axis) are shown for the silver-like (left) and gold-like mirrors (right).

Figure 6.5 displays the progressive chirping effect on the transmittance of the samples. The addition of 5 periods increased the stopband by nearly 50 nm each time until it reached 750 nm, the end of the visible light spectrum. Figures 6.5.c and 6.5.d also shows the coating appearances as a function of the chirping, either in transmission (using white background) or in reflection (using black background). The first pictures are related to the tuning of the initial Bragg wavelengths. The silver-like sample started by reflecting the blue part of the spectrum, then green and red were progressively added while the gold-like device reflected green first and then moved to the red region. The complementary colours can be observed in transmittance too. For example, the silvery structures let through only long wavelengths after 51 layers, therefore looked red. The sample appeared completely colourless once all the wavelengths were more or less affected (white in reflection and black in transmission). Conversely, the gold-like device stayed transparent to the blue all along the fabrication. The orange and red were progressively reflected, thus, the transmission started from light purple to darker purple to deep blue.

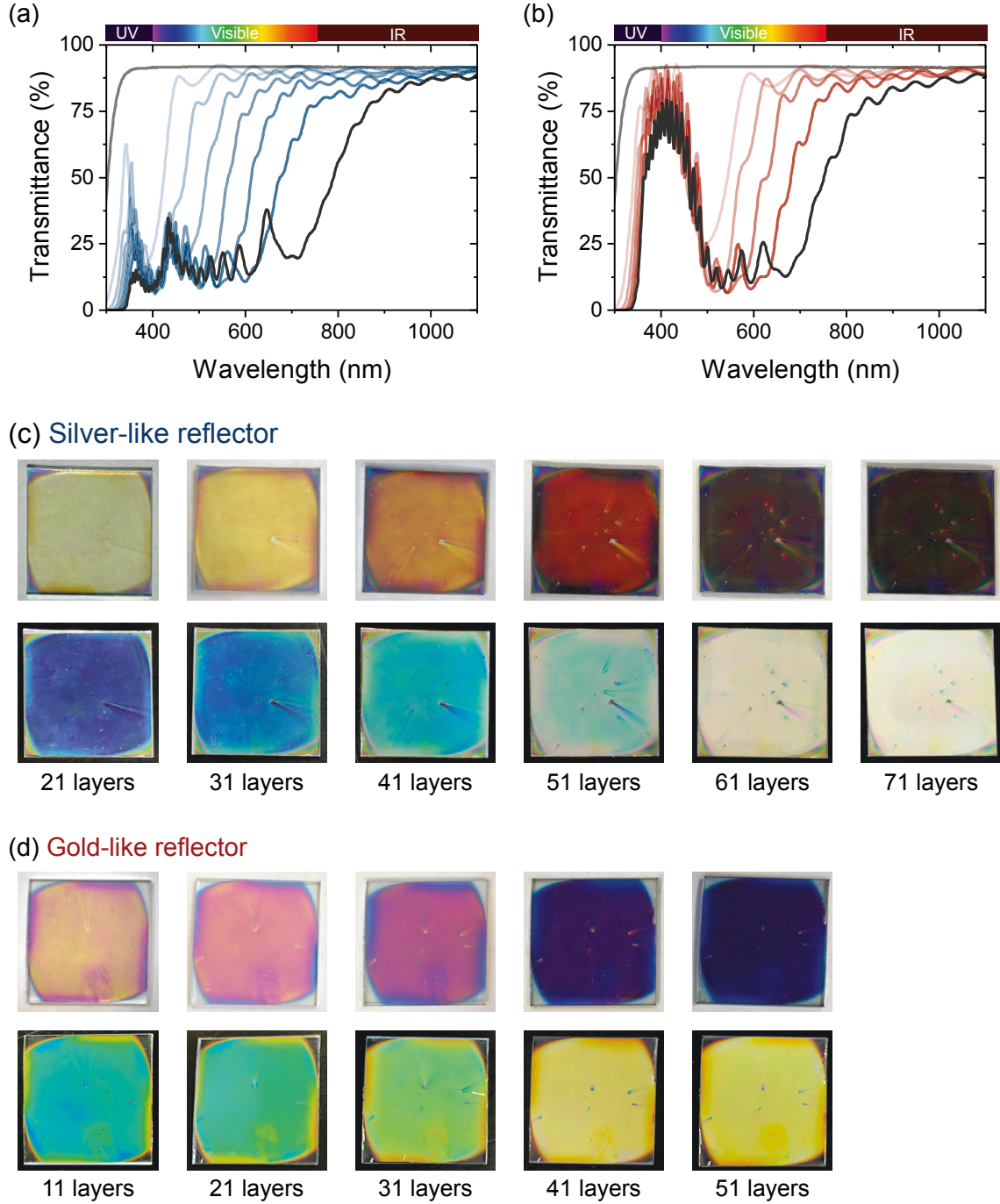


Figure 6.5: Chirping of one-dimensional photonic structures for broadband metal-like reflectors. 60 vol% hybrid and PMMA were combined and annealed at 100 °C. Transmittance spectra every 10 layers (11, 21, 31,...) are plotted in (a) and (b), from the lighter to the darker curve, for the silver and the gold-like mirrors, respectively. (c) and (d) show the devices at various stages of the fabrication. Transmission and reflection can be observed using white and black backgrounds behind samples, corresponding to the top and bottom rows of photographs, respectively.

For direct comparison, silver and gold reflectance spectra are plotted along with the chirped devices in Figure 6.6. The colourless appearance of metals such as silver was replicated by an overall reflection of 76 % in the visible. Conversely to silver, the photonic crystal is transparent to infrared with a transmittance of 88 % from 750 to 2500 nm. The gold-like sample reflects from 500 nm only with an average reflectance of 77 %. It is also fairly transmissive in the infrared (89 % from 750 to 2500 nm). By adding more layers and reducing the chirping common ratio, even higher reflectance could be achieved and the oscillations observed in Figure 6.6 removed while still being entirely transparent to other wavelengths. This type of structure is often referred as interference edge filter and extremely sharp steps can be made with advanced designs.⁶²

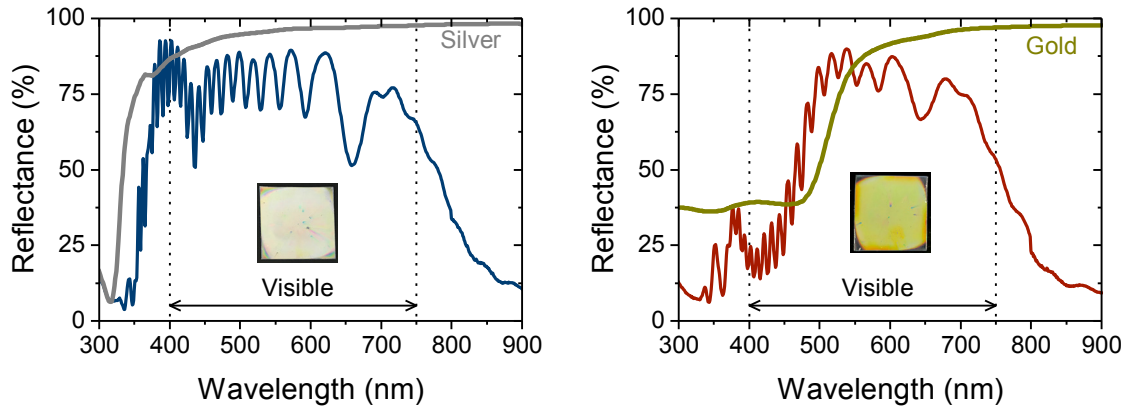


Figure 6.6: Reflectance spectra of chirped metal-like mirrors along with silver and gold spectra. The broadband reflector covering all the wavelengths appears colourless like silver while the gold-looking sample does not reflect the blue part of the visible spectrum, similar to gold. Metal spectra were calculated from their complex refractive indices.⁷⁰

6.2.4 Dip-coating of photonic mirrors

We have demonstrated the remarkable compatibility of the hybrid with PMMA which greatly facilitates the processing of multilayers devices. Spin-coating is, however, a relatively limited technique in term of upscaling and large-area manufacturing. As mentioned in Section 3.2.3, dip-coating has been used industrial for panes up to 3×4 m.⁸ This method can produced incredibly uniform coatings with high control over the thicknesses. Nevertheless, the impact of dust, particles or even bubbles present either in the solution or the atmosphere is extremely high. Yet, for better industrial compatibility, no clean-room environment was used in the following studies.

To first confirm the suitability of the material system for the scalable dip-coating, mirrors were initially fabricated on 1×3 in glass slides. That time, 80 vol% hybrid was used for DBRs centred around two different wavelengths to confirm the good control over the coating thicknesses. Spectra of 7.5-period DBRs at $\lambda_0 = 525$ nm and $\lambda_0 = 700$ nm are plotted in Figure 6.7 along with TMM calculated structures. Longer Bragg wavelengths were initially designed, however, a higher annealing temperature was accidentally applied which blue-shifted stopbands but also increased hybrid refractive index. Parameters of the designs and after calculation are reported in Tables 6.2 and 6.3.

Quarter-wave conditions were not exactly obtained in this case due to the annealing issue, nevertheless, transmittance lower than 10 % with 15 alternating layers were achieved. As discussed in more depth in Section 3.3.4, the detuning of the layers does not have a substantial impact on the transmittance at the Bragg wavelength, partly due to the refractive index dispersion, thus inducing an increase in the contrast when blue-shifted. On the other hand, transmittance outside the stopband region carries essential information about the stack quality. The positions of the side interference fringes of experimental data correspond exactly with the ones of calculated spectra (considering for the higher temperature used) proving the high-quality of the reflectors. However, the envelopes of the oscillations are relatively irregular in the shorter wavelength re-

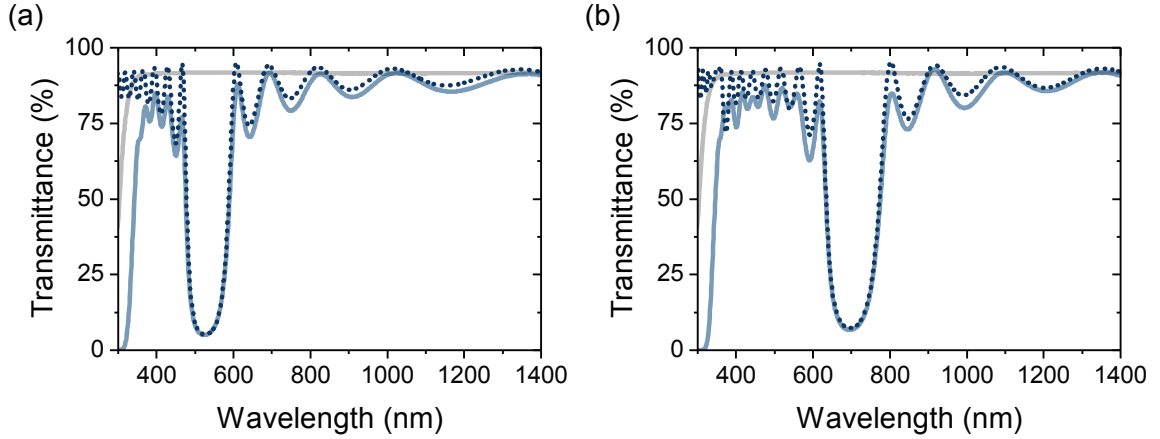


Figure 6.7: Transmittance spectra of 7.5-period DBRs (solid lines) tuned at $\lambda_0 = 525$ nm and $\lambda_0 = 700$ nm. PMMA and 80 vol% hybrid were dip-coated on 1×3 in substrates following design parameters given in Tables 6.2 and 6.3 and annealed at 125 °C. Corresponding calculated spectra by TMM are plotted in dotted lines.

gion. A combination of several factors can be the reason of such optical behaviours like an error in one layer, a lack of repeatability between each coating or some layer roughness.

The presence of scattering in this type of structure is often problematic. It can be caused by the bulk of the layers being inhomogeneous or the poor quality of interfaces. The first one has been investigated and crossed-out in Chapter 4. On the other side, dip-coating is a relatively harsh technique for the interfaces compared to spin-coating due to long time the sample spends in liquids. Furthermore, the hybrid solution is rather acidic which considerably increases the risk of degradation of the underneath PMMA layers like for cellulose acetate (see part 6.2.1). Therefore, it is important to check the quality of the interfaces of dip-coated samples.

Figure 6.8.a displays a cross-sectional TEM image of a dip-coated multilayer sample made using PMMA and 80 vol% hybrid. The quality between each coating is exceptional both in term of thickness and roughness. The irregularities noticed in the side interferences in the samples discussed above is, therefore, probably due to a mistake in only one or a couple of layers, as it has been proven to be possible in Section 3.3.4. It is indeed quite straightforward to have a change in the thickness of one single layer by dip-coating due to the strong effect of the atmosphere and air draft on the layers (see Section 3.2.3). The TEM image also confirms the

Table 6.2: Design parameters for a DBR centred at $\lambda_0 = 550$ nm and annealed at 100 °C using PMMA and 80 vol% hybrid. Measured parameters from a dip-coated device shown in Figure 6.7.a are reported after TMM modelling of the transmittance spectrum. Sample was unfortunately annealed at 125 °C which induced higher refractive index and thinner layers, thus, shifting the λ_0 to 525 nm.

<i>Design $\lambda_0 = 550$ nm</i>	n_{550nm}	d	nd/λ_0	
PMMA	1.50 ($n_a=1.49$ / $n_b=0.003$)	92 nm	0.25	
80 vol% hybrid (100 °C)	1.83 ($n_a=1.75$ / $n_b=0.025$)	75 nm	0.25	
<i>Fitting $\lambda_0 = 525$ nm</i>	n_{525nm}	d	nd/λ_0	<i>Speed</i>
PMMA	1.50 ($n_a=1.49$ / $n_b=0.003$)	92 nm	0.26	24 mm min ⁻¹
80 vol% hybrid (125 °C)	1.92 ($n_a=1.81$ / $n_b=0.03$)	66 nm	0.24	16 mm min ⁻¹

Table 6.3: Design parameters for a DBR centred at $\lambda_0 = 700$ nm and annealed at 100 °C using PMMA and 80 vol% hybrid. Measured parameters from a dip-coated device shown in Figure 6.7.a are reported after TMM modelling of the transmittance spectrum. Sample was unfortunately annealed at 125 °C which induced higher refractive index and thinner layers, thus, shifting the λ_0 to 700 nm.

<i>Design $\lambda_0 = 750$ nm</i>	n_{750nm}	d	nd/λ_0	
PMMA	1.50 ($n_a=1.49$ / $n_b=0.003$)	125 nm	0.25	
80 vol% hybrid (100 °C)	1.79 ($n_a=1.75$ / $n_b=0.025$)	104 nm	0.25	
<i>Fitting $\lambda_0 = 700$ nm</i>	n_{700nm}	d	nd/λ_0	<i>Speed</i>
PMMA	1.50 ($n_a=1.49$ / $n_b=0.003$)	125 nm	0.27	54 mm min ⁻¹
80 vol% hybrid (125 °C)	1.88 ($n_a=1.81$ / $n_b=0.03$)	86 nm	0.23	33 mm min ⁻¹

absence of large crystalline aggregate in hybrid layers with considerably high titanium content (80 %).

Additionally, an elemental analysis was performed to control the interaction between the material when exposed for a long time to solutions. The EDS images showed in Figure 6.8.b confirm the confinement of titanium atoms in hybrid layers with relatively sharp interfaces. As a result, it can be concluded that the diffusion of hybrid solution in PMMA and *vice versa* does not happen.[†]

[†]Thank you to Claire Burgess, Department of Materials, Imperial College London, for assistance with these measurements.

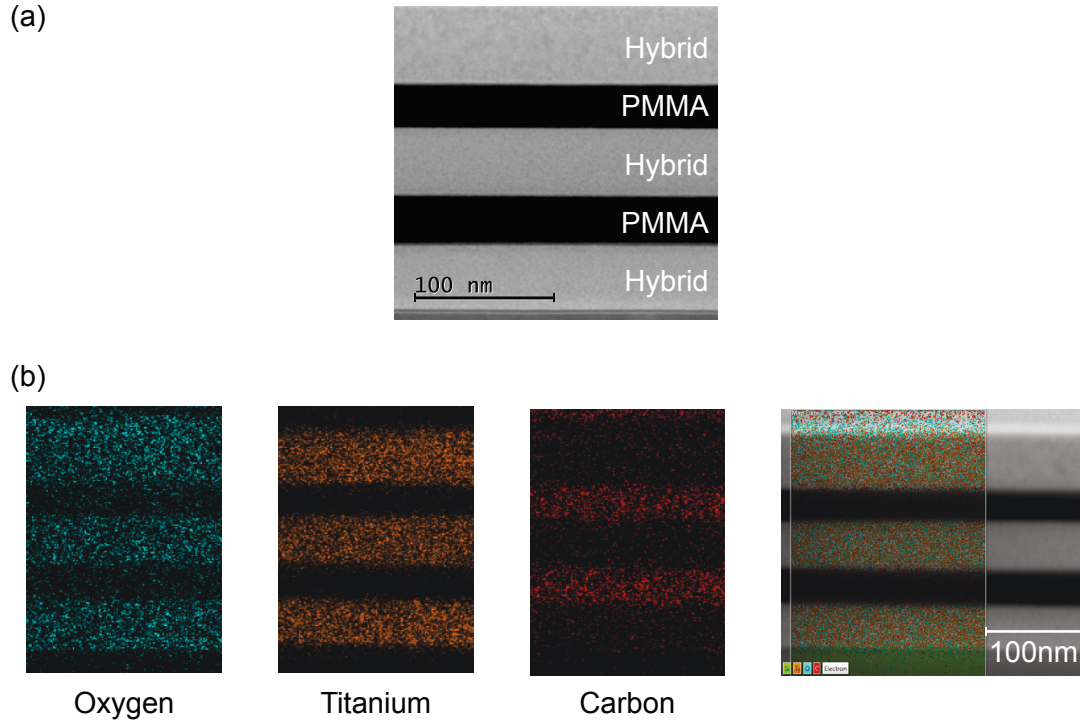


Figure 6.8: Cross-sectional TEM of dip-coated multilayer sample of 80 vol% hybrid and PMMA after annealing at 100 °C. (a) Extremely smooth interfaces and no crystalline particles are observed. (b) shows the elementary mapping confirming the absence of titanium diffusion within the PMMA layers.

6.2.5 Upscaling

Dip-coating has the advantage of being upscalable, nevertheless, different challenges can be encountered. Longer substrates have a substantial impact on the time spent in the solutions. Moreover, the shape and filling of the beakers can also play a considerable role, especially when much solution is lost after each coating which diminishes the level in the tank, thus, the drying process.

In this part, 10 × 10 cm borofloat™ 33 glass substrates from Schott were used. Rectangular square beakers were designed to minimise the amount of solution. After new calibration of the thicknesses, large one-dimensional photonic reflectors were designed at different wavelengths by changing the dip-coating speeds. 100 cm² blue, green and red-reflecting mirrors were successfully produced with 21 layers coated on each side of the substrate. As displayed in Fig-

ure 6.9.a, high-quality spectra could be obtained, in particular with the DBR at $\lambda_0 = 700$ nm. The blue and green reflectors seemed to suffer from an irregular stack resulting in low-transmittance side oscillations. Nevertheless, they all exhibited minimum transmittance as low as 10 % around the Bragg wavelengths.

Photographs of the reflectors are shown in Figure 6.9.b. Thickness gradients, an inherent problem of the dip-coating method, produced colour changes in the withdrawing direction. It resulted in blue-shifted DBRs on the bottom of the samples, with the green becoming blue and the red turning yellow. This was not as pronounced on the blue device because of the thinner layers and slower coating speeds. This particular processing effect could be limited by the use of very dilute solutions (low viscosity) and slower withdrawing velocities (like for the blue DBR). It is worth mentioning again that those samples were not produced in clean-room conditions neither in a humidity and temperature-controlled environment, however, high optical quality and low defect density could be accomplished even with 42 layers. The compatibility of the dip-coating technique and the use of commodity polymers such as PVAI and PMMA are also of great interest for potential applications such as heat control windows (see Chapter 7).

6.2.6 Circular substrates

Dip-coating is also an attractive method to cover complex shapes such as curved surfaces. It was applied in the large-scale production of rear-view mirrors from solution-processed oxides for instance.⁷¹ There are still very few technologies on the market able to coat high-quality thin-films on tubes and more specifically on the inside wall. Methods like pulsed laser deposition, ion beam sputtering or plasma CVD are possible but particularly challenging and restricted.^{72–74} On the other hand, dip-coating of sol-gel films on tubes has been successfully investigated recently.^{75–77} The major problem has been generally the quality of the inside film (roughness, lack of reproducibility) due to the restricted solvent evaporation, thus, a saturation of the atmosphere inside the cylinder. They managed to force a laminar flow inside the tube by inserting an exhausting pipe linked to a pump. Yet, the impact of solvent saturation on the

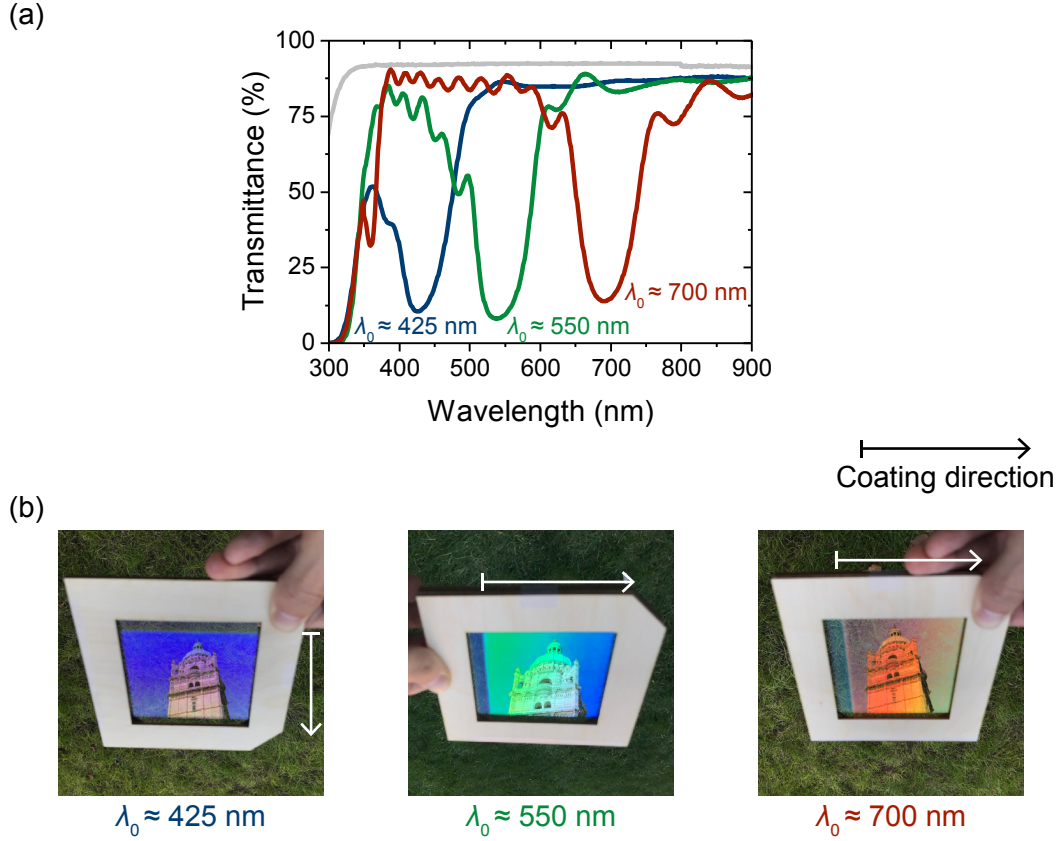


Figure 6.9: Upscaling of solution-processed 10.5-period DBRs by dip-coating on 10×10 cm glass substrates. PMMA and 80 vol% hybrid were used and annealed only once at 100°C after finishing all coatings. High reflectance were achieved by coating 21 layers on each side of the glass. (a) displays the transmittance spectra at different λ_0 and (b) the blue, green and red-looking reflectors along with the coating direction.

coating quality is primarily a sol-gel problem which can be avoided with the use of polymers and polymer hybrids.

Antireflection coatings (ARCs) are widely used in everyday applications and require a limited number of layer, therefore, a bilayer ARC was first designed to investigate the feasibility of the technique. As explained in Section 2.3.2, high transmittance can be produced by stacking a medium index layer with a low index one, following half-wave and quarter-wave conditions, respectively (see part 2.3.2). For these reasons, a 20 vol% hybrid was combined with the ultra-low refractive index PFP ($n = 1.3$, chemical structure shown in Figure 6.1). Furthermore, the simultaneous deposition on the outside and inside of the tube automatically creates a

double ARC with high efficiency. The spectrum exhibits a transmittance close to 100 % around 650 nm. Despite the unoptimised position of the destructive interference, the structure reduced the average reflectance across the visible by two-thirds from 7.5 % to 2.5 %. The photograph in Figure 6.10.b shows clearly the antireflection effect of the coating compared to the bare glass tube. Consequently, this initial experiment confirmed that high-quality polymer and hybrid films could be deposited on tubes by dip-coating without any particular problem.

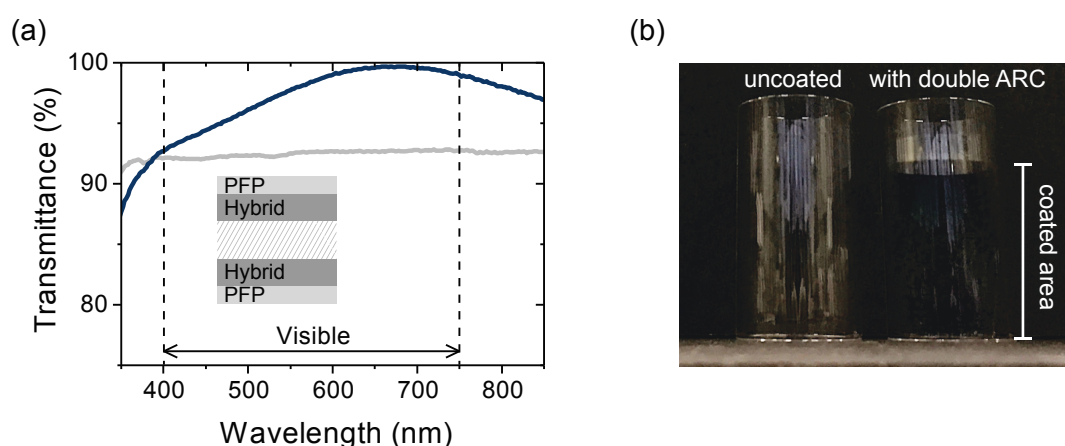


Figure 6.10: Bilayer sandwich ARC structure on glass tube by dip-coating of 20 vol% hybrid and PFP. The transmittance spectra of the bare tube and the ARC are shown in (a) with the multilayer structure in inset and a photograph of untreated and treated glass tube in (b). Diameter of the tube is 4 cm.

From the successful coating of a glass tube by dip-coating, the production of more complex multilayer structures such as DBRs was considered. Hollow cylindrical photonic fibres are mostly applied in infrared because of the thicker layers involved, so easier manufacturing. Those structures led to developments in a wide range of applications such as optical sensors, short distance lightening and photonic fibres for textile.^{78,79} Firstly mentioned theoretically by Yeh et al.,⁸⁰ all-dielectric hollow fibres were initially produced by chemical vapour deposition.⁸¹ However, polymers are particularly attractive to add flexibility and potentially low-cost to the lightguides. Many reported structures were produced by thermal evaporation of high refractive index inorganics (As_2Se_3) onto a free-standing layer of polymer (poly(ether sulfone)) which were then rolled-up to create alternating multilayers.^{82–85} Using this straightforward fabrication method does not allow to change thickness and composition within the stack. Fully organic structures

were also made with this technique recently.⁸⁶ Other processing techniques used for circular DBRs entirely based on polymers were deposition by solvent evaporation with a rotation of the tube,⁸⁷ co-rolling and drawing of preforms^{79,87,88} and co-extrusion followed by a roll-up method.²⁴ Finally, dip-coating was also alternated with the evaporation of tellurium to produce organic/inorganic stacks.⁸⁹

By using the dip-coating procedure described in Section 3.2.3, a fully-solution processed circular DBR was fabricated. 31 layers of 80 vol% hybrid and PMMA were successfully coated on each side of the tube to produce the hollowed structure displayed in Figure 6.11 along with the unusual transmittance spectrum. Two distinct optical stopbands with $T_{min} \approx 13\%$ centred around $\lambda_1 = \sim 490$ nm and $\lambda_2 = \sim 590$ nm were measured. This spectrum is similar to the one shown in Figure 3.5 where a different drying rate caused a shift in thickness on the back-side of the glass slide, resulting ultimately in the superposition of two photonic stopbands. It is believed that this phenomenon happened here with the saturation of the atmosphere by the solvent inside the tube and the lack of laminar flow. It implied slower drying, therefore, thicker films on the inside than on the outside. If needed, this particular feature could be reduced by forcing a laminar flow inside the tube as discussed by Puetz et al.⁷⁶

Furthermore, the dip-coating calibration was performed on flat substrates for experimental reasons. While a Bragg wavelength at 700 nm was originally targeted with the chosen conditions, both stacks occurred at shorter wavelengths ($\lambda_1 = \sim 490$ nm and $\lambda_2 = \sim 590$ nm) *i.e.* thinner layers. Consequently, in addition to the difference between the inside and outside coatings, it is believed that the geometrical effect of the tube considerably amplified the downward viscous drag by capillarity effect for both of them. This force was not fully balanced by the lack of airflow inside the tube since λ_2 was still off-set by more than 100 nm.

The simultaneous fabrication of two multilayer stacks on each side of the substrate enabled the juxtaposition of two optical stopbands (Figure 6.11.a). While a single DBR with these materials would typically induce a 100 nm wide photonic band, low transmittance spanned over an extended spectral region of 200 nm in this case. Furthermore, the observed iridescent effect is caused by the angular dependence of dielectric mirrors. The larger the angle of incidence (or

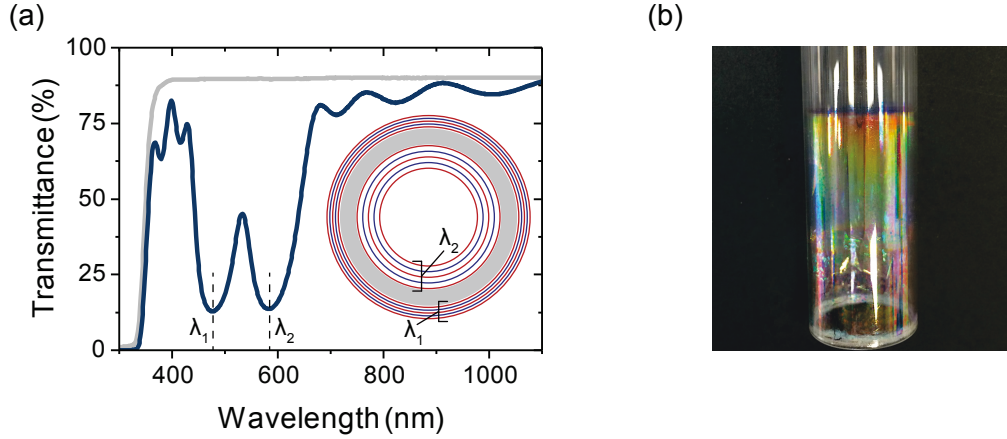


Figure 6.11: Broadband dielectric reflectors on the inside and outside of a 1 in diameter glass tube fabricated by dip-coating of 80 vol% hybrid and PMMA. 15.5 periods (31 layers) on each side were first deposited and then annealed at 100 °C. The downward viscous drag decreased the thickness and blue-shifted the optical stopbands while the slower drying rate and atmosphere inside the tube produced thicker films ($\lambda_2 = \sim 590$ nm vs. $\lambda_1 = \sim 490$ nm). The simultaneous coating of multilayer structures with two distinct λ_0 is at the origin of the extended reflectance band from $\lambda = 450$ nm to $\lambda = 650$ nm.

observation), the larger the shift of the band toward shorter wavelengths (discussed in further details in Section 7.2.2). As a result, the yellow turns to green and blue on the side of the tube in the photograph shown in Figure 6.11.b.

The annealing of the tube performed after the fabrication was performed at 100 °C. Generally, both single and multilayer structures do not experience any degradation during heating despite the hybrid contraction (see Section 4.3.1). In this particular configuration, however, the inside coating experienced slight cracking and delamination certainly due to the geometry of the substrate and the continuous circular film (no side edges). Nevertheless, this happened mainly at the bottom of the device.

6.3 Conclusion and Outlook

To summarise, high-quality and reproducible photonic reflectors could be solution-processed using high refractive index PVAI/TiO_xH hybrid materials. Low-loss PMMA has proven to be an adequate solution for up-scaling and toward complex optical structures compared to expensive and challenging fluorinated polymers. The study of the coating interfaces and thorough comparison with optical simulations demonstrated the suitability of the material system for high-standard optical devices. Furthermore, as the doping of PMMA with optically active dyes already been reported in the literature, this work enabled further investigations in active light management photonic structures.⁹⁰

More specifically, we reported spin-coated DBRs with quasi-perfect quarter-wave structures but also with chirped superlattices able to reflect extended part of the light spectrum. On-demand designs were highlighted with silver-like and gold-like reflectors while being fully transparent to IR radiation. Often referred to as cold mirrors, they can be applied as cooling structures or beamsplitters but also enable multi-functionality such as the integration of infrared sensors through mirrors.

Dip-coating being more suitable for industrial large-area manufacturing, the processing compatibility has been validated with the production of dielectric mirrors with sizes spanning from 10 cm² to 100 cm². This coating method also allowed the fabrication of ARC and broadband reflectors on glass tubes, something usually challenging when conventional materials such as inorganics are used. The proof-of-concept devices shown in this chapter could be of interest to technologies like lightning and optical sensors, in particular, thanks to the broadband reflection achieved thanks to the different drying rate inside and outside the circular substrate.

To conclude, the remarkable versatility of printed dielectric mirrors open the way to many large-area and potentially low-cost applications. Other than the visible light, the manipulation of infrared radiation is a primary concern for the coming century considering the increase in energy demand, thus, will be investigated in the following chapter.

6.4 References

1. Parker, A. R. 515 Million Years of Structural Colour. *Journal of Optics A: Pure and Applied Optics* **2**, R15 (2000).
2. Zhou, H., Xu, J., Liu, X., Zhang, H., Wang, D., Chen, Z., Zhang, D. & Fan, T. Bio-Inspired Photonic Materials: Prototypes and Structural Effect Designs for Applications in Solar Energy Manipulation. *Advanced Functional Materials* **28**, 1705309 (2018).
3. Sun, J., Bhushan, B. & Tong, J. Structural Coloration in Nature. *RSC Advances* **3**, 14862–14889 (2013).
4. Kinoshita, S., Yoshioka, S. & Miyazaki, J. Physics of Structural Colors. *Reports on Progress in Physics* **71**, 076401 (2008).
5. Karthaus, O. *Biomimetics in Photonics* 277 pp. (CRC Press, 2012).
6. Vukusic, P. & Sambles, J. R. Photonic Structures in Biology. *Nature* **424**, 852–855 (2003).
7. Kinoshita, S. & Yoshioka, S. Structural Colors in Nature: The Role of Regularity and Irregularity in the Structure. *ChemPhysChem* **6**, 1442–1459 (2005).
8. Dislich, H. & Hussmann, E. Amorphous and Crystalline Dip Coatings Obtained from Organometallic Solutions: Procedures, Chemical Processes and Products. *Thin Solid Films* **77**, 129–140 (1981).
9. Calvo, M. E., Colodrero, S., Hidalgo, N., Lozano, G., López-López, C., Sánchez-Sobrado, O. & Míguez, H. Porous One Dimensional Photonic Crystals: Novel Multifunctional Materials for Environmental and Energy Applications. *Energy & Environmental Science* **4**, 4800–4812 (2011).
10. Bensaid, M. O., Miloua, R., Ghalouci, L., Godey, F. & Soldera, A. Multiscale Design and Optimization of Polymer-Based Photonic Crystals for Solar Shielding. *Solar Energy Materials and Solar Cells* **171**, 166–179 (2017).
11. Yu, W., Shen, L., Shen, P., Long, Y., Sun, H., Chen, W. & Ruan, S. Semitransparent Polymer Solar Cells with 5% Power Conversion Efficiency Using Photonic Crystal Reflector. *ACS Applied Materials & Interfaces* **6**, 599–605 (2014).
12. Smirnov, J. R. C., Calvo, M. E. & Míguez, H. Selective UV Reflecting Mirrors Based on Nanoparticle Multilayers. *Advanced Functional Materials* **23**, 2805–2811 (2013).

13. Bronnbauer, C., Gasparini, N., Brabec, C. J. & Forberich, K. Guideline for Efficiency Enhancement in Semi-Transparent Thin-Film Organic Photovoltaics with Dielectric Mirrors. *Advanced Optical Materials* **4**, 1098–1105 (2016).
14. Shen, H., Wang, Z., Wu, Y. & Yang, B. One-Dimensional Photonic Crystals: Fabrication, Responsiveness and Emerging Applications in 3D Construction. **6**, 4505–4520 (2016).
15. Goldenberg, L. M., Lisinetskii, V. & Schrader, S. Fast and Simple Fabrication of Organic Bragg Mirrors—Application to Plastic Microchip Lasers. *Laser Physics Letters* **10**, 055808 (2013).
16. Canazza, G., Scotognella, F., Lanzani, G., Silvestri, S. D., Zavelani-Rossi, M. & Comoretto, D. Lasing from All-Polymer Microcavities. *Laser Physics Letters* **11**, 035804 (2014).
17. Goldenberg, L. M., Lisinetskii, V. & Schrader, S. All-Polymer Spin-Coated Organic Vertical-Cavity Surface-Emitting Laser with High Conversion Efficiency. *Applied Physics B* **120**, 271–277 (2015).
18. Valkama, S., Kosonen, H., Ruokolainen, J., Haatainen, T., Torkkeli, M., Serimaa, R., ten Brinke, G. & Ikkala, O. Self-Assembled Polymeric Solid Films with Temperature-Induced Large and Reversible Photonic-Bandgap Switching. *Nature Materials* **3**, 872–876 (2004).
19. Kang, Y., Walish, J. J., Gorishnyy, T. & Thomas, E. L. Broad-Wavelength-Range Chemically Tunable Block-Copolymer Photonic Gels. *Nature Materials* **6**, 957–960 (2007).
20. Wang, Z., Zhang, J., Xie, J., Li, C., Li, Y., Liang, S., Tian, Z., Wang, T., Zhang, H., Li, H., Xu, W. & Yang, B. Bioinspired Water-Vapor-Responsive Organic/Inorganic Hybrid One-Dimensional Photonic Crystals with Tunable Full-Color Stop Band. *Advanced Functional Materials* **20**, 3784–3790 (2010).
21. Wang, Z., Zhang, J., Li, J., Xie, J., Li, Y., Liang, S., Tian, Z., Li, C., Wang, Z., Wang, T., Zhang, H. & Yang, B. Colorful Detection of Organic Solvents Based on Responsive Organic/Inorganic Hybrid One-Dimensional Photonic Crystals. *Journal of Materials Chemistry* **21**, 1264–1270 (2011).
22. Alfrey, T., Gurnee, E. F. & Schrenk, W. J. Physical Optics of Iridescent Multilayered Plastic Films. *Polymer Engineering & Science* **9**, 400–404 (1969).
23. Radford, J. A., Alfrey, T. & Schrenk, W. J. Reflectivity of Iridescent Coextruded Multilayered Plastic Films. *Polymer Engineering & Science* **13**, 216–221 (1973).
24. Weber, M. F., Stover, C. A., Gilbert, L. R., Nevitt, T. J. & Ouderkirk, A. J. Giant Birefringent Optics in Multilayer Polymer Mirrors. *Science* **287**, 2451–2456 (2000).

25. Álvarez, A. L., Tito, J., Vaello, M. B., Velásquez, P., Mallavia, R., Sánchez-López, M. M. & Fernández de Ávila, S. Polymeric Multilayers for Integration into Photonic Devices. *Thin Solid Films. Proceedings from the 12th International Conference on Thin Films* **433**, 277–280 (2003).
26. Mönch, W., Dehnert, J., Prucker, O., Rühle, J. & Zappe, H. Tunable Bragg Filters Based on Polymer Swelling. *Applied Optics* **45**, 4284 (2006).
27. Scotognella, F., Monguzzi, A., Meinardi, F. & Tubino, R. DFB Laser Action in a Flexible Fully Plastic Multilayer. *Physical Chemistry Chemical Physics* **12**, 337–340 (2009).
28. Komikado, T., Inoue, A., Masuda, K., Ando, T. & Umegaki, S. Multi-Layered Mirrors Fabricated by Spin-Coating Organic Polymers. *Thin Solid Films* **515**, 3887–3892 (2007).
29. Bailey, J. & Sharp, J. S. Infrared Dielectric Mirrors Based on Thin Film Multilayers of Polystyrene and Polyvinylpyrrolidone. *Journal of Polymer Science Part B: Polymer Physics* **49**, 732–739 (2011).
30. Lova, P., Grande, V., Manfredi, G., Patrini, M., Herbst, S., Würthner, F. & Comoretto, D. All-Polymer Photonic Microcavities Doped with Perylene Bisimide J-Aggregates. *Advanced Optical Materials* **5**, 1700523 (2017).
31. Giusto, P., Lova, P., Manfredi, G., Gazzo, S., Srinivasan, P., Radice, S. & Comoretto, D. Colorimetric Detection of Perfluorinated Compounds by All-Polymer Photonic Transducers. *ACS Omega* **3**, 7517–7522 (2018).
32. Edrington, A. C., Urbas, A. M., DeRege, P., Chen, C. X., Swager, T. M., Hadjichristidis, N., Xenidou, M., Fetters, L. J., Joannopoulos, J. D., Fink, Y. & Thomas, E. L. Polymer-Based Photonic Crystals. *Advanced Materials* **13**, 421–425 (2001).
33. Yoon, J., Lee, W. & Thomas, E. L. Optically Pumped Surface-Emitting Lasing Using Self-Assembled Block-Copolymer-Distributed Bragg Reflectors. *Nano Letters* **6**, 2211–2214 (2006).
34. Walish, J. J., Kang, Y., Mickiewicz, R. A. & Thomas, E. L. Bioinspired Electrochemically Tunable Block Copolymer Full Color Pixels. *Advanced Materials* **21**, 3078–3081 (2009).
35. Kang, C., Kim, E., Baek, H., Hwang, K., Kwak, D., Kang, Y. & Thomas, E. L. Full Color Stop Bands in Hybrid Organic/Inorganic Block Copolymer Photonic Gels by Swelling-Freezing. *Journal of the American Chemical Society* **131**, 7538–7539 (2009).
36. Song, D.-P., Li, C., Li, W. & Watkins, J. J. Block Copolymer Nanocomposites with High Refractive Index Contrast for One-Step Photonics. *ACS Nano* **10**, 1216–1223 (2016).

37. Druffel, T., Mandzy, N., Sunkara, M. & Grulke, E. A. Polymer Nanocomposite Thin Film Mirror for the Infrared Region. *Small* **4**, 459–461 (2008).
38. Calvo, M. E., Sobrado, O. S., Lozano, G. & Míguez, H. Molding with Nanoparticle-Based One-Dimensional Photonic Crystals: A Route to Flexible and Transferable Bragg Mirrors of High Dielectric Contrast. *Journal of Materials Chemistry* **19**, 3144–3148 (2009).
39. Russo, M., Campoy-Quiles, M., Lacharmoise, P., Ferenczi, T. A. M., Garriga, M., Caseri, W. R. & Stingelin, N. One-Pot Synthesis of Polymer/Inorganic Hybrids: Toward Readily Accessible, Low-Loss, and Highly Tunable Refractive Index Materials and Patterns. *Journal of Polymer Science Part B: Polymer Physics* **50**, 65–74 (2012).
40. Wang, Z., Zhang, J., Xie, J., Yin, Y., Wang, Z., Shen, H., Li, Y., Li, J., Liang, S., Cui, L., Zhang, L., Zhang, H. & Yang, B. Patterning Organic/Inorganic Hybrid Bragg Stacks by Integrating One-Dimensional Photonic Crystals and Macrocavities through Photolithography: Toward Tunable Colorful Patterns as Highly Selective Sensors. *ACS Applied Materials & Interfaces* **4**, 1397–1403 (2012).
41. Ogata, T., Yagi, R., Nakamura, N., Kuwahara, Y. & Kurihara, S. Modulation of Polymer Refractive Indices with Diamond Nanoparticles for Metal-Free Multilayer Film Mirrors. *ACS Applied Materials & Interfaces* **4**, 3769–3772 (2012).
42. Bronnbauer, C., Hornich, J., Gasparini, N., Guo, F., Hartmeier, B., Luechinger, N. A., Pflaum, C., Brabec, C. J. & Forberich, K. Printable Dielectric Mirrors with Easily Adjustable and Well-Defined Reflection Maxima for Semitransparent Organic Solar Cells. *Advanced Optical Materials* **3**, 1424–1430 (2015).
43. Howell, I. R., Li, C., Colella, N. S., Ito, K. & Watkins, J. J. Strain-Tunable One Dimensional Photonic Crystals Based on Zirconium Dioxide/Slide-Ring Elastomer Nanocomposites for Mechano-chromic Sensing. *ACS Applied Materials & Interfaces* **7**, 3641–3646 (2015).
44. Bronnbauer, C., Riecke, A., Adler, M., Hornich, J., Schunk, G., Brabec, C. J. & Forberich, K. Printing of Large-Scale, Flexible, Long-Term Stable Dielectric Mirrors with Suppressed Side Interferences. *Advanced Optical Materials* **6**, 1700518 (2017).
45. Strang, A. *Organic/Inorganic Hybrid Materials for Solution-Processed Photonic Applications* Ph.D. (Imperial College London, 2015).
46. Grosso, D. How to Exploit the Full Potential of the Dip-Coating Process to Better Control Film Formation. *Journal of Materials Chemistry* **21**, 17033–17038 (2011).

47. Brinker, C. J., Hurd, A. J., Schunk, P. R., Frye, G. C. & Ashley, C. S. Review of Sol-Gel Thin Film Formation. *Journal of Non-Crystalline Solids. Advanced Materials from Gels* **147-148**, 424–436 (1992).
48. Brinker, C. J., Frye, G. C., Hurd, A. J. & Ashley, C. S. Fundamentals of Sol-Gel Dip Coating. *Thin Solid Films* **201**, 97–108 (1991).
49. Bindini, E., Naudin, G., Faustini, M., Grosso, D. & Boissière, C. Critical Role of the Atmosphere in Dip-Coating Process. *The Journal of Physical Chemistry C* **121**, 14572–14580 (2017).
50. Komikado, T., Yoshida, S. & Umegaki, S. Surface-Emitting Distributed-Feedback Dye Laser of a Polymeric Multilayer Fabricated by Spin Coating. *Applied Physics Letters* **89**, 061123 (2006).
51. Scotognella, F., Monguzzi, A., Cucini, M., Meinardi, F., Comoretto, D. & Tubino, R. One Dimensional Polymeric Organic Photonic Crystals for DFB Lasers. *International Journal of Photoenergy* **2008**, e389034 (2008).
52. Manfredi, G., Mayrhofer, C., Kothleitner, G., Schennach, R. & Comoretto, D. Cellulose Ternary Photonic Crystal Created by Solution Processing. *Cellulose* **23**, 2853–2862 (2016).
53. Amim, J., Kosaka, P. M. & Petri, D. F. S. Characteristics of Thin Cellulose Ester Films Spin-Coated from Acetone and Ethyl Acetate Solutions. *Cellulose* **15**, 527–535 (2008).
54. Edgar, K. J., Buchanan, C. M., Debenham, J. S., Rundquist, P. A., Seiler, B. D., Shelton, M. C. & Tindall, D. Advances in Cellulose Ester Performance and Application. *Progress in Polymer Science* **26**, 1605–1688 (2001).
55. Zubia, J. & Arrue, J. Plastic Optical Fibers: An Introduction to Their Technological Processes and Applications. *Optical Fiber Technology* **7**, 101–140 (2001).
56. Ma, Y., Cao, X., Feng, X., Ma, Y. & Zou, H. Fabrication of Super-Hydrophobic Film from PMMA with Intrinsic Water Contact Angle below 90°. *Polymer* **48**, 7455–7460 (2007).
57. Ali, U., Karim, K. J. B. A. & Buang, N. A. A Review of the Properties and Applications of Poly (Methyl Methacrylate) (PMMA). *Polymer Reviews* **55**, 678–705 (2015).
58. Carroll, D. R., Constantinou, A. P., Stingelin, N. & Georgiou, T. K. Scalable Syntheses of Well-Defined Pentadecablock Bipolymer and Quintopolymer. *Polymer Chemistry* **9**, 3450–3454 (2018).
59. Jansson, P. A. *Deconvolution: With Applications in Spectroscopy* 370 pp. (Academic Press, 1984).
60. Hecht, E. *Optics* 698 pp. (Addison-Wesley, 2002).
61. Parker, A. R., Mckenzie, D. R. & Large, M. C. J. Multilayer Reflectors in Animals Using Green and Gold Beetles as Contrasting Examples. *Journal of Experimental Biology* **201**, 1307–1313 (1998).

62. Macleod, H. A. *Thin-Film Optical Filters, Third Edition* 682 pp. (CRC Press, 2001).
63. Hooke, R. *Micrographia* (Allestry, 1965).
64. Steinbrecht, R. A., Mohren, W., Pulker, H. K. & Schneider, D. Cuticular Interference Reflectors in the Golden Pupae of Danaine Butterflies. *Proc. R. Soc. Lond. B* **226**, 367–390 (1985).
65. Gur, D., Leshem, B., Oron, D., Weiner, S. & Addadi, L. The Structural Basis for Enhanced Silver Reflectance in Koi Fish Scale and Skin. *Journal of the American Chemical Society* **136**, 17236–17242 (2014).
66. Jordan, T. M., Partridge, J. C. & Roberts, N. W. Disordered Animal Multilayer Reflectors and the Localization of Light. *Journal of The Royal Society Interface* **11**, 20140948 (2014).
67. Libby, E., Azofeifa, D. E., Hernández-Jiménez, M., Barboza-Aguilar, C., Solís, A., García-Aguilar, I., Arce-Marenco, L., A Hernández & Vargas, W. E. Light Reflection by the Cuticle of C. Aurigans Scarabs: A Biological Broadband Reflector of Left Handed Circularly Polarized Light. *Journal of Optics* **16**, 082001 (2014).
68. Zhao, S., Brady, P. C., Gao, M., Etheredge, R. I., Kattawar, G. W. & Cummings, M. E. Broadband and Polarization Reflectors in the Lookdown, Selene Vomer. *Journal of The Royal Society Interface* **12**, 20141390 (2015).
69. Bossard, J. A., Lin, L. & Werner, D. H. Evolving Random Fractal Cantor Superlattices for the Infrared Using a Genetic Algorithm. *Journal of The Royal Society Interface* **13**, 20150975 (2016).
70. Johnson, P. B. & Christy, R. W. Optical Constants of the Noble Metals. *Physical Review B* **6**, 4370–4379 (1972).
71. Dislich, H. & Hinz, P. History and Principles of the Sol-Gel Process, and Some New Multicomponent Oxide Coatings. *Journal of Non-Crystalline Solids. Proceedings of the International Workshop on Glasses and Glass Ceramics from Gels* **48**, 11–16 (1982).
72. Fujiyama, H., Kawasaki, H., Fujiyama, T. & Takagi, S. Sputter Coating on High Speed Steel Tube Using a Hybrid Plasma Produced by Coaxial ECR and Magnetron Discharges. *Surface and Coatings Technology* **59**, 140–143 (1993).
73. Schumacher, A., Frech, G. & Wolf, G. K. A Novel Method for Inside-Coating of Tubes and Hollow Cylinders by Ion Beam Sputtering. *Surface and Coatings Technology* **89**, 258–261 (1997).
74. Dietsch, R., Mai, H. & Mucha, A. *European pat.* 0729520B1 (2000).

75. Puetz, J., Chalvet, F. N. & Aegerter, M. A. *Transparent Conducting Coatings on Glass Tubes in Sol-Gel Optics VI* Sol-Gel Optics VI. **4804** (International Society for Optics and Photonics, 2002), 73–81.
76. Puetz, J., Chalvet, F. N. & Aegerter, M. A. Wet Chemical Deposition of Transparent Conducting Coatings in Glass Tubes. *Thin Solid Films. Selected Papers from the 4th International Conference on Coatings on Glass* **442**, 53–59 (2003).
77. Aegerter, M. A., Puetz, J., Gasparro, G. & Al-Dahoudi, N. Versatile Wet Deposition Techniques for Functional Oxide Coatings. *Optical Materials. Proceedings of the Second International Conference on Sol-Gel Materials. Research, Technology, Applications (SGM'03)* **26**, 155–162 (2004).
78. Knight, J. C. Photonic Crystal Fibres. *Nature* (2003).
79. Gauvreau, B., Guo, N., Schicker, K., Stoeffler, K., Boismenu, F., Ajji, A., Wingfield, R., Dubois, C. & Skorobogatiy, M. Color-Changing and Color-Tunable Photonic Bandgap Fiber Textiles. *Optics Express* **16**, 15677–15693 (2008).
80. Yeh, P., Yariv, A. & Marom, E. Theory of Bragg Fiber. *Journal of the Optical Society of America* **68**, 1196 (1978).
81. Elder, M., Jancaitis, K., Milam, D. & Campbell, J. Optical Characterization of Damage Resistant “Kilolayer” Rugate Filters. *Laser-Induced Damage in Optical Materials: 1990* (eds Bennett, H., Chase, L., Guenther, A., Newnam, B. & Soileau, M.) 237–10 (1991).
82. Hart, S. D., Maskaly, G. R., Temelkuran, B., Prideaux, P. H., Joannopoulos, J. D. & Fink, Y. External Reflection from Omnidirectional Dielectric Mirror Fibers. *Science* **296**, 510–513 (2002).
83. Temelkuran, B., Hart, S. D., Benoit, G., Joannopoulos, J. D. & Fink, Y. Wavelength-Scalable Hollow Optical Fibres with Large Photonic Bandgaps for CO₂ Laser Transmission. *Nature* **420**, 650–653 (2002).
84. Shapira, O., Kuriki, K., Orf, N. D., Abouraddy, A. F., Benoit, G., Viens, J. F., Rodriguez, A., Ibanescu, M., Joannopoulos, J. D., Fink, Y. & Brewster, M. M. Surface-Emitting Fiber Lasers. *Optics Express* **14**, 3929–3935 (2006).
85. Abouraddy, A. F., Bayindir, M., Benoit, G., Hart, S. D., Kuriki, K., Orf, N., Shapira, O., Sorin, F., Temelkuran, B. & Fink, Y. Towards Multimaterial Multifunctional Fibres That See, Hear, Sense and Communicate. *Nature Materials* **6**, 336–347 (2007).
86. Kolle, M., Lethbridge, A., Kreysing, M., Baumberg, J. J., Aizenberg, J. & Vukusic, P. Bio-Inspired Band-Gap Tunable Elastic Optical Multilayer Fibers. *Advanced Materials* **25**, 2239–2245 (2013).

87. Gao, Y., Guo, N., Gauvreau, B., Rajabian, M., Skorobogata, O., Pone, E., Zabeida, O., Martinu, L., Dubois, C. & Skorobogatiy, M. Consecutive Solvent Evaporation and Co-Rolling Techniques for Polymer Multilayer Hollow Fiber Preform Fabrication. *Journal of Materials Research* **21**, 2246–2254 (2006).
88. Pone, E., Dubois, C., Guo, N., Gao, Y., Dupuis, A., Boismenu, F., Lacroix, S. & Skorobogatiy, M. Drawing of the Hollow All-Polymer Bragg Fibers. *Optics Express* **14**, 5838–5852 (2006).
89. Fink, Y., Ripin, D., Fan, S., Chen, C., Joannopoulos, J. & Thomas, E. Guiding Optical Light in Air Using an All-Dielectric Structure. *Journal of Lightwave Technology* **17**, 2039–2041 (1999).
90. Yuan, H.-K. *Sub-Wavelength Photonics from Solution-Processing (in Preparation)* Ph.D. (Imperial College London, 2019).

7 | Solar radiation management for sustainable buildings

Global energy needs will rise by a considerable 25 % by 2040 worldwide with electricity demand growing by 40 % at the same time.¹ This trend will have many impacts like higher pollution and CO₂ emissions which, on the opposite, should be largely reduced to meet Paris agreement targets. Moreover, it is known that energy consumption in buildings is around 40 % of the total energy produced, thus, nearly-zero energy buildings are required. With strong policy objectives given by the European Commission, new technological advances will be crucial.²⁻⁴

Ventilation, heating and air conditioning are responsible for a large part of the energy loss in buildings, mainly due to poor insulation and human behaviours. Many efforts are put into better wall insulation, but little is done to improve windows heat management.⁵ This is particularly of interest when the ratio window to wall becomes large such as business premises and new architectures. In addition, more than 25 % of the building heat loss happens through windows.⁶ At the same time, daylight is a must-have for human comfort and lightning energy savings.^{7,8}

Furthermore, automotive windshields have always been problematic with significant heat-loss during winter and high solar heating under the sun.⁹ This last one especially results in the considerable use of air-conditioning, consequently consuming more energy and emitting more. With the recent development of electric vehicles, consumption and autonomy will strongly benefit from advanced infrared windows.

While silver and transparent conductive oxides (TCO) are commonly used in the construction of new edifices, there are still a lot of efforts to do. In particular, evaporation of metals is energy and capital intensive compared to solution-based manufacturing. In this chapter, a novel solar-heat control window coating is proposed based on advanced photonic design and enabled by the work discussed previously.

7.1 Background

Building and car windows are made of common silica-based glass which does not block IR radiation. The development of visibly transparent and thermally reflective coatings is therefore necessary for energy savings as mentioned above.

First, it is important to describe the different radiations involved in windows. All objects emit heat radiation, simply explained by the blackbody concept. An ideal blackbody absorbs all radiation and emits the energy at different wavelengths depending on its equilibrium temperature (Figure 7.1.a). The amplitude of the blackbody radiation is given by Planck's Law:

$$W_{\lambda}(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1} \quad (7.1)$$

From the spectra at room temperature, it is noticed that a blackbody emits only in the IR between $2.5 \mu\text{m} < \lambda_{bb} < 50 \mu\text{m}$. When the temperature increases, the intensity is blue-shifted (Wien's displacement law) and becomes stronger (Stefan-Boltzmann law). As a result, the sun can be seen as a blackbody at about 5800°C radiating between $250 \text{ nm} < \lambda_{sol} < 5 \mu\text{m}$. Solar spectrum observed at the surface of the Earth (generally known as Air Mass 1.5 spectrum) is displayed in Figure 7.1.a, the difference compared to a perfect blackbody spectrum being due to the absorption of the atmosphere elements.¹⁰

Solar radiation can be segregated in three parts: the UV emission up to 400 nm, the visible region between 400 nm and 750 nm with a maximum around 555 nm which corresponds to the maximum sensitivity of the human eye in daylight (photopic vision) and the near-IR radiation from 750 nm. More than 50 % of the solar energy is radiated in the IR. It is also noteworthy that there is almost no overlap between the solar spectrum and the blackbody radiation at room temperature.

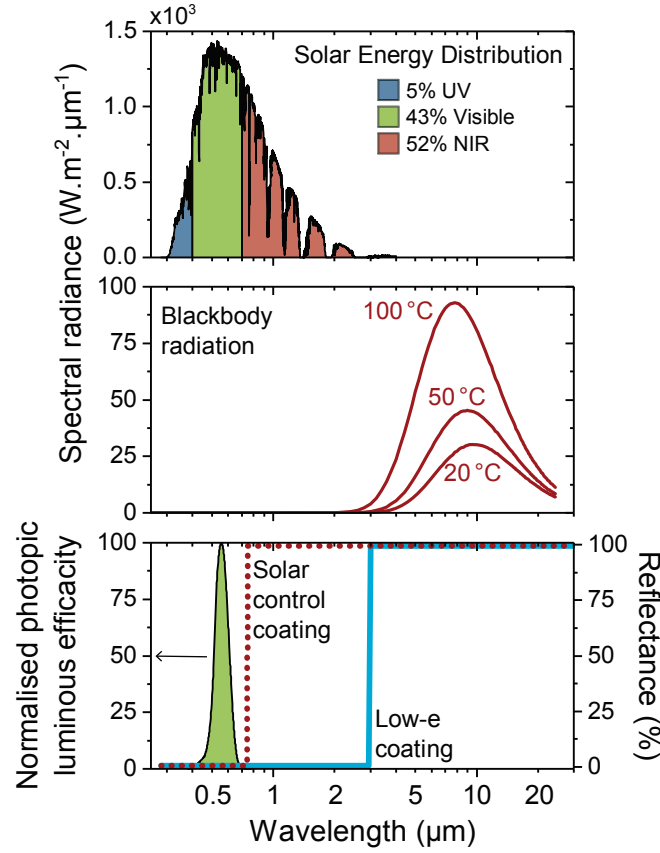


Figure 7.1: (Top) Standard terrestrial solar intensity spectrum (AM1.5, ASTM G173-03) in logarithmic scale. (Middle) Blackbody radiation at three different temperatures (25 °C, 50 °C and 100 °C). (Bottom) The human eye photopic response (daylight) is shown in green. The ideal reflectance spectra of low-emissivity coating and solar-control coating are plotted in solid blue line and red dotted line, respectively.

There are three main situations for window coating technologies depending on the climate:

1. In cold climates, windows should stop heat loss, transmit the visible light for human well-being and lightning purposes and allow infrared solar radiation to pass through. These high-solar heat gain (SHG) technologies are also called low-emissivity (low-e) coatings as we will discuss later. It results in:

$$T(\lambda) = 1 \quad \& \quad R(\lambda) = 0 \quad \text{for} \quad 0.4 < \lambda < 2.5 \, \mu\text{m}$$

$$T(\lambda) = 0 \quad \& \quad R(\lambda) = 1 \quad \text{for} \quad 2.5 < \lambda < 50 \, \mu\text{m}$$

2. In hot climate, while the two first parameters are similar, as much IR as possible must be kept outside. These low-SHG coatings are commonly referred as solar-control coating

and follow the parameters:

$$T(\lambda) = 1 \quad \& \quad R(\lambda) = 0 \quad \text{for} \quad 0.4 < \lambda < 0.75 \mu m$$

$$T(\lambda) = 0 \quad \& \quad R(\lambda) = 1 \quad \text{for} \quad 0.75 < \lambda < 50 \mu m$$

3. Finally, for climate where ambient temperatures are not constant, dynamic technologies are needed such as chromogenic materials. Their properties can change as a function of temperature, light or electrical potential, therefore, adapt to the environment. Specific oxides have been the main focus of the research in this field like MoO₃, VO₂, NiO and WO₃.⁵

As discussed in Chapter 2, the sum of transmittance, reflectance and absorptance is equal to 1 following the conservation of energy (Equation 2.9). Furthermore, for a body in thermodynamic equilibrium, Kircchoff's law of thermal radiation states that the energy absorbed by a material is equal to the emitted energy, thus:

$$E(\lambda) = A(\lambda) \tag{7.2}$$

where $A(\lambda)$ is the spectral absorptance and $E(\lambda)$ the spectra emittance. It is evident that in the context of this work, the emittance is only relevant for $\lambda > 2.5 \mu m$, thus is often integrated over this spectral range.¹¹

Achieving total reflectance in the blackbody spectral range eliminates any absorptance *i.e.* emittance from the material. This reduces the heat loss through windows but also blocks the non-solar radiation from outside (pavement, buildings). In this regards, metals have the ability to completely reflect IR. Silver fulfils all the requirement for low-e coating and has become predominant on the market. Its poor adhesion and durability are addressed by encapsulating oxide layers which also improve the transmittance in the visible by antireflective interferences. Yet, silver is still relatively expensive as well as its deposition at industrial scale.^{4,10}

On the other hand, the development of TCO can be processed using less demanding methods. They also effectively reflect the blackbody IR but usually transmit relatively well near-IR crucial for SHG. As a result, they became one of the main technology for the low-e coating market.

The most common coatings are made of indium tin oxide and fluorine-doped tin oxide (FTO). Thanks to their fundamental wide band gap, both the absorbance in the visible and the solar IR emission are low.^{3,12}

However, one of the main drawback of both metal and TCO coatings, is the interference in the range of the electromagnetic signals used for telecommunication. Only recent studies demonstrated the transparency to radio-waves using complex lithography.^{13,14}

Dielectric mirrors are on the other hand entirely transparent to those long wavelengths. Despite their transparency to blackbody radiation, they can be fully transparent to visible light while reflecting near-IR. Yet, the investigation of DBR for solar IR management has been few and far between. The main work in this area has been done by Weber et al. from 3M Corporate Research Laboratory who developed a chirped polymer dielectric reflectors.^{15–17} The film, reflecting between $0.8 \mu\text{m} < \lambda_{sol} < 1.1 \mu\text{m}$, can be found under the commercial name *Sun Control Windows Film Prestige 90*. In order to increase the photonic stopband, the DBR needed almost 500 layers of low-index PMMA and polyester. The fabrication was performed by melting, co-extrusion and successive folding.¹⁵ Another interesting theoretical study was also published on polymer-based IR shield by Bensaid et al. where the advantages of chirped structure for solar-control were proved.¹⁸

7.2 Results and Discussion

Based on the results of the previous chapter, photonic structures based on the PVAI/TiO_xH hybrid and PMMA for window applications are discussed here. Straightforward quarter-wave transparent BDRs tuned in the near-IR are initially explored. Advanced superlattices are then investigated for both UV and IR shielding with remarkable broadband responses with an additional low-e feature given by a TCO substrate. The produced solar-control device is finally put into a low-carbon building context using international standards and solar emission data for different cities provided by the National Renewable Energy Laboratory (NREL).

7.2.1 Near-IR DBRs

The position of the optical stopband in dielectric mirrors can be tuned with the optical path length of each layer following the quarter-wave condition. Since this photonic structures exhibit a harmonic band at a third of the Bragg wavelength, λ_0 is limited to 1200 nm to maintain transparency. Thus, a DBR with a λ_0 around 1.1 μm was first produced by dip-coating using the procedure described in Section 3.2.3. 30 layers were deposited (15 on each side) to reach a transmittance as low as 9 % (Figure 7.2). The device shows great transparency to the visible.

The as-cast sample exhibited a second harmonic around $\lambda = 600\text{ nm}$ (usually missing in the quarter-wave design) and a third harmonic around $\lambda = 410\text{ nm}$ compromising the transmission of the visible light. The device revealed very smooth interferences from 400 to 750 nm from the change in refractive index and thickness after annealing at 100 °C. By altering the optical path length, the thermal post-tuning of the hybrid induced a blue-shift of both the main and the third bands; the last one moving away from the visible region. At the same time, the second harmonic reduced as expected for this type of structure. Parameters of the initial design and the calculated spectra after fitting of the data are reported in Table 7.1. The comparison of the experimental and modelled spectra highlight the high-quality of the device.

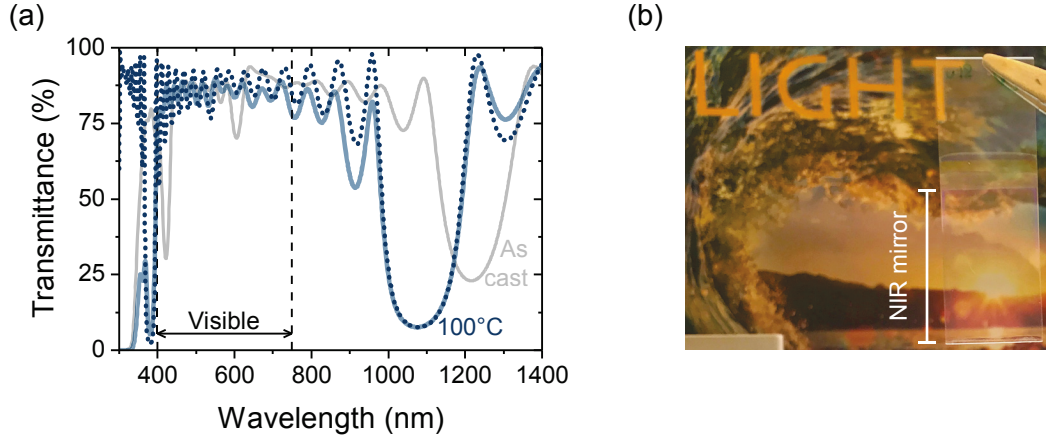


Figure 7.2: Near-IR dielectric mirror ($\lambda_0 = 1 \mu\text{m}$) made of 80 vol% hybrid and PMMA. Using dip-coating, the simultaneous deposition of 7.5-period DBRs on each side was possible. (a) shows the transmittance spectra of the sample as-cast (grey line), after annealing (solid blue line) and from the TMM model (dotted blue line). A photograph of the highly transmissive structure is displayed in (b).

Table 7.1: Design parameters for a DBR centred at $\lambda_0 = 1100 \text{ nm}$ and annealed at 100°C using PMMA and 80 vol% hybrid. Measured parameters from the dip-coated device shown in Figure 7.2.a are reported after TMM modelling of the transmittance spectrum.

Design $\lambda_0 = 1100 \text{ nm}$	$n_{1100 \text{ nm}}$	d	nd/λ_0	
PMMA	1.49 ($n_a=1.49 / n_b=0.003$)	184 nm	0.25	
80 vol% hybrid (100°C)	1.77 ($n_a=1.75 / n_b=0.025$)	155 nm	0.25	
Fitting $\lambda_0 = 1078 \text{ nm}$	$n_{1078 \text{ nm}}$	d	nd/λ_0	Speed
PMMA	1.49 ($n_a=1.49 / n_b=0.003$)	181 nm	0.25	10 mm min^{-1}
80 vol% hybrid (125°C)	1.78 ($n_a=1.76 / n_b=0.03$)	151 nm	0.25	12 mm min^{-1}

Despite the thicker layers needed for IR reflectors, no particular difficulty was encountered during the fabrication of the DBR. Nevertheless, with the upscaling of dip-coated structures, layers spend a much longer time in solution which could easily be the source of difficulties. As a result, large coatings were explored to confirm the suitability of the system for large-area applications using $10 \times 10 \text{ cm}$ glass substrates (see Section 6.2.5). Another sandwich 3.5-period near-IR mirror was produced (Figure 7.3). Once again, high transmittance across the visible was observed while the reflectance around $\lambda_0 = 1 \mu\text{m}$ started to build-up. This confirmed the potentially low-cost and large-area manufacturing using this technique.

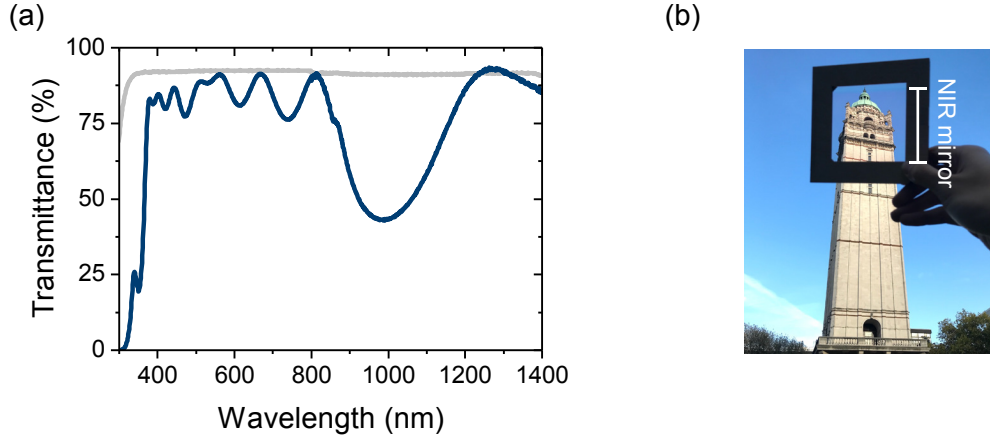


Figure 7.3: Large-area IR reflector of 3.5 periods on each side produced by dip-coating of 80 vol% hybrid and PMMA and annealed at 100 °C.

7.2.2 Design of chirped photonic coating at specific angle

In the context of this study, broadband reflection of IR is required to reduce the solar effect as much as possible. This is also of interest for many other optical applications where heat is a problem for components such as in microscopes.

Superlattices

The quarter-wave DBR shown in the previous part exhibited a ~ 200 nm wide stopband which is relatively similar to the one of the commercial chirped structure, yet, still limited compared to the solar IR radiations (750 nm to 2500 nm). As investigated in Chapter 6, chirped superlattices proved to be an elegant way to extend the reflection range. In a similar fashion, λ_0 can be geometrically changed in a solar coating, following Equation 7.3:

$$\lambda_0^i = \Lambda_0 \cdot k^{N-i} \quad (7.3)$$

where λ_0^i is the wavelength for the quarter-wave condition of layer i , Λ_0 the initial Bragg wavelength of the stack, k the common ratio of the geometrical sequence and N the number of layers in the structure.

Superlattices with a geometrical increase, however, do not suppress the third harmonic when still based on a quarter-wave design. As a result, transparency could be impacted if the Bragg wavelength becomes larger than 1200 nm since the second stopband approaches $\lambda = 400$ nm. Consequently, the maximum theoretical mirror would reflect between $750 \text{ nm} < \lambda < 1200 \text{ nm}$ and $250 \text{ nm} < \lambda < 400 \text{ nm}$ simultaneously. This latter range is, without a doubt, beneficial since it protects from energetic UV emission, responsible for the degradation of materials inside and health-related issues like skin and eye damage.

Angular aspect

Another aspect to consider when window coatings are discussed is the incident angle of the solar rays. While all previous devices were designed and measured at normal incidence (0°), this is rarely the case for a window. In the last part of this chapter, several cities will be considered to simulate the effect of the photonic design on windows at different latitudes. As a proof-of-concept, an angle of incidence of 50° was chosen for the study. This is close to the average incident angle of sunlight on a vertical south-facing window when the sun is at its highest point during the day for mid-latitudes.

Designing a DBR for it to be perfectly tuned at a specific angle is highly challenging in term of fabrication. Regarding the design, the angular dependency as to be discussed first. It is indeed known that the position of the stopband of an one-dimensional photonic crystal is variable as a function of the angle. To begin with, the phase shift δ in each layer of a dielectric mirror, including the angle of the wave in the layer θ , was given by Equation 2.11. The latter is adapted below for a chirped lattice (indices i). The condition for high reflectance is that δ should always be equal to $\pi/2$ to create destructive interferences in reflection.

$$\delta_X = 2\pi n_X^i d_X^i \cos\theta_X / \lambda_0^i = \pi/2 \quad (7.4)$$

where θ is the angle of the wave in the layer, d^i the thickness of the layer i and λ_0^i the Bragg wavelength of layer i to satisfy the quarter-wave condition ($\delta = \pi/2$). Index X stands either for the high-index hybrid or the low-index PMMA, as shown in Figure 7.4.

Intuitively, and misleadingly, a tilted angle would imply a longer optical path length experienced by the wave in each layer, therefore, red-shifting the optical stopband in a similar way as when increasing the thickness of the layers. This is however incorrect since the cosine of θ decreases for larger angles, thus, λ_0 at which the quarter-wave condition is satisfied has to become smaller too. Consequently, a higher angle of incidence causes a blue-shift of the photonic band-gap.

Consequently, for the design, each thickness d_X^i must be calculated as a function of the angle θ_X , which is different in the air, the hybrid layers and the PMMA layers due to refraction. Using the Equation 7.4 and Snell's law as shown in Figure 7.4.b, thicknesses are given by the following equation:

$$d_X^i = \frac{\lambda_0^i}{4n_X^i \cos\theta_X} = \frac{\lambda_0^i}{4 \sqrt{n_X^i{}^2 - \sin^2(\theta_0)}} \quad (7.5)$$

where θ_0 is the angle of incidence on the structure and considering air as the incident medium.

Experimental design

Subsequently, using Equations 7.3 and 7.5, the design of a near-IR broadband reflector tuned at a 50° incident angle could be designed. The parameters, reported in Table 7.2, were used to compute the thicknesses shown in Figure 7.4.a, with the thickest layers on the bottom (largest λ_0) and the thinnest on the top (smaller λ_0) of the device. The corresponding Bragg wavelengths are shown in the top axis.

Table 7.2: Designed parameters for solar-control chirped dielectric mirror starting at the Bragg wavelength Λ_0 at an angle of incidence of 50° .

<i>Design at $\theta_0 = 50^\circ$</i>	
PMMA	$n_a=1.49 / n_b=0.003$
80 vol% hybrid (100 °C)	$n_a=1.75 / n_b=0.025$
Λ_0 (nm)	800
Number of layers	81
Common ratio k	1.0045

The calculated reflectance spectra of the structure are plotted in Figure 7.5 at normal incidence, 25° and 50° with respect to the normal. The spectrum at the designed angle 50° confirms the photonic stopband starting from $\lambda = 750$ nm up to 1200 nm. This ~ 450 nm extended reflectance band of about 90 % in average can reflect most of the solar radiation at these wavelengths,

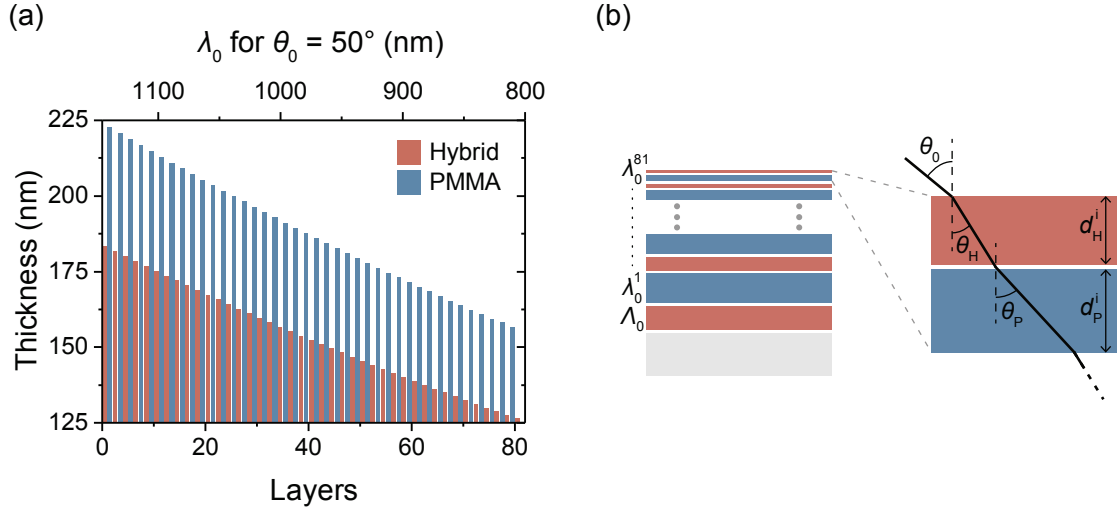


Figure 7.4: Structure of near-IR superlattice based on the parameters given in Table 7.2. (a) displays the thicknesses of each layer along the stack and as a function of the Bragg wavelength λ_0 (top axis). (b) shows a schematic of the chirped structure as well as the refraction of light in the top hybrid/PMMA bi-layer.

also corresponding to the most intensive part of the IR emission. Furthermore, the second reflective region is located in the UV as designed, therefore, not compromising the transparency. Consequently, this clear coating would allow good solar control for low-SHG but also effective UV blocking which is generally not fully absorbed by glass. This is done thanks to the photonic stopband but also the absorption of the titanium species.

Reflectance spectra in Figure 7.5 were calculated considering an averaged polarisation as it is the case with the solar radiation. Nevertheless, when discussing angular behaviours in optics, it is also important to analyse *s*- and *p*-polarisations separately since the refractive index behaves differently. Figure 7.6 shows the reflectance as a function of the angle of incidence for both polarisations. While a small part of the visible blue light is reflected at low angles, it is noticed that the stopband moves towards shorter wavelengths and crosses the 400 nm dashed line at an incident angle of 50° . This confirms the angular design of the device. Furthermore, the reflectance is low across the visible spectrum for most angles which demonstrates the omnidirectional transparency of the structure, only the deep-blue being reflected around normal incidence.

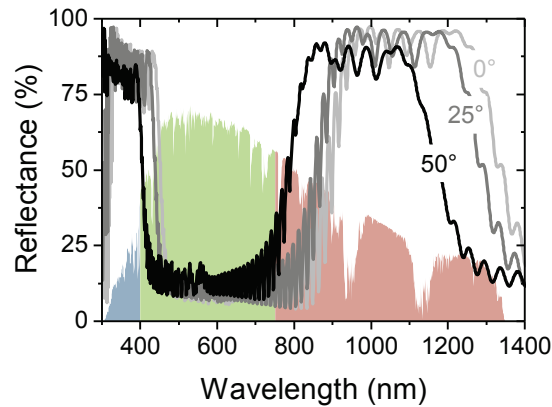


Figure 7.5: Calculated reflectance spectra of near-IR chirped mirror at normal incidence, 25° and 50°. Shaded area behind the data represent the solar spectrum with UV (blue area), visible (green area) and IR (red area) regions.

The difference between both polarisations is related to the Fresnel's Equations 2.4 and 2.5 expressing the angular dependence of the reflection and transmission coefficients (see Chapter 2). In the general case, *s*-polarised light experiences an increase in reflectance with the angle of incidence while the reflectance decreases with *p*-polarised light down to the Brewster angle before increasing sharply (see Figure 2.1). These trends are also observed here with the reflectance becoming less strong with *p*-polarised light for both the transparent part and the photonic band-gap. Moreover, the width of the latter shrinks with *p*-polarised light compared to the *s*-polarisation.

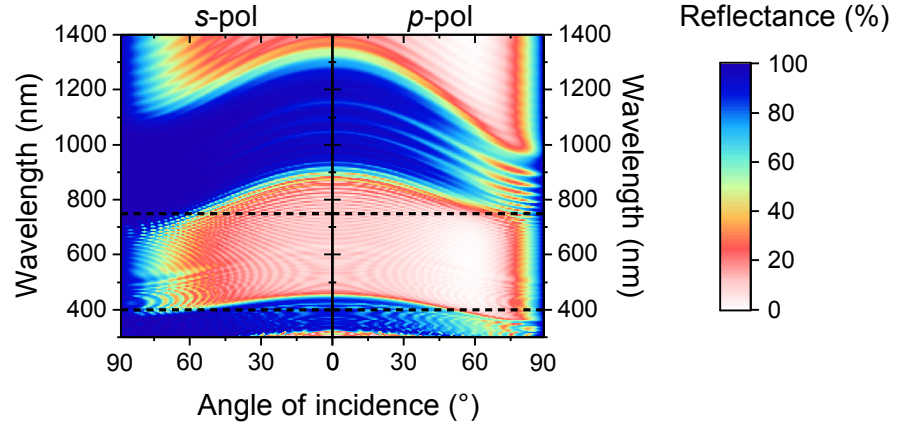


Figure 7.6: Calculated angular reflectance of the near-IR chirped mirror for *s*- and *p*-polarised light. Horizontal dashed lines, delimiting the visible spectrum, shows the omnidirectional transmittance band of the structure.

7.2.3 Solar-control coating with low-emissivity

Despite the efficient solar-control thanks to the photonic stopband, DBRs do not insulate the window from the blackbody radiation ($\lambda > 2.5 \mu\text{m}$). As seen in part 7.1, TCOs are highly reflective in this spectral region, remarkably simple to process and affordable. For example, NSG TECTM 15, a low-e window pane widely commercialised by Pilkington exhibits an emissivity as low as 0.16 with a visible transmittance of 76 % and a SHG coefficient of 0.78.² It is based on a transparent 300 nm FTO layer. Consequently, applying the near-IR chirped reflector to a low-e substrate would allow the control of both types of IR radiation, as well as reflecting the near-UV.

In the following section, the fabrication of the structure is discussed. NSG TECTM 15 is used as a substrate (optical and material characterisation can be found in Appendix C). For the calculations, a glass made of BK7 is considered since it appears relatively similar to the one used by the company. The refractive indices of BK7 and FTO were taken from Schott datasheet and the literature, respectively.^{19,20}

The near-IR superlattice designed above was fabricated by spin-coating on the back of the FTO substrate. A more viscous 60 vol% hybrid solution than previously used for the visible chirped mirrors was required this time to deposit thicker layers (formulated from a 20 mg mL⁻¹ PVAI solution and a 1.5 M TiO_xH solution). The low molecular weight PMMA ($M_n \approx 35\,000$ g mol⁻¹) developed in Section 6.2.1 was used in butyl acetate with a concentration of 60 mg mL⁻¹. Fabrication method is described in the Experimental Section 3.2.4 and spin-coating parameters can be found in Appendix D.

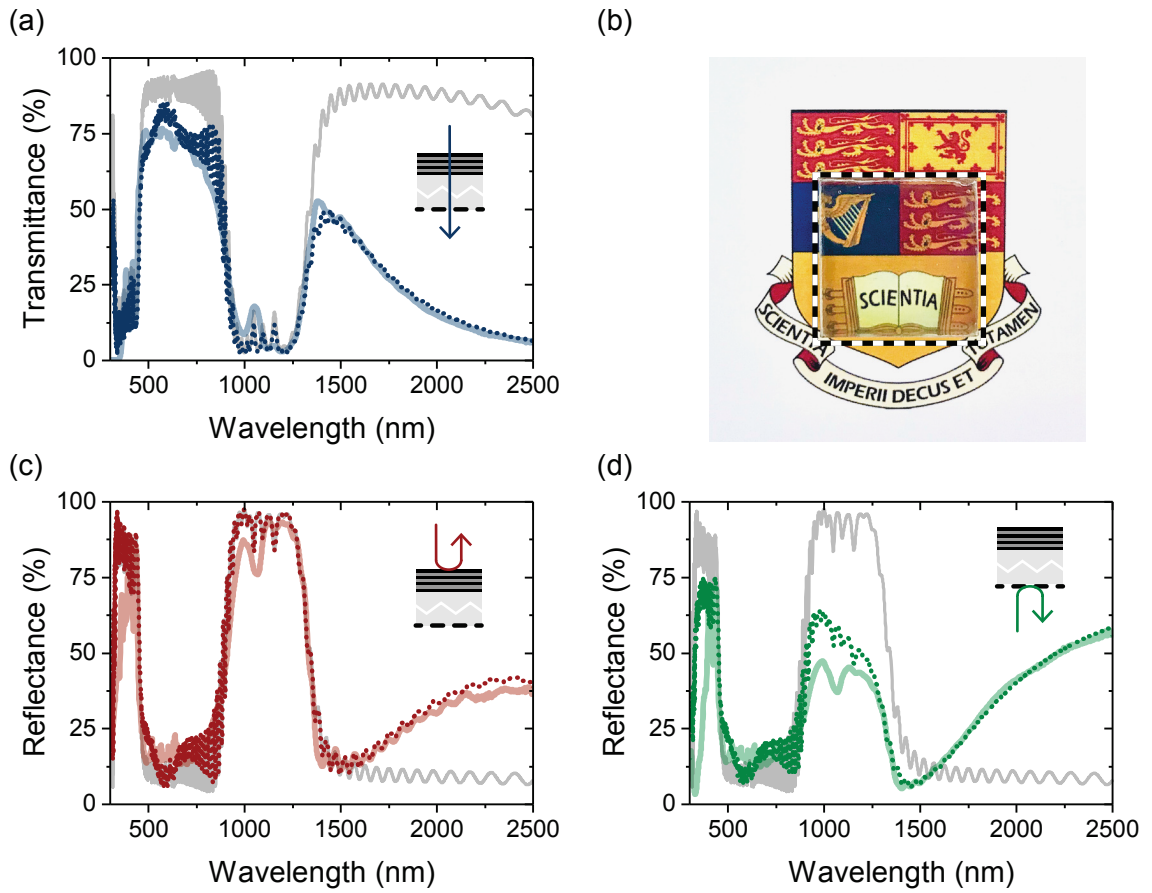


Figure 7.7: Broadband near-IR reflector based on 81 layers with additional low-e film for solar-control window coating. Transmittance, reflectance from the dielectric mirror side and reflectance from the low-e FTO side are reported in (a), (c) and (d), respectively. Calculated spectra of the photonic structure only (no FTO) are plotted in light grey lines. Dotted lines correspond to the calculated spectra of the design including a 300 nm FTO film. Schematics of the structure and the direction of characterisation are shown in inset. Finally, the sample is displayed in (b) which confirms the high transparency even at the unoptimised $\sim 0^\circ$ incidence.

Measured transmittance and reflectance spectra are plotted in Figure 7.7 along with the calculated spectra. The light grey curves show calculated spectra from the DBR alone (no FTO) and the dotted lines the modelled structure including the FTO layer. For technical reasons, transmittance was measured at normal incidence only and reflectance at an 8° angle (see Section 3.3.1).

It can be noticed that calculated and experimental data are in excellent agreement. Reflectance bands are perfectly superimposed which confirms the omnidirectional transparency but also what would be the optimum reflectivity at $\sim 50^\circ$. The averaged transmittance in the range $450\text{ nm} < \lambda < 850\text{ nm}$ (corresponding to the visible range at the angle of incidence of the design) is $\sim 70\%$. This is just a few percents lower than the one of the low-e substrate (76 %) confirming the high transmittance of the superlattice. It also emphasises the low optical losses of the materials and the good interfaces considering the 81 layers of the structure. The photograph of the sample on the Imperial College London crest is displayed in Figure 7.7.b.

Furthermore, the reflectance within the optical stopband was measured to be as high as 87 % for the extended region of $\lambda = 950\text{ nm}$ to $\lambda = 1300\text{ nm}$. The position of the harmonic also replicates exactly the calculated spectrum. As a consequence, the reflectance is higher than 50 % at normal incidence for $\lambda < 445\text{ nm}$ (at 8° incident angle) which gives a slight blue reflection and a yellowish colouration in transmission. This can be observed in the photograph (Figure 7.7.b) where the book "*scientia*" appears slightly yellow while it is originally white. Regarding the UV part of the spectrum, measured and calculated spectra differ lightly due to the absence of absorption for the hybrid and the PMMA in the model used.

It is also important to notice that the transmittance is the same both ways, conversely, different optical responses are measured in reflection depending on the direction. The reflectance from the DBR side (Figure 7.7.c) matches with the one from the photonic crystals alone. This side would be intended to block the solar radiation, thus, facing the outside. Beneficially, the "inside" (FTO) reflectivity (Figure 7.7.d) is considerably lower in the near-IR but stronger in the mid-IR, the only IR wavelength range in play inside a building and crucial for good thermal insulation.

7.2.4 Solar radiation glazing factors

Window panes can be characterised and compared using several solar radiation glazing factors. The following study focuses on the calculation of the total solar transmittance (T_{solar}), visible solar transmittance ($T_{visible}$), UV solar transmittance (T_{UV}) and IR solar transmittance ($T_{sol\ IR}$). While in practice, windows often include two or three-glass layers, only single panes are discussed here. The solar properties of the chirped near-IR DBR alone (part 7.2.2) and its combination with a low-e FTO coating (part 7.2.3) were compared with a bare glass window (BK7) and benchmark technologies. For this purpose, FTO films (based on NSG TEC™ 15 windows), high-SHG silver-based coating and low-SHG triple-silver coatings were modelled.

Solar radiation glazing factors are defined by the ratio of the energy passing through the window to the global energy reaching the window for a specific spectral region. For consistency with the industry, the international standards were used except for $T_{sol\ IR}$ which is not included in their method (in this case *ISO 9050:2003(E) - Glass in buildings - Determination of light transmittance, solar direct transmittance, total solar energy transmittance, ultraviolet transmittance and related glazing factors*).^{21,22}

T_{solar} , T_{UV} , $T_{visible}$ and $T_{sol\ IR}$ are given by the following equations:

$$T_{solar} = \frac{\sum_{\lambda=300nm}^{2500nm} T(\lambda) S_{\lambda} \Delta\lambda}{\sum_{\lambda=300nm}^{2500nm} S_{\lambda} \Delta\lambda} \quad (7.6)$$

where S_{λ} is the relative spectral distribution of solar radiation and $T(\lambda)$ the spectral transmittance of the window. $S_{\lambda} \Delta\lambda$ values are given in Table E.1.^{21,22}

$$T_{UV} = \frac{\sum_{\lambda=300nm}^{380nm} T(\lambda) S_{\lambda} \Delta\lambda}{\sum_{\lambda=300nm}^{380nm} S_{\lambda} \Delta\lambda} \quad (7.7)$$

where S_λ is the relative spectral distribution of UV solar radiation. $S_\lambda \Delta\lambda$ values are given in Table E.2.^{21,22}

$$T_{visible} = \frac{\sum_{\lambda=380nm}^{780nm} T(\lambda) D_\lambda V(\lambda) \Delta\lambda}{\sum_{\lambda=380nm}^{780nm} D_\lambda V(\lambda) \Delta\lambda} \quad (7.8)$$

where D_λ is the relative spectral distribution of illuminant D65 and $V(\lambda)$ the spectral luminous efficiency for photopic vision.²³ $D_\lambda V(\lambda) \Delta\lambda$ values are given in Table E.3.^{21,22}

$$T_{sol IR} = \frac{\sum_{\lambda=780nm}^{2500nm} T(\lambda) S_\lambda \Delta\lambda}{\sum_{\lambda=780nm}^{2500nm} S_\lambda \Delta\lambda} \quad (7.9)$$

where S_λ is the relative spectral distribution of IR solar radiation. $S_\lambda \Delta\lambda$ values are given in Table E.4.^{21,22}

Those factors are commonly given at normal incidence, even for the standards, despite of the position of the sun. Table 7.3 shows the characteristics at 0° for the sample discussed previously along with the calculated values of other modelled coatings. As expected, the bare glass BK7 transmits above 90 % across the whole spectrum. The 300 nm FTO low-e coating is also relatively transparent to all solar spectral regions (T between 60 and 80 %). Another benchmark product for high-SHG coating, *i.e.* high solar transmission, is based on a thin layer of silver. A common structure made of TiO₂ (25 nm)/Ag (9 nm)/TiO₂ (25 nm) was used in this study. The spectrum can be found in Appendix F along with the other window spectra. Comparatively, the chirped DBR alone (no FTO coating) exhibits higher transmittance in the visible by 6 % and a 4-fold stronger UV control.

The low-SHG sample fabricated above (DBR + FTO) was put in regards with a triple-silver coating, the most common technology on the market nowadays. It was modelled using a seven-layer structure alternating TiO₂ and silver films, such as: TiO₂ (20 nm)/Ag (9 nm)/TiO₂ (35 nm)/Ag (9 nm)/TiO₂ (35 nm)/Ag (9 nm)/TiO₂ (20 nm).⁴ The spectrum is given in Appendix F.

The total solar transmittance of the triple-Ag structure is relatively similar to the one of the measured DBR on the FTO substrate (50 % against 46 %). The silver-based window transmits better in the visible by ~ 10 % and reflects 10 % more solar IR, however, it is much less efficient in blocking the solar UV ($T_{UV} = 69$ % against 16 %).

Table 7.3: Solar radiation glazing factors of designed and measured photonic structures along with benchmark window coatings. T_{solar} , T_{UV} , $T_{visible}$ and $T_{sol\ IR}$ are reported for high- and low-SHG films at normal incidence following international standards. Transmittance spectra are given in Appendix F.

	T_{solar} (%)	T_{UV} (%)	$T_{visible}$ (%)	$T_{sol\ IR}$ (%)
BK7 substrate	92	90	92	92
FTO	70	67	80	61
Single-layer silver	73	63	84	57
Chirped near-IR DBR (modelled)	65	15	90	49
Triple-layer silver	50	69	87	9
Chirped DBR + FTO (modelled)	50	12	78	29
Chirped DBR + FTO (measured)	46	16	76	20

Despite international standards, it seems also crucial to consider the solar position when dealing with solar-control radiation for windows. Unfortunately, the transmittance of the sample could not be measured as a function of angle for experimental reasons. Consequently, the calculated spectra, which was shown to fit remarkably well with the experimental data (see Figure 7.7) and exhibited similar glazing factors at normal incidence (Table 7.3), are used in the following part.

The angular transmittance of the structures are given in Appendix F for non-polarised light as it is the case for solar radiation. Incorporating $T(\lambda, \theta)$ in Equations 7.6, 7.7, 7.8 and 7.9, angular glazing factors $T_{solar}(\theta)$, $T_{UV}(\theta)$, $T_{visible}(\theta)$ and $T_{sol\ IR}(\theta)$ could be computed.

Figure 7.8 displays factors as a function of the angle of incidence. While all coatings transmit well the visible light, the distinction between high- and low-SHG windows, respectively shown by dotted and solid lines, is immediate. Transmittance of solar IR and total solar radiation is indeed much higher for the high-SHG structures. As expected, the superlattice combined with a low-e film exhibits a low-SHG similar to the one of the triple-Ag benchmark window. As for the dielectric structure alone, it shows an intermediate SHG. On the other hand, both photonic structures (red curves) have a unique UV control aspect with $T_{UV}(\theta)$ much lower than for

the other coatings, independently of the angle. Finally, all films become more opaque to solar radiation at higher angles due to the Fresnel's coefficients (see Section 2.1).

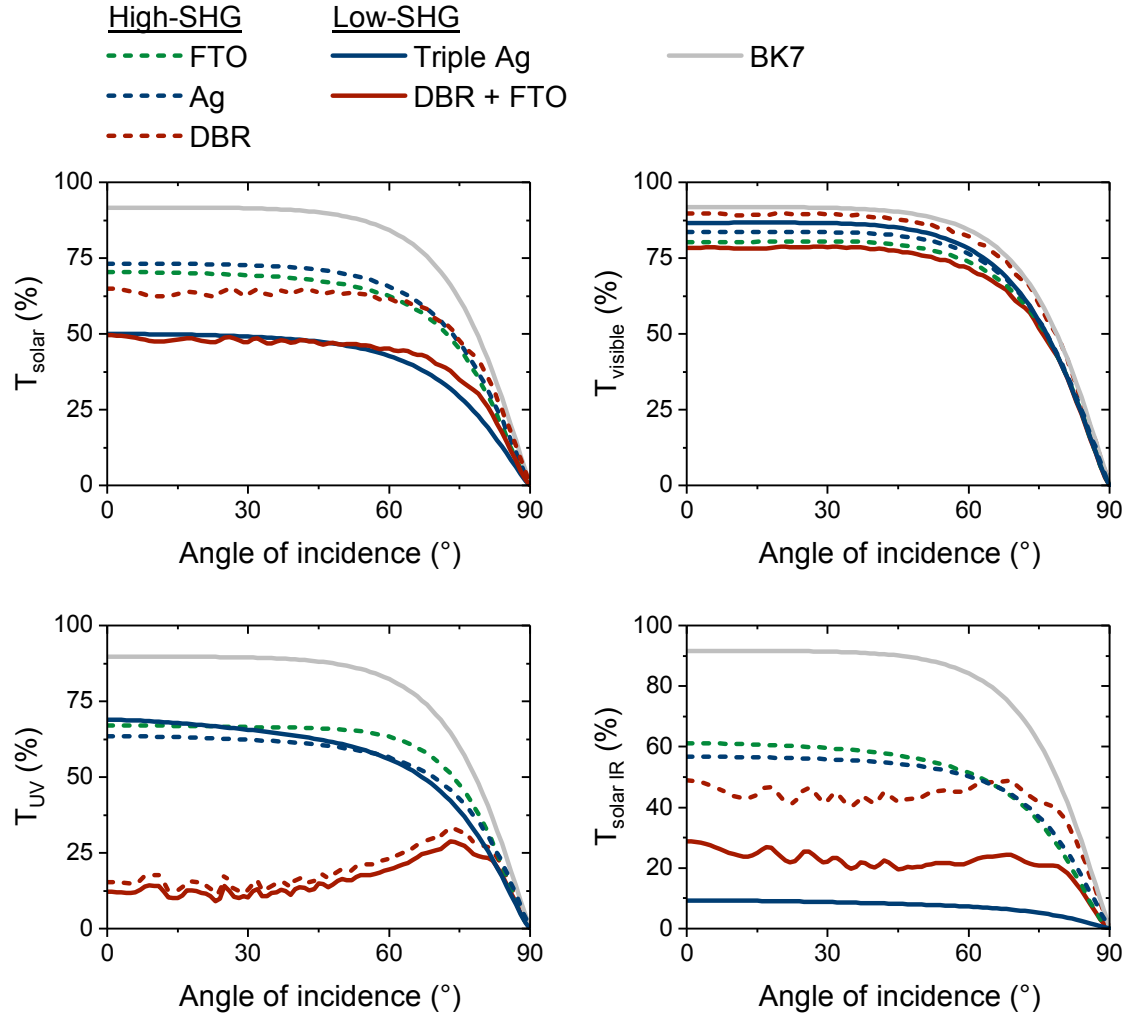


Figure 7.8: Angular solar radiation glazing factors T_{solar} , T_{UV} , $T_{visible}$ and $T_{solar IR}$ for designed photonic structures and benchmark window coatings. Angular transmittance spectra are given in Appendix F.

7.2.5 Energy efficiency analysis

To compare the energy efficacy of the chirped photonic glazings with the benchmark coatings, a south-facing window was considered. To account for different solar positions and climate, London with a relatively high latitude (51° North) and moderate climate, Atlanta with a subtropical climate (34° N) and Dubai with a tropical desert climate (25° N) were chosen. The diverse weather conditions imply distinct requirements in term of solar heat management. Solar radiation is preferred for about three-quarter of the year in London, but only during winter in Atlanta and almost never in Dubai. Nevertheless, high transmission in the visible is always expected for windows and additional UV opacity an advantage.

The position of the sun also differs between these locations and during the year. Figure 7.9 shows the sun position for the three latitudes during particular days of the year: summer and winter solstices where the sun is at its highest and lowest position, respectively, and the vernal and autumnal equinoxes which represent the intermediate sun inclination (equal day and night length). The angle of incidence of sun's rays on the south-facing window, *i.e.* the angle between the window plane and the incoming ray, was generated every 10 minutes using NREL's Solar Position and Intensity function (SOLPOS 2.0).²⁴ As predicted from the latitudes, London exhibits the most grazing angles, especially during winter times.

Another observation is that the solar intensity also changes during the year due to the Earth's elliptical orbit and during the day due to the different lengths of atmosphere the light experienced. For the study, the solar intensity was also computed every 10 minutes using NREL's SOLPOS 2.0 code along with the clearness index for a vertical surface K_t which is the ratio of global to extraterrestrial irradiance.^{25,26}

The Solar Factor is generally defined as the total solar energy transmitted by the window, the closer to 0 meaning that most of the solar radiation is blocked. It corresponds to the sum of spectral solar transmittance and secondary heat transfer factor toward the inside (q_i). The latter is the energy absorbed by the glazing and re-emitted to the inside, thus, accounting for the heat transfer by convection and blackbody IR radiation.^{21,22} Yet, in order to calculate the energy

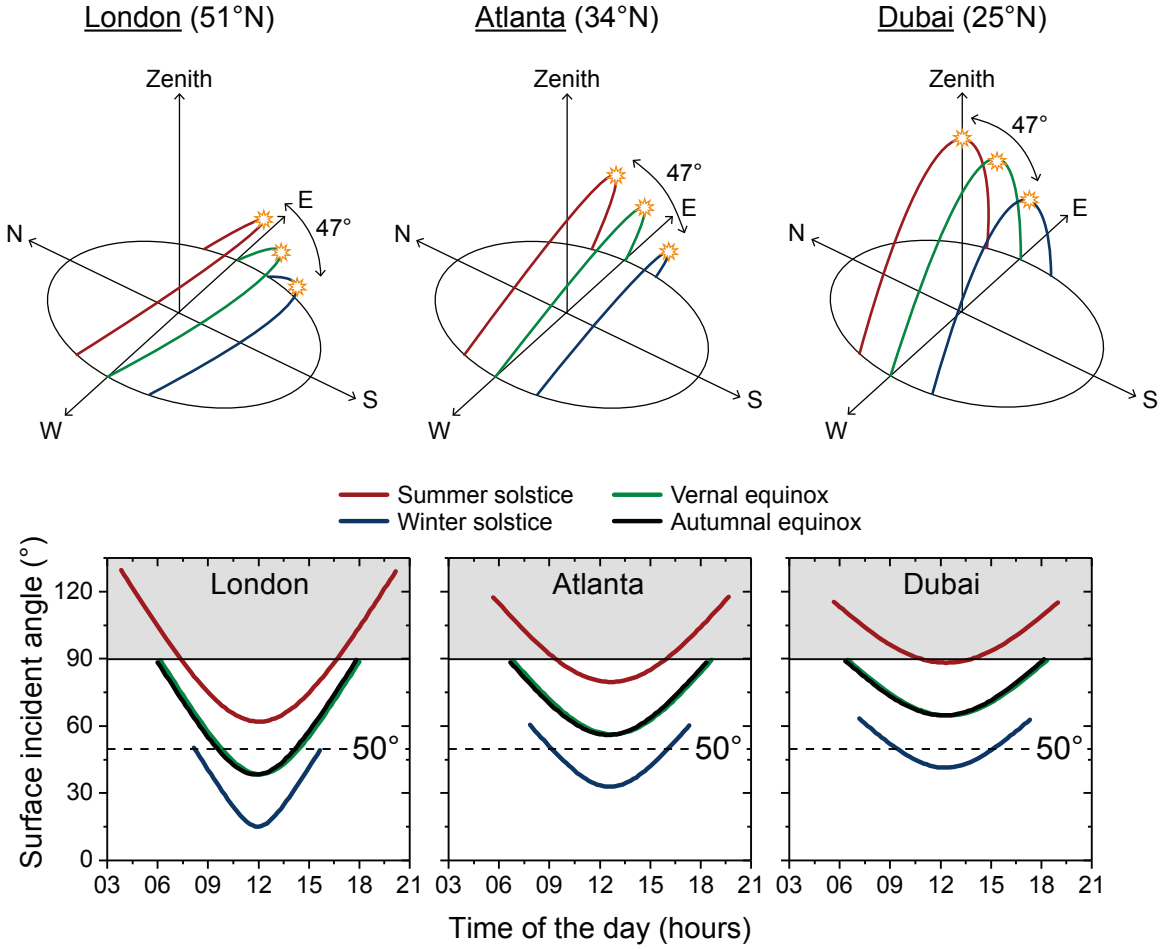


Figure 7.9: Incident angle of solar rays on a vertical south-facing window, *i.e.* the angle between the window plane and the incoming ray, during daytime in London, Atlanta and Dubai. Blue and red solid lines represent the extremal position of the sun during the year (winter and summer solstices) and black and green are the averaged one (autumnal and vernal equinoxes). Rays above 90° do not reach the windows. Data were acquired from NREL's SOLPOS 2.0.²⁴

transfer towards the inside, the solar absorptance and the emissivity of the inside surface are needed. Since most of the coatings in this study have a low-e coating (TCO or silver), q_i is relatively small and can be ignored. Therefore, only the solar factor of the DBR alone and the bare substrate are slightly underestimated in this study.

Consequently, the efficacies of the coatings were calculated by integrated the solar factor over time, taking in account solar intensity and angle of incidence variations. Thus, both daily and yearly factors are defined by the ratio of the solar intensity transmitted by the window integrated

over time to the total solar energy reaching the surface integrated over time, assuming clear sky. For more clarity, instead of the solar factor, the solar control factor (SCF) is defined by Equation 7.10. The higher the SCF, the more solar energy is kept outside.

$$SCF = 1 - \frac{\int_{t_i}^{t_f} I_{sol}(t)T_{sol}(t)dt}{\int_{t_i}^{t_f} I_{sol}(t)dt} \quad (7.10)$$

where I_{sol} is the global solar intensity given by SOLPOS 2.0 for a vertical window facing south and $T_{sol}(t)$ the total solar transmittance as a function of time. Thanks to the known position of the sun during the day and the year, time can be directly related to the angle of incidence θ , leading to $T_{sol}(\theta)$ and $I_{sol}(\theta)$. t_i and t_f are the initial and final limits of the integration depending on the daily or yearly SCF calculation.

In Figures 7.10 and 7.11, glazing technologies are compared for the solstices and equinoxes and also averaged over the year for the three different locations. High-SHG films are plotted in Figure 7.10 where the yearly solar control factor increased by $\sim 20\%$ compared to the bare substrate for all cities. Furthermore, they allow more solar energy to pass through during winter time while they are much more efficient in blocking radiations during summer when the sun is higher on average. In general, the solar control is stronger when the latitude becomes lower. This is particularly true during summer which corresponds to the most intense solar radiation. The sun being much closer to the zenith in these conditions, the sunlight is highly reflected because of the Fresnel's coefficients at large angles. The DBR alone exhibits very similar solar control as the other high-SHG coatings in all conditions. Nevertheless, applications would be different since it permits heat exchange through the window (no low-e) while blocking UV light more effectively.

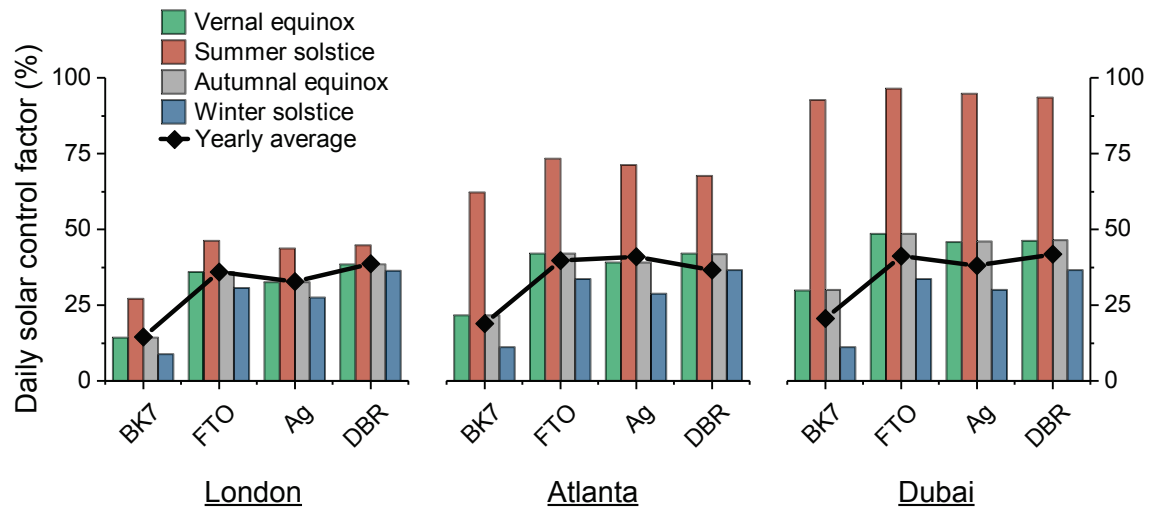


Figure 7.10: Bar plots of daily solar control factors during four specific days of the year in London, Atlanta and Dubai. High-SHG glazings are compared. The black line shows the yearly average solar energy control. The near-IR dielectric mirror exhibits similar solar factor but permits heat exchange (no low-e) and UV blocking.

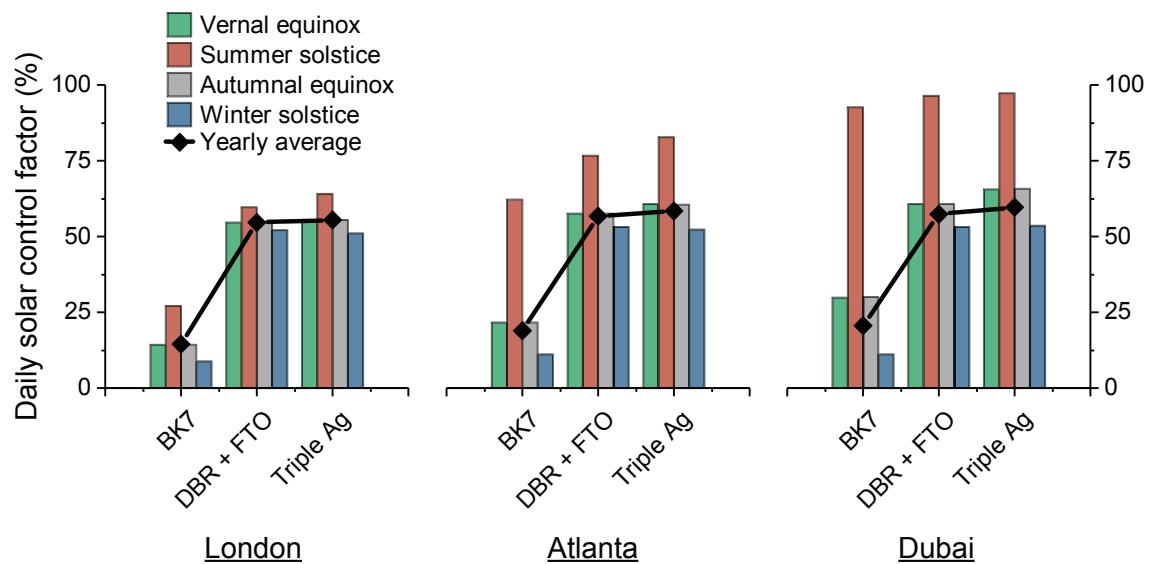


Figure 7.11: Bar plots of daily solar control factors during four specific days of the year in London, Atlanta and Dubai. Low-SHG glazings are compared. The black line shows the yearly average solar energy control. The printed DBR with FTO substrate is as efficient as the triple-silver coating in controlling the solar radiation while being transparent to telecommunication wavelengths and opaque to solar UV light.

Meanwhile, the use of photonic crystal for solar control windows becomes probably more attractive when combined with a low-e film. Figure 7.11 shows the daily and yearly SCF for the low-SHG window. The benchmark triple-silver glazing and the chirped dielectric mirror on FTO both reduce the yearly solar energy transmittance by 40 % independently of the location. Daily optical responses are also very similar by leaving through more energy during winter and less during summer as required. In summary, the printed dielectric device allows a solar energy control and a low-emissivity as valuable as the silver-based window and appears as a potential solution for low-SHG glazing. Yet, the choice between the two would be made on other properties such as UV blocking, essential to protect inside materials from degradation, electromagnetic transparency for telecommunications and optical appearance. While the silver-based film is more transparent to the visible, the dielectric mirror excels in the two other spectral domains.

To discuss the energy saving, the solar irradiance is plotted in Figure 7.12 for London during the summer solstice. A horizontal surface would receive the equivalent of $\sim 5 \text{ kWh m}^{-2}$ with a peak irradiance around 1 kW m^{-2} . In the case of a vertical window facing south, the peak irradiance received is only 625 W m^{-2} while the total energy (the area under the solar irradiance curve) is about 3.7 kWh m^{-2} . As discussed above with Figure 7.11, the fabricated photonic structure allows a daily solar control factor as high as 60 % during summer in London. This would be equivalent to a total energy of 2.2 kWh m^{-2} blocked by the glazing (grey area of Figure 7.12) with only 1.5 kWh m^{-2} remaining radiating inside the room (blue area).

Keeping in mind that electrical energy is far superior "quality" than thermal energy, it is still interesting, as an example, to give the amount of energy produced by a domestic photovoltaic panel in similar conditions. When considered on a horizontal roof with an efficiency of 20 %, the electrical energy output would be $\sim 1 \text{ kWh m}^{-2}$ during a day in June in London (daily irradiance of $\sim 5 \text{ kWh m}^{-2}$). Despite that electrical and thermal energy are not directly equivalent, it seems reasonable to say that the use of coating for heat management should play an important role in a sustainable future.

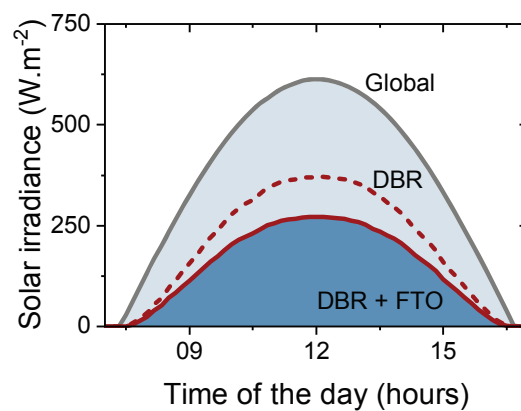


Figure 7.12: Solar irradiance reaching a vertical south-facing window in London during the summer solstice. The global irradiance is plotted in grey with the resulting energy being the area underneath. The solar irradiance radiating inside the room after passing through the DBR and the DBR + FTO glazings are plotted in dashed and solid red curves, respectively. The energy transmitted through the window during the day with the printed photonic structure with the low-e coating is equal to 1.5 kWh m^{-2} (blue area), only 40 % of the global daily solar power shining on the window (3.7 kWh m^{-2}).

7.3 Conclusion and Outlook

Solving the global energy equation that the world is currently facing and to meet regulations, better control of the solar energy in buildings is crucial. In particular, with 50 % of the solar radiation in the IR and ventilation, air-conditioning and heating standing for 40 % of the energy consumed in buildings, the development of advanced windows is central.

Based on previous chapters, classic quarter-wave IR dielectric mirrors were first produced. Then, based on a more sophisticated design, a broadband near-IR and UV reflector was modelled and fabricated with exceptional agreement. The mirror was also arranged at a specific angle, in regards to the solar incident angle on windows and to demonstrate the remarkable control over the processability of the materials. Thanks to a superlattice of 81 layers, an extended photonic stopband with a reflectance around 90 % over 450 nm in the IR was achieved.

It was finally shown that the photonic structure could be as efficient as benchmark window glazings to control the solar radiation. The printed photonic structure on a low-e substrate resulted in high solar control, thus, low-SHG independently of the solar conditions. It can reflect more than 50 % of the total solar energy while leaving the visible passing through (accounting for 43 % of the total solar energy). Comparatively, a triple-silver coating appeared slightly more transparent but, conversely, did not block the solar UV radiation.

To conclude, we have shown that near-IR printed photonic reflectors could be an efficient technology for solar control windows. This could lead to potential low-cost and large-area manufacturing thanks to the use of solution-processed materials. Moreover, the advanced design discussed in this chapter could be applied to other applications where wavelength-selective, broadband reflectors are also required and where costly photonic inorganic-based filters are the only solution.

7.4 References

1. IEA. *World Energy Outlook 2018* 661 pp. (International Energy Agency, Paris, 2018).
2. Jelle, B. P., Kalnæs, S. E. & Gao, T. Low-Emissivity Materials for Building Applications: A State-of-the-Art Review and Future Research Perspectives. *Energy and Buildings* **96**, 329–356 (2015).
3. Granqvist, C. G. Transparent Conductors as Solar Energy Materials: A Panoramic Review. *Solar Energy Materials and Solar Cells* **91**, 1529–1598 (2007).
4. Ding, G. & Clavero, C. Silver-Based Low-Emissivity Coating Technology for Energy-Saving Window Applications. *Modern Technologies for Creating the Thin-film Systems and Coatings* (2017).
5. Kanu, S. S. & Binions, R. Thin Films for Solar Control Applications. *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* **466**, 19–44 (2010).
6. Kim, J.-J. & Moon, J. W. *Impact of Insulation on Building Energy Consumption in Eleventh International IBPSA Conference, Building Simulation* (Citeseer, 2009).
7. Solovyev, A. A., Rabotkin, S. V. & Kovsharov, N. F. Polymer Films with Multilayer Low-E Coatings. *Materials Science in Semiconductor Processing* **38**, 373–380 (2015).
8. Anderson, A.-L., Chen, S., Romero, L., Top, I. & Binions, R. Thin Films for Advanced Glazing Applications. *Buildings* **6**, 37 (2016).
9. Ebisawa, J. & Ando, E. Solar Control Coating on Glass. *Current Opinion in Solid State and Materials Science* **3**, 386–390 (1998).
10. Martín-Palma, R. J. Spectrally Selective Coatings on Glass: Solar-Control and Low-Emissivity Coatings. *Journal of Nanophotonics* **3**, 030305 (2009).
11. Granqvist, C. G. Solar Energy Materials. *Advanced Materials* **15**, 1789–1803 (2003).
12. Granqvist, C. G. & Hultåker, A. Transparent and Conducting ITO Films: New Developments and Applications. *Thin Solid Films. Proceedings of the 2nd International Symposium on Transparent Oxide Thin Films for Electronics and Optics* **411**, 1–5 (2002).
13. Liu, L., Chang, H., Xu, T., Song, Y., Zhang, C., Hang, Z. H. & Hu, X. Achieving Low-Emissivity Materials with High Transmission for Broadband Radio-Frequency Signals. *Scientific Reports* **7**, 4840 (2017).

14. Bouvard, O., Lanini, M., Burnier, L., Witte, R., Cuttat, B., Salvadè, A. & Schöler, A. Structured Transparent Low Emissivity Coatings with High Microwave Transmission. *Applied Physics A* **123**, 66 (2017).
15. Weber, M. F., Stover, C. A., Gilbert, L. R., Nevitt, T. J. & Ouderkirk, A. J. Giant Birefringent Optics in Multilayer Polymer Mirrors. *Science* **287**, 2451–2456 (2000).
16. Wheatley, J. A. & Ouderkirk, A. J. *US Patent* 6049419A (2000).
17. Wheatley, J. A., Weber, M. F. & Ouderkirk, A. J. *US Patent* 6157490A (2000).
18. Bensaid, M. O., Miloua, R., Ghalouci, L., Godey, F. & Soldera, A. Multiscale Design and Optimization of Polymer-Based Photonic Crystals for Solar Shielding. *Solar Energy Materials and Solar Cells* **171**, 166–179 (2017).
19. Schott. *Optical Glass Collection Datasheets* (2017).
20. Von Rottkay, K. & Rubin, M. Optical Indices of Pyrolytic Tin-Oxide Glass. *MRS Proceedings* **426** (1996).
21. *ISO 9050:2003 - Glass in Building – Determination of Light Transmittance, Solar Direct Transmittance, Total Solar Energy Transmittance, Ultraviolet Transmittance and Related Glazing Factors* (2003).
22. Jelle, B. P. Solar Radiation Glazing Factors for Window Panes, Glass Structures and Electrochromic Windows in Buildings—Measurement and Calculation. *Solar Energy Materials and Solar Cells* **116**, 291–323 (2013).
23. *ISO 11664-2:2007 - Colorimetry – Part 2: CIE Standard Illuminants* (2007).
24. Michalsky, J. J. The Astronomical Almanac’s Algorithm for Approximate Solar Position (1950–2050). *Solar Energy* **40**, 227–235 (1988).
25. Maxwell, E. L. *A Quasi-Physical Model for Converting Hourly Global Horizontal to Direct Normal Insolation* (1987).
26. Reda, I. & Andreas, A. *Solar Position Algorithm for Solar Radiation Applications (Revised)* NREL/TP-560-34302, 15003974 (2008).

8 | Summary and Outlook

8.1 Summary

The development of advanced functional materials to control light is fundamental for many current and future technologies. Solution-processed hybrids offer many advantages compared to inorganics. While the latter can give access to exceptional optical properties, they also generally require energy and capital intensive deposition techniques. Meanwhile, a novel poly(vinyl alcohol)/titanium oxide hydrates hybrid has demonstrated that high refractive indices and low-optical losses can also be achieved with inks. Consequently, fields such as solar energy, building efficiency, sensing and optical data storage could benefit from their potential low-cost and large-area manufacturing as well as low-embodied carbon and mechanical flexibility.

This work investigated the potential of the PVAI/TiOxH hybrid for thin-film photonics and, in particular, planar local patterning of refractive index and solution-processed dielectric mirrors. After introducing the underlying concepts behind light-matter interactions, inorganic/organic hybrids and solution-processed photonic devices in Chapter 2, a thorough characterisation of the primary material was presented in Chapter 4. Then, a time-resolved study of the annealing process and its implication for the refractive index control were discussed (Chapter 5). In Chapter 6, solution-processed DBRs were explored with scalability and straightforward deposition in mind to facilitate the often complex fabrication of photonic structures. Such one-dimensional crystals were then applied in Chapter 7 specifically to heat management as solar-control window glazings. Details on the materials, experimental setups and optical modelling were reported in Chapter 3.

The measurements discussed in Chapter 4 demonstrated the exceptional intrinsic properties of the PVAI/TiOxH hybrid. When this type of materials generally suffer from large particles formation, thus strong scattering, it was shown that inorganic loads as high as 80 vol% could

be used. Only in the extreme case, extremely small (<5 nm) and well-dispersed clusters were observed without having a negative effect on the optical properties. Therefore, outstanding refractive indices between 1.6 and 2 can easily and reproducibly be achieved along with low-optical losses as a result of fine morphology, smooth interfaces and low absorption.

The in-situ characterisation of films during thermal annealing, presented in Chapter 5, demonstrated the fast thermal response of the material. It enables the straightforward local patterning of refractive index with large contrast, of great interest for the fabrication of planar waveguides and lenses, solar concentrators or even data storage. Uncommon multiple coplanar indices and large refractive index gradients were also successfully produced. Finally, a novel process called μ -contact photo-annealing showed great promise for the patterning of the hybrid but also, more generally, for sub-second micro-fabrication on thermally sensitive substrates such as plastic.

The work in Chapter 6 allowed the combination of high titanium content hybrid with the commodity polymer PMMA for the fabrication of solution-processed dielectric mirrors. Complex broadband chirped designs, larger-scale devices, circular photonic mirror and ARC were produced. Then, optical responses were systematically compared with modelling which proved the high quality and control of the fabrication technique. While spin-coating is simpler to use at the lab scale, the compatibility with the scalable dip-coating technique on relatively large substrates demonstrates the potential of the hybrid/PMMA reflectors for large-area, high-throughput manufacturing.

Mainly investigated within the visible spectrum, printed one-dimensional photonic crystal can also play a role in the control of infrared and ultraviolet light. These radiations are particularly relevant for solar energy, therefore, for building-integrated solar control technologies. An exceptionally complex structure for printed photonics based on fine chirping and designed for a specific angle was possible. It was demonstrated that, when combined with a low-emissivity coating, it could substantially limit the energy consumption in buildings similarly to benchmark low solar-heat gain window glazings. Additionally to the near-IR control, the dielectric mirrors reflected UV light more effectively than others.

8.2 Overall Outlook

This thesis has presented a comprehensive investigation of the PVAI/titanium oxide hydrates hybrid and some of its potential applications. Nevertheless, implications could be considerably broader if we consider that optical thin-films play a crucial role in many components, from conventional anti-reflection coatings for lenses or solar panels, integrated optics for planar light-wave circuits to dielectric mirrors in lasers. As a more general remark, the tunable and readily accessible high refractive index, the patterning of multiple coplanar indices and the extremely advanced multilayer coatings discussed in the last chapters of this work could enable the use of printed photonics in many other optical fields where expensive inorganic devices are currently the sole option.

It is believed that, among other possibilities, the patterning of planar two-dimensional crystal and photonic waveguides using the μ -contact photo-annealing method or the elaboration of printed light pipes on cylindrical support could be for example considered. Meanwhile, a few ideas were explored with colleagues from the group and other research institutes. For example, the solution-processed embossing of the hybrid at room temperature was recently demonstrated. Thanks to the hybrid contraction and refractive index increase during annealing, the diffraction efficiency could be altered by applying different temperatures, opening the way to thermo-responsive devices. Furthermore, the development of PMMA-based devices enabled the introduction of optical dyes in the low-index medium, studied by Kevin (Hua-Kang) Yuan in our group, moving toward optically active devices.

Finally, the advanced multilayer design reported in the last chapter could also be relevant to photovoltaic cells. Light conversion would not be strongly affected thanks to the high averaged visible transparency. A broadband near-IR reflector would, however, decrease solar heating, responsible for a drastic reduction in efficiency, at the same time as protect from UV radiation. Similarly, this type of wavelength-selective filter could be applied to flexible printed electronics to limit the performance degradation from UV light but also for use as an encapsulating structure.

Appendices

A | Hybrid formulation details

As explained in Section 3.1.3, the hybrid is produced from PVAI and TiOxH solutions. The concentration of each can be adjusted for different final viscosities. Before mixing the solutions, the precise amount of each must be known to achieve the specific ratio of inorganic/organic, independently of the solvent.

Firstly, it is simpler to calculate the volume of each solutions for a final amount of 1 g of PVAI:

$$V_{TiOxH} = \frac{n_{Ti}}{[TiOxH]_{mol}} = \frac{C_{Ti}}{[TiOxH]_{mol}} \quad (A.1)$$

$$V_{PVAI} = \frac{m_{PVAI}}{[PVAI]_{mass}} = \frac{1}{[PVAI]_{mass}} \quad (A.2)$$

where $[TiOxH]_{mol}$ is the molar concentration of titanium oxide hydrate in mol L^{-1} and C_{Ti} is the hybrid concentration expressed in mol Ti/g PVAI i.e. the number of moles of titanium expected for 1 g of PVAI. $[PVAI]_{mass}$ is the mass concentration of PVAI in g L^{-1} .

Considering that the ratio of each component should always be the same, we can write Equation A.3 with V' referring to the volumes in the final solution.

$$\frac{V'_{TiOxH}}{V'_{PVAI}} = \frac{V_{TiOxH}}{V_{PVAI}} \quad (A.3)$$

Moreover, the final volume is given by:

$$V'_{Hybrid} = V'_{TiOxH} + V'_{PVAI} \quad (A.4)$$

Therefore, both volumes can be expressed as:

$$V'_{TiOxH} = \frac{V_{TiOxH}}{V_{TiOxH} + V_{PVAl}} \times V'_{Hybrid} \quad (A.5)$$

$$V'_{PVAl} = \frac{V_{PVAl}}{V_{TiOxH} + V_{PVAl}} \times V'_{Hybrid} \quad (A.6)$$

Finally, by combining Equation A.1 and A.2 with Equation A.5 and A.6, final volumes of pre-solutions can be calculated.

B | Optical and experimental design of broad-band visible reflectors

In order to chirped a reflector, the Bragg wavelength λ_0 is progressively changed in the superlattice. A geometrical increase was use to extend the stop-band of silver-like and gold-like mirrors.

$$\lambda_0^i = \Lambda_0 \cdot k^{i-1} \quad (\text{B.1})$$

where λ_0^i is the wavelength for the quarter-wave condition of layer i , Λ_0 the initial Bragg wavelength of the stack and k the common ratio of the geometrical sequence.

Parameters and resulting spectra for each mirror are reported in Table B.1 and Figure B.1.

Table B.1: Design parameters for silver-like and gold-like chirped reflectors.

<i>Appearance</i>	<i>Reflectance range</i>	Λ_0	<i>Number of layers</i>	k
Silver	400 - 750 nm	400 nm	71	1.011
Gold	500 - 750 nm	525 nm	51	1.009

Precise calibration curves are required for the fabrication of chirped superlattices. 60 vol% hybrid formulated from 20 mg mL⁻¹ PVAI and 1 mol L⁻¹ TiOxH was used. However, two solutions of PMMA were needed for the silver-like reflectors. Figure B.2 displays the spin-curves for the 3 solutions involved in this experiment along with their fit.

After fitting the spin-curves using Equation B.2, spin-speeds were calculated. All parameters are reported in Tables B.2 and B.3.

$$d = a + b/s^c \quad (\text{B.2})$$

where d is the thickness, s the spin-speed and a, b and c the fitting parameters.

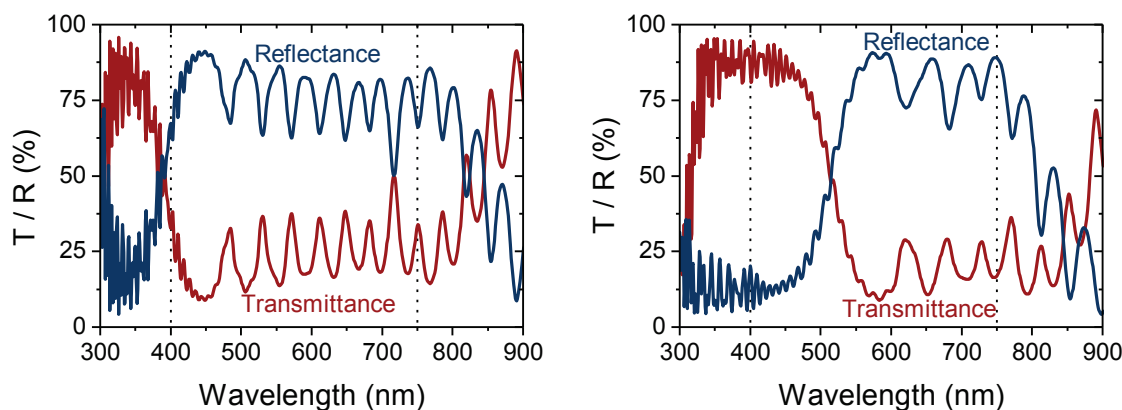


Figure B.1: Calculated transmittance and reflectance spectra of silver-like and gold-like chirped reflectors using TMM.

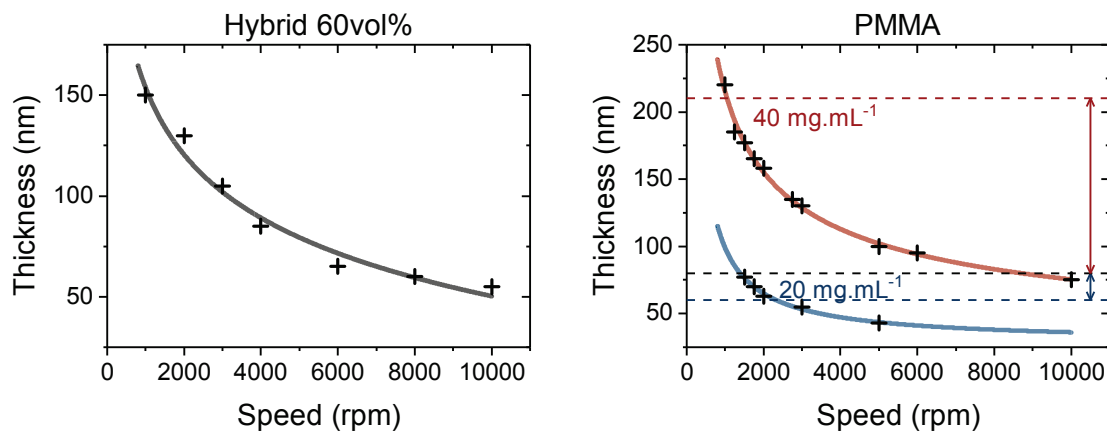


Figure B.2: Spin-coating calibrations for 60 vol% hybrid formulated from 20 mg mL^{-1} PVAI and 1 mol L^{-1} TiOxH and PMMA with two concentrations of 20 mg mL^{-1} and 40 mg mL^{-1} . Fitting curves were used to back calculated the speeds needed for the chirped devices.

Table B.2: Parameters used for the fabrication of silver-like reflector. The 8 first layers of PMMA were produced with a 20 mg mL^{-1} solution while the rest was with a 40 mg mL^{-1} solution.

Period	Hybrid			PMMA		
	λ_0	d_H	Spin-speed (rpm)	λ_0	d_L	Spin-speed (rpm)
1	400	53	9304	404	67	1886
2	409	55	8998	413	69	1811
3	418	56	8697	422	70	1740
4	427	57	8402	432	72	1672
5	437	59	8111	441	73	1609
6	446	60	7826	451	75	1548
7	456	62	7546	461	77	1491
8	466	63	7272	471	78	1437
9	477	65	7003	482	80	8674
10	487	67	6740	492	82	8239
11	498	68	6482	503	84	7827
12	509	70	6230	514	86	7438
13	520	72	5984	526	88	7069
14	532	73	5744	537	90	6720
15	543	75	5509	549	92	6389
16	555	77	5280	561	94	6076
17	568	79	5057	574	96	5779
18	580	81	4840	587	98	5497
19	593	83	4629	600	100	5231
20	606	85	4424	613	102	4978
21	620	87	4224	626	105	4737
22	633	89	4031	640	107	4510
23	647	91	3843	654	109	4293
24	662	93	3661	669	112	4088
25	676	95	3485	684	114	3893
26	691	97	3314	699	117	3708
27	707	100	3149	714	119	3532
28	722	102	2990	730	122	3365
29	738	104	2836	746	125	3207
30	754	107	2688	763	128	3056
31	771	109	2546	780	130	2912
32	788	112	2408	797	133	2776
33	806	114	2276	814	136	2646
34	823	117	2150	833	139	2523
35	842	120	2028	851	142	2405
36	860	123	1912			

Table B.3: Parameters used for the fabrication of gold-like reflector.

<i>Period</i>	Hybrid			PMMA		
	λ_0	d_H	<i>Spin-speed (rpm)</i>	λ_0	d_L	<i>Spin-speed (rpm)</i>
1	525	72	5880	530	88	6949
2	534	74	5685	539	90	6667
3	544	75	5494	549	92	6397
4	554	77	5306	559	93	6139
5	564	78	5123	569	95	5892
6	574	80	4943	579	97	5655
7	585	81	4767	590	98	5429
8	595	83	4596	601	100	5212
9	606	85	4428	611	102	5005
10	617	86	4264	622	104	4806
11	628	88	4104	634	106	4616
12	639	90	3948	645	108	4433
13	651	91	3796	657	110	4259
14	663	93	3647	669	112	4091
15	675	95	3503	681	114	3931
16	687	97	3362	693	116	3777
17	699	99	3226	706	118	3629
18	712	101	3093	718	120	3488
19	725	102	2963	731	122	3352
20	738	104	2838	745	124	3222
21	751	106	2716	758	127	3097
22	765	108	2598	772	129	2978
23	779	110	2484	786	131	2863
24	793	113	2373	800	134	2753
25	807	115	2266	814	136	2647
26	822	117	2162			

C | Low-emissivity NSG TECTM 15

NSG TECTM 15 was bought from Pilkington UK. UV-vis spectroscopy was performed between 300 nm and 2500 nm (Figure C.1.a) within which the reflectance starts to increase considerably. It is highly reflective for wavelengths from 5 μm to 30 μm leading to its low-emissivity of 0.16. SEM images are shown in Figure C.1.b where the 300 nm FTO layer is observed as well as a thin underneath coating, probably acting as an adhesive layer and improving the transmittance across the visible.*

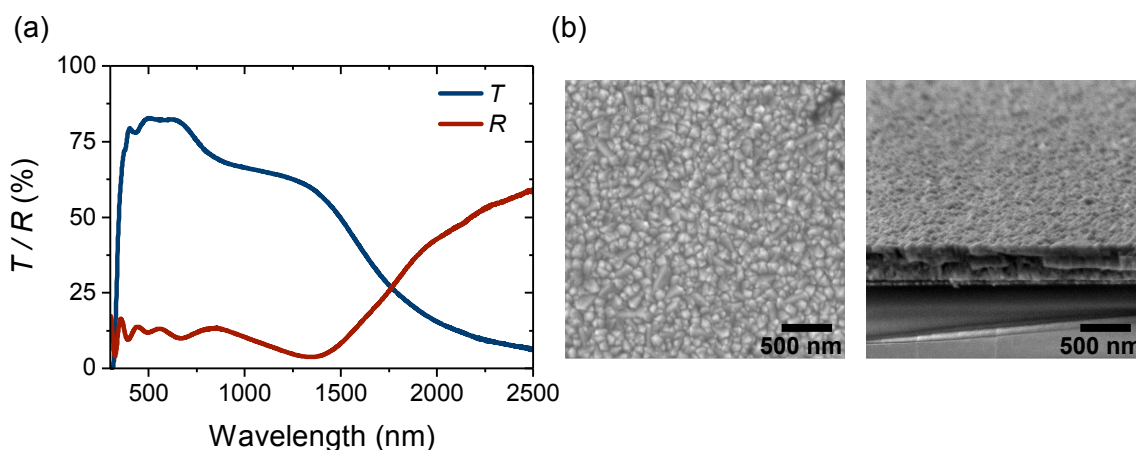


Figure C.1: (a) Transmittance and reflectance spectra of NSG TECTM 15 substrate. (b) Top-view (left) and cross-section (right) SEM images of NSG TECTM 15 substrate.

*Thank you to Riley Sinclair Ratnasingham, Department of Materials, Imperial College London, for assistance with these measurements.

D | Experimental design of broadband solar-control coating

Similarly to the chirped reflectors discussed in Chapter 6, the Bragg wavelength λ_0 is geometrically changed in the structure in order to widen the optical stop-band.

Precise calibration curves are required for the fabrication of chirped superlattices. A 40 mg mL⁻¹ PMMA solution was deposited by spin-coating using calibration curve displayed in Figure B.2. A 60 vol% hybrid solution formulated from 20 mg mL⁻¹ PVAI and 1.5 mol L⁻¹ TiOxH was used for the infrared reflector following the spin-curve plotted in Figure D.1.

After fitting the spin-curves using Equation B.2, spin-speeds were calculated for each thickness. All parameters are reported in Tables D.1.

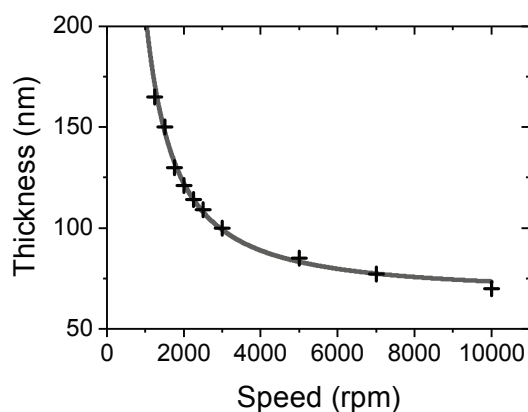


Figure D.1: Spin-coating calibrations for 60 vol% hybrid formulated from 20 mg mL⁻¹ PVAI and 1.5 mol L⁻¹ TiOxH. Fitting curves were used to back calculated the speeds needed for the chirped device.

Table D.1: Experimental parameters used for the fabrication of broadband near-infrared reflector.

<i>Period</i>	Hybrid			PMMA		
	λ_0	d_H	<i>Spin-speed (rpm)</i>	λ_0	d_L	<i>Spin-speed (rpm)</i>
1	1146	183	1149	1141	223	929
2	1135	182	1156	1130	221	946
3	1125	180	1172	1120	219	964
4	1115	178	1187	1110	217	983
5	1105	177	1195	1100	215	1002
6	1095	175	1212	1091	213	1021
7	1086	173	1229	1081	211	1040
8	1076	172	1238	1071	209	1060
9	1066	170	1255	1062	207	1081
10	1057	169	1265	1052	205	1101
11	1047	167	1284	1043	203	1123
12	1038	166	1293	1033	202	1144
13	1029	164	1313	1024	200	1166
14	1019	163	1323	1015	198	1189
15	1010	161	1344	1006	196	1212
16	1001	160	1355	997	194	1235
17	992	158	1377	988	193	1259
18	984	157	1389	979	191	1283
19	975	155	1412	970	189	1308
20	966	154	1424	962	188	1333
21	957	152	1449	953	186	1359
22	949	151	1462	945	184	1385
23	940	149	1489	936	183	1412
24	932	148	1502	928	181	1439
25	924	147	1516	919	179	1467
26	915	145	1545	911	178	1496
27	907	144	1560	903	176	1525
28	899	143	1576	895	174	1554
29	891	141	1607	887	173	1585
30	883	140	1624	879	171	1616
31	875	139	1640	871	170	1647
32	867	137	1675	863	168	1679
33	860	136	1693	856	167	1712
34	852	135	1712	848	165	1745
35	844	134	1731	841	164	1779
36	837	132	1771	833	162	1814
37	829	131	1791	826	161	1850
38	822	130	1813	818	159	1886
39	814	129	1834	811	158	1923
40	807	127	1880	804	157	1961
41	800	126	1904			

E | Tables for calculations of solar radiation glazing factors

Table E.1: Normalised relative spectral distribution of total solar radiation for the calculation of T_{solar} and $T_{solar}(\theta)$. The sum of all $S_{\lambda}\Delta\lambda$ is equal to 1 for the wavelength range 300 to 2500 nm. Table is given in ISO 9050 considering air mass 1.5.¹

λ (nm)	$S_{\lambda}\Delta\lambda$	λ (nm)	$S_{\lambda}\Delta\lambda$	λ (nm)	$S_{\lambda}\Delta\lambda$	λ (nm)	$S_{\lambda}\Delta\lambda$
300	0	440	0.013246	680	0.012838	1400	0.000741
305	0.000057	450	0.015343	690	0.011788	1450	0.003792
310	0.000236	460	0.016166	700	0.012453	1500	0.009693
315	0.000554	470	0.016178	710	0.012798	1550	0.013693
320	0.000916	480	0.016402	720	0.010589	1600	0.012203
325	0.001309	490	0.015794	730	0.011233	1650	0.010615
330	0.001914	500	0.015801	740	0.012175	1700	0.007256
335	0.002018	510	0.015973	750	0.012181	1750	0.007183
340	0.002189	520	0.015357	760	0.009515	1800	0.002157
345	0.002260	530	0.015867	770	0.010479	1850	0.000398
350	0.002445	540	0.015827	780	0.011381	1900	0.000082
355	0.002555	550	0.015844	790	0.011262	1950	0.001087
360	0.002683	560	0.015590	800	0.028718	2000	0.003024
365	0.003020	570	0.015256	850	0.048240	2050	0.003988
370	0.003359	580	0.014745	900	0.040297	2100	0.004229
375	0.003509	590	0.014330	950	0.021384	2150	0.004142
380	0.003600	600	0.014663	1000	0.036097	2200	0.003690
385	0.003529	610	0.015030	1050	0.034110	2250	0.003592
390	0.003551	620	0.014859	1100	0.018861	2300	0.003436
395	0.004294	630	0.014622	1150	0.013228	2350	0.003163
400	0.007812	640	0.014526	1200	0.022551	2400	0.002233
410	0.011638	650	0.014445	1250	0.023376	2450	0.001202
420	0.011877	660	0.014313	1300	0.017756	2500	0.000475
430	0.011347	670	0.014023	1350	0.003743		

Table E.2: Normalised relative spectral distribution of UV solar radiation for the calculation of T_{UV} and $T_{UV}(\theta)$. The sum of all $S_\lambda \Delta\lambda$ is equal to 1 for the wavelength range 300 to 380 nm. Table is given in ISO 9050 considering air mass 1.5.¹

λ (nm)	$S_\lambda \Delta\lambda$	λ (nm)	$S_\lambda \Delta\lambda$	λ (nm)	$S_\lambda \Delta\lambda$
300	0	330	0.062108	360	0.087039
305	0.001859	335	0.065462	365	0.097963
310	0.007665	340	0.071020	370	0.108987
315	0.017961	345	0.073326	375	0.113837
320	0.029732	350	0.079330	380	0.058351
325	0.042466	355	0.082894		

Table E.3: Normalised relative spectral distribution of illuminant D65 (D_λ) and spectral luminous efficiency for photopic vision ($V(\lambda)$) for the calculation of $T_{visible}$ and $T_{visible}(\theta)$. The sum of all $D_\lambda V(\lambda) \Delta\lambda$ is equal to 1 for the wavelength range 380 to 780 nm. Table is given in ISO 9050 considering air mass 1.5.¹

λ (nm)	$D_\lambda V(\lambda) \Delta\lambda$	λ (nm)	$D_\lambda V(\lambda) \Delta\lambda$	λ (nm)	$D_\lambda V(\lambda) \Delta\lambda$
380	0	520	0.070523	660	0.004612
390	0.000005	530	0.087990	670	0.002485
400	0.000030	540	0.094427	680	0.001255
410	0.000103	550	0.098077	690	0.000536
420	0.000352	560	0.094306	700	0.000276
430	0.000948	570	0.086891	710	0.000146
440	0.002274	580	0.078994	720	0.000057
450	0.004192	590	0.063306	730	0.000035
460	0.006663	600	0.053542	740	0.000021
470	0.009850	610	0.042491	750	0.000008
480	0.015189	620	0.031502	760	0.000001
490	0.021336	630	0.020812	770	0
500	0.033491	640	0.013810	780	0
510	0.051393	650	0.008070		

Table E.4: Normalised relative spectral distribution of solar IR radiation for the calculation of $T_{sol\ IR}$ and $T_{sol\ IR}(\theta)$. The sum of all $S_{\lambda}\Delta\lambda$ is equal to 1 for the wavelength range 800 to 2500 nm.

λ (nm)	$S_{\lambda}\Delta\lambda$	λ (nm)	$S_{\lambda}\Delta\lambda$	λ (nm)	$S_{\lambda}\Delta\lambda$
800	0.069970	1400	0.001805	2000	0.007368
850	0.117534	1450	0.009239	2050	0.009717
900	0.098181	1500	0.023616	2100	0.010304
950	0.052101	1550	0.033362	2150	0.010092
1000	0.087948	1600	0.029732	2200	0.008990
1050	0.083107	1650	0.025863	2250	0.008752
1100	0.045954	1700	0.017679	2300	0.008372
1150	0.032229	1750	0.017501	2350	0.007706
1200	0.054944	1800	0.005255	2400	0.005441
1250	0.056954	1850	0.000970	2450	0.002929
1300	0.043261	1900	0.000200	2500	0.001157
1350	0.009120	1950	0.002648		

E.1 References

1. *ISO 9050:2003 - Glass in Building – Determination of Light Transmittance, Solar Direct Transmittance, Total Solar Energy Transmittance, Ultraviolet Transmittance and Related Glazing Factors* (2003).

F | Angular transmittance of glazing

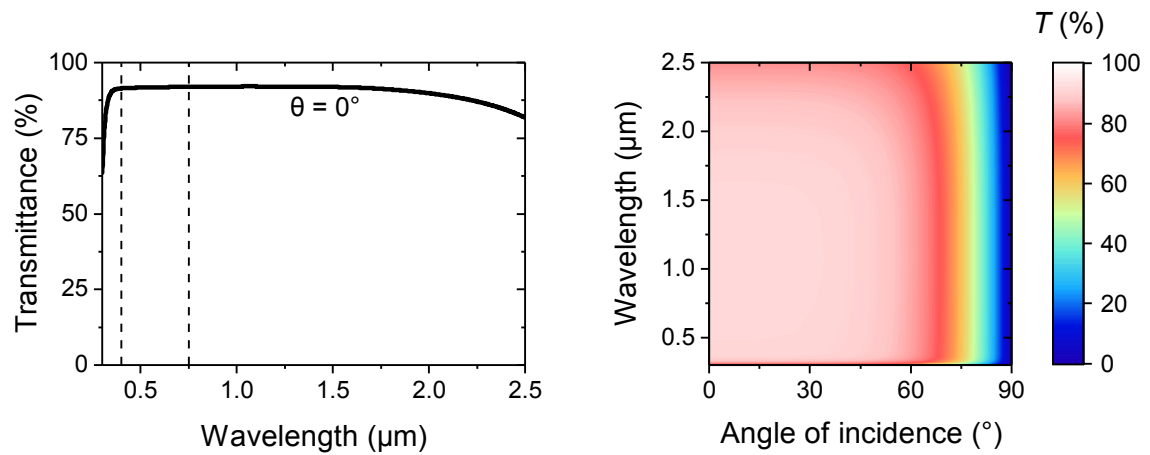


Figure F.1: Angular transmittance of BK7 substrate (3 mm). Left panel shows the transmittance at normal incidence. Spectra were calculated using TMM and complex refractive index.¹

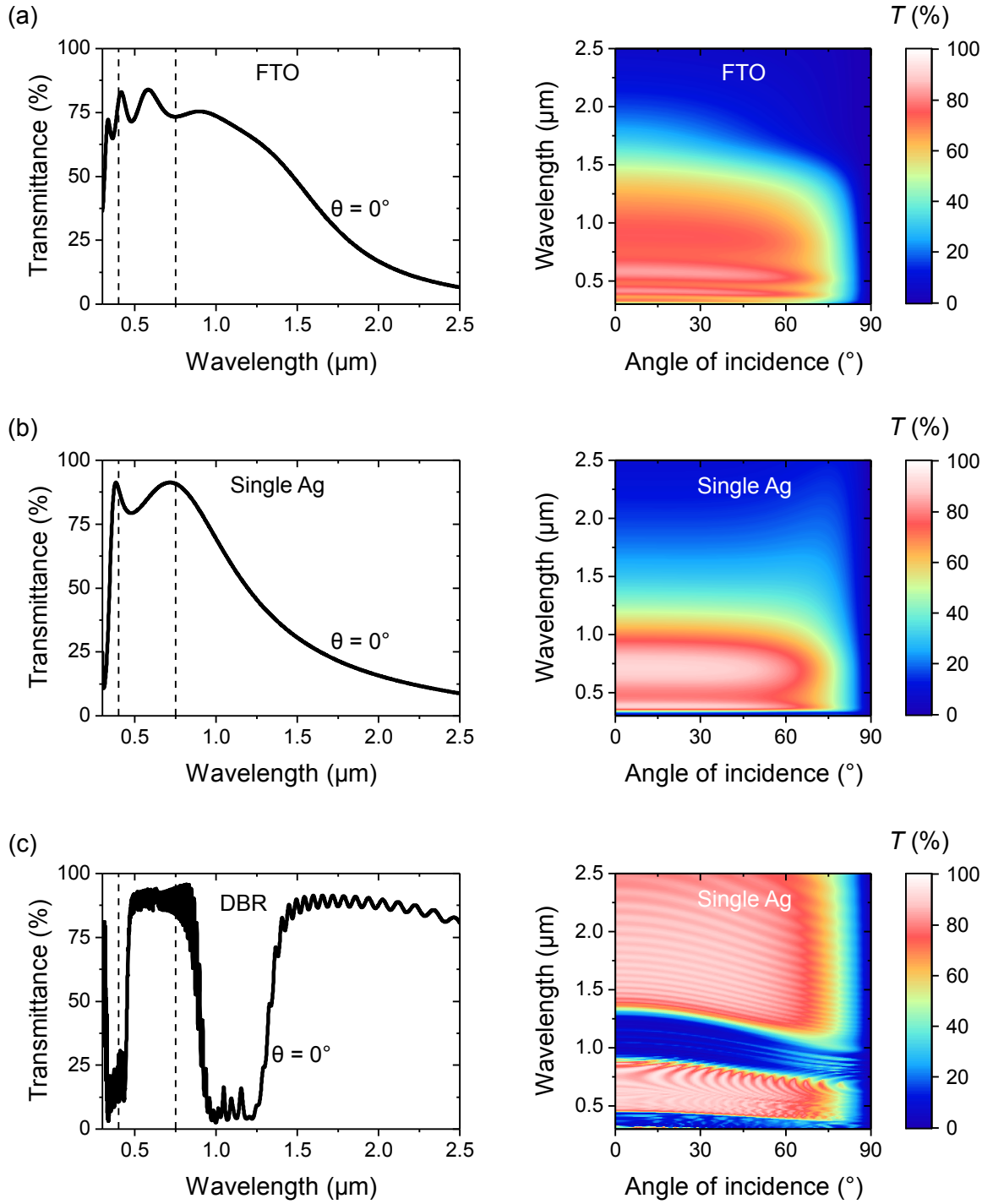


Figure F.2: Angular transmittance of FTO (300 nm), single-silver coating (TiO₂ (25 nm)/Ag (9 nm)/TiO₂ (25 nm)) and chirped DBR on BK7. Left panels show the transmittance at normal incidence. Spectra were calculated using TMM and complex refractive indices for BK7,¹ FTO,² TiO₂³ and Ag.⁴

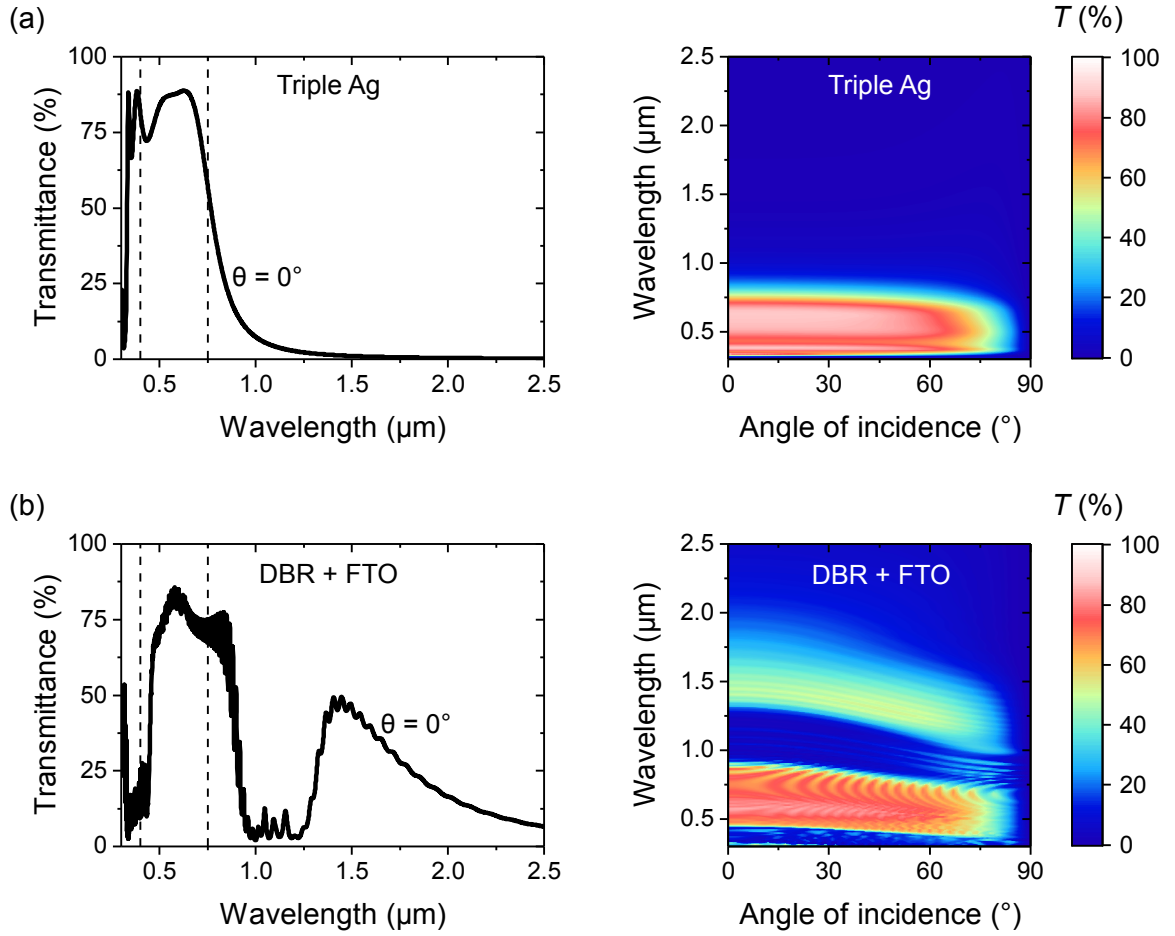


Figure F.3: Angular transmittance of triple-silver coating (TiO_2 (20 nm)/Ag (9 nm)/ TiO_2 (35 nm)/Ag (9 nm)/ TiO_2 (35 nm)/Ag (9 nm)/ TiO_2 (20 nm)) and chirped DBR on BK7 substrate with a 300 nm FTO film on the back. Left panels show the transmittance at normal incidence. Spectra were calculated using TMM and complex refractive indices for BK7,¹ FTO,² TiO_2 ³ and Ag.⁴

F.1 References

1. Schott. *Optical Glass Collection Datasheets* (2017).
2. Von Rottkay, K. & Rubin, M. Optical Indices of Pyrolytic Tin-Oxide Glass. *MRS Proceedings* **426** (1996).
3. DeVore, J. R. Refractive Indices of Rutile and Sphalerite. *JOSA* **41**, 416–419 (1951).
4. Johnson, P. B. & Christy, R. W. Optical Constants of the Noble Metals. *Physical Review B* **6**, 4370–4379 (1972).

Publications, Prizes, Talks & Posters

List of publications:

- Stefan Bachevillier, Hua-Kang Yuan, Andrew Strang, Artem Levitsky, Gitti L. Frey, Andreas Hafner, Donal D. C. Bradley, Paul N. Stavrinou & Natalie Stingelin, *Fully Solution-Processed Photonic Structures from Inorganic/Organic Molecular Hybrid Materials and Commodity Polymers*, Advanced Functional Materials, (2019), Published
- Stefan Bachevillier, Hua-Kang Yuan, Kornelius Tetzner, Jan Gebers, Irene Votta, Donal D. C. Bradley, Thomas D. Anthopoulos, Andreas Hafner, Paul N. Stavrinou & Natalie Stingelin, *Planar Refractive Index Patterning through Heat and Microcontact Photothermal-Annealing of Printable Organic-Inorganic Hybrid*, Manuscript In Preparation
- Stefan Bachevillier, Hua-Kang Yuan, Dean Carroll, Theoni K. Georgiou, Jan Gebers, Artem Levitsky, Gitti L. Frey, Donal D. C. Bradley, Andreas Hafner, Paul N. Stavrinou & Natalie Stingelin, *Bio-Inspired Solution-Processed Chirped Dielectric Mirrors for Visible and Infrared Radiation Control*, Manuscript In Preparation
- Ester Buchaca-Domingo/Hanlin Hu, Lucía Serrano-Luján, Stefan Bachevillier, Hua-Kang Yuan, Taesoo Kim, Andrew Strang, Natalie Stingelin & Aram Amassian, *Solution-Processable Photonic Structures for Highly Efficient Semi-transparent Organic Solar Cells: Is this approach actually worth?*, Manuscript In Preparation

List of prizes:

- 2nd prize for Best Poster, March 2017, Imperial College London - Materials Postgraduate Research Day, London, UK
- 1st prize for Best Poster, April 2017, University of Oxford - Oxford Photonic Day, Oxford, UK
- 1st prize for Best Talk, September 2017, Imperial College London - CPE symposium, London
- The Don Pashley Memorial Prize for Best Public Speaker, March 2018, Imperial College London - Materials Postgraduate Research Day, London, UK

List of talks:

- *Solution-Processed Hybrids for Light Management Devices*, January 2016, BASF AG, Basel, Switzerland
- *Tunable High-Refractive Index Hybrid for Solution-Processed Light Management Devices*, August 2016, SPIE Optics + Photonics, Conference OP306 Polymer Optics and Molded Glass Optics, San Diego, USA
- *Refractive Index Patterning of Molecular Hybrid for Photonics*, September 2016, Imperial College London - CPE symposium, London, UK
- *Tunable High-Refractive Index Hybrid for Solution-Processed Light Management Devices*, February 2017, King Abdullah University of Science and Technology - Prof. Amassian group, Thuwal, Saudi Arabia
- *BASF Annual Meeting - State of the Projects*, March 2017, BASF AG, Basel, Switzerland
- *Tunable High-Refractive Index Hybrid for Solution-Processed Light Management Devices*, May 2017, Laboratoire de l'Intégration du Matériau au Système, Bordeaux, France
- *Polymer/Inorganic Hybrid Systems toward Heat and Light Management Photonic Devices*, September 2017, Imperial College London - CPE symposium, London, UK
- *Polymer/Inorganic Hybrid Systems toward Heat and Light Management Photonic Devices*, October 2017, Georgia Institute of Technology - Stingelin and Silva research groups, Atlanta, USA
- *Multilayer Photonic Structures toward Light and Heat Management*, November 2017, MRS Fall meeting, Symposium EM10 Solution-Processed Inorganics for Electronic and Photonic Device Applications, Boston, USA
- *Solution-Cast Photonic Structures toward Light and Heat Management*, December 2017, BASF AG, Basel, Switzerland
- *Solution-Cast Photonic Structures toward Light and Heat Management*, March 2018, Imperial College London - Materials Postgraduate Research Day, London, UK

- *Solution-Cast Photonic Structures toward Light and Heat Management*, July 2018, Georgia Institute of Technology - National Institute of Standards and Technology, Atlanta, USA
- *Printed Dielectric Mirrors for Light and Heat Management*, September 2018, Imperial College London - CPE symposium, London, UK

List of poster presentations:

- *Refractive Index Patterning of Molecular Hybrid for Photonics*, September 2016, Imperial College London - CPE symposium, London, UK
- *Refractive Index Patterning of Molecular Hybrid for Photonics*, January 2017, Innovations in Large-Area Electronics Conference (innoLAE), Cambridge, UK
- *Refractive Index Patterning of Molecular Hybrid for Photonics*, February 2017, King Abdullah University of Science and Technology - KAUST Catalysis Center Conference, Thuwal, Saudi Arabia
- *Refractive Index Patterning of Molecular Hybrid for Photonics*, March 2017, Imperial College London - Materials Postgraduate Research Day, London, UK
- *Refractive Index Patterning of Molecular Hybrid for Photonics*, April 2017, University of Oxford - Oxford Photonic Day, Oxford, UK
- *Solution-Cast Multilayer Photonic Structures for Light and Heat Management*, March 2018, 21st Sede Boqer Symposium on Solar Electricity Production, Beer-Sheva, Israel
- *Solution-Cast Multilayer Photonic Structures for Light and Heat Management*, June 2018, 14th International Conference on Organic Electronics, Bordeaux, France
- *Low-Cost Solution-Processed Heat Mirrors for Sustainable Buildings*, July 2018, Imperial College London - PhD Summer Showcase, London, UK
- *Printed Dielectric Mirrors for Light and Heat Management*, September 2018, Imperial College London - CPE symposium, London, UK