



A scalable route to mixed and layered sandwich-structured carbonaceous–anatase TiO₂ coatings with bi-functional photocatalytic activity for air pollution remediation and solar water splitting

Paransa Alimard^{a,b,c,*}, Longren Li^a, Stanley Cazaly^d, Flurin Eisner^d, Brian Tam^a,
Andreas Kafizas^{a,c,**}

^a Department of Chemistry, Molecular Science Research Hub, 82 Wood Lane, White City Campus, Imperial College London, London, W12 0BZ, UK

^b Science and Solutions for a Changing Planet DTP, Grantham Institute for Climate Change and the Environment, Exhibition Road, South Kensington Campus, Imperial College London, London, SW7 2AZ, UK

^c London Centre for Nanotechnology, South Kensington Campus, Imperial College London, London, SW7 2AZ, UK

^d School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, London, E1 4NS, UK

ARTICLE INFO

Keywords:

Aerosol-assisted chemical vapour deposition (AA-CVD)
Graphene
Composites
Nitrogen oxide (NO_x
NO + NO₂)
Solar water splitting

ABSTRACT

This study showcases how carbonaceous materials, including graphene (G), fullerene (F), and multi-walled carbon nanotubes (MWCNTs), can be integrated within titanium dioxide (TiO₂) films as either: (i) mixed or (ii) layered sandwich structures (TiO₂/carbonaceous material/TiO₂) and show bifunctional photocatalytic activity. Our composites are engineered to address both NO_x pollution and water splitting within the same platform. In the mixed composite (TGmix), graphene's high conductivity and electron-accepting ability enhance the photo-oxidation of NO_x, where under UVA light 17.6 % NO and 9.6 % total NO_x removal was seen, which was significantly higher than TiO₂ alone, which showed 6.8 % NO and 1.3 % total NO_x removal. Whereas in the sandwich-layered composite (TGT), the architecture promotes hole accumulation on the surface, favouring water splitting, with incident-photon-to-current efficiency (IPCE) reaching 68 % at 1.23 V_{RHE} (pH = 7) under 250 nm illumination; a factor of ~2 increase compared to TiO₂ alone. Transient photocurrent (TPC) and diffuse reflectance transient absorption spectroscopy (DR-TAS) were employed operando to probe the kinetics of electron extraction and hole-mediated water oxidation. At 1.23 V_{RHE}, the TGT sample showed slightly faster electron extract kinetics to T (TGT: t_{50 %}–0.25 ms and T: t_{50 %}–0.268 ms), along with a significantly higher long-lived hole carrier population that drove water oxidation, which were found to linearly correlate with the observed photocurrent density.

Our wholistic study, including in operando investigations, informs the rational design of active carbonaceous composite coatings within anatase TiO₂ that can be grown at scale for applications in NO_x air pollution remediation and solar water splitting.

1. Introduction

Although renewable energy shares are increasing, fossil fuels remain the dominant global energy source, with transportation relying heavily on petroleum. The burning of fossil fuels — coal, oil, and natural gas — is the primary contributor to climate change, releasing carbon dioxide (CO₂) and other greenhouse gases (GHGs) [1,2]. In 2024, global

temperatures reached their highest levels on record, surpassing 1.5 °C above the estimated pre-industrial baseline (1850–1900) [3]. Since CO₂ can remain in the atmosphere for hundreds of years, the environmental impact of today's emissions can persist for generations [1]. The use of fossil fuels is also a significant source of air pollution, releasing a range of pollutants, among which nitrogen oxides (NO_x = NO + NO₂) are of particular concern. NO_x compounds are major contributors to

* Corresponding author. Department of Chemistry, Molecular Science Research Hub, 82 Wood Lane, White City Campus, Imperial College London, London, W12 0BZ, UK.

** Corresponding author. Department of Chemistry, Molecular Science Research Hub, 82 Wood Lane, White City Campus, Imperial College London, London, W12 0BZ, UK.

E-mail addresses: p.alimard22@imperial.ac.uk (P. Alimard), a.kafizas@imperial.ac.uk (A. Kafizas).

<https://doi.org/10.1016/j.carbon.2025.120939>

Received 23 August 2025; Received in revised form 1 October 2025; Accepted 13 October 2025

Available online 19 October 2025

0008-6223/© 2025 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

environmental issues such as photochemical smog, acid rain, tropospheric ozone formation, ozone layer depletion, and global warming through secondary reactions. In addition to environmental damage, high concentrations of NO_x pose serious health risks to humans.

Considering the growing global energy demand and the non-renewable nature of fossil fuels, the search for sustainable energy sources is a major focus of scientific research [4]. Our largest source of renewable energy – solar – remains relatively untapped, with only 7 % of electricity produced from solar power in 2024. Hydrogen, if produced using solar energy, offers a promising solution to global warming and air pollution caused by fossil fuel combustion [5]. This renewable form of “green hydrogen”, which can be used as a direct fuel or a feedstock for synthetic liquid and gaseous fuels, serves as a vital link between clean energy and the decarbonisation of the power, transport, and industrial sectors, while also eliminating air pollution associated with fossil fuel combustion [6]. In addition to transitioning to green hydrogen, it is vitally important to address existing levels of NO_x generated and already present in the air. Therefore, alongside the development of sustainable energy solutions, effective strategies for the remediation of NO_x pollution are essential to improving air quality and protecting human health and the environment.

Titanium dioxide (TiO_2) is one of the most extensively studied n-type semiconductors, renowned for its strong oxidizing valence band and versatility in driving a wide range of photocatalytic reactions [7]. It is widely studied as a photoanode in photoelectrochemical (PEC) water splitting devices to drive water oxidation to oxygen and as a photocatalyst for remediating NO_x pollution by oxidation to nitrate (NO_3^-) [8–12]. Despite the many promising attributes of TiO_2 , one weakness is the relatively low minority carrier (holes) mobility, which can hinder efficient charge separation and transport [13]. In photocatalytic applications, the effective migration of charge carriers through the material bulk is crucial, as they must travel to the surface of the photocatalyst to participate in redox reactions [14]. Limited mobility increases the likelihood of electron–hole recombination before reaching reaction sites, thereby reducing the overall efficiency of the photocatalytic process [15]. To address this limitation, strategies such as surface doping [16], defect engineering [17], and impurity doping have been employed to enhance charge carrier mobility, reduce recombination, and improve the overall photocatalytic performance of TiO_2 [18].

One emerging strategy to enhance the mobility of photogenerated carriers in TiO_2 is to integrate carbonaceous materials [19,20]. This can significantly improve photocatalytic performance, primarily through the transfer of photogenerated electrons into the carbonaceous component, promoting the efficient separation of photogenerated electron–hole pairs [21]. Effective carbonaceous materials should possess good electrical conductivity, where graphene-based materials, in particular, are well known for their exceptionally high electron conductivity [22].

Graphene refers to a single, flat layer of carbon atoms arranged in a tightly packed two-dimensional (2D) honeycomb structure that serves as the fundamental building block for all other forms of graphitic materials. Depending on how it is manipulated, graphene can be shaped into zero-dimensional (0D) fullerenes, rolled into one-dimensional (1D) nanotubes, or stacked to form three-dimensional (3D) graphite [22]. Graphene, as a zero-gap semiconductor, possesses a range of remarkable characteristics, including massless charge carriers (Dirac fermions) [23], carrier mobilities surpassing $15,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under ambient conditions [24], a large theoretical specific surface area of $2600 \text{ m}^2/\text{g}$ [25], and excellent optical transparency [26]. The various roles of reduced graphene oxide (rGO) in hydrogen generation reactions were previously studied by Xie et al., including its functions as an electron acceptor and transporter, cocatalyst, photocatalyst, and photosensitiser [27]. Graphene, fullerene, and multi-walled carbon nanotubes (MWCNTs) have also been studied in NO_x pollution remediation applications [28]. Sysoev et al. studied the absorption and reactivity of NO_x on graphene oxide using *in situ* X-ray photoelectron spectroscopy (XPS), confirming the adsorption of both NO and NO_2 through surface oxygen-functional

groups [29]. Using DFT calculations, Tang et al. reported that graphene adsorbs NO_2 in a nitro configuration to its surface [30] and can act as an electron acceptor [31]. Carbon nanotubes (CNTs), depending on their diameter and chirality, can behave either as semiconductors or metals [32] and can enhance the performance of photocatalysts by modifying their electronic and catalytic properties. Previous XPS studies by Goldoni et al. demonstrated that NO_2 molecules can react on the surface of CNTs, leading to the formation of NO and NO_3^- [33]. Further, fullerene-based photocatalysts can improve catalytic performance through various mechanisms: acting as an electron acceptor that promotes effective charge separation [34] or serving as an electron donor due to its strong photosensitivity [35]. Additionally, fullerene has attracted considerable research interest for its ability to capture gas molecules such as NO and N_2O through catalytic adsorption, particularly when incorporated into a composite with a catalyst. In such systems, the adsorption on the surface of the pristine fullerene cage is typically weak, necessitating the presence of a catalytic component to enhance interaction [28,36]. Given the potential of carbon materials for efficient charge transport and separation, as well as their role as adsorbents and active sites for NO and NO_2 interactions, integrating graphitic materials into TiO_2 films with controlled architectures offers a promising strategy to simultaneously enhance pollutant oxidation and water splitting.

Graphene (2D) and metallic carbon nanotubes (CNTs, 1D) are typically classified as semi-metallic or zero-band-gap materials [37], and monolayer fullerene (0D) possesses a narrow energy gap of approximately 1.67–1.88 eV between its HOMO and LUMO levels [38]. Owing to their ability to facilitate rapid charge-carrier separation, all of these carbon-based materials have been widely reported to function as electron donors/acceptors [39–41], or as charge-transfer mediators [42,43]. Consequently, their incorporation into semiconductor systems can enhance photoinduced charge transfer, thereby improving the overall photo-efficiency of their semiconductor neighbours [44]. One promising strategy to improve the photoactivity of carbon–semiconductor composite photocatalysts is to increase the interfacial contact between the carbon phase and the semiconductor to increase charge transfer [45]. For instance, Zhang et al. demonstrated that intimate interfacial contact in an RGO– TiO_2 composite resulted in significantly higher photo-efficiency compared to a CNT– TiO_2 composite, where the poorer interface led to inferior photoactivity [46]. In another study, the influence of interfacial contact area was investigated. The findings suggest that the dimensionality of the carbon nanomaterial, which dictates whether interfacial contact is poor or efficient, is a critical factor governing the spectral response and reaction selectivity of carbon-based composite photocatalysts [47].

However, the scalable fabrication of architecturally controlled carbon– TiO_2 films, systematically optimised for both NO_x remediation and water splitting, remains largely unexplored. TiO_2 thin film coatings can be fabricated using a variety of methods, with one promising method capable of growing materials with tailored morphology at scale being chemical vapour deposition (CVD) [48–50]. Aerosol-assisted chemical vapour deposition (AA-CVD) is a branch of CVD where the chemical precursors are first dissolved in a volatile solvent and then transferred into the reactor in the form of an aerosol [51]. This enables one to transfer heavier precursors [52], or even pre-formed nanoparticles [53], into the reactor. Herein, we believe that we demonstrate for the first time how AA-CVD can be used to deposit coatings of pre-formed graphene, fullerene, and MWCNTs, where specifically, we produce mixed composites within TiO_2 films or sandwich structures between two layers of TiO_2 . These coatings were grown on the 50 cm^2 ($5 \times 10 \text{ cm}$) scale, and their capacity to drive photocatalytic NO_x pollution and PEC water splitting was studied in detail. Our findings were rationalised through in-depth physicochemical analyses and in operando studies of the charge carrier dynamics, providing unique insight into the materials design rules that govern activity in carbonaceous/ TiO_2 composite coatings for applications in NO_x air pollution remediation and solar

water splitting. We systematically compared 0D, 1D, and 2D carbon materials within TiO_2 matrices and found that graphene's superior conductivity delivers the highest NO_x remediation, whereas the structured electron pathways in the layered graphene composite best support water oxidation, thereby highlighting the strong impact of structural design on the role of carbon nanomaterials in dual-function photocatalytic systems. Thus, for the first time, we demonstrate a single, scalable material platform, fabricated by AA-CVD, that delivers high performance in both NO_x remediation and solar-driven water splitting.

2. Experimental

2.1. Synthesis

2.1.1. Chemicals and materials

Titanium tetraisopropoxide (TTIP) (97 %), graphite powder (<20 μm), carbon nanotube multi-walled carboxylic acid functionalized (>90 %) (9.5 nm diameter and 1.5 μm length), potassium phosphate mono-basic (≥ 99 %), nitric acid (70 %), and potassium chlorate (≥ 99.0 %) were purchased from Sigma-Aldrich. Toluene and ethanol absolute (99.5 %), sulfuric acid (98 %), sodium sulphate anhydrous (100 %), and hydrochloric acid (37 %) were purchased from VWR. Potassium phosphate dibasic was purchased from Fluorochem. Buckminsterfullerene C_{60} (99.5 %) was purchased from Tokyo Chemical Industry. NO and NO_2 gases (100 ppm in N_2) were purchased from BOC UK. Float glass substrates (2.2 mm thick) that contain an ultra-thin (~ 50 nm) silicon dioxide barrier layer and fluorine-doped tin oxide (FTO; TEC 15) coated glass substrates (3.0 mm thick) were supplied by Pilkington NSG.

2.1.2. Graphene oxide (GO) synthesis

Graphene oxide (GO) was synthesised using a modified Staudenmaier method, which was reported in our previous paper [54–58]. In an ice bath, 9 mL concentrated nitric acid and 18 mL sulfuric acid in a 1:2 vol% ratio were combined. Subsequently, 1.0 g of graphite powder was introduced into the acid mixture under vigorous stirring, ensuring uniform dispersion and preventing agglomeration. To mitigate abrupt temperature increases and explosive chlorine dioxide gas formation, a gradual addition of 11 g of potassium chlorate was made over the course of 1 h, while stirring and maintaining the reaction flask within the ice bath. After the complete dissolution of potassium chlorate, the mixture was vigorously stirred for 96 h at room temperature. Upon completion of the reaction, the mixture was poured into 1 L of deionised water (DI), followed by a decantation process. To eliminate sulphate ions, the GO underwent a process of re-dispersion in 5 vol% HCl solutions, followed by multiple rounds of centrifugation and redispersion in DI water. Subsequently, the GO slurry was dried in an oven at 60 °C for 48 h.

2.1.3. Graphene (G) coatings using a spray coater

To prepare a graphene (G) coating, 10 mg of GO was dissolved in 10 mL of absolute ethanol and spray-coated onto a 5 cm $\times$ 10 cm piece of float glass. The coating was then annealed in a tubular furnace at 450 °C under a N_2 gas flow of 4 L min^{-1} for 15 min, and then in a muffle furnace (Nabertherm Electric Muffle Furnace, L 9/11/B410) at 500 °C for 5 h in air.

2.1.4. TiO_2 (T), TiO_2 : graphene (TGmix), TiO_2 : fullerene (TFmix) and TiO_2 : MWCNTs (TCTmix) coatings using AA-CVD

Our synthesis method was inspired by previous work, with some modifications [59]. In all cases, 1 mL TTIP (3.28 mmol) was added to 20 mL toluene, followed by sonication using an ultrasonic bath (SHESTO UT8031/EUK) for 30 min at 25 °C. For the synthesis of mixed composite coatings, 10 mg of the carbon-based material (GO for TGmix, MWCNT for TCTmix, and fullerene for TFMix) was added to the TTIP/toluene solution and sonicated using the ultrasonic bath for 30 min at 25 °C (Fig. S1). For the synthesis of T, no carbon-based material was added to the TTIP/toluene solution. Coatings were grown using a cold-wall

horizontal CVD reactor at 450 °C under an N_2 flow of 4 L min^{-1} . In each reaction, a float glass sheet (5 cm $\times$ 10 cm) and FTO glass (1.3 cm $\times$ 2.5 cm) were positioned inside the reactor. The precursor suspension/solution was carried in the form of an aerosol into the reactor, using an ultrasonic humidifier (Liquifog®, Johnson Matthey, ~ 1.6 MHz operating frequency). The deposition was carried out until the whole suspension/solution was transferred (~ 15 min). Subsequently, the reactor was allowed to cool to room temperature under a N_2 flow. Samples were then annealed in a muffle furnace at 500 °C for 5 h in air to remove any organic impurities.

2.1.5. TiO_2 /graphene/ TiO_2 (TGT) coatings using AA-CVD

The synthesis method is similar to that of TGmix with some modifications. Instead of an mixed composite, a layered structure was formed, with TiO_2 sandwiching a graphene central layer. For all AA-CVD steps, the same conditions as above were used. All steps were carried out in succession, with the AA-CVD reactor temperature held at 450 °C. A layer of TiO_2 was first grown using AA-CVD from a precursor solution of 0.5 mL TTIP (1.64 mmol) in 10 mL toluene, sonicated for 30 min at 25 °C. Then, a central graphene layer was grown using AA-CVD from a precursor suspension of 10 mg of GO in 10 mL of absolute ethanol, sonicated for 30 min at 25 °C (Fig. S1). And a final TiO_2 layer was grown using AA-CVD from a precursor solution of 0.5 mL TTIP (1.64 mmol) in 10 mL toluene, sonicated for 30 min at 25 °C.

2.1.6. Sample nomenclature

Table 1 presents the nomenclature of the sample coatings, along with the mass of TiO_2 , the mass of carbon-based materials, and the weight percentage of the carbon-based material in each composite.

3. Physical characterisation

Details of our physical characterisation is provided in the Supplementary Information.

4. Results and discussion

4.1. Overview of the samples produced

Using AA-CVD, mixed and sandwich-structured carbonaceous-anatase TiO_2 coatings were deposited on float glass and FTO-coated glass. Graphene (G), fullerene (F), and multi-walled carbon nanotubes (MWCNTs) were incorporated at 1 wt% to produce TGmix, TFMix, and TCTmix samples, respectively. A layered TiO_2 /G/ TiO_2 structure (TGT) and a carbon-free TiO_2 coating (T) were also prepared. Coatings on float glass were evaluated for photocatalytic NO_x removal, while those on FTO-glass were tested for PEC water splitting.

Graphene oxide (GO), synthesised via a modified Staudenmaier method [60]. G was then prepared by annealing coatings containing GO under N_2 and air. served as the G precursor by being thermally reduced first under N_2 and then air. MWCNTs and F were obtained commercially. In AA-CVD, toluene was selected as an anhydrous, non-polar solvent to suppress premature TTIP hydrolysis and ensure its decomposition in the heated reactor. Under N_2 at 450 °C, TTIP in toluene yields phase-pure

Table 1
Nomenclature and chemical amounts used to prepare T, TGmix, TCTmix, TFMix and TGT samples.

Sample name	Titanium (mmole)	Carbonaceous material	Carbonaceous material (mg)	Carbonaceous material (wt%)
G	0	Graphene	10	100
T	3.28	n/a	0	0
TGmix	3.28	Graphene	10	1
TFmix	3.28	Fullerene	10	1
TCTmix	3.28	MWCNT	10	1
TGT	3.28	Graphene	10	1

anatase TiO_2 [61,62]. Interactions between TTIP and carbonaceous additives likely proceed via ligand exchange: TTIP isopropoxide groups coordinate to fullerenes at 6:6 ring junctions [63], while GO [64], and carboxylated CNTs [65], facilitate coordination expansion through oxygen-containing surface functionalities.

4.2. Physical characterisation

4.2.1. Coating topography

4.2.1.1. SEM and TEM imaging. Fig. 1 presents top-down SEM images of T, TGmix, TGT, TFmix, and TCTmix, with hierarchical porous columnar particles, each composed of numerous substructures. In Fig. 1a–d, the SEM images of T show columnar particles composed of flakes. Previously, Gardecka et al. [66] reported dendritic nanostructures of TiO_2 from the low-pressure CVD of TTIP in toluene, which is consistent with the shape of the crystallites observed in our TiO_2 sample. The column's length, measured in Fig. 1b, is 1.5 μm , while the diameter, measured in Fig. 1c, is 3 μm . The morphology and particle length are similar to findings of Wong et al., who synthesised TiO_2 via AA-CVD using a solution of titanium (IV) n-butoxide ($\text{Ti}(\text{O}i\text{Bu})_4$) in toluene at 500 $^\circ\text{C}$ [67]. In Fig. S4, the length of the columnar structures in TGmix is shown to have dramatically decreased to $\sim 0.5 \mu\text{m}$ compared to the pristine TiO_2 in sample T. No significant change was observed in the diameter of the columnar grains (Fig. 1f), although the flake substructures were replaced by compressed spherical particles. Fig. 1g and h presents the SEM images of TGT, indicating that both the length and diameter of the columnar structures were reduced to $\sim 0.5 \mu\text{m}$ as well. Furthermore, each columnar grain is composed of numerous finer, nanoscale substructures, which are themselves made up of nanoscale spherical particles. Fig. 1i–j and Fig. 1k–l displays the SEM images of TFmix and TCTmix, showing that the diameter of the flake-based columns was reduced to $\sim 0.5 \mu\text{m}$ in both cases.

Side-on SEM images were used to determine the approximate thickness of each coating, as shown in Fig. S5. Sample T exhibits the greatest thickness ($\sim 1.2 \mu\text{m}$), which is reduced by the incorporation of carbonaceous materials to $\sim 0.5 \mu\text{m}$. Additionally, TGmix and TCTmix displayed columnar growth and thus a higher degree of porosity. In contrast, the remaining samples formed more densely packed films.

A TEM image of TGmix (Fig. S6) revealed the high porosity of the sample and d-spacing of 3.52 nm at the tips of the substructures, belonging to the anatase (101) crystal plane [68].

4.2.1.2. AFM. Surface roughness was quantified using atomic force microscopy (AFM) over a $10 \mu\text{m} \times 10 \mu\text{m}$ scan area (Fig. S7). The average roughness (R_a), root mean square roughness (R_q), and maximum height (R_{max}) were determined for all samples (Table 2). T, TGT, and TCTmix have similarly low R_a (~ 0.7 – 0.72 nm) and R_q values (~ 0.97 – 1.1 nm), indicating very smooth surfaces. On the other hand, TGmix shows a slightly rougher surface ($R_a \sim 1.4 \text{ nm}$ and $R_q \sim 2.6 \text{ nm}$) compared to T, TGT, and TCTmix. The AFM topography image of the TFmix sample reveals a highly irregular surface with numerous sharp peaks reaching heights over 150 nm. These protrusions, distributed non-uniformly across the surface, contribute to the elevated roughness values observed ($R_a = 11.6 \text{ nm}$, $R_q = 31.8 \text{ nm}$, $R_{\text{max}} = 467 \text{ nm}$), indicating lower homogeneity within the TFmix sample.

4.2.2. Structural and compositional characterisation

4.2.2.1. XRD and Raman spectroscopy. Fig. 2a presents XRD patterns of GO, G, CNT, and F. The XRD pattern of GO, synthesised using the Staudenmaier method [58], shows that the characteristic (002) crystal plane of graphite has been replaced by a sharp, intense peak at $2\theta = 12.95^\circ$, indicating the complete oxidation of graphite to GO [69]. After heat treatment, G is formed, with the appearance of a peak at $2\theta = 24.80^\circ$ corresponding to the (002) crystal plane of graphite, confirming complete reduction of GO back to G. The XRD pattern of CNTs is

Table 2

Surface roughness properties from AFM imaging of the T, TGmix, TGT, TCTmix, and TFmix coatings.

Sample	R_q (nm)	R_a (nm)	R_{max} (nm)
T	1.1 ± 0.37	0.71 ± 0.22	33 ± 3.4
TGmix	2.6 ± 0.5	1.4 ± 0.04	49 ± 2.6
TGT	0.97 ± 0.1	0.72 ± 0.1	24 ± 1.2
TCTmix	0.98 ± 0.3	0.70 ± 0.3	21 ± 5.4
TFmix	32 ± 0.3	12 ± 0.8	47 ± 5.8

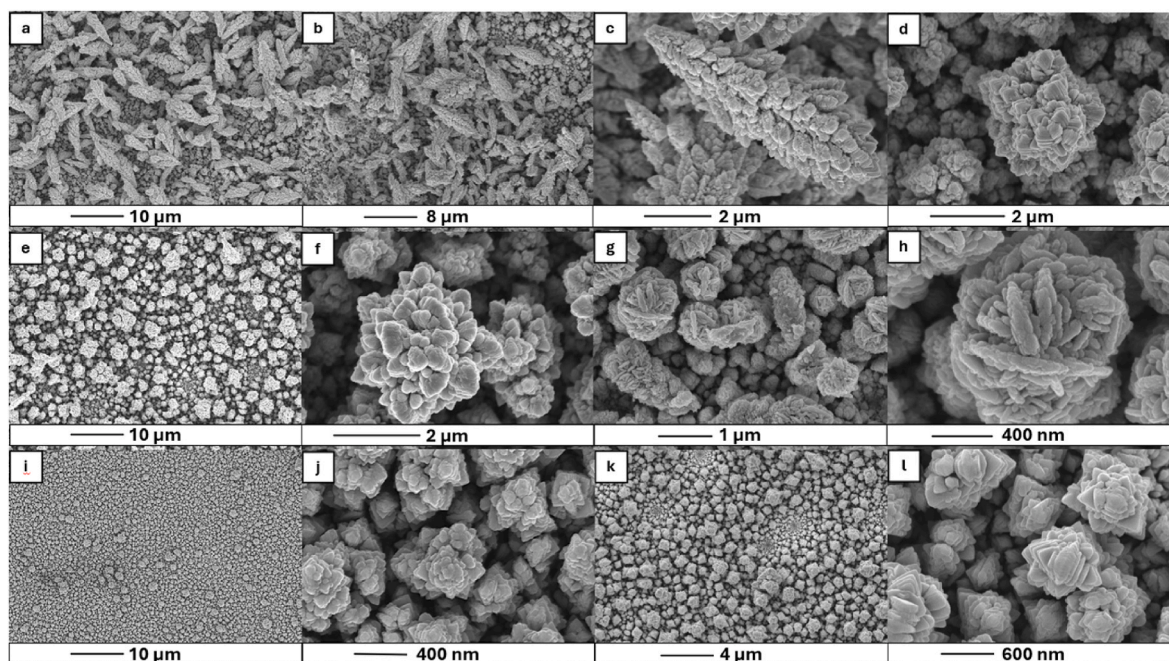


Fig. 1. SEM of (a, b, c, d) T, (e, f) TGmix, (g, h) TGT, (i, j) TFmix, and (k, l) TCTmix

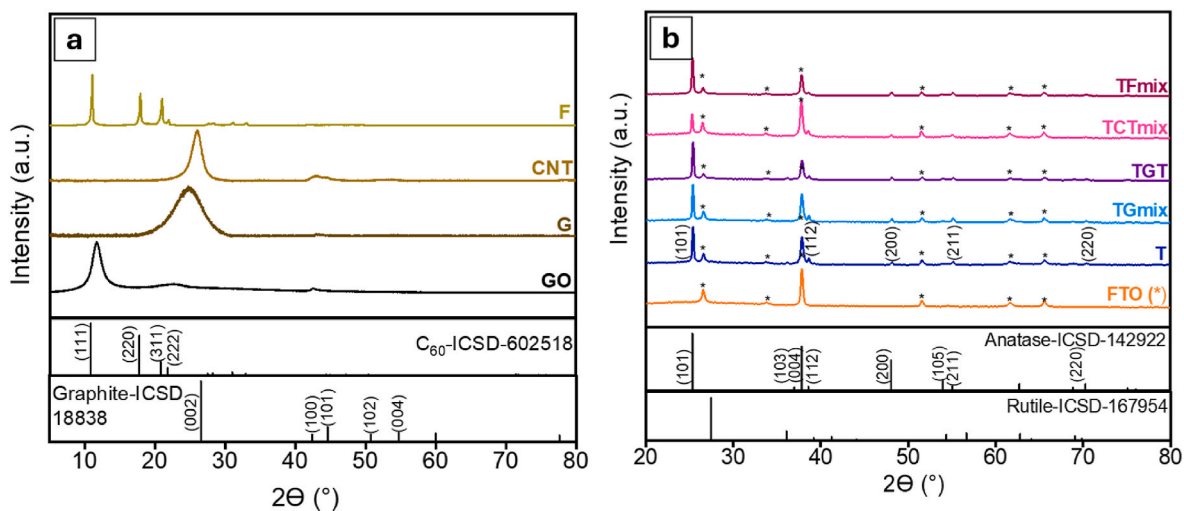


Fig. 2. XRD patterns of (a) GO, G, CNT, and F, and (b) T, TGmix, TGT, TCTmix, and TFmix coatings, with peaks corresponding to the FTO substrate marked with asterisks.

dominated by the (002) crystal plane at $2\theta = 26.06^\circ$ [70]. Crystalline C_{60} fullerene typically adopts a face-centred cubic (fcc) structure. The XRD pattern displays prominent peaks corresponding to the (111), (220), and (311) planes, located at 2θ values of 11.05° , 17.88° , and 20.93° , respectively (Fig. 2a) [71]. In Fig. 2b, the XRD patterns of FTO, T, TGmix, TGT, TCTmix, and TFmix coated on FTO-glass, with characteristic Miller indices labelled, confirming the formation of the anatase TiO_2 phase. While the dominant crystal facet in samples T, TGmix, TGT, and TFmix is the (101) plane, the dominant crystal facet in TCTmix

appears to be the (004) plane (albeit with overlap in this region with FTO). Notably, the XRD patterns of the composites show no detectable peaks corresponding to G, CNT, or F, indicating that the amounts of these additives were too low to be observed by XRD. The lattice interplanar space (d_{hkl}) can be measured using Equation S(1), where the d_{hkl} of GO was found to be ~ 0.69 nm, which is in agreement with the reported d-spacing of GO from other studies [72].

Fig. 3a shows the Raman spectra of T, TGmix, TGT, TCTmix, and TFmix from 50 to 1000 cm^{-1} . The results show peaks at 142 cm^{-1} , 396

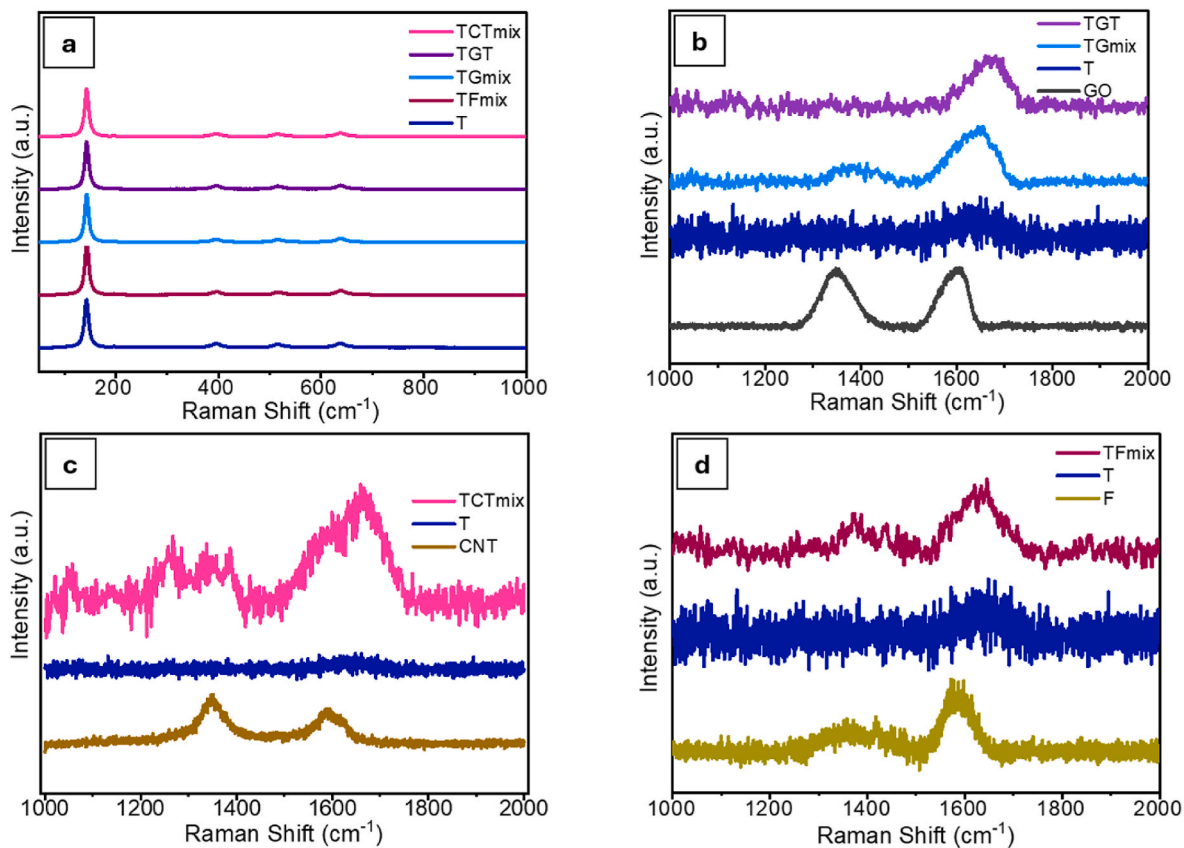


Fig. 3. Raman spectra of (a) T, TGmix, TGT, TCTmix, and TFmix from 50 to 1000 cm^{-1} , (b) GO, T, TGmix, and TGT from 1000 to 2000 cm^{-1} , (c) CNT, T, and TCTmix from 1000 to 2000 cm^{-1} , (d) F, T, and TFmix from 1000 to 2000 cm^{-1} .

cm^{-1} , 515 cm^{-1} , and 639 cm^{-1} , corresponding to the E_g , B_{1g} , $A_{1g} + B_{1g}$, and E_g vibrational modes of the anatase TiO_2 phase, respectively [62, 73–75]. In Fig. 3b, GO shows two distinct peaks at 1346 cm^{-1} and 1599 cm^{-1} , CNT at 1346 cm^{-1} and 1590 cm^{-1} , and F at 1390 cm^{-1} and 1588 cm^{-1} , corresponding to the D and G-band, respectively. The G-band, usually found near 1560 cm^{-1} , represents the presence of well-ordered sp^2 -bonded carbon atoms in the graphene structure. In contrast, the D-band, which appears strongly around 1350 cm^{-1} , reflects the presence of sp^3 -type defects disrupting the sp^2 carbon lattice [54]. Interestingly, no D-band was observed in the G layer when incorporated into the TGT coating. The intensity ratio of the D and G bands (I_D/I_G) is a widely used indicator of structural disorder in carbon materials. The I_D/I_G ratio of GO, CNT, F, TGMix, TGT, TCTmix, and TFMix were calculated to be 0.85, 1.5, 0.46, 0.36, 0, 0.58, and 0.42, respectively. No significant shifts in the peaks are observed compared to their parent materials.

The obtained I_D/I_G ratio of the synthesised GO is in close agreement with the disorder levels reported for GO produced using the Staudenmaier method [76]. The I_D/I_G ratio of the synthesised GO was found to be 0.85, signifying a scarcity of sp^3 defects within the sp^2 lattice. The average crystallite size (L_a) was determined using Equation S(2) [54, 77]. The calculated crystal size of GO was 16.4 nm. Using the crystal size and the d_{hkl} of GO ($\sim 0.69 \text{ nm}$), the number of GO layers in the measured crystallite size was therefore approximately 25, using Equation S(3) [78].

4.2.2.2. XPS. As shown in Figs. S8–12, XPS measurements were conducted on GO, T, TGMix, TGT, TCTmix, and TFMix, respectively. In addition, XPS measurements were carried out on GO, CNT, and F in our previous work [60]. In Fig. S8a–c, the XPS measurements of the C 1s and O 1s core levels of GO confirm the successful oxidation of graphite to GO, resulting in a high sp^3/sp^2 carbon ratio [79]. Table S1 summarises the binding energies of the key environments found in the samples, and Table S2 contains the abundances. In the XPS spectra of T, TGMix, TGT, TCTmix, and TFMix, the Ti 2p core-level peak can be observed in the range of 458.49 eV–458.9 eV, representing Ti^{4+} ; in agreement with literature [59,80]. The ΔE between the Ti 2p_{3/2} and Ti 2p_{1/2} in all samples is $\sim 5.8 \text{ eV}$, in good agreement with the reported values (Fig. S13) [80]. The Ti 2p core-level of TGT was shifted slightly towards higher energies compared to sample T. The O 1s core-level of T, TGMix, TGT, TCTmix, and TFMix, the O–Ti band in all samples is located approximately in the same place as T (529.89 eV), apart from TGT sample (530.22 eV), which was shifted towards higher energies, revealing that the O 1s and Ti 2p core-levels for all the composites, apart from TGT, are akin to the parent material. The shift of the O 1s and Ti 2p core levels of TGT to higher energies compared to T indicates a change in the chemical environment of titanium due to its interaction with graphene oxide, suggesting the formation of chemical bonds between GO and TiO_2 [81]. The C 1s core-level of all composites confirms the presence of sp^2 (C=C) and sp^3 (C–C) carbon. The ratio of sp^2/sp^3 in GO, CNT, F, TGMix, TGT, TCTmix, and TFMix are ~ 0.16 , 10, 5.0, 2.0, 2.0, 2.0, and 2.0, respectively. This showed that the amount of sp^2 carbon in TGMix and TGT dramatically increased compared to the sp^2 carbon level in GO, revealing that GO was reduced to G during the synthesis process. On the other hand, the sp^2/sp^3 values of CNT and F were reduced in the composite coatings compared to parent CNT and F materials, which can be attributed to their amorphization during synthesis. The valence band maximum (VBM) energies relative to the Fermi level for T, TGMix, TGT, TCTmix, and TFMix were determined to be 2.67 eV, 2.54 eV, 3.05 eV, 3.02 eV, and 2.99 eV, respectively (Fig. S13). Based on these values, the band gap (E_g), measured using Equation S(6), the conduction band minimum (CBM) energies for T, TGMix, TGT, TCTmix, and TFMix were calculated using Equation S(4), and determined to be -0.53 eV , -0.66 eV , -0.15 eV , -0.18 eV , and -0.21 eV with respect to their Fermi level, respectively.

4.2.3. Optical characterisation

4.2.3.1. UV–visible spectroscopy. The optical properties of all samples were studied using UV–Vis spectroscopy (Fig. 4). The optical properties of the GO, G, CNT, and F were investigated using UV–visible diffuse reflectance spectroscopy (DRS) (Fig. 4a). The recorded diffuse reflectance spectra were subsequently transformed into relative absorption (F(R)) values via the Kubelka–Munk function. All the carbon-based materials exhibited notable absorption in the visible region, with the trend observed as $\text{CNT} > \text{F} > \text{GO} \approx \text{G}$. However, the visible light absorption behaviour of the corresponding composites does not strictly follow this trend, likely due to differences in dispersion and deposition efficiency. Transmittance and total reflectance spectra of all TiO_2 -containing coatings were used to determine their absorptance, and subsequently, a Tauc plot (Fig. 4a and b). Fig. 4b shows the absorptance spectra of the samples, indicating that in the UV ($< 350 \text{ nm}$) region, all the samples have the same high level of UV light absorption, while in the visible region (400–800 nm), TFMix and TGMix show the highest levels ($\sim 40\%$) of visible absorption. Unexpectedly, sample T exhibits some visible light absorption, the lowest among the samples ($< 20\%$). This absorption may be attributed to residual carbon from TTIP or toluene that was not fully decomposed during the annealing process [59]. In comparison, TCTmix and TGT exhibit intermediate absorption levels (20–30%) in the visible range, differing from what would be expected in the case of TCTmix based on the strong visible light absorption of CNT.

Fig. 4c illustrates the Tauc plots of T, TGMix, TGT, TCTmix, and TFMix. No difference in the band gap of the anatase TiO_2 component was seen across this series of samples, where the band gaps were analogous to the T parent material, being $\sim 3.2 \text{ eV}$. GO is reduced to graphene (G) during the high-temperature AA-CVD process and subsequent annealing.

4.3. Photocatalytic activity

4.3.1. NO_x remediation

The photocatalytic activity of all coatings produced herein was evaluated against NO gas under both UVA and visible light using ISO protocol (22197–1:2016). Going further than the ISO protocol, we also investigated their activity against NO_2 gas under both UVA and visible light irradiation. All photocatalysts examined in this study facilitate the photo-oxidation of NO and NO_2 pollutants rather than their reduction.

The process begins with a 15-min equilibration period in the dark under an atmosphere containing approximately 1 ppm of NO. Following this, the sample is exposed to UVA light (1.00 mW cm^{-2}) to initiate photocatalytic reactions for 1 h, preceded by a second 15-min equilibration period in the dark under the same NO conditions (Fig. S14). For TiO_2 , UV illumination causes a rapid, remarkable drop in NO concentration. This decrease is attributed to the reaction between gas-phase NO and adsorbed superoxide anions (O_2^-), leading to the formation of nitrate species. These superoxide anions are generated when photoexcited electrons reduce adsorbed oxygen molecules [82,83]. Because the resulting nitrate species do not readily desorb, the catalyst surface gradually becomes saturated, causing the NO concentration at the reactor outlet to rise again over time. Simultaneously, a part of NO is photo-oxidised to NO_2 on the illuminated TiO_2 surface through its reaction with photogenerated hydroxyl radicals, although this transformation is considered undesirable, as NO_2 is more toxic than NO [84].

The results for NO gas removal under UVA (300–400 nm with a light intensity of 1 mW cm^{-2}) and visible (~ 360 –800 nm) illumination are summarised in Fig. 5a and b, respectively, and Fig. S15 for all materials. All samples show higher performance under UVA light. Under visible light, no photocatalytic activity was expected for TiO_2 , due to its wide band gap. However, under visible irradiation, a small amount of UV light (250–320 nm) is transmitted through the Pyrex filter from the white light source. With the addition of carbonaceous material, the NO_x

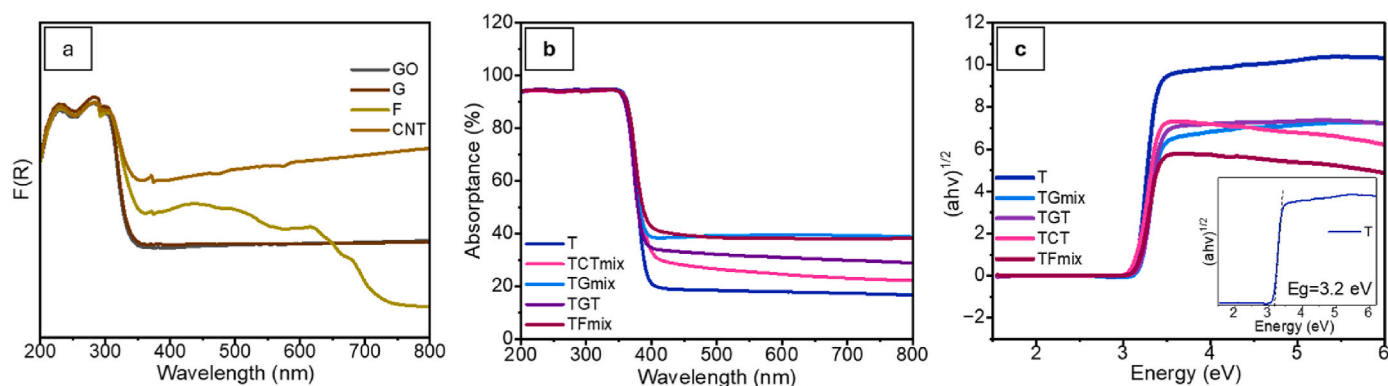


Fig. 4. Optical properties of all samples. (a) UV-visible absorption spectra of GO, G, CNT, and F obtained by converting the measured values of diffuse reflectance to relative absorbance using the Kubelka-Munk relation. (b) UV-visible absorbance spectra of TiO₂-containing coatings: T, TGmix, TGT, TCTmix, and TFmix, calculated from the measured values of total reflectance and transmittance to absorbance (%). (c) Tauc plots of T, TGmix, TGT, TCTmix, and TFmix, and the inset shows Tauc plot extrapolation for T.

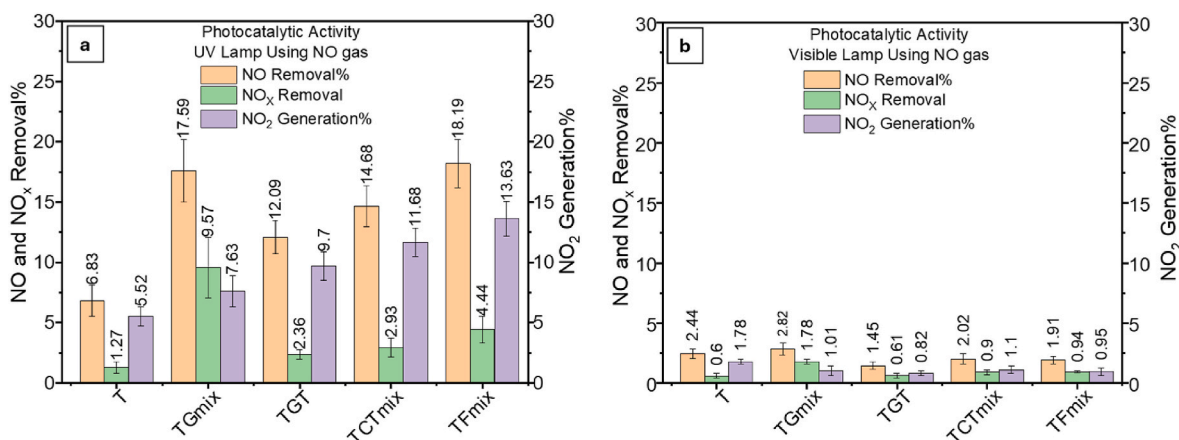


Fig. 5. Photocatalytic NO removal tests for the series of T, TGmix, TGT, TCTmix, TFmix samples summarising their NO removal (%), NO_x removal (%), and NO₂ generation (%) examined under (a) UVA light (1 mW cm⁻²), and (b) visible light (~360–800 nm)(2.6 mW cm⁻²).

removal (green bars) improves and selectivity to form NO₂ (purple bars) reduces under both UV and visible light. The most significant increase in activity was observed in TGmix, indicating a synergistic interaction between the parent materials, with graphene serving as both an electron acceptor and an adsorption site for NO_x, thereby accelerating NO photo-oxidation and reduces the NO₂ generation. Under UVA light, TGmix showed ~3 times higher NO and ~8 times higher NO_x removal (17.59

and 9.57 %, respectively) than its parent material T (6.83 and 1.27 %, respectively). Importantly, TGmix showed approximately half the selectivity to form NO₂ (~44 %) than its parent material T (~81 %). Under visible light, TGmix showed slightly higher NO and NO_x (2.82 and 1.78 %, respectively) removal compared to T (2.44 % and 0.60 %, respectively), with NO₂ selectivity again showing a significant reduction (~39 %) compared to T (~68 %).

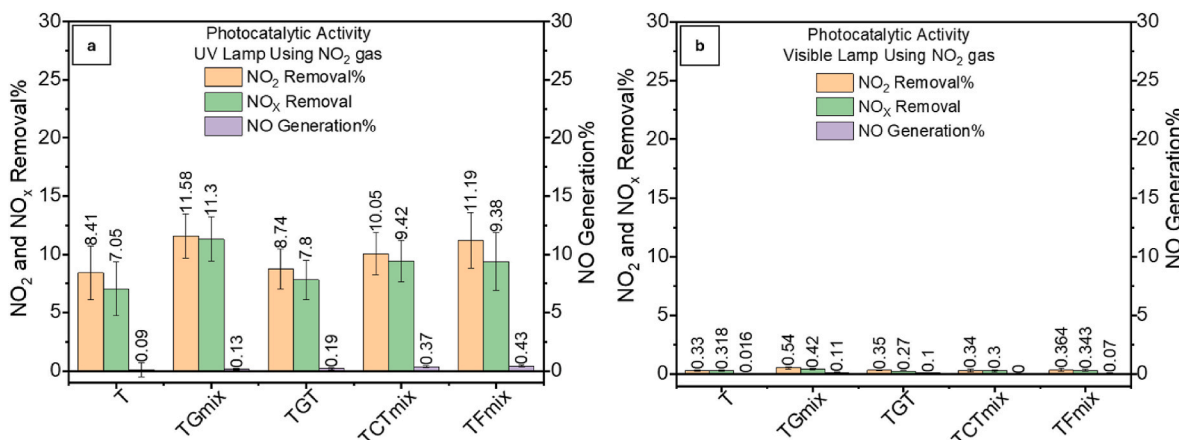


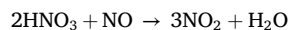
Fig. 6. Photocatalytic NO₂ removal tests for the series of T, TGmix, TGT, TCTmix, TFmix samples summarising their NO₂ removal (%), NO_x removal (%), and NO generation (%) examined under (a) UVA light, and (b) visible light.

The results for NO_2 photo-oxidation under UVA and visible light are summarised in Fig. 6. As with our NO photo-oxidation tests, all samples showed higher activity under UVA light than under visible light. In the NO_2 photo-oxidation tests, NO_2 is oxidised to nitrate (NO_3^-), while a minor amount of NO may be generated due to competing reduction processes involving photogenerated electrons (e^-). In either case, all carbon-containing samples showed better performance compared to the parent material T. TGmix was the most active sample once more, where under visible light it removed 0.54 % of NO_2 compared to 0.33 % for sample T, and under UVA light it removed 11.68 % of NO_2 compared to 8.41 % for sample T.

To investigate the mechanism of the photo-oxidation of NO using TGmix and the role of $\text{OH}^\bullet$ and $\text{O}_2^{\bullet-}$, TGmix was tested against NO removal in two different conditions (Fig. S16a). One of the experiments was conducted using air as the carrier gas in the absence of relative humidity (0 % RH) to monitor the role of $\text{O}_2^{\bullet-}$, and the other was in the absence of air using N_2 as the carrier gas and relative humidity of 50 % to study the role of $\text{OH}^\bullet$. Both tests were conducted under UVA light, and the results were compared to NO removal carried out under ISO conditions, in which the carrier gas is air and the relative humidity is 50 %. The results show that in the ISO condition, NO removal is superior to the other conditions, meaning that both $\text{OH}^\bullet$ and $\text{O}_2^{\bullet-}$ are essential for NO removal. However, since NO removal in the presence of air and 0 % relative humidity is higher than NO removal in the absence of air and 50 % relative humidity, the role of $\text{O}_2^{\bullet-}$ is postulated to be more important than the role of $\text{OH}^\bullet$.

Finally, to study the durability of TGmix, 4 cycles of NO removal

were tested under UVA light and ISO conditions with a 30-min gap between each test, as shown in Fig. S16b. The results show that in the second cycle of NO removal, the NO_x removal value reduces to 0.1 %, indicating that NO gas was being converted primarily to NO_2 . This is due to nitric acid build-up on the surface of the photocatalyst that blocks active sites, and can back-react with NO to form NO_2 [85]:



Equation 1

The results indicate that the surface eventually reached a saturation point with HNO_3 , at which the rate of HNO_3 formation matched the rate of photocatalytic removal [85]. However, by the fourth cycle, both NO_x and NO removal show a noticeable decline. Importantly, the activity can be recovered through a simple wash, where the TGmix sample was immersed in DI water for 30 min, air dried, and tested again under the same conditions. As shown in Fig. S16b, the NO_x remediation performance of the composite was restored to within the error of the fresh sample.

Interestingly, the architecture that excelled in NO_x removal (TGmix) was not the top performer in water splitting, indicating different charge-separation requirements, as explored next.

4.3.2. PEC water splitting

The PEC water splitting activity of all coatings produced herein was evaluated by recording current-voltage (J-V) curves and incident photon-to-current efficiency (IPCE) spectra, and chronoamperometry.

The PEC water splitting JV curves shown in Fig. 7a were performed under front 350 nm illumination, sweeping the voltage 0 to 2.8 V_{RHE} at

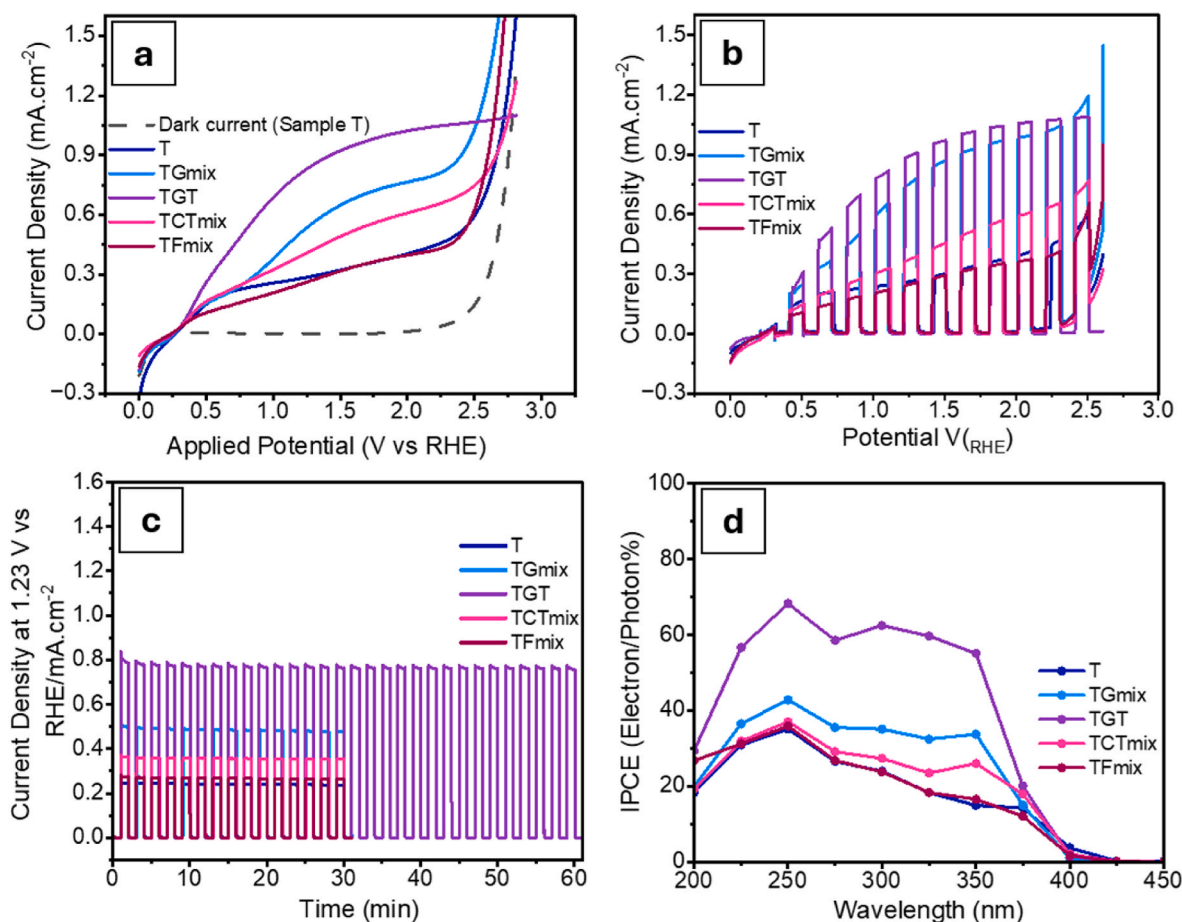


Fig. 7. PEC performance data for all samples in a pH = 7 aqueous buffered solution (0.1 M $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ and 0.2 M Na_2SO_4) under front illumination. (a) J-V curves (scan rate: 10 mV s^{-1}) using 350 nm light (5.26 mW cm^{-2}), (b) LSV under chopped 350 nm light irradiation (5.26 mW cm^{-2}) with a 0.1 Hz chopper frequency, (c) Chopped chronoamperometry stability test for 30/60 min under 350 nm light irradiation (5.26 mW cm^{-2}) with a 0.016 Hz chopper frequency, (d) IPCE measured at 1.23 V_{RHE} .

10 mV s⁻¹. The TGMix, TGT, and TCTmix composites exhibited a higher photocurrent density than T, indicating enhanced charge carrier separation facilitated by the addition of carbonaceous material. At an applied potential of 1.23 V_{RHE}, the photocurrent density of 0.28 mA cm⁻² for sample T increased to 0.53 mA cm⁻² for TGMix, 0.82 mA cm⁻² for TGT, and 0.4 mA cm⁻² for TCTmix; however, the photocurrent density for TFmix worsened to 0.25 mA cm⁻². The photocurrent onsets of all the samples at 10 mV.s⁻¹ scan rate are similar, located at ~0.25 V_{RHE}.

Fig. 7b presents the JV curves under chopped 350 nm light irradiation with the potential swept from 0 to 2.8 V_{RHE} at 10 mV s⁻¹. The chopped-light JV curves matched data from dark and light measurements in Fig. 7a, with data for the TGT sample compared in Fig. S17a. Upon turning the light on (and off), there was a sharp rise (fall) and stabilisation of the photocurrent, indicating efficient charge extraction. Fig. S17b shows the CV of all samples, under front 350 nm illumination, sweeping the voltage from 0 to 2.8 V_{RHE} at 10 mV s⁻¹. All samples exhibit low hysteresis between the forward and reverse scans, supporting our assessment from chopped light measurements of efficient charge extraction and no photo-charging effect [86]. The photocurrent onsets of T, TGMix, TGT, TCTmix, and TFmix were measured under chopped 350 nm light irradiation (with 0.3 Hz chopping frequency) at a very slow scan rate of 1 mV s⁻¹, from 0 to 0.32 V_{RHE} to obtain the approximate flat band. The measured flat bands are approximately located at +0.02 V, +0.01 V, +0.03 V, 0.00 V, and +0.01 V_{RHE} at pH 7 (Fig. S18).

Fig. 7c shows the CA photocurrent response for all samples at 1.23 V_{RHE} under chopped 350 nm light irradiation with 0.016 Hz chopping frequency over a 30-min period. The TGT sample was tested for an extended duration of 1 h under the same conditions. All samples showed highly stable photocurrent generation, with little loss in initial performance over the testing period (<5 % drop). TGT was later tested for 5 h, showing only a 5.2 % decrease in photogenerated current density after this extended testing (Fig. S19).

The IPCE of all samples was measured using monochromatic illumination from 200 to 450 nm, at 1.23 V_{RHE} (Fig. 7d). The samples exhibit an increase in IPCE from 200 nm to 250 nm, reaching their highest value at 250 nm. From 350 nm, the IPCE of all samples declines and drops to zero between 425 and 450 nm. Among all samples, TGT showed the highest IPCE values. At 250 nm, the IPCE values for T, TGMix, TGT, TCTmix, and TFmix are 35.1 %, 42.9 %, 68.2 %, 37 %, and 35.9 %, respectively. And at 350 nm, the IPCE values for T, TGMix, TGT, TCTmix, and TFmix the IPCE results at this wavelength are 14.9 %, 33.7 %, 55 %, 26 % and 16.6 %, respectively.

The solar predicted photocurrent (SPP) was determined from IPCE measurements at 1.23 V_{RHE} for all samples (Table 3), and shown diagrammatically for T (Fig. 8a) and the best performing sample, TGT (Fig. 8b). The utilised portion of the solar flux is shown, highlighting the enhancement in solar harvesting in TGT, resulting in a more than double increase in SPP from 0.20 mA cm⁻² in T to 0.49 mA cm⁻² in TGT.

The photocurrent density trends were consistent across all tests (JV, CV, CA, IPCE and SPP), and showed the following order: T ~ TFmix < TCTmix < TGMix < TGT. These results suggest that graphene contributes most effectively to charge separation at early timescales, particularly in the sandwich-layered structure, where improved charge carrier

separation and transfer kinetics are observed [87]. The electron carrier kinetics were investigated using transient photocurrent (TPC) measurements. Fig. S20 shows the normalised TPC response of all samples at 1.23 V_{RHE} under 365 nm illumination. The electron extraction kinetics were assessed by monitoring the anodic photocurrent half-rise time (t_{50 %}) after the illumination onset. Table 4 shows the half-rise time (t_{50 %}) extracted from TPC response curves. The t_{50 %} values reflect the characteristic times required for the photocurrent to reach 50 % of its maximum value after illumination, serving as a proxy for the electron extraction kinetics. A shorter t_{50 %} indicates faster charge extraction. The TPC measurements showed that electron extraction kinetics were similar in all samples except TFmix, which was approximately twice as slow as the parent material, T. This indicates that the incorporation of MWCNTs and G were not disruptive to electron extraction in TiO₂, however, the incorporation of F (C₆₀) was disruptive, revealing that these sites acted as electron traps [88].

4.4. Charge carrier characterisation

4.4.1. PL

We now turn to photoluminescence (PL) spectroscopy to investigate the electronic and surface processes in the materials. Unnormalised PL spectra are shown for TFmix, TCTmix, TGMix and TGT in Fig. 9a, b and 9c, respectively, along with the spectra of their respective individual constituent materials. Corresponding normalised spectra are shown in Fig. S21. All samples were excited with a 345 nm laser, and all measurements were carried out in air.

Examining first the spectrum of neat T, in agreement with previous literature on anatase TiO₂, we observe broad emission extending from 400 (3.1 eV) to beyond 800 nm (1.55 eV) [89–91].

In agreement with these works, this broad emission comprises two distinct components, centred in the blue-green (~450 - 480 nm corresponding to an energy of 2.8-2.6 eV) and in the red (~600 nm; 2.1 eV), noting that the overall shape and relative intensities of the emission peaks have been shown to be strongly dependent on both structure and interaction with external species. As convincingly shown in recent work by Pallotti et al. [89], emission from these two regions can be assigned to the recombination of photogenerated electrons in the conduction band with trapped holes near the valence band (green emission), and the recombination of photogenerated holes with electrons trapped in mid-gap states (red emission). These two phenomena were assigned to chemical defects arising from surface and subsurface oxygen vacancies, respectively.

Turning now to the emission of the composite materials, it is immediately evident that none show the high energy emission band observed in neat T, with all instead showing red-shifted emission peaking beyond 550 nm (TGMix and TGT) or 610 nm (TCTmix and TFmix). The absence of this emission band indicates the charge transfer of photogenerated electrons from the conduction band of T to the carbonaceous material in all composite materials, leading to the quenching of emission of the recombination of photogenerated electrons with surface trapped holes.

Looking in more detail at the emission from TCTmix and TFmix (Fig. 9a and b), the emission spectra of both materials are centred around a single peak around 600–610 nm, and the emission of neither material correspond to that of its parent carbon material (CNT or F, respectively). This suggests that photogenerated electrons that are under charge transfer to the carbonaceous material are either rapidly scavenged by chemisorbed O₂ at the carbon surface or undergo non-radiative recombination in the bulk. Further, the strong overlap of the emission of both carbonaceous materials with the low-energy emission band of neat T suggests that the bulk recombination in TiO₂ of photogenerated holes with trapped electrons is unaffected by the presence of the carbonaceous materials on the TiO₂ surface, as may be expected.

Finally, the emission of both TGT and TGMix (Fig. 9c) shows a strong emission peak around 570–580 nm, in addition to a broad shoulder

Table 3

The solar predicted photocurrent (SPP) values for T, TGMix, TGT, TCTmix, and TFmix, determined from IPCE performance measurements at 1.23 V_{RHE}.

Sample	SPP (mA cm ⁻²)
T	0.20
TGMix	0.40
TGT	0.49
TCTmix	0.27
TFmix	0.20

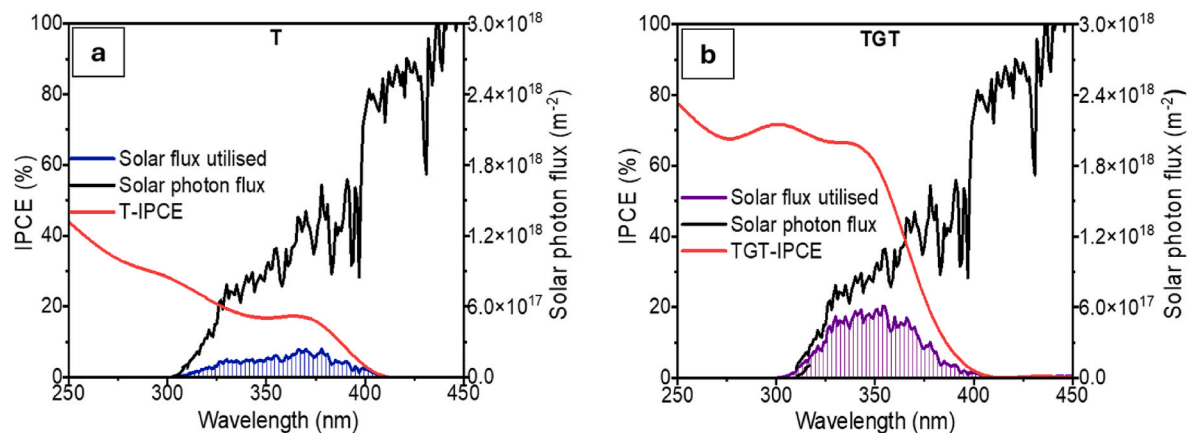


Fig. 8. The solar predicted photocurrent at 1.23 V_{RHE} for (a) T and (b) TGT sample under front irradiation.

Table 4

Half-rise time (t_{50} %) extracted from transient photocurrent response curves of pristine T, TCTmix, TFmix, TGMix, and TGT, measured at 1.23 V_{RHE} under 365 nm illumination with a light power of $\sim 10 \text{ mW cm}^{-2}$ (~ 1 sun equivalent UV component).

	T	TCTmix	TFmix	TGMix	TGT
t_{50} % (ms)	0.268	0.243	0.449	0.220	0.250

beyond 650 nm (which can be assigned to bulk TiO_2 emission, as above). The high-energy emission peak centred around 570–580 nm can be confidently assigned to emission from GO, which shows the same emission feature in its neat state. Given the low concentration (1 %) of GO compared to T in the composites and the absence of the low energy GO emission peak ($< 700 \text{ nm}$) in the composition materials, we believe that most of this emission stems from the radiative recombination of photogenerated electrons (with holes in the GO) transferred following photoexcitation of TiO_2 , although recombination of charges from the direct photoexcitation of GO cannot be completely ruled out. In either case, the strong emission feature from GO suggests a strongly increased lifetime of photogenerated electrons in the GO-based composites compared to the composites based on CNT or F.

4.4.2. DR-TAS

Using diffuse reflectance transient absorption spectroscopy (DR-TAS), the behaviour of the photogenerated charge carriers was studied in all samples. From our previous work, the carbon-based materials studied herein do not show any photoexcitation behaviour themselves on the measured timescale of the microsecond to second [60]. Ultrafast transient absorption spectroscopy (TAS) is commonly used to investigate the rapid electronic excitation and relaxation dynamics in materials such as GO [92], CNT [93], and F [94], showing that these processes occur faster than the time resolution of the instrument employed in this study.

All samples were measured in operando, at applied potential of 1.23 V_{RHE} , for probe wavelengths 500–1100 nm from 10 μs to 1 s after a 355 nm laser pulse excitation. Fig. S22 shows the DR-TAS kinetics of all samples from 10 μs to 1 s at all probe wavelengths 500–1100 nm. Fig. S23 shows the DR-TAS spectra from 500 to 1100 nm at the selected times of 10 μs , 100 μs , 1 ms, and 10 ms following 355 nm laser pulse excitation. Among the samples, TGMix and TGT exhibit the strongest transient absorption intensities. Although TGMix and TGT display higher overall transient absorption, their spectral evolution over time closely follows the trend observed for T. Sample T shows a distinct absorption peak in the 500–600 nm range shortly after excitation. In contrast, TGMix and TGT feature broad absorption spanning the entire monitored range (500–1100 nm), with a pronounced peak centred around 500 nm. Notably, both TGMix and TGT exhibit enhanced absorption at 700 nm at 10 μs post-excitation. TCTmix shows its highest absorption at 600 nm, while TFmix exhibits maximum absorption in the 700–900 nm range, which shifts to 500 nm at 100 μs after the laser pulse. Past studies have shown that photogenerated holes in TiO_2 are primarily located in the blue region of the electromagnetic spectrum, at energies below the band edge of the material, whereas photogenerated electrons are primarily located in the red region [95].

To study the behaviour of photogenerated hole carriers in our

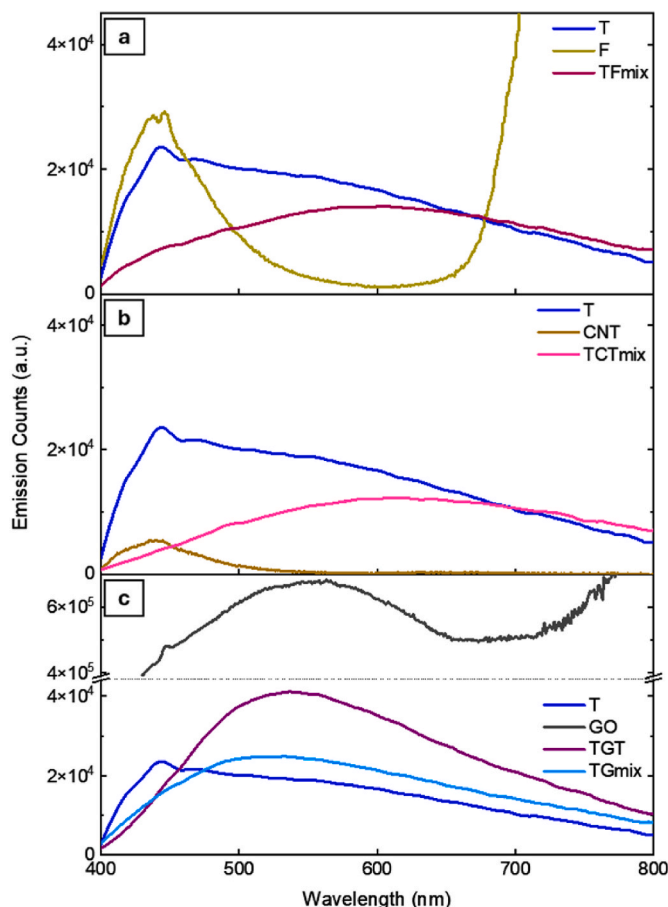


Fig. 9. Photoluminescence (PL) emission over the 400–800 nm range after excitation with 345 nm light for (a) T, F, TFmix, (b) T, CNT, TCTmix, and (c) T, GO, TGMix and TGT.

materials, we probed the DR-TAS behaviour at 500 nm. Fig. S24 illustrates the DR-TAS kinetics of all samples at applied potentials from 0 to 2 V_{RHE} from 10 μ s to 1 s after a 355 nm laser pulse. At 0 V and 0.2 V_{RHE} , no changes in optical density were observed, which closely matches the JV curves of all samples, where the photocurrent onset was observed from $\sim +0.25 V_{RHE}$ (Fig. 7). Above the onset potential, recombination is inhibited due to increased band-bending and stronger electric fields in the space charge layer, significantly increasing the yield and lifetimes of photogenerated holes observed on the time scale. All samples showed increased charge carrier absorption and lifetime at 500 nm at 0.4 V_{RHE} . With further increases in applied potential, further increases in hole carrier population and lifetime were observed, with this being most prominent in the TGT sample. Fig. 10 compares the DR-TAS spectra of the samples at 500 nm probe light at the applied potential of 1.23 V_{RHE} . Fig. 10 shows that the charge carrier population is higher in TGT > TGmix > TFmix compared to T, with the exception of TCTmix, which displays a lower population. This suggests that, at early timescales (10 μ s–100 μ s), charge carrier recombination is suppressed in these composites, likely contributing to the increased carrier populations observed. An ultrafast transient absorption spectroscopy (uf-TAS) study could provide further insight into this phenomenon. These results closely align with the photocurrent generation observed in the PEC measurements (Fig. 7a and b), in which the composites generate more photocurrent compare to T. Charge carrier lifetimes, represented by the half-life (t_{50} %), defined as the time for the transient absorption to decay to 50 % of its initial value at 10 μ s after the laser pulse, were extracted, with t_{50} % values of 82 ms, 88 ms, 10.3 ms, 3.1 ms, and 63 ms for T, TGT, TGmix, TCTmix, and TFmix, respectively.

Fig. S25 presents the diffuse reflectance-transient absorption spectra of T, TGmix, TGT, TCTmix, and TFmix, recorded at time delays of (a) 10 μ s, (b) 100 μ s, (c) 1 ms, and (d) 10 ms following 355 nm laser pulse excitation (6 ns pulse width, 0.67 Hz repetition rate, $\sim 220 \mu$ J cm^{-2} per pulse), across a range of 0–2 V_{RHE} applied potential. In all of the time scales (10 μ s, 100 μ s, 1 ms, and 10 ms), the transient absorption increases after the onset potential (≥ 0.4), and the highest transient absorption can be observed at 100 μ s for all the samples. At 100 μ s, the highest transient absorption is seen in TGT, which correlates with this sample showing the highest water splitting performance. Fig. S25 shows the optical density changes of the samples at 500 nm probe light under

355 nm laser excitation and an applied potential of 1.23 V_{RHE} , plotted against the current density of the same samples measured at 1.23 V_{RHE} from JV-curve measurements under 350 nm irradiation at various time points: 10 μ s, 100 μ s, 1 ms, and 10 ms. At 100 μ s—where the linear fit shows the strongest correlation—the $\Delta O.D.$ values reach their peak, serving as the most reliable indicator of photoelectrochemical water oxidation activity (Fig. S26). This trend confirms that charge carrier recombination is effectively suppressed up to the 1 ms timescale, beyond which the $\Delta O.D.$ begins to decline.

4.4.3. Mechanisms of photocatalytic action

To rationalise why the optimal structure differs in composites containing anatase and graphene, with mixed and layered architectures, for NO_x removal and water splitting, we constructed band alignment diagrams and propose the following mechanisms.

Fig. 11a illustrates the mechanism behind the enhanced photocatalytic performance of TGmix for NO_x removal. The comparison between the conduction and valence band positions of anatase TiO₂ and the Fermi level of G, relative to the redox potential of O₂ reduction to $\bullet O_2^-$ radicals ($-0.33 V_{NHE}$) [96], as well as the oxidation potentials of OH[−] to $\bullet OH$ ($+1.99 V_{NHE}$) and H₂O to $\bullet OH$ ($+2.30 V_{NHE}$), are shown. Using the measured flat band, conduction band, valence band, and band gap, the band energy diagram was constructed relative to the RHE and NHE reference scales (Fig. 11a and b). It has been reported that the conduction band (CB) of anatase at pH 7 is located at $-0.5 V_{NHE}$, while its valence band (VB) is positioned at $+2.7 V_{NHE}$ [97], which approximately matches the values we measured for our CB ($-0.86 V_{NHE}$) and VB ($2.34 V_{NHE}$) based on the flat band potential and the band gap (3.2 eV) of sample T. This indicates that the CB of anatase is more negative than the redox potential for O₂ reduction to $\bullet O_2^-$, and its VB is more positive than the oxidation potentials of OH[−] to $\bullet OH$ and H₂O to $\bullet OH$. Therefore, anatase can effectively oxidise NO_x to nitrate.

To understand the role of graphitic materials in the composites and their contribution to the photo-oxidation of NO_x, it is essential to consider their work function, which corresponds to their Fermi level. Since these graphitic materials exhibit metallic behaviour, their conduction and valence bands can be considered continuous. The reported work functions (vs vacuum) for intrinsic graphene, multi-walled carbon nanotubes (MWCNTs), and C₆₀ are 4.57 eV vs vacuum [98], 4.54 eV vs vacuum [99], and 4.69 eV vs vacuum [100], respectively. The Fermi level of graphene was also reported to be $-0.08 V_{NHE}$ in a previous report [101]. These values indicate that the Fermi levels of graphene, CNTs, and C₆₀ are more positive than the conduction band of anatase TiO₂. Consequently, photogenerated electrons migrate from the conduction band of anatase to the Fermi level of these graphitic materials, effectively suppressing the recombination of electron-hole pairs [27]. Additionally, the ability of graphitic materials to adsorb NO and NO₂ [28], helps explain the superior performance of TGmix, TGT, TCTmix, and TFmix compared to their parent sample T.

Importantly, the TGmix sample exhibited significantly higher activity than all other samples produced in this study. This enhancement is attributed to the superior electron conductivity of graphene compared to MWCNTs and C₆₀, which facilitates more efficient electron delocalisation and reduces the likelihood of charge recombination at the interface [102]. Nevertheless, the TGmix sample showed a higher activity in a mixed composite form as opposed to a layered sandwich structure form, TGT, in the photo-oxidation of NO_x. Notably, even TCTmix and TFmix outperform TGT. We attribute this to the uniform dispersion of G throughout the composite, which increases the interfacial contact with TiO₂, facilitating more effective electron transfer from the conduction band of TiO₂ to G and enhancing charge separation. Moreover, the fact that G is mixed allows photogenerated electrons to be separated to surface sites where G resides, and O₂ can be reduced to $\bullet O_2^-$ radicals. In the layered form, G acts as a conduit for electrons in the bulk of the material, impeding this reaction.

On the other hand, TGT outperforms TGmix and all other samples in

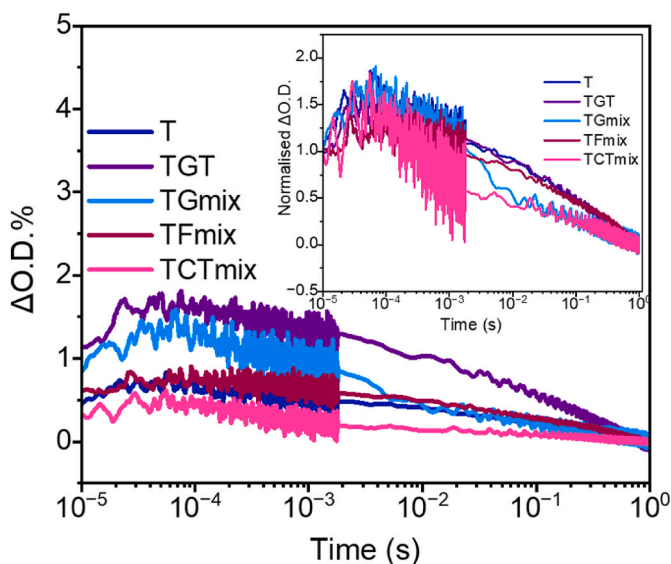


Fig. 10. Diffuse reflectance-transient absorption decay kinetics for all samples measured from 10 μ s to 1 s after laser excitation (355 nm, 6 ns width, $\sim 220 \mu$ J cm^{-2} per pulse) at a probe wavelength of 500 nm under an applied potential of 1.23 V_{RHE} in a pH 7 buffered aqueous electrolyte (0.1 M KH₂PO₄/K₂HPO₄ and 0.2 M Na₂SO₄).

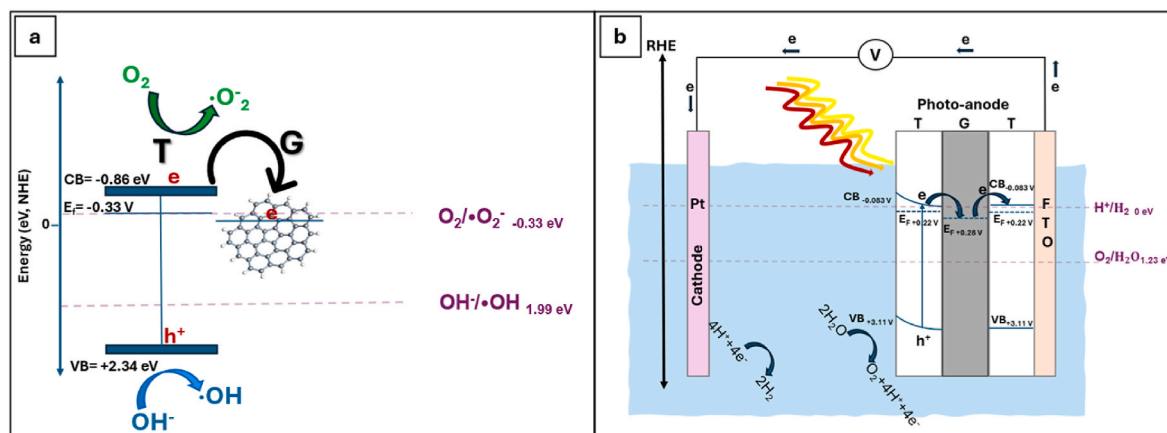


Fig. 11. (a) Band energy diagram showing the TGMix forming reactive oxygen species (ROS) that can drive the oxidation of NO_x. (b) Band energy diagram of the TGT layered structure in a water splitting device.

PEC water oxidation due to its long-lived photogenerated charge carriers, as shown by the DR-TA decay kinetics under 1.23 V_{RHE} (Fig. 10), where TGT exhibits both the highest charge-carrier population and the longest lifetime. This enhanced charge separation arises from the layered architecture, in which rGO is sandwiched between the top and bottom TiO₂ layers. It can be concluded that the combination of rGO's two-dimensional structure, large interfacial area, and high electrical conductivity with this layered arrangement promotes efficient interfacial transfer and long-lived charge carriers, which are the key factors driving the superior PEC performance (Fig. 11b). In contrast, TGMix shows lower performance due to potential light scattering and partial blockage by G, less efficient charge separation, and more random electron transport pathways, all of which contribute to reduced water splitting efficiency.

To investigate the generation of oxygen (O₂) during water oxidation

at our photoanode, operando mass spectrometry was carried out during chronoamperometry under several light and dark cycles for our best-performing sample, TGT (Fig. S27). The films were deposited on FTO glass substrates (0.7 cm × 0.7 cm × 0.1 cm) and tested at pH 7 in a 0.1 M KH₂PO₄/K₂HPO₄ buffer solution. Measurements were conducted under front-side 350 nm illumination over an active area of 0.196 cm² at an applied potential of 1.23 V_{RHE}. O₂ was seen to form and then drop to background levels with each light and dark cycle, showing that our photoanode was producing O₂ from the photocatalytic oxidation of water.

Table 5

A summary of photocatalytic NO removal activity of TiO₂ and carbon-based composites with TiO₂ from the literature compared with the best-performing material produced herein, TGMix.

Material	Synthesis method	Precursor	Phase	Deposition temperature (°C)	ISO	NO removal (%)	Light source	NO (ppm)	Ref.
TiO ₂	APCVD	Ti(OEt) ₄	Anatase	600	No	22.6	2 × Sankyo (UV lamp), 15 W	3	[103]
TiO ₂	APCVD	TTIP	Anatase/Rutile	600	No	14.9	2 × Sankyo (UV lamp), 15 W	3	[103]
TiO ₂	APCVD	Ti(OBu) ₄	Anatase	600	No	12.7	2 × Sankyo (UV lamp), 15 W	3	[103]
TiO ₂	AA-CVD	Ti(OBu) ₄ /ethanol	Anatase	500	Yes	10.3	2 × Sankyo (UV lamp), 15 W	1	[67]
TiO ₂	AA-CVD	Ti(OBu) ₄ /toluene	Anatase	500	Yes	9.3	2 × Sankyo (UV lamp), 15 W	1	[67]
TiO ₂	AA-CVD	TTIP/IPA	Anatase	500	Yes	6.8	2 × Sankyo (UV lamp), 15 W	1	[67]
TiO ₂	AA-CVD	TTIP/Methanol	Anatase/Rutile	550	Yes	6.6	2 × Sankyo (UV lamp), 15 W	1	[67]
TiO ₂	AA-CVD	TTIP	Anatase	500	Yes	6.3	2 × Sankyo (UV lamp), 15 W	1	[67]
TiO ₂ /GO 0.1 wt%	Solvothermal	TTIP	Anatase	na	No	52.3	Philips Cleo Compact 15 W lamps	1	[104]
Black TiO ₂ /GO 3 wt% (>420 nm)	Sol-gel	Ti(OBu) ₄	Anatase	na	No	50.4	1 × Xe lamp (350 W)		
TiO ₂ /MWCNT 8 wt%	Hydrothermal	[105] TiOSO ₄	Anatase	na	ns	37.1	1 × Black UV lamp	1	[106]
T	AA-CVD	TTIP/toluene	Anatase	450	Yes	6.8	2 × Sankyo (UV lamp), 15 W	1	Herein
TGMix	AA-CVD	TTIP/toluene	Anatase	450	Yes	17.6	2 × Sankyo (UV lamp), 15 W	1	Herein

ns = not stated.

na = not applicable.

5. Photocatalytic performance comparisons with related carbonaceous TiO₂ materials in the literature

5.1. NO_x remediation

Several studies have investigated the photocatalytic activity of composites containing carbonaceous material in TiO₂ for NO_x remediation, some of which are listed in Table 5.

First, we will consider TiO₂ produced using CVD methods, which was used herein to produce our samples. Lin et al. fabricated TiO₂ using atmospheric pressure chemical vapour deposition (APCVD) [103]. By heating titanium tert-ethoxide (Ti(OEt)₄), TTIP, and titanium butoxide (Ti(OBu)₄) at 160 °C and depositing at 600 °C, the resulting samples achieved NO removal efficiencies of 22.6 %, 14.97 %, and 12.68 %, respectively, using non-standard ISO conditions with an NO concentration of 3 ppm and a flow rate of 1 L/min [103]. The best-performing TiO₂ coating achieved a NO and NO_x removal efficiency of 22.6 % and 6.62 %, respectively, with a NO₂ selectivity of 70.2 %. In comparison, the TiO₂ sample (sample T) in this study showed a higher NO₂ selectivity of 80.8 %, which was significantly reduced in the best-performing sample (TGmix), exhibiting a NO₂ selectivity of 44 %. Wong et al. coated TiO₂ on float glass using AA-CVD from solutions of Ti(OBu)₄ in toluene and ethanol at a deposition temperature of 500 °C. NO removal efficiencies of 10.3 % and 9.35 % were achieved at ISO conditions, with corresponding NO₂ selectivity of 26 ± 12 % and 27 ± 14 %, respectively [67]. They reported a NO removal efficiency of 6.8 % and 6.65 %, when IPA and methanol were used as solvents, respectively, at a deposition temperature of 500 °C, and were nearly analogous in performance to our TiO₂ sample, T, which achieved 6.83 %.

Now we will compare the NO_x remediation activity of composites of TiO₂ with carbonaceous materials, although none were examined under ISO conditions. Trapolis et al. investigated the NO_x removal efficiency of TiO₂/G and TiO₂/GO composites, identifying the TiO₂/GO sample with 0.1 wt% GO as the most effective. This sample, which was pressed in a holder with an area of 19.6 cm², achieved a NO removal efficiency of 52.3 % [104]. Zhu et al. prepared a black TiO₂/GO composite containing 3 wt% GO through a sol-gel process followed by solvothermal treatment [105]. The photocatalytic NO removal performance was tested under illumination from a 350 W Xenon lamp ($\lambda > 420$ nm), in the presence of 30 wt% H₂O₂, with a gas flow rate of 0.1 L/min. The findings showed that their black TiO₂ sample removed 33.9 % of NO, whereas incorporating 3 wt% GO enhanced the efficiency to 50.4 % [105]. Since the initial concentration of NO was 400 times higher than ISO conditions (400 ppm), the results of this study cannot be directly compared with our measurements. Yen et al. studied the photocatalytic activity of sol-gel synthesised TiO₂/MWCNT composites [106]. They found that the addition of 8 wt% MWCNT enhanced NO removal efficiency to 37.1 % [106]. However, the quantity of the sample used to perform the NO_x removal test was not specified.

Notably, the composites containing carbonaceous materials listed in Table 5 from other studies are in powder form rather than coated films. This complicates direct comparison, as powders typically exhibit higher porosity and surface area, which can enhance NO removal efficiency. Furthermore, when the initial NO concentration exceeds 1 ppm, NO_x removal efficiencies cannot be directly compared, as one tends to see a linear relationship between pollutant concentration and removal performance, with higher concentrations increasing the likelihood of adsorption and subsequent photo-oxidation. To the best of our knowledge, no CVD-coated TiO₂-GO composites have been reported for NO_x remediation to date, limiting direct comparisons. It can be concluded that the T sample in this study performs comparably, in terms of NO removal efficiency, to TiO₂ anatase samples prepared via AA-CVD by Yang et al. previously [67]. However, our mixed anatase TiO₂/G composite, TGmix, exhibits superior NO_x removal efficiency compared to both T and the other anatase TiO₂ samples listed in Table 5.

5.2. PEC water splitting

In Table 6, The PEC water splitting activity of TiO₂ and its composites with carbonaceous materials are also compared with the best-performing material synthesised in this study, TGT.

Considering CVD routes first, Gardecka et al. coated an anatase/rutile heterojunction containing carbon on FTO, using pulsed-pressure metal organic chemical vapour deposition (PP-MOCVD) with different thicknesses by varying the deposition duration and by adjusting the number of pulses [66]. They reported a photocurrent density of 1.2 mA cm⁻² at 1.23 V_{RHE} (under 365 nm illumination with an intensity of 44 mW cm⁻²). Under 1 Sun, the same coating achieved a SSP of 1.2 mA cm⁻², along with an IPCE of 85 % at 350 nm. This performance was achieved with a coating thickness of 0.6 µm [66]. Using an aerosol-assisted CVD method, Tahir et al. fabricated anatase TiO₂ photoelectrodes with a cauliflower-like morphology. Under 1 sun illumination (100 mW cm⁻², Xe lamp), these electrodes exhibited photocurrent densities of approximately 0.2 mA cm⁻² at 1.23 V_{RHE} [107]. Harris-Lee et al. synthesised a composite of anatase: rutile TiO₂ with a ratio of 93.3 %:6.4 % using AA-CVD at 450 °C [110]. The TiO₂ film generated photocurrent densities of 1.06 mA cm⁻² at 1.23 V_{RHE} and achieved a maximum incident photon-to-current efficiency of 95.6 % at 380 nm (70 % at 350 nm) [110].

Cho et al. reported a hierarchical branched rutile nanorods synthesised using a dip-coating method followed by an annealing at 450 °C [108]. Under near 1 sun illumination (88 mW cm⁻², Xe lamp), these photoelectrodes demonstrated light conversion efficiencies of nearly 70 % at 380 nm and generated photocurrent densities of approximately 0.83 mA cm⁻² at 0.8 V_{RHE} [108]. Nanostructured TiO₂ photoelectrodes were synthesised by Liu et al. using a two-step hydrothermal approach, resulting in highly oriented rutile nanorods adorned with anatase branches with a thickness of 2 µm [109]. These electrodes achieved light conversion efficiencies exceeding 60 % in the UV range and delivered photocurrent densities of approximately 1.0 mA cm⁻² at 0.8 V_{RHE} under 1 sun illumination (100 mW cm⁻², Xe lamp) [109].

Now considering carbonaceous composites with TiO₂, Morais et al. investigated the effect of reduced graphene oxide (rGO) incorporation in TiO₂/rGO composites for water splitting applications [111]. Their study demonstrated that incorporating 0.1 wt% rGO increases the population of photogenerated charge carriers in the composite and increases the photogenerated current density (0.20 mA cm⁻² at 1.23 V_{RHE}) and water splitting performance compared to pristine TiO₂.

When comparing photocurrent density results in Table 6, the highest performance at 1 sun light intensity conditions was seen by Liu et al., achieving ~1.0 mA cm⁻² [109], and the highest SPP was seen by Gardecka et al., achieving ~1.2 mA cm⁻² [66]. Both samples contained anatase and rutile TiO₂, and therefore, had access to a greater portion of the visible spectrum from the rutile component (E_g ~ 3.0 eV). Herein, the best performing sample was a layered anatase TiO₂/G/anatase TiO₂ sandwich structure, TGT, achieving an SPP of 0.49 mA cm⁻² that was more than double seen in pure anatase TiO₂, T.

6. Conclusions

In this study, carbonaceous materials – including graphene (G), fullerene (F), and multi-walled carbon nanotubes (MWCNTs) – were integrated within titanium dioxide (TiO₂) films as either (i) mixed composites or (ii) layered sandwich structures (TiO₂/carbonaceous material/TiO₂). All materials showed bifunctional photocatalytic activity for nitrogen oxide (NO_x = NO + NO₂) pollution remediation and solar water splitting. These composite structures were produced using a novel aerosol-assisted chemical vapour deposition (AA-CVD) route, with coatings up to 50 cm² in area produced.

The incorporation of G, F, and MWCNTs with anatase TiO₂ enhanced the photocatalytic activity for both NO_x remediation and solar water splitting. Among all samples investigated, the sample that contained an

Table 6

A summary of the PEC water splitting activity of TiO₂ and carbon-based composites of TiO₂ from the literature compared with the best-performing material produced herein.

Material	Synthesis method	Precursor	Phase	Deposition temperature (°C)	IPCE (%) / wavelength (nm)	Photocurrent density / light source (mA cm ⁻²) ^a	SPP (mA cm ⁻²)	Light source	Ref.
TiO ₂ /C	PP-MOCVD	TTIP/toluene	Anatase/ Rutile	525	85/350	4.5/365 nm (44 mW cm ⁻²)	1.2	75 W xenon lamp	[66]
TiO ₂	AA-CVD	TTIP/toluene	Anatase	400	n/a	0.2/1 Sun	ns	Halogen lamp	[107]
TiO ₂	Dip-coating / annealing	TiCl ₃	Rutile	n/a	32/350	0.85/1 Sun	ns	Xenon lamp	[108]
TiO ₂	Hydrothermal	TiCl ₄	Anatase/ Rutile	n/a	57/350	1.0/1 Sun	ns	150 W xenon lamp	[109]
TiO ₂	AA-CVD	(EtO)Ti [OCMe ₂ CH ₂] ₃ N / hexane	Anatase/ Rutile	450	70/350	0.2/1 Sun	ns	Xenon lamp	[110]
T	AA-CVD	TTIP/toluene	Anatase	450	33.7/350	0.28/350 nm (5.3 mW cm ⁻²)	0.2	75 W Xe lamp	Herein
TGT	AA-CVD	TTIP/toluene	Anatase	450	55/350	0.82/350 nm (5.3 mW cm ⁻²)	0.49	75 W Xe lamp	Herein

ns = not stated.

na = not applicable.

^a When held at 1.23 V_{RHE} and irradiated from the front (semiconductor-electrolyte interface).

intimate mixture of G (i.e. TGmix) exhibited the highest NO_x removal efficiencies under UVA light of 17.6 % for NO and 9.6 % for total NO_x. And a layered sandwich structure containing anatase TiO₂/G/anatase TiO₂ (i.e. TGT) exhibited the highest solar water splitting activity, with incident-photon-to-current efficiency (IPCE) reaching 68 % at 1.23 V_{RHE} (pH = 7) under 250 nm illumination; a factor of ~2 increase compared to TiO₂ alone. Transient photocurrent (TPC) and transient absorption spectroscopy (TAS) revealed the kinetics of electron extraction and hole oxidation of water. At 1.23 V_{RHE}, the TGT sample showed similar electron extract kinetics to T (t_{50 %} ~0.25 ms) but significantly higher long-lived hole carrier populations that drive water oxidation (Δ.O.D. ~1.4 % at 1 ms for TGT vs Δ.O.D. ~0.5 % at 1 ms for T), which were found to linearly correlate with the observed photocurrent densities (~0.85 mA cm⁻² for TGT and ~0.25 mA cm⁻² for T). It can be concluded that, in the mixed composites containing graphene (TGmix), the graphene is uniformly dispersed within the TiO₂ matrix, maximising electron transfer and NO_x adsorption, thereby delivering superior NO_x remediation. In contrast, the sandwich-layered architecture (TGT) promotes hole accumulation on the surface, favours water splitting, and maximises the rate of charge extraction, as evidenced by TPC results, yielding higher water-splitting currents.

The development of versatile photocatalytic coatings that can be grown at scale to combat various environmental challenges, including air pollution and clean fuel production, remains a significant materials challenge. Our comprehensive study, incorporating operando investigations, demonstrates a scalable CVD approach for integrating carbon-based materials into anatase TiO₂ to create coatings effective for both NO_x air pollution control and solar water splitting. The results show that a homogeneous dispersion of graphene in TiO₂ matrix (TGmix) is optimal for NO_x photo-oxidation, whereas a TiO₂-graphene-TiO₂ layered architecture (TGT) better supports water splitting, providing design principles to guide future large-scale photocatalyst development.

CRedit authorship contribution statement

Paransa Alimard: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Longren Li:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Stanley Cazaly:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Flurin Eisner:** Writing – review & editing, Supervision, Resources, Methodology, Investigation, Formal analysis. **Brian Tam:** Writing – review & editing, Supervision, Methodology, Investigation,

Formal analysis. **Andreas Kafizas:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Project administration, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Acknowledgements

The authors gratefully acknowledge Lee Tooley, Steve Atkins and Stefanos Karapanagiotidis for their invaluable contributions in constructing and maintaining the chemical vapour deposition apparatus used in this study. P. A. thanks the Science and Solutions for a Changing Planet DTP (NE/S007415/1), hosted at the Grantham Institute for Climate Change and the Environment, Imperial College London, United Kingdom, for funding this research. A.K. thanks the EPSRC for a Programme Grant (EP/W017075/1) and the Royal Society for an Equipment Grant (RSG/R1/180434). B.T. thanks the CPLAS: Catalysis Meets Plasmonics programme grant. L. L. acknowledges funding by the Imperial College London President's PhD Scholarships. F.E. thanks the support from the Royal Society through grant RGS\R2\242510.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.carbon.2025.120939>.

References

- [1] H. Orru, K. Ebi, B. Forsberg, The interplay of climate change and air pollution on health, *Curr. Environ. Health Rep.* 4 (2017) 504–513.
- [2] L. Berrang-Ford, J.D. Ford, J. Paterson, Are we adapting to climate change? *Glob. Environ. Change* 21 (1) (2011) 25–33.
- [3] E. Bevacqua, C.-F. Schleussner, J. Zscheischler, A year above 1.5° C signals that Earth is most probably within the 20-year period that will reach the paris agreement limit, *Nat. Clim. Change* (2025) 1–4.
- [4] C. Breyer, et al., On the history and future of 100% renewable energy systems research, *IEEE Access* 10 (2022) 78176–78218.

- [5] M.K. Singla, P. Nijhawan, A.S. Oberoi, Hydrogen fuel and fuel cell technology for cleaner future: a review, *Environ. Sci. Pollut. Control Ser.* 28 (13) (2021) 15607–15626.
- [6] F. Dawood, M. Anda, G. Shafiullah, Hydrogen production for energy: an overview, *Int. J. Hydrogen Energy* 45 (7) (2020) 3847–3869.
- [7] A. Fujishima, X. Zhang, D.A. Tryk, TiO₂ photocatalysis and related surface phenomena, *Surf. Sci. Rep.* 63 (12) (2008) 515–582.
- [8] S. Chen, T. Takata, K. Domen, Particulate photocatalysts for overall water splitting, *Nat. Rev. Mater.* 2 (10) (2017) 1–17.
- [9] A. Miyoshi, S. Nishioka, K. Maeda, Water splitting on rutile TiO₂-based photocatalysts, *Chem.-Eur. J.* 24 (69) (2018) 18204–18219.
- [10] A. Kafizas, et al., Water oxidation kinetics of accumulated holes on the surface of a TiO₂ photoanode: a rate law analysis, *ACS Catal.* 7 (7) (2017) 4896–4903.
- [11] G. Wang, et al., Hydrogen-treated TiO₂ nanowire arrays for photoelectrochemical water splitting, *Nano Lett.* 11 (7) (2011) 3026–3033.
- [12] H. Ma, Y. Li, C. Wang, Y. Li, X. Zhang, TiO₂-based photocatalysts for removal of low-concentration NO_x contamination, *Catalysts* 15 (2) (2025) 103.
- [13] T. Luttrell, S. Halpegamage, J. Tao, A. Kramer, E. Sutter, M. Batzill, Why is anatase a better photocatalyst than rutile?-Model studies on epitaxial TiO₂ films, *Sci. Rep.* 4 (1) (2014) 4043.
- [14] Y. Mohammed, H.Y. Hafeez, J. Mohammed, A.B. Suleiman, C.E. Ndikilar, M. G. Idris, Hydrogen production via photocatalytic water splitting using spinel ferrite-based photocatalysts: recent and future perspectives, *Next Energy* 4 (2024) 100145.
- [15] J. Alberro, D. Mateo, H. García, Graphene-based materials as efficient photocatalysts for water splitting, *Molecules* 24 (5) (2019) 906.
- [16] A. Zaleska, Doped-TiO₂: a review, *Recent Pat. Eng.* 2 (3) (2008) 157–164.
- [17] J. Nowotny, et al., Defect chemistry and defect engineering of TiO₂ 2-based semiconductors for solar energy conversion, *Chem. Soc. Rev.* 44 (23) (2015) 8424–8442.
- [18] R. Shwetharani, M. Sakar, C. Fernando, V. Binas, R.G. Balakrishna, Recent advances and strategies to tailor the energy levels, active sites and electron mobility in titania and its doped/composite analogues for hydrogen evolution in sunlight, *Catal. Sci. Technol.* 9 (1) (2019) 12–46.
- [19] X. An, C.Y. Jimmy, Graphene-based photocatalytic composites, *RSC Adv.* 1 (8) (2011) 1426–1434.
- [20] H. Yi, et al., Selective prepared carbon nanomaterials for advanced photocatalytic application in environmental pollutant treatment and hydrogen production, *Appl. Catal. B Environ.* 239 (2018) 408–424.
- [21] R. Li, T. Li, Q. Zhou, Impact of titanium dioxide (TiO₂) modification on its application to pollution treatment—a review, *Catalysts* 10 (7) (2020) 804.
- [22] A.K. Geim, K.S. Novoselov, The rise of graphene, *Nat. Mater.* 6 (3) (2007) 183–191.
- [23] K.S. Novoselov, et al., Two-dimensional gas of massless dirac fermions in graphene, *nature* 438 (7065) (2005) 197–200.
- [24] K.S. Novoselov, et al., Electric field effect in atomically thin carbon films, *science* 306 (5696) (2004) 666–669.
- [25] N.-G. Park, J. Van de Lagemaat, A.J. Frank, Comparison of dye-sensitized rutile and anatase-based TiO₂ solar cells, *J. Phys. Chem. B* 104 (38) (2000) 8989–8994.
- [26] Q. Xiang, J. Yu, M. Jaroniec, Graphene-based semiconductor photocatalysts, *Chem. Soc. Rev.* 41 (2) (2012) 782–796.
- [27] G. Xie, K. Zhang, B. Guo, Q. Liu, L. Fang, J.R. Gong, Graphene-based materials for hydrogen generation from light-driven water splitting, *Adv. Mater.* 25 (28) (2013) 3820–3839.
- [28] P.S. Agrawal, P.N. Belkhole, D.S. Brijpuriya, S.P. Gouda, S.L. Rokhum, Stimulation in fullerene for adsorbing pollutant gases: a review, *Chem. Phys. Impact* 6 (2023) 100156.
- [29] V.I. Sysoev, A.V. Okotrub, A.V. Gusel'nikov, D.A. Smirnov, L.G. Bulusheva, In situ XPS observation of selective NO_x adsorption on the oxygenated graphene films, *physica status solidi (b)* 255 (1) (2018) 1700267.
- [30] S. Tang, Z. Cao, Adsorption of nitrogen oxides on graphene and graphene oxides: insights from density functional calculations, *J. Chem. Phys.* 134 (4) (2011).
- [31] F. Schedin, et al., Detection of individual gas molecules adsorbed on graphene, *Nat. Mater.* 6 (9) (2007) 652–655.
- [32] D.-M. Tang, et al., Chirality engineering for carbon nanotube electronics, *Nat. Rev. Electr. Eng.* 1 (3) (2024) 149–162.
- [33] A. Goldoni, R. Larciprete, L. Petaccia, S. Lizzit, Single-wall carbon nanotube interaction with gases: sample contaminants and environmental monitoring, *J. Am. Chem. Soc.* 125 (37) (2003) 11329–11333.
- [34] V. Krishna, N. Noguchi, B. Koopman, B. Moudgil, Enhancement of titanium dioxide photocatalysis by water-soluble fullerenes, *J. Colloid Interface Sci.* 304 (1) (2006) 166–171.
- [35] P.V. Kamat, M. Haria, S. Hotchandani, C60 cluster as an electron shuttle in a Ru (II)-polypyridyl sensitizer-based photochemical solar cell, *J. Phys. Chem. B* 108 (17) (2004) 5166–5170.
- [36] I.M. Ismail, S.L. Rodgers, Comparisons between fullerene and forms of well-known carbons, *Carbon* 30 (2) (1992) 229–239.
- [37] T. Ando, The electronic properties of graphene and carbon nanotubes, *NPG Asia Mater.* 1 (1) (2009) 17–21.
- [38] B. Peng, Monolayer fullerene networks as photocatalysts for overall water splitting, *J. Am. Chem. Soc.* 144 (43) (2022) 19921–19931.
- [39] D. Ma, J. Zhong, R. Peng, J. Li, R. Duan, Effective photoinduced charge separation and photocatalytic activity of hierarchical microsphere-like C60/BiOCl, *Appl. Surf. Sci.* 465 (2019) 249–258.
- [40] X.-F. Zhang, Q. Xi, A graphene sheet as an efficient electron acceptor and conductor for photoinduced charge separation, *Carbon* 49 (12) (2011) 3842–3850.
- [41] M. Berd, K. Moussi, Y. Aouabdia, L. Benchallal, G. Chahi, B. Kahouadji, From metallic to semiconductor conversion of single-walled carbon nanotubes by chlorination, *Chem. Phys. Lett.* 781 (2021) 138988.
- [42] G.D. Panagiotou, et al., Development of [60] fullerene supported on silica catalysts for the photo-oxidation of alkenes, *Appl. Catal. Gen.* 372 (1) (2010) 16–25.
- [43] A.I. Inozemtseva, et al., Graphene electrochemistry: 'adiabaticity' of electron transfer, *Electrochim. Acta* 427 (2022) 140901.
- [44] X. Li, J. Yu, S. Wageh, A.A. Al-Ghamdi, J. Xie, Graphene in photocatalysis: a review, *Small* 12 (48) (2016) 6640–6696.
- [45] N. Zhang, Y. Zhang, M.-Q. Yang, Z.-R. Tang, Y.-J. Xu, A critical and benchmark comparison on graphene-, carbon nanotube-, and fullerene-semiconductor nanocomposites as visible light photocatalysts for selective oxidation, *J. Catal.* 299 (2013) 210–221.
- [46] Y. Zhang, Z.-R. Tang, X. Fu, Y.-J. Xu, Engineering the unique 2D mat of graphene to achieve graphene-TiO₂ nanocomposite for photocatalytic selective transformation: what advantage does graphene have over its forebear carbon nanotube? *ACS Nano* 5 (9) (2011) 7426–7435.
- [47] Y.T. Liang, B.K. Vijayan, O. Lyandres, K.A. Gray, M.C. Hersam, Effect of dimensionality on the photocatalytic behavior of carbon–titania nanosheet composites: charge transfer at nanomaterial interfaces, *J. Phys. Chem. Lett.* 3 (13) (2012) 1760–1765.
- [48] B.J. Blackburn, C. Drosos, D.B. Brett, M.A. Parkes, C.J. Carmalt, I.P. Parkin, In situ mass spectrometry analysis of chemical vapour deposition of TiO₂ thin films to study gas phase mechanisms, *RSC Adv.* 6 (113) (2016) 111797–111805.
- [49] A. Perraudau, C. Dublanche-Tixier, P. Tristant, C. Chazelas, Dynamic mode optimization for the deposition of homogeneous TiO₂ thin film by atmospheric pressure PECVD using a microwave plasma torch, *Appl. Surf. Sci.* 493 (2019) 703–709.
- [50] A. Lepcha, et al., Electrospun black titania nanofibers: influence of hydrogen plasma-induced disorder on the electronic structure and photoelectrochemical performance, *J. Phys. Chem. C* 119 (33) (2015) 18835–18842.
- [51] P. Marchand, I.A. Hassan, I.P. Parkin, C.J. Carmalt, Aerosol-assisted delivery of precursors for chemical vapour deposition: expanding the scope of CVD for materials fabrication, *Dalton Trans.* 42 (26) (2013) 9406–9422.
- [52] B. Tam, S.D. Pike, J. Nelson, A. Kafizas, The scalable growth of high-performance nanostructured heterojunction photoanodes for applications in tandem photoelectrochemical-photovoltaic solar water splitting devices, *Chem. Sci.* 16 (2025) 7794–7810.
- [53] X. Hou, K.-L. Choy, V. Serin, N. Fleischer, Processing and characterization of nanocomposite coatings using Aerosol-assisted chemical vapor deposition (AACVD) method, *ECS Trans.* 25 (8) (2009) 1135.
- [54] H.L. Poh, F. Šaněk, A. Ambrosi, G. Zhao, Z. Sofer, M. Pumera, Graphenes prepared by staudenmaier, hofmann and hummers methods with consequent thermal exfoliation exhibit very different electrochemical properties, *Nanoscale* 4 (11) (2012) 3515–3522.
- [55] K. Gerani, H.R. Mortaheb, B. Mokhtarani, Enhancement in performance of sulfonated PES cation-exchange membrane by introducing pristine and sulfonated graphene oxide nanosheets synthesized through hummers and staudenmaier methods, *Polym.-Plast. Technol. Eng.* 56 (5) (2017) 543–555.
- [56] Z. Ai, W. Ho, S. Lee, Efficient visible light photocatalytic removal of NO with BiOBr-graphene nanocomposites, *J. Phys. Chem. C* 115 (51) (2011) 25330–25337.
- [57] M. Hakimi, P. Alimard, Fabrication and properties of Nd-La doped Sr₂CuMgFe₂O₄ nanoparticles anchored with sheets of reduced graphene oxide, *Ceram. Int.* 40 (9) (2014) 14501–14507.
- [58] L. Staudenmaier, Verfahren zur darstellung der graphitsäure, *Ber. Dtsch. Chem. Ges.* 31 (2) (1898) 1481–1487.
- [59] M. Taylor, R.C. Pullar, I.P. Parkin, C. Piccirillo, Nanostructured titanium dioxide coatings prepared by aerosol assisted chemical vapour deposition (AACVD), *J. Photochem. Photobiol. Chem.* 400 (2020) 112727.
- [60] P. Alimard et al., "Exploring the influence of carbonaceous material on the photocatalytic performance of composites containing Bi-BiOBr and P25 TiO₂ for NO_x remediation," *ChemPhysChem*, p. e202500237.
- [61] C. Piccirillo, et al., Aerosol assisted chemical vapour deposition of hydroxyapatite-embedded titanium dioxide composite thin films, *J. Photochem. Photobiol. Chem.* 332 (2017) 45–53.
- [62] L. Romero, C. Piccirillo, P.M. Castro, C. Bowman, M.E. Warwick, R. Binions, Titanium dioxide thin films deposited by electric field-assisted CVD: effect on antimicrobial and photocatalytic properties, *Chem. Vap. Depos.* 21 (1–2-3) (2015) 63–70.
- [63] A.L. Balch, M.M. Olmstead, Reactions of transition metal complexes with fullerenes (C₆₀, C₇₀, etc.) and related materials, *Chem. Rev.* 98 (6) (1998) 2123–2166.
- [64] G. Peng, J.E. Ellis, G. Xu, X. Xu, A. Star, In situ grown TiO₂ nanospindles facilitate the formation of holey reduced graphene oxide by photodegradation, *ACS Appl. Mater. Interfaces* 8 (11) (2016) 7403–7410.
- [65] K. Hemalatha, A. Prakash, M. Jayakumar, TiO₂ coated carbon nanotubes for electrochemical energy storage, *J. Mater. Chem. A* 2 (6) (2014) 1757–1766.
- [66] A.J. Gardecka, et al., High efficiency water splitting photoanodes composed of nano-structured anatase-rutile TiO₂ heterojunctions by pulsed-pressure MOCVD, *Appl. Catal. B Environ.* 224 (2018) 904–911.

- [67] Y. Wong, Y. Li, Z. Lin, A. Kafizas, Studying the effects of processing parameters in the aerosol-assisted chemical vapour deposition of TiO₂ coatings on glass for applications in photocatalytic NO_x remediation, *Appl. Catal. Gen.* 648 (2022) 118924.
- [68] X. Xin, T. Xu, J. Yin, L. Wang, C. Wang, Management on the location and concentration of Ti³⁺ in anatase TiO₂ for defects-induced visible-light photocatalysis, *Appl. Catal. B Environ.* 176 (2015) 354–362.
- [69] G. Yasin, et al., Exploring the nickel–graphene nanocomposite coatings for superior corrosion resistance: manipulating the effect of deposition current density on its morphology, mechanical properties, and erosion-corrosion performance, *Adv. Eng. Mater.* 20 (7) (2018) 1701166.
- [70] R. Das, S. Bee Abd Hamid, M. Eaqub Ali, S. Ramakrishna, W. Yongzhi, Carbon nanotubes characterization by X-ray powder Diffraction—a review, *Curr. Nanosci.* 11 (1) (2015) 23–35.
- [71] M. Sathish, K.I. Miyazawa, Synthesis and characterization of fullerene nanowhiskers by liquid-liquid interfacial precipitation: influence of C60 solubility, *Molecules* 17 (4) (2012) 3858–3865.
- [72] W. Li, W. Wu, Z. Li, Controlling interlayer spacing of graphene oxide membranes by external pressure regulation, *ACS Nano* 12 (9) (2018) 9309–9317.
- [73] P. Alimard, C. Gong, I. Itskou, A. Kafizas, Achieving high photocatalytic NO_x removal activity using a Bi/BiOBr/TiO₂ composite photocatalyst, *Chemosphere* 368 (2024) 143728.
- [74] H.C. Choi, Y.M. Jung, S.B. Kim, Size effects in the Raman spectra of TiO₂ nanoparticles, *Vib. Spectrosc.* 37 (1) (2005) 33–38.
- [75] E. Villabona-Leal, et al., Semiconducting polypyrrole@ TiO₂ pure anatase nanoparticles for photodegradation of reactive red 120 azo dye, *J. Mater. Sci. Mater. Electron.* 31 (2020) 12178–12190.
- [76] Z. Li, L. Deng, I.A. Kinloch, R.J. Young, Raman spectroscopy of carbon materials and their composites: Graphene, nanotubes and fibres, *Prog. Mater. Sci.* (2023) 101089.
- [77] L. Cançado, et al., General equation for the determination of the crystallite size La of nanographite by Raman spectroscopy, *Appl. Phys. Lett.* 88 (16) (2006).
- [78] A. Popova, Crystallographic analysis of graphite by X-Ray diffraction, *Coke Chem.* 60 (2017) 361–365.
- [79] M.C. Biesinger, Accessing the robustness of adventitious carbon for charge referencing (correction) purposes in XPS analysis: insights from a multi-user facility data review, *Appl. Surf. Sci.* 597 (2022) 153681.
- [80] S. Naseem, et al., Epitaxial growth of cobalt doped TiO₂ thin films on LaAlO₃ (100) substrate by molecular beam epitaxy and their opto-magnetic based applications, *Appl. Surf. Sci.* 493 (2019) 691–702.
- [81] M. Xing, F. Shen, B. Qiu, J. Zhang, Highly-dispersed boron-doped graphene nanosheets loaded with TiO₂ nanoparticles for enhancing CO₂ photoreduction, *Sci. Rep.* 4 (1) (2014) 6341.
- [82] Q. Wu, R. van de Krol, Selective photoreduction of nitric oxide to nitrogen by nanostructured TiO₂ photocatalysts: role of oxygen vacancies and iron dopant, *J. Am. Chem. Soc.* 134 (22) (2012) 9369–9375.
- [83] Y. Komazaki, H. Shimizu, S. Tanaka, A new measurement method for nitrogen oxides in the air using an annular diffusion scrubber coated with titanium dioxide, *Atmos. Environ.* 33 (27) (1999) 4363–4371.
- [84] H. Wang, Z. Wu, W. Zhao, B. Guan, Photocatalytic oxidation of nitrogen oxides using TiO₂ loading on woven glass fabric, *Chemosphere* 66 (1) (2007) 185–190.
- [85] A. Mills, S. Elouali, The nitric oxide ISO photocatalytic reactor system: measurement of NO_x removal activity and capacity, *J. Photochem. Photobiol. Chem.* 305 (2015) 29–36.
- [86] A. Mir, M. Shah, Cyclic voltammetry response of TiO₂ nanostructures prepared via fast and facile microwave irradiation, *Bull. Mater. Sci.* 45 (3) (2022) 119.
- [87] C. Ban, et al., Plasmonic Au–TiO₂ interactions for augmented photocatalytic hydrogen evolution, *Ceram. Int.* 50 (9) (2024) 15444–15451.
- [88] S. Collavini, J.L. Delgado, Fullerenes: the stars of photovoltaics, *Sustain. Energy Fuels* 2 (11) (2018) 2480–2493.
- [89] D.K. Pallotti, L. Passoni, P. Maddalena, F. Di Fonzo, S. Lettieri, Photoluminescence mechanisms in anatase and rutile TiO₂, *J. Phys. Chem. C* 121 (16) (2017) 9011–9021.
- [90] N.D. Abazović, M.I. Čomor, M.D. Dramićanin, D.J. Jovanović, S.P. Ahrenkiel, J. M. Nedeljković, Photoluminescence of anatase and rutile TiO₂ particles, *J. Phys. Chem. B* 110 (50) (2006) 25366–25370.
- [91] C. Mercado, Z. Seeley, A. Bandyopadhyay, S. Bose, J.L. McHale, Photoluminescence of dense nanocrystalline titanium dioxide thin films: effect of doping and thickness and relation to gas sensing, *ACS Appl. Mater. Interfaces* 3 (7) (2011) 2281–2288.
- [92] N. Liaros, S. Couris, E. Koudoumas, P. Loukakos, Ultrafast processes in graphene oxide during femtosecond laser excitation, *J. Phys. Chem. C* 120 (7) (2016) 4104–4111.
- [93] D.J. Styers-Barnett, et al., Exciton dynamics and biexciton formation in single-walled carbon nanotubes studied with femtosecond transient absorption spectroscopy, *J. Phys. Chem. C* 112 (12) (2008) 4507–4516.
- [94] H.S. Cho, S.I. Yang, S.K. Kim, E.-j. Shin, D. Kim, Comparative study of exciton relaxation dynamics in C60 and C70 solid, *J. Phys. Chem. B* 103 (31) (1999) 6504–6508.
- [95] A. Kafizas, et al., Where do photogenerated holes go in anatase: rutile TiO₂? A transient absorption spectroscopy study of charge transfer and lifetime, *J. Phys. Chem.* 120 (5) (2016) 715–723.
- [96] J. Sun, et al., Insight into the synergistic effect of metal surface plasmon resonance and clay loading to boost the antibiotics degradation of bentonite/biOBr/bismuth, *Mater. Sci. Semicond. Process.* 166 (2023) 107739.
- [97] R. Deas, S. Pearce, K. Goss, Q. Wang, W.-T. Chen, G.I. Waterhouse, Hierarchical Au/TiO₂ nanoflower photocatalysts with outstanding performance for alcohol photoreforming under UV irradiation, *Appl. Catal. Gen.* 602 (2020) 117706.
- [98] Y.-J. Yu, Y. Zhao, S. Ryu, L.E. Brus, K.S. Kim, P. Kim, Tuning the graphene work function by electric field effect, *Nano Lett.* 9 (10) (2009) 3430–3434.
- [99] P. Liu, et al., Thermionic emission and work function of multiwalled carbon nanotube yarns, *Phys. Rev. B Condens. Matter* 73 (23) (2006) 235412.
- [100] H. Liang, et al., Modulation of the work function of fullerenes C60 and C70 by alkali-metal adsorption: a theoretical study, *Phys. Lett.* 377 (38) (2013) 2676–2680.
- [101] E. Gao, W. Wang, M. Shang, J. Xu, Synthesis and enhanced photocatalytic performance of graphene-Bi₂WO₆ composite, *Phys. Chem. Chem. Phys.* 13 (7) (2011) 2887–2893.
- [102] X. Wang, et al., Comparative study of three carbon additives: carbon nanotubes, graphene, and fullerene-c60, for synthesizing enhanced polymer nanocomposites, *Nanomaterials* 10 (5) (2020) 838.
- [103] Z.-P. Lin, Y. Li, S.A. Haque, A.M. Ganose, A. Kafizas, Insights from experiment and machine learning for enhanced TiO₂ coated glazing for photocatalytic NO_x remediation, *J. Mater. Chem. A* 12 (22) (2024) 13281–13298.
- [104] A. Trapalis, et al., TiO₂/graphene composite photocatalysts for NO_x removal: a comparison of surfactant-stabilized graphene and reduced graphene oxide, *Appl. Catal. B Environ.* 180 (2016) 637–647.
- [105] C. Zhu, et al., Effect of synergy between oxygen vacancies and graphene oxide on performance of TiO₂ for photocatalytic NO removal under visible light, *Sep. Purif. Technol.* 276 (2021) 119362.
- [106] C.-Y. Yen, et al., The effects of synthesis procedures on the morphology and photocatalytic activity of multi-walled carbon nanotubes/TiO₂ nanocomposites, *Nanotechnology* 19 (4) (2008) 045604.
- [107] A.A. Tahir, T.N. Peiris, K.U. Wijayantha, Enhancement of photoelectrochemical performance of AACVD-produced TiO₂ electrodes by microwave irradiation while preserving the nanostructure, *Chem. Vap. Depos.* 18 (4-6) (2012) 107–111.
- [108] I.S. Cho, et al., Branched TiO₂ nanorods for photoelectrochemical hydrogen production, *Nano Lett.* 11 (11) (2011) 4978–4984.
- [109] J. Liu, et al., Surface-phase junctions of branched TiO₂ nanorod arrays for efficient photoelectrochemical water splitting, *Appl. Catal. B Environ.* 158 (2014) 296–300.
- [110] T.R. Harris-Lee, E. Della Gaspera, F. Marken, J. Zhang, C.L. Bentley, A.L. Johnson, Aerosol-assisted chemical vapour deposition of highly efficient mixed anatase-rutile TiO₂ for photoelectrochemical water splitting, *Mater. Adv.* 4 (17) (2023) 3708–3713.
- [111] A. Morais, C. Longo, J.R. Araujo, M. Barroso, J.R. Durrant, A.F. Nogueira, Nanocrystalline anatase TiO₂/reduced graphene oxide composite films as photoanodes for photoelectrochemical water splitting studies: the role of reduced graphene oxide, *Phys. Chem. Chem. Phys.* 18 (4) (2016) 2608–2616.