Thermochromic VO$_2$—SiO$_2$ Nanocomposite Smart Window Coatings with Narrow Phase Transition Hysteresis and Transition Gradient Width

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Abstract

Thermochromic vanadium dioxide (VO$_2$) window coatings hold the promise of reducing the energy consumption of the built environment by passively regulating solar heat gain in response to changing conditions. Composite materials with embedded VO$_2$ particles have shown greatly improved optical performances compared with thin films, however they typically exhibit broadened phase transition hysteresis and gradient widths, which negatively impacts the overall performance. Here, we present a scalable one-step solution based synthesis for a thermochromic smart window coating based on a vanadium dioxide sol-gel containing silica (SiO$_2$) nanoparticles. We compare the performance of our nanoparticle composite with thin film VO$_2$ along with composites formed by mixing VO$_2$ and SiO$_2$ sol-gels and find that both composites achieve an acceptable visible transmittance ($\sim$ 50 %) along with a comparable and competitive solar modulation (12.5 % and 16.8 % respectively), roughly double that of the plain VO$_2$ film (6.7 %). However, our SiO$_2$ nanoparticle containing composite also benefits from a narrow transition hysteresis and gradient width (9.4 °C and 2.9 °C respectively). We predict that

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this method may subsequently be combined with metal ion doping to control both the optical and phase transition characteristics to achieve composite films with high overall energy saving performances.

**Keywords:** vanadium dioxide, thermochromic, energy-efficient glazing, smart windows, nanocomposites, optical coatings, silica nanoparticles, thin films, dynamic solar control coatings

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1. Introduction

Static solar control coatings have become an essential part of modern energy-efficient windows due to their ability to control the heat gain in buildings resulting from solar radiation[1]. Solar heat gain can be beneficial in winter or in colder climates when it acts to passively heat the building. However, in summer or warmer climates a high solar heat gain often results in an undesired overheating of the building[2]. The prevailing climatic conditions can be subject to rapid and fluctuating changes due to weather conditions and seasonal variations. There are times when it is more beneficial to let solar radiation enter the building and at other times it is more beneficial to block it out[3]. A window with a static solar control coating must compromise between these two opposing goals.

Dynamic solar control technologies such as thermochromic coatings are able to overcome the limitations of static solar control coatings by modulating their transmission of solar energy as a function of temperature. Vanadium dioxide (VO$_2$) is the prime candidate material for thermochromic coatings due to its first order phase transition from a monoclinic semiconducting state to a tetragonal metallic state at a transition temperature of 68 °C[4, 5]. The transition results in a large change in optical properties. The transmittance in the infrared drops significantly upon switching, however the coating remains relatively transparent in the visible region in both states.

Work on thermochromic window coatings has mainly been focused on optimising the luminous transmittance $T_{\text{lum}}$ and the solar modulation $\Delta T_{\text{sol}}$ as defined by,

$$T_{\text{lum},\text{sol}} = \frac{\int \phi_{\text{lum,sol}}(\lambda) T(\lambda) \, d\lambda}{\int \phi_{\text{lum,sol}}(\lambda) \, d\lambda},$$  

$$\Delta T_{\text{sol}} = T_{\text{sol,cold}} - T_{\text{sol,hot}}$$

where $T(\lambda)$ denotes the transmittance at wavelength $\lambda$, $\phi_{\text{lum}}(\lambda)$ is the photometric spectral sensitivity of human vision[6], and $\phi_{\text{sol}}(\lambda)$ is the AM 1.5
solar irradiance spectrum. To increase the solar modulation, film thickness must be increased, however this results in a reduction in luminous transmittance due to the non-zero visible absorption and high reflectance of vanadium dioxide. Improvements to luminous transmittance can be achieved by suppressing reflection of visible light with anti-reflective multilayer systems[7, 8, 9, 10, 11, 12, 13] or graded index nanostructures[14, 15] however this adds to the complexity of design. Alternative methods to improve the optical performance in a single coating step are composite films comprised of VO₂ nanoparticles embedded in a dielectric matrix[16, 17, 18, 19, 20]. The low density and sub-wavelength dimensions of vanadium dioxide domains means that visible reflectance is minimal. Additionally, most composite coatings with high solar modulations exhibit a broad hysteresis and transition gradient. The reason for this is that the probability of phase transition in vanadium dioxide depends on the density of suitable heterogeneous nucleating sites such as surface defects, dislocations and grain boundaries[21, 22, 23, 24]. Consequently, the onset temperature of the phase transition increases (decreases) during heating (cooling) as the sizes of the nanocrystals are reduced. Several theoretical works[25, 26, 27] have highlighted the importance of reducing the hysteresis width of thermochromic films to improve their overall energy saving performance, as wide hysteresis loops mean that coatings are less responsive to changing climate conditions. Several previous works have shown that the hysteresis width can be reduced significantly by doping vanadium dioxide with metal ions[5, 18], however this generally results in an increase in transition gradient[5] which has also been shown to be detrimental to the overall energy saving performance[25, 28, 27]. Table 1 shows a summary of literature for composite thermochromic coatings, from which we can see that improvements in solar modulation and visible transmission for composite coatings generally result in increased hysteresis width. It must also be noted how infrequently the transition gradient is discussed in the literature, despite having been shown to be critical to the overall energy saving performance[25, 28, 27]. In the only study found with a high optical performance ($T_{\text{lum}} = 48.5\%$ & $T_{\text{sol}} = 15.7\%$) that reports both the transition hysteresis and gradient width, both hysteresis and gradient widths were found to be wide (17.4 & 11.3 °C respectively)[29].

In light of these factors, this work aims to demonstrate the influence of the
Table 1: Optical Properties of thermochromic films based on VO$_2$–SiO$_2$. The highest solar modulation values are accompanied by large hysteresis widths.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$T_{\text{lum,c}}$ (%)</th>
<th>$T_{\text{lum,h}}$ (%)</th>
<th>$\Delta T_{\text{lum}}$ (%)</th>
<th>$\Delta T_{\text{sol}}$ (%)</th>
<th>$\Delta T_t$ (°C)</th>
<th>$w_{1/2}$ (°C)</th>
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<tr>
<td>[17]</td>
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<td>57.4</td>
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<td>14.6</td>
<td>54.4</td>
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</tr>
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<td>[18]</td>
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<tr>
<td>[18]</td>
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<td>17.3</td>
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</tr>
<tr>
<td>[19]</td>
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<td>3.1</td>
<td>14.7</td>
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<td>N/A</td>
</tr>
<tr>
<td>[19]</td>
<td>55.3</td>
<td>54.2</td>
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<td>7.5</td>
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</tr>
<tr>
<td>[20]</td>
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<td>14.3</td>
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</tr>
<tr>
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<td>46.9</td>
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</tr>
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<tr>
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<td>N/A</td>
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<td>N/A</td>
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</tr>
<tr>
<td>[29]</td>
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<td>43.2</td>
<td>5.3</td>
<td>15.7</td>
<td>17.4</td>
<td>11.3</td>
</tr>
</tbody>
</table>

$^a(T_{\text{lum,c}} + T_{\text{lum,h}})/2$

$T_{\text{lum,x}}$: Luminous transmittance in the low temperature ($x = c$) and high temperature ($x = h$) state; $\Delta T_{\text{sol}}$: transmittance modulation of solar radiation; $\Delta T_t$: hysteresis width; $w_{1/2}$: gradient width.

Nanostructure of composite films on both the hysteresis and gradient width of a thermochromic coating. Nanocomposite films of silica and vanadium dioxide with different film structures were prepared by sol-gel methods. We compare three different sample types: plain VO$_2$ (sample V), VO$_2$ sol with SiO$_2$ nanoparticles dispersed within (samples A1-A4), and VO$_2$ sol mixed with SiO$_2$ sol (samples B1-B4). We demonstrate that by dispersing SiO$_2$ nanoparticles within the VO$_2$ sol, the optical performance can be improved significantly whilst the hysteresis and gradient width remain minimal. Whilst the focus of discussion in this work is on smart window applications, the control of transition hysteresis and gradient in VO$_2$ is important for many applications such as thermal emittance control, microbolometers, infrared modulators, and reconfigurable optical and electronic devices.

2. Methods & Materials

2.1. Synthesis of VO$_2$ sol

In a typical reaction, 3.78 g (30 mmol) of oxalic acid dihydrate (98%, Alfa Aesar) was added to a suspension of 1.82 g (10 mmol) V$_2$O$_5$ (general
purpose grade, Fisher Chemical) in 10 mL anhydrous ethanol (99.8%, denat. 1% MEK + 0.001% denat. benzoate, Acros Organics). The reaction mixture was heated to 80°C for 12 h. The blue solution was filtered and used without further purification.

2.2. Synthesis of SiO$_2$ sol

A mixture of hydrochloric acid (37%, extra pure, Fisher Chemical), H$_2$O and half of the prescribed amount of anhydrous ethanol was slowly added at room temperature to a solution of tetraethyl orthosilicate ([Si(OEt)$_4$], TEOS, 98%, Acros Organics) in the remaining ethanol. The clear solution was stirred for 24 h in a sealed glass vial and was used without further purification. The molar ratios of the reactants were as follows: TEOS:H$_2$O:HCl:ethanol = 1:4:0.01:20.

2.3. Synthesis of SiO$_2$ Nanoparticles Dispersion

SiO$_2$ nanoparticle dispersions were prepared according to a previously described, slightly modified procedure[35]. In short, a mixture of 50 mL of absolute ethanol, 1 ml of deionized water and 1 mL of ammonia (25%, Fisher Chemical) was heated to 40 °C. Afterward, 3 mL of TEOS were added dropwise to the reaction mixture under vigorous stirring. After 2 h additional 2 mL of TEOS were added. This step was repeated in 2 h intervals (4x) amounting to 11 mL of TEOS in total. The nanoparticles dispersion was used as obtained without any further purification steps.

2.4. Fabrication of Thermochromic Films

To an appropriate amount of VO$_2$ sol the prescribed amount of SiO$_2$ sol or SiO$_2$ nanoparticles dispersion was added. The mixture was stirred for at least 1 h before usage. Glass substrates consisted of a 3.4 mm thick silica-coated barrier glass (50 nm SiO$_2$ layer) obtained from Pilkington. Prior to deposition all substrates (2x2 cm) were cleaned with detergent solution, deionized water and 2-propanol, respectively, and were blown dry in a nitrogen stream. Afterwards the substrates were treated with oxygen plasma for 3 min (Zepto Plasma System, Diener). The spin solutions were uniformly cast onto the float glass substrates by spin-coating with the speed of 5000 r/min for 25 s (SCS G3 Spin Coater). The spin-cast films were dried in a box furnace at 100 °C for 10 min. Afterwards the dried films were annealed in a vacuum tube furnace at 550 °C for 1 h (p < 20 mbar). The furnace was ramped up to the set temperature at a ramp rate of 20 °C/min and was allowed to
cool down naturally. The elemental composition and purity of the crystalline phase were found to very similar for both samples A3 and B3 as evidenced by Raman and EDX analysis (see Supplementary Fig. S11 and S12).

2.5. Characterisation

X-ray diffraction (XRD) studies were carried out using a Bruker-Axs D8 (GADDS) diffractometer. Raman spectroscopy was performed using an in-Via confocal Raman microscope with laser power set to 1% to avoid sample heating. Atomic Force Microscopy (AFM) studies were performed using a Bruker Dimension-Icon. Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) were carried out using a Zeiss XB1540 Crossbeam FIB-SEM Microscope with scans collected in the range 0-1200 eV. Transmission electron microscopy (TEM) images were obtained using a JEOL 2100 microscope with a LaB6 cathode operating at an acceleration voltage of 200 kV. Images were recorded on a Gatan Orius SC200 CCD Camera. Samples were prepared by drop-casting a nanoparticle dispersion onto a holey carbon film on 300 mesh copper grid (Agar Scientific).

Thin films samples were prepared by scratching parts of the film with a scalpel onto the TEM grid. Optical constants of the plain VO$_2$ film were measured using a Semilabs SE-2000 spectroscopic ellipsometer at room temperature and at 90 °C.

Thermochromic properties of the films were tested by measuring their transmittance and reflectance spectra using a Perkin Elmer Lambda 950 UV/Vis/NIR spectrophotometer. The samples were heated in-situ using an aluminium high-temperature cell controlled by a Eurotherm temperature controller and k-type thermocouple. In order to remove any contribution of the glass slide and to isolate the optical properties attributed to the VO$_2$ films alone, a plain glass slide was measured as a background reference before the measurement of the samples. For hysteresis measurement the transmittance at 2500 nm was measured at small temperature increments during the heating and cooling cycle using a Shimazdu Prestige 21 Fourier Transform Infrared Spectrophotometer. The hysteresis curves for heating and cooling were fitted to a Boltzmann function, separately. The transition temperature for each curve was determined by calculating the minimum of the first derivative. The transition gradient width ($w_{1/2}$) is defined as the full width half maximum (FWHM) of the first derivative. The scattering behaviour of the films was measured in transmission using a Radiant Zemax Imaging Sphere.
for Scatter and Appearance Measurement (IS-SA). Samples were illuminated at a normal angle of incidence with blue light (450 nm).

3. Results and discussion

3.1. Sol-gel synthesis of thermochromic coatings

Plain VO$_2$ films were prepared by spin casting a 1 M vanadyl oxalate solution in ethanol on a pre-treated glass substrate followed by a vacuum annealing step at 550 °C for 1 h. Spin solutions for the nanocomposite films were synthesised by mixing the vanadium sol with the silica nanoparticle dispersion (samples A1-A4) or silica sol (samples B1-B4) respectively. The molar concentration of vanadium was kept constant at 1 M. Monodisperse, spherical silica nanoparticles with a mean diameter of $\sim$ 14 nm (SD 1.6 nm) (Figure S1) were synthesized by a modified Stöber method. To obtain the pure VO$_2$(M) phase, the annealing conditions must be tightly controlled. The oxygen partial pressure must be adjusted within tight tolerance limits as slightly higher oxygen contents resulted in the oxidation of the films whereas films annealed under lower oxygen partial pressures are still amorphous[36]. Consequently, the spin coated films were annealed in a vacuum tube furnace and the oxygen content in the furnace was controlled by adjusting the internal pressure to 10-20 mbar. Different annealing temperatures were screened with films annealed at 550 °C showing the highest NIR modulation (Figure S2), above this temperature the surface of the film was found to be oxidized to V$_2$O$_5$. For the fabricated films, Raman and XRD measurements only show peaks indicative of VO$_2$(M1) (see Supplementary Fig. S10 & S11).

3.2. Simulation of performance limits for composite films

The performance metrics $\Delta T_{\text{sol}}$ and $T_{\text{lum}}$ of vanadium dioxide composite films were simulated via a transfer matrix method[37]. The optical constants of silica and vanadium dioxide were measured via ellipsometry (Figure S3 & S4). The optical constants of composite films with varying compositions were calculated via the Bruggeman effective medium theory, which is well suited to modelling composite materials with both high and low fill fractions and non-spatially separated domains[38, 39]. Figure 1 shows $\Delta T_{\text{sol}}$ and $T_{\text{lum}}$ plotted together for coating of varying thickness and compositions.

It can be seen from Figures 1a & 1b that as the silica fill fraction ($FF$) is increased, the optical performance range increases due to the suppressed
visible reflectance of the silica-VO$_2$ composite, which is a result of silica having a lower refractive index ($\sim$ 1.45) than that of VO$_2$ (see Figures S3 & S4).

Figure 1b shows that the thickness of these coatings is also key to maximizing luminous transmittance since the peaks observed in Figure 1b are the result of thickness dependent optical interference in the thin films. Whilst optimisation of the composite thickness was outside of the scope of this study, this shows the potential optical improvements that can be achieved via the formation of such composites with precise thicknesses. These simulations, however, give no indication of the hysteresis and gradient properties of the films, both of which are key to the overall energy saving performances. This is particularly important to determine for nanocomposites, since as the size of vanadium dioxide domains decreases, the hysteresis width increases due to a decrease in suitable phase change nucleation sites[21, 22, 23, 24]. Additionally many composite materials exhibit significant polydispersity in their components which in the case of vanadium dioxide can lead to large gradients in the phase transition since the different sized grains have different hysteretic behaviour[21].

3.3. Thermochromic properties

The optical properties of all samples: plain VO$_2$ (sample V), VO$_2$ sol with SiO$_2$ nanoparticles dispersed within (samples A1-A4), and VO$_2$ sol mixed with SiO$_2$ sol (samples B1-B4), were evaluated by measuring the transmittance and reflectance at room temperature and 90 $^\circ$C. All coatings showed a
Figure 2: (a) Spectral transmittance in hot and cold states for samples A1-A4 and plain VO$_2$ film (V). (b) Spectral transmittance in hot and cold states for samples B1-B4 and plain VO$_2$ film (V).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si:V</th>
<th>FF</th>
<th>$T_{\text{lum,c}}$ (%)</th>
<th>$T_{\text{lum,h}}$ (%)</th>
<th>$\Delta T_{\text{lum}}$ (%)</th>
<th>$T_{\text{sol,c}}$ (%)</th>
<th>$T_{\text{sol,h}}$ (%)</th>
<th>$\Delta T_{\text{sol}}$ (%)</th>
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<tr>
<td>V</td>
<td>0.00</td>
<td>0</td>
<td>52.2</td>
<td>52.5</td>
<td>0.3</td>
<td>51.1</td>
<td>44.3</td>
<td>6.69</td>
</tr>
<tr>
<td>A1</td>
<td>0.25</td>
<td>0.24</td>
<td>42.3</td>
<td>45.9</td>
<td>3.6</td>
<td>47.9</td>
<td>39.3</td>
<td>8.60</td>
</tr>
<tr>
<td>A2</td>
<td>0.50</td>
<td>0.38</td>
<td>48.1</td>
<td>48.9</td>
<td>0.8</td>
<td>54.6</td>
<td>44.6</td>
<td>10.0</td>
</tr>
<tr>
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<td>0.75</td>
<td>0.48</td>
<td>48.9</td>
<td>49.2</td>
<td>0.3</td>
<td>55.6</td>
<td>42.8</td>
<td>12.8</td>
</tr>
<tr>
<td>A4</td>
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<td>0.56</td>
<td>52.7</td>
<td>52.4</td>
<td>-0.3</td>
<td>57.4</td>
<td>46.1</td>
<td>11.3</td>
</tr>
<tr>
<td>B1</td>
<td>0.25</td>
<td>0.24</td>
<td>49.1</td>
<td>47.7</td>
<td>1.4</td>
<td>49.0</td>
<td>39.5</td>
<td>9.58</td>
</tr>
<tr>
<td>B2</td>
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<td>0.38</td>
<td>43.1</td>
<td>45.5</td>
<td>-2.4</td>
<td>51.1</td>
<td>39.7</td>
<td>11.4</td>
</tr>
<tr>
<td>B3</td>
<td>0.75</td>
<td>0.48</td>
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<td>0.2</td>
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<td>53.6</td>
<td>37.5</td>
<td>16.1</td>
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large reduction in transmittance in the infrared part of the spectrum at temperatures of 90 °C due to the transition from the insulating to the metallic phase (Figure 2). The metrics $\Delta T_{\text{sol}}$ and $T_{\text{lum}}$ of all coatings are detailed in Table 2.

All nanocomposite films show a higher solar modulation than plain VO$_2$ with comparable visible transmittance. The highest solar modulation of the mixed sol-gel films was 16.1% compared to the 6.79% solar modulation of the plain VO$_2$ sample, whilst the highest solar modulation of the nanoparticle containing films was 12.8%. The composites are able to achieve a higher solar modulation with comparable visible transmittance since they are less reflective in the visible region than the pure VO$_2$ film. Reflectance spectra showed a drop in reflectance with increasing amount of Si for both nanocomposite
Table 3: Transition temperature, hysteresis width and transition gradient width for plain VO$_2$ films and nanocomposite films.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$T_{t,c}$ ($^\circ$C)</th>
<th>$T_{t,h}$ ($^\circ$C)</th>
<th>$T_t$ ($^\circ$C)</th>
<th>$\Delta T_t$ ($^\circ$C)</th>
<th>$w_{1/2}$ ($^\circ$C)</th>
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<td>8.0</td>
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<td>61.3</td>
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<td>2.9</td>
</tr>
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<td>B3</td>
<td>58.1</td>
<td>75.8</td>
<td>67.0</td>
<td>17.7</td>
<td>11.1</td>
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</table>

The phase transition of plain VO$_2$ and the nanocomposite films A3 and B3, were investigated by temperature dependent transmittance measurements. The samples were heated up in small temperature steps to above the transition temperature and were cooled down slowly. As can be seen from the hysteresis loops in Figure 3 and as detailed in Table 3 the hysteresis width of plain VO$_2$ is much narrower than the one for the sol-gel film B3. In contrast, the nanoparticle-based film showed a loop width similar to plain VO$_2$. Hysteresis width and transition temperatures $T_t$ were obtained by plotting the first derivative $d(T_r)/d(T)$ against $T$ and determining the position of the minimum (Table 3). The average transition temperature $T_t$ of A3 (61.3 $^\circ$C) is similar to the one of plain VO$_2$ (64.6 $^\circ$C) whereas the sol-gel film exhibit a higher $T_c$ of ca. 68 $^\circ$C. The hysteresis width is following a similar trend, with $\Delta T_t$ of B3 (17.7 $^\circ$C) more than double the size as the one for plain VO$_2$ and A3. The transition gradient width was determined by the FWHM of the transition peaks in Figure 3. A sharp phase transition was observed for plain VO$_2$ and A3, with gradient widths of 5.6 $^\circ$C & 2.6 $^\circ$C respectively, whereas the larger hysteresis width in B3 is accompanied by a more gradual transition with a gradient width of 11.1%.

In brief, the differences in phase transition can be correlated to the different domain size of VO$_2$ in the nanocomposite films. The narrower transition hysteresis and gradient in A3 can be explained by the larger and more uniform grain size of VO$_2$ which gives rise to more simultaneous nucleation within a small temperature window. SEM and AFM analysis of the sol-gel and nanoparticle nanocomposite films showed clear differences in film structure and morphology (Figure 4). The mixed VO$_2$-SiO$_2$ sol-gel films (B1-B4) exhibit a smooth surface texture with small particles of $\sim$ 13 nm diameter on the film surface. All of the composite films containing silica nanoparticles show a higher surface roughness with a granular structure of the films clearly visible in the SEM images (Figure S7 & S8). The size of the individual films (Figure S5 & S6).
Figure 3: Measured hysteresis loops used to calculate transition hysteresis and gradient width of samples V, A3, B3. The first derivative $d(T_r)/dT$ against $T$ is given for both heating (red) and cooling (blue) of samples V, A3, and B3.
grains measured by AFM (d = 25 nm, SD = 4 nm) is larger than the average diameter of the silica nanoparticles (14 nm).

The influence of the silica nanoparticles on the film structures can be clearly seen in Figure 4. In the composite formed by sol-gel mixing, the silica sol acts to encapsulate the in-situ formed VO$_2$ and prevents further growth of the crystallites, resulting in the formation of relatively small, polydisperse particles embedded in a silica matrix. Conversely in the composite containing silica nanoparticles, the silica particles allow for the formation of much larger crystalline domains of VO$_2$ in the film which can have a pronounced effect on the phase transition properties of the films as shown in Table 3. It has been shown that the hysteresis width is strongly correlated with grain size because of the increased probability of nucleation[21, 40, 41]. The controlled size of the domains means that grain sizes are large enough such that hysteresis width is narrow and grain sizes are small enough such that the composite is non-scattering. Additionally, the uniformity in domain size means that the transition gradient is in fact sharper than for our plain VO$_2$ sample (2.9 °C
vs 5.6 °C).

The XRD pattern of all fabricated films showed exclusively diffraction peaks for the monoclinic VO$_2$(M) phases (011, 211, 220)\cite{42,43}, though the patterns for sample type A are slightly more defined, with the FWHM of the main peak narrower than for type B (Figure S9 & S10) indicating that the crystallites are larger in type A than type B. Additionally, the structure of the coatings were investigated further by TEM. Parts of the films were delaminated with a scalpel and were transferred on a TEM grid coated with a holey carbon film. In the case of sample A3 shown in Figure 5 the coexistence of two nanoscale structures can be identified by their diffraction pattern from selected area electron diffraction (SAED). Crystalline domains with a sizes $\sim 50$ nm were observed and indentified as monoclinic VO$_2$(M) phases (011, 211, 220)\cite{42, 43}. The spacing of the lattice fringes of 3.19 Å is in good agreement with the d-spacing of the (011) planes in monoclinic VO$_2$. The amorphous phase is formed by the silica nanoparticles. The particles form a network of aggregated, spherical nanoparticles with a mean diameter of around 22 nm which is in good agreement with the particle size measured by AFM. For the case of sample B3 shown in Figure 6 the amorphous phase is more polydisperse and the VO$_2$(M) crystallites observed are generally smaller.
Figure 6: TEM image of sample B3. SAED analysis shows VO$_2$(M) phases (011, 211, 220).

than in sample A3 which is in agreement with the calculated crystallite sizes from XRD.

Transparent coatings for glazing applications are subject to tight limits on visible haze. Since diffuse scattering of light is correlated to the structure size in the film and the optical properties of the materials, agglomeration of particles in composite films can introduce scattering sites due to the larger structure size of the agglomerates compared with single nanoparticles. The scattering behaviour of both nanocomposites (A3 and B3) was measured in transmission using an imaging sphere. Both samples were illuminated at a normal angle of incidence with blue light (450 nm) and only a small amount of transmitted light was detected outside of the 2° haze cone surrounding the incident path of light (see Figure S13); Samples A3 and B3 had 98±0.5% and 99±0.5% of transmitted light within the 2.5° cone respectively. The slightly increased scattering in A3 can be explained by the larger grain sizes observed from SEM and AFM. Overall, the low degree of diffuse scattering in both samples shows that the VO$_2$ domains are evenly distributed within in the film and no larger agglomerates of the vanadium oxide or silica nanoparticles are formed.
4. Conclusions

In summary, we have demonstrated the synthesis and improved performance of a nanocomposite thermochromic smart window coating based on a VO$_2$ sol with SiO$_2$ nanoparticles dispersed within. The composite can be considered as an effective medium between VO$_2$ and SiO$_2$ which reduces visible reflectivity. When deposited onto the substrate, the silica particles act as a matrix within which uniform sized domains of VO$_2$ form, the uniformity in domain size means that the transition gradient is sharper than for the plain VO$_2$ film (2.6 °C vs 5.6 °C). Additionally, the SiO$_2$ particles allow for the in-situ formation of larger VO$_2$ domains in the nanocomposite which reduces the hysteresis width compared to the mixed sol-gel films due to an increased nucleation probability (9.4 °C vs 17.7 °C). All films exhibit a good luminous transmittance of around 50% combined with a competitive solar modulation of up to 16.1% for the mixed sol-gel films (B1-B4) and up to 12.8% for the composites containing silica nanoparticles (A1-A4). We expect that in the future our method may be combined with doping to control both the optical and phase transition characteristics to achieve composite films with high overall energy saving performances. Specifically, magnesium doping has been shown to improve visible transparency by raising the optical bandgap[44], whilst tungsten doping has been shown to effectively reduce the transition temperature to near room temperature[5].

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6. Supplementary information

Additional supporting information is available online. This information includes TEM images and size distribution of SiO$_2$ nanoparticles, SEM and XRD of A1-4, B1-4, reflectance spectra for V, A1-4, B1-4, measured angular
distribution of transmitted light for A3, B4, and EDX and Raman spectra for A3 and A4.

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