Thermochromic VO₂–SiO₂ Nanocomposite Smart Window Coatings with Narrow Phase Transition Hysteresis and Transition Gradient Width

Johannes Schläfer^{a,1}, Christian Sol^{a,1}, Tao Li^a, Delphine Malarde^b, Mark Portnoi^a, Thomas J. Macdonald^b, Sophia K. Laney^a, Michael J. Powell^b, Işıl Top^c, Ivan P. Parkin^b, Ioannis Papakonstantinou^{a,*}

^aUniversity College London, Department of Electronic & Electrical Engineering, Torrington Place, London WC1E 7JE, United Kingdom

^bUniversity College London, Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom

^cQueen Mary University of London, School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom

---

Abstract

Thermochromic vanadium dioxide (VO₂) 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 VO₂ 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 (SiO₂ nanoparticles). We compare the performance of our nanoparticle composite with thin film VO₂ along with composites formed by mixing VO₂ and SiO₂ sol-gels and find that both composites achieve an acceptable visible transmittance (~ 50 %) along with a comparable and competitive solar modulation (12.5 % and 16.8 % respectively), roughly double that of the plain VO₂ film (6.7 %). However, our SiO₂ nanoparticle containing composite also benefits from a narrow transition hysteresis and gradient width (9.4 °C and 2.9 °C respectively). We predict that

---

*i.papakonstantinou@ucl.ac.uk

¹These authors contributed equally

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

---

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_{lum} and the solar modulation ΔT_{sol} as defined by,

$$T_{\text{lum,sol}} = \frac{\int \phi_{\text{lum,sol}}(\lambda) T(\lambda) d\lambda}{\int \phi_{\text{lum,sol}}(\lambda) d\lambda}, \quad (1)$$

$$\Delta T_{\text{sol}} = T_{\text{sol,cold}} - T_{\text{sol,hot}} \quad (2)$$

where $T(\lambda)$ denotes the transmittance at wavelength λ , $\phi_{\text{lum}}(\lambda)$ is the photoscopic spectral sensitivity of human vision[6], and $\phi_{\text{sol}}(\lambda)$ is the AM 1.5

28 solar irradiance spectrum. To increase the solar modulation, film thickness
 29 must be increased, however this results in a reduction in luminous transmit-
 30 tance due to the non-zero visible absorption and high reflectance of vanadium
 31 dioxide. Improvements to luminous transmittance can be achieved by sup-
 32 pressing reflection of visible light with anti-reflective multilayer systems[7, 8,
 33 9, 10, 11, 12, 13] or graded index nanostructures[14, 15] however this adds
 34 to the complexity of design. Alternative methods to improve the optical
 35 performance in a single coating step are composite films comprised of VO_2
 36 nanoparticles embedded in a dielectric matrix[16, 17, 18, 19, 20]. The low
 37 density and sub-wavelength dimensions of vanadium dioxide domains means
 38 that visible reflectance is minimal. Additionally vanadium dioxide nanoparti-
 39 cles have the benefit of exhibiting a plasmon resonance in their metallic state
 40 which greatly improves the solar modulating performance around 1000 nm
 41 where solar irradiance is high[16]. However, most composite coatings with
 42 high solar modulations exhibit a broad hysteresis and transition gradient.
 43 The reason for this is that the probability of phase transition in vanadium
 44 dioxide depends on the density of suitable heterogeneous nucleating sites
 45 such as surface defects, dislocations and grain boundaries[21, 22, 23, 24].
 46 Consequently, the onset temperature of the phase transition increases (de-
 47 creases) during heating (cooling) as the sizes of the nanocrystals are reduced.
 48 Several theoretical works[25, 26, 27] have highlighted the importance of re-
 49 ducing the hysteresis width of thermochromic films to improve their overall
 50 energy saving performance, as wide hysteresis loops mean that coatings are
 51 less responsive to changing climate conditions. Several previous works have
 52 shown that the hysteresis width can be reduced significantly by doping vana-
 53 dium dioxide with metal ions[5, 18], however this generally results in an
 54 increase in transition gradient[5] which has also been shown to be detrimen-
 55 tal to the overall energy saving performance[25, 28, 27]. Table 1 shows a
 56 summary of literature for composite thermochromic coatings, from which we
 57 can see that improvements in solar modulation and visible transmission for
 58 composite coatings generally result in increased hysteresis width. It must
 59 also be noted how infrequently the transition gradient is discussed in the
 60 literature, despite having been shown to be critical to the overall energy sav-
 61 ing performance[25, 28, 27]. In the only study found with a high optical
 62 performance ($T_{\text{lum}} = 48.5\%$ & $T_{\text{sol}} = 15.7\%$) that reports both the transi-
 63 tion hysteresis and gradient width, both hysteresis and gradient widths were
 64 found to be wide (17.4 & 11.3 °C respectively)[29].

65 In light of these factors, this work aims to demonstrate the influence of the

Table 1: Optical Properties of thermochromic films based on $\text{VO}_2\text{-SiO}_2$. The highest solar modulation values are accompanied by large hysteresis widths.

Reference	$T_{lum,c}$ (%)	$T_{lum,h}$ (%)	ΔT_{lum} (%)	ΔT_{sol} (%)	ΔT_t ($^{\circ}\text{C}$)	$w_{1/2}$ ($^{\circ}\text{C}$)
[17]	62.2	57.4	4.8	14.6	54.4	N/A
[18]	56.2	49.7	6.5	21.4	50.5	N/A
[18]	52.2	48.3	3.9	17.3	22.3	N/A
[18]	50.6	47.5	3.1	14.7	8.5	N/A
[19]	55.3	54.2	0.9	7.5	9.3	N/A
[20]	71.0	56.6	14.5	14.3	N/A	N/A
[30]	41.5	46.9	5.4	3.1	N/A	N/A
[31]	47.7 ^a	N/A	N/A	7.6	12.8	N/A
[32]	55.4	51.2	3.67	8.4	N/A	N/A
[33]	63.3	65.2	1.9	5.1	32.2	N/A
[34]	43.5 ^a	N/A	N/A	5.2	N/A	N/A
[29]	48.5	43.2	5.3	15.7	17.4	11.3

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

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

66 nanostructure of composite films on both the hysteresis and gradient width
67 of a thermochromic coating. Nanocomposite films of silica and vanadium
68 dioxide with different film structures were prepared by sol-gel methods. We
69 compare three different sample types: plain VO_2 (sample V), VO_2 sol with
70 SiO_2 nanoparticles dispersed within (samples A1-A4), and VO_2 sol mixed
71 with SiO_2 sol (samples B1-B4). We demonstrate that by dispersing SiO_2
72 nanoparticles within the VO_2 sol, the optical performance can be improved
73 significantly whilst the hysteresis and gradient width remain minimal. Whilst
74 the focus of discussion in this work is on smart window applications, the
75 control of transition hysteresis and gradient in VO_2 is important for many
76 applications such as thermal emittance control, microbolometers, infrared
77 modulators, and reconfigurable optical and electronic devices.

78 2. Methods & Materials

79 2.1. Synthesis of VO_2 sol

80 In a typical reaction, 3.78 g (30 mmol) of oxalic acid dihydrate (98%,
81 Alfa Aesar) was added to a suspension of 1.82 g (10 mmol) V_2O_5 (general

82 purpose grade, Fisher Chemical) in 10 mL anhydrous ethanol (99.8%, denat.
83 1% MEK + 0.001% denat. benzoate, Acros Organics). The reaction mixture
84 was heated to 80°C for 12 h. The blue solution was filtered and used without
85 further purification.

86 2.2. *Synthesis of SiO₂ sol*

87 A mixture of hydrochloric acid (37%, extra pure, Fisher Chemical), H₂O
88 and half of the prescribed amount of anhydrous ethanol was slowly added at
89 room temperature to a solution of tetraethyl orthosilicate ([Si(OEt)₄], TEOS,
90 98%, Acros Organics) in the remaining ethanol. The clear solution was stirred
91 for 24 h in a sealed glass vial and was used without further purification. The
92 molar ratios of the reactants were as follows: TEOS:H₂O:HCl:ethanol =
93 1:4:0.01:20.

94 2.3. *Synthesis of SiO₂ Nanoparticles Dispersion*

95 SiO₂ nanoparticle dispersions were prepared according to a previously
96 described, slightly modified procedure[35]. In short, a mixture of 50 mL of
97 absolute ethanol, 1 ml of deionized water and 1 mL of ammonia (25%, Fisher
98 Chemical) was heated to 40 °C. Afterward, 3 mL of TEOS were added drop-
99 wise to the reaction mixture under vigorous stirring. After 2 h additional
100 2 mL of TEOS were added. This step was repeated in 2 h intervals (4x)
101 amounting to 11 mL of TEOS in total. The nanoparticles dispersion was
102 used as obtained without any further purification steps.

103 2.4. *Fabrication of Thermochromic Films*

104 To an appropriate amount of VO₂ sol the prescribed amount of SiO₂ sol or
105 SiO₂ nanoparticles dispersion was added. The mixture was stirred for at least
106 1 h before usage. Glass substrates consisted of a 3.4 mm thick silica-coated
107 barrier glass (50 nm SiO₂ layer) obtained from Pilkington. Prior to deposi-
108 tion all substrates (2x2 cm) were cleaned with detergent solution, deionized
109 water and 2-propanol, respectively, and were blown dry in a nitrogen stream.
110 Afterwards the substrates were treated with oxygen plasma for 3 min (Zepto
111 Plasma System, Diener). The spin solutions were uniformly cast onto the
112 float glass substrates by spin-coating with the speed of 5000 r/min for 25 s
113 (SCS G3 Spin Coater). The spin-cast films were dried in a box furnace at
114 100 °C for 10 min. Afterwards the dried films were annealed in a vacuum
115 tube furnace at 550 °C for 1 h (p < 20 mbar). The furnace was ramped
116 up to the set temperature at a ramp rate of 20 °C/min and was allowed to

117 cool down naturally. The elemental composition and purity of the crystalline
118 phase were found to very similar for both samples A3 and B3 as evidenced
119 by Raman and EDX analysis (see Supplementary Fig. S11 and S12).

120 2.5. Characterisation

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

133 Thin films samples were prepared by scratching parts of the film with a
134 scalpel onto the TEM grid. Optical constants of the plain VO_2 film were
135 measured using a Semilabs SE-2000 spectroscopic ellipsometer at room tem-
136 perature and at 90 °C.

137 Thermochromic properties of the films were tested by measuring their
138 transmittance and reflectance spectra using a Perkin Elmer Lambda 950
139 UV/Vis/NIR spectrophotometer. The samples were heated in-situ using
140 an aluminium high-temperature cell controlled by a Eurotherm temperature
141 controller and k-type thermocouple. In order to remove any contribution
142 of the glass slide and to isolate the optical properties attributed to the VO_2
143 films alone, a plain glass slide was measured as a background reference before
144 the measurement of the samples. For hysteresis measurement the transmit-
145 tance at 2500 nm was measured at small temperature increments during the
146 heating and cooling cycle using a Shimadzu Prestige 21 Fourier Transform
147 Infrared Spectrophotometer. The hysteresis curves for heating and cooling
148 were fitted to a Boltzmann function, separately. The transition temperature
149 for each curve was determined by calculating the minimum of the first deriva-
150 tive. The transition gradient width ($w_{1/2}$) is defined as the full width half
151 maximum (FWHM) of the first derivative. The scattering behaviour of the
152 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 VO₂ 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 ~ 14 nm (SD 1.6 nm) (Figure S1) were synthesized by a modified Stöber method. To obtain the pure VO₂(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 V₂O₅. For the fabricated films, Raman and XRD measurements only show peaks indicative of VO₂(M1) (see Supplementary Fig. S10 & S11).

3.2. Simulation of performance limits for composite films

The performance metrics ΔT_{sol} and T_{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 ΔT_{sol} and T_{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

Figure 1: (a) Performance limits of vanadium dioxide composite coatings with different silica fill fractions (FF) with the target performance shown as a gold star. (b) Luminous reflectance as a function of film thickness for coatings with different silica fill fractions.

187 visible reflectance of the silica-VO₂ composite, which is a result of silica hav-
 188 ing a lower refractive index (~ 1.45) than that of VO₂ (see Figures S3 & S4).
 189 Figure 1b shows that the thickness of these coatings is also key to maximizing
 190 luminous transmittance since the peaks observed in Figure 1b are the result
 191 of thickness dependent optical interference in the thin films. Whilst opti-
 192 misation of the composite thickness was outside of the scope of this study,
 193 this shows the potential optical improvements that can be achieved via the
 194 formation of such composites with precise thicknesses. These simulations,
 195 however, give no indication of the hysteresis and gradient properties of the
 196 films, both of which are key to the overall energy saving performances. This
 197 is particularly important to determine for nanocomposites, since as the size
 198 of vanadium dioxide domains decreases, the hysteresis width increases due
 199 to a decrease in suitable phase change nucleation sites[21, 22, 23, 24]. Addi-
 200 tionally many composite materials exhibit significant polydispersity in their
 201 components which in the case of vanadium dioxide can lead to large gra-
 202 dients in the phase transition since the different sized grains have different
 203 hysteretic behaviour[21].

204 3.3. Thermochromic properties

205 The optical properties of all samples: plain VO₂ (sample V), VO₂ sol with
 206 SiO₂ nanoparticles dispersed within (samples A1-A4), and VO₂ sol mixed
 207 with SiO₂ sol (samples B1-B4), were evaluated by measuring the transmit-
 208 tance and reflectance at room temperature and 90 °C. All coatings showed a

Figure 2: (a) Spectral transmittance in hot and cold states for samples A1-A4 and plain VO₂ film (V). (b) Spectral transmittance in hot and cold states for samples B1-B4 and plain VO₂ film (V).

Table 2: Luminous and solar transmittance of plain VO₂ and nanocomposite films

Sample	Si:V	FF	$T_{lum,c}$ (%)	$T_{lum,h}$ (%)	ΔT_{lum} (%)	$T_{sol,c}$ (%)	$T_{sol,h}$ (%)	ΔT_{sol} (%)
V	0.00	0	52.2	52.5	0.3	51.1	44.3	6.69
A1	0.25	0.24	42.3	45.9	3.6	47.9	39.3	8.60
A2	0.50	0.38	48.1	48.9	0.8	54.6	44.6	10.0
A3	0.75	0.48	48.9	49.2	0.3	55.6	42.8	12.8
A4	1.00	0.56	52.7	52.4	-0.3	57.4	46.1	11.3
B1	0.25	0.24	49.1	47.7	1.4	49.0	39.5	9.58
B2	0.50	0.38	43.1	45.5	-2.4	51.1	39.7	11.4
B3	0.75	0.48	44.5	44.7	0.2	52.3	38.7	13.6
B4	1.00	0.56	46.1	43.7	2.4	53.6	37.5	16.1

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 ΔT_{sol} and T_{lum} of all coatings are detailed in Table 2.

All nanocomposite films show a higher solar modulation than plain VO₂ 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 VO₂ 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 VO₂ 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 VO₂ films and nanocomposite films.

Sample ID	$T_{t,c}$ (°C)	$T_{t,h}$ (°C)	T_t (°C)	ΔT_t (°C)	$w_{1/2}$ (°C)
V	60.6	68.6	64.4	8.0	5.6
A3	56.6	66.0	61.3	9.4	2.9
B3	58.1	75.8	67.0	17.7	11.1

221 films (Figure S5 & S6).

222 The phase transition of plain VO₂ and the nanocomposite films A3 and
 223 B3, were investigated by temperature dependent transmittance measure-
 224 ments. The samples were heated up in small temperature steps to above
 225 the transition temperature and were cooled down slowly. As can be seen
 226 from the hysteresis loops in Figure 3 and as detailed in Table 3 the hystere-
 227 sis width of plain VO₂ is much narrower than the one for the sol-gel film
 228 B3. In contrast, the nanoparticle-based film showed a loop width similar to
 229 plain VO₂. Hysteresis width and transition temperatures T_t were obtained
 230 by plotting the first derivative $d(T_r)/d(T)$ against T and determining the
 231 position of the minimum (Table 3). The average transition temperature T_t
 232 of A3 (61.3 °C) is similar to the one of plain VO₂ (64.6 °C) whereas the
 233 sol-gel film exhibit a higher T_c of ca. 68 °C. The hysteresis width is following
 234 a similar trend, with ΔT_c of B3 (17.7 °C) more than double the size as the
 235 one for plain VO₂ and A3. The transition gradient width was determined
 236 by the FWHM of the transition peaks in Figure 3. A sharp phase transition
 237 was observed for plain VO₂ and A3, with gradient widths of 5.6 °C & 2.6 °C
 238 respectively, whereas the larger hysteresis width in B3 is accompanied by a
 239 more gradual transition with a gradient width of 11.1%.

240 In brief, the differences in phase transition can be correlated to the differ-
 241 ent domain size of VO₂ in the nanocomposite films. The narrower transition
 242 hysteresis and gradient in A3 can be explained by the larger and more uni-
 243 form grain size of VO₂ which gives rise to more simultaneous nucleation
 244 within a small temperature window. SEM and AFM analysis of the sol-gel
 245 and nanoparticle nanocomposite films showed clear differences in film struc-
 246 ture and morphology (Figure 4). The mixed VO₂-SiO₂ sol-gel films (B1-B4)
 247 exhibit a smooth surface texture with small particles of ~ 13 nm diameter
 248 on the film surface. All of the composite films containing silica nanoparticles
 249 show a higher surface roughness with a granular structure of the films clearly
 250 visible in the SEM images (Figure S7 & S8). The size of the individual

Figure 3: Measured hysteresis loops used to calculate transition hysteresis and gradient width of samples V, A3, B3. The first derivative $d(T_r)/d(T)$ against T is given for both heating (red) and cooling (blue) of samples V, A3, and B3.

Figure 4: From left to right, top-view SEM, side-on SEM, and AFM images of $\text{VO}_2\text{-SiO}_2$ -nanocomposites formed via two different methods: A3 - vanadium(IV) sol-gel containing SiO_2 nanoparticles (top row), B3 - mixed vanadium(IV) and silica sol-gels (bottom row).

grains measured by AFM ($d = 25$ nm, $\text{SD} = 4$ 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

Figure 5: TEM image of sample A3. SAED analysis shows $\text{VO}_2(\text{M})$ phases (011, 211, 220).

vs 5.6 °C).

The XRD pattern of all fabricated films showed exclusively diffraction peaks for the monoclinic $\text{VO}_2(\text{M})$ phases (011, 211, 220)[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 ~ 50 nm were observed and indentified as monoclinic $\text{VO}_2(\text{M})$ phases (011, 211, 220)[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 $\text{VO}_2(\text{M})$ crystallites observed are generally smaller

Figure 6: TEM image of sample B3. SAED analysis shows $\text{VO}_2(\text{M})$ 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 $98 \pm 0.5\%$ and $99 \pm 0.5\%$ 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.

304 4. Conclusions

305 In summary, we have demonstrated the synthesis and improved perfor-
306 mance of a nanocomposite thermochromic smart window coating based on
307 a VO_2 sol with SiO_2 nanoparticles dispersed within. The composite can be
308 considered as an effective medium between VO_2 and SiO_2 which reduces vis-
309 ible reflectivity. When deposited onto the substrate, the silica particles act
310 as a matrix within which uniform sized domains of VO_2 form, the unifor-
311 mity in domain size means that the transition gradient is sharper than for
312 the plain VO_2 film (2.6 °C vs 5.6 °C). Additionally, the SiO_2 particles allow
313 for the in-situ formation of larger VO_2 domains in the nanocomposite which
314 reduces the hysteresis width compared to the mixed sol-gel films due to an
315 increased nucleation probability (9.4 °C vs 17.7 °C). All films exhibit a good
316 luminous transmittance of around 50% combined with a competitive solar
317 modulation of up to 16.1% for the mixed sol gel films (B1-B4) and up to
318 12.8% for the composites containing silica nanoparticles (A1-A4). We ex-
319 pect that in the future our method may be combined with doping to control
320 both the optical and phase transition characteristics to achieve composite
321 films with high overall energy saving performances. Specifically, magnesium
322 doping has been shown to improve visible transparency by raising the optical
323 bandgap[44], whilst tungsten doping has been shown to effectively reduce the
324 transition temperature to near room temperature[5].

325 5. Acknowledgements

326 This work was supported by the European Research Council (ERC) In-
327 telglazing, Project ID: 679891 and by the Horizon H2020 research and in-
328 novation program EENSULATE under grant agreement No. 723868. C.S.
329 was supported by the EPSRC Centre for Doctoral Training (CDT) in In-
330 tegrated Photonic and Electronic Systems (IPES) (EP/L015455/1). The
331 authors thank Dr. Stefan Guldin and Dr. László Makai for access to ellip-
332 sometry facilities and Mr. Péter Rutka for assistance with IR ellipsometry.

333 6. Supplementary information

334 Additional supporting information is available online. This information
335 includes TEM images and size distribution of SiO_2 nanoparticles, SEM and
336 XRD of A1-4, B1-4, reflectance spectra for V, A1-4, B1-4, measured angular

337 distribution of transmitted light for A3, B4, and EDX and Raman spectra
338 for A3 and A4.

339 References

- 340 [1] Solar Control Glass, Pilkington, [http://www.pilkington.com/en-](http://www.pilkington.com/en-gb/uk/products/product-categories/solar-control)
341 [gb/uk/products/product-categories/solar-control](http://www.pilkington.com/en-gb/uk/products/product-categories/solar-control), 2018. (Accessed: 26
342 February 2018).
- 343 [2] T. A. Markus, E. N. Morris, Buildings, climate, and energy, Pitman
344 Pub., 1980.
- 345 [3] C. Granqvist, Spectrally selective coatings for energy efficiency and solar
346 applications, *Physica Scripta* 32 (1985) 401.
- 347 [4] S. Babulanam, T. Eriksson, G. Niklasson, C. Granqvist, Thermochromic
348 VO₂ films for energy-efficient windows, *Solar energy materials* 16 (1987)
349 347–363.
- 350 [5] T. D. Manning, I. P. Parkin, M. E. Pemble, D. Sheel, D. Vernardou,
351 Intelligent window coatings: atmospheric pressure chemical vapor depo-
352 sition of tungsten-doped vanadium dioxide, *Chemistry of Materials* 16
353 (2004) 744–749.
- 354 [6] L. T. Sharpe, A. Stockman, W. Jagla, H. Jäggle, A luminous efficiency
355 function, $v^*(\lambda)$, for daylight adaptation, *Journal of Vision* 5 (2005) 3–3.
- 356 [7] D. Li, Y. Shan, F. Huang, S. Ding, Sol-gel preparation and charac-
357 terization of SiO₂ coated VO₂ films with enhanced transmittance and
358 high thermochromic performance, *Applied Surface Science* 317 (2014)
359 160–166.
- 360 [8] M.-H. Lee, J.-S. Cho, Better thermochromic glazing of windows with
361 anti-reflection coating, *Thin Solid Films* 365 (2000) 5–6.
- 362 [9] N. Mlyuka, G. A. Niklasson, C.-G. Granqvist, Thermochromic multi-
363 layer films of VO₂ and TiO₂ with enhanced transmittance, *Solar Energy*
364 *Materials and Solar Cells* 93 (2009) 1685–1687.

- [10] M. J. Powell, R. Quesada-Cabrera, A. Taylor, D. Teixeira, I. Papakonstantinou, R. G. Palgrave, G. Sankar, I. P. Parkin, Intelligent multifunctional VO₂/SiO₂/TiO₂ coatings for self-cleaning, energy-saving window panels, *Chemistry of Materials* 28 (2016) 1369–1376.
- [11] T. Chang, X. Cao, L. R. Dedon, S. Long, A. Huang, Z. Shao, N. Li, H. Luo, P. Jin, Optical design and stability study for ultrahigh-performance and long-lived vanadium dioxide-based thermochromic coatings, *Nano Energy* 44 (2018) 256–264.
- [12] C. Sol, J. Schläfer, T. Li, S. Guldin, I. P. Parkin, I. Papakonstantinou, A combined experimental and theoretical study into the performance of multilayer vanadium dioxide composite films for energy saving applications, in: *Photonics for Solar Energy Systems VII*, volume 10688, International Society for Optics and Photonics, p. 106880D.
- [13] I. Top, R. Binions, C. Sol, I. Papakonstantinou, M. Holdynski, S. Gaiaschi, I. Abrahams, Improved thermochromic properties in bilayer films of VO₂ with ZnO, SnO₂ and WO₃ coatings for energy efficient glazing, *Journal of Materials Chemistry C* 6 (2018) 12555–12565.
- [14] A. Taylor, I. Parkin, N. Noor, C. Tummeltshammer, M. S. Brown, I. Papakonstantinou, A bioinspired solution for spectrally selective thermochromic VO₂ coated intelligent glazing, *Optics express* 21 (2013) A750–A764.
- [15] X. Qian, N. Wang, Y. Li, J. Zhang, Z. Xu, Y. Long, Bioinspired multifunctional vanadium dioxide: improved thermochromism and hydrophobicity, *Langmuir* 30 (2014) 10766–10771.
- [16] S.-Y. Li, G. A. Niklasson, C.-G. Granqvist, Nanothermochromics: calculations for VO₂ nanoparticles in dielectric hosts show much improved luminous transmittance and solar energy transmittance modulation, *Journal of Applied Physics* 108 (2010) 063525.
- [17] Y. Zhou, A. Huang, Y. Li, S. Ji, Y. Gao, P. Jin, Surface plasmon resonance induced excellent solar control for VO₂@SiO₂ nanorods-based thermochromic foils, *Nanoscale* 5 (2013) 9208–9213.
- [18] J. Zhu, Y. Zhou, B. Wang, J. Zheng, S. Ji, H. Yao, H. Luo, P. Jin, Vanadium dioxide nanoparticle-based thermochromic smart coating: high

luminous transmittance, excellent solar regulation efficiency, and near room temperature phase transition, *ACS applied materials & interfaces* 7 (2015) 27796–27803.

[19] Y. Gao, S. Wang, H. Luo, L. Dai, C. Cao, Y. Liu, Z. Chen, M. Kanehira, Enhanced chemical stability of VO₂ nanoparticles by the formation of VO₂/SiO₂ core/shell structures and the application to transparent and flexible VO₂-based composite foils with excellent thermochromic properties for solar heat control, *Energy & Environmental Science* 5 (2012) 6104–6110.

[20] M. Wang, J. Tian, H. Zhang, X. Shi, Z. Chen, Y. Wang, A. Ji, Y. Gao, Novel synthesis of pure VO₂@SiO₂ core@shell nanoparticles to improve the optical and anti-oxidant properties of a VO₂ film, *RSC Advances* 6 (2016) 108286–108289.

[21] R. Lopez, L. C. Feldman, R. F. Haglund Jr, Size-dependent optical properties of VO₂ nanoparticle arrays, *Physical Review Letters* 93 (2004) 177403.

[22] T.-H. Yang, C. Jin, H. Zhou, R. J. Narayan, J. Narayan, Role of twin boundaries in semiconductor to metal transition characteristics of VO₂ films, *Applied Physics Letters* 97 (2010) 072101.

[23] W. Fan, J. Cao, J. Seidel, Y. Gu, J. Yim, C. Barrett, K. Yu, J. Ji, R. Ramesh, L. Chen, et al., Large kinetic asymmetry in the metal-insulator transition nucleated at localized and extended defects, *Physical Review B* 83 (2011) 235102.

[24] K. Appavoo, D. Y. Lei, Y. Sonnefraud, B. Wang, S. T. Pantelides, S. A. Maier, R. F. Haglund Jr, Role of defects in the phase transition of VO₂ nanoparticles probed by plasmon resonance spectroscopy, *Nano letters* 12 (2012) 780–786.

[25] C. Sol, J. Schläfer, I. P. Parkin, I. Papakonstantinou, Mitigation of hysteresis due to a pseudo-photochromic effect in thermochromic smart window coatings, *Scientific Reports* 8 (2018) 13249.

[26] M. E. Warwick, I. Ridley, R. Binions, The effect of transition gradient in thermochromic glazing systems, *Energy and Buildings* 77 (2014) 80–90.

- [27] M. E. Warwick, I. Ridley, R. Binions, The effect of variation in the transition hysteresis width and gradient in thermochromic glazing systems, *Solar Energy Materials and Solar Cells* 140 (2015) 253–265.
- [28] M. E. Warwick, I. Ridley, R. Binions, The effect of transition gradient in thermochromic glazing systems, *Energy and Buildings* 77 (2014) 80–90.
- [29] L. Zhao, L. Miao, C. Liu, C. Li, T. Asaka, Y. Kang, Y. Iwamoto, S. Tanemura, H. Gu, H. Su, Solution-processed VO₂-SiO₂ composite films with simultaneously enhanced luminous transmittance, solar modulation ability and anti-oxidation property, *Scientific Reports* 4 (2014) 7000.
- [30] Y. Ke, I. Balin, N. Wang, Q. Lu, A. I. Y. Tok, T. J. White, S. Magdassi, I. Abdulhalim, Y. Long, Two-dimensional SiO₂/VO₂ photonic crystals with statically visible and dynamically infrared modulated for smart window deployment, *ACS Applied Materials & interfaces* 8 (2016) 33112–33120.
- [31] J.-H. Yu, S.-H. Nam, J. W. Lee, J.-H. Boo, Enhanced visible transmittance of thermochromic VO₂ thin films by SiO₂ passivation layer and their optical characterization, *Materials* 9 (2016) 556.
- [32] Z. Cao, Y. Lu, X. Xiao, Y. Zhan, H. Cheng, G. Xu, Tunable simultaneously visible-light and near-infrared transmittance for VO₂-SiO₂ composite films to enhance thermochromic properties, *Materials Letters* 209 (2017) 609–612.
- [33] C. Wang, L. Zhao, Z. Liang, B. Dong, L. Wan, S. Wang, New intelligent multifunctional SiO₂/VO₂ composite films with enhanced infrared light regulation performance, solar modulation capability, and superhydrophobicity, *Science and Technology of Advanced Materials* 18 (2017) 563–573.
- [34] L. Zhou, J. Liang, M. Hu, P. Li, X. Song, Y. Zhao, X. Qiang, Enhanced luminous transmittance of thermochromic VO₂ thin film patterned by SiO₂ nanospheres, *Applied Physics Letters* 110 (2017) 193901.
- [35] D. Erdem, N. S. Bingham, F. J. Heiligt, N. Pilet, P. Warnicke, L. J. Heyderman, M. Niederberger, CoFe₂O₄ and CoFe₂O₄-SiO₂ nanoparticle thin films with perpendicular magnetic anisotropy for magnetic and

- 463 magneto-optical applications, *Advanced Functional Materials* 26 (2016)
464 1954–1963.
- 465 [36] A. P. Peter, K. Martens, G. Rampelberg, M. Toeller, J. M. Ablett,
466 J. Meersschaut, D. Cuypers, A. Franquet, C. Detavernier, J.-P. Rueff,
467 Metal insulator transition in ald VO₂ ultrathin films and nanoparticles:
468 Morphological control, *Advanced Functional Materials* 25 (2015) 679–
469 686.
- 470 [37] P. Yeh, *Optical Waves in Layered Media*, volume 61, Wiley-Interscience,
471 2005.
- 472 [38] S. Berthier, J. Lafait, Effective medium theory: mathematical deter-
473 mination of the physical solution for the dielectric constant, *Optics*
474 *Communications* 33 (1980) 303–306.
- 475 [39] D. Bruggeman, Dielectric constant and conductivity of mixtures of
476 isotropic materials, *Ann. Phys.(Leipzig)* 24 (1935) 636–679.
- 477 [40] R. Lopez, T. Haynes, L. Boatner, L. Feldman, R. Haglund Jr, Size
478 effects in the structural phase transition of VO₂ nanoparticles, *Physical*
479 *Review B* 65 (2002) 224113.
- 480 [41] I. Khakhaev, F. Chudnovskii, E. Shadrin, Martensitic effects in the
481 metal-insulator phase transition in a vanadium dioxide film, *Physics of*
482 *the Solid State* 36 (1994) 898–901.
- 483 [42] X. Cao, M. N. Thet, Y. Zhang, S. C. J. Loo, S. Magdassi, Q. Yan,
484 Y. Long, Solution-based fabrication of VO₂(M) nanoparticles via
485 lyophilisation, *RSC Advances* 5 (2015) 25669–25675.
- 486 [43] Y. Jo, M. Kim, B. Kim, Direct correlation of structural and electrical
487 properties of electron-doped individual VO₂ nanowires on devised tem
488 grids, *Nanotechnology* 27 (2016) 435704.
- 489 [44] S.-Y. Li, N. R. Mlyuka, D. Primetzhofer, A. Hallén, G. Possnert, G. A.
490 Niklasson, C. G. Granqvist, Bandgap widening in thermochromic mg-
491 doped VO₂ thin films: Quantitative data based on optical absorption,
492 *Applied Physics Letters* 103 (2013) 161907.