Showcasing a study on micro-patterned vanadium dioxide thermochromic windows by Dr Yi Long at School of Materials Science and Engineering, Nanyang Technological University, and Prof. Shlomo Magdassi and Prof. Daniel Mandler at Institute of Chemistry, The Hebrew University.

Periodic micro-patterned VO$_2$ thermochromic films by mesh printing

Facile meshing printing is employed to fabricate periodic micro-patterned structures of vanadium dioxide. Such structure is able to favorably transmit visible light without sacrificing large near-infrared modulation, with overall enhanced thermochromic properties.

As featured in:

Periodic micro-patterned VO₂ thermochromic films by mesh printing†

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VO₂ has garnered much attention in recent years as a promising candidate for thermochromic window applications due to rising awareness about energy conservation. However, the trade-off between improving the luminous transmittance (Tlum) and solar modulation ability (ΔTsol) limits the commercialization of VO₂-based smart windows. Four major nanostructuring approaches were implemented to enhance both Tlum and ΔTsol, namely nanocomposites, nanoporous films, biomimetic moth-eye structures and anti-reflection coating (ARC) multilayers. This work demonstrates a novel approach that fabricates periodic, micro-patterned structures of VO₂ using a facile screen printing method. The micro-patterned structure is able to favorably transmit visible light without sacrificing high near-infrared modulation, and the patterned film shows improved Tlum (67% vs. 60%) and ΔTsol (8.8% vs. 6.9%) compared with continuous films. By varying the thickness, periodicity and solid concentration, this approach can give a ΔTsol of 14.9% combined with a Tlum of 43.3%, which is comparable, if not superior to, some of the best reported results found using other approaches.

Introduction

20 to 40 percent of energy consumption in developed countries can be attributed to buildings, and 10 to 20 percent of the primary energy usage of buildings account for heating or cooling purposes.1,2 This provides a strong impetus for novel energy-saving solutions, and in particular, building-facade solutions have become increasingly popular. Thermochromic films are the most cost-effective chromogenic material as they exhibit an automatic change in solar transmission with changes in temperature.3 Vanadium dioxide (VO₂) is one of the leading thermochromic materials.4–6 Below the critical temperature of $\tau_c = 68 \, ^\circ\text{C}$, VO₂ is in the monoclinic phase and is transparent to infrared light. As it transforms into a tetragonal structure at $T > \tau_c$, it becomes highly absorptive of IR radiation.7–9 Ideally, thermochromic coatings should have both high luminous transmittance ($T_{\text{lum}}$) and solar modulation ability ($\Delta T_{\text{sol}}$), but VO₂’s inherently high luminous absorption in both states renders it challenging to simultaneously increase $T_{\text{lum}}$ and $\Delta T_{\text{sol}}$. Most conventional VO₂ single layer films are able to achieve a $T_{\text{lum}}$ around 50% with a $\Delta T_{\text{sol}}$ of 5%.10 Many endeavors to improve the performance of VO₂ based films have been attempted,11 employing doping,10,12–18 anti-reflection coating,19 nanoporous structuring,20,21 nanoparticle-based composites,22–26 biomimetic nanostructuring,27,28 organic materials,29 and hybridization30 as means to enhance both $T_{\text{lum}}$ and $\Delta T_{\text{sol}}$.

Liu Chang et al.31 proposed the first finite difference time domain (FDTD) simulation work on nano-gridded, VO₂-based perforated films. The nano-sized opening would improve the transmission of short-wavelength visible light, while the abundant volume of VO₂ retained in the pattern maintains the film’s good long-wavelength near-infrared (NIR) modulation abilities. The best-performing theoretical combination of 79% $T_{\text{lum}}$ and 14% $\Delta T_{\text{sol}}$ surpasses other theoretical work such as biomimetic nanostructuring,28 nanothermochromism,32 and nanoporous structuring.33

We report, for the first time, a micro-gridded structure inspired by Liu’s design. It was fabricated using screen printing meshes with controlled film thickness, concentration and periodicity. Such structures could improve both $T_{\text{lum}}$ and $\Delta T_{\text{sol}}$ simultaneously, thus opening a new research direction in thermochromic VO₂ studies.

Materials and equipment

VO₂ nanoparticles (Jingcheng Chemicals, China), dipropylene glycol methyl ether (DPM, 4.5 wt%), Disperbyk 180, and silica aluminum gel were used without further purification. Deionized water (18.2 MΩ) was used throughout the experiments.
A VO₂/Si–Al gel mixture was prepared as reported, which serves to provide structural support to the VO₂ grid films upon drying. 5 wt% mg of the filtered colloid was diluted to 0.5 wt%, 0.25 wt%, 0.167 wt% and 0.125 wt% with Si–Al gel. The solution was then vortexed and sonicated for 15 minutes for better dispersion and homogeneity.5

A soda glass substrate was sonicated with deionized water, followed by 95% ethanol solution, and finally with deionized water again for cleaning. The glass slide was dried in a furnace set at 100 °C. As illustrated in Fig. 1, the glass substrate was placed at the center of a hot plate. The screen printing mesh (Ponger 2000, Israel) was mounted directly above the glass substrate, and the vertical distance, D, between the bottom of the mesh and the top surface of the glass substrate, was carefully controlled. Using a 100 μL pipette, the VO₂/Si–Al gel mixture was applied onto the glass substrate through the meshes. When the nanoparticle (NP) dispersion was placed on top of the mesh (Fig. 1), upon contact, the liquid immediately wetted the mesh walls and filled up the space between the mesh and the glass substrate, resulting in the alignment of the NPs along the threads of the mesh (Fig. 1 inset side view). The substrate was heated at 50 °C for 12 hours to evaporate water from the matrix. Upon removal of the mesh, a periodic, waffle textured VO₂ film was formed (Fig. 1 inset top view).

Characterization

The morphology and the SAED (selected area electron diffraction) of the purchased VO₂ nanoparticles were characterized using a transmission electron microscope (JEM-2010, JEOL, Japan) with an accelerating voltage of 200 kV.

The transmittance spectrum from 250 to 2500 nm was analysed using a UV-Vis-NIR spectrometer (Cary 5000, Agilent, USA) at normal incidence. A heating stage (PE120, Linkam, UK) was employed to control the temperature of the samples mounted on the spectrophotometer.

The sample films’ morphology was studied using a field emission scanning electron microscope (JEM-7600F, JEOL, Japan) with an accelerating voltage of 5 kV.

The following equation was employed in the calculation of the film’s performance in terms of its luminous transmittance (380–780 nm), IR transmittance (780–2500 nm), and solar transmittance, T_{sol} (250–2500 nm):

$$ T_{\text{lum/IR/sol}} = \frac{\int \varphi_{\text{lum/IR/sol}}(\lambda) T(\lambda) d\lambda}{\int \varphi_{\text{lum/IR/sol}}(\lambda) d\lambda} $$

where \( T(\lambda) \) refers to the spectral transmittance and \( \varphi_{\text{lum}} \) is the standard luminous efficiency function of photopic vision at the corresponding wavelength.36 \( \varphi_{\text{IR}} \) and \( \varphi_{\text{sol}} \) denote the IR/solar irradiance spectrum distribution for air mass 1.5 (which corresponds to the sun standing at 37° above the horizon with 1.5 atmosphere thickness,37 and in the presence of a solar zenith angle of 48.2°). \( \Delta T_{\text{lum/IR/sol}} \) is obtained as the difference between \( \Delta T_{\text{lum/IR/sol}} \) at 20 °C and \( \Delta T_{\text{lum/IR/sol}} \) at 90 °C.

Results and discussion

Effects of thickness on optical properties

The particle size of the starting VO₂ powders is less than 100 nm with an oval shape and a uniform size distribution, as shown in Fig. 2a. The selected area electron diffraction (SAED) pattern (inset Fig. 2a) suggests the high purity of the polycrystalline VO₂ NPs. The thickness of the samples fabricated has been varied according to Fig. 1, using a mesh of size 100 nm with an oval shape and a uniform size distribution, periodically alternating crests and troughs. The cross-section view of the samples is shown in Fig. 2d and e. The increase in the thickness of film is observed to reduce the size of the crater and allows more solution to remain at the centre. The thickness of the film formed at the bottom of the crater also increases (Fig. 2c). In this case, the film is no longer a hollow grid; it forms a cone textured structure with periodically alternating crests and troughs. The cross-section view of the samples is shown in Fig. 2d and e. The increase in the thickness does not afford the formation of the patterned structure, albeit the film starts to adopt a waffle-like structure instead of a gridded structure when the thickness becomes greater.

As illustrated in Fig. 2f, increasing thickness (D) results in a gradual decrease in the transmittance in samples prepared with 0.25 wt% VO₂ dispersions at all wavelengths (250–2500 nm) at 90 °C. This is also observed in the visible range (380–780 nm) at 20 °C, thus accounting for decreasing averaged \( T_{\text{lum}} \), as shown in Fig. 2g. A similar trend was observed for 0.5 wt% samples. The reduction in \( T_{\text{lum}} \) is attributed to greater solar absorption due to the increased VO₂ content. However, such thickness-transmission correlation was not observed in the IR range (780–2500 nm) at 20 °C, as the 400 μm size sample gives the highest IR transmission. This is
reflected by the trend in the IR contrast ($\Delta T_{IR}$), which increases with thickness up to 1000 µm. Enhanced $\Delta T_{IR}$ is correlated with higher $\Delta T_{sol}$ for both concentrations because large portions of $\Delta T_{sol}$ come from the IR contrast. $\Delta T_{sol}$ starts to decrease when the thickness increases to 1200 µm, and such thickness/performance correlation was predicted by Liu Chang et al., who suggested that a grid-design will enhance $\Delta T_{sol}$ up to a certain thickness before it becomes a static absorber with much reduced contrast. It is worth noting that the satellite peaks in the 1000 to 2500 nm range (Fig. 2f) are due to the pure Si–Al gel matrix as shown in Fig. S1 (ESI†).

**VO₂ concentration effect**

By fixing the distance $D$ to 1000 µm, the performance of different VO₂ content ranging from 0.125 to 0.5 wt% was investigated. The varying VO₂ content results in different solution properties, thereby changing the surface morphology of the patterned films. By changing the concentration from 0.25 wt% to the 0.5 wt%, as shown in Fig. 3a and b, we observe increasing aggregation of VO₂ towards the center, and the groove formed under the thread of the mesh starts to become more uniform and well defined. Fig. 3c and d illustrate the real samples prepared using the aforementioned concentrations. The 0.5 wt% sample appears darker than the 0.25 wt% sample, indicating the higher solid concentration.

As illustrated in Fig. 3e, the concentration has an inverse correlation with transmittance. Samples prepared with $D = 1000$ µm experience a drop in transmittance in the visible spectrum (380–780 nm) at both 20 °C and 90 °C as the
concentration increases. This corroborates with the observation that the average $T_{\text{film}}$ depreciates with rising concentration. The same trend is not observed in the IR spectrum (780–2500 nm) at $20\,^\circ\text{C}$, with the 0.25 wt% sample having a higher transmittance. This accounts for the highest $\Delta T_{\text{IR}}$ displayed by the 0.25 wt% sample, as $\Delta T_{\text{IR}}$ is the difference in transmittance in the IR range at the two temperatures. As $\Delta T_{\text{IR}}$ accounts for a large portion of solar contrast, higher $\Delta T_{\text{IR}}$ leads to higher $\Delta T_{\text{sol}}$, as observed in Fig. 3f for both distances $D$. The increasing trend in both $\Delta T_{\text{sol}}$ and $\Delta T_{\text{IR}}$ does not continue indefinitely. They both peak at 0.25 wt% concentration and decrease when the concentration is higher.\textsuperscript{31} This could be accounted for by excessive absorption in both states, which suggests that an optimal design requires one to avoid excessively concentrated dispersions.

**Effect of mesh periodicity**

The SEM image (Fig. 4a–c) shows that a smaller mesh opening size results in a smaller center crater size. Meanwhile, the groove under each mesh thread becomes more pronounced compared with a larger mesh opening. Fig. 4d–f illustrate the real samples prepared. The reduction in the mesh size results in less pronounced gridded structures on the surface of the films formed.

As shown in Fig. 4g, samples prepared with $D = 1000\,\mu\text{m}$ and a concentration of 0.5 wt% have higher transmittance in the
visible spectrum (380–780 nm) at both 20 and 90 °C when a smaller mesh periodicity is used, and this trend is consistent with the theoretical calculation. The 325 μm mesh sample produces inferior results even compared to continuous samples due to low transmittance in both the luminous and IR ranges in both states. Indeed, the highest average $T_{\text{lum}}$ is produced using a mesh opening of 55 μm. In contrast to $D_{T_{\text{lum}}}$, $D_{T_{\text{IR}}}$ is very sensitive to the change of mesh periodicity as shown in Fig. 4h, and the high $D_{T_{\text{IR}}}$ results in a corresponding change in $D_{T_{\text{sol}}}$. Compared with the continuous sample, both the 230 and 55 μm mesh samples show much higher transmittance over the entire spectrum in both states with higher average $T_{\text{lum}}$ and more importantly $D_{T_{\text{sol}}}$. It is interesting to note that the 230-mesh size sample can obtain $T_{\text{lum}}$ of 21.4% with a $D_{T_{\text{sol}}}$ as high as 17.2%. This exceeds the highest reported $D_{T_{\text{sol}}}$ of 16.5% coupled with a poor $T_{\text{lum}}$ of 10.5%, as predicted by theoretical calculation. This is due to the fact that the simulation is based on a perforated continuous VO$_2$ film while nanocomposite VO$_2$ is used in this project to form such a periodic gridded structure.

A similar trend is also observed in the 0.25 wt% samples (Fig. S2, ESI†). Both the 230 and 55 μm mesh samples show much higher transmittance over the entire spectrum in both states with higher average $T_{\text{lum}}$ compared with the continuous sample.

**Optimization of performance**

Previous discussions have established the importance of VO$_2$ concentration, thickness, and mesh size (periodicity) for the optical properties of the film. Generally, a higher concentration has been shown to increase the solar modulation ability due to the increased VO$_2$ content, albeit with the inevitable trade-off with luminous transmittance. Meanwhile, increasing the thickness further enhances $D_{T_{\text{sol}}}$ but only to a maximum thickness of $D = 1000$ μm, as further thickening would result in excessive absorption of incident rays and, therefore, degrade the performance. Finally, a smaller mesh size offers a significantly higher $T_{\text{lum}}$.

Therefore, we set $D$ to 1000 μm and prepared samples using 230 and 55 μm meshes since both were proven to offer better
Table 1 Optimized thermochromic properties with a fixed thickness (1000 μm) and concentration (0.25 wt%) with two different mesh sizes 230 and 55 μm

<table>
<thead>
<tr>
<th>Mesh (μm)</th>
<th>Ave. $T_{\text{lam}}$</th>
<th>$\Delta T_{\text{sol}}$</th>
<th>$T_{\text{lam}}$ (20 °C)</th>
<th>$T_{\text{lam}}$ (90 °C)</th>
<th>$\Delta T_{\text{lam}}$ (20 °C)</th>
<th>$T_{\text{ir}}$ (20 °C)</th>
<th>$T_{\text{ir}}$ (90 °C)</th>
<th>$\Delta T_{\text{ir}}$ (90 °C)</th>
<th>$T_{\text{sol}}$ (20 °C)</th>
<th>$T_{\text{sol}}$ (90 °C)</th>
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<tr>
<td>230</td>
<td>40.1</td>
<td>15.0</td>
<td>40.1</td>
<td>40.1</td>
<td>0.1</td>
<td>63.3</td>
<td>30.9</td>
<td>32.4</td>
<td>47.5</td>
<td>32.5</td>
</tr>
<tr>
<td>55</td>
<td>43.3</td>
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<td>44.4</td>
<td>42.2</td>
<td>2.2</td>
<td>64.0</td>
<td>32.2</td>
<td>29.8</td>
<td>48.9</td>
<td>34.0</td>
</tr>
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</table>

performance compared to continuous samples. The best results obtained were with 0.5 wt% and 0.25 wt% solutions. From the tabulated results (Table 1), the best combination of $T_{\text{lam}}$ and $\Delta T_{\text{sol}}$ is 43.3% and 14.9%, respectively. As shown in Fig. 5, this result is comparable to some of the best reported porous and antireflective multilayered structure results, and is significantly higher than that of biomimetic moth eyed VO$_2$. Compared with the theoretical results of nano-gridded VO$_2$, the current work can still improve its performance by further reducing its mesh periodicity.

Furthermore, two samples prepared with 0.5 wt% and 0.25 wt% dispersions were tested for their cycling stability. Samples were cycled between 20 °C and 90 °C using an oven for 40 cycles. The UV-Vis-NIR results (Fig. S3, ESI†) show stable performance in terms of $T_{\text{lam}}$ and $\Delta T_{\text{sol}}$.

Conclusion

In this report, a simple mesh printing method is employed to produce micro-patterned VO$_2$ films with different periodicities. Compared with continuous nanocomposite film samples, such a structure could enhance $T_{\text{lam}}$ due to the opening of the grid, and enables the formation of thicker samples that better capitalize on the additional VO$_2$ content for better $\Delta T_{\text{sol}}$. Compared with theoretical work based on a gridded thin film structure, this experimental work can achieve a $\Delta T_{\text{sol}}$ as high as 17.2%, which exceeds the calculated $\Delta T_{\text{sol}}$ of 16.5%, and an even higher $T_{\text{lam}}$ (experimental 21.4% versus theoretical 10.5%). This is mainly due to the integration of a gridded structure and nanocomposite VO$_2$. The best performing sample gives 43.3% $T_{\text{lam}}$ and 14.9% $\Delta T_{\text{sol}}$, which are comparable to most approaches used to enhance thermochromic properties. The facile fabrication method and novel micro-patterned structures open a new and promising direction of VO$_2$ thermochromic materials for smart window applications.

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