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2020

Zhou, C., Li, D., Tan, Y., Ke, Y., Wang, S., Zhou, Y., . . . Long, Y. (2020). 3D printed smart windows for adaptive solar modulations. *Advanced Optical Materials*, 8(11), 2000013-. doi:10.1002/adom.202000013

<https://hdl.handle.net/10356/141502>

<https://doi.org/10.1002/adom.202000013>

This is the peer reviewed version of the following article: Zhou, C., Li, D., Tan, Y., Ke, Y., Wang, S., Zhou, Y., . . . Long, Y. (2020). 3D printed smart windows for adaptive solar modulations. *Advanced Optical Materials*, xxx, 2000013-, which has been published in final form at <http://doi.org/10.1002/adom.202000013>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions.

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3D Printed Smart Windows for Adaptive Solar Modulations

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Vanadium dioxide (VO_2) based thermochromic smart window is considered as the most promising approach for economizing building energy consumption. However, the high phase transition temperature (τ_c), low luminous transmission (T_{lum}), and solar modulation (ΔT_{sol}) impose an invertible challenge for commercialization. Currently, smart window research surprisingly assumes that the sunlight radiates in one direction which is obviously not valid as most regions receive solar radiation at various angles in different seasons. For the first time, solar elevation angle is considered and 3D printing technology is employed to fabricate tilted microstructures for modulating solar transmission dynamically. To maximize energy-saving performance, the architecture of the structures (tilt, thickness, spacing, and width) and tungsten (W) doped VO_2 can be custom-designed according to the solar elevation angle variation at the midday between seasons and tackle the issue of compromised T_{lum} and ΔT_{sol} with W-doping. The energy consumption simulations in different cities prove the efficiency of such dynamic modulation. This first attempt to adaptively regulate the solar modulation by considering the solar elevation angle together with one of the best reported thermochromic properties ($\tau_c = 40^\circ\text{C}$, $T_{\text{lum(average)}} = 40.8\%$, $\Delta T_{\text{sol}} = 23.3\%$) may open a new era of real-world-scenario smart window research.

1. Introduction

Due to the rapid development of modern society and growth of global population, the energy consumption has been increasing dramatically. Among all the energy consumed, the building energy usage alarmingly contributes a major portion, which is up to 40% of the entire energy requirement.^[1] While for the energy consumed by the buildings, approximately half of it is used up for the services and maintenances, especially the heating, ventilation and air conditioning (HVAC) system. As a result, reducing the energy consumption of the HVAC system becomes one of the most practicable solutions to lower the energy usage globally.^[2,3] In order to achieve such objective, windows modification and transformation have always attracted the most attention as windows are considered as the least energy-efficient units of all building envelopes as heat is always transferred in the unfavorably opposite direction.

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DOI: 10.1002/adom.202000013

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Smart windows have been brought up as a reliable method to economize the building energy consumption due to their abilities to modulate the solar transmittance going through the windows “smartly” depending on the stimulations.^[4–6] Smart windows are categorized as electrochromic smart window, photochromic smart window, mechanochromic and thermochromic smart window, based on the different stimulation sources as summarized in recent review.^[7] Thermochromic smart windows are usually considered as a promising technology due to passive response, rational stimulus, easy fabrication, simple configuration and cost-effective materials.^[8–11]

Vanadium dioxide (VO_2), the most studied thermochromic material, undergoes a metal-to-insulator (MIT) phase transition at the critical temperature, τ_c (68 °C), which is accompanied with a huge transmittance contrast at the near-infrared (NIR) range with relatively unchanged luminous transmission (T_{lum}).^[12–14] Nevertheless, due to its intrinsic physical properties, the application of VO_2 on energy-saving smart window still faces one major challenge which is to reduce τ_c while maintaining both high luminous transmission (T_{lum}) and the solar modulation ability (ΔT_{sol}) simultaneously.^[15] Various approaches have been applied to address this issue including but not limited to doping,^[16–20] antireflection coating,^[21–23] biomimetic structuring,^[24–26] compositing,^[27–31] photonic structuring,^[32,33] kirigami-inspired structuring.^[34] However, the usual trade-off relationship between these three major index τ_c , ΔT_{sol} , and T_{lum} is often observed, especially for doping techniques.^[16–20]

However, so far all researches assume the static vertical solar transmission, ignoring the fact that solar radiation is a dynamic process due to the rotation of the earth and its revolution around the sun. The solar radiation intensity is heavily depended on the latitude of the sun, known as solar elevation angle, which is the angle between the sun’s disc and the horizon.^[35,36] Since the solar radiation intensity reaches the maximum at the midday (11 a.m. to 1 p.m.) and significantly overrides the early morning and late afternoon,^[37] only the solar elevation angles at the midday are considered in this project. From June to December, the declination of the sun moves from the Tropic of Cancer to the Tropic of Capricorn and moves back from December to June of the next year, which leads to a large solar elevation angle variation between summer and winter for a specific location. For example, in the places located around the Tropic of Cancer, the solar elevation angle difference reaches as large as 45°. Therefore, measurements with the incident light perpendicular to the solar modulation devices at low and high temperatures may not be able to reflect the actual solar modulation ability precisely, especially for the location with distinct four seasons. Meanwhile, by taking advantage of the dynamic feature of solar radiation, enhanced solar modulation ability may be achieved as well as reasonable transmittance of visible light. (Scheme 1).

Herein, we, for the first time, developed a custom-designed tilted 1D grating-shape composite structure of polymer and VO_2/W -doped VO_2 nanoparticles on glass substrates targeting

Scheme 1. a) Schematic diagram of the 3D printing process for the structured composite targeting solar modulation. b) Schematic diagram of the solar modulation mechanism for the 3D-printed composite structures together with the side-view pictures and the top-view pictures. In wintertime, some of the solar radiation transits through the gaps between every two composite structures, leading to a relatively high T_{lum} . In summertime, before transmitting indoors, the solar radiation passes through the composite structures with the longest path length, resulting in superior solar modulation ability.

the real scenario applications in different latitude cites. By using the 3D printing technology (digital light processing 3D printing, DLP) (Scheme 1b) the tilted angle of the composite structures can be controlled according to the real solar elevation angle difference between hot and cold seasons. As schematically demonstrated in the Scheme 1a, while considering the windows are placed parallel to the ground surface, in summertime, solar radiation is perpendicular to the tilted structures so that the majority of solar transmission will be absorbed due to the NIR blocking effect of metallic VO₂ at high temperature and high effective blocking volume. However, in winter-time, solar transmission will be largely enhanced due to the parallel solar irradiation to the tilted surface which effectively reduces the blocking volume together with the NIR transparency characteristic of insulating VO₂. In this project, the tilted angle was designed according to a location around the Tropic of Cancer. We need to emphasize that because of the elegance and flexibility of 3D printing technique, customized design can be made up for various latitudes, window facings and real temperature conditions. Both pure VO₂ nanoparticles and tungsten (W) doped VO₂ nanoparticles were applied for producing the

solar modulation composite structures. Compared with flat surface, the structured composite can offer much enhanced thermochromic performance: for VO₂ samples, the T_{lum} increases from 34.4% to 43.3% and ΔT_{sol} increasing from 8.4% to 25.8%; more importantly, for W-doped VO₂ samples, ΔT_{sol} increases from 2.1% to 23.3% and this tackles the invertible challenge of often compromised thermochromic performance in W-doped VO₂, which paves a way to real-world applications.

2. Results and Discussion

For the flat films, the incident light was directed perpendicular to the windows (Figure 1a). VO₂ nanoparticles size ranging from 80 to 120 nm were used to form a continuous film together with SR-9035 monomers and the transmission electron microscopic (TEM) mapping and high-resolution imaging (Figure S1, Supporting Information and Figure 1a) together with the X-ray diffractometric (XRD) pattern (Figure S2, Supporting Information) suggest the pure phase of VO₂ and good crystallinity. As observed in Figure S1d in the Supporting Information, the

Figure 1. a) Schematic illustration of the conventional approach with vertical incident light for transmittance measurement on flat films. The insert is the TEM picture of the VO₂ nanoparticles. b) UV-vis-NIR transmittance spectrum of the flat polymer-VO₂ composite films with 200 μm thickness and various VO₂ concentration varying from 0.5 to 2.0 wt% at both high and low temperatures. c) T_{lum} and ΔT_{sol} diagram of the flat polymer-VO₂ composite films with 1.5 wt% VO₂ concentration and different film thickness varying from 200 to 800 μm. d) T_{lum} and ΔT_{sol} diagram of the flat polymer-VO₂ composite films with 1.5 wt% VO₂ concentration and different film thickness varying from 200 to 800 μm. e) Schematic illustration of the transmittance measurement approach for the structured polymer-VO₂ composite. The angle of the incident light is labeled according to the angle between light source and the tilted surface of the structures as the simulation of various solar elevations at the midday for different seasons. The dimensional parameters of the structured polymer-VO₂ composite are defined as labeled, including width, thickness, and spacing. f) UV-vis-NIR transmittance spectrum of the 3D printed composite structures of 45° tilted angle, 200 μm spacing (S) and 400 μm thickness (T) with 0° incident light at 20 °C and 45° incident light at 90 °C together with the flat polymer-VO₂ composite film with identical thickness and VO₂ concentration at high and low temperatures, respectively. g) Simulated UV-vis-NIR transmittance spectrum of the structured VO₂-polymer composite and flat VO₂-polymer composite film with the identical dimensions as (f) at both high and low temperatures.

d spacing between every two planes is 0.21 nm. The scanning electron microscopic (SEM) images of the VO₂ nanoparticles distribution of the VO₂-polymer composite and the single particles are shown in Figure S3 in the Supporting Information. As shown in Figure S4 in the Supporting Information, which is the transmittance spectrum of the same sample measured with and without the integration sphere, the calculated T_{lum} (30.6% vs 30.0%) and T_{IR} (55.5% vs 53.0%) between the measurements with and without the integration sphere suggest that no obvious scattering effect has been observed and the major reason could be due to the low volume ratio of VO₂ nanoparticles, which is less than 0.4%.^[38] Flat VO₂-polymer composite films of 200 μ m thickness were fabricated with the VO₂ concentration ranging from 0.5 to 2.0 wt%. The transmittance spectrum of both high and low temperatures of these films are shown in Figure 1b. The calculation suggests that when the VO₂ concentration is increased from 0.5 to 2.0 wt%, a significant reduction of T_{lum} can be observed from 73.6% to 22.2% (Figure 1c). The maximum ΔT_{sol} of 7.7% is achieved at the concentration of 1.5 wt% followed with a decrease of ΔT_{sol} for further increasing concentration. This is because of the intrinsic thermochromism property limits, the turning point of VO₂, which is defined as the point where effective modulating volume loses its effect on ΔT_{sol} .^[39] Since the most promising combination of T_{lum} and ΔT_{sol} was obtained at the concentration of 1.5 wt%, flat films with various thicknesses ranging from 200 to 800 μ m (the temperature-dependent transmission spectrum are shown in Figure S5 in the Supporting Information) were printed to further enhance the solar modulation performance. While the thickness increases from 200 to 400 μ m, ΔT_{sol} is increased from 7.7% to 8.4% with negligible variation of T_{lum} and continued increase of thickness jeopardizes the ΔT_{sol} with a similar effect as the concentrations (Figure 1d).

To overcome this intrinsic issue of VO₂, by fixing the concentration of 1.5 wt%, 400 μ m thickens and 45° tilted angle, a structured VO₂-polymer composite with 200 μ m spacing and 200 μ m width was designed and printed. As shown in Figure 1e, while determining the solar modulation ability of the tilted composite structure, the incident light source was placed at 0° and 45° with respect to the tilted surface to simulate the wintertime and summertime, respectively. The transmittance spectrum of the abovementioned composite structures with the incident light at 0° and 20 °C and the incident light at 45° and 90 °C are shown in Figure 1f. In contrast to flat VO₂-polymer composite film with the same concentration and thickness, a large contrast occurred in both visible and IR ranges. Thereby ΔT_{sol} has been improved significantly from 8.4% to 21.3%. Meanwhile, because of the gaps between each two structures, the proportion of the visible light can pass through especially in the wintertime has been enhanced, where $T_{lum(winter)}$ is increased from 36.1% to 51.0%, $T_{lum(summer)}$ is increased from 32.8% to 33.1% and $T_{lum(average)}$ is increased from 34.5% to 42.0%. As a result, compared with the thermochromism performance of flat films, such structured VO₂-polymer composite is more applicable for real-world sceneries. We further verified this conclusion by finite-different time-domain (FDTD, Lumerical Solutions, Inc.) simulations. First an unconstrained formulation of the nonlinear programming model implemented by the software PUMA was conducted to estimate the reflective index (n) and

absorption coefficient (k) of the VO₂-polymer composite film at 20 and 90 °C, which are shown in Figures S6 and S7 in the Supporting Information, respectively. The transmittance of VO₂-polymer composite thin film and structured VO₂-polymer composite with the incident light at 0° and 20 °C and the incident light at 45° and 90 °C are calculated by FDTD (Figure 1g). It can be observed that the experimental results match well with the theoretical simulation, especially for the flat VO₂-polymer composite film. For the structured VO₂-polymer composite, $T_{lum(average)}$ and ΔT_{sol} are 24.6% and 46.3% according to the simulation, resulting in an increase of 4.3% and 3.3% for each one of them compared with the experimental results. This discrepancy could be due to the morphology variation from the designed structure, which will be elaborated more in the next section. Those initial results suggest the significant potential of the precisely designed tilted composite structures to largely enhance the thermochromics properties in real-world applications.

To further reinforce the solar modulation ability and transparency of visible light for the printed VO₂-polymer composite structures of 1.5 wt% concentration, studies have been done systematically through varying the three parameters, thickness, spacing, and width. Each one of them is modified from 200 to 800 μ m while maintaining the rest as a constant of 200 μ m. The optical cross-sectional images of the printed composite structures with the variation of thickness, spacing, and width are shown in Figure 2a–c, respectively. The corresponding calculated T_{lum} and ΔT_{sol} (solar transmittance difference between 0° incident angle at 20 °C and 45° incident angle at 90 °C are shown in Figure 2d,e and the detailed information are shown in Tables S1–S3 in the Supporting Information, respectively. Meanwhile, the related transmittance spectrums are shown in Figures S8–S10 in the Supporting Information. For the thickness variation from 200 to 800 μ m (Figure 2d), T_{lum} drops from 43.3% to 28.9% since more visible light is blocked by the increasing structure thickness together with the loss of printing precision; while ΔT_{sol} drops from 25.8% to 10.3% due to the intrinsic limit of VO₂, the turning point issue. It can be observed in Figure 2a, with increasing thickness, the bottom in the trench could not be printed and the spacing in between is filled with continuous films; such loss of precision in printing is more severe for 600 and 800 μ m samples. This is due to the intrinsic drawback of 3D printing which limits its application in high aspect ratio trench structures.

While the spacing increases from 200 to 800 μ m, since less proportion is covered with the effective composite structures, T_{lum} increases from 43.3% to 60.2%, but ΔT_{sol} decreases from 25.8% to 12.2%. For the variation of width from 200 to 800 μ m, a trend which is similar to the thickness is observed (Figure 2f). The increased coverage portion of the composite structure leads to a decrease of T_{lum} from 43.3% to 29.1% and a decrease of ΔT_{sol} from 25.8% to 15.1%. It is worth noting that with increasing width, the printing resolution is lost. Therefore, by tuning the thickness, spacing and width of the printed composite structures, it can be determined that among all of the printed samples, the best thermochromism properties is achieved by the one with 200 μ m thickness, 200 μ m spacing and 200 μ m width, where $T_{lum} = 43.3\%$ and $\Delta T_{sol} = 25.8\%$. The large solar transmittance contrast is mainly due to the 1:1 ratio

Figure 2. a) Optical microscopic pictures of the printed composite structures with identical 0° tilted angle, 200 μm spacing, 200 μm width but different thicknesses, ranging from 200 to 800 μm . b) Optical microscopic pictures of the printed composite structures with identical 0° tilted angle, 200 μm width, 200 μm thickness but different spacing, ranging from 200 to 800 μm . c) Optical microscopic pictures of the printed composite structures with identical 0° tilted angle, 200 μm thickness, 200 μm spacing but different width, ranging from 200 to 800 μm . d) $T_{\text{lum}}(\text{avg})$, $T_{\text{lum}}(0^\circ\text{--}20^\circ\text{C})$, $T_{\text{lum}}(45^\circ\text{--}90^\circ\text{C})$, ΔT_{sol} and ΔT_{IR} diagram of the printed composite structures with identical 200 μm thickness, 200 μm width but different thickness ranging from 200 to 800 μm . e) $T_{\text{lum}}(\text{avg})$, $T_{\text{lum}}(0^\circ\text{--}20^\circ\text{C})$, $T_{\text{lum}}(45^\circ\text{--}90^\circ\text{C})$, ΔT_{sol} and ΔT_{IR} diagram of the printed composite structures with identical 200 μm thickness, 200 μm width but different spacing ranging from 200 to 800 μm . f) $T_{\text{lum}}(\text{avg})$, $T_{\text{lum}}(0^\circ\text{--}20^\circ\text{C})$, $T_{\text{lum}}(45^\circ\text{--}90^\circ\text{C})$, ΔT_{sol} and ΔT_{IR} diagram of the printed composite structures with identical 200 μm thickness, 200 μm spacing but different width ranging from 200 to 800 μm .

between spacing and width which could effectively block the solar incidence at 45° and provide the high printing quality. Compared with the other printed samples, it gives the largest coverage percentage difference while the incident light source comes from 0° and 45°, respectively. Moreover, the relatively small thickness of 200 μm contributes to the high T_{lum} as well.

In addition, to identify the effectiveness of the polymer matrix and VO_2 nanoparticles, pure polymer matrix structures with 200 μm thickness, 200 μm spacing, 200 μm width, and 45° tilting angle were printed and the transmittance spectrum was measured with the incident angle at 0°, 15°, 30°, and 45°, respectively (Figure 3a). The inset shows the photo taken at 0°, which indicates the high transparency of the matrix material. The solar transmission of pure polymer matrix is barely dependent on the incident angle. By adding 1.5 wt% VO_2 concentration into the matrix with the identical size and tilted angle, the transmittance spectrum for the 0° incident angle at the room temperature of 20 °C and the incident angle of 0°, 15°, 30°, and 45° at high temperature of 90 °C were measured, respectively (Figure 3b). The corresponding T_{lum} , ΔT_{IR} , and ΔT_{sol} are calculated and shown in Figure 3c, where the solar transmittance at 20 °C with 0° incident angle is assigned as the baseline, meanwhile the detailed information is shown in Table S4 in the Supporting Information. While the incident angle is increased from 0° to 45°, ΔT_{sol} increases together with the incident angle from 9.7% to 25.8% but a relatively smooth variation of T_{lum} is observed from 52.8% to 43.30%. It simulates the solar modulation process from winter to summer. In the

wintertime, only minimal solar radiation is blocked by the layer of composite material and most of the solar light is allowed to pass through and maintaining a relatively high luminous level. Whereas, during the summertime, due to the significant increase of ΔT_{sol} from 9.7% to 25.7%, the heat absorbed by the indoor environment from the sunshine is dramatically reduced while retaining a reasonable luminous level of 43.3%. Furthermore, because of the large solar modulation ability contrast between summer and wintertime, such composite structures conform even better with the requirements of energy-saving smart window targeting daily applications. Additionally, structured composite with various tilted angles was printed and the microscopic pictures are shown in Figure 3d. It implies the capability and flexibility of the 3D printed structures for customized fabrication depending on different requirements or latitudes. However, as can be observed, with increasing tilting angle, more trenches are filled and less resolution are achieved with such printing techniques.

Due to the high τ_c of the pure VO_2 nanoparticles, W-doped VO_2 nanoparticles are applied for the composite fabrication as well. The XRD pattern of W-doped VO_2 nanoparticles (Figure S11, Supporting Information) and the TEM mapping images (Figure 3e,f) identify the composition and purity. As confirmed by the energy-dispersive X-ray spectroscopy (EDX) measurement (Figure S12, Supporting Information), the W dopant concentration is around 2 wt%. Additionally, the high magnification TEM picture (Figure 3g) suggests that the particle size of W-doped VO_2 ranges from 60 to 120 nm.

Figure 3. a) UV-vis-NIR transmittance spectrum of the printed pure polymer structures with 45° tilted angle, 200 μm thickness, 200 μm spacing, 200 μm width but different angles of the incident light, varying from 0° to 45°. The insert is the pictures of the polymer structures with 0° tilting angle and 45° tilting angle. b) UV-vis-NIR transmittance spectrum of the printed VO₂-polymer composite structures with 1.5 wt% VO₂ concentration, 45° tilted angle, 200 μm thickness, 200 μm spacing, 200 μm width but different angles of the incident light, varying from 0° to 45°. For 0° incident angle, measurements are conducted at both 20 and 90 °C. For 15°, 30°, and 45° incident angle, measurements are conducted at 90 °C. c) T_{lum} , ΔT_{sol} and ΔT_{IR} diagram of the printed composite structures with identical 200 μm thickness, 200 μm spacing, 200 μm width and 1.5 wt% VO₂ concentration, while the incident angle varies from 0° to 45°. d) Optical microscopic pictures of the printed composite structures with identical 200 μm thickness, 200 μm spacing, 200 μm width, 1.5 wt% VO₂ concentration but different tilted angle, ranging from 0° to 45°. e) TEM image of the W-doped VO₂ nanoparticles. f) TEM mapping image of W-doped VO₂ nanoparticles, V K α 1 and TEM mapping image of W-doped VO₂ nanoparticles, W K α 1. g) High resolution TEM image of the W-doped VO₂ nanoparticles. h) Normalized transmittance at 2000 nm as a function of temperature for the VO₂-polymer composite structures and the W-doped VO₂-polymer composite structures, respectively. i) UV-vis-NIR transmittance spectrum of the printed W-doped VO₂-polymer composite structures with 1.5 wt% W-doped VO₂ concentration, 45° tilted angle, 200 μm thickness, 200 μm spacing, 200 μm width but different angles of the incident light, varying from 0° to 45°. For 0° incident angle, measurements are conducted at both 20 and 60 °C. For 15°, 30° and 45° incident angle, measurements are conducted at 60 °C. j) T_{lum} , ΔT_{sol} , and ΔT_{IR} diagram of the printed composite structures with identical 200 μm thickness, 200 μm spacing, 200 μm width and 1.5 wt% VO₂ concentration, while the incident angle varies from 0° to 45°.

The hysteresis curves of both VO₂ and W-doped VO₂ nanoparticles are shown in Figure 3h and the transmittance at 20 °C is normalized to 100%. The calculated τ_c of the VO₂ and W-doped VO₂ are 68 and 40 °C, respectively. Meanwhile, W-doped VO₂-polymer composite structures of 1.5 wt% concentration with 200 μ m thickness, 200 μ m spacing, 200 μ m width and 45° tilting angle are printed and the transmittance measurements were performed under the conditions that for the incident angle of 0° at the room temperature of 20 °C and the incident angle of 0°, 15°, 30°, and 45° at high temperature of 60 °C (Figure 3i). While the incident angle is varied from 0° to 45°, a sharp increase of ΔT_{sol} from 4.8% to 23.3% and a slight drop of T_{lum} from 40.8% to 32.3% are observed, respectively (Figure 3j), detailed information is shown in Table S5 in the Supporting Information. The commonly and severely compromised thermochromic properties due to the W dopant^[4] can be resolved with such design. We have assumed a device with constant metallic state without phase transition with 200 μ m thickness, 200 μ m spacing, 200 μ m width and 45° tilted angle, and the simulated results are shown in Figure S13 in the Supporting Information, where $\Delta T_{sol} = 14.3\%$, $T_{lum(average)} = 26.5\%$ and $\Delta T_{IR} = 14.7\%$ are calculated. Compared with the system with phase transition with $\Delta T_{sol} = 23.3\%$, $T_{lum(average)} = 40.3\%$ and $\Delta T_{IR} = 22.4\%$, the thermochromic properties could be enhanced by such simple structuring. Furthermore, it can be observed that the small transmittance difference for 0° incident angle data at high and low temperatures could be dramatically enhanced by tilting.

A comparison has been conducted with the selected works of best-reported VO₂ and elemental doping VO₂ devices with the similar critical temperature regarding the thermochromism performances. For the pure VO₂ samples, the solar modulation ability of VO₂-polymer composite structure stands out from all the other reported data with a ΔT_{sol} of 25.8% and a competitive $T_{lum} = 43.3\%$.^[4,7] As for the W-doped VO₂ samples, the ΔT_{sol} of 23.3% outperforms all the previous reported results as shown in Figure 4a, where the previously reported data were categorized depending on the doping elements.^[40–50] Since it is always a trading-off relationship between T_{lum} and ΔT_{sol} , compared with the other reported performance, our W-doped VO₂-polymer composite sample gives one of the most promising combinations of $T_{lum} = 40.8\%$ and $\Delta T_{sol} = 23.3\%$.

To demonstrate the actual energy-saving performance of such structured W-doped VO₂ thermochromic smart window, a simulation of the annual energy consumption is performed for various cities including Athens, Guangzhou and Miami, which locates near the Tropic of Cancer in Europe, Asia and America, thereby having similar solar incident angle difference between winter and summer. Four windows are adopted to evaluate the performance, including double glazed glass, low-e glass (IGDB 2191), flat W-doped VO₂ composite film (1.5 wt%, 200 μ m thickness) and structured W-doped VO₂ composite (1.5 wt%, 200 μ m thickness, 200 μ m spacing, and 200 μ m width) (Figure 4b). The UV-vis-NIR spectrums of the flat W-doped VO₂ composites of 1.5 wt% concentration but various thicknesses, ranging from 200 to 800 μ m are shown in Figure S14 in the Supporting Information. In all three cities, compared with the benchmark of the double glazed glass and low-e glass, both thermochromic smart windows give better

energy saving, while the structured window gives the best performance among all four windows. Such phenomenon is more pronounced in Miami, compared with the double-glazed glass, by applying the structured W-doped VO₂ composite smart window, over 20% of the energy consumption can be saved annually, which is significant considering the huge amount of building energy consumption each year. Moreover, taking the energy-saving capability in Guangzhou as an example, compared with the flat W-doped VO₂ composite film, performance enhancement of 13.8 % is achieved due to such unique design. According to the monthly energy consumption diagram of all three cities (Figure 4c–e), the gap between the double-glazed glass and the structure W-doped VO₂ composite reaches the maximum in summer, which indicates that the energy usage for cooling can be dramatically reduced by the application of the as-designed smart window. Additionally, to further study the energy-saving related properties, the solar heat gain coefficient (SHGC) of the abovementioned windows is derived and shown in Figure S15 in the Supporting Information. For SHGC, the structured W-doped VO₂ composite has the lower SHGC than that of the flat W-doped VO₂ composite at the same temperature. However, at the high temperature of 90 °C, the SHGCs of both smart windows decline due to the reduction of solar transmittance at high temperature. According to the SHGC results, it is determined that both the smart windows have better energy saving potential compared to the double-glazed glass window. Furthermore, the structured W-doped VO₂ composite window has better performance than that of the flat one because it takes the solar incident angle into account.

While assigning the double clear glass as the baseline, the energy conservation ability of the low-e glass (IGDB 2191), flat W-VO₂ composite and structured W-VO₂ composite at the three cities are shown in Figure 4f–h. Compared with the conventional energy-saving low-e glass, the structured W-VO₂ composite surpasses for over 1000% regarding the energy conservation ability in all three cities, especially in the summertime. Moreover, comparisons have been done between the flat W-doped VO₂ composite smart window and the structure W-doped VO₂ composite smart window. Regarding the energy conservation ability, average performance enhancement of 23.4%, 22.5%, and 22.7% have been achieved during the summertime in Athens, Guangzhou, and Miami, respectively, which indicates the advantage of such structures with unique design. Both the simulation and comparison have illustrated the great potential for the application of the VO₂/W-doped VO₂ structured composite smart window targeting energy saving.

3. Conclusion

For the first time, the variation of solar elevation angle in different seasons has been taken into consideration for the energy-saving smart window applications. By integrating the flexibility of 3D printing and the diversity of solar elevation angle in structure design, superior thermochromism performances have been achieved, where $T_{lum} = 43.3\%$, $\Delta T_{sol} = 25.8\%$ for VO₂ samples and $T_{lum} = 40.8\%$ and $\Delta T_{sol} = 23.3\%$ for W-doped VO₂ samples, which outperform the previously reported results. The optical response confirmed by physical

Figure 4. a) Comparison of thermochromism performances (τ_c , T_{lum} , and ΔT_{sol}) between the best-reported and selected works and the tilted VO₂ and W-doped VO₂ composite structures. b) Annual energy consumption of the double clear glass, low-e glass (IGDB 2191), flat W-doped VO₂ composite and structured W-doped VO₂ composite at various cities including Athens, Guangzhou and Miami. c) Monthly energy consumption of the double clear glass, low-e glass (IGDB 2191), flat W-doped VO₂ composite and structured W-doped VO₂ composite in Athens. d) Monthly energy consumption of the double clear glass, low-e glass (IGDB 2191), flat W-doped VO₂ composite and structured W-doped VO₂ composite in Guangzhou. e) Monthly energy consumption of the double clear glass, low-e glass (IGDB 2191), flat W-doped VO₂ composite and structured W-doped VO₂ composite in Miami. f) Monthly energy conservation of the low-e glass (IGDB 2191), flat W-doped VO₂ composite and structured W-doped VO₂ composite in Athens while using the double clear glass as the baseline. g) Monthly energy conservation of the low-e glass (IGDB 2191), flat W-doped VO₂ composite and structured W-doped VO₂ composite in Guangzhou while using the double clear glass as the baseline. h) Monthly energy conservation of the low-e glass (IGDB 2191), flat W-doped VO₂ composite and structured W-doped VO₂ composite in Miami while using the double clear glass as the baseline.

simulation and the actual energy-saving performance in three cities confirms the efficiency of the new concept. The 3D printing technology offers customized designs which are feasible for various application requirements considering the different location latitudes, facing and weather conditions. The idea of combining the concept of solar elevation angle and 3D printing technology with conventional thermochromic material, VO₂, starts a new phase for energy-saving smart window in real-word applications.

4. Experimental Section

Materials and Equipment: VO₂ nanoparticles and W-doped VO₂ nanoparticles (Ji-cheng, China), ethanol absolute (99.9%, Merck), monomer solution SR-9035 (Sartomer, France), and photoinitiator

diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide (TPO) (Sigma Aldrich, US) were used for the fabrication of the composite. All chemicals were used as received without any further purification.

Preparation of Printing Formulation and 3D Printing: SR-9035 was mixed with TPO with the weight ratio of 1:0.015. VO₂/W-doped VO₂ nanoparticles were dispersed in ethanol absolute ultrasonically. The concentration of VO₂/W-doped VO₂ nanoparticles was 5 wt%. An appropriate amount of the well-dispersed VO₂/W-doped VO₂-ethanol absolute solution was added with the SR-9035-TPO mixture depending on the desired VO₂/W-doped VO₂ concentration. Then the solution was left for stirring for 24 h for homogeneous mixing and the evaporation of the ethanol. Before printing, the glass substrates were washed with acetone followed by deionized (DI) water ultrasonically for 15 min each. Both the composite structures and flat composite films were printed using a DLP 3D printer (Asiga Pico 2, Australia). The printing parameters are provided in Table S6 in the Supporting Information. A schematic demonstration of the printing process is shown in Scheme 1b.

After printing, the printed objects were washed with isopropyl alcohol to remove the unpolymerized residues.

Characterization: The morphology and shape of the printed composite structures were observed using the optical microscope (Olympus SZ61, Olympus, Japan). The crystal morphology and composition of the VO₂/W-doped VO₂ nanoparticles were observed using a TEM (JOEL JEM2010, US) at an accelerating voltage of 200 kV. The VO₂ nanoparticle distribution of the VO₂-polymer composite was observed with a field-emission SEM (JEOL JSM-7600F) at an accelerating voltage of 5 kV. The composition characterization of the VO₂ and W-doped VO₂ powders was performed using an XRD (Bruker D8 Advance XRD, Bruker, US). The transmittance spectra were measured with the UV-vis-NIR spectrophotometer system equipped with the integration sphere (AvaSpec-ULS2048L StarLine Versatile Fiber-optic Spectrometer and AvaSpec-NIR256-2.5-HSC-EVO, Avantes, Netherlands). A heating and cooling stage (PE1200, Linkam, UK) was attached to the spectrophotometer.

The calculation of the integrated luminous transmittance T_{lum} (380–780 nm) and solar transmittance T_{sol} (250–2500 nm) is done by using Equation (1)

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

where $T(\lambda)$ representing spectral transmittance, $\phi_{lum}(\lambda)$ is the standard luminous efficiency function of photopic vision in the wavelength range of 380–780 nm, and $\phi_{sol}(\lambda)$ is the solar irradiance spectrum distribution for air mass 1.5 (corresponding to the sun standing 37° above the horizon with 1.5 atmosphere thickness and the presence of a solar zenith angle of 48.2°).^[51] As for the calculation of $\Delta T_{lum/sol/IR}$, it is calculated by $\Delta T_{lum/sol/IR} = T_{lum/sol/IR}(\text{low temperature}) - T_{lum/sol/IR}(\text{high temperature})$.

The calculation of the structured composite (with gratings) coating varies from above calculation. $\Delta T_{lum/sol/IR} = T_{lum/sol/IR}(\text{low temperature}) - T_{lum/sol/IR}(\text{high temperature})$ (nonvertical transmission) – $T_{lum/sol/IR}(\text{high temperature})$ (vertical transmission)

Simulation: The optical constants (refractive index and absorption coefficient) of both flat and structured VO₂-polymer composite films at low and high temperature were estimated through PUMA from the one-film system by using experimental transmittance data.^[52,53] The PUMA software is freely available from the PUMA Project web page (<https://www.ime.usp.br/~egbirgin/puma/#related>). A 2D FDTD (Lumerical Solutions, Inc.) method was used to calculate transmittance of the VO₂-polymer composite thin film and tilted VO₂-polymer composite structure at low and high temperature. For details of simulation methods, refer to the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The principal investigator of this project (Y.L.) wishes to thank National Research Foundation, Prime Minister's Office, Singapore, under its Campus for Research Excellence and Technological Enterprise (CREATE) program, the Singapore Ministry of Education (MOE) Academic Research Fund Tier one RG200/17, and the Sino-Singapore International Joint Research Institute for the funding support. The computational work for this article was partially performed on resources of the National Supercomputing Center, Singapore.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

C.Z. and D.L. contributed equally to this work. Y.L. designed and proposed the manuscript. C.Z. performed most of the experiments and drafted the manuscript. D.L. and S.L., conducted the FDTD simulation. Y.T. and J.P. conducted the building energy consumption simulation. Y.L. revised the manuscript. All authors checked the manuscript.

Keywords

3D printing, energy-saving, smart windows, thermochromic, vanadium dioxide

Received: January 2, 2020

Revised: February 6, 2020

Published online:

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