VO₂ thermochromic smart window for energy savings and generation

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The ability to achieve energy saving in architectures and optimal solar energy utilisation affects the sustainable development of the human race. Traditional smart windows and solar cells cannot be combined into one device for energy saving and electricity generation. A VO₂ film can respond to the environmental temperature to intelligently regulate infrared transmittance while maintaining visible transparency, and can be applied as a thermochromic smart window. Herein, we report for the first time a novel VO₂-based smart window that partially utilises light scattering to solar cells around the glass panel for electricity generation. This smart window combines energy-saving and generation in one device, and offers potential to intelligently regulate and utilise solar radiation in an efficient manner.

Most efforts to efficiently utilise solar energy have been focused on improving the efficiency in the conversion and storage using solar cells¹–⁷ and large capacity batteries⁸, respectively. However, these cells, which have been used on housetops and wall periphery, could not be integrated into windows that require the material to be transparent. Traditionally designed energy-saving windows, such as electrochromic, thermochromic, and gasochromic, typically function by exterior stimuli involving either an electric field, heat stimulus or a gas⁹. It is not possible to alter the optical performance, which involves intelligently passing or blocking solar energy in response to environmental changes, and simultaneously generate electricity¹⁰,¹¹. Herein, a novel smart window was designed such that the VO₂ films or particles regulate solar infrared radiation and scatter partial light to a solar cell for electricity generation.

It is known that VO₂ undergoes a fully reversible metal-semiconductor transition (MST) at a critical temperature (Tc) of 68 °C¹². Below Tc (T<Tc), VO₂ is a monoclinic crystalline structure, which is insulating and transparent to infrared light, but it becomes a tetragonal crystalline structure that is metallic and reflective to infrared light above Tc (T>Tc)¹³,¹⁴. This phase transition property makes VO₂ an attractive material for smart windows¹⁵. Current research efforts have been primarily focused on enhancing the optical properties of VO₂ films (e.g., the improvement of the solar energy modulation ability and visible transmittance of VO₂ using multi-layered structures by designing high-reflective-index dielectric top or under layers (i.e., SiO₂/VO₂¹⁶,¹⁷, TiO₂/VO₂¹⁸,¹⁹ and In₉O₄:Sn/VO₂/In₉O₄:Sn²⁰), forming nanoparticle composite foils (i.e., SiO₂/VO₂ core-shell²¹, VO₂/ATO²²) or enhancing the visible transmittance by doping (i.e., F-doped VO₂²³ and Mg-doped VO₂²⁴). The focal points of the above-mentioned studies involve changing the transmittance, absorption and reflection characteristics of VO₂. However, the scattering interaction between the material and light has been ignored, resulting in a loss of the energy associated with scattering.

Results

Three devices that can save energy and simultaneously generate electricity were designed. Scattering can be defined as Tyndall, Mie or Rayleigh types based on the interactional relationship between wavelength (λ) of light and size of material, which implies the possibility to size-dependent control the strength of scattering²⁵. A finite-difference-time-domain (FDTD) algorithm is useful for designing and investigating a variety of devices and applications involving the propagation of electromagnetic radiation through complicated media, and was employed to investigate the interaction between VO₂ particles and light (Figure 1a). The electric field distribution of different particle sizes with light²⁶ (Figures 1b through 1f) indicates that light bypasses the particle propagation and that the scattering is so weak at a VO₂ particle size of less than 50 nm. However, the scattering is significantly enhanced with an increase in the particle size (i.e., 100 nm, 150 nm, 200 nm and...
300 nm). The scattering behaviour between VO₂ particle arrays and light was further simulated by FDTD to illustrate the potential use of scattered light for electricity generation (Figure 2). In this simulation, both the radius of the VO₂ particle and the distance between two particles are 100 nm. The scattering of normal incident light in a wavelength range of 350–780 nm along the z-direction and polarised along the y/x-direction was simulated25 (Figure 2a). The far field angular scattering shown in Figure 2b suggests that the scattering field intensity extended to a far zone, which means the scattering field is obvious and large. The scattering energy distribution in the y-z plane is larger than that in the x-y plane, which changed the transmittance of the film in x-y plane.

Based on this model, a solar cell module possessing energy-saving characteristics was designed and is shown in Figures 3a–3d. The structure consisted of three sections, including a low reflective index medium (e.g., VO₂-based particle or film), light guider layers and solar cells. To collect scattered light using this structure, the light guider layers should have a high reflective index associated with the reflective material, which enables the scattering light to propagate between the light guider layers and be reflected to the solar cells. The total internal reflection occurs when light propagates into an optically thinner medium from a denser medium with an incident angle larger than the total internal reflection angle c. The VO₂-based particle can scatter some of light to solar cells for generation.

In Figure 3e–3f, the three devices (i.e., C_a, C_b and C_c) have been designed, a polycarbonate plate (PC plate, refractive index: 1.59) is employed as the light guider layer to gather scattering light to poly-silicon solar cells. In Figure 3e–3b, the low reflective index medium for the device C_a (Figure 3b) and C_b (Figure 3c) was a VO₂ particle film on a quartz plate and VO₂-based power arrays, respectively. The latter was designed as a core-shell-shell structure (i.e., VO₂@SiO₂@TiO₂) to decrease the absorption of VO₂ while maintaining the overall size of the particles to fulfil the scattering conditions26. In Figure 3f, the low reflective index medium for the device C_c (Figure 3d) was a smooth VO₂ thin film. The thickness of the PC is about 4 mm and thickness of the low reflective index medium is about 200 nm in these devices.

Discussion

Figure 4 shows the optical scattering spectra, the transmittance spectra and the I-V curves of devices C_a, C_b and C_c. The scattering measured by the bidirectional reflectance distribution function (BRDF) method27 indicated that the scattering of C_a is larger than C_b and C_c (Figure 4a) because the absorption of the film cast in PDMS for the C_b is enhanced. The scattering of C_c that used a smooth thin film as medium decreased, and the corresponding value of the BRDF for C_c is lower than C_a and C_b. The BRDF curve is consistent with the simulation of FDTD, which indicates that the scattering is large enough for generation. Figure 4b shows the optical transmittance spectra of C_a, C_b and C_c before and after the MST. Consistently, the transmittance in the wavelength range of 300–1,000 nm for the device C_a at a high temperature (i.e., 90 °C) is higher than that at a low temperature (i.e., 25 °C), which is due to the enhanced scattering while the absorption is weakened. In addition, the transmittance of C_a is higher than that of C_b due to the structural difference.

Figure 1 | The scatter electric field distribution of the interaction between a single VO₂ particle and light was simulated by FDTD. (a), The interaction of a single VO₂ particle with light, where the colour represents the incident light. The particle size of VO₂ is 50, 100, 150, 200 and 300 nm for (b, c, d, e and f), respectively. The scattering was enhanced as the particle size increased.

Figure 2 | The scattering of a VO₂ particle arrays film and the electric field intensity profiles of scattered light were simulated. (a), The simulation scheme (inset shows coordinate directions). The normal incident light was along the z-direction and polarised along the y/x-direction. (b), Far field angular scattering, which shows the behaviour of the scattered field in the far zone in the x-y and y-z planes. The vertical direction numbers represent the relative intensity. (c and d), The electric field intensity scattered by the VO₂-based particle film is indicated by a colour scale in the x-y and y-z planes.
To investigate the optical properties of the devices, the solar modulation efficiency ($\Delta T_{\text{sol}}$) was calculated to characterise the thermochromic smart window properties of the devices. $T_{\text{vis}}$ denotes the integral visible transmittance of the devices. The calculated results of the three devices are shown in Table 1. These results indicate that the $\Delta T_{\text{sol}}$ of the Ca is only 2.0%, and the $T_{\text{vis}}$ values at high and low temperatures are 65.6% and 61.7%, respectively. The $\Delta T_{\text{sol}}$ of Cb is 7.5%, which is much higher than Ca, and the $T_{\text{vis}}$ values at high and low temperatures are 45.6% and 42.7%, respectively. The results suggest that the VO$_2$-based core-shell-shell structure is beneficial for energy saving. For the Cc with a smooth VO$_2$ thin film, the solar energy modulation ability of VO$_2$ was maintained.

The I-V curves are shown in Figure 4c, and the results are summarised in Table 2. The Ca and Cc devices show efficiencies of 0.50% and 0.52%, $V_{\text{oc}}$ values of 0.501 V and 0.498 V, $FF$ values of 50.18% and 59.68% and $J_{\text{sc}}$ values of 2.0 mA/cm$^2$ and 1.74 mA/cm$^2$ for Ca and Cc, respectively. The efficiency and $FF$ values of Cc are higher than those of Ca, which shows that the Cc structure is more efficient compared to that of Ca in terms of gathering scattering energy. Note that the area of Ca is larger than Cc, so the scattering light in Ca attenuated bigger than that in Cc. The properties of the device Cc are worse than Ca and Cc, probably because of decreased scattering.

Buildings and other man-made structures consume 30–40% of the primary energy for heating, cooling, ventilation and lighting. This phenomenon will increase with the growth of the population and the associated energy consumption. The ability to reduce energy consumption has become an urgent priority. The successful design and preparation of a novel smart window that combines energy-saving and electricity generation achieves comprehensive utilisation of solar energy, which supports an important new insight into resolving the energy consumption.

Figure 3 | The work principle scheme and the structure description of the VO$_2$-based thermochromic/generating smart window. (a), Three-dimensional structure of the prepared VO$_2$-based smart window. The solar cells are assembled in a manner that surrounds the module. Here, 3 sides are shown. (b), (c) and (d) are the cross-sectional views of a with different DP. (b), A VO$_2$ film on quartz that served as a scattering medium. The scattering medium in c is a smooth VO$_2$ thin film. SC, LGL and DP refer to the solar cell, light guider layer and low reflective index medium, respectively. (b, c and d) show the principle scheme of the devices Ca, Cc (Figure 3e) and Cc (Figure 3f), respectively. When light interacts with the VO$_2$ particle, partial light was scattered and reflected to the solar cell to generate electricity. Cl is a 1.5-V lamp, which was employed to demonstrate whether the smart window works for generation. The two devices in series in Figure 3e could light a 1.5 V lamp.

Figure 4 | The results of the BRDF curve, transmittance spectra of three windows and I-V curves of the three devices. In Figure 4a, the BRDF curve under the measurement conditions has a polarisation incidence with an incident wavelength of 635 nm. Ca, Cb and Cc represent the curve of the Ca, Cb and Cc devices in Figure 3e and 3f, respectively. The incident angle was fixed at 30°, 45° and 60°, and the intensity of the reflective light was measured from 10° to 80°. The results indicate that the scattering intensity of Ca is larger than Cb and Cc. In the Figures 4b and 4c, the optical transmittance spectra at low and high temperatures and the I-V curves under AM 1.5 illumination of the three devices in Figure 3e (Ca, Cb and Cc) and 3f-Cc are shown.
Preparation of VO₂@SiO₂@TiO₂/PU composite film. The VO₂ nanoparticles were prepared according to a previously reported protocol. Vanadium pentoxide (V₂O₅, analytically pure), diamide hydrochloride (N₂H₄·HCl, analytically pure) and PVP (K90, average molecular weight: 1,300,000) were used as starting materials to prepare vanadium precursors. Quartz glass was used as the substrate and was subsequently cleaned in H₂O₂, HCl, and NH₃·H₂O. Precursor films were prepared by spin-coating at 3,000 rpm for 40 s. Then, the films were annealed at 520°C in N₂ (100%) and N₂·O₂·H₂·O. Precursor films were prepared according to a previously reported protocol. In a typical procedure, vanadium pentoxide (V₂O₅, analytically pure) powder was added to an oxalic acid dehydrate aqueous solution to form a yellowish slurry. Then, the slurry was transferred to a 50 mL teflon-lined stainless-steel autoclave, which was maintained at 240°C for 24 h, and then was air-cooled to room temperature.

Preparation of VO₂@SiO₂ nanoparticles. First, VO₂ nanoparticles were pretreated with polyvinylpyrrolidone (PVP) K-30. Then, the VO₂@SiO₂ core-shell structure was prepared by the hydrolysis of TEOS, which is known as the modified Stöber method. Finally, the prepared sample was collected by centrifugation and washed with deionized water and ethanol several times.

Preparation of VO₂@SiO₂@TiO₂ nanoparticles. First, the as-prepared VO₂@SiO₂ nanoparticles were dispersed in an ethanol solution under strong stirring for 30 min. Then, the required amount of tetraethyl titanate (TBT) was quickly added. Finally, an ethanol solution containing 0.03 mL of NH₃·H₂O was added drop-wise to the solution over 5 min. The reaction was maintained at 45°C for 24 h. When the reaction was complete, the sample was collected by centrifugation, washed with deionized water and ethanol several times, and dried at 50°C for 6 h.

Table 1 | The visible transmission, solar energy transmittance and solar modulation ability of the windows in Figure 3e and 3f

| Sample | Visible transmittance Tᵥ(%) | Solar transmittance Tₛ(%) | Solar modulation ability |
|--------|----------------------------|--------------------------|-------------------------|
|        | 25°C                      | 90°C                     |                         |
| Cᵥ     | 61.7                      | 65.6                     |                         |
| Cᵥ     | 45.6                      | 42.7                     |                         |
| Cᵥ     | 31.5                      | 28.0                     |                         |
| Cᵥ     | 56.2                      | 58.2                     | 2.0                     |
| Cᵥ     | 46.9                      | 39.3                     | 7.5                     |
| Cᵥ     | 32.1                      | 24.1                     | 8.0                     |

to 2600 nm were measured using a Hitachi U-4100 spectrometer. The scattering interaction between the VO₂ particles and light was simulated by the finite difference time domain solution (FDTD). The scattering of the VO₂-based smart windows was measured using the method of the bidirectional reflectance distribution function.

| Sample | Jᵥc (mA/cm²) | FF (%) | ER (%) | Area (cm²) |
|--------|--------------|--------|--------|------------|
| Cᵥ     | 0.501        | 2.00   | 50.18  | 0.50       | 76         |
| Cᵥ     | 0.498        | 1.74   | 59.68  | 0.52       | 60         |
| Cᵥ     | 0.497        | 1.32   | 52.06  | 0.34       | 70         |

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28. Table 2 | The efficiency, open-circuit voltage Vᵥc, fill factor FF and short-circuit current density Jᵥc under AM 1.5 illumination for three devices

| cell | Vᵥc [V] | Jᵥc [mA/cm²] | FF (%) | ER (%) | Area (cm²) |
|------|---------|--------------|--------|--------|------------|
| Cᵥ   | 0.501   | 2.00         | 50.18  | 0.50   | 76         |
| Cᵥ   | 0.498   | 1.74         | 59.68  | 0.52   | 60         |
| Cᵥ   | 0.497   | 1.32         | 52.06  | 0.34   | 70         |
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**Author contributions**
J.Z., Z.Z. and Y.G. designed the experiment. J.Z. performed synthesis experiments and characterization. Z.Z. and J.Z. performed simulation and analysis. J.Z. and Y.G. wrote the paper. J.Z., Z.Z., Y.G., H.L., C.C., Z.C., L.D. and X.L. contributed to analysis the experimental data.

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