

Review on thermochromic vanadium dioxide based smart coatings: from lab to commercial application

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Abstract With an urgent demand of energy efficient coatings for building fenestrations, vanadium dioxide (VO₂)-based thermochromic smart coatings have been widely investigated due to the reversible phase transition of VO₂ at a critical transition temperature of 68 °C, which is accompanied by the modulation of solar irradiation, especially in the near-infrared region. As for commercial applications in our daily life, there are still some obstacles for VO₂-based smart coatings, such as the high phase transition temperature, optical properties (luminous transmittance and solar modulation ability), environmental stability in a long-time period, as well as mass production. In this review, recent progress of thermochromic smart coatings to solve above obstacles has been surveyed. Meanwhile, future development trends have also been given to promote the goal of commercial production of VO₂ smart coatings.

Keywords Vanadium dioxide (VO₂) · Thermochromic · Multilayer films · Nanoparticles · Commercial production

1 Introduction

Due to environmental deterioration and energy shortage in human society, people pay more attention to finding effective energy efficient materials to reduce the energy consumption and greenhouse gas emission. According to the survey, buildings are responsible for about 40% of the energy consumption and almost 30% of the anthropogenic greenhouse gas emissions, which are owing to the use of lighting, air-conditioning, and heating [1–5]. This has driven an urgent demand and research for energy efficient applications to reduce the building energy consumption. The heat exchange between the interior of the building and the outdoor environment through fenestrations leads to the largest energy consumption of buildings. Therefore, managing heat exchange through fenestrations is a feasible approach to reduce the building energy consumptions. In summers, solar radiation entering buildings should be controlled to reduce the air-conditioning energy consumption. On the contrary, thermal radiations from the buildings must be limited to consume lesser energy for heating in winters.

An effective way to achieve this goal would be using smart coatings on building fenestrations to control the solar radiation and thermal radiation. Therefore, smart coatings based on electrochromism [6–10], thermochromism [11–19], gasochromism [20–22] and photochromism [23–26] have been widely studied for energy efficient coatings. Thermochromic smart coatings can modulate near-infrared radiation from transmissive to opaque in response to the environmental temperature from low to

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high, which does not require extra stimuli and can save more energy consumption.

Vanadium dioxide (VO_2) is a typical thermochromic material that has been widely studied. VO_2 exhibits an automatic reversible semiconductor-metal phase transition (SMT) at a critical transition temperature (T_c) of 68°C [27], which has been widely investigated as smart coatings for buildings fenestrations [28–32]. As shown in Fig. 1, for temperatures below the T_c , VO_2 is monoclinic ($P2_1/c$, M1) phase with the transmittance of infrared (IR) radiation. On the contrary, the material is a tetragonal structure ($P4_2/mmm$, R), which is reflective for IR radiation [33, 34]. This feature makes VO_2 an amazing material for thermochromic smart coatings [34–42].

VO_2 smart coatings are usually used in two forms including flexible foils based on VO_2 nanoparticles [31, 43–49] and VO_2 based multilayer films [11, 12, 30, 50–52]. However, for commercial application as smart coatings on energy efficient fenestrations, there are still several obstacles severely limiting the relative

applicability of VO_2 smart coatings. (i) The phase transition temperature (T_c) for pure bulk VO_2 (68°C) is too high to be applied on building fenestrations, while T_c around 40°C is acceptable. (ii) For conventional VO_2 coatings, relative modulation abilities are not efficient enough for energy saving. That can be explained by the fact that the modulation of VO_2 for solar radiation is most attributed to the transmittance switch in the near-infrared region, which only accounts for 43% of solar energy in the solar spectrum [23]. (iii) The luminous transmittance T_{lum} for single layer VO_2 with desirable (ΔT_{sol}) is usually less than 40% (even 30%) due to the absorption in the short-wavelength range in both the semiconducting and metallic states of VO_2 , which should be larger than 50% at least for daily applications. (iv) For practical applications as smart coatings, VO_2 must maintain excellent thermochromic performances during a long-time period—at least ten years. However, VO_2 will finally transform into the V_2O_5 phase in the real environment, which is the most thermodynamically stable phase of vanadium oxide but does not possess the

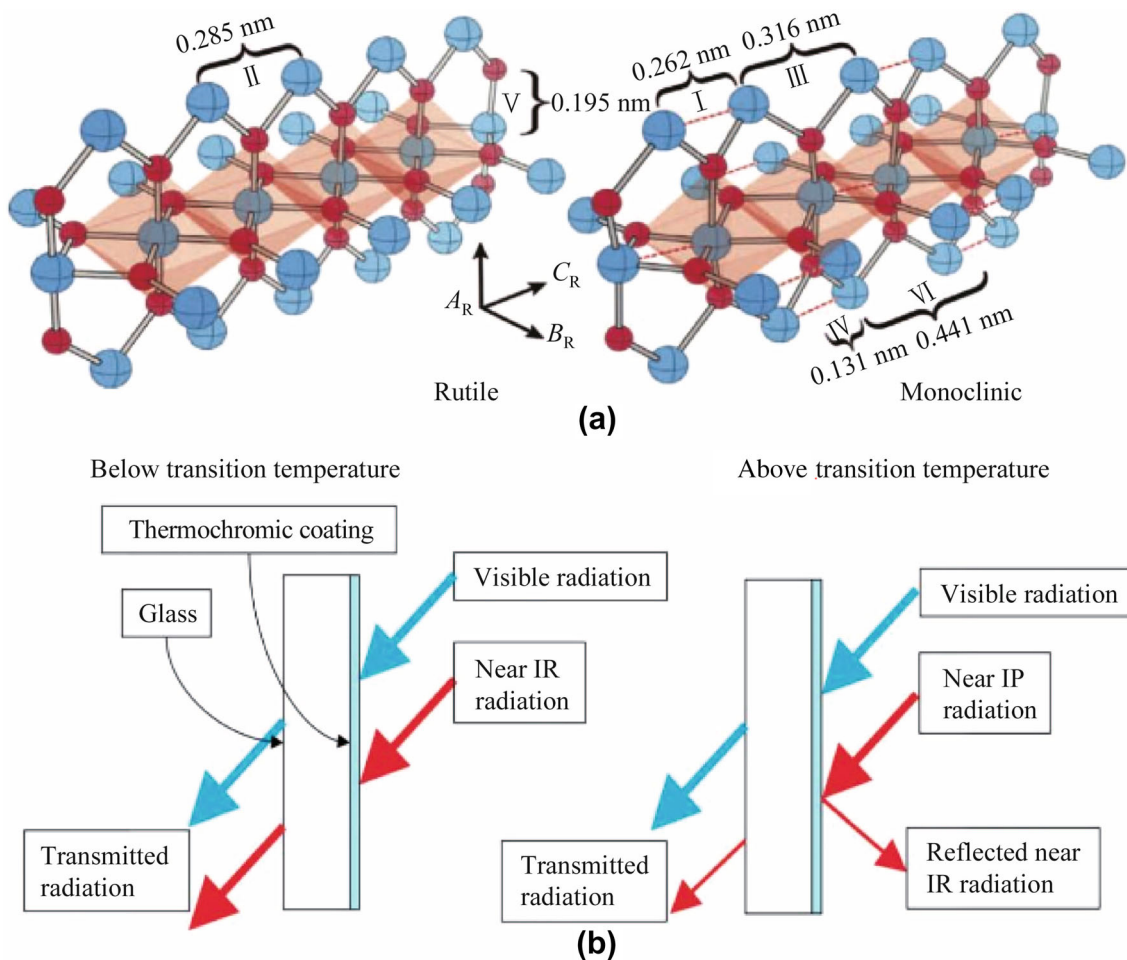


Fig. 1 **a** The crystallographic structure of VO_2 (rutile) and VO_2 (monoclinic) [53] and **b** schematic of thermochromic behavior before and after the phase transition [33]

thermochromic property [54]. Therefore, environmental stability of VO₂ is a great challenge for practical applications as smart coatings.

These obstacles must be overcome for practical applications and many efforts have been made to achieve this goal. Doping of proper ions can effectively reduce the phase transition temperature of VO₂: cations larger than V⁴⁺, such as W⁶⁺ [55], Mo⁶⁺ [56] and Nb⁵⁺ [57], and anions smaller than O²⁻, such as F⁻ [58], have been utilized to reduce the T_c . However, obstacles in (ii)–(iv) have not been solved. Although several reviews about VO₂ coatings have been reported [32, 33, 59, 60], most of them are still in lab scale and few prospects of commercial applications are available.

In this review, we are going to view strategies of thermochromic VO₂ smart coatings for improved thermochromic performance, environmental stability and large-scale production for commercial applications on building fenestrations. Firstly, strategies to enhance thermochromic performance (T_{lum} and ΔT_{sol}) of VO₂ coatings have been introduced as well as the balance between T_{lum} and ΔT_{sol} (Section 2). Then, methods to improve the durability of VO₂ coatings, including protective layers for multilayer films and core-shell structures for nanoparticles, will be summarized in Section 3. Meanwhile, multifunctional design of VO₂ smart coatings such as photocatalysis and self-cleaning function has been discussed in Section 4. Recent progress for large-scale production of VO₂ smart coatings has been surveyed in Section 5. Finally, future development trends of VO₂ coatings have prospected for large-scale production as practical and commercial applications.

2 Improvements of optical properties

T_{lum} and ΔT_{sol} are the most important indexes of thermochromic properties for VO₂ smart coatings. The integral T_{lum} and T_{sol} of the samples can be obtained by the following equations

$$T_{lum, sol} = \int \Phi_{lum, sol}(\lambda) T(\lambda) d\lambda / \int \Phi_{lum, sol}(\lambda) d\lambda,$$

where $T(\lambda)$ represents the transmittance at wavelength λ ; Φ_{lum} is the standard efficiency function for photopic vision; and Φ_{sol} is the solar irradiance spectrum for an air mass of 1.5, which corresponds to the sun standing 37° above the horizon. While the ΔT_{sol} of the films was calculated by $\Delta T_{sol} = T_{sol, lt} - T_{sol, ht}$, where lt and ht represent low temperature and high temperature, respectively.

VO₂ smart coatings always suffer from the problem of low luminous transmittance due to the absorption in the short-wavelength range in both the semiconducting and the

metallic states [61]. The luminous transmittance of VO₂ coatings is largely dependent on relative thicknesses. Based on optical calculation, a single layer VO₂ film (80 nm), for example, exhibits an integrated T_{lum} of 30.2% and 25.1% for semiconducting and metallic VO₂ (see Fig. 2a). As for solar modulation ability, the majority of reported modulation abilities are less than 10%, which are not efficient enough for energy saving function [62–65]. For VO₂ coatings before and after the phase transition, the contrast of relative optical transmittance is mainly in the near-infrared region (780–2500 nm), which only accounts for 43% of solar energy in the solar spectrum (see Fig. 2b).

2.1 Strategies for enhanced luminous transmittance and solar modulation ability

Many efforts have been made to improve the luminous transmittance and solar modulation ability of VO₂ based smart coatings. For VO₂ films fabricated by deposition, the design of multilayer structures is an effective way to improve the optical properties [11, 52, 66]. As for VO₂ nanoparticles prepared by solution methods, the formation of composite films is the most commonly used strategy [67, 68].

2.1.1 Multilayer design for VO₂ thin films

Thermochromic smart coatings incorporating VO₂ films with additional layers have been fabricated for improved thermochromic performances including desirable luminous transmittance and effective solar modulation ability. Schematic illustration of additional layers such as antireflection layers and buffer layers have been shown in Fig. 3 with three typical structures for VO₂ thin films and relative SEM images.

An effective way to improve the luminous transmittance of VO₂ coatings is to introduce an antireflection (AR) layer, such as SiO₂ [69–72], TiO₂ [73], ZrO₂ [74], etc. Lee and Cho [70, 71] reported that SiO₂ antireflection layer successfully increased the luminous transmittance of the VO₂ films. However, the luminous transmittance is still not sufficient. TiO₂ was selected as AR layer for VO₂ films [73] because TiO₂ has a higher refractive index and is a more effective antireflection material for VO₂ than the reported SiO₂. The optimized VO₂/TiO₂ structure has been fabricated and demonstrated the highest T_{lum} improvement among the reported at that time. The optical calculation was performed upon a basic structure of a VO₂ layer with an AR layer of refractive index n and thickness d [74]. Optimization was carried out on n and d for a maximum integrated T_{lum} . The calculation demonstrates that the optimal n value changes with the thickness of VO₂, and at $n \approx 2.2$ it gives the highest T_{lum} enhancement from 32%

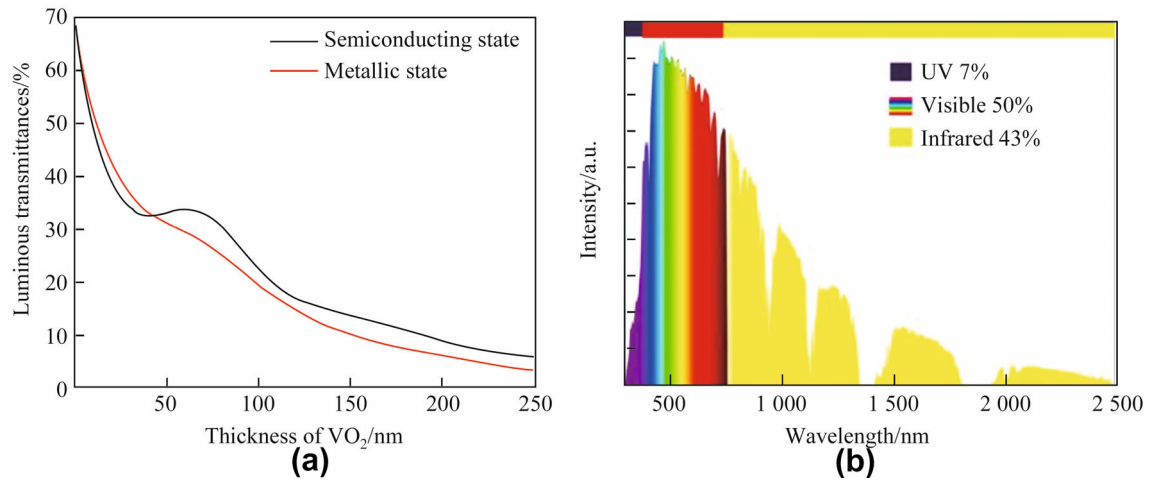


Fig. 2 **a** Calculated luminous transmittance for single layer VO_2 films with various thicknesses at semiconducting state (black line) and metallic state (red line) and **b** the solar spectrum and relative energy distribution [23]

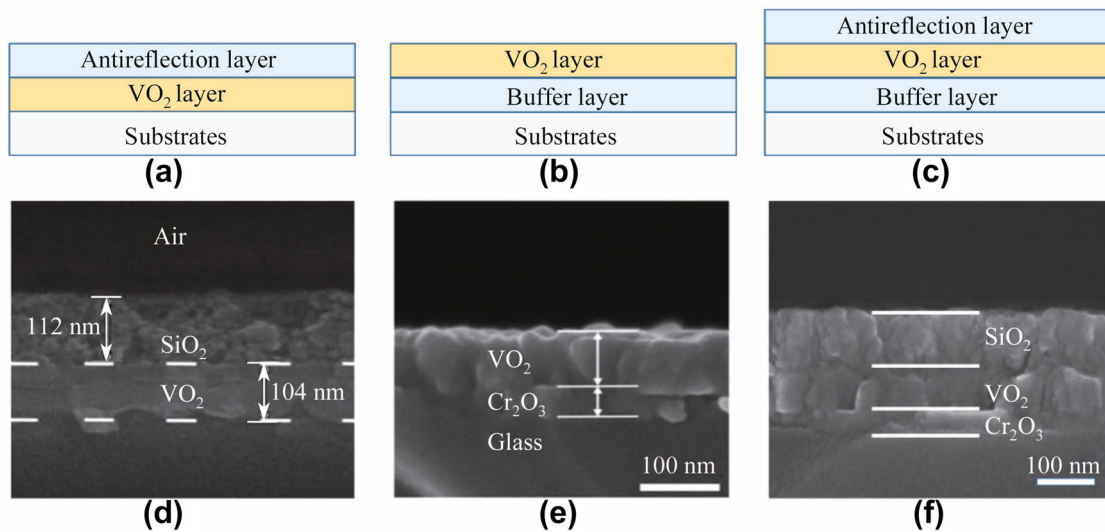


Fig. 3 Schematic illustration of VO_2 based films with **a** antireflection layer, **b** buffer layer, and **c** both of antireflection layer and buffer layers, respectively. Relative SEM images of three typical structures have been shown in Figs. **d–f** corresponding to Figs. **a–c** [12, 30, 69], respectively

(without AR coating) to 55% for 50 nm VO_2 . They deposited an optimized structure of VO_2/ZrO_2 and an improvement from 32.3% to 50.5% in T_{lum} was confirmed for the semiconductor phase of VO_2 , which was in good agreement with the calculations.

Besides the antireflection layers on the top of VO_2 films, buffer layers between the substrates and VO_2 films also play important roles in the optical performances of integrated coatings. Some buffer layers as SiO_2 , TiO_2 , SnO_2 , ZnO , CeO_2 , and SiN_x have been investigated in reported works [75–78]. Nevertheless, thermochromic performances of VO_2 coatings obtained based on above buffer layers are fair, which still can not match the requirements for practical applications.

In our recent work, Cr_2O_3 has been selected to act as a structural template for the growth of VO_2 films as well as the AR layer for improving the luminous transmittance [12]. The suitable refractive index (2.2–2.3) is predicted to be beneficial for the optical performance of VO_2 thin films. Refractive index of Cr_2O_3 is between the glass and the VO_2 , which is considered to enhance the luminous transmittance. Meanwhile, Cr_2O_3 has similar lattice parameters with $\text{VO}_2(\text{R})$, which can act as the structural template layer to lower the lattice mismatch between VO_2 thin films and glass substrates and to reduce the deposition temperature of VO_2 thin films (see Figs. 4a, b). Different crystallization of VO_2 films can be obtained by introducing Cr_2O_3 layers with various thicknesses at a competitive temperature

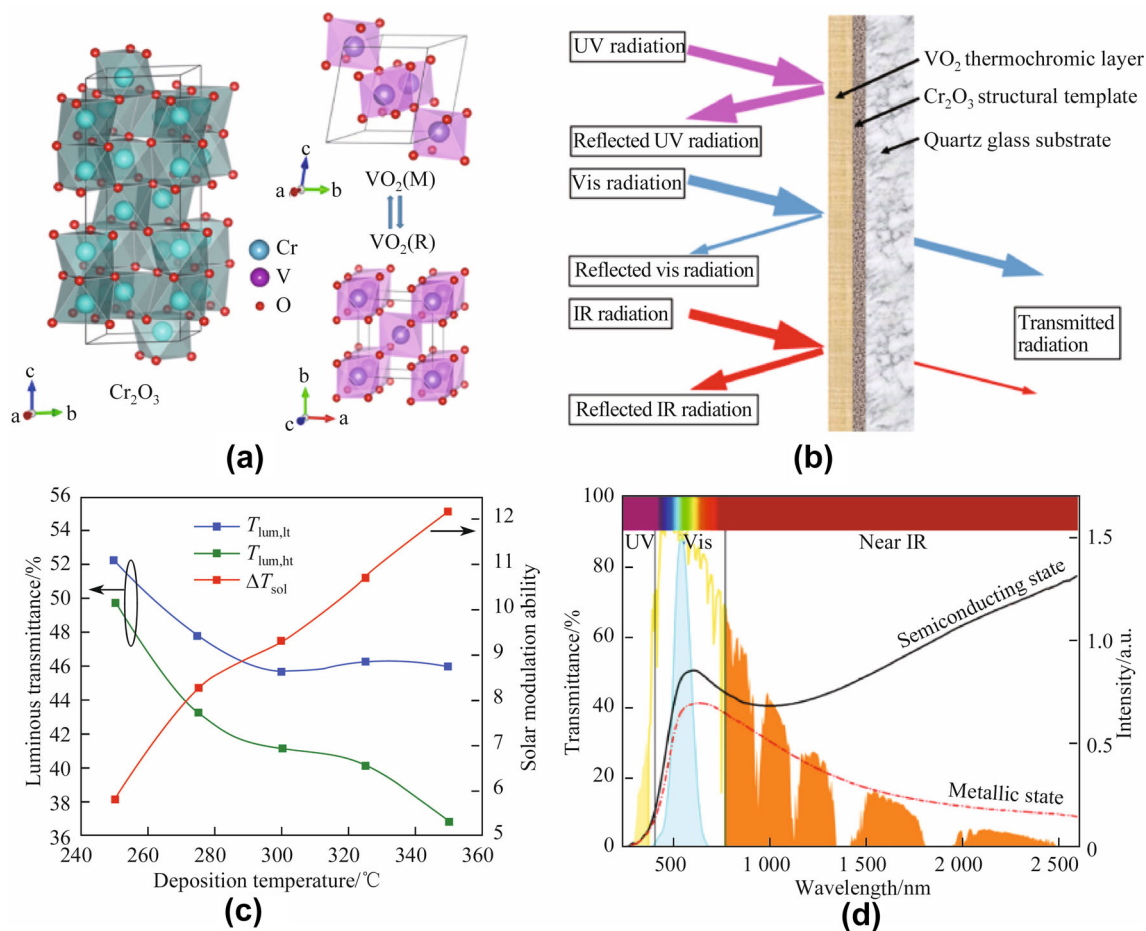


Fig. 4 **a** Crystal structure of hexagonal Cr_2O_3 , monoclinic VO_2 , and rutile VO_2 , respectively, **b** schematic illustration of $\text{Cr}_2\text{O}_3/\text{VO}_2$ bilayer thermochromic film, **c** variation curve of $T_{\text{lum,lt}}$, $T_{\text{lum,ht}}$ and ΔT_{sol} for VO_2 films deposited with 40 nm Cr_2O_3 structural template layer at different temperatures, **d** transmittance spectra (250–2600 nm) at 25 $^{\circ}\text{C}$ and 90 $^{\circ}\text{C}$ for VO_2 films deposited with 40 nm Cr_2O_3 structural template layer at 350 $^{\circ}\text{C}$ and standard solar spectra [12]

range from 250 $^{\circ}\text{C}$ to 350 $^{\circ}\text{C}$, where different thermochromic performance can be obtained (see Fig. 4c). The $\text{Cr}_2\text{O}_3/\text{VO}_2$ bilayer film deposited at 350 $^{\circ}\text{C}$ with optimal thickness shows an excellent $\Delta T_{\text{sol}} = 12.2\%$ with an enhanced $T_{\text{lum,lt}} = 46.0\%$ (see Fig. 4d), while the value of ΔT_{sol} and $T_{\text{lum,lt}}$ for the single layer VO_2 film deposited high temperature at 450 $^{\circ}\text{C}$ is 7.8% and 36.4%, respectively. The Cr_2O_3 insertion layer dramatically increased the visible light transmission, as well as improved the solar modulation of the original films, which arised from the structural template effect and antireflection function of Cr_2O_3 to VO_2 .

For better thermochromic performance, sandwich structures based on VO_2 films have been fabricated. Double-layer antireflection incorporating TiO_2 and VO_2 ($\text{TiO}_2/\text{VO}_2/\text{TiO}_2$) has been proposed [61] and a maximum increase in T_{lum} by 86% (from 30.9% to 57.6%) has been obtained, which is better than the sample with single-layer antireflection (49.1%) [73]. The same structure of $\text{TiO}_2/$

VO_2/TiO_2 has also been investigated by Zheng et al. [11] and Sun et al. [35] for improved thermochromic performance and skin comfort design. A novel sandwich structure of $\text{VO}_2/\text{SiO}_2/\text{TiO}_2$ has been described by Powell et al. [66], where the SiO_2 layers acts as ion-barrier interlayers to prevent diffusion of Ti ions into the VO_2 lattice. The best performing multilayer film obtained in this work showed an excellent solar modulation ability (15.29%), which was very close to the maximum possible solar modulation for VO_2 thin films. Unfortunately, the corresponding luminous transmittance is weak of around 18% for both semiconducting and metallic states.

A novel $\text{Cr}_2\text{O}_3/\text{VO}_2/\text{SiO}_2$ (CVS) sandwich structures have been proposed and fabricated based on optical design and calculations [30]. The bottom Cr_2O_3 layer provides a structural template for improving the crystallinity of VO_2 and increasing the luminous transmittance of the structure. Then, the VO_2 layer with a monoclinic (M) phase at low temperature undergoes a reversible phase-transition to

rutile (R) phase at high temperature for solar modulation. The top SiO₂ layer not only acts as an antireflection layer but also greatly enhances the environmental stability of the multilayer structures as well as providing a self-cleaning layer for the versatility of smart coatings. Optical simulation of luminous transmittances (semiconducting state) for the CVS structure has been shown in Fig. 5a (3-dimensional image). The thickness of the VO₂ layer was fixed at 80 nm to demonstrate significant thermochromic performance while varying thicknesses of Cr₂O₃ and SiO₂ were investigated for optimized optical properties. Four clear peaks are observed in the luminous transmittance simulations, which can be attributed to the interference effect of the multilayer structure. The highest value of $T_{lum,lt}$ is about 44.0% at approximately 40 nm and 90 nm of Cr₂O₃ and SiO₂, respectively. In this work, the proposed CVS multilayer thermochromic film shows an ultrahigh $\Delta T_{sol} = 16.1\%$ with an excellent $T_{lum,lt} = 54.0\%$, which

gives a commendable balance between ΔT_{sol} and $T_{lum,lt}$ (see Figs. 5b, c). The demonstrated structure shows the best optical performance in the reported structures grown by magnetron sputtering and even better than most of the structures fabricated by solution methods. To date, the proposed CVS structure exhibits the most recommendable balance between the solar modulation ability and the luminous transmittance to reported VO₂ multilayer films (see Fig. 5d).

There is some work focus on multilayer films with more layers for enhanced thermochromic performances. A five-layer thermochromic coating based on TiO₂/VO₂/TiO₂/VO₂/TiO₂ has been studied [52]. A featured wave-like optical transmittance curve has been measured by the five-layer coating companying an improved luminous transmittance (45.0% at semiconducting state) and a competitive solar modulation ability (12.1%). Multilayer structure like SiN_x/NiCrO_x/SiN_x/VO_x/SiN_x/NiCrO_x/SiN_x exhibits

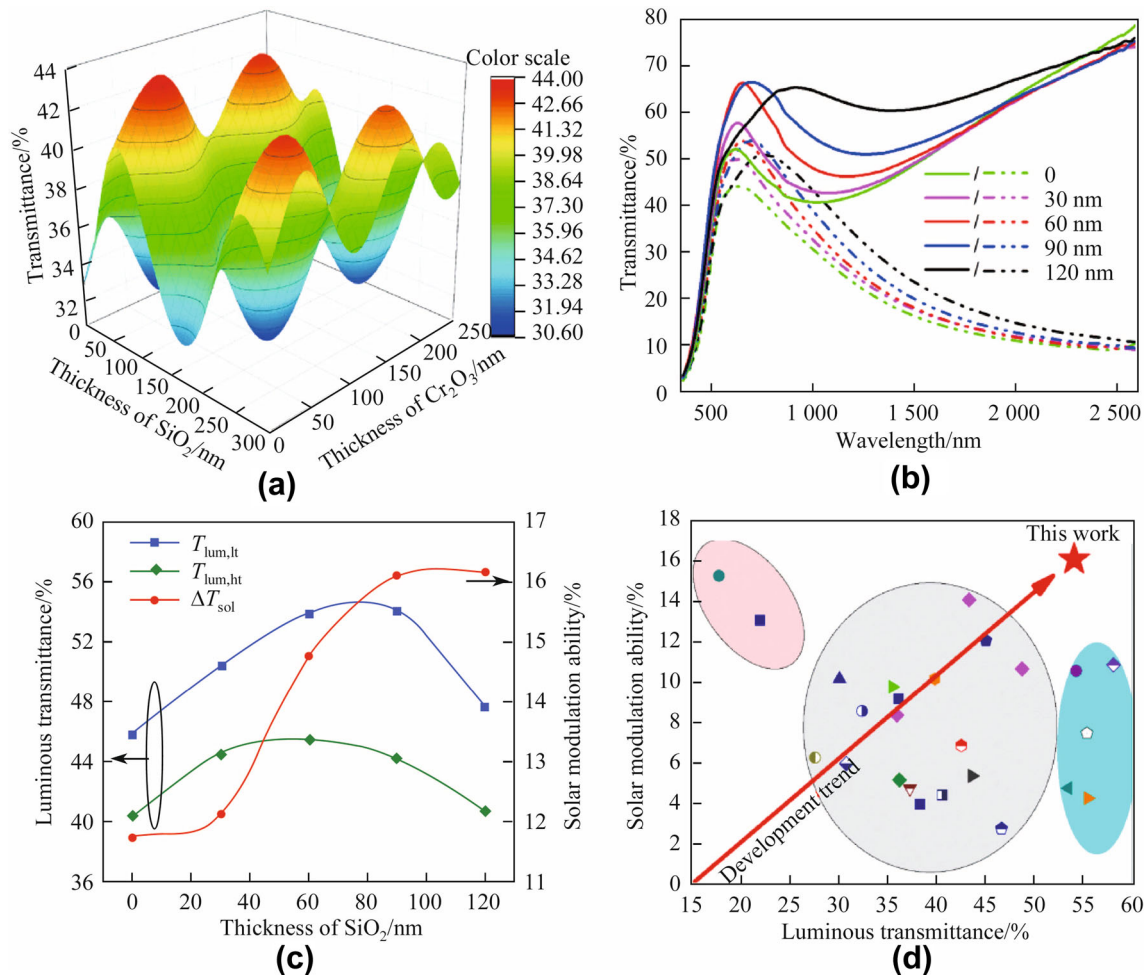


Fig. 5 **a** 3D surface image of the luminous transmittance ($T_{lum,lt}$) calculation of the Cr₂O₃/VO₂ (80 nm)/SiO₂ multilayer structure on the thickness design of Cr₂O₃ (bottom layer) and SiO₂ (top layer), **b** transmittance spectra (350–2600 nm) at 25 °C (solid lines) and 90 °C (dashed lines) for the CVS structures with various thicknesses of SiO₂ layers, **c** corresponding variation curves of $T_{lum,lt}$, $T_{lum,ht}$, and ΔT_{sol} for **b**, **d** comparison of this work with recently reported VO₂-based thermochromic films [30]

superior solar modulation ability of 18.0%, but the luminous transmittance (32.7%) and the complicated structure pose an enormous obstacle for practical application of this structure.

2.1.2 Composite films based on VO₂ nanoparticles

Composite films incorporating VO₂ nanoparticles with inorganic or/and organic materials have many advantages. On the one hand, the structure of composite films may induce strains, which may have positive effects on the T_c and hysteresis-loop width of VO₂ films [79]. On the other hand, according to the optical calculations performed by Li et al. [80], VO₂ nanoparticles dispersed in suitable dielectric hosts show much higher luminous transmittance and solar energy transmittance modulation than pure VO₂ films [80].

VO₂-ZrV₂O₇ composite films have been successfully prepared by polymer-assisted deposition using V-Zr-O solution [79]. With similar thickness, the composite films exhibited significantly enhanced luminous transmittances with increasing Zr/V ratios (from 32.3% at Zr/V = 0 to 53.4% at Zr/V = 0.12), which can be attributed to the absorption-edge changes in the composite films. Nevertheless, the solar modulation ability of the samples showed slightly weakened increasing Zr/V ratios (from 6.0% at Zr/V = 0 to 4.8% at Zr/V = 0.12). Crystallized TiO₂-VO₂ composite films were prepared by dispersing VO₂ nanoparticles in TiO₂ sol and annealing by an optimized two-step annealing process [81]. The optical performance of these composite films could be improved by increasing their porosity by controlling annealing rate or by introducing mesopores.

Inorganic host BaSO₄ has also been investigated due to its numerous advantages, such as stronger chemical inertness, acid and alkali resistance, relatively high density and whiteness, especially the high dispersion, good refractive index and transparency [82]. VO₂-BaSO₄ composite powders were prepared by a one-step hydrothermal process, and the existence of the BaSO₄ could improve the optical properties of the VO₂ by 43.0% in T_{lum} (from 30.4% to 43.5%) and 10.7% in ΔT_{sol} (from 11.2% to 12.4%).

Besides the inorganic hosts as ZrV₂O₇, TiO₂, and BaSO₄, organic hosts also show great potentials in smart coatings. A temperature-responsive hydrogel based on poly(*N*-iso-propylacrylamide) (PNIPAm) has been reported [83]. The PNIPAm can undergo a hydrophilic to hydrophobic transition at the lower critical solution temperature (LCST). By tuning the thickness of the hydrogel and designing a suitable glass panel set-up, the PNIPAm exhibited an unprecedented good combination of the near-doubled average T_{lum} (70.7%), higher ΔT_{sol} (25.5%) and lower transition temperature (32 °C). Further

investigations have been carried out by dispersing VO₂ nanoparticles into a PNIPAm hydrogel to form a hybrid thermochromic material [67]. The VO₂/hydrogel hybrid nanothermochromic material makes a dramatically higher ΔT_{sol} up to 35%, while still maintaining higher average T_{lum} (63%) (see Fig. 6).

Some transition metal complexes (TMCs) that exhibit thermochromism with little T_{lum} loss at high temperature are chosen to be hybridized with VO₂ nanoparticles [45, 68, 84]. The used TMCs can partly absorb visible light and change color as a response to temperature change upon interaction with an appropriate donor solvent and effectively avoid severe damage to T_{lum} at high temperature because the absorption peaks are staggered with the extremum of the light-adapted eye sensitivity function. The thermochromic ionic liquid (IL) has been used by Zhu et al. [68]. Briefly, when heating from room temperature, the ionic liquid-nickel-chlorine (IL-Ni-Cl) complexes absorb increasing visible light around 656 nm and 705 nm, and gradually change color from colorless to blue. Compared with a pure VO₂ film, the composite film of VO₂ nanoparticles and IL-Ni-Cl complexes not only expresses more excellent optical performance ($\Delta T_{sol} = 26.45\%$ and $T_{lum,lt} = 66.44\%$, $T_{lum,lt} = 43.93\%$) but also adds a function of an obvious color change from brown to green as temperature rises, facilitating application and function exhibiting of smart windows (see Fig. 7). TMCs like IL-Ni-Br and IL-Co-Br have also been studied with robust improvements of thermochromic performances of VO₂ nanoparticles [45, 84].

2.2 Balance between luminous transmittances and solar modulation ability

Regarding practical application of VO₂ based thermochromic smart coatings, high solar modulation ability accompanied by high luminous transmittance is required. Nevertheless, we can find that it is tough to make a good balance between luminous transmittance and solar modulation ability or ultrahigh luminous transmittances is meaningless.

Most work on VO₂ based smart coatings pursue large contrast of optical transmittance in the near infrared region (780–2500 nm), while inconspicuous contrast in the visible light region (380–780 nm) is desirable for both semiconducting and metallic states. In the solar spectrum, ultraviolet light, visible light and infrared light is responsible for about 7%, 50%, 43% of solar energy, respectively [23]. Therefore, if there is an increased contrast in the visible light region for VO₂ based smart coatings between the semiconducting and the metallic state, relative solar

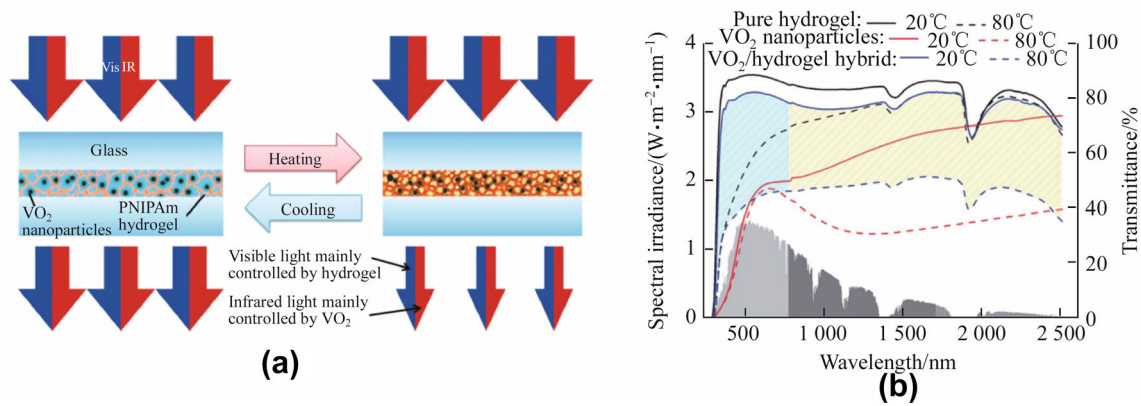


Fig. 6 **a** Solar modulation mechanism of the VO₂/hydrogel hybrid, **b** UV-Vis spectra of pure hydrogel (black), pure VO₂ (red), and VO₂/hydrogel hybrid (blue) at low and high temperature (the grey area indicates the normalized values of the visible (light) and IR(dark) spectra spectral irradiance. The light cyan area with sparse slashes is the luminous transmission difference, and the light yellow area is the IR transmission difference of the VO₂/hydrogel hybrid) [67]

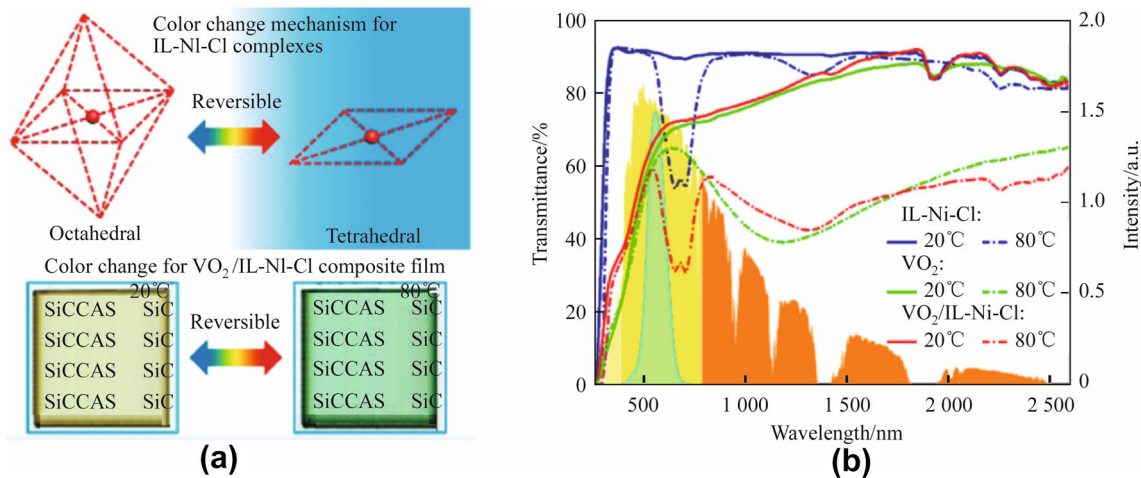


Fig. 7 **a** Color change mechanism for IL-Ni-Cl complexes (upper) and color change of VO₂/IL-Ni-Cl composites film, **b** UV-Vis-NIR transmittance spectra of pure IL-Ni-Cl complexes film, pure VO₂ nanoparticles film, and VO₂/IL-Ni-Cl composite film at 20 °C and 80 °C (the yellow-orange area indicates the normalized values of the visible (yellow) and NIR (orange) spectra spectral irradiance, and the cyan area indicates the values of eyes ensitivity function) [68]

modulation ability can be robustly enhanced due to the contribution from the visible light region. That means that the transmittance in the visible light region for VO₂ smart coating of metallic state should be maintained at least 50%, while the coating shows higher luminous transmittance of semiconducting state. Some works have been reported to increase ΔT_{sol} of VO₂ by mixing with specific materials shows a robust contrast in the visible light region in different temperatures [45, 68]. However, more investigations are required for a facile and cheap method to achieve the balance between luminous transmittances and solar modulation ability of VO₂ based smart coatings.

3 Methods to improve the stability of VO₂ for long-time use

In previous work, researchers usually focus on the thermochromic properties of VO₂ to improve the luminous transmittances and solar modulation ability. However, environmental stability is another great challenge for VO₂ coatings from lab to industrial production. Vanadium is a multivalent element and there are several kinds of vanadium oxide, such as VO, V₂O₃, VO₂, V₆O₁₃, V₄O₉, V₃O₇, and V₂O₅. Among them, V₂O₅ is the most thermodynamically stable phase and VO₂ will gradually transform into the intermediate phases of V₆O₁₃ and V₃O₇ and finally into V₂O₅ [54]. However, unlike VO₂, V₂O₅ does not possess thermochromic optical change properties near the room temperature. Therefore, how to maintain the

thermochromic performance of VO₂ coatings during a long-time period is an inevitable problem that must be overcome.

3.1 Protective layers for VO₂ films

To prevent VO₂ films from degradation, introducing of protective layers above VO₂ is an effective way that has been widely used. Chemically stable oxide films such as Al₂O₃ [54, 85], CeO₂ [86, 87], WO₃ [64], etc., have been studied to keep VO₂ away from oxidant like water and O₂ in air. It should be noted that the selected materials to be used as protective layers might affect the optical properties of VO₂, where dual enhancement in the optical properties and the stability is preferred.

Al oxide is a typical material that has been investigated as a protection layer for VO₂ coatings. In work reported by Ji et al. [54], different thicknesses of Al oxide protective layers have been deposited for VO₂ by DC magnetron sputtering. The durability of the samples was evaluated at a high temperature around 300 °C in dry air and highly humid environment. They found that the Al oxide protective layers provided good protection and delayed the degradation process of VO₂ in dry air at 300 °C and humid environment. The similar structure was also investigated [85], while the Al₂O₃ protective layers were fabricated by atomic layer deposition (ALD). The Al₂O₃ films can protect the VO₂ from oxidation in the heating test but not sufficient in the damp environment, which can be attributed to the corrosion of water to Al₂O₃. It is worthy to mention that in above cases, the test period of the samples is less than one week (168 h), which is far from the request for practical applications.

Long et al. [64] proposed a novel sandwich structure of WO₃/VO₂/WO₃, where WO₃ not only functions as an AR layer to enhance the T_{lum} of VO₂ but also performs as a good protective layer for thermochromic VO₂. The stability of samples was investigated in a constant-temperature humid environment with 90% relative humidity at 60 °C. For the single layer VO₂, the thermochromism nearly vanishes after 20 day treatment in the tough environment. On the contrary, there shows almost no change in the optical transmittance of WO₃/VO₂/WO₃ multilayer films with the same treatment. However, though the protection provided by the WO₃, the solar modulation ability of the sample is weakly reduced due to the diffusion of W⁶⁺ to VO₂.

In works above, the protective layers are usually single layer films. To enhance the durability of thermochromic VO₂ films, bilayer coatings as VO₂/TiO₂/ZnO, VO₂/SiO₂/ZnO, and VO₂/SiO₂/TiO₂ have been studied [88]. In this study, VO₂ films with TiO₂/ZnO protective coatings have been demonstrated higher antioxidant activity under aging

tests, which can be attributed to the different oxygen permeability through different inorganic films [89]. Zhan et al. [90] fabricated a complicated multilayer structure of SiN_x/NiCrO_x/SiN_x/VO_x/SiN_x/NiCrO_x/SiN_x, which exhibits enhanced thermal stability up to 375 °C. However, aging test in a humid environment is not applied to the samples.

The Cr₂O₃/VO₂/SiO₂ structure proposed by our lab shows robust environmental stability for long-time use [30]. The top SiO₂ layer is chemically stable and makes the static water contact angle of the films change abruptly from 24.1° (hydrophilicity) to 115.0° (hydrophobicity) (see Figs. 8a, b). Hydrophilicity of the single layer VO₂ indicates well contact with water, which will accelerate the degradation process of relative thermochromic performance. On the contrary, the hydrophobicity that exhibited by the CVS structure is helpful to keep the VO₂ isolated from the water, which can protect the coatings against oxidation. Wettability is dependent on the chemical composition and structure of the surface. The surface of silicon is normally hydrophilic without additional treatments, but previous studies have demonstrated that the wettability of the silicon surface can be significantly changed by structuring the surfaces. So, fabrication of SiO₂ top coatings in this work has been deliberately optimized with enhanced roughness for hydrophobic surfaces (see Fig. 8b). The double-protection from Cr₂O₃ and SiO₂ makes an excellent promotion for the environmental stability of the CVS coatings, which is desirable for long-time use. The proposed CVS structure shows remarkable environmental stability due to the dual-protection from the Cr₂O₃ and the SiO₂ layer, which shows negligible deterioration even after accelerated aging (60 °C and 90% relative humidity) of 10³ h and 4 × 10³ fatigue cycles, while VO₂ single layer samples almost become invalid (see Figs. 8c, d).

3.2 Core-shell structures

Unlike VO₂ films prepared PVD methods, thermochromic coatings based on VO₂ nanoparticles have different surface morphologies and larger specific area. Therefore, protective layers may not be suitable for VO₂ nanoparticles. Core-shell structures for VO₂ nanoparticles have been demonstrated to be an effective way to improve performances of the VO₂ core by using selected materials as shells [29, 55, 91–93].

Silica (SiO₂) is the most studied material utilized as shell to improve the durability of VO₂ nanoparticles [29, 55, 94, 95]. Firstly, the SiO₂ layer is optically transparent and chemically stable. Secondly, the utilization of SiO₂ layer can prevent nanoparticles from agglomeration [95]. Thirdly, the SiO₂ layer is helpful to improve the chemical stability and mechanical stability of VO₂ nanoparticles. Gao et al. [29] synthesized VO₂@SiO₂ core-

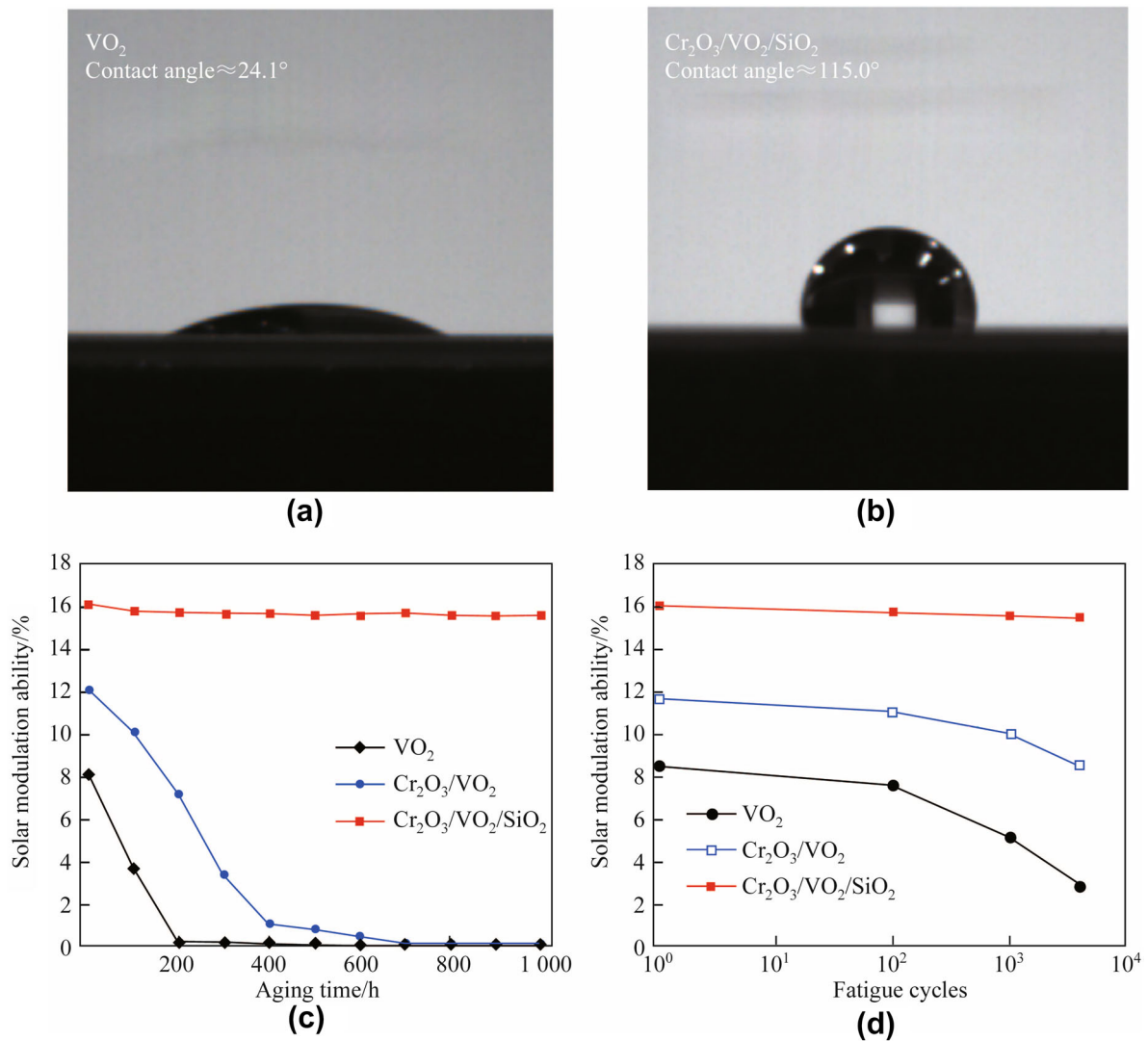


Fig. 8 Images of contact angle measurement of **a** the single layer VO₂ and **b** the proposed Cr₂O₃/VO₂/SiO₂ structure. Variation curves of ΔT_{sol} for VO₂, Cr₂O₃/VO₂ and Cr₂O₃/VO₂/SiO₂ with different duration time **c** and different fatigue cycles **d** [30]

shell structure via solution method with PVP pretreatment. The proposed VO₂@SiO₂ structures can effectively enhance the anti-oxidation and acid-resisting properties of VO₂. After annealing at 300 °C in air for 2 h, most VO₂ nanoparticles without SiO₂ shell have transformed into V₂O₅, while no trace of V₂O₅ can be observed in the VO₂@SiO₂ sample. The acid-corrosion experiment of the samples in a hydrochloric acid solution (pH = 1) also confirmed the chemical stability of VO₂@SiO₂.

Al oxide is a promoted material as the shell to protect nanoparticles from corrosion, which has been demonstrated to protect perovskite solar cells from corrosion [96]. VO₂/Al-O core-shell structures have been fabricated, where different duration tests have been carried out [97]. For the uncoated sample, the VO₂ nanoparticles were oxidized into V₂O₅ when heated at 300 °C, while the coated VO₂/Al-O remains stable even heated up to 350 °C. While treated in

the damp heating environment, the uncoated sample loses thermochromic properties only after 48 h, while the VO₂ nanoparticles coated with Al-O shell remains stable even after 20 days.

In the study by Chen et al. [43], ZnO was selected as the shell to prevent VO₂ nanoparticles from being oxidized. From the TEM images of VO₂@ZnO shown in Figs. 9a, b, it can be observed that VO₂ nanoparticles were closely surrounded by ZnO shells. Compared with uncoated VO₂ film, ZnO coating VO₂ films show greater effects on the properties (see Fig. 9c). The ΔT_{sol} and T_{lum} are improved from 38.9% and 17.2% to 51.0% and 19.1% (see Fig. 9d). An extreme environment for a constant temperature of 60 °C and humidity of 90% which will accelerate samples losing the thermochromic performance in this condition of the environment and evaluated relative durability. For the uncoated VO₂ film, the thermochromism vanishes

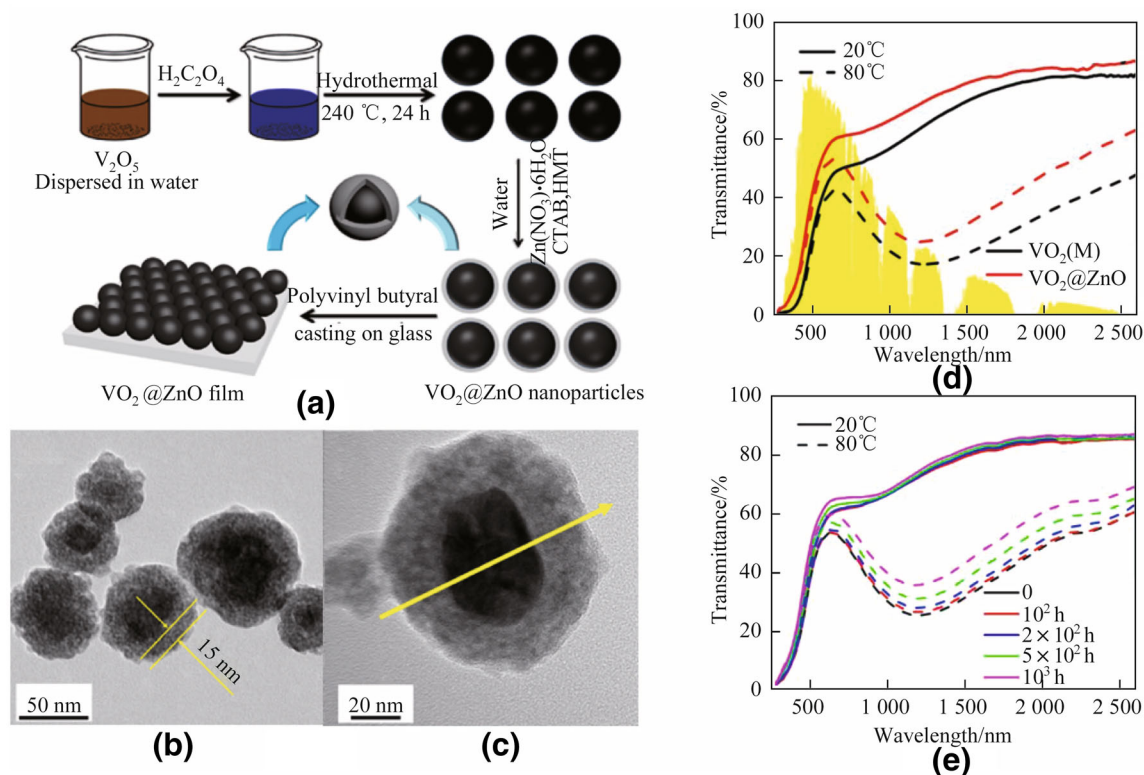


Fig. 9 a Experimental flow chart for the synthesis of $VO_2@ZnO$ core-shell structure nanoparticles and $VO_2@ZnO$ film, b–c TEM images of $VO_2@ZnO$ core-shell structure nanoparticle, d optical transmittance spectra at $20\text{ }^\circ\text{C}$ and $80\text{ }^\circ\text{C}$ of uncoated VO_2 film and $VO_2@ZnO$ film, e optical transmittance spectra of $VO_2@ZnO$ in a constant temperature ($60\text{ }^\circ\text{C}$) and humidity (90%) [43]

completely after 30 h treatment. Compared with the uncoated VO_2 , the $VO_2@ZnO$ shows striking durability. The transmittance curve at different temperatures of $VO_2@ZnO$ film remains almost intact after 10^3 h testing, which means that it still has good thermochromic performance (see Fig. 9e).

4 Multifunctional design and construction

Nowadays, multifunctional fenestrations of the buildings are favored by customers. As is known to all, the fenestrations of the buildings and vehicles always need to be cleaned, which would lead to additional pollutants from the use of detergents and wasting a mass of labors. Semiconductor photocatalysts like TiO_2 are widely and frequently employed to decompose pollutants. There are three different polymorphs of crystalline TiO_2 : rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Rutile TiO_2 ($TiO_2(R)$) is a thermodynamically stable phase at all temperatures and the most common natural form of TiO_2 . Due to similar lattice parameters, $TiO_2(R)$ films are acted as buffer layer and growth template of $VO_2(M)$ films. Nevertheless, $TiO_2(R)$ films are less efficient photocatalysts than anatase TiO_2 ($TiO_2(A)$) films, which occupy an

important position in the studies of photocatalytic active. Zheng et al. [11] constructed a $TiO_2(R)/VO_2(M)/TiO_2(A)$ multilayer film, while the photocatalytic and photoinduced hydrophilic properties from the top $TiO_2(A)$ layer for self-cleaning effects (see Fig. 10a).

Self-cleaning property of the $TiO_2(R)/VO_2(M)/TiO_2(A)$ multilayer film was evaluated by the decomposition of stearic acid under UV radiation. The degradation of stearic acid was related to the decrease in IR absorption of the C—H stretches, which has been summarized in Fig. 10b. Before UV light irradiation, the characteristic alkyl C—H bond stretching vibrations of CH_2 and CH_3 groups ($3000\text{--}2800\text{ cm}^{-1}$) can be distinctly detected. After UV light irradiation of 20 min, the absorbance of C—H bond stretching vibrations decreased drastically, which meant that a considerable proportion of stearic acid was decomposed. The IR absorbance slowly became weak with the increase of irradiation time, and finally almost faded away after 180 min irradiation time. In addition, the degradation of stearic acid also can be confirmed by the changes of the contact angle of the multilayer film. The contact angles of the surface transform from 99.5° (hydrophobic) to 11.5° (hydrophilic) (see Fig. 10c), which can be ascribed to the degradation of stearic acid and the photoinduced hydrophilicity of multilayer film. The photocatalytic activity of $TiO_2(R)/VO_2(M)/$

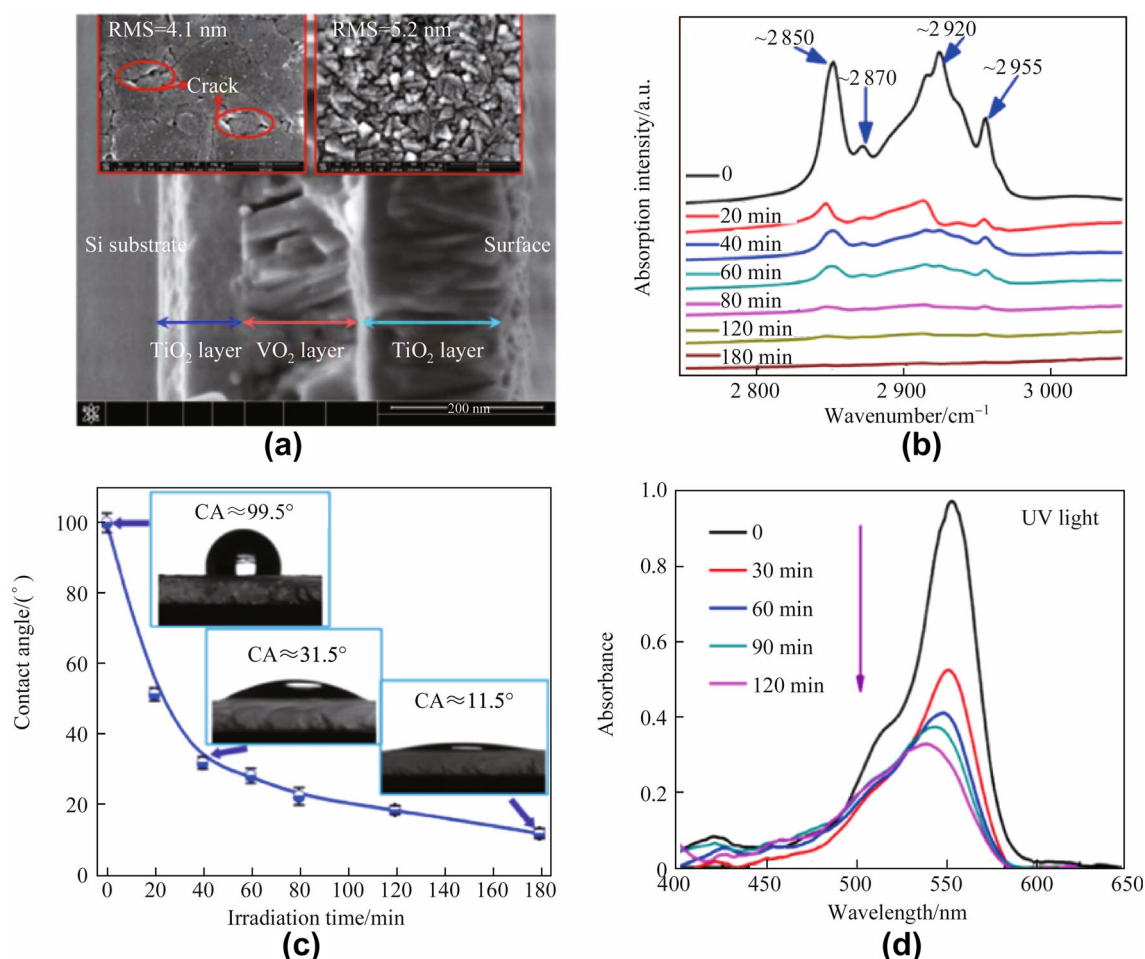


Fig. 10 **a** FESEM image of a fractured cross-section of the multilayer film (the insets are surface morphology of $\text{VO}_2(\text{M})$ (left) and $\text{TiO}_2(\text{A})$ layers (right)), **b** IR absorbance spectra of $\text{TiO}_2(\text{R})/\text{VO}_2(\text{M})/\text{TiO}_2(\text{A})$ multilayer film with stearic acid overlayer at various irradiation time under UV light, **c** CAs of the multilayer film with stearic acid overlayer dependence on irradiation time (the insets are corresponding water droplet shapes on the surface), **d** variation of absorption spectra of RhB aqueous solution degraded by the multilayer film [11]

$\text{TiO}_2(\text{A})$ multilayer film also has been demonstrated by the decomposition rate of RhB under UV light irradiation. Figure 10d shows that the absorption spectra of RhB aqueous solution degraded by the multilayer film under UV light irradiation. Thermochromic smart coatings with self-cleaning function have also been achieved by the $\text{VO}_2/\text{SiO}_2/\text{TiO}_2$ structure where the SiO_2 layer act as the ion-barrier inter-layer [66]. The proposed VST structure shows a significant degradation rate of stearic acid and is comparable to that of a standard Pilkington Activ glass, which is a commercially available self-cleaning glass that contains a thin TiO_2 layer (15 nm) deposited by CVD methods.

For self-cleaning function and improved stability, VO_2 thermochromic smart coatings with hydrophobic surface have been favored and studied by researchers. VO_2 films with moth-eye nanostructures have been fabricated to enhance the thermochromic properties and the hydrophobic surface (contact angle 120°) can be achieved with

additional overcoat [98]. Fused silica substrates with AR patterns of different periods (0, 210, 440, 580 and 1 000 nm) were prepared by reactive ion etching using 2D polystyrene colloidal crystals as a mask. A nipple arrays based on VO_2/SiO_2 have been realized and the additional fluorooctyltriethoxysilane (FOS) overcoat provides hydrophobicity of the surface (see Fig. 11).

The biosafety of VO_2 is also under consideration, while the ZnO layer has been used to provide the antibacterial property [99]. ZnO coated VO_2 thin films exhibited excellent antibacterial property proved by SEM observation results that ZnO coated samples cause the membrane disruption and cytoplasm leakage of *E. coli* cells and fluorescence staining results that the amounts of viable bacteria are evidently lower on the surface of ZnO coated films than that of uncoated films (see Fig. 12). The sterilization mechanism of ZnO films is believed to be attributed to the synergistic effect of released zinc ions and ZnO

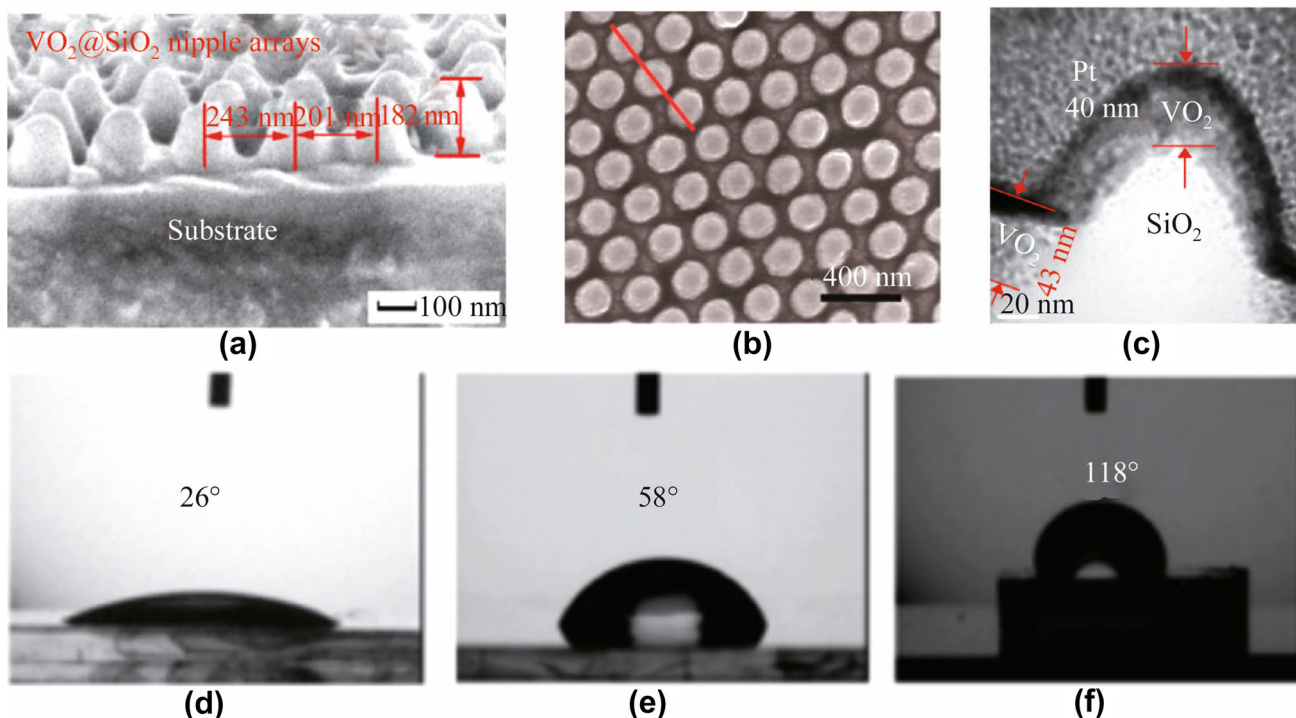


Fig. 11 **a** SEM cross-sectional profile of the sample with 210 nm period, **b** top-view SEM image of the sample with 440 nm period, **c** TEM cross-sectional image to show the thickness of VO₂ coatings on SiO₂, **d** planar VO₂, 210 nm patterned VO₂ with 40 nm thickness, and 210 nm patterned VO₂ with FOS overcoat [98]

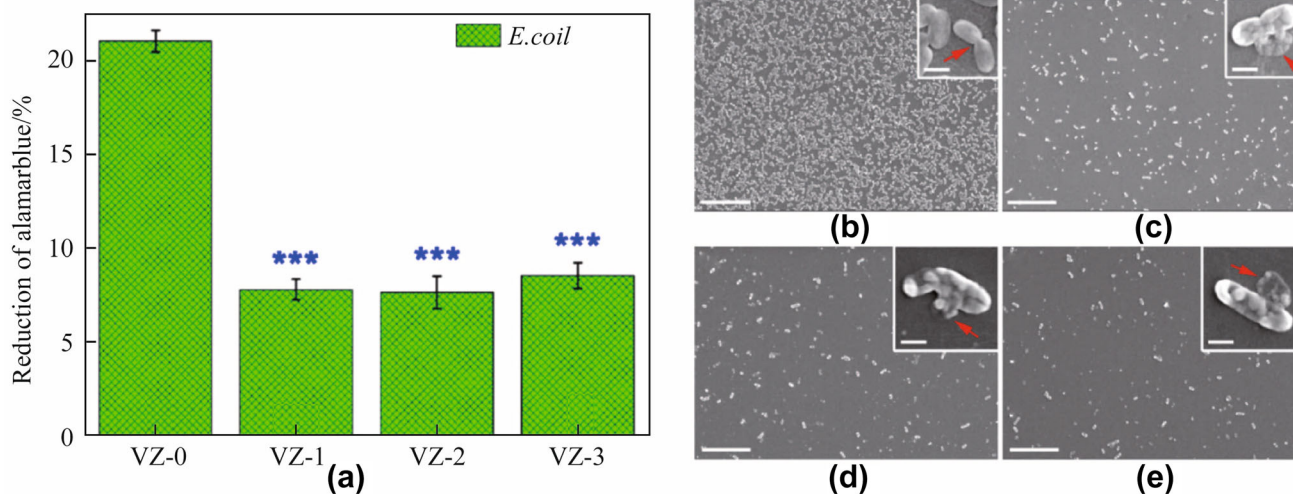


Fig. 12 **a** Proliferation viability of *E. coli* after culture of 24 h on samples VZ-0, VZ-1, VZ-2 and VZ-3, accompanied by the SEM morphology of *E. coli* after culture of 24 h on surfaces of **b** VZ-0, **c** VZ-1, **d** VZ-2 and **e** VZ-3 (the scale bar is 20 μ m. The insets show the corresponding partially enlarged SEM images and the scale bar is 1 μ m) [99]

nanoparticles by elaborately designing a verification experiment. More importantly, the ZnO layer with an appropriate thickness can significantly reduce the cytotoxicity of VO₂ and thus promote the VO₂ biosafety.

5 Large-scale production of VO₂ smart coatings

For commercial applications on building fenestrations in our daily life, large-scale production of VO₂ based smart coatings is a great challenge that must be developed. For VO₂ based films, magnetron sputtering is the most

commonly used method and several works about large-scale production of VO₂ based films by magnetron sputtering have been reported. A large-scale TiO₂(R)/VO₂(M)/TiO₂(A) multilayer film was prepared on a glass with the area of 400 mm × 400 mm using magnetron sputtering method by Zheng et al. [11], where a combination of energy-saving, antifogging and self-cleaning functions has been achieved (see Fig. 13a). TiO₂(R)/VO₂(M)/TiO₂(A) multilayer film was deposited using medium frequency reactive magnetron sputtering (MFRMS, see Fig. 13b) system to sputter planar rectangular metal targets in a suitable atmosphere. The proposed structure shows excellent ability to block out infrared irradiation, which causes a temperature reduction of 12 °C compared with the blank glass (see Fig. 13c).

The magnetron sputtering coating system could be applied in architecture commercial glasses and the designed large area sputtering cathode can make the coating on large area glass substrates. The optimized design and precise manufacturing can guarantee to get a higher vacuum and a shorter cycle time by using a smaller pumping system. Sputtering is a vacuum process used to

deposit thin films on substrates. It is performed by applying a high voltage across a low-pressure gas (usually argon) to create a “plasma”, which consists of electrons and gas ions in a high-energy state. During sputtering, energized plasma ions strike the target, which is composed of the desired coating material, and caused atoms from that target to be ejected with enough energy to travel to and bond with the substrate (see Fig. 13d).

In terms of VO₂ nanoparticles, which are usually synthesized by solution methods, the first requirement for commercial application is the preparation of VO₂ nanoparticles with uniform particle sizes. Then, VO₂ nanoparticles would be dissolved in suitable resins and coated on substrates such as glasses and PET. Calculations based on effective medium theory made by Li et al. [80] shows that dilute composites with VO₂ nanoparticles embedded in hosts with properties mimicking glass or polymer can yield significantly decreased luminous absorption jointly with much enhanced transmittance modulation of solar energy. These results demonstrate that VO₂-based nanothermochromics open new avenues toward energy-efficient fenestration. Polymer hosts such as

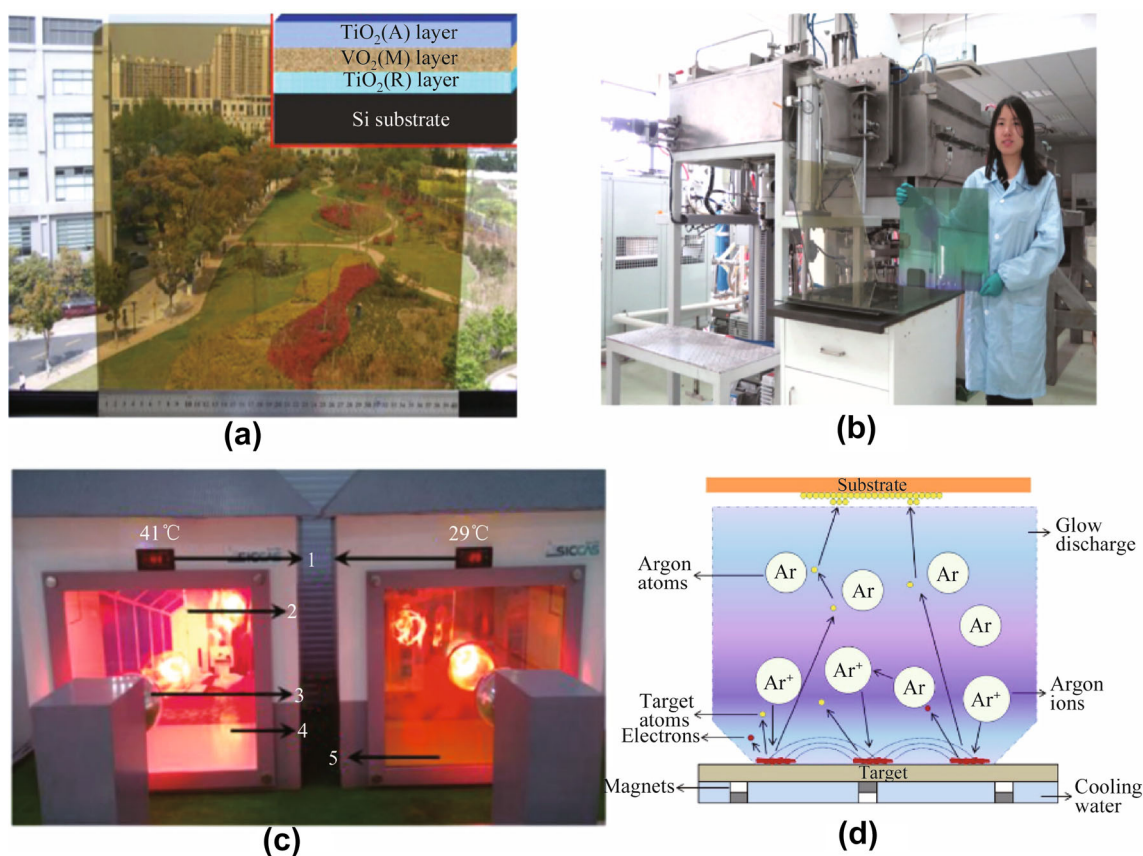


Fig. 13 **a** Photograph of large-scale (400 mm × 400 mm) multilayer film at room temperature (the inset is corresponding structure diagram of the multilayer film), **b** photograph of the magnetron sputtering system, **c** photographic illustration of the testing system, 1: temperature monitor, 2: temperature probe, 3: infrared lamps, 4: blank glass, 5: glass with TiO₂(R)/VO₂(M)/TiO₂(A) multilayer film, **d** schematic diagram illustrating the basic components of a magnetron sputtering system [11, 100]

polyurethane (PU), poly(vinylpyrrolidone) (PVP) and polyamide (PA) have been used. Surface modulation of VO_2 nanoparticles will be carried out and the treated nanoparticles will be dispersed in the polymer hosts to form the suspension. The VO_2 based coatings are prepared by casting the suspension on the substrates. Preparation procedure for $\text{VO}_2@ \text{SiO}_2$ nanoparticles and flexible composite films has been shown in Fig. 14a [29]. Thermal stable PET film covered with VO_2 has been stuck on the glass on which has a size of $1.65 \text{ m} \times 1.65 \text{ m}$ of a model house (see Fig. 14b) [101–104]. The demonstration of the VO_2 glazing's application indicated that compared with the use of the ordinary glazing, the use of VO_2 glazing could save 10.2%–19.9% cumulative cooling load (see Fig. 14c).

6 Conclusions and prospects

As the most attractive thermochromic technology, VO_2 -based smart coatings have gained great attention by researchers and many efforts have been made to promote the real commercialization. Methods such as multilayer stacks, composite films, core-shell structures have been carried out to improve thermochromic performance with enhanced luminous transmittance, solar modulation ability and environmental stability. However, more efforts are still needed to make this technology into our daily lives.

- (i) Optical performances of VO_2 thermochromic smart coatings can be improved by methods, such as element doping, fabricating multilayer

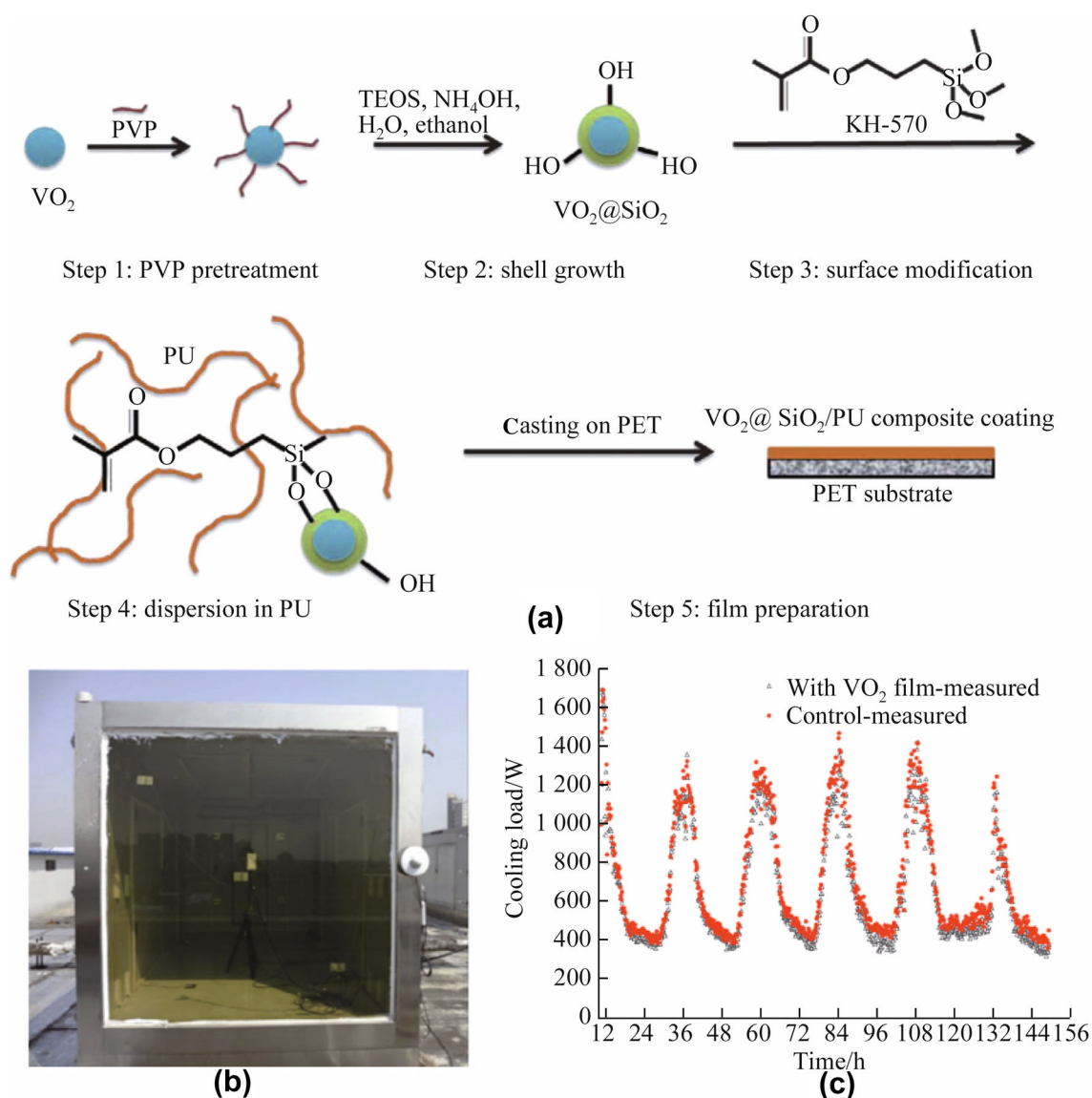


Fig. 14 **a** Preparation procedure for $\text{VO}_2@ \text{SiO}_2$ nanoparticles and flexible composite films, **b** photograph of a model room with VO_2 glazing ($1.65 \text{ m} \times 1.65 \text{ m}$), **c** cooling load comparison during the demonstration of VO_2 glazing [29, 101]

structures, and designing nanostructures. For practical applications, VO₂ smart coatings should have 50% luminous transmittance and 15% solar modulation ability for sufficient energy-saving effect. Optical properties of VO₂ smart coatings can be further improved by computational calculations and simulations for better luminous transmittance and solar modulation ability.

- (ii) Environmental stability of VO₂ coatings is a great challenge for long-time use. Protective layers for VO₂ films as well as core-shell structures for VO₂ nanoparticles can effectively improve the environmental stability of VO₂ coatings. Future work can be carried out by choosing materials with versatility for protective, antireflection and self-cleaning functions.
- (iii) Large-scale production of VO₂ smart coatings is necessary to turn this technology from the lab into the industrial and commercial application. Traditional methods, such as hydrothermal synthesis, spray pyrolysis and sol-gel, etc., are limited due to their low production and complicated process. An effective way to solve this problem is fabricating VO₂ based smart coatings during the production of glasses, just like the deposition of low-emissivity (low-E) coatings on the glass production lines.

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