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Solar Modulation Utilizing VO₂-Based Thermochromic Coatings for Energy-Saving Applications

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.75584>

Abstract

Energy consumption has become an urgent issue not only for the global environment, but also for people's lives. Among total energy consumption, buildings take nearly 40%. For buildings, energy exchange through windows accounts for over 50% by means of conduction, convection, and radiation. To reduce energy consumption, new structures should be developed for glass surfaces to enhance their thermal insulation properties. Vanadium dioxide (VO₂) is the most well-known thermochromic material, which exhibits a notable optical change from transparent to reflecting in the infrared upon a semiconductor-to-metal phase-transition. In this chapter, we provide a comprehensive summary of advances on the VO₂-based thermochromic coatings. Although the research on VO₂ smart window has been carried on for several decades, the real commercial use of it has not yet been achieved. The hindrance factors against commercial use are conventionally known as the unsatisfactory intrinsic properties of VO₂ material and have recently emerged as new challenges.

Keywords: solar modulation, vanadium dioxide, optical design, multilayer structures, energy-saving

1. Introduction

Nowadays, for environmental deterioration and energy shortage in modern human society, people are paying more attention to finding 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 owing to the use of lighting, air-conditioning, and heating [1–5]. Energy

exchange through windows accounts for over 50% of energy consumed through a building's envelope by means of conduction, convection and radiation, as shown in **Figure 1(a)**. Therefore, energy saving of windows contributes the critical and important roles in building energy-efficient projects. Managing heat exchange through windows is a feasible approach to reduce the building energy consumptions. In summer, solar radiation entering buildings should be controlled to reduce the air-conditioning energy consumption. On the contrary, thermal radiation from the buildings must be limited to consume lesser energy for heating.

An effective route to achieve this goal would be using smart coatings on building windows to control the solar radiation. Therefore, smart coatings based on electrochromism [6–10], thermochromism [11–19], gasochromism [20–22] and photochromism [23–26] have been widely investigated for energy-efficient coatings. Thermochromic-coated window can modulate near-infrared radiation (NIR) from transmissive to opaque in response to the environmental temperature from low to high, which does not require extra stimuli and can save more energy consumption. It has two states: a transparent state with a higher solar transmittance and an opaque state with a lower solar transmittance. The thermochromic window [27–29], whose transition depends on the temperature, is widely investigated type of chromogenic window.

Vanadium dioxide (VO_2) is one of the most promising thermochromic materials, which has been widely studied. VO_2 exhibits an automatic reversible semiconductor–metal phase transition (SMT) at a critical transition temperature (T_c) at 68°C [30], which has been widely investigated as smart coatings for building fenestrations [31–35]. As shown in **Figure 1(b)**, for temperatures below the T_c , VO_2 is monoclinic ($\text{P}2_1/c$, M1) phase with the transmittance of NIR. On the contrary, the material is a tetragonal structure ($\text{P}4_2/mnm$, R), which is reflective for NIR [36, 37]. This feature makes VO_2 an amazing material for thermochromic smart coatings [37–45]. Based on VO_2 -thermochromic coatings, smart windows can let the solar energy (mainly caused by NIR) in and out during the cold and hot days, respectively, which are shown in **Figure 1(c)**.

VO_2 smart coatings are usually used in two forms including flexible foils based on VO_2 nanoparticles [34, 46–52] and VO_2 -based multilayer films [11, 12, 33, 53–55]. However, for commercial application as smart coatings on windows, there are still many 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 windows, 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 solar modulation (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 10 years. However, VO_2 can easily transform into the V_2O_5 phase in the real environment,

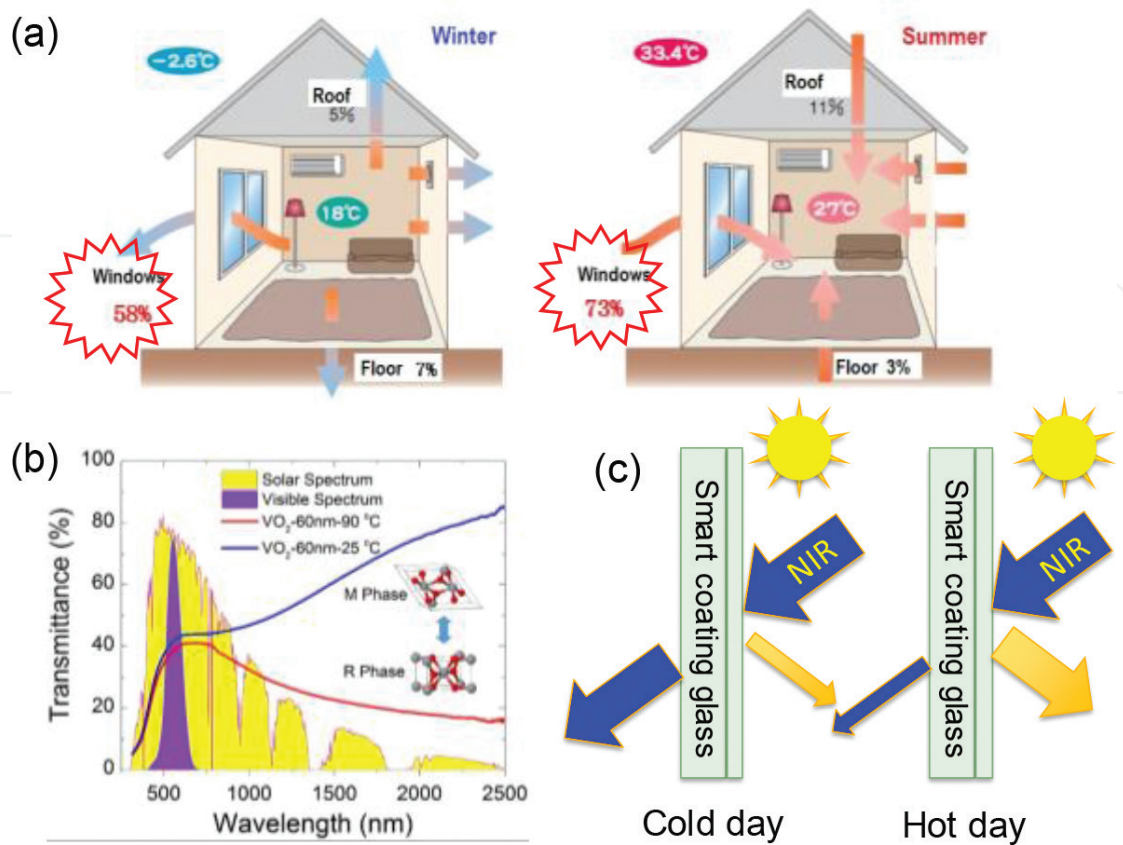


Figure 1. (a) Schematic of energy exchange in winter and summer days. (b) Typical optical properties of thermochromic coatings before and after phase-transition temperature. Inset is the crystallographic structure of VO₂ (monoclinic phase) and VO₂ (rutile phase). (c) Schematic of energy-efficiency based on thermochromic smart coatings.

which is the most thermodynamically stable phase of vanadium oxide but does not possess the thermochromic property [56]. Therefore, environmental stability of VO₂ is a great challenge for practical applications as smart coatings.

These obstacles have to 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⁺ [57], Mo⁶⁺ [58] and Nb⁵⁺ [59], and anions larger than O²⁻, such as F⁻ [60], have been utilized to reduce the T_c . However, obstacles in (II)–(IV) mentioned above have not yet been solved. Although several reviews about VO₂ coatings have been reported [35, 36, 61, 62], most of them are still in lab scale and few prospects of commercial applications are available.

In this chapter, we will review 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, 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 of VO₂

Luminous transmittances (T_{lum}) and solar modulation ability (ΔT_{sol}) are the most important indexes of thermochromic properties for VO₂ smart coatings. The integral luminous transmittances (T_{lum}) and solar transmittances (T_{sol}) of the samples can be obtained by the following equations:

$$T_{lum, sol} = \int \Phi_{lum, sol}(\lambda) T(\lambda) d\lambda / \int \Phi_{lum, sol}(\lambda) d\lambda \quad (1)$$

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. The solar modulation ability (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 [63]. 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 luminous transmittance (T_{lum}) of 30.2% and 25.1% for semiconducting and metallic VO₂ (see **Figure 2(a)**). As for solar modulation ability, the majority of reported modulation abilities are less than 10%, which are not efficient enough for energy-saving function [64–67]. 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 account for 43%.

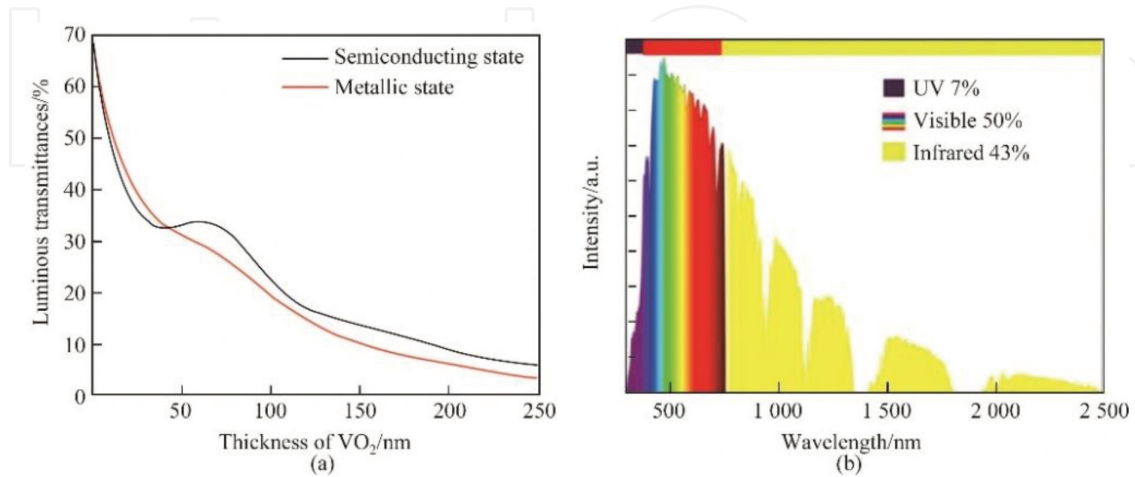


Figure 2. (a) Calculated luminous transmittance for single-layer VO₂ films with various thickness at semiconducting state (black line) and metallic state (red line) and (b) the solar spectrum and relative energy distribution.

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, 55, 68]. 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 has been shown in **Figure 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 employ an anti-reflection (AR) layer, such as SiO₂ [69–72], TiO₂ [73], ZrO₂ [74], etc. Lee et al. [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 anti-reflection 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 luminous transmittance (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 (without AR coating) to 55% for 50 nm VO₂. They deposited an optimized structure of VO₂/ZrO₂, and an improvement from 32.3 to 50.5% in T_{lum} was confirmed for the semiconductor phase of VO₂, which was in good agreement with the calculations.

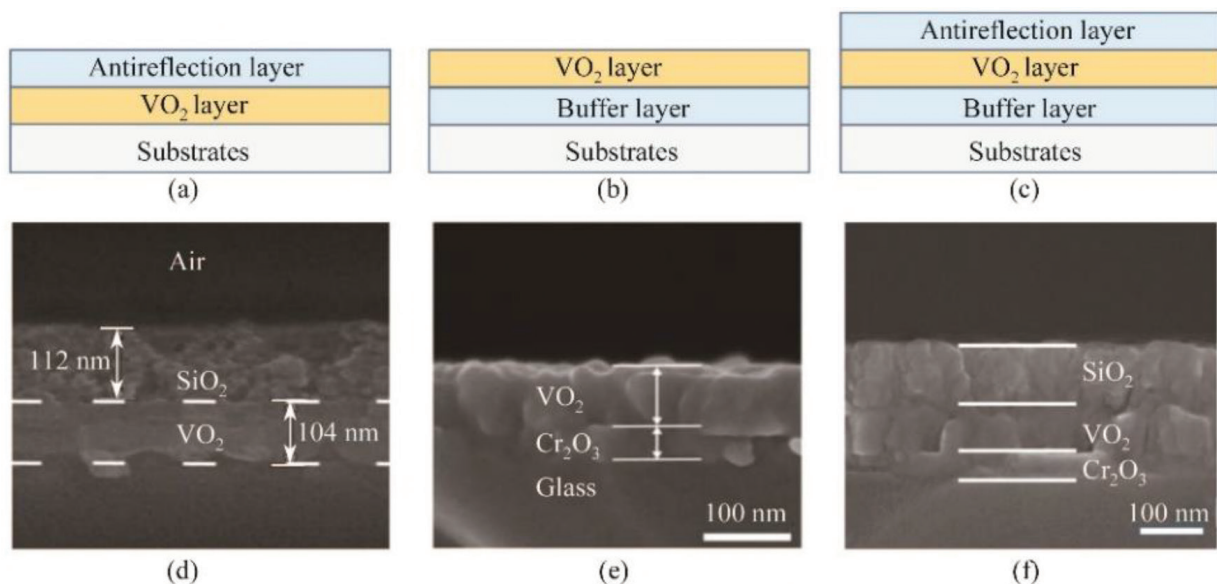


Figure 3. Schematic illustration of VO₂-based films with (a) antireflection layer, (b) buffer layer, and (c) both of antireflection layer and buffer, respectively. Relative SEM images of three typical structures have been shown in figures. (d)–(f) corresponding to figures. (a)–(c) [12, 33, 72], respectively.

Besides the antireflection layers on the top of VO₂ films, buffer layers between the substrates and VO₂ films also play important roles in the optical performances of integrated coatings. Some buffer layers as SiO₂, TiO₂, SnO₂, ZnO, CeO₂, and SiN_x have been investigated in reported work [64, 75–77]. Nevertheless, thermochromic performances of VO₂ coatings obtained based on above buffer layers were fair, which still cannot match the requirements for practical applications.

In our recent work, Cr₂O₃ has been selected to act as a structural template for the growth of VO₂ 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 VO₂ thin films. Refractive index of Cr₂O₃ is between the glass and the VO₂, which is considered to enhance the luminous transmittance. Meanwhile, Cr₂O₃ has similar lattice parameters with VO₂(R), which can act as the structural template layer to lower the lattice mismatch between VO₂ thin films and glass substrates and to reduce the deposition temperature of VO₂ thin films (see **Figure 4(a), (b)**). Different crystallization of VO₂ films can be obtained by introducing Cr₂O₃ layers with various thicknesses at a competitive temperature range from 250 to 350°C, where different thermochromic performance can be obtained (see **Figure 4(c)**). The Cr₂O₃/VO₂ bilayer film deposited 350°C with optimal thickness shows an excellent $\Delta T_{\text{sol}} = 12.2\%$ with an enhanced $T_{\text{lum,lt}} = 46.0\%$ (see **Figure 4(d)**), while the value of ΔT_{sol} and $T_{\text{lum,lt}}$ for the single-layer VO₂ film deposited high temperature at 450°C is 7.8 and 36.4%, respectively. The Cr₂O₃ insertion layer dramatically increased the visible light transmission as well as improved the solar modulation of the original films, which arose from the structural template effect and antireflection function of Cr₂O₃ to VO₂.

For better thermochromic performance, sandwich structures based on VO₂ films have been fabricated. Double-layer antireflection incorporating TiO₂ and VO₂ (TiO₂/VO₂/TiO₂) has been proposed [63], 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 TiO₂/VO₂/TiO₂ has also been investigated by Zheng et al. [11] and Sun et al. [38] for improved thermochromic performance and skin comfort design. A novel sandwich structure of VO₂/SiO₂/TiO₂ has been described by Powell et al. [68], where the SiO₂ layers act as ion-barrier interlayers to prevent diffusion of Ti ions into the VO₂ lattice. The best-performing multilayer film obtained in this work showed excellent solar modulation ability (15.29%), which was very close to the maximum possible solar modulation for VO₂ thin films. Unfortunately, the corresponding luminous transmittance is weak around 18% for both semiconducting and metallic states.

A novel Cr₂O₃/VO₂/SiO₂ (CVS) sandwich structure has been proposed and fabricated based on optical design and calculations [33]. The bottom Cr₂O₃ layer provides a structural template for improving the crystallinity of VO₂ and increasing the luminous transmittance of the structure. Then, the VO₂ 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

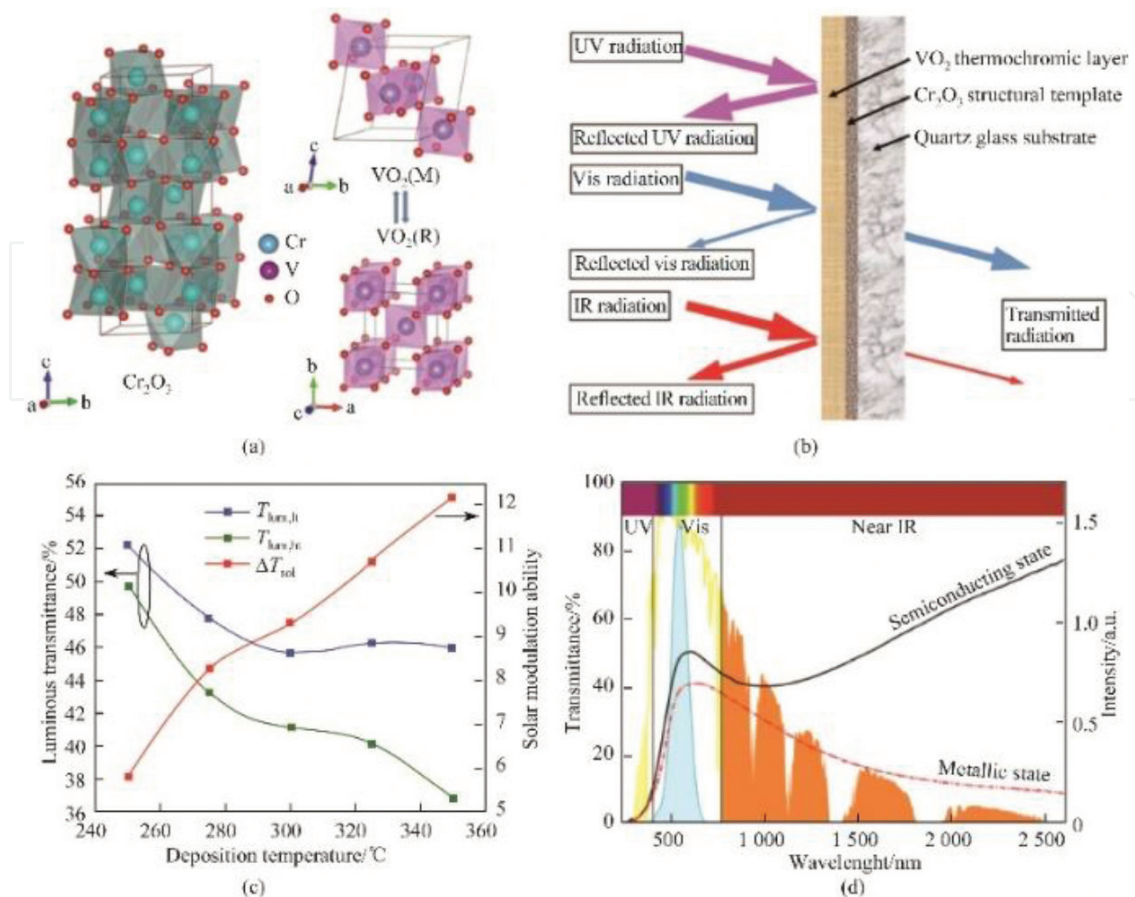


Figure 4. (a) Crystal structure of hexagonal Cr₂O₃, monoclinic VO₂, and rutile VO₂, respectively, (b) schematic illustration of Cr₂O₃/VO₂ bilayer thermochromic film, (c) variation curve of $T_{lum,lt}$, $T_{lum,ht}$ and ΔT_{sol} for VO₂ films deposited with 40 nm Cr₂O₃ structural template layer at different temperatures, (d) transmittance spectra (250–2600 nm) at 25 and 90 °C for VO₂ films deposited with 40 nm Cr₂O₃ structural template layer at 350 °C and standard solar spectra [12].

structure has been shown in **Figure 5(a)** (three-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 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 **Figure 5(b), (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 **Figure 5(d)**).

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

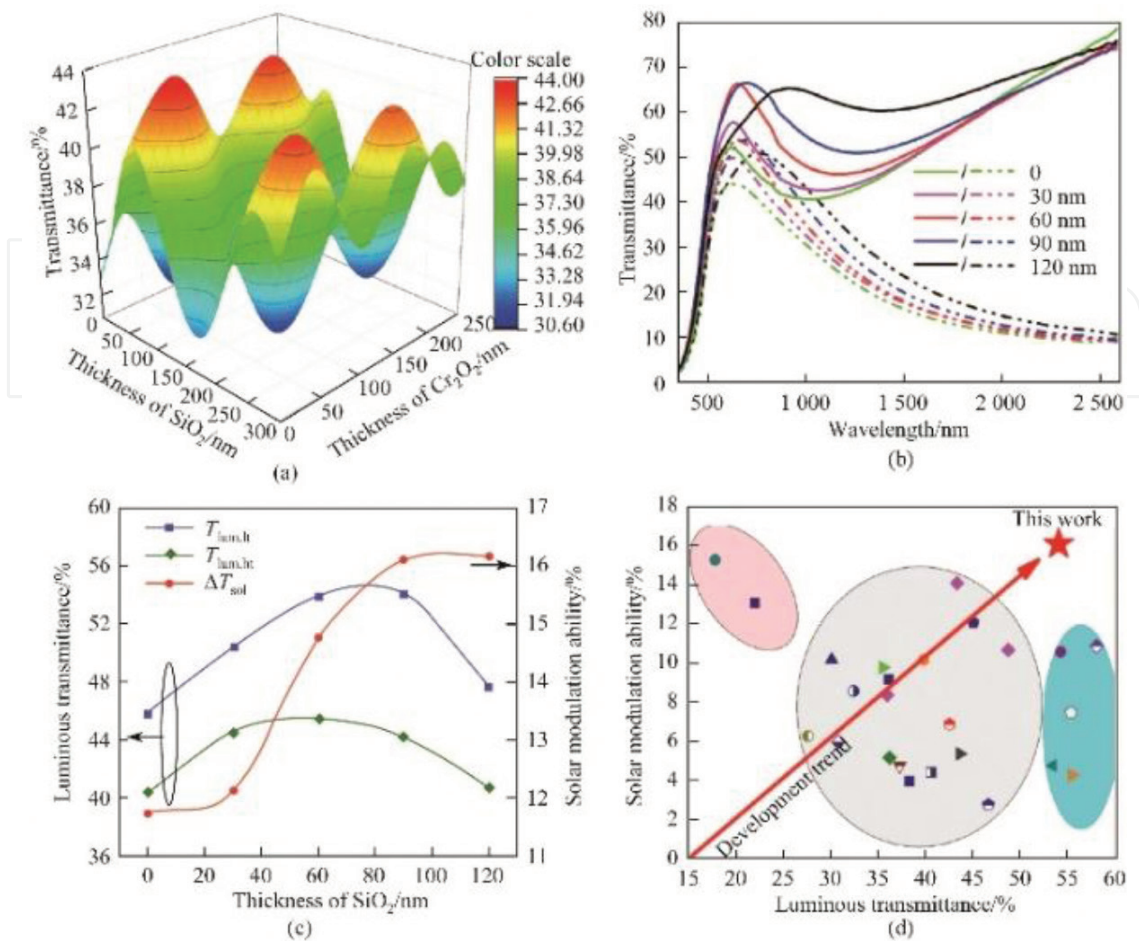


Figure 5. (a) 3D surface image of the luminous transmittance ($T_{lum,lt}$) calculation of the Cr_2O_3/VO_2 (80 nm)/ SiO_2 multilayer structure on the thickness design of Cr_2O_3 (bottom layer) and SiO_2 (top layer), (b) transmittance spectra (350–2600 nm) at 25 (solid lines) and 90°C (dashed lines) for the CVS structures with various thickness of SiO_2 layers, (c) corresponding variation curves of $T_{lum,lt}$, $T_{lum,lt'}$ and ΔT_{sol} for (b), (d) comparison of this work with recently reported VO_2 -based thermochromic films.

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 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.

2.2. Balance between luminous transmittances and solar modulation ability

Regarding practical application of VO_2 -based thermochromic smart coatings, high solar modulation ability (ΔT_{sol}) accompanied by high luminous transmittance (T_{lum}) is required. Nevertheless, we can find that it is tough to make a good balance between luminous transmittance (T_{lum}) and solar modulation ability (ΔT_{sol}). A unilateral pursuit of distinguished solar modulation ability or ultrahigh luminous transmittances is meaningless.

Most work on VO_2 -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 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, which shows a robust contrast in the visible light region in different temperatures [48, 78]. However, more investigations are required for a facile and low-cost 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 thermochemical 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 [57]. However, unlike VO₂, V₂O₅ does not possess thermochemical optical change properties near the room temperature. Therefore, how to maintain the thermochemical performance of VO₂ coatings during a long-time period is an inevitable problem that must be overcome.

To prevent VO₂ films from degradation, introduction of protective layers above VO₂ is an effective way that has been widely used. Chemically stable oxide films such as Al₂O₃ [56, 79], CeO₂ [80, 81], WO₃ [66], 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 [56], 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 [79], 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 1 week (168 h), which is far from the request for practical applications.

Long et al. [66] proposed a novel sandwich structure of $\text{WO}_3/\text{VO}_2/\text{WO}_3$, where WO_3 not only functions as an AR layer to enhance the luminous transmittance (T_{lum}) of VO_2 but also performs as a good protective layer for thermochromic VO_2 . The stability of samples was investigated in a constant-temperature humid environment with 90% relative humidity at 60°C . For the single-layer VO_2 , the thermochromism nearly vanishes after 20 day's treatment in the tough environment. On the contrary, there shows almost no change in the optical transmittance of $\text{WO}_3/\text{VO}_2/\text{WO}_3$ multilayer films with the same treatment. However, though protection is provided by WO_3 , the solar modulation ability of the sample is weakly reduced due to the diffusion of W^{6+} to VO_2 .

In the works above, the protective layers are usually single-layer films. To enhance the durability of thermochromic VO_2 films, bilayer coatings such as $\text{VO}_2/\text{TiO}_2/\text{ZnO}$, $\text{VO}_2/\text{SiO}_2/\text{ZnO}$, and $\text{VO}_2/\text{SiO}_2/\text{TiO}_2$ have been studied [82]. In this study, VO_2 films with TiO_2/ZnO protective coatings have demonstrated higher antioxidant activity under aging tests, which can be attributed to the different oxygen permeability through different inorganic films [83].

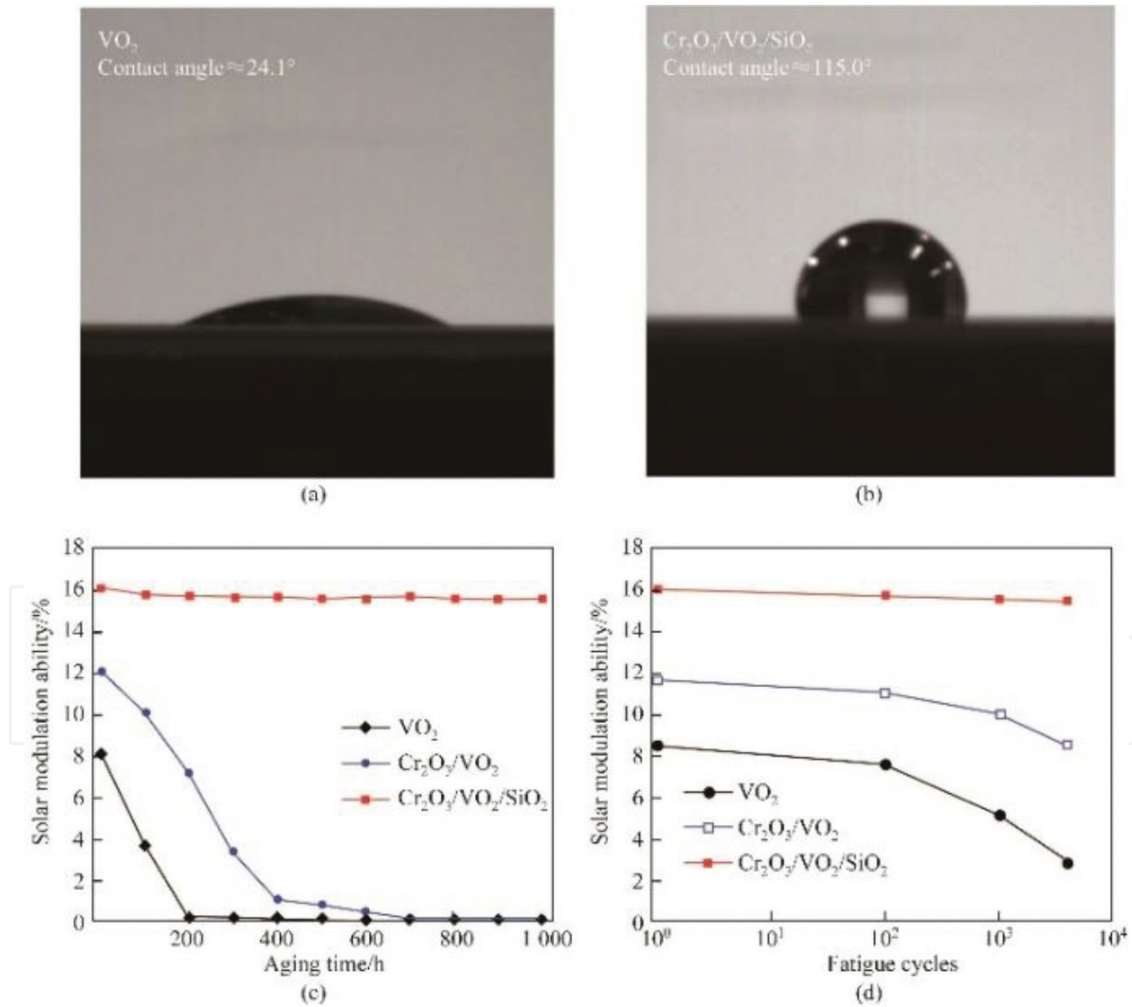


Figure 6. Images of contact angle measurement of (a) the single-layer VO_2 and (b) the proposed $\text{Cr}_2\text{O}_3/\text{VO}_2/\text{SiO}_2$ structure. Variation curves of ΔT_{sol} for VO_2 , $\text{Cr}_2\text{O}_3/\text{VO}_2$, and $\text{Cr}_2\text{O}_3/\text{VO}_2/\text{SiO}_2$ with different duration time (c) and different fatigue cycles (d).

Zhan et al. [84] 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 [33]. 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 **Figure 6(a), (b)**). Hydrophilicity of the single-layer VO₂ indicates contact with water, which will accelerate the degradation process of relative thermochromic performance. On the contrary, the hydrophobicity 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 **Figure 6(b)**). 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 **Figure 6(c), (d)**).

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 TiO₂ are widely and frequently employed to decompose pollutants. There are three different polymorphs of crystalline TiO₂: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Rutile TiO₂ (TiO₂ (R)) is a thermodynamically stable phase at all temperatures and the most common natural form of TiO₂. Due to similar lattice parameters, TiO₂ (R) films are acted as buffer layer and growth template of VO₂ (M) films. However, TiO₂ (R) films are less efficient photocatalysts than anatase TiO₂ (TiO₂ (A)) films, which occupy an important position in the studies of photocatalytic active materials. Zheng et al. [11] constructed a TiO₂(R)/VO₂(M)/TiO₂(A) multilayer film, while the photocatalytic and photo-induced hydrophilic properties from the top TiO₂(A) layer were studied for self-cleaning effects (see **Figure 7(a)**).

Self-cleaning property of the TiO₂(R)/VO₂(M)/TiO₂(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 **Figure 7(b)**. Before UV light irradiation, the characteristic alkyl C—H bond stretching

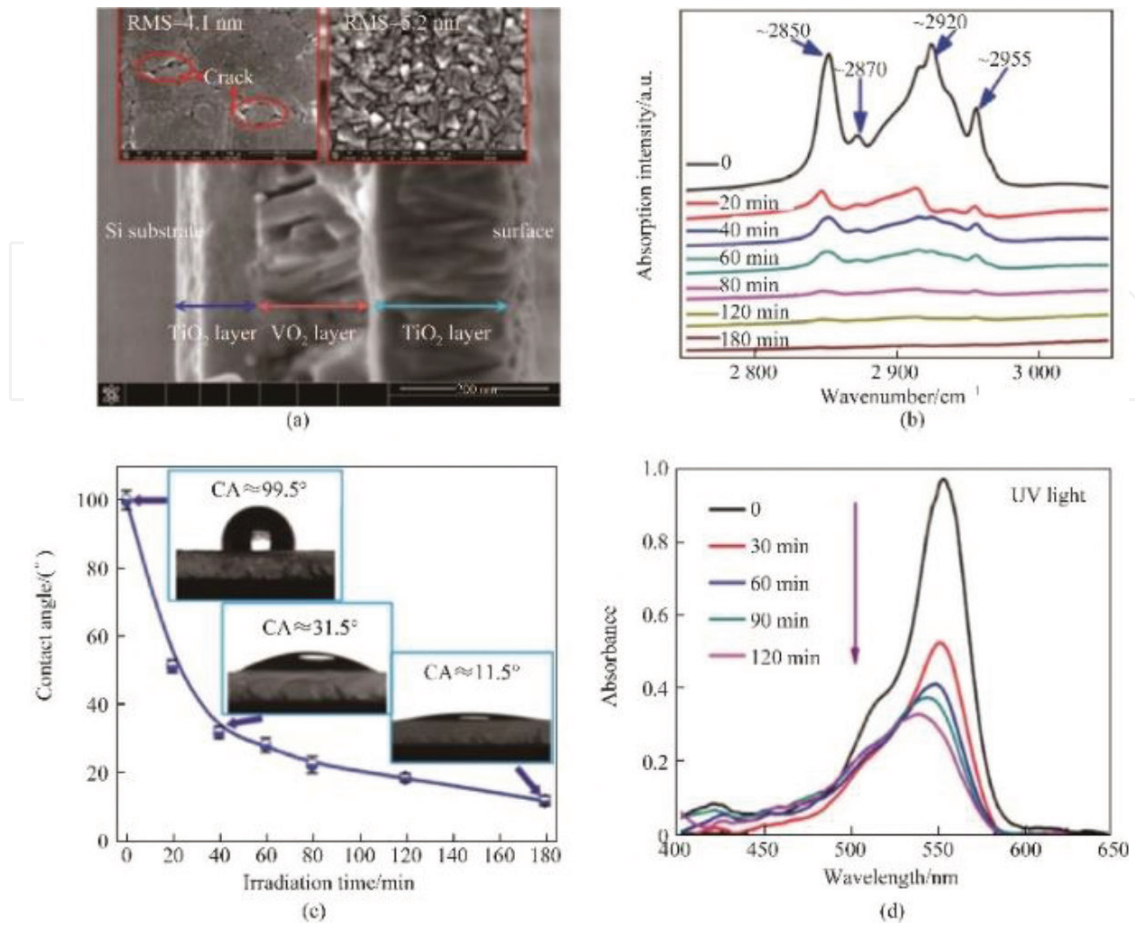


Figure 7. (a) FESEM image of a fractured cross section of the multilayer film (the insets are surface morphology of $\text{VO}_2(\text{M})$ (left) and $\text{TiO}_2(\text{A})$ layers (right), respectively), (b) IR absorbance spectra of $\text{TiO}_2(\text{R})/\text{VO}_2(\text{M})/\text{TiO}_2(\text{A})$ 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 correspond to water droplet shapes on the surface), (d) variation of absorption spectra of RhB aqueous solution degraded by the multilayer film.

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 means 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 **Figure 7(c)**), which can be ascribed to the degradation of stearic acid and the photoinduced hydrophilicity of multilayer film. The photocatalytic activity of $\text{TiO}_2(\text{R})/\text{VO}_2(\text{M})/\text{TiO}_2(\text{A})$ multilayer film also has been demonstrated by the decomposition rate of RhB under UV light irradiation. **Figure 7(d)** 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 acts as the ion-barrier interlayer [68]. 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, which contains a thin TiO₂ layer (15 nm) deposited by CVD methods.

For self-cleaning function and improved stability, VO₂ thermochromic smart coatings with hydrophobic surface have been favored and studied by researchers. VO₂ films with moth-eye

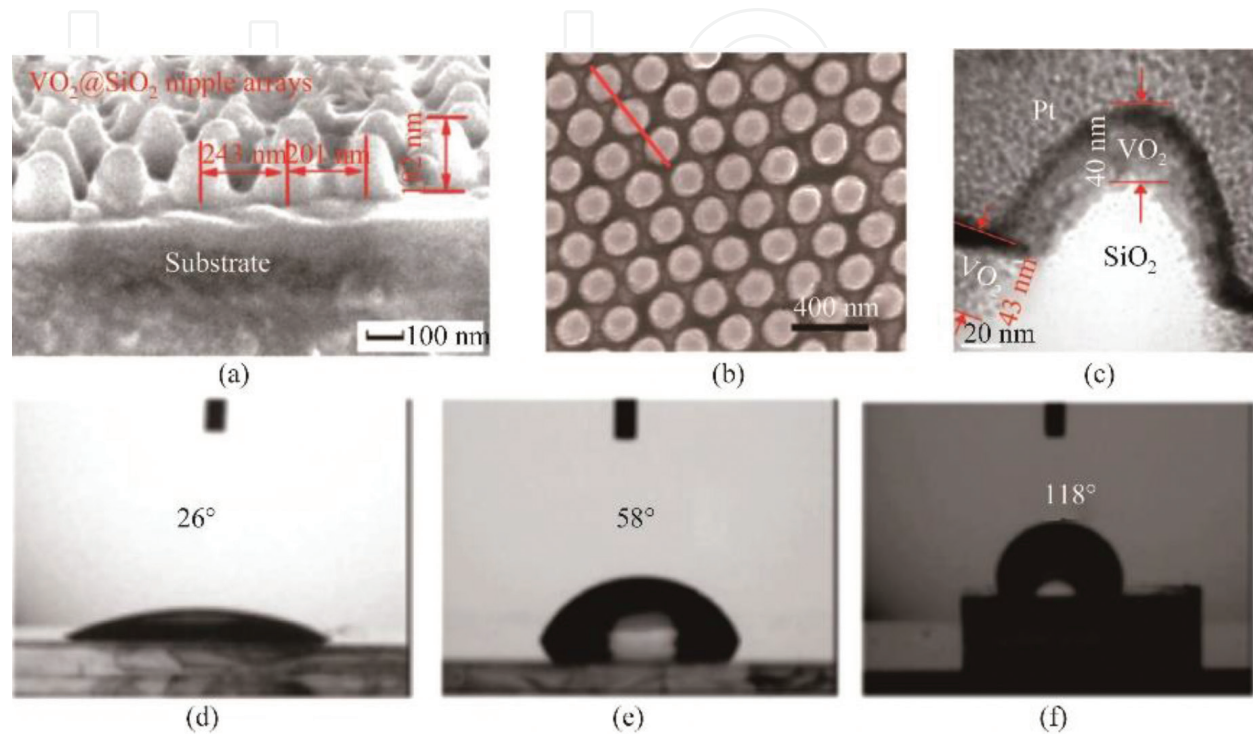


Figure 8. (a) SEM cross-sectional profile of the sample with 210 nm period, (b) top-view SEM image of the sample with 440 nm period, (c) TEM cross-sectional image to show the thickness of VO₂ coatings on SiO₂, (d) planar VO₂, 210 nm patterned VO₂ with 40 nm thickness, and 210 nm patterned VO₂ with fluorooctyl triethoxysilane (FOS) overcoat.

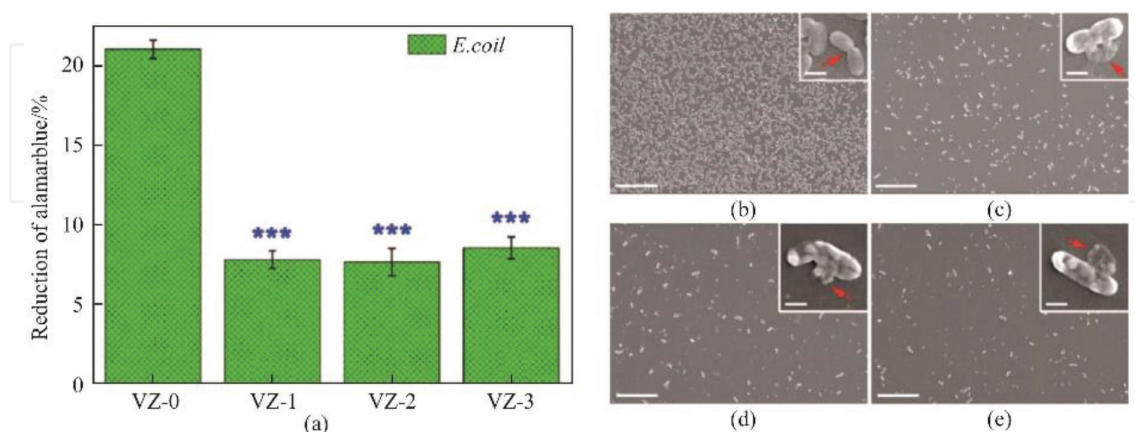


Figure 9. (a) Proliferation viability of *Escherichia coli* after culture of 24 h on samples VZ-0, VZ-1, VZ-2 and VZ-3, accompanied by the SEM morphology of *E. coli* after culture of 24 h on surfaces of (b) VZ-0, (c) VZ-1, (d) VZ-2 and (e) VZ-3 (the scale bar is 20 μ m). The insets show the corresponding partially enlarged SEM images and the scale bar is 1 μ m).

nanostructures have been fabricated to enhance the thermochromic properties, and the hydrophobic surface (contact angle 120°) can be achieved with additional overcoat [85]. Fused silica substrates with AR patterns of different periods (0, 210, 440, 580, and 1000 nm) were prepared by reactive ion etching using 2D polystyrene colloidal crystals as a mask. Nipple arrays based on VO_2/SiO_2 have been realized and the additional fluorooctyl triethoxysilane (FOS) overcoat provides hydrophobicity of the surface (see **Figure 8**).

The biosafety of VO_2 is also under consideration, while the ZnO layer has been used to provide the antibacterial property [86]. 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 **Figure 9**). The sterilization mechanism of ZnO films is believed to be attributed to the synergistic effect of released zinc ions and ZnO nanoparticles by elaborately designing a verification experiment. More importantly, the ZnO layer with an appropriate thickness can significantly reduce the cytotoxicity of VO_2 and thus promote the VO_2 biosafety.

5. Large-scale production of VO_2 smart coatings

For commercial applications on building fenestrations in our daily life, large-scale production of VO_2 -based smart coatings is a great challenge that must be developed. For VO_2 -based films, magnetron sputtering is the most commonly used method and several works about large-scale production of VO_2 -based films by magnetron sputtering have been reported. A large-scale $\text{TiO}_2(\text{R})/\text{VO}_2(\text{M})/\text{TiO}_2(\text{A})$ multilayer film was prepared on a glass with the area of $400 \times 400 \text{ mm}^2$ using magnetron sputtering method by Zheng et al. [11], where a combination of energy-saving, antifogging, and self-cleaning functions has been achieved (see **Figure 10(a)**). $\text{TiO}_2(\text{R})/\text{VO}_2(\text{M})/\text{TiO}_2(\text{A})$ multilayer film was deposited using medium frequency reactive magnetron sputtering (MFRMS, see **Figure 10(b)**) 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 **Figure 10(c)**).

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 causes atoms from that target to be ejected with enough energy to travel to and bond with the substrate (see **Figure 10(d)**).

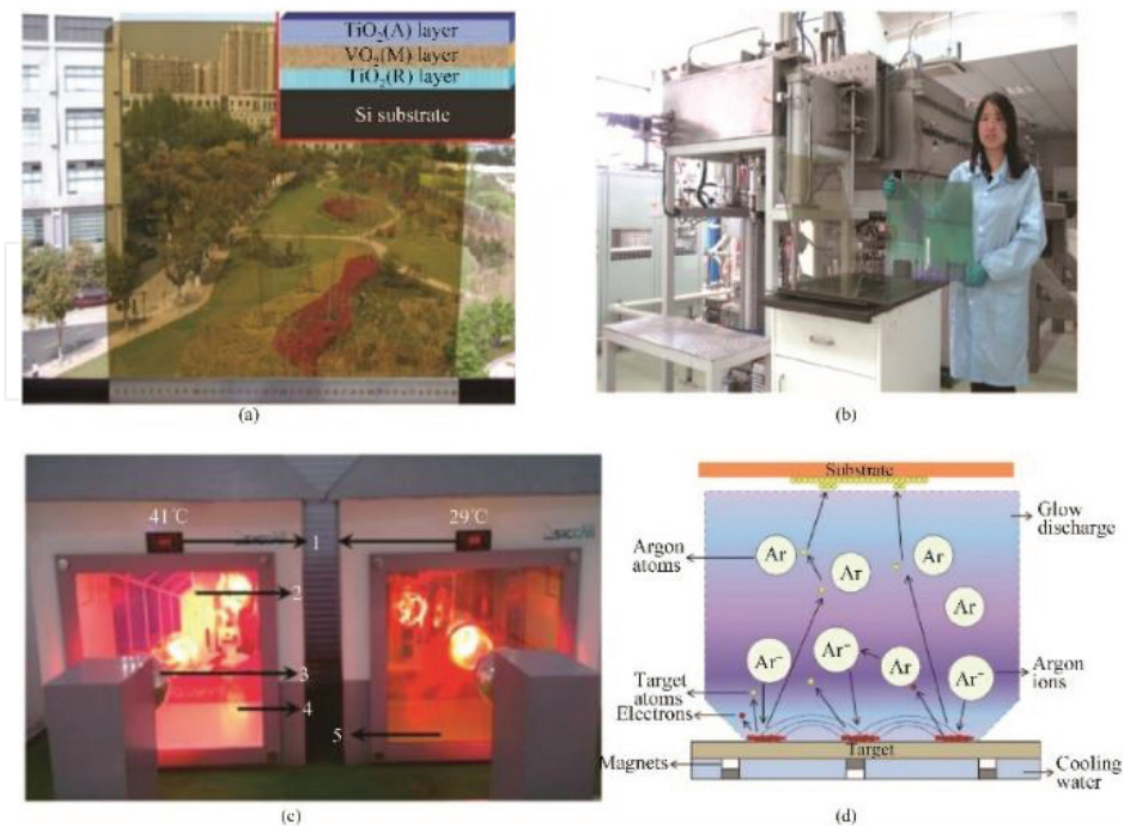


Figure 10. (a) Photograph of large-scale (400 × 400 mm) multilayer film at room temperature (the inset is corresponding structure diagram of the multilayer film), (b) photograph of the magnetron sputtering system, (c) photographic illustration of the testing system, 1: Temperature monitor, 2: Temperature 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.

6. Conclusion and prospects

As the most attractive thermochromic technology, VO₂-based smart coatings have gained great attention by researchers and many efforts have been made to promote the real commercialization. Method of multilayer structures has 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 VO₂ thermochromic smart coatings can be improved by methods, such as element doping, fabricating multilayer structures, and designing nanostructures. For practical applications, VO₂-based 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 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 VO_2 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 VO_2 -based smart coatings during the production of glasses, just like the deposition of low-emissivity (low-E) coatings on the glass production lines.

Acknowledgements

We want to thank Tianci Chang for discussion about the VO_2 materials. This chapter was financially supported by the National Natural Science Foundation of China (Grant No. 51572284) and the “Youth Innovation Promotion Association, Chinese Academy of Sciences” (Grant No.2018288).

Conflict of interest

There is no conflict of interest to declare.

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