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# Solar Modulation Utilizing VO<sub>2</sub>-Based Thermochromic Coatings for Energy-Saving Applications

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## 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 (VO<sub>2</sub>) 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 VO<sub>2</sub>-based thermochromic coatings. Although the research on VO<sub>2</sub> 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 VO<sub>2</sub> material and have recently emerged as new challenges.

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

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## 1. Introduction

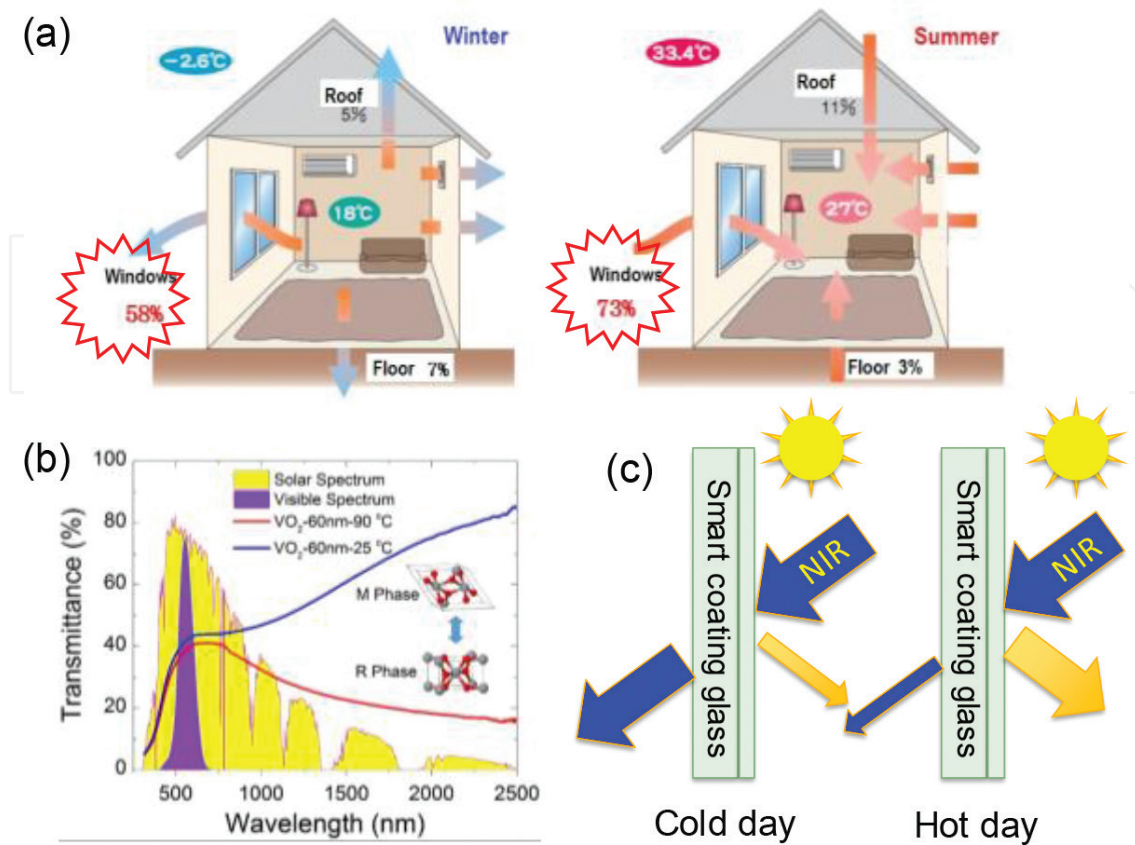
Nowadays, for environmental deterioration and energy shortage in modern human society, people are paying more attention to finding energy-efficient materials to reduce the energy consumption and greenhouse gas emission. According to the survey, buildings are responsible for about 40% of the energy consumption 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 ( $\text{VO}_2$ ) is one of the most promising thermochromic materials, which has been widely studied.  $\text{VO}_2$  exhibits an automatic reversible semiconductor–metal phase transition (SMT) at a critical transition temperature ( $T_c$ ) at  $68^\circ\text{C}$  [30], which has been widely investigated as smart coatings for building fenestrations [31–35]. As shown in **Figure 1(b)**, for temperatures below the  $T_c$ ,  $\text{VO}_2$  is monoclinic ( $\text{P2}_1/c$ , M1) phase with the transmittance of NIR. On the contrary, the material is a tetragonal structure ( $\text{P4}_2/mnm$ , R), which is reflective for NIR [36, 37]. This feature makes  $\text{VO}_2$  an amazing material for thermochromic smart coatings [37–45]. Based on  $\text{VO}_2$ -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)**.

$\text{VO}_2$  smart coatings are usually used in two forms including flexible foils based on  $\text{VO}_2$  nanoparticles [34, 46–52] and  $\text{VO}_2$ -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  $\text{VO}_2$  smart coatings. (I) The phase-transition temperature ( $T_c$ ) for pure bulk  $\text{VO}_2$  ( $68^\circ\text{C}$ ) is too high to be applied on building windows, while  $T_c$  around  $40^\circ\text{C}$  is acceptable. (II) For conventional  $\text{VO}_2$  coatings, relative modulation abilities are not efficient enough for energy saving. That can be explained by the fact that the modulation of  $\text{VO}_2$  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 ( $T_{\text{lum}}$ ) for single layer  $\text{VO}_2$  with desirable solar modulation ( $\Delta T_{\text{sol}}$ ) is usually less than 40% (even 30%) due to the absorption in the short-wavelength range in both the semiconducting and metallic states of  $\text{VO}_2$ , which should be larger than 50% at least for daily applications. (IV) For practical applications as smart coatings,  $\text{VO}_2$  must maintain excellent thermochromic performances during a long-time period-at least 10 years. However,  $\text{VO}_2$  can easily transform into the  $\text{V}_2\text{O}_5$  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 VO<sub>2</sub> (monoclinic phase) and VO<sub>2</sub> (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 VO<sub>2</sub> 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 VO<sub>2</sub>: cations larger than V<sup>4+</sup>, such as W<sup>6+</sup> [57], Mo<sup>6+</sup> [58] and Nb<sup>5+</sup> [59], and anions larger than O<sup>2-</sup>, such as F<sup>-</sup> [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 VO<sub>2</sub> 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 VO<sub>2</sub> 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  $\Delta T_{sol}$ ) of VO<sub>2</sub> coatings have been introduced as well as the balance between  $T_{lum}$  and  $\Delta T_{sol}$  (Section 2). Then, methods to improve the durability of VO<sub>2</sub> coatings, including protective layers for multilayer films, will be summarized in Section 3. Meanwhile, multi-functional design of VO<sub>2</sub> smart coatings such as photocatalysis and self-cleaning function has

been discussed in Section 4. Recent progress for large-scale production of VO<sub>2</sub> smart coatings has been surveyed in Section 5. Finally, future development trends of VO<sub>2</sub> coatings have prospected for large-scale production as practical and commercial applications.

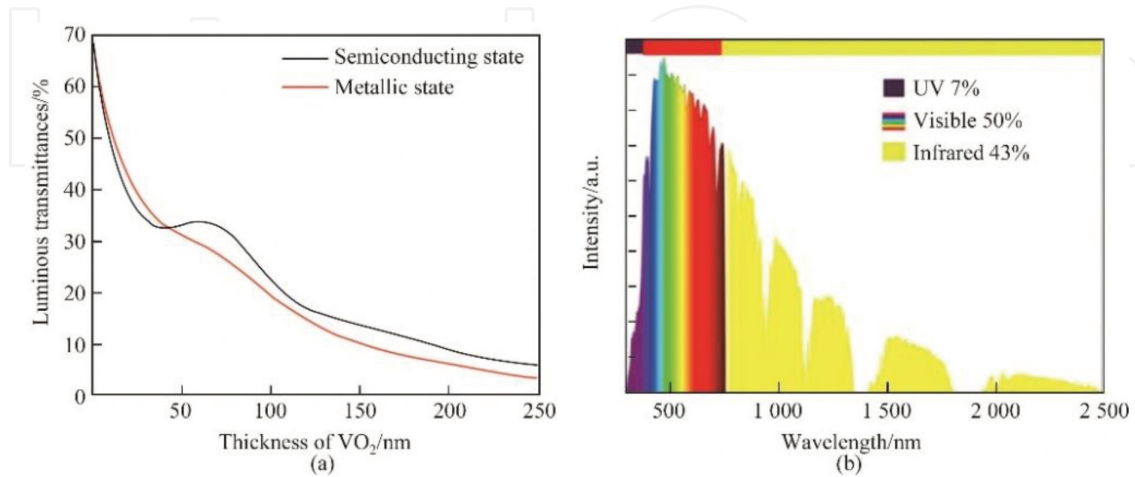
## 2. Improvements of optical properties of VO<sub>2</sub>

Luminous transmittances ( $T_{lum}$ ) and solar modulation ability ( $\Delta T_{sol}$ ) are the most important indexes of thermochromic properties for VO<sub>2</sub> 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  $\lambda$ ;  $\Phi_{lum}$  is the standard efficiency function for photopic vision; and  $\Phi_{sol}$  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 ( $\Delta T_{sol}$ ) 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.

VO<sub>2</sub> 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 VO<sub>2</sub> coatings is largely dependent on relative thicknesses. Based on optical calculation, a single layer VO<sub>2</sub> film (80 nm), for example, exhibits an integrated luminous transmittance ( $T_{lum}$ ) of 30.2% and 25.1% for semiconducting and metallic VO<sub>2</sub> (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 VO<sub>2</sub> 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%.



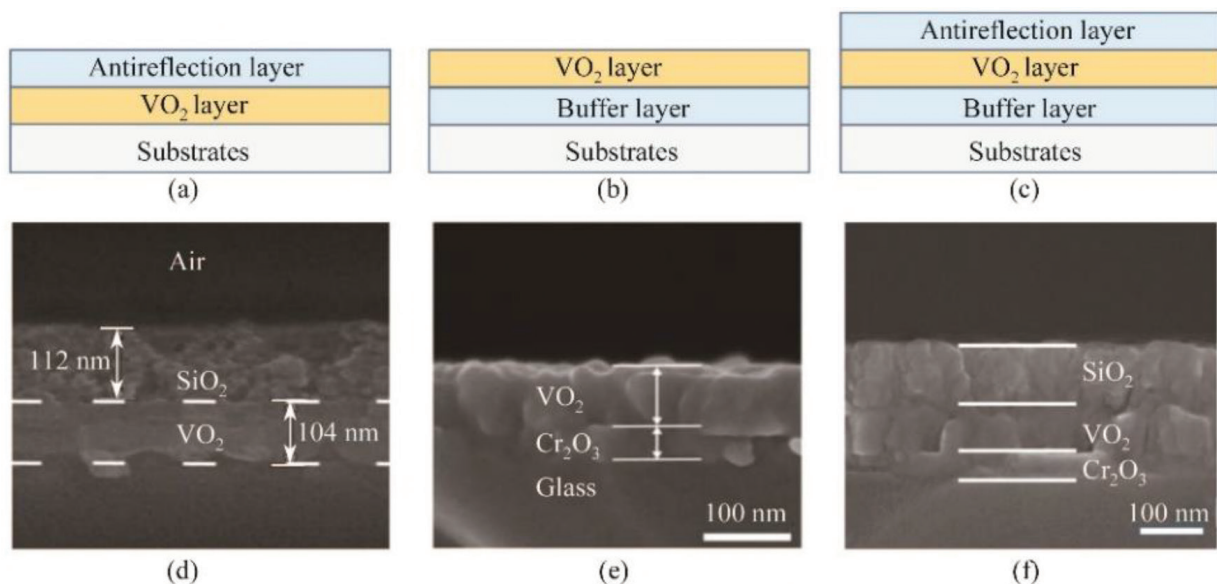
**Figure 2.** (a) Calculated luminous transmittance for single-layer VO<sub>2</sub> films with various thickness at semiconducting state (black line) and metallic state (red line) and (b) the solar spectrum and relative energy distribution.



## 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 VO<sub>2</sub>-based smart coatings. For VO<sub>2</sub> 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 VO<sub>2</sub> 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 VO<sub>2</sub> thin films and relative SEM images.

An effective way to improve the luminous transmittance of VO<sub>2</sub> coatings is to employ an anti-reflection (AR) layer, such as SiO<sub>2</sub> [69–72], TiO<sub>2</sub> [73], ZrO<sub>2</sub> [74], etc. Lee et al. [70, 71] reported that SiO<sub>2</sub> antireflection layer successfully increased the luminous transmittance of the VO<sub>2</sub> films. However, the luminous transmittance is still not sufficient. TiO<sub>2</sub> was selected as AR layer for VO<sub>2</sub> films [73] because TiO<sub>2</sub> has a higher refractive index and is a more effective anti-reflection material for VO<sub>2</sub> than the reported SiO<sub>2</sub>. The optimized VO<sub>2</sub>/TiO<sub>2</sub> 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 VO<sub>2</sub> 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 VO<sub>2</sub>, and at  $n \approx 2.2$  it gives the highest  $T_{lum}$  enhancement from 32 (without AR coating) to 55% for 50 nm VO<sub>2</sub>. They deposited an optimized structure of VO<sub>2</sub>/ZrO<sub>2</sub>, and an improvement from 32.3 to 50.5% in  $T_{lum}$  was confirmed for the semiconductor phase of VO<sub>2</sub>, which was in good agreement with the calculations.



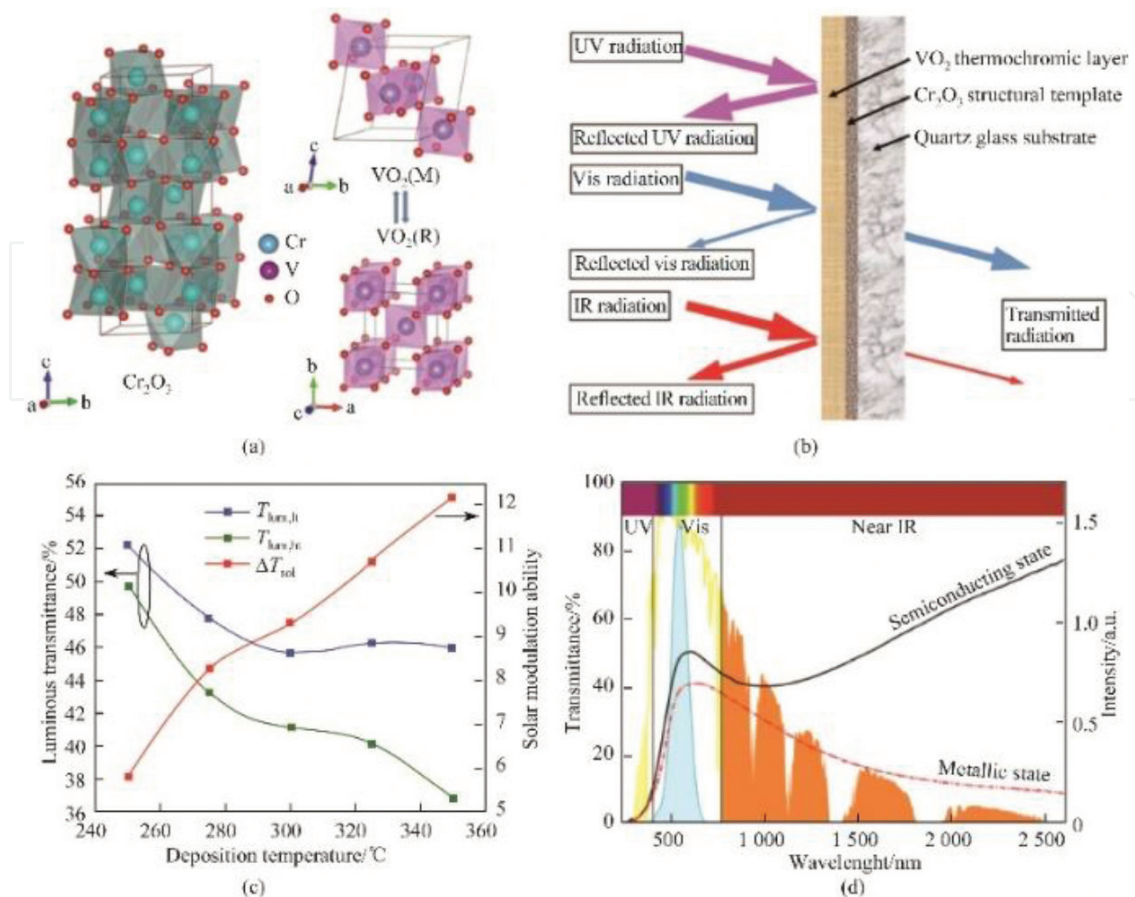
**Figure 3.** Schematic illustration of VO<sub>2</sub>-based films with (a) antireflection layer, (b) buffer layer, and (c) both of antireflection layer and buffer, respectively. Relative SEM images of three typical structures have been shown in figures. (d)–(f) corresponding to figures. (a)–(c) [12, 33, 72], respectively.

Besides the antireflection layers on the top of VO<sub>2</sub> films, buffer layers between the substrates and VO<sub>2</sub> films also play important roles in the optical performances of integrated coatings. Some buffer layers as SiO<sub>2</sub>, TiO<sub>2</sub>, SnO<sub>2</sub>, ZnO, CeO<sub>2</sub>, and SiN<sub>x</sub> have been investigated in reported work [64, 75–77]. Nevertheless, thermochromic performances of VO<sub>2</sub> coatings obtained based on above buffer layers were fair, which still cannot match the requirements for practical applications.

In our recent work, Cr<sub>2</sub>O<sub>3</sub> has been selected to act as a structural template for the growth of VO<sub>2</sub> 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<sub>2</sub> thin films. Refractive index of Cr<sub>2</sub>O<sub>3</sub> is between the glass and the VO<sub>2</sub>, which is considered to enhance the luminous transmittance. Meanwhile, Cr<sub>2</sub>O<sub>3</sub> has similar lattice parameters with VO<sub>2</sub>(R), which can act as the structural template layer to lower the lattice mismatch between VO<sub>2</sub> thin films and glass substrates and to reduce the deposition temperature of VO<sub>2</sub> thin films (see **Figure 4(a), (b)**). Different crystallization of VO<sub>2</sub> films can be obtained by introducing Cr<sub>2</sub>O<sub>3</sub> 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 Cr<sub>2</sub>O<sub>3</sub>/VO<sub>2</sub> 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  $\Delta T_{\text{sol}}$  and  $T_{\text{lum,lt}}$  for the single-layer VO<sub>2</sub> film deposited high temperature at 450°C is 7.8 and 36.4%, respectively. The Cr<sub>2</sub>O<sub>3</sub> 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 Cr<sub>2</sub>O<sub>3</sub> to VO<sub>2</sub>.

For better thermochromic performance, sandwich structures based on VO<sub>2</sub> films have been fabricated. Double-layer antireflection incorporating TiO<sub>2</sub> and VO<sub>2</sub> (TiO<sub>2</sub>/VO<sub>2</sub>/TiO<sub>2</sub>) has been proposed [63], and a maximum increase in  $T_{\text{lum}}$  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 TiO<sub>2</sub>/VO<sub>2</sub>/TiO<sub>2</sub> 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 VO<sub>2</sub>/SiO<sub>2</sub>/TiO<sub>2</sub> has been described by Powell et al. [68], where the SiO<sub>2</sub> layers act as ion-barrier interlayers to prevent diffusion of Ti ions into the VO<sub>2</sub> 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 VO<sub>2</sub> thin films. Unfortunately, the corresponding luminous transmittance is weak around 18% for both semiconducting and metallic states.

A novel Cr<sub>2</sub>O<sub>3</sub>/VO<sub>2</sub>/SiO<sub>2</sub> (CVS) sandwich structure has been proposed and fabricated based on optical design and calculations [33]. The bottom Cr<sub>2</sub>O<sub>3</sub> layer provides a structural template for improving the crystallinity of VO<sub>2</sub> and increasing the luminous transmittance of the structure. Then, the VO<sub>2</sub> 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 SiO<sub>2</sub> 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

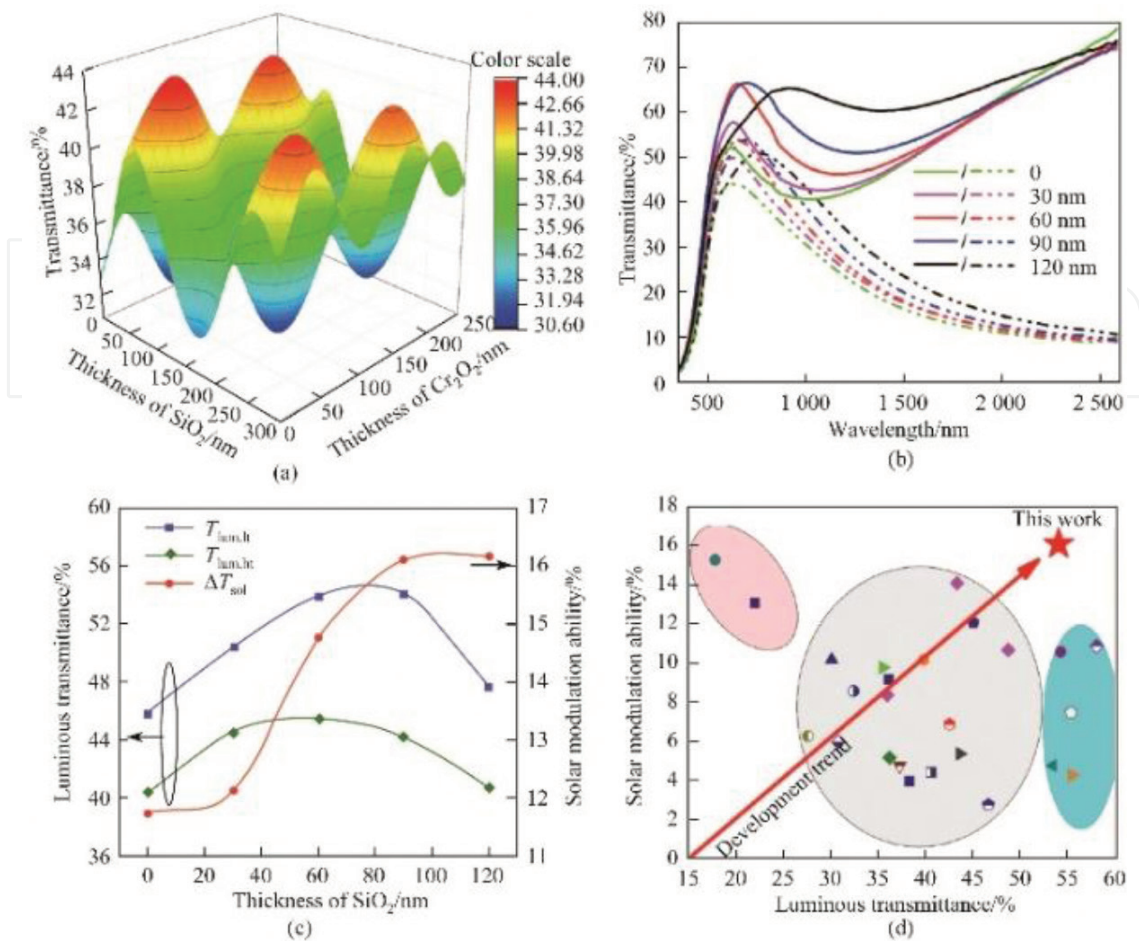


**Figure 4.** (a) Crystal structure of hexagonal Cr<sub>2</sub>O<sub>3</sub>, monoclinic VO<sub>2</sub>, and rutile VO<sub>2</sub>, respectively, (b) schematic illustration of Cr<sub>2</sub>O<sub>3</sub>/VO<sub>2</sub> bilayer thermochromic film, (c) variation curve of  $T_{lum,lt}$ ,  $T_{lum,ht}$  and  $\Delta T_{sol}$  for VO<sub>2</sub> films deposited with 40 nm Cr<sub>2</sub>O<sub>3</sub> structural template layer at different temperatures, (d) transmittance spectra (250–2600 nm) at 25 and 90 °C for VO<sub>2</sub> films deposited with 40 nm Cr<sub>2</sub>O<sub>3</sub> 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 VO<sub>2</sub> layer was fixed at 80 nm to demonstrate significant thermochromic performance while varying thicknesses of Cr<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> 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 Cr<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, 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  $\Delta T_{sol}$  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 VO<sub>2</sub> 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 TiO<sub>2</sub>/VO<sub>2</sub>/TiO<sub>2</sub>/VO<sub>2</sub>/TiO<sub>2</sub> 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  $\Delta T_{sol}$  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 ( $\Delta T_{sol}$ ) 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 ( $\Delta T_{sol}$ ). 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 VO<sub>2</sub>-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 VO<sub>2</sub> 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  $\Delta T_{\text{sol}}$  of VO<sub>2</sub> 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 VO<sub>2</sub>-based smart coatings.

### 3. Methods to improve the stability of VO<sub>2</sub> for long-time use

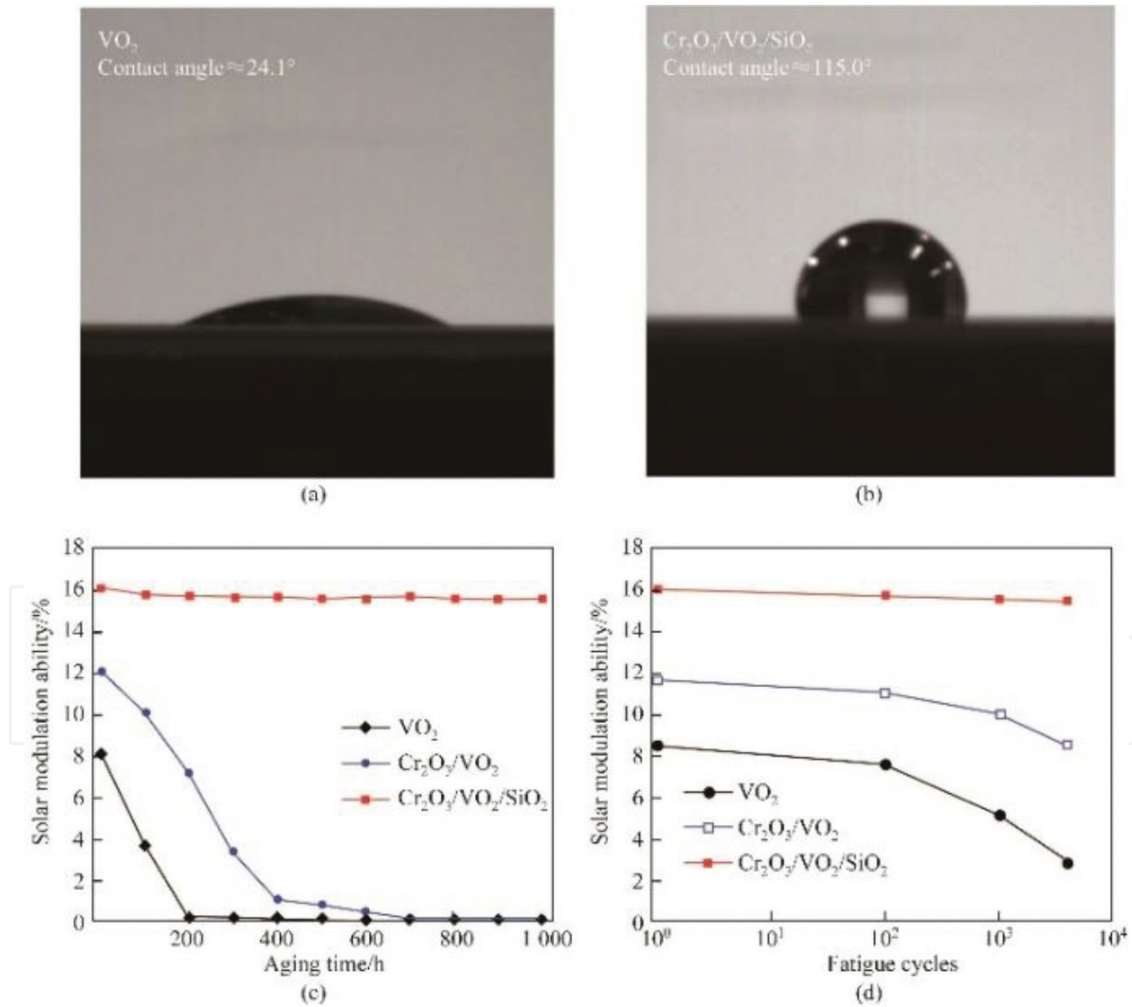
In previous work, researchers usually focus on the thermochemical properties of VO<sub>2</sub> to improve the luminous transmittances and solar modulation ability. However, environmental stability is another great challenge for VO<sub>2</sub> coatings from lab to industrial production. Vanadium is a multivalent element and there are several kinds of vanadium oxide, such as VO, V<sub>2</sub>O<sub>3</sub>, VO<sub>2</sub>, V<sub>6</sub>O<sub>13</sub>, V<sub>4</sub>O<sub>9</sub>, V<sub>3</sub>O<sub>7</sub>, and V<sub>2</sub>O<sub>5</sub>. Among them, V<sub>2</sub>O<sub>5</sub> is the most thermodynamically stable phase and VO<sub>2</sub> will gradually transform into the intermediate phases of V<sub>6</sub>O<sub>13</sub> and V<sub>3</sub>O<sub>7</sub> and finally into V<sub>2</sub>O<sub>5</sub> [57]. However, unlike VO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub> does not possess thermochemical optical change properties near the room temperature. Therefore, how to maintain the thermochemical performance of VO<sub>2</sub> coatings during a long-time period is an inevitable problem that must be overcome.

To prevent VO<sub>2</sub> films from degradation, introduction of protective layers above VO<sub>2</sub> is an effective way that has been widely used. Chemically stable oxide films such as Al<sub>2</sub>O<sub>3</sub> [56, 79], CeO<sub>2</sub> [80, 81], WO<sub>3</sub> [66], etc. have been studied to keep VO<sub>2</sub> away from oxidant like water and O<sub>2</sub> in air. It should be noted that the selected materials to be used as protective layers might affect the optical properties of VO<sub>2</sub>, 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 VO<sub>2</sub> coatings. In work reported by Ji [56], different thicknesses of Al oxide protective layers have been deposited for VO<sub>2</sub> 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 VO<sub>2</sub> in dry air at 300°C and humid environment. The similar structure was also investigated [79], while the Al<sub>2</sub>O<sub>3</sub> protective layers were fabricated by atomic layer deposition (ALD). The Al<sub>2</sub>O<sub>3</sub> films can protect the VO<sub>2</sub> from oxidation in the heating test but not sufficient in the damp environment, which can be attributed to the corrosion of water to Al<sub>2</sub>O<sub>3</sub>. 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  $\text{WO}_3$  not only functions as an AR layer to enhance the luminous transmittance ( $T_{\text{lum}}$ ) of  $\text{VO}_2$  but also performs as a good protective layer for thermochromic  $\text{VO}_2$ . The stability of samples was investigated in a constant-temperature humid environment with 90% relative humidity at  $60^\circ\text{C}$ . For the single-layer  $\text{VO}_2$ , 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  $\text{WO}_3$ , the solar modulation ability of the sample is weakly reduced due to the diffusion of  $\text{W}^{6+}$  to  $\text{VO}_2$ .

In the works above, the protective layers are usually single-layer films. To enhance the durability of thermochromic  $\text{VO}_2$  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,  $\text{VO}_2$  films with  $\text{TiO}_2/\text{ZnO}$  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  $\text{VO}_2$  and (b) the proposed  $\text{Cr}_2\text{O}_3/\text{VO}_2/\text{SiO}_2$  structure. Variation curves of  $\Delta T_{\text{sol}}$  for  $\text{VO}_2$ ,  $\text{Cr}_2\text{O}_3/\text{VO}_2$ , 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<sub>x</sub>/NiCrO<sub>x</sub>/SiN<sub>x</sub>/VO<sub>x</sub>/SiN<sub>x</sub>/NiCrO<sub>x</sub>/SiN<sub>x</sub>, which exhibits enhanced thermal stability up to 375°C. However, aging test in a humid environment is not applied to the samples.

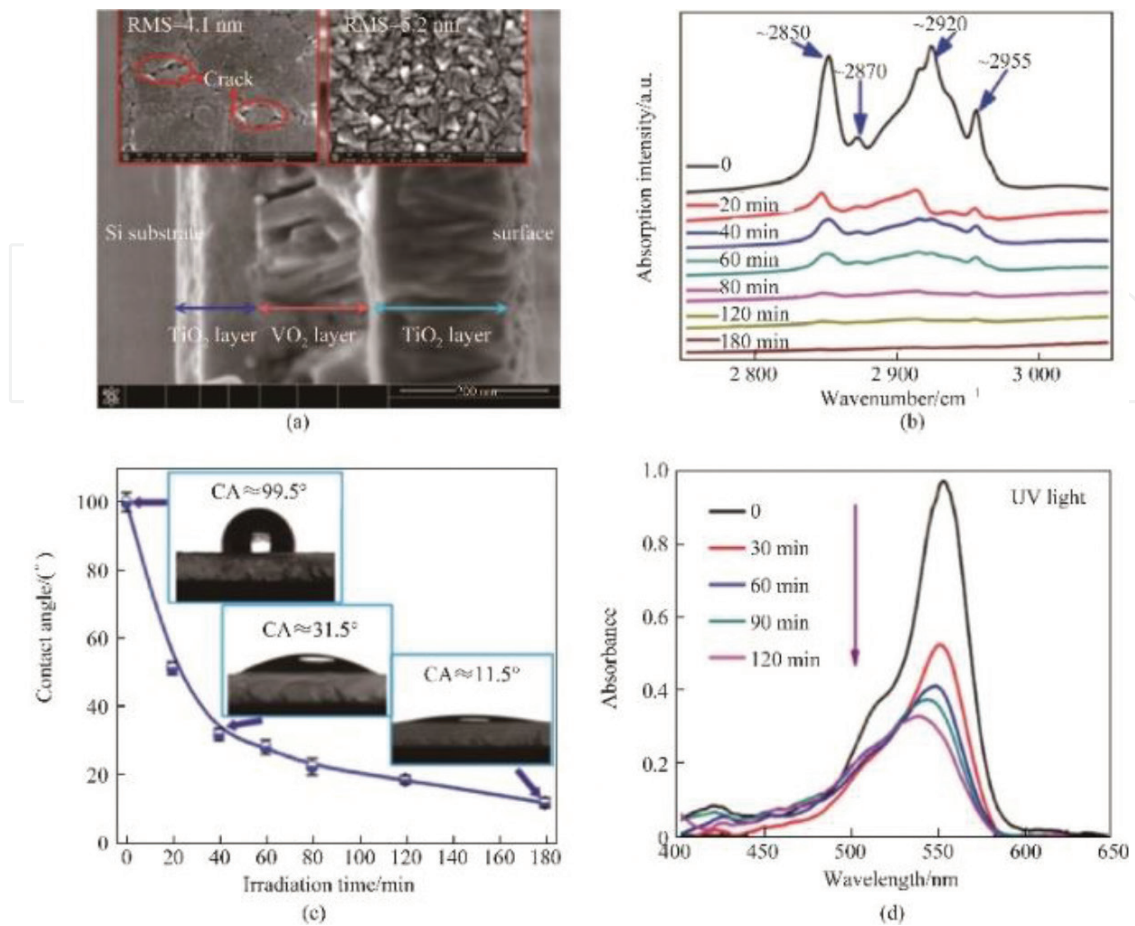
The Cr<sub>2</sub>O<sub>3</sub>/VO<sub>2</sub>/SiO<sub>2</sub> structure proposed by our lab shows robust environmental stability for long-time use [33]. The top SiO<sub>2</sub> layer is chemically stable and makes the static water contact angle of the films change abruptly from 24.1° (hydrophilicity) to 115.0° (hydrophobicity) (see **Figure 6(a), (b)**). Hydrophilicity of the single-layer VO<sub>2</sub> 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 VO<sub>2</sub> 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 SiO<sub>2</sub> top coatings in this work has been deliberately optimized with enhanced roughness for hydrophobic surfaces (see **Figure 6(b)**). The double protection from Cr<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> 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 Cr<sub>2</sub>O<sub>3</sub> and the SiO<sub>2</sub> layer, which shows negligible deterioration even after accelerated aging (60°C and 90% relative humidity) of 10<sup>3</sup> h and 4 × 10<sup>3</sup> fatigue cycles, while VO<sub>2</sub> 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 TiO<sub>2</sub> are widely and frequently employed to decompose pollutants. There are three different polymorphs of crystalline TiO<sub>2</sub>: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Rutile TiO<sub>2</sub> (TiO<sub>2</sub> (R)) is a thermodynamically stable phase at all temperatures and the most common natural form of TiO<sub>2</sub>. Due to similar lattice parameters, TiO<sub>2</sub> (R) films are acted as buffer layer and growth template of VO<sub>2</sub> (M) films. However, TiO<sub>2</sub> (R) films are less efficient photocatalysts than anatase TiO<sub>2</sub> (TiO<sub>2</sub> (A)) films, which occupy an important position in the studies of photocatalytic active materials. Zheng et al. [11] constructed a TiO<sub>2</sub>(R)/VO<sub>2</sub>(M)/TiO<sub>2</sub>(A) multilayer film, while the photocatalytic and photo-induced hydrophilic properties from the top TiO<sub>2</sub>(A) layer were studied for self-cleaning effects (see **Figure 7(a)**).

Self-cleaning property of the TiO<sub>2</sub>(R)/VO<sub>2</sub>(M)/TiO<sub>2</sub>(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



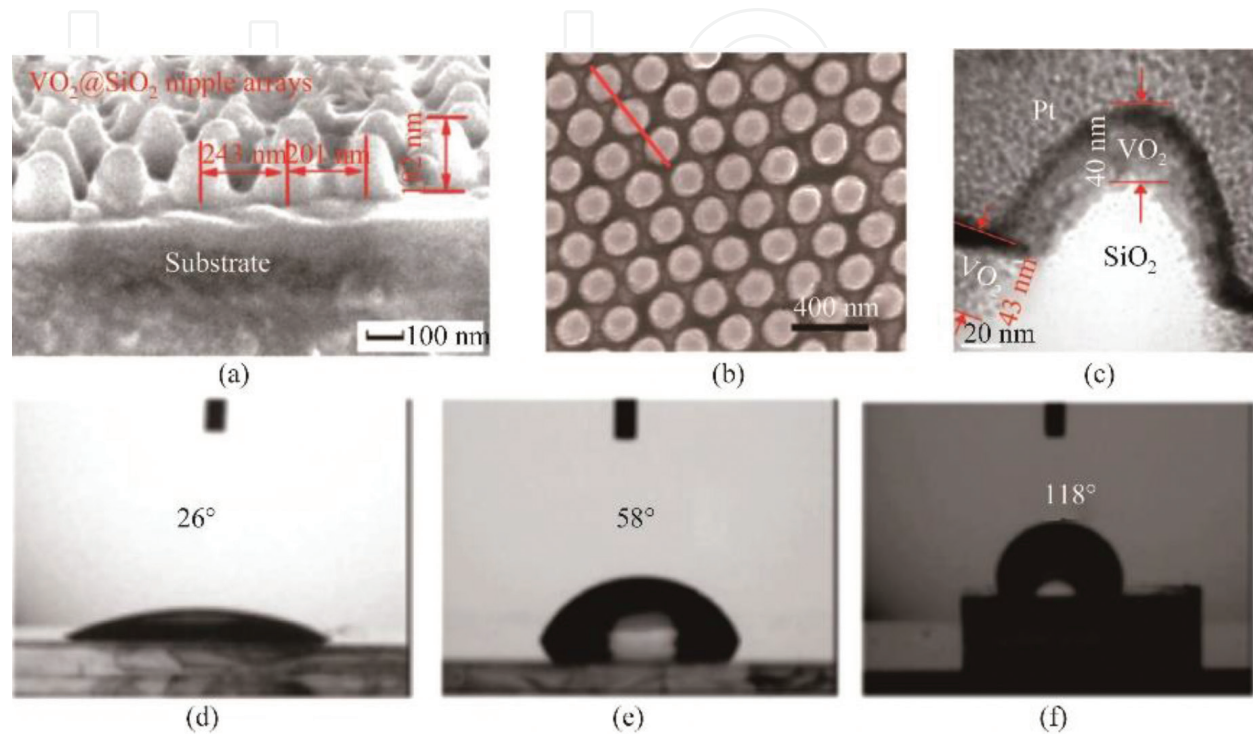


**Figure 7.** (a) FESEM image of a fractured cross section of the multilayer film (the insets are surface morphology of  $\text{VO}_2(\text{M})$  (left) and  $\text{TiO}_2(\text{A})$  layers (right), respectively), (b) IR absorbance spectra of  $\text{TiO}_2(\text{R})/\text{VO}_2(\text{M})/\text{TiO}_2(\text{A})$  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.

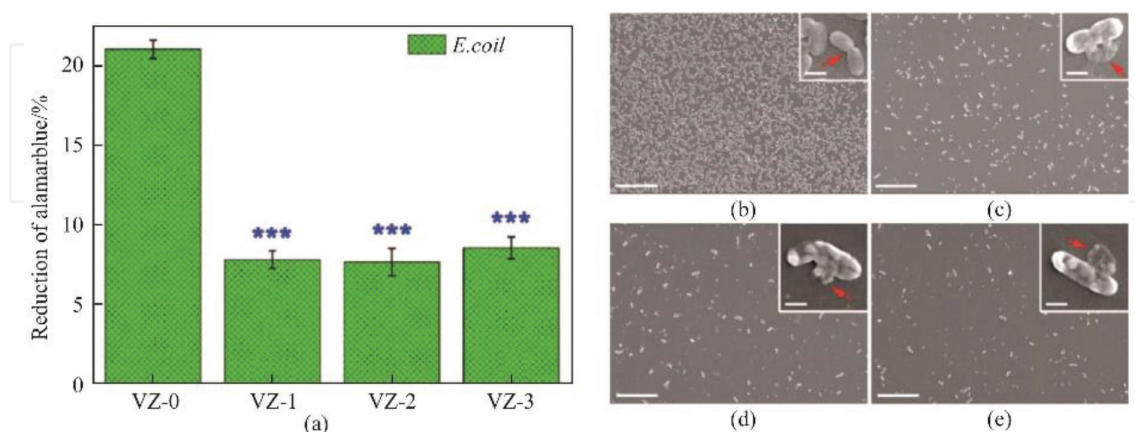
vibrations of  $\text{CH}_2$  and  $\text{CH}_3$  groups ( $3000\text{--}2800\text{ cm}^{-1}$ ) can be distinctly detected. After UV light irradiation of 20 min, the absorbance of C—H bond stretching vibrations decreased drastically, which means that a considerable proportion of stearic acid was decomposed. 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  $99.5^\circ$  (hydrophobic) to  $11.5^\circ$  (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  $\text{SiO}_2$  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 TiO<sub>2</sub> layer (15 nm) deposited by CVD methods.

For self-cleaning function and improved stability, VO<sub>2</sub> thermochromic smart coatings with hydrophobic surface have been favored and studied by researchers. VO<sub>2</sub> 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 VO<sub>2</sub> coatings on SiO<sub>2</sub>, (d) planar VO<sub>2</sub>, 210 nm patterned VO<sub>2</sub> with 40 nm thickness, and 210 nm patterned VO<sub>2</sub> 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  $\mu$ m). The insets show the corresponding partially enlarged SEM images and the scale bar is 1  $\mu$ m).

nanostructures have been fabricated to enhance the thermochromic properties, and the hydrophobic surface (contact angle  $120^\circ$ ) 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  $\text{VO}_2/\text{SiO}_2$  have been realized and the additional fluorooctyl triethoxysilane (FOS) overcoat provides hydrophobicity of the surface (see **Figure 8**).

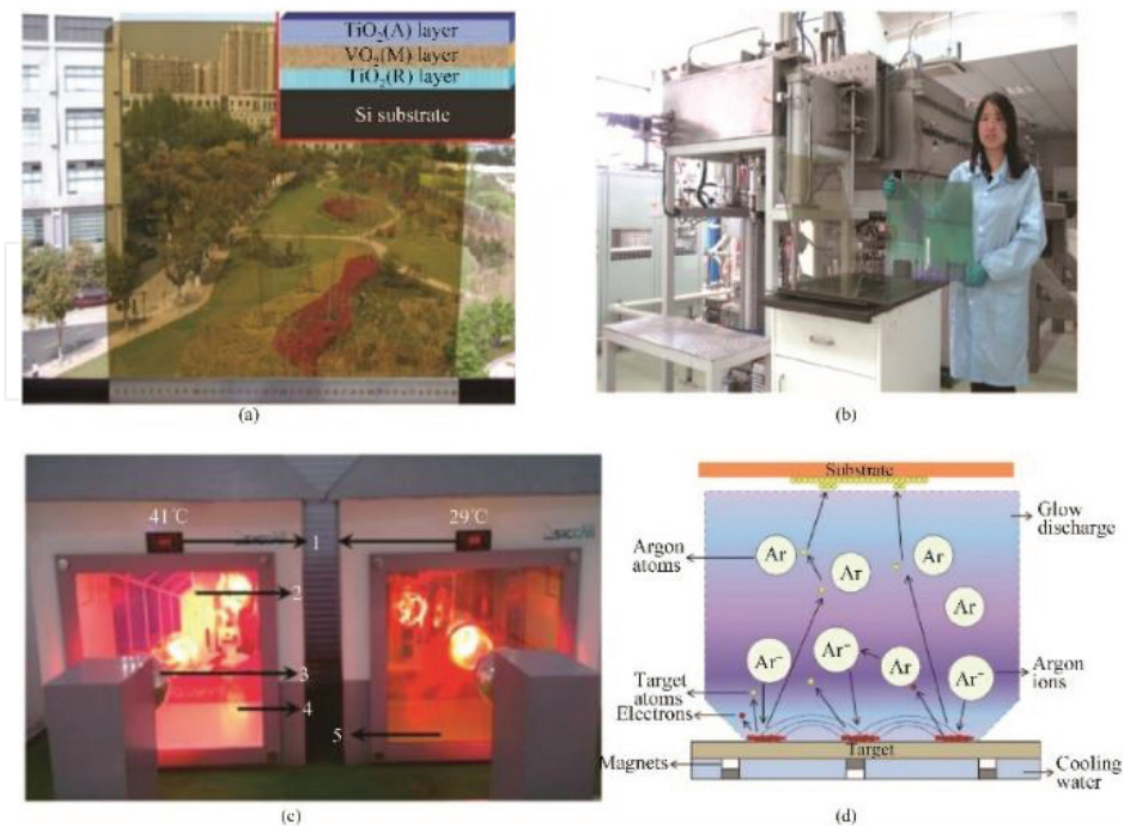
The biosafety of  $\text{VO}_2$  is also under consideration, while the ZnO layer has been used to provide the antibacterial property [86]. ZnO-coated  $\text{VO}_2$  thin films exhibited excellent antibacterial property proved by SEM observation results that ZnO-coated samples cause the membrane disruption 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  $\text{VO}_2$  and thus promote the  $\text{VO}_2$  biosafety.

## 5. Large-scale production of $\text{VO}_2$ smart coatings

For commercial applications on building fenestrations in our daily life, large-scale production of  $\text{VO}_2$ -based smart coatings is a great challenge that must be developed. For  $\text{VO}_2$ -based films, magnetron sputtering is the most commonly used method and several works about large-scale production of  $\text{VO}_2$ -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  $12^\circ\text{C}$  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 TiO<sub>2</sub>(R)/VO<sub>2</sub>(M)/TiO<sub>2</sub>(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, VO<sub>2</sub>-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 VO<sub>2</sub> thermochromic smart coatings can be improved by methods, such as element doping, fabricating multilayer structures, and designing nanostructures. For practical applications, VO<sub>2</sub>-based smart coatings should have 50% luminous transmittance and 15% solar modulation ability for sufficient energy-saving effect. Optical properties of VO<sub>2</sub> smart coatings can be further improved by computational calculations and simulations for better luminous transmittance and solar modulation ability.
- II. Environmental stability of VO<sub>2</sub> coatings is a great challenge for long-time use. Protective layers for VO<sub>2</sub> films can effectively improve the environmental stability of VO<sub>2</sub> coatings.



Future work can be carried out by choosing materials with versatility for protective, antireflection, and self-cleaning functions.

- III.** Large-scale production of  $\text{VO}_2$  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  $\text{VO}_2$ -based smart coatings during the production of glasses, just like the deposition of low-emissivity (low-E) coatings on the glass production lines.

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## Conflict of interest

There is no conflict of interest to declare.

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