Transparent hydrophobic thermal insulation Cs\textsubscript{x}WO\textsubscript{3}-ZnO-SiO\textsubscript{2} coatings: Energy saving, anti-dust and anti-fogging performance

Mengyuan Li, Zhiyang Zhao, Xianli Fang*, Zefeng Zhang and Min Deng*
College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, People's Republic of China
*Author to whom any correspondence should be addressed
E-mail: xianlif@njtech.edu.cn and dengmin@njtech.edu.cn

Keywords: Cs\textsubscript{x}WO\textsubscript{3}, ZnO, nano-SiO\textsubscript{2} resin, anti-dust, thermal insulation

Abstract
Cs\textsubscript{x}WO\textsubscript{3}-ZnO-SiO\textsubscript{2} smart coatings were proposed to achieve multiple functions, such as thermal insulation, anti-dust, anti-fogging and blocking harmful ultraviolet light, etc. The transparent hydrophobic hybrid resins were prepared from methyltriethoxysilane (MTES) and SiO\textsubscript{2} sol, which was used as the substrate of the composite coating. The Cs\textsubscript{x}WO\textsubscript{3} is served as the near-infrared (NIR) absorber, and the ZnO is functioned as the ultraviolet (UV) blocking agent. Coatings with different ratios of Cs\textsubscript{x}WO\textsubscript{3} and ZnO were successfully prepared by co-blending with nano-SiO\textsubscript{2} resin. The morphology, microstructure, surface composition, hydrophobicity, thermal stability, anti-dust and optical property of the composite coatings were investigated comprehensively. The transmittance of C10Z10 (Cs\textsubscript{x}WO\textsubscript{3} 10%, ZnO 10%, nano-SiO\textsubscript{2} resin 80%) coating at 370 nm is 2.3%, and the value of Solar Energy Transmittance Selectivity (SETS) is 0.665, which exhibits excellent NIR shielding ability. Compared with nano-SiO\textsubscript{2} resin coating, the thermal insulation temperature difference can reach 7.0 °C. The C10Z10 coating showed good durability in the twenty times anti-dust repeated tests and the efficiency could maintain 70.3% after the repeating tests. The coating showed excellent sustainability after a 45-day outdoor exposure experiment and a 240 h of artificial accelerated aging experiment. Thus, the proposed Cs\textsubscript{x}WO\textsubscript{3}-ZnO-SiO\textsubscript{2} coatings are promising for outdoor smart windows.

1. Introduction

Energy crisis has become a worldwide topic of widespread concern owing to the rapid development of the industrialization and the increasing energy depletion [1]. According to the International Energy Agency reports, the building energy consumption accounts for 41% of the total global energy depletion. This has caused serious energy burdens and environmental pollution, so improving energy efficiency has become an extremely concerned issue. In the past ten years, solar thermal insulation coatings for building glass have become more and more important for sustainable development from an energy-saving point of view [2–5].

Cs-doped tungsten bronze (Cs\textsubscript{x}WO\textsubscript{3}) nanoparticles can selectively shield NIR light while keeping high visible transparency. It belongs to a kind of non-toxic and cheap material for solar thermal insulation [6–8]. The near-infrared shielding properties and thermal insulation of the Cs\textsubscript{x}WO\textsubscript{3} have been extensively investigated in recent years. For instance, a wide-band two-component near-infrared shielding coating with Cs\textsubscript{x}WO\textsubscript{3} and antimony doped tin oxide (ATO) was prepared [9], the coating could shield NIR light as much as 90.9% and maintain high transparency in visible light of 70.6%, as the optimized mass ratio value of Cs\textsubscript{x}WO\textsubscript{3} to ATO is 1. Wu et al. [10] proposed a novel Cs\textsubscript{x}WO\textsubscript{3}/ZnO smart coating, whose thermal insulation performance was superior to the indium tin oxide coating and the photocatalytic purification of toxic gas was better than the commercial P25 (TiO\textsubscript{2}). However, the NIR shielding properties of Cs\textsubscript{x}WO\textsubscript{3} nanoparticles exhibited significant instabilities in weathering evaluations [11–13]. One of these serious problems is that when the Cs\textsubscript{x}WO\textsubscript{3} is dispersed in resin coatings, photochromism will inevitably occur, leading to a dark appearance of the coating.
Another problem is the NIR shielding ability of Cs\textsubscript{x}WO\textsubscript{3} easily deteriorates in hot humid and alkaline environment, which hinders further applications of Cs\textsubscript{x}WO\textsubscript{3}. Thus, Zeng et al \cite{14} made use of the ultraviolet absorber and SiO\textsubscript{2} composite resin to enhance the UV resistance of Cs\textsubscript{x}WO\textsubscript{3} coating and it showed good near infrared shielding ability as well as excellent optical stability. Meanwhile, Cs\textsubscript{x}WO\textsubscript{3}@ZnO may improve the stability in the humid alkaline environment, owing to its high performance of NIR shielding and enhanced stability as a core–shell structure nanocomposite \cite{15}. Furthermore, a novel bio-based material which combined Cs\textsubscript{x}WO\textsubscript{3} with transparent wood was synthesized. The composite bio-based material showed both excellent NIR shielding ability and good mechanical property \cite{16}. However, the preparation methods of these materials are too complex and costly to realize large-scale industrial application in spite of their improved performances. In addition, dust in the natural environment will decrease the light transmittance of the glass when the solar thermal insulation coating is applied outdoors \cite{17}. So, more resources are needed to clean it. Obviously, the enhancement of anti-dust ability to prevent contamination is indispensable for Cs\textsubscript{x}WO\textsubscript{3} served as window glass coatings.

The optical stability of Cs\textsubscript{x}WO\textsubscript{3} and the sustainability in outdoor surroundings are crucial for the coating to be applied into the practical applications. Therefore, recent works focus on developing coatings with both solar thermal insulation and anti-dust properties simultaneously. In this study, nano-SiO\textsubscript{2} resins were prepared via sol-gel method from MTES and SiO\textsubscript{2} sol. Then, the Cs\textsubscript{x}WO\textsubscript{3}-ZnO-SiO\textsubscript{2} coating were prepared by simple co-blending of Cs\textsubscript{x}WO\textsubscript{3}, ZnO nanoparticles and the previous as-prepared resins. The morphology, chemical structure, optical transparency, thermal insulation, and anti-dust property of the composite coatings were investigated. Besides, the durability of the prepared Cs\textsubscript{x}WO\textsubscript{3}-ZnO-SiO\textsubscript{2} coating were verified. The results indicated that Cs\textsubscript{x}WO\textsubscript{3}-ZnO-SiO\textsubscript{2} coatings are promising for outdoor thermal insulation.

2. Experimental

2.1. Materials

N-butanol, absolute ethanol (EtOH) and zinc oxide dispersed in EtOH (30\%, 30–40 nm) are all purchased from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). Hydrochloric acid (HCl) is provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). SiO\textsubscript{2} sol dispersed in isopropanol (30\%, 10–15 nm) is purchased from Nissan Chemical Industries, Ltd. Dispersion of Cs\textsubscript{x}WO\textsubscript{3} NPs in EtOH, the solid content is 30\% is obtained from Nanomaterials Technology Pte. Ltd. (Xiamen, China). MTES is purchased from Qufu Chenguang Chemical Co., Ltd. (Qufu, China) and distillated before use.

2.2. Synthesis of nano-SiO\textsubscript{2} resin

Typically, 35.6 g of MTES, 35.6 g of n-butanol and 66.7 g of SiO\textsubscript{2} sol were added into a four-neck flask equipped with a mechanical stirrer, thermometer and reflux condenser. Then, the mixed system was heated to 70 °C and stirred for 30 min. Then, 10.8 g of HCl aqueous solution (pH 3) was added dropwise into the flask at 70 °C for 5 h. Subsequently, the system temperature was raised to 110 °C, and major solvent (about 100 g) in the bottle was removed by atmospheric distillation. After cooling down to 60 °C, the unreacted MTES was removed through vacuum distillation at the pressure of −0.095 MPa. Finally, a nano-SiO\textsubscript{2} resin with solid content of about 50\% was obtained from the bottom.

2.3. Preparation of the Cs\textsubscript{x}WO\textsubscript{3}-ZnO-SiO\textsubscript{2} coatings

The preparation process of the Cs\textsubscript{x}WO\textsubscript{3}-ZnO-SiO\textsubscript{2} coatings were presented in figure 1. A mixture was formed by directly mixing Cs\textsubscript{x}WO\textsubscript{3} dispersion, ZnO dispersion, n-butanol and nano-SiO\textsubscript{2} resin. Then, the mixture was sonicated for 30 min to form a uniform colloidal suspension coating. The main components of the coatings are listed in table 1. The solid content of the coating was about 30\%. Afterwards, the Cs\textsubscript{x}WO\textsubscript{3}-ZnO-SiO\textsubscript{2} coatings were brushed onto a glass and cured at room temperature for 1 h. And then moved to an oven at 120 °C baked for 2 h to get the cured coatings. The average thickness of the coating was about 7 μm. Herein, they were designated as CXZY (X, Y represents the content of Cs\textsubscript{x}WO\textsubscript{3} and ZnO in the solid coating, respectively).

2.4. Characterization

The transmittance of the coatings was measured by UV–vis-NIR spectrophotometer (Hitachi, Japan). The near infrared (NIR) shielding performance was accurately analyzed by the Solar Energy Transmittance Selectivity (SETS). And the SETS was calculated by the following equation:
where \( T(\lambda) \) represents the transmittance spectrum, and \( E(\lambda) \) represents the solar radiation spectrum of 1.5 air mass corresponding to the Sun at 37\(^\circ\) above the horizon. The chemical structure of the coating samples was characterized by using a Nexus-670 Fourier transform infrared (FTIR) spectrometer. X-ray diffraction (XRD) patterns were obtained through a 3 kW x-ray diffractometer (Smart Lab, Rigaku, Japan), using Cu K\( \alpha \) radiation (\( \lambda = 0.154 \) nm) from 10 to 80\(^\circ\) at a constant scanning rate of 10\(^\circ\) min\(^{-1}\). The water contact angle (WCA) was performed on a DSA 100 contact angle goniometer tester (KRUSS, Germany) by using a 2 \( \mu \)l deionized water droplet each time. Every coating sample was measured at least five times to minimize the random errors during the WCA test. The micromorphology of the coating was studied by field emission scanning electron microscopy (FESEM) method (Zeiss, LEO-1530VP, Germany). The film thickness was measured by SEM test on the cross-section of the coatings. Energy dispersive x-ray spectroscopy (EDS) (H-7650, Hitachi, Japan) provided mapping images regarding the cross-sectional surface of the coatings. The thermal performance of the coatings was evaluated by TG-DTA method on a thermo-gravimetric analyzer (NETZSCH STA449C, USA). The hardness test was carried out on Cs\(_x\)WO\(_3\)-ZnO-SiO\(_2\) coating by using Zhonghua® pencils (China) ranging from 6B to 6H.

### 2.5. Anti-dust and anti-fogging test

In a typical anti-dust test, as shown in figure 2(a), the fly ash was used as the model to simulate the dust in natural surroundings. Before the test, all samples, including the fly ash, should be treated in an oven at 100 \(^\circ\)C for 30 min to remove the moisture. Cool to room temperature and spray about 100 mg ash uniformly on each sample using a 100-mesh sieve (\( d = 0.15 \) mm). Slowly tilt the dust-treated sample until the angle between it and the horizontal plane reached 90\(^\circ\), then stopped and kept for 3 s. The mass percentage reduced by the ash during the process is obtained by the following formula: 

\[
SETS = \frac{1}{2} \left( 1 + \frac{\int_{\text{UV}}^{\text{VIS}} E(\lambda) T(\lambda) \, d\lambda}{\int_{\text{VIS}}^{\text{NIR}} E(\lambda) \, d\lambda} - \frac{\int_{\text{VIS}}^{\text{NIR}} E(\lambda) T(\lambda) \, d\lambda}{\int_{\text{VIS}}^{\text{NIR}} E(\lambda) \, d\lambda} \right)
\]  

(1)

Figure 1. Schematic diagram of the preparation process of Cs\(_x\)WO\(_3\)-ZnO-SiO\(_2\) coatings.

Table 1. The different formulations of the solid in Cs\(_x\)WO\(_3\)-ZnO-SiO\(_2\) coatings.

| Sample | C20 | C15Z5 | C10Z10 | C5Z15 | Z20 |
|--------|-----|-------|--------|-------|-----|
| nano-SiO\(_2\) resin/wt% | 80  | 80    | 80     | 80    | 80  |
| Cs\(_x\)WO\(_3\)/wt%   | 20  | 15    | 10     | 5     | 0   |
| ZnO/wt%     | 0   | 5     | 10     | 15    | 20  |
and the remaining ash, respectively. The anti-dust performance of the coating under gravity is evaluated by calculating the weight loss of the ash. And each measurement is taken out for three times.

Typically, in an anti-fog test [18–20], as shown in figure 2(b), the sample was placed on the opening of a round-bottom flask filled with boiling water to simulate the foggy conditions. The sample was kept in the opening of the flask for 1 min, and the anti-fog performance was comprehensively evaluated by observing the image clarity under the steam.

2.6. Thermal insulation test

The thermal insulation test was conducted in a designed device as illustrated in figure 3. The device is composed of a xenon lamp, a test chamber and a temperature recording system. The test chamber is divided into three parts by two pieces of installed glass samples. One is coated glass, and the other is bare glass. A xenon lamp with power of 1000 W is located at the middle chamber, which serves as a heat source to simulate sunlight. Upon light irradiation, the temperatures at both ends gradually increased, and the data of temperatures was automatically recorded every 30 s.

3. Results and discussion

3.1. FTIR analysis of the nano-SiO2 resin

The chemical structures of nano-SiO2 resin, the original SiO2 sol and MTES were identified by FTIR spectra in figure 4. In the FTIR spectra of nano-SiO2 resin [21, 22], the band around 3428 cm\(^{-1}\) is assigned to the O-H stretching vibration of hydrogen-bonded water. Correspondingly, the deformation vibration of absorbed water is indicated by band around 1634 cm\(^{-1}\). All samples exhibit two absorption bands at 1107 and 780 cm\(^{-1}\), corresponding to antisymmetric stretching and symmetric stretching vibrations of Si–O–Si bond, respectively. The band at 475 cm\(^{-1}\) corresponds to the deformation vibration of Si–O–Si. The bands around 2972, 2927 and 1272 cm\(^{-1}\) correspond to the C–H symmetric stretching vibration of –CH\(_3\), antisymmetric stretching vibration of –CH\(_2\) and symmetric deformation vibration of Si–CH\(_3\), respectively. The absorption band at 955 cm\(^{-1}\) is
ascribed to the hydroxyl group of Si–OH, the intensity of which weakens after reactions. In addition, the area of Si–O–Si peak increased after reaction. The FTIR results demonstrate that the hydroxyl groups on the SiO2 sol particles were replaced and the condensation between MTES and SiO2 sol particles occurred effectively.

3.2. XRD analysis of the CsxWO3-ZnO-SiO2 coatings

As shown in figure 5, XRD analysis was further used to investigate compositions in the solid coatings. The first diffraction peak around 10° in nano-SiO2 resin can be explained with incomplete hydrolysis of the precursor, while the second diffraction peak around 22° is attributed to the SiO2 network [23]. All diffraction peaks of the CsxWO3 and the ZnO samples could be well indexed to the hexagonal phase of cesium tungsten bronze (JCPDS No. 831334) and the hexagonal phase of zinc oxide (JCPDS No. 890510), respectively [10]. With increasing amounts of ZnO in the composites, the diffraction peaks corresponding to ZnO increased, as expected. These results suggest that the as-prepared CsxWO3-ZnO-SiO2 coatings are composed of nano-SiO2 resin, CsxWO3 and ZnO definitely.
3.3. Morphology of the $\text{Cs}_x \text{WO}_3 - \text{ZnO} - \text{SiO}_2$ coatings

Since the formation of special surface structure is essential for anti-dust properties of coatings, morphology and microstructure of the $\text{C10Z10}$ coating were examined by FESEM and the results are shown in figure 6. The image showed that the surface of $\text{C10Z10}$ coating was covered with nanoparticles with a diameter less than 50 nm on average. These nanoparticles have created the roughness on the surface of coating. Besides, the surface of the coating is continuous and dense, owing to the product after the MTES hydrolysis reaction enhances the attraction force between the polymer and the nanoparticles through generating hydrogen bonds or other long-range forces \[24\]. Elemental mapping under EDS mode was also employed to further investigate the microstructure and compositional distribution of the composite coating, which is shown from the inset picture in figure 6(a). The elemental analysis result shows that the $\text{C10Z10}$ coating contained O, Cs, W, Si and Zn elements, indicating the as-prepared coating has a high purity, which is in agreement with the results from the XRD analysis. The uniform distribution of $\text{Cs}_x \text{WO}_3$ and $\text{ZnO}$ in the composites is also observed in elemental mapping from figures 6(b)–(e). The uniform distribution of elements in elemental mapping reflects the nanoparticles dispersed homogeneously.

3.4. TG analysis of the $\text{Cs}_x \text{WO}_3 - \text{ZnO} - \text{SiO}_2$ coatings

The TG and DSC curves of the nano-$\text{SiO}_2$ resin and $\text{Cs}_x \text{WO}_3 - \text{ZnO} - \text{SiO}_2$ coatings in air atmosphere are shown in figure 7. There are two main degradation stages in TG curves in nano-$\text{SiO}_2$ resin. The first step showing a weight loss of 6.25% from 180 to 320 °C corresponds to the loss of water molecules caused by the condensation reaction between Si-OH groups in nano-$\text{SiO}_2$ resin. The second step takes place within the temperature range 420 °C–600 °C, accompanied by weight loss of 2.25%, it is assigned to the degradation of Si–O–Si and oxidation removal of the organic species, such as $-\text{CH}_3$ and $-\text{OH}$ from the Si–O–Si side chains \[25, 26\]. Similarly, there also two main stages in TG curves for $\text{Cs}_x \text{WO}_3 - \text{ZnO} - \text{SiO}_2$ coatings. However, with the temperature higher than 450 °C,
the thermal stability for Cs$_x$WO$_3$-ZnO-SiO$_2$ coatings is much better than that of nano-SiO$_2$ resin. Comparing with nano-SiO$_2$ resin, the decomposition temperature of the Cs$_x$WO$_3$-ZnO-SiO$_2$ coatings ascend to around 620 °C after the addition of Cs$_x$WO$_3$ and ZnO nanoparticles. A possible explanation is that when nanocomposites are heated, nanoparticles migrate to the surface of the material due to their relatively low surface potential energy, blocking the huge heat transfer to silicon resin to a certain extent [27]. This indicates that the incorporation of the nanoparticles can improve the thermal stability of the Cs$_x$WO$_3$-ZnO-SiO$_2$ coatings significantly.

3.5. Optical analysis of the Cs$_x$WO$_3$-ZnO-SiO$_2$ coatings

The optical transparency of the Cs$_x$WO$_3$-ZnO-SiO$_2$ coatings are presented in figure 8. The UV–vis-NIR spectra of the nano-SiO$_2$ resin and the bare glass are presented in figure S1 (available online at stacks.iop.org/MRX/8/025004/mmedia). From the figure, ultraviolet light with a wavelength of less than 300 nm is shielded due to the unique optical properties of the bare glass. At the same time, the nano-SiO$_2$ coating will not reduce the light transmittance of the bare glass. Figure 8(a) exhibits the appearance of the Cs$_x$WO$_3$-ZnO-SiO$_2$ coatings at various mass ratio of Cs$_x$WO$_3$ to ZnO in macroscopic scale, showing the tendency to be more transparent with an increase in the ZnO content.

Figure 8(b) illustrates the UV–vis-NIR transmittance spectra of the Cs$_x$WO$_3$-ZnO-SiO$_2$ coatings. It can be observed that the C20 coating shows excellent shielding effect of NIR light ranging from 780 to 2500 nm and good visible light transmittance. While the Z20 coating exhibits almost transparency for NIR light, along with good UV light absorption. The UV shielding ability of Cs$_x$WO$_3$-ZnO-SiO$_2$ coatings were improved with an increase of ZnO content while the NIR blocking ability decreased. All the compound coatings of Cs$_x$WO$_3$-ZnO-SiO$_2$ were prepared by the simple co-blending method and they all exhibit good NIR light shielding ability and excellent Vis light transmittance as well as good blocking of UV light. The excellent NIR shielding performance of these coatings are caused by the absorption of Cs$_x$WO$_3$ to near-infrared light, which is derived from the localized surface plasmon resonance (LSPR) and a small-polaron absorption [28, 29]. To compare the NIR shielding performances of these Cs$_x$WO$_3$-ZnO-SiO$_2$ coatings quantitatively, some optical indices are listed in table 2. The second column in table 2 presents the transmittance at a wavelength of 370 nm which is an important judge basis of UV blocking capability. It can be seen that Z20 coating exhibits much lower transmittance at a wavelength of 370 nm than that of C20 coating, since Cs$_x$WO$_3$ contributes to UV shielding much less than ZnO. In addition, the values in fourth column reflect the effect of Cs$_x$WO$_3$ content on the NIR shielding performance of these coatings, solar energy transmittance of NIR lights of C15Z5, C10Z10 and C5Z15 are 0.159, 0.243 and 0.411 respectively, which are significantly enhanced comparing with control sample Z20.

Table 2. The optical indices of the Cs$_x$WO$_3$-ZnO-SiO$_2$ coatings.

| Coatings | Transmittance at 370 nm (%) | Solar energy transmittance of visible lights | Solar energy transmittance of NIR lights | SETS |
|----------|-----------------------------|---------------------------------------------|----------------------------------------|------|
| C20      | 48.2                        | 0.591                                       | 0.111                                  | 0.740 |
| C15Z5    | 12.1                        | 0.569                                       | 0.159                                  | 0.705 |
| C10Z10   | 2.13                        | 0.572                                       | 0.243                                  | 0.665 |
| C5Z15    | 0.513                       | 0.576                                       | 0.411                                  | 0.583 |
| Z20      | 0.017                       | 0.617                                       | 0.829                                  | 0.394 |

Figure 8. (a) The as-prepared and (b) the UV–vis-NIR transmittance spectra of Cs$_x$WO$_3$-ZnO-SiO$_2$ coatings.
In conclusion, the C10Z10 coating owes a SETS value of 0.665 and offers excellent resistance to both near-infrared and ultraviolet light, making it the most suitable composition for the CsxWO3-ZnO-SiO2 coating.

### 3.6. Ultraviolet aging analysis of the CsxWO3-ZnO-SiO2 coatings

CsxWO3 nanoparticles are relatively stable in the natural environment, but when they are dispersed in organic resins to prepare coatings, significant photochromism appears in the weathering evaluation [6, 12, 15]. A large amount of hydrogen atoms on alkyl groups are existed in the resin. The typical reactions of RH → R + H⁺ and H → H⁺ + e⁻ in organic resin are initiated under ultraviolet light. In general, hydrogen atoms on alkyl groups in organic resin tend to generate H⁺ and e⁻ under ultraviolet light, and the generated H⁺ and e⁻ can further be inserted into the crystal lattice of CsxWO3 and make the coating darken [14]. A 45-day outdoor exposure experiment to be verified the sustainability of CsxWO3-ZnO-SiO2 coatings. The optical properties of the as-prepared coatings did not change significantly after a 45-day outdoor exposure experiment, which was shown in figure S2, indicating that the coating has excellent sustainability.

The ultraviolet aging test was performed to evaluate the optical stability of the prepared CsxWO3-ZnO-SiO2 coatings. Changes in the transmittance spectra of different coatings before and after UV illumination are shown in figures 9(a)–(d). The TVis of C20 coating dropped obviously under UV illumination. After 240 h of UV light illumination, TVis for C20 coating decreased by 9.0% compared to the initial value, while for C15Z5 and C10Z10, that decreasing values are 7.1% and 3.8%, respectively. Figure 9(e) shows the curves of the net change of TVis of the coatings over time, it can be clearly seen that with the addition of ZnO, this value tends to decrease under an equal intensity of UV illumination. Since ZnO can effectively absorb ultraviolet light [30], leading to the less production of H⁺ and e⁻ in resin, the photochromic effect can be suppressed to a certain extent.

### 3.7. Thermal insulation analysis of the CsxWO3-ZnO-SiO2 coatings

The self-made device shown in figure 2 was used to characterize the thermal insulation performance of the coatings. Two side chambers were designed to imitate enclosed rooms with the coated window and the blank glass window, respectively. For better comparison of thermal insulation performance between different coatings, the variation of temperatures as a function of radiation time in two chambers were recorded simultaneously. As shown in figure 10(a), under the luminous xenon light, the chamber temperature gradually increases with the lapse of time, and reaches peak value within 1200 s. Apparently, all the temperatures of the chamber with CsxWO3-ZnO-SiO2 coated glass after 1200 s light irradiation are lower than with nano-SiO2 resin coated glass. The highest temperature difference between chambers with C20 coated glass and with nano-SiO2 resin coated glass is 9.4 °C. While C10Z10 coating, with well overall optical performance, also obtains a good temperature difference of 7.0 °C. As indicated in figure 10(b), it is observed that temperature difference increases with the concentration of the CsxWO3 in the coating. Considering that NIR light accounts for as high as about 45% of total solar energy, CsxWO3 obviously plays a dominant role in achieving well thermal insulation effect owing to its proved excellent NIR shielding performance. Consequently, this observation is in good accordance with optical measurement results.
3.8. Anti-dust and anti-fogging analysis of the CsxWO3-ZnO-SiO2 coatings

The wettability of the bare glass, nano-SiO2 resin coating, C10Z10 coating were measured by static WCA measurement. All the error bars represent the standard deviation of at least five replicate measurements. Studies have shown that low surface energy and surface roughness are the key factors that determine the hydrophobicity of the coating [31, 32]. Concerning nano-SiO2 resin was obtained by the hydrolytic condensation reaction of MTES and silica sol in this study, it is supposed that the hydrophobic group (–CH3) reduces the surface energy of the coating, and the addition of SiO2 nanoparticles improves the surface roughness. As shown in figure 11(a), the WCA of the bare glass, nano-SiO2 resin and C10Z10 coating were measured by static WCA measurement. All the error bars represent the standard deviation of at least five replicate measurements. Studies have shown that low surface energy and surface roughness are the key factors that determine the hydrophobicity of the coating [31, 32]. Concerning nano-SiO2 resin was obtained by the hydrolytic condensation reaction of MTES and silica sol in this study, it is supposed that the hydrophobic group (–CH3) reduces the surface energy of the coating, and the addition of SiO2 nanoparticles improves the surface roughness. As shown in figure 11(a), the WCA of the nano-SiO2 resin coating is 109°, much higher than 57° of bare glass. Besides, with the incorporation of the CsxWO3 and ZnO nanoparticles, the WCA of the coating increases to 118°. Since both the CsxWO3 and ZnO nanoparticles are irrelevant to low surface energy, their participation probably benefited the construction

Figure 10. (a) Insulation curves (temperature versus time) of nano-SiO2 resin, Cx3WO3-ZnO-SiO2 coatings; (b) The temperature difference between the Cx3WO3-ZnO-SiO2 coatings and nano-SiO2 resin after 1200s.

Figure 11. (a) Water contact angle of the bare glass, nano-SiO2 resin and C10Z10 coating before and after a 45-day outdoor exposure experiment. (b) The bare glass, nano-SiO2 resin and C10Z10 coated glass were placed on 90 °C water for one minute respectively. (c) Photos of the bare glass, nano-SiO2 resin and C10Z10 coated glass with 100 mg fly ashes and their corresponding ones after anti-dust tests. (d) The anti-dust percentage of the bare glass, nano-SiO2 resin and C10Z10 coated glass as the functions of repeated testing time.
of enhanced surface roughness in this case. Meanwhile, after a 45-day outdoor exposure experiment, the WCA of nano-SiO$_2$ resin and C10Z10 coating slightly descended to 103° and 112° respectively, indicating the excellent sustainability of the as-prepared coatings.

To investigate the anti-fogging ability of the nano-SiO$_2$ resin coating and C10Z10 coating, the corresponding samples were placed on the opening of a round-bottom flask filled with boiling water to simulate the foggy conditions. Figure 11(b) showed the simulation diagram of the anti-fogging test. From the Video 1, it only takes 4 s for the water droplets to completely cover the surface of the bare glass, the words under the bottle cannot be recognized through the bare glass apparently. With respect to nano-SiO$_2$ resin coating and C10Z10 coating, as can be seen in Video 2 and Video 3, the words under the bottle were still seen after a 1-minute hot water vapor experiment. Figure 11(b) shows the photos of three kinds of coated glass after a 1-minute hot water vapor experiment. Many large mist droplets attached to the surface of the bare glass, while only tiny droplets attached to the surface of the nano-SiO$_2$ resin coating and C10Z10 coating. The tiny mist droplets entirely evaporated on the nano-SiO$_2$ resin coated glass and C10Z10 coated glass after about 3 min while it took about 10 min on the bare glass.

The anti-dust performance of the two above mentioned coatings under gravity were investigated, along with the bare glass served as the comparison sample. Figure 11(c) shows the photos of the anti-dust effect of different samples. Evidently, most of fly ashes slipped from the coated glass slides while only a little fly ash fell off from the bare glass. The anti-dust percentage of the coating was calculated and presented in table 3 with the corresponding WCA. The results show that the dust-reducing performance is associated with the WCA values, as exemplifying by C10Z10 coating that a large WCA couples with a better anti-dust performance. In repeated anti-dust tests, as can be seen in figure 11(d), the anti-dust efficiency of all three samples decreases as the repeated times increases, other researchers have also reported the similar phenomenon [32]. Nevertheless, 70.1% of anti-dust efficiency was kept even after twenty repeated tests, indicating that the C10Z10 coating has a durable anti-dust performance. In comparison, the nano-SiO$_2$ resin coating could maintain 64.3% of anti-dust efficiency after multiple cycles, while the bare glass almost lost its anti-dust performance.

The hardness test was carried out on $\text{Cs}_x\text{WO}_3$-ZnO-SiO$_2$ coating by using Zhonghua® pencils (China) ranging from 6B to 6H, from the softest to the hardest, correspondingly. The grade of the hardest pencil that did not cause surface lacerations was taken as the pencil hardness. The test results show that all the $\text{Cs}_x\text{WO}_3$-ZnO-SiO$_2$ coatings are rather hard with pencil hardness as high as 4H, due to their dense structure, which is similar with and even a little superior to the previous published works [9, 32, 33].

4. Conclusions

The nanocomposite materials of $\text{Cs}_x\text{WO}_3$-ZnO-SiO$_2$ coatings were developed to be used as smart windows. The transparent hybrid resin was prepared from MTES and SiO$_2$ sol by the sol-gel method is used as the substrate, $\text{Cs}_x\text{WO}_3$ is used as the infrared shielding phase, and ZnO is used as the ultraviolet blocking agent. The composite coating has excellent anti-dust and anti-fogging properties due to the hydrophobicity of the nano-SiO$_2$ resin. The addition of SiO$_2$ nanoparticles improved the surface roughness and the hydrophobic group (-CH$_3$) reduced the surface energy of the coating. The efficient thermal insulation performance of the composite coating due to the wonderful NIR shielding properties of the $\text{Cs}_x\text{WO}_3$ nanoparticles. The composite coating could shield most of the ultraviolet light and effectively inhibit the photochromism of $\text{Cs}_x\text{WO}_3$, which is related to the proper band gap of ZnO. Meanwhile, the addition of nanoparticles improved the thermal stability of the composite coating.

Table 3. The anti-dust property of different coated glass.

| Glass          | WCA/° | $M_0$/mg | $M_1$/mg | Anti-dust average percentage/% |
|----------------|-------|----------|----------|--------------------------------|
| bare glass     | 57°   | 93.2     | 87.2     | 6.6                            |
|                | 62°   | 86.7     | 76.4     |                                |
|                | 59°   | 79.9     | 74.7     |                                |
| nano-SiO$_2$ resin | 109° | 86.1     | 2.1      | 95.9                           |
|                | 107°  | 91.4     | 4.3      |                                |
|                | 106°  | 83.2     | 4.2      |                                |
| C10Z10         | 115°  | 89.2     | 3.2      | 96.4                           |
|                | 116°  | 90.1     | 2.1      |                                |
|                | 118°  | 85.2     | 4.2      |                                |

of enhanced surface roughness in this case. Meanwhile, after a 45-day outdoor exposure experiment, the WCA of nano-SiO$_2$ resin and C10Z10 coating slightly descended to 103° and 112° respectively, indicating the excellent sustainability of the as-prepared coatings.

To investigate the anti-fogging ability of the nano-SiO$_2$ resin coating and C10Z10 coating, the corresponding samples were placed on the opening of a round-bottom flask filled with boiling water to simulate the foggy conditions. Figure 11(b) showed the simulation diagram of the anti-fogging test. From the Video 1, it only takes 4 s for the water droplets to completely cover the surface of the bare glass, the words under the bottle cannot be recognized through the bare glass apparently. With respect to nano-SiO$_2$ resin coating and C10Z10 coating, as can be seen in Video 2 and Video 3, the words under the bottle were still seen after a 1-minute hot water vapor experiment. Figure 11(b) shows the photos of three kinds of coated glass after a 1-minute hot water vapor experiment. Many large mist droplets attached to the surface of the bare glass, while only tiny droplets attached to the surface of the nano-SiO$_2$ resin coating and C10Z10 coating. The tiny mist droplets entirely evaporated on the nano-SiO$_2$ resin coated glass and C10Z10 coated glass after about 3 min while it took about 10 min on the bare glass.

The anti-dust performance of the two above mentioned coatings under gravity were investigated, along with the bare glass served as the comparison sample. Figure 11(c) shows the photos of the anti-dust effect of different samples. Evidently, most of fly ashes slipped from the coated glass slides while only a little fly ash fell off from the bare glass. The anti-dust percentage of the coating was calculated and presented in table 3 with the corresponding WCA. The results show that the dust-reducing performance is associated with the WCA values, as exemplifying by C10Z10 coating that a large WCA couples with a better anti-dust performance. In repeated anti-dust tests, as can be seen in figure 11(d), the anti-dust efficiency of all three samples decreases as the repeated times increases, other researchers have also reported the similar phenomenon [32]. Nevertheless, 70.1% of anti-dust efficiency was kept even after twenty repeated tests, indicating that the C10Z10 coating has a durable anti-dust performance. In comparison, the nano-SiO$_2$ resin coating could maintain 64.3% of anti-dust efficiency after multiple cycles, while the bare glass almost lost its anti-dust performance.

The hardness test was carried out on $\text{Cs}_x\text{WO}_3$-ZnO-SiO$_2$ coating by using Zhonghua® pencils (China) ranging from 6B to 6H, from the softest to the hardest, correspondingly. The grade of the hardest pencil that did not cause surface lacerations was taken as the pencil hardness. The test results show that all the $\text{Cs}_x\text{WO}_3$-ZnO-SiO$_2$ coatings are rather hard with pencil hardness as high as 4H, due to their dense structure, which is similar with and even a little superior to the previous published works [9, 32, 33].

4. Conclusions

The nanocomposite materials of $\text{Cs}_x\text{WO}_3$-ZnO-SiO$_2$ coatings were developed to be used as smart windows. The transparent hybrid resin was prepared from MTES and SiO$_2$ sol by the sol-gel method is used as the substrate, $\text{Cs}_x\text{WO}_3$ is used as the infrared shielding phase, and ZnO is used as the ultraviolet blocking agent. The composite coating has excellent anti-dust and anti-fogging properties due to the hydrophobicity of the nano-SiO$_2$ resin. The addition of SiO$_2$ nanoparticles improved the surface roughness and the hydrophobic group (-CH$_3$) reduced the surface energy of the coating. The efficient thermal insulation performance of the composite coating due to the wonderful NIR shielding properties of the $\text{Cs}_x\text{WO}_3$ nanoparticles. The composite coating could shield most of the ultraviolet light and effectively inhibit the photochromism of $\text{Cs}_x\text{WO}_3$, which is related to the proper band gap of ZnO. Meanwhile, the addition of nanoparticles improved the thermal stability of the composite coating.
and the pencil hardness could reach 4H. Moreover, the CsₓWO₃-ZnO-SiO₂ coatings showed an amazing temperature difference of 9.4 °C in the thermal insulation test. The dust reduction rate of the C10Z10 coating still maintain 70.4% after multiple cycles. Due to the combination of its excellent UV/NIR blockage ability, anti-dust and anti-fogging performance, the CsₓWO₃-ZnO-SiO₂ nanocomposite is expected to further applied as smart window coatings for energy-saving materials.

Acknowledgments

We thank the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) to support this work and thanks eceshi (www.eceshi.cn) for the FESEM analysis.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Xianli Fang https://orcid.org/0000-0003-1495-0114

References

[1] Downie C 2020 Strategies for survival: the international energy agency’s response to a new world Energy Policy 141 111452
[2] Shao G F, Wu X D, Kong Y, Cui S, Shen X D, Jiao C R and Jiao J 2015 Thermal shock behavior and infrared radiation property of integrative insulations consisting of MoO₃/ borosilicate glass coating and fibrous ZrO₂ ceramic substrate Surf. Coat. Technol. 270 154–63
[3] Yao Y J, Zhang L M, Chen Z, Cao C X, Gao Y F and Luo H J 2018 Synthesis of CsₓWO₃ nanoparticles and their NIR shielding properties Ceram. Int. 44 13469–75
[4] Qu J et al 2014 Transparent thermal insulation coatings for energy efficient glass windows and curtain walls Energy Build. 77 1–10
[5] Lu X D, Yu G, Tan Q, Hu B N, Zhang J J and Dong Q Z 2014 Preparation and characterization of transparent fluorocarbon emulsion doped with antimony tin oxide and TiO₂ as thermal-insulating and self-cleaning coating J. Coat. Technol. Res. 11 567–74
[6] Chao L, Bao L, Wei W and Tegus O 2019 A review of recent advances in synthesis, characterization and NIR shielding property of nanocrystalline rare-earth hexaborides and tungsten bronze Sol. Energy Mater. 190 10–27
[7] Guo C S, Yin S, Huang L J, Yang L and Sato T 2011 Discovery of an excellent IR absorbent with a broad working wavelength: CsₓWO₃ nanorods Chem. Commun. 47 8853–5
[8] Guo C S, Yin S, Zhang P L, Yan M, Adachi K, Chonan T and Sato T 2010 Novel synthesis of homogenous CsₓWO₃ nanorods with excellent NIR shielding properties by a water controlled-release solvothermal process J. Mater. Chem. 20 8227–9
[9] Xu X Y, Zhang W L, Hu Y, Wang Y H, Lu L and Wang S J 2017 Preparation and overall energy performance assessment of wide waveband two-component transparent NIR shielding coatings Sol. Energy Mater. Sol. Cells 168 119–29
[10] Wu X Y, Yin S, Xue D F, Komarneni S and Sato T 2015 A CsₓWO₃ nanocomposite as a smart coating for photocatalytic environmental cleanup and heat insulation Nanoscale 7 17048–54
[11] Adachi K, Ota Y, Tanaka H, Okada M, Oshimura N and Togukawa A 2013 Chromatic instabilities in cesium-doped tungsten bronze nanoparticles J. Appl. Phys. 114
[12] Xu W J, Meng Z Q, Yu N, Chen Z G, Sun B, Jiang X Z and Zhu M F 2015 PEGylated CsₓWO₃ nanorods as an efficient and stable 915 nm-laser-driven photothermal agent against cancer cells RSC Adv. 5 7074–82
[13] Zhou Y J, Li N, Xin Y C, Cao X, Ji S D and Jin P 2017 CsₓWO₃ nanoparticle-based organic polymer transparent foils: low haze, high near infrared-shielding ability and excellent photochromic stability J. Mater. Chem. C 5 6251–8
[14] Zheng X Z, Zhou Y J, Ji S D, Luo H J, Yao H L, Huang X and Jin P 2015 The preparation of a high performance near-infrared shielding CsₓWO₃/SiO₂ composite resin coating and research on its optical stability under ultraviolet illumination, J. Mater. Chem. C 3 8050–60
[15] Chen Y X, Zeng X Z, Zhou Y J, Li R, Yao H L, Cao X and Jin P 2018 core–shell structured CsₓWO₃@ZnO with excellent stability and high performance on near-infrared shielding Ceram. Int. 44 2738–44
[16] Yu Z Y, Yao Y J, Yao J N, Zhang L M, Chen Z, Gao Y F and Luo H J 2017 Transparent wood containing CsₓWO₃ nanoparticles for heat-shielding window applications, J. Mater. Chem. A 5 6019–24
[17] Quan Y and Zhang L J 2017 Experimental investigation of the anti-dust effect of transparent hydrophobic coatings applied for solar cell covering glass Sol. Energy Mater. Sol. Cells 168 382–9
[18] Joshi D N, Achuta S R, Reddy Y L, Arkoti N K and Sakthivel S 2019 Super-hydrophilic broadband anti-reflective coating with high weather stability for solar and optical applications Sol. Energy Mater. Sol. Cells 200 110023
[19] Huang L, Wang T, Li X, Wang X, Zhang W, Yang Y and Tang Y 2020 UV-to-NIR highly transparent ultrathin diamond nanofilms with intriguing performances: anti-fogging, self-cleaning and self-lubricating Appl. Surf. Sci. 527 146733
[20] Chen Y, Zhang Y B, Shi L, Li J, Xin Y, Yang T T and Guo Z G 2012 Transparent superhydrophobic/superhydrophilic coatings for self-cleaning and anti-fogging Appl. Phys. Lett. 101 033701
[21] Al-Owaysi R and El-Rassy H 2009 Synthesis and characterization by FTIR spectroscopy of silica aerogels prepared using several Si(OR)₄ and R′Si(OR)₃ precursors J. Mol. Struct. 919 140–5
[22] Ren T T and He J H 2017 Substrate-versatile approach to robust antireflective and superhydrophobic coatings with excellent self-cleaning property in varied environments ACS Appl. Mater. Interfaces 9 34367–76
[23] Chernyev G, Rangelova N, Djambazki P, Nenkova S, Salvador I, Fernandes M, Wu A Y and Kabanovana L 2011 Sol-gel silica hybrid biomaterials for application in biodegradation of toxic compounds J. Sol-Gel Sci. Techn. 58 619–24
[24] Xu Q F, Wang J N and Sanderson K D 2010 Organic–inorganic composite nanocoatings with superhydrophobicity, good transparency, and thermal stability Acs Nano 4 2201–9
[25] Yang Z G, Zhao Z J, Yu J B, Ren Z M, Ma S Q and Wang Z 2019 Effect of silicone resin as precursor and binder on the properties of alumina-based ceramic cores using ball-shaped powders Ceram. Int. 45 2170–7
[26] Yang Z G, Zhao Z J, Yu J B and Ren Z M 2019 Preparation of silica ceramic cores by the preceramic pyrolysis technology using silicone resin as precursor and binder Mater. Chem. Phys. 223 676–82
[27] Wang L Y, Hang J Z, Shi L Y, Sun X Y and Xu F 2012 Preparation and characterization of NIR cutoff antimony doped tin oxide/hybrid silica coatings Mater. Lett. 85 33–8
[28] Willets K A and Van Duyne R P 2007 Localized surface plasmon resonance spectroscopy and sensing. Annu. Rev. Phys. Chem. 58 267–97
[29] Adachi K and Asahi T 2012 Activation of plasmons and polarons in solar control cesium tungsten bronze and reduced tungsten oxide nanoparticles J. Mater. Res. 27 965–70
[30] Liang X P, Wang X H, Xin S B and Liu Y J 2006 Ultraviolet spectrum of nanometer zinc oxide prepared by sol-gel process Rare Metal. Mat. Eng. 35 567–9
[31] Cai S, Zhang Y L, Zhang H L, Yan H W, Lv H B and Jiang B 2014 Sol–gel preparation of hydrophobic silica antireflective coatings with low refractive index by base/acid two-step Catalysis. Appl. Mater. Inter. 6 11470–5
[32] Zhang J W, Wang W Q, Zhou S X, Yang H D and Chen C 2019 Transparent dust removal coatings for solar cell on Mars and its Anti-dust mechanism Prog. Org. Coat. 134 312–22
[33] Li T and He J H 2016 A facile hybrid approach to high-performance broadband antireflective thin films with humidity resistance as well as mechanical robustness J. Mater. Chem. C 4 5342–8