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ARTICLE

Cs_xWO₃/ZnO nanocomposite as a smart coating for photocatalytic environmental cleanup and heat insulation

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A novel Cs_xWO₃/ZnO smart coating was proposed to achieve multiple functions, such as heat insulation, photodecomposition of toxic NO gas, blocking of harmful UV light, etc. In this composite coating, the Cs_xWO₃ nanorods were used as a NIR and UV light shielding material while the ZnO nanoparticles were utilized as a photocatalyst and a material to enhance visible light transmittance and block UV light. When the mass ratio of Cs_xWO₃/ZnO was 1, the composite coating possessed a very good visible light transmittance of over 80% and excellent UV-shielding ability. This novel coating showed heat insulation that is superior to that of the ITO coating and photocatalytic decontamination of NO gas that is superior to that of the standard TiO₂ (P25). The proposed Cs_xWO₃/ZnO smart coating is a promising material for not only energy savings but also for environmental cleanup.

Introduction

With the rapid industrial development, energy depletion and environmental pollution have become two of the most serious problems. Therefore, there is an enormous interest in energy savings and environmental decontamination. Solar light accounts for ca. 50% of the heat-producing near infrared (NIR, 780-2500 nm) light. Every year about a quarter of the total energy is spent on heating and cooling buildings and vehicles throughout the world. If a technique could be developed to shield the NIR but transmit the visible (VIS) light, it would have a huge impact on energy savings. In order to save energy, low-E coatings, electrochromic coatings, thermochromic coatings, etc.¹⁻⁹ have been developed previously to block heat-producing NIR from solar light. However, all of the above types of coatings have some disadvantages. For example, low-E coating of silver leads to relatively low VIS transmittance and silver is also easily oxidized leading to deterioration of properties while electrochromic coatings need extra electric power and require complicated preparation process. As for the thermochromic coatings, they generally show a lower VIS transmittance and relatively lower efficiency for NIR shielding compared to other coatings. Therefore, a simple coating with high NIR light absorption i.e., high NIR shielding and good VIS transmittance is still needed. Recently, several materials have been developed to shield NIR light such as black compounds,

rare-earth hexaborides, tin-doped indium oxide (ITO) and so on.¹⁰⁻¹³ However, they also have some disadvantages. For instance, black compounds usually lead to very low VIS transmittance;¹⁰ rare-earth hexaborides generally can only shield a small amount of the NIR light in the range of 780-2500 nm and they also require special reducing atmosphere and high temperature for preparation;¹¹ as for frequently used ITO, it can't shield the main heat source of NIR light from 780 nm to 1500 nm, which limits its NIR shielding property.^{12,13} Because of the above drawbacks of the above materials, our group has successfully developed a series of W related mixed valence state compounds (e.g. W₁₈O₄₉, Na_xWO₃, etc.) as the NIR shielding materials especially for Cs_xWO₃, which exhibited excellent VIS transmittance and NIR light shielding property in the range of 780-2500 nm using a simple preparation process.¹⁴⁻¹⁷ In addition, because of the relatively narrow band gap of Cs_xWO₃, it can also shield UV light, which is generally detrimental to our health. Thus, the Cs_xWO₃ coating is promising for shielding NIR and UV light along with over 65% transmittance of VIS light.

Air pollution with NO_x is a serious problem from vehicular emissions, emissions by cooking stoves using liquefied petroleum gas, the combustion of nitrogen and oxygen gases in the air, agricultural fertilization and natural lightning, etc..¹⁸ The toxic NO_x gas is generally remediated by filtration and adsorption methods, which are of relatively low efficiency and these techniques also have disposal and regeneration problems.¹⁹ Photocatalysis is a green chemical method, which has been considered to be one of the most effective ways to decompose toxic gases including NO_x using solar light as the energy source for environmental cleanup.²⁰⁻²⁴

Therefore, the objective of the present research is to develop a novel composite, which will have both the NIR shielding property and photocatalytic performance simultaneously. In

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this work, we report a novel $\text{Cs}_x\text{WO}_3/\text{ZnO}$ composite coating, which achieves a high NIR shielding efficiency, good UV light blocking, excellent toxic gas decontamination and high VIS light transmittance. In this $\text{Cs}_x\text{WO}_3/\text{ZnO}$ composite, the Cs_xWO_3 serves as the NIR shielding phase with strong NIR light absorption ability while the ZnO not only works as UV absorbent but also as a photocatalyst. In addition, both of Cs_xWO_3 and ZnO have high transmittance for the VIS light. To demonstrate the effectiveness of the current composite for practical application, a simulated house system was employed by using quartz glass, ITO coated quartz glass or $\text{Cs}_x\text{WO}_3/\text{ZnO}$ coated quartz glass as window material in order to check the variation of temperature by irradiation with NIR containing light source. Also, the destruction of toxic NO gas was tested to check for the photocatalytic activity of $\text{Cs}_x\text{WO}_3/\text{ZnO}$ composite based on established criteria for NO gas release by Japanese Industrial Standard, JIS.²⁵

Experimental

Sample preparation

Synthesis of Cs_xWO_3 nanorods. The Cs_xWO_3 nanorods were prepared by a controlled water release solvothermal process (CWRSP) as follows:¹⁴ First 0.2976 g WCl_6 was dissolved in 40 mL of dehydrated ethanol with fast stirring for 15 min or so until the solution color turned to yellow. Then 0.063 g $\text{CsOH}\cdot\text{H}_2\text{O}$ was introduced into the above solution followed by stirring for 5 min. Subsequently, 10 mL of acetic acid were added into the mixed solution and then the solution was transferred into a Teflon-lined autoclave, followed by heat-treatment at 240°C for 20 h. After cooling down to room temperature, the blue products were centrifuged to separate solids, washed with ethanol for 3 times and then vacuum dried at 60°C overnight.

Preparation of $\text{Cs}_x\text{WO}_3/\text{ZnO}$ composite. The composite was prepared by a simple soft solution method as follows: first, 0.1 g of the as-prepared blue Cs_xWO_3 nanorods were put into 80 mL ethanol followed by sonication for 30 min and fast stirring for 30 min. Then 0.27 g $\text{Zn}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$ was introduced into the solution followed by another 30 min of rapid stirring. After that, the mixed solution was heated at 85°C with continuous stirring. Then, 20 mL of ethanol containing 2 mL distilled water and 0.06 g NaOH were added dropwise into the above solution followed by stirring for another 4 h. After cooling, the solid was separated from solution by centrifugation, washed with ethanol for 5 times and then vacuum dried at 60°C overnight. By changing the amounts of Cs_xWO_3 , different $\text{Cs}_x\text{WO}_3/\text{ZnO}$ weight ratios (0.5/1.0, 1.0/1.0, 1.5/1.0) of composites were obtained, and they were designated as C-Z-0.5, C-Z-1.0 and C-Z-1.5, respectively. In addition, pure ZnO and Cs_xWO_3 powders were also prepared by the same procedure for comparison.

Characterization

The crystalline phases of the samples were determined by X-ray diffraction (XRD) analysis using Bruker AXS D2 Phaser unit with graphite-monochromated $\text{CuK}\alpha$ radiation. The specific surface area was evaluated by the BET method (Quantachrome Instruments, NOVA4200e). The morphology

and size of the solid phases were observed by transmission electron microscopy (TEM, JEOLJEM-2010). The surface composition and elemental status of the specimens were determined by X-ray photoelectron spectroscopy (XPS, Perkin Elmer PHI 5600). The shift of the binding energy owing to the surface state charge was corrected using the C 1s level at 284.6 eV as an internal standard. The transmittance of a sample film was checked by a UV-vis spectrophotometer (Shimadzu, UV-2450). The sample film was prepared as follows: First, the sample powder was dispersed into collodion-ethanol mixed solution at a weight ratio of sample:collodion:ethanol=0.15:0.93:1.0 followed by fast stirring for 24 h. After that, the above mixed solution was dropped onto a quartz glass by an applicator to make a film of ca. 33 μm thickness. The ITO film was also prepared by the same process using commercial ITO ($10\Omega/\square$) powder (bought from Mitsubishi Materials Corporation).

Photocatalytic activity tests

The photocatalytic property of samples was evaluated by the destruction of toxic NO gas (deNO_x) according to JIS criteria using a flow type reactor under the irradiation of a 450 W high pressure mercury lamp at room temperature. The specimen was spread in the hollow (20 mm \times 16 mm \times 0.5 mm) of a glass plate and then was placed at the bottom center of the reactor (373 cm^3 of internal volume), into which a 1:1 mixed gas of air and nitrogen containing 1 ppm of NO was continuously flowed at the rate of 200 $\text{cm}^3\cdot\text{min}^{-1}$. The product powder was held in the dark for 30 min to reach the adsorption and desorption equilibrium of NO gas. After that, the light was turned on to irradiate the sample for 10 min, followed by another 10 min without the irradiation. The concentration of NO gas was measured by a NO_x analyzer (Yanaco, ECL-88A).²⁰ The deNO_x ability of the sample film of ca. 34 μm thickness was also measured. The sample film was prepared on a glass by a squeegee method²⁶ with the above mentioned sample powder dispersed in collodion/ethanol solution using a squeegee tape. The film was also used for the investigation of heat insulation performance using a simulated house system.

Results and discussion

Figure 1 shows the XRD patterns of a series of composites of C-Z-0.5, C-Z-1.0, C-Z-1.5 and pure samples of Cs_xWO_3 and ZnO. All diffraction peaks of the pure Cs_xWO_3 sample could be well indexed to the hexagonal phase of cesium tungsten bronze (JCPDS No. 831334), indicating that the single phase of Cs_xWO_3 was successfully prepared by the one-pot controlled water release solvothermal process. The C-Z composites showed both Cs_xWO_3 and ZnO reflections without any impurities. With increasing amounts of ZnO in the composites, the diffraction peaks corresponding to ZnO increased, as expected.

To confirm the intimate contact between Cs_xWO_3 and ZnO in the C-Z composites, TEM was used to check the morphologies of samples. Figure 2 presents the TEM images of products along with the HRTEM and EDX of C-Z-1.0 composite. Pure Cs_xWO_3 sample (Fig. 2a) showed nanorods with a length of ca.

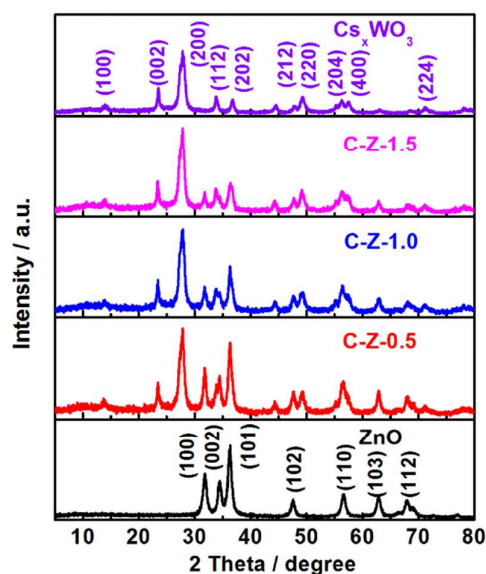


Fig. 1 XRD patterns of pure ZnO, Cs_xWO_3 and their composites with various weight ratios.

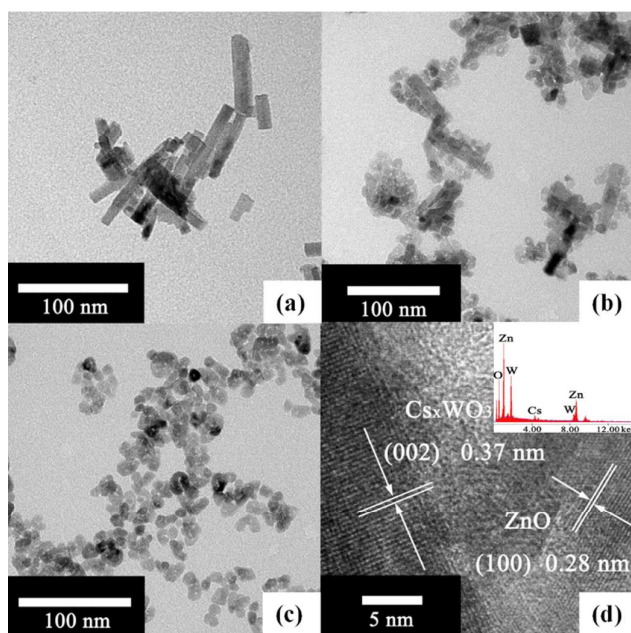


Fig. 2 TEM images of pure Cs_xWO_3 (a), C-Z-1.0 composite (b) and pure ZnO (c), and the HRTEM image of the C-Z-1.0 composite (the inset is the EDX profile of C-Z-1.0).

80 nm and a width of ca. 10 nm, and the pure ZnO sample (Fig. 2c) exhibited well-dispersed nanoparticles of ca. 8 nm in size. The composite, C-Z-1.0 (Fig. 2b), shows that the nanoparticles of ZnO were deposited on the surfaces of Cs_xWO_3 nanorods, implying a good contact, which can lead to multi-functional properties. In addition, HRTEM image in Fig. 2d indicates that the Cs_xWO_3 nanorods grew along the [002] direction and also shows that ZnO nanoparticles are in close contact with the nanorods. EDX profile of C-Z-1.0 composite shows the elements of Cs, W, Zn and O in the inset as expected. Thus,

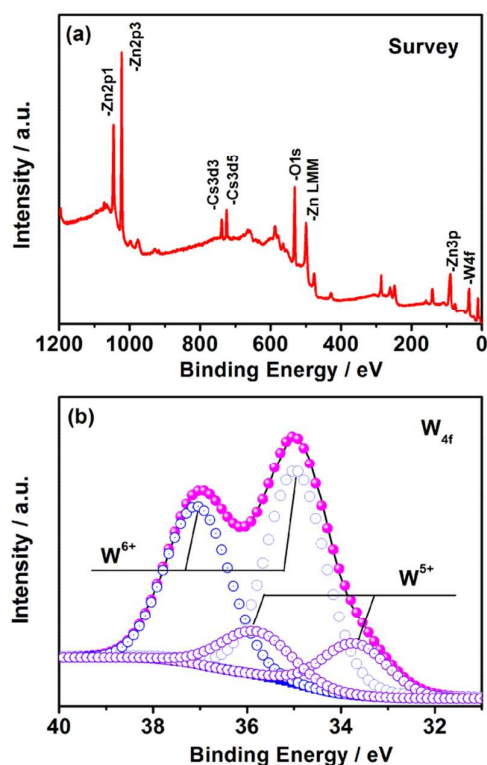


Fig. 3 XPS spectra: survey spectrum (a) and W_{4f} spectrum (b) of composite C-Z-1.0.

XRD and TEM results confirmed that the C-Z composite is a nanocomposite.

Since the existence of reductive W^{5+} in the product is essential for NIR property as mentioned above, a XPS analysis was carried out (see Figure 3) to evaluate the W status in the C-Z composite. A survey spectrum (Fig. 3a) shows that W, Cs, Zn and O existed in the composite without any impurity. This is in agreement with the result of EDX shown in Fig. 2 (d). Moreover, XPS shows that W in the composite not only partially existed as W^{6+} , corresponding to energy peaks at 34.9 and 37.0 eV, but also partially existed as W^{5+} relating to the energy peaks at 33.7 and 35.9 eV.^{14,27,28} The reduced W^{5+} ion in the Cs_xWO_3 of C-Z composite was probably formed by reduction with ethanol during the CWRSP process resulting in the blue color of Cs_xWO_3 particles.¹⁴ Thus, the W_{4f} XPS spectrum of C-Z-1.0 (Fig. 3b) composite clearly shows the presence of both W^{5+} and W^{6+} ions, which are needed for the NIR shielding property.

Detailed characterization of samples for the NIR shielding (heat insulation) property and photocatalytic activity is described below. Figure 4 illustrates the transmittance spectra of the sample films in the range of UV, VIS and NIR. It is clear from the spectrum that the pure Cs_xWO_3 film showed excellent shielding of NIR light ranging from 780 to 2600 nm and UV light less than 400 nm but with relatively good VIS light transmittance. On the other hand, the pure ZnO film was almost transparent for NIR light, but showed excellent absorption for UV light and outstanding transmittance for VIS

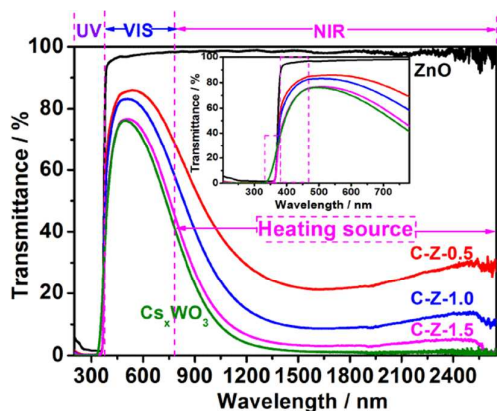


Fig. 4 Transmittance spectra of the films of pure Cs_xWO_3 , ZnO, C-Z-0.5, C-Z-1.0 and C-Z-1.5 (The inset is the enlarged transmittance spectra in the range of 200–780 nm, which covers the areas of UV and VIS lights).

light. It can also be seen from Fig. 4 that the UV shielding ability of ZnO is superior to Cs_xWO_3 , especially in the wavelength range of 330–380 nm (see inset in Fig. 4), the superiority of the former is due to its intrinsic band gap, which is perfectly located at the edge of UV and VIS lights. More importantly, when Cs_xWO_3 was combined with ZnO, the composites inherited the merits of both Cs_xWO_3 and ZnO. The inheritance of NIR absorption capability of composite from Cs_xWO_3 could be attributed to the use of soft chemical method in synthesizing ZnO/ Cs_xWO_3 composite in which the reduced W^{5+} ion was preserved. All the composites of C-Z-0.5, C-Z-1.0 and C-Z-1.5 were prepared by the soft chemical method and they all exhibited good NIR light shielding ability and excellent VIS light transmittance as well as good blocking of UV light. In addition, the UV-shielding ability and visible light transparency could be improved with an increase in the ZnO content, i.e., the composites of C-Z-0.5 and C-Z-1.0 revealed better UV shielding and VIS light transmittance than pure Cs_xWO_3 and C-Z-1.5 composite (Fig. 4). The composites showed more of the desired VIS light transmittance and UV light shielding for practical application, although the NIR shielding property was decreased, to some extent (see, inset of Fig. 4) when compared to pure Cs_xWO_3 . Based on these results, it can be inferred that the appropriate composition of C-Z film would lead to excellent heat insulation properties and good light transmittance as well as excellent blocking of UV light in the daytime. As for the outstanding NIR light absorption capability of Cs_xWO_3 in C-Z composite, it was probably caused by the following reasons: firstly, Cs was doped into WO_3 by the partial reduction of W^{6+} to W^{5+} forming hexagonal Cs_xWO_3 where some electrons will be produced to form localized levels just below the conduction band of Cs_xWO_3 . In this case, the electromagnetic wave of NIR light can be absorbed by the so-called polaron mechanism by which the localized electrons at W^{5+} are either excited to the conduction band and/or transferred to the adjoining W^{6+} sites by hopping.^{29,30} Secondly, as Cs_xWO_3 was strongly reduced with a large value of x as presented in this work, the produced electrons are not only used to form the localized levels below conduction band but

also accommodated as free electrons in the conduction band of Cs_xWO_3 . The free electrons can be utilized to produce localized surface plasma resonance, which then induces the absorption of NIR light.³¹ If the x in Cs_xWO_3 was large enough (more than 0.25), the second mechanism will be dominant, otherwise the first one.

In order to confirm the heat insulation ability of the C-Z films from the viewpoint of practical application, a simulated heat ray shielding test was conducted by irradiating with a 50W halogen lamp to the boxes covered by the quartz glass, C-Z sample coated quartz glass and ITO coated quartz glass and measuring the temperature inside the boxes (Fig. 5).

ITO is well-known as an NIR light shielding material and ITO glass has been widely used in our daily life.^{32,33} Therefore, the ITO coating was used as a control. The change in temperatures inside the boxes as a function of irradiation time is plotted in Fig. 5 (b). It can be seen that the inside temperature of the pure quartz glass equipped box increased from 17.5°C to 27.8°C i.e., by about 10°C after 60 min irradiation. In contrast, the temperature in the box covered with the C-Z-1.0 composite film increased only from 17.5°C to 22.4°C. This temperature change was much lower than that of the box covered with the quartz glass. More importantly, the C-Z-1.0 composite film showed the heat ray shielding performance superior to ITO film (Fig. 5), although the visible light transmittance of C-Z-1.0 composite coated glass and ITO coated glass are almost identical. According to the above discussion, it could be inferred that the C-Z-1.0 composite coated film was effective for heat insulation and therefore, very promising for practical application.

Figure 6 shows the transmittance and reflectance spectra of the C-Z-1.0 composite film and ITO film to further explain the superior heat insulation ability of the composite film. It is well known that the solar light consists of ca. 5% UV light (280–380 nm), ca. 45% VIS light (400–780 nm) and ca. 50% NIR light (780–2500 nm). In these three types of lights, the NIR light is the main heat source. Moreover, the NIR light located at the wavelength of 780–1500 nm is the majority of the heat-rays of sunlight.¹⁴ Both the C-Z-1.0 composite film and ITO film showed very good VIS transmittance of above 80% with excellent NIR light shielding ability. However, some difference could be observed between the two films. On one hand, the C-Z-1.0 composite film showed much better UV light blocking property compared with the ITO film, as depicted in region I, and the comparable VIS light transmittance as marked in regions II and III (Fig. 6). On the other hand, the C-Z-1.0 composite film presented much higher NIR light shielding property in the range of 780–1450 nm as labelled in region IV than ITO film in spite of the weaker NIR light blocking in the range of 1450–2500 nm. As mentioned above, the short wavelength of NIR is the main part of the heat source in sunlight. Therefore, the C-Z-1.0 composite film demonstrated the heat insulation performance superior to that of ITO film as shown in Fig. 5. Besides, both the C-Z-1.0 composite film and ITO film made from the powders showed no reflectance in the NIR light, indicating that the shielding of NIR light was achieved by the NIR light absorption.

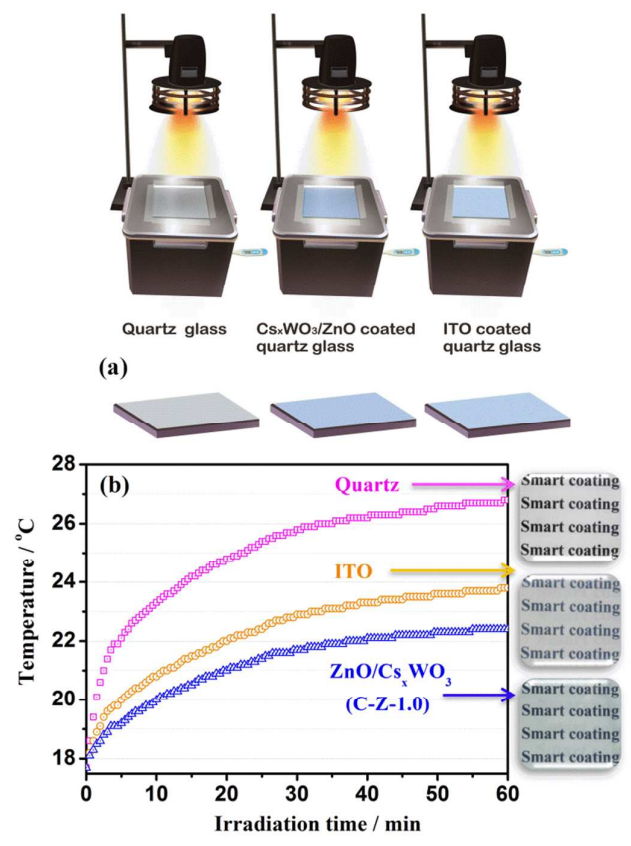


Fig. 5 Schematic illustration of the simulated heat ray shielding test using the boxes covered by pure quartz glass, C-Z-1.0 composite coated quartz glass and ITO coated quartz glass under the irradiation of a 50 W halogen lamp (a), and the detailed temperature variation with light irradiation time as well as the visual images of the three sample glasses (b).

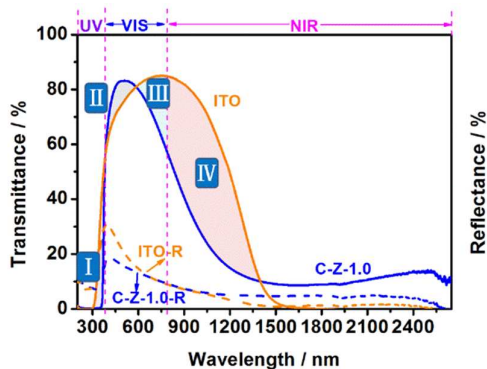


Fig. 6 Transmittance and reflectance spectra of the C-Z-1.0 film and ITO film.

Subsequently, the photocatalytic performance of the powder samples was tested by decomposing toxic NO gas by flowing over the sample. Figure 7 shows the deNO_x performance of the pure ZnO, pure Cs_xWO₃, C-Z-0.5, C-Z-1.0, C-Z-1.5 and commercial TiO₂ (P25). It is clear from these results that the

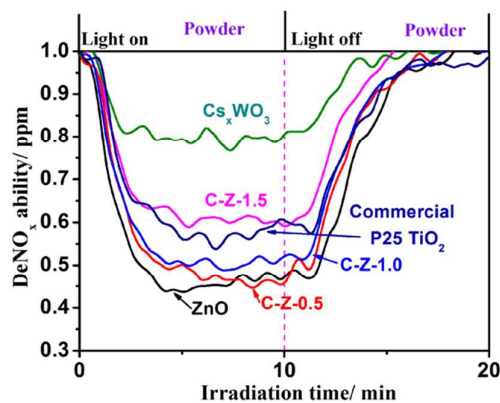


Fig. 7 DeNO_x performances of various sample powders.

pure Cs_xWO₃ displayed very poor deNO_x property owing to its poor separation ability of the photoinduced electrons and holes regardless of absorption property. In contrast, the pure ZnO possessing a specific surface area of 90.1 m²/g exhibited excellent deNO_x capability of nearly 60% under the irradiation of UV light, as expected since ZnO is one of the best photocatalysts³⁴⁻³⁸. When Cs_xWO₃ was combined with ZnO, the photocatalytic activity of ZnO decreased a little, however, it is notable that the deNO_x activities of C-Z-1.0 and C-Z-0.5 composites were even better than that of P25 (Fig. 7). In addition, the NO gas concentration would recover to the original content after light off with these composites, which indicates that these novel composites are highly efficient for air purification by decomposing NO under the light irradiation. Similar deNO_x tests were also performed using the films of the pure Cs_xWO₃, ZnO and C-Z-1.0 composite and the results are shown in Fig. 8. The results further confirmed that the C-Z-1.0 composite film possessed similar photocatalytic performance to that of ZnO film and definitely superior to that of pure Cs_xWO₃.

Based on the results obtained here, a potential application of the C-Z composite film for photocatalytic cleanup and heat-ray insulation is shown in Fig. 9. When the C-Z composite film coated glass is irradiated by solar light, the NIR light contained in solar light can be shielded by Cs_xWO₃ component to achieve the heat insulation and the UV light will be absorbed by both ZnO and Cs_xWO₃ to protect health while the majority of VIS light can pass through the film. In addition, the absorbed UV light by ZnO can further be used to excite the ZnO to produce photogenerated hole-electron pairs, which will then migrate to the surface of C-Z film and react with the surface absorbed H₂O and O₂ molecules to produce active radicals. These radicals then participate in reduction and oxidation processes to decompose toxic gas in air. Thus we have shown here that the C-Z composite film is not only effective for the heat insulation but also active for the toxic gas decontamination. In addition, the composite films developed here are useful for UV light blocking yet retaining very good visible light transparency. These novel C-Z composite coatings are expected to have promising application in the area of energy savings and environmental protection.

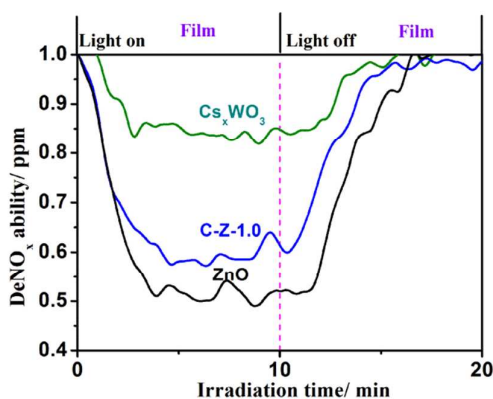


Fig. 8 DeNO_x performances of the films of the pure Cs_xWO₃, ZnO and C-Z-1.0 composite.

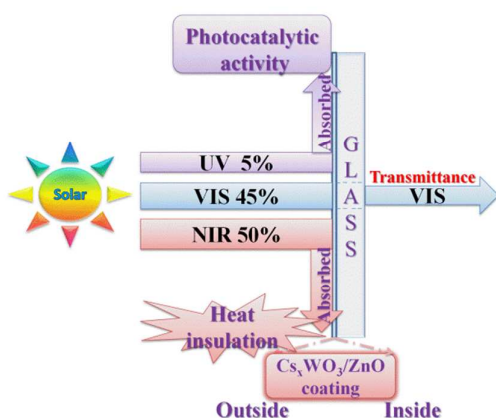


Fig. 9 Schematic illustration of the potential application of the C-Z composite for photocatalytic cleanup as well as heat-ray insulation.

Conclusions

Novel composites of Cs_xWO₃/ZnO were developed to be used as smart coatings. The Cs_xWO₃ was prepared by a controlled water release solvothermal process (CWRSP), and then the ZnO was combined by a soft chemical method to form target composites. The prepared Cs_xWO₃/ZnO composite films were not only highly efficient for heat insulation due to their excellent NIR shielding property of Cs_xWO₃ component, but also active for photocatalytic cleanup, due to the superior photocatalytic performance of ZnO component. These composite films also showed good harmful UV light blocking along with improved VIS light transparency and these properties are related to the suitable band gap of ZnO component. When the weight ratio of Cs_xWO₃ to ZnO is 1:1, the heat insulation ability of the composite was superior to ITO coating. Furthermore, the deNO_x ability of the 1:1 composite was also found to be much better than that of P25.

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Notes and references

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- 1 C. G. Granqvist, *Solar Energy Materials and Solar Cells*, 2007, **91**, 1529-1598.
- 2 Y. Z. Gao, X. Zhi, Y. Ren and T. Zhu, *Materials Science Forum*, 2009, **620-622**, 5-8.
- 3 C. Bechinger, J. N. Bullock, J. G. Zhang, E. E. Tracy, D. K. Benson, S. K. Deb and H. M. Branz, *J. Appl. Phys.*, 1996, **80**, 1226-1232.
- 4 J. Livage and D. Ganguli, *Solar Energy Materials & Solar Cells*, 2001, **68**, 365-381.
- 5 P. R. Somani and S. Radhakrishnan, *Mater. Chem. Phys.*, 2002, **77**, 117-133.
- 6 C. Bechinger, S. Ferrere, A. Zaban, J. Sprague and B. Gregg, *Nature*, 1996, **383**, 608-610.
- 7 U. Quershi, T. D. Manning, C. Blackman and I. P. Parkin, *Polyhedron*, 2006, **25**, 334-338.
- 8 S. D. Ji, Y. Zhao, F. Zhang and P. Jin, *Journal of Crystal Growth*, 2010, **312**, 282-286.
- 9 Y. M. Li, S. D. Ji, Y. F. Gao, H. J. Luo and M. Kanehira, *Sci. Rep.*, 2013, **3**, 1370.
- 10 U. Kreibitz and M. Vollmer, *Springer Ser. Mater. Sci.*, 1995, **25**, 25.
- 11 H. Takeda and K. Adachi, *J. Am. Ceram. Soc.*, 2007, **90**, 4059-4061.
- 12 K. Purvis, G. Lu and J. Schwartz, *J. Am. Chem. Soc.*, 2000, **122**, 1808-1809.
- 13 A. Hjortsberg and I. Hamberg, *Thin Solid Films*, 1982, **90**, 323-326.
- 14 C. Guo, S. Yin, P. Zhang, M. Yan, K. Adachi, T. Chonan and T. Sato, *J. Mater. Chem.*, 2010, **20**, 8227-8229.
- 15 C. S. Guo, S. Yin, M. Yan, M. Kobayashi, M. Kakahana and T. Sato, *Inorg. Chem.*, 2012, **51**, 4763-4771.
- 16 C. S. Guo, S. Yin and T. Sato, *J. Am. Ceram. Soc.*, 2012, **95**, 1634-1639.
- 17 J. Schneider, M. Matsuoka, M. Takeuchi, J. L. Zhang, Y. Horiuchi, M. Anpo and D. W. Bahnemann, *Chem. Rev.*, 2014, **114**, 9919-9986.
- 18 Y. Huang, W. Ho, S. Lee, L. Z. Zhang, G. Li and J. C. Yu, *Langmuir* 2008, **24**, 3510-3516.
- 19 C. H. Ao, S. C. Lee, C. L. Mak and L. Y. Chan, *Appl. Catal. B: Environ.*, 2003, **42**, 119-129.
- 20 X. Y. Wu, S. Yin, B. Liu, M. Kobayashi, M. Kakahana and T. Sato, *J. Mater. Chem. A*, 2014, **2**, 20832-20840.
- 21 X. Y. Wu, S. Yin, Q. Dong, B. Liu and T. Sato, *Appl. Catal. B: Environ.*, 2014, **156-157**, 257-264.
- 22 X. Y. Wu, S. Yin, Q. Dong, B. Liu, Y. H. Wang, T. Sekino, S. W. Lee and T. Sato, *Sci. Rep.*, 2013, **3**, 2918.
- 23 X. Y. Wu, S. Yin, Q. Dong and T. Sato, *Phys. Chem. Chem. Phys.*, 2013, **15**, 20633-20640.
- 24 C. Cheng, A. Amini, C. Zhu, Z. L. Xu, H. S. Song and N. Wang, *Sci. Rep.*, 2013, **4**, 4181.
- 25 Japanese Industrial Standard [JIS R 1701-1:2004(J)], Test method for air purification performance of photocatalytic materials-Part 1: Removal of nitric oxide, Japanese Standards Association, established on 2004-01-20.

- 26 F. Amano, D. Li and B. Ohtani, *ECS Transactions*, 2010, **28**, 127-133.
- 27 Z. J. Gu, Y. Ma, T. Y. Zhai, B. Gao, W. S. Yang and J. N. Yao, *Chem. Eur. J.*, 2006, **12**, 7717-772.
- 28 D. G. Barton, M. Shtein, R. D. Wilson, D. G. Barton, S. L. Soled and E. Iglesia, *J. Phys. Chem. B.*, 1999, **103**, 630-640.
- 29 K. Adachi and T. Asahi, *J. Mater. Res.*, 2012, **27**, 965-970.
- 30 O. F. Shirmer, V. Wittwer, G. Baur, and G. Brandt, *J. Electrochem. Soc.*, 1977, **124**, 749-753.
- 31 M. Miyakawa, H. Hosono, and H. Kawazoe, *Mater. Res. Bull.*, 1999, **34**, 115-121.
- 32 K. Purvis, G. Lu, J. Schwartz and S. Bernasek, *J. Am. Chem. Soc.*, 2000, **122**, 1808-1809.
- 33 O. N. Mryasov and A. J. Freeman, *Phys. Rev. B*, 2001, **64**, 233111-233113.
- 34 J. Q. Hu, Q. Li, X. M. Meng, C. S. Lee and S. T. Lee, *Chem. Mater.*, 2003, **15**, 305-308.
- 35 Y. Huang, Y. Wei, J. Wu, C. Guo M. Wang, S. Yin and T. Sato, *Appl. Catal. B: Environ.*, 2012, **123-124**, 9-17.
- 36 T. G. Xu, L. W. Zhang, H. Y. Cheng and Y. F. Zhu, *Appl. Catal. B: Environ.*, 2011, **101**, 382-387.
- 37 C. Q. Tian, Q. Zhang, A. P. Wu, M. J. Jiang, Z. L. Liang, B. J. Jiang and H. Q. Fu, *Chem. Commun.*, 2012, **48**, 2858-2860.
- 38 X. J. Bai, L. Wang, R. L. Zong, Y. H. Lv, Y. Q. Sun and Y. F. Zhu, *Langmuir*, 2013, **29**, 3097-3105.