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Short Communication

Photoprotective and multifunctional polymer film with excellent near-infrared and UV shielding properties

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ABSTRACT

Polymeric optical composites have played an important role in selectively shielding solar light to satisfy the increasing requirements of photoprotection and environmental comfort as well as improving the energy saving efficiency of buildings and cars. In the present work, a smart polymer film with high near-infrared (NIR) and ultraviolet (UV) light shielding, acceptable visible light transmittance was developed on basis of CuS nanoplate. The influences of the CuS nanoplate size and the thickness of polymer composite films on the optical and shielding properties were studied. In particular, the composite film can shield 86.5% of the near-infrared light from 800 to 1800 nm and at the same time permitting acceptable visible light (63.4%) with the film thickness of 30 μm. In order to improved UV-shielding performance, CuS nanoplate coated by polydopamine (PDA) was used for preparation of polymer composite film. It was found that UV-shielding performance was further promoted in the entire UV region and exhibited a synergistic relationship between PDA and CuS, which certificating the outstanding contribution of PDA layer on the surface of CuS nanoplate. In a word, the comprehensive research on nanocomposite fabrication, surface modification, and integration techniques enable us to fabricate highly flexible, transparent and reliable composite films with outstanding UV and NIR shielding performance. This novel film is potential to be used as smart windows of buildings and cars for the application of cooling energy saving and UV protection.

1. Introduction

The rapid growth of energy consumption has attracted worldwide concerns about climate change, wanton depletion of petroleum fuel, and global warming [1–3]. Sunlight is a great energy, approximately one-half of the total sun energy is heat rays, which includes the electromagnetic radiation from near-infrared (NIR) to infrared, that causes room temperature to rise is in the infrared region [4,5]. The world primary energy spent on air conditioning and heating accounts for more than 50% of the total energy, and what's worse is that a large proportion of this energy is wasted due to the poor light shielding or insulation of windows. Consequently, no matter in industrial or transportation sectors, energy saving and effective utilization are very important in both buildings and automobiles [6–8]. To minimize the energy loss, one promising and feasible approach to reduce energy consumption is to cut off the infrared light from the sun to achieve heat shielding and maintain appropriate visible light transparency. Although the energy of UV light only accounts for about 7% of the total energy of sunlight, long term exposure to UV radiation appears to cause significant damage to human health or polymeric materials. Prolonged UV radiation is also the biggest inducement of degradation of most polymer materials, which affect their mechanical properties and shorten their service life [9,10]. Therefore, to avoid the harmful effect of UV irradiation and energy consumption, it is essential to design effective UV-shielding and NIR shielding optical materials.

In the field of optical materials, polymers blended with fillers have been considered to be one of the most effective methods, and has a wide range of applications in building, industry, and national defense field. Recent studies have reported various polymer materials to shield the UV or NIR light, including metals (Ag and Au) [11,12], antimony-tin oxide [13,26], metal-doped semiconductors (e.g., $BiP_{1-x}V_xO_4$, Sn–In_2O_3, Pt-K_xWO_3, $Na_xCs_yWO_z$) [14–19], and inorganic oxides (e.g., TiO_2, In_2O_3,

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ZnO, SiO_2, Al_2O_3) [19–24]. However, these research studies have used either expensive metals or complicated doping procedures to design polymer materials, and also these materials usually suffer from a narrow absorption in a specific wavelength range rather than the entire NIR and UV regions. Many efforts have been done to solve this problem. Chen et al. [25] synthesized polypyrrole (PPy) nanoparticles by one-step aqueous dispersion polymerization and fabricated polyacrylic acid (PAA)/PPy composite films by adopting coating/drying technology. The PPy/PAA composite films can transmit 63.1% visible light (400–780 nm) but shield 80.9% NIR light. However, the UV-shielding performance is still at a relatively low level, over 50% UV light can still pass through the composite film. Qiu et al. [26] adopted antimony-doped tin oxide (ATO) as filler and used 3-(Trimethoxysily)propyl methacrylate (KH570) to modify the ATO nanoparticles. The ATO/TW composite was successfully fabricated via ATO modification and infiltration with PMMA, which exhibited excellent NIR shielding and UV-shielding properties. Unfortunately, the ATO/TW composite was no more transparent after the incorporation of ATO. Wu et al. [27] fabricated a smart Cs_xWO_3/PAM-PNIPAM window system, in which Cs_xWO_3 was selected as a light absorber and the transmittance of the window can be modulated by the phase change of PNIPAM microgels. This spectral selective smart window can block more than 75% of the solar energy, but still allow more than 40% of the visible light to pass through. But the need to pay attention to is that these Cs-based and W-based materials involve in the utilization of expensive and/or rare metal, thus increasing its manufacturing cost, what's worse is that the abandon of these materials would cause great damage to the environment.

To solve the problem mentioned above, a cheap, abundant and environmentally friendly copper sulfide (CuS) nanoplate has been found, which shows excellent absorption capacity in both UV and NIR band. A common solution mixing manufacturing method by introducing CuS nanoplate into PVA matrix was used to fabricate composite films. In this work, we synthesized three different sizes of CuS nanoplates by a simple hydrothermal method and the influence of their sizes on the NIR shielding and UV-shielding properties were further investigated. In our previous work, we have prepared a series of polydopamine (PDA) particles with different morphology and structure and studied their UV-shielding properties [28–30]. On the basis of our previous work, we covered the surface of CuS nanoplate with PDA to further improve its UV-shielding performance. These results have important practical value for preparing multifunctional polymer films with transparent thermal insulation and UV protection for the application in the field of energy saving and emission reduction.

2. Materials and methods

2.1. Materials

Dopamine (DA, 98%) was purchased from Aladdin. Copper chloride dihydrate ($CuCl_2{\cdot}2H_2O$), tris(hydroxymethyl)aminomethane, polyvinylpyrrolidone (PVP, K30), and sulphide ammonia solution ($(NH_4)_2S$, ≥17 wt %) were provided by Sinopharm Chemical Reagent Co., Ltd. Poly (vinyl alcohol) (PVA-1799) was supplied from Sinopec Sichuan Vinylon Works.

2.2. Preparation of CuS nanoplates with different diameters

The synthesis of CuS nanoplates with a diameter of ~250, ~180 and ~110 nm are as follows. A common hydrothermal method was adopted to fabricate CuS nanoplate. The diameter of the CuS nanoplates can be turned by simply varying the PVP content. For a typical preparation, $CuCl_2{\cdot}2H_2O$ (0.085 g, 0.5 mmol) and PVP (0.25 g, 0.5 g, 2 g) were dissolved in deionized water (30 mL) with magnetic stirring to form a transparent blue solution, respectively. After that, $(NH_4)_2S$ solution (≥17 wt%, 0.6 mL) was added quickly into the above blue solution and magnetically stirred for another 30 min, and then the homogeneous solution was transferred into a Teflon-lined autoclave and heated at 180 °C for 12 h. The black products were collected via centrifugation (12 000 rpm, 20 min) and then washed with deionized water several times. Finally, the products were dried in air-circulating oven at 50 °C for 24 h.

2.3. Preparation of CuS-PDA

In a typical procedure, 0.1 g CuS and dopamine (0.01g) were added to 150 mL deionized water by ultrasonication into a uniform dispersion, and the pH of the mixing solution was adjusted to ~ 8 by adding tris (hydroxymethyl)aminomethane. After that, the mixture was stirred at 520 rpm for 1 h at room temperature (25 °C). CuS-PDA nanoplates were collected by centrifugation (12 000 rpm) and then washed with deionized water several times.

2.4. Preparation of composite films

PVA composite films were prepared by a doctor blade method. 0.01 g CuS (or CuS-PDA) powder was dispersed in 15 mL of deionized water by ultrasonication for 30 min to form a homogeneous suspension. Then 20 g PVA solution (in water, 5 wt%) was added, and the mixture was stirred at 60 °C for 4 h to form a 11 wt% PVA aqueous solution. Composite films were prepared by using a doctor blade with a height of 200 μm at a speed of 1 cm/s. Films were dry at room temperature for 12 h and then further dried in air-circulating oven at 50 °C for 6 h to remove the water completely.

2.5. Characterization

The morphologies of the CuS and CuS-PDA were characterized by transmission electron microscope (TEM JEM-2100 plus, Japan). The average size of CuS nanoplates were tested by Zeta potential and nanoparticle analyzer (ZetaPALS, US). The UV-visible-NIR absorption spectrum were observed by a UV-3600 plus spectrophotometer. Heat-insulation performance was investigated by measuring the change in the temperature of an insulating box in real time by an electronic thermometer expose to a 300 W xenon lamp irradiation.

3. Results and discussion

3.1. Morphology and optical property of CuS nanoplate with different sizes

As shown in Fig. 1, the CuS nanoplate with three different sizes were characterized by TEM. All CuS nanoplates present a hexagonal shape [25]. Meanwhile, the diameters of each sample measured by Zeta were estimated to be 110, 180, 250 nm, respectively. Furthermore, with the increase of PVP content, the CuS nanoplates show a better monodispersity and more regular hexagonal morphology.

The optical properties of CuS dispersion with different size were measured using UV-vis-NIR spectroscopy. As shown in Fig. 2, the absorption intensity of CuS is relatively weak between 400 and 780 nm (visible region), which means that the majority of visible light can directly pass through the CuS-based polymer films. However, the CuS nanoplate represents a very high absorption capacity in both the UV region (220–400 nm) and NIR region (780–1300 nm) [35,36]. Those wide and strong spectral absorption capabilities are usually related to the photoprotective function. Importantly, the absorption intensity of the CuS nanoplate with a smaller size shows a better light absorption performance in the whole wavelength region, especially in the NIR region and UV region. Since the aqueous dispersions of the CuS have the same concentration, the change of absorption intensity should be attributed to the difference of CuS nanoplates number, which can help to improve its light absorption performance [29].

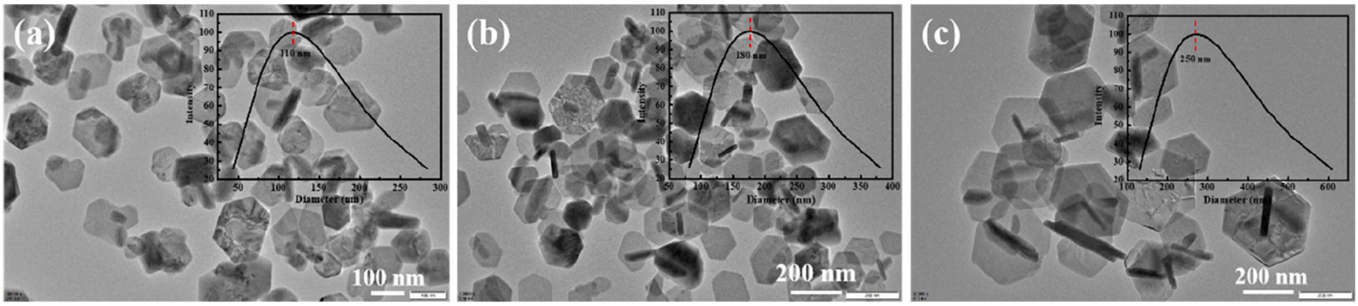

Fig. 1. TEM images of CuS nanoplates with an average diameter of (a) 110, (b) 180, (c) 250 nm. The inset was the corresponding DLS of CuS nanoplates.

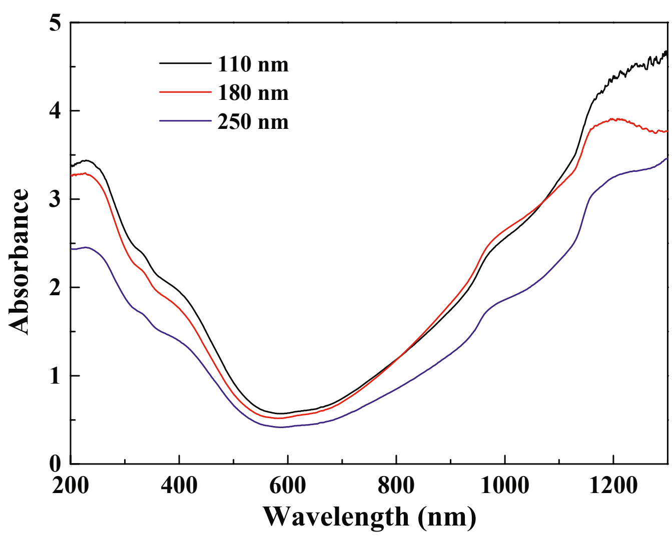

Fig. 2. UV-vis-NIR absorption spectrum of the aqueous dispersion containing CuS nanoplates (0.1 mg/mL) with different size.

3.2. Design of PVA/CuS composite films and optical property measurements

Fig. 3 generalizes the optical performance of the composite films. For the optimization of film fabrication, the influence of the CuS nanoplate size and film thickness on optical performance were studied. Fig. 3 (a, b) shows the UV-vis transmittance spectra of PVA composite films with different film thickness, which contains only 1 wt % CuS nanoplate load. It can be clearly found out from Fig. 3 (a, b) that the UV and NIR shielding properties of composite films are partly decided by the size of CuS nanoplate. The pure PVA film was almost transparent in the whole UV-vis-NIR region (300–1800 nm), meaning the inappreciable light absorption capacity [9,38]. After 250 nm CuS nanoplate was added, the composite film with a height of 15 μm is able to block NIR light in the range of 780–1800 nm and UV light below 400 nm, the maximum transmittance is about 37.7% at 1370 nm and 50.8% at 320 nm, respectively (Fig. 3a). More interesting is the fact that as the nanoplate size decreases from 250 to 110 nm (Fig. 3a), both UV and NIR shielding properties are improved, while transmittance of visible light is still very high (≥74%). What's more, the influence of the film thickness on its transmittance was studied. Obviously, with the increase of film thickness from 15 to 30 μm, the overall transmittance of the visible region (400–780 nm) slightly decreases, and the maximum transmittance at 580 nm reduces to 63.4%. At the same time, the increase of the film thickness promotes the shielding property of the composite film in the NIR region (780–1800 nm), the total transmittance in the wavelength of 780–1800 nm decreases from ~34% to ~13%. Similar phenomena can also been observed in the UV region. It is interesting to note that the UV-shielding and NIR shielding performance will not change significantly when further increase the thickness of the composite film, the only change is the transparency of the composite film (Fig. 3 c). The high transparency of visible light is an important prerequisite for the preparation of optical materials [36]. However, how to achieve a good balance between the shielding property and visible light transparency is still a great challenge [9,13]. Consequently, the material characterization demonstrates a highly reliable fabrication of multifunctional films with the film thickness of 30 μm, which yields excellent UV-shielding and NIR shielding properties, and a relatively high transmittance (63.4% at 580 nm).

3.3. Heat-shielding properties of the PVA/CuS composite film

In order to assess the practical application value of composite films, we carried out a simulated experiment where the sealed foam box was covered by the PVA/CuS film as the window, as demonstrated in Fig. 4 a. At first, the temperature in the box was ~27.8 °C. After the direct exposure in real sunlight for 8 min, the temperature in the box rose to 44.3 °C, 5.2 °C higher than the box protected by the PVA/CuS composite film. Under the irradiation of the xenon lamp with an intensity of 150 W cm^{-2}, the air temperature in the box was real-time recorded. As shown in Fig. 4 b, when pure PVA was covered as the window, the interior air temperature goes up sharply with the increase of the irradiation time to 400 s, then exhibits a relatively flat section and reaches a maximum of about 43.4 °C (ΔT = 20.6 °C) at 1400 s. For the PVA/CuS composite film with a particle size of 110 nm, the temperature increases to 35.5 °C (ΔT = 12.4 °C), 7.9 °C lower compared with pure PVA film. These results show that PVA/CuS can be used as a thermal shielding material and has a wide potential application in the field of energy conversation [13,36].

3.4. Preparation of CuS-PDA and the optical performance of CuS-PDA based composite films

For further improvement of the UV-shielding property of the PVA composite film, we covered the CuS with a polydopamine (PDA) layer for the first time and investigate the synergistic relationship between PDA and CuS in UV-shielding performance. By control the ratio of CuS to dopamine and the reaction time, we can obtain PDA coated CuS nanoplate with different PDA layer thickness [37]. When the mass ratio of CuS to dopamine is 10:1 and the reaction time is 1 h, the thickness of PDA layer is about 5 nm (Fig. 5 a). Further improving the content of dopamine and the reaction time, the PDA layer can be increased to about 20 nm (Fig. 5 b). Absolutely, PDA layer with different thickness can also affect the UV and NIR shielding properties of the composite film. Definitely, a 5-nm-thick PDA layer was of vital importance in reducing the UV transmittance of the composite film, the maximum transmittance at 250 (UVC), 300 (UVB), 360 nm (UVA) drops from 15.1% to 7.2%, 20.2%–14.7%, 25.5%–21.5%, respectively, demonstrating the improvement of the UV-shielding performance. Meanwhile, the presence of the PDA layer does not have a great influence on the visible light transmittance and NIR shielding performance of the composite film

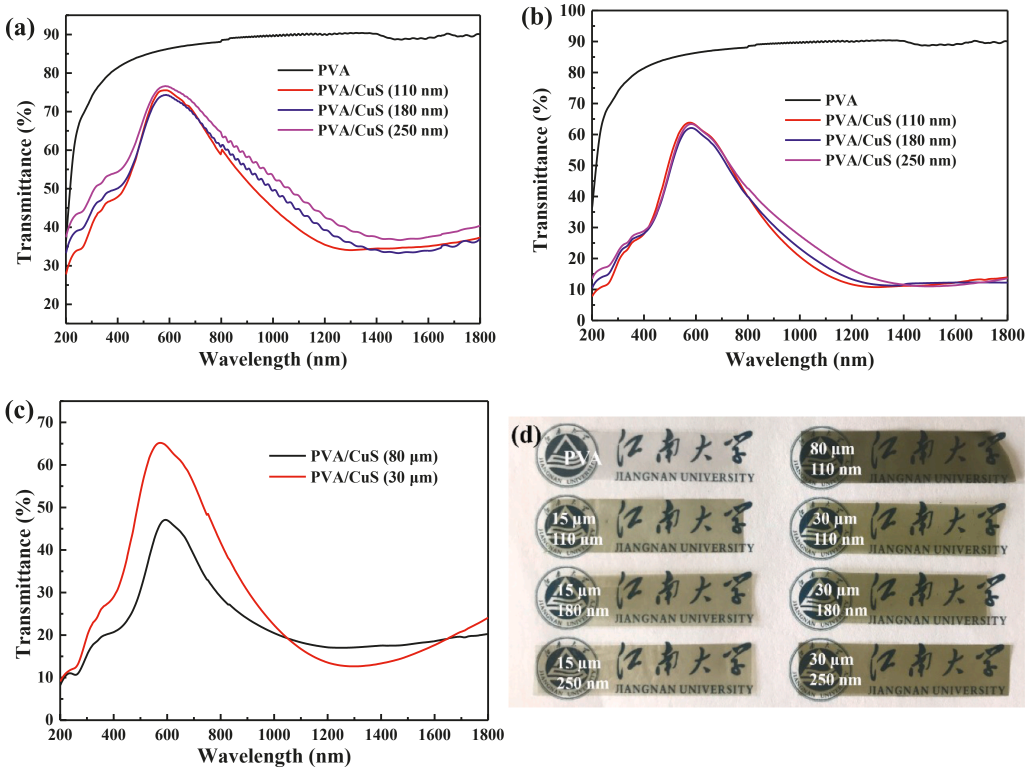

Fig. 3. UV-vis transmittance of the composite films composed of CuS with (a) 15 μm thickness and (b) 30 μm thickness. (c) Comparation between different thickness composite films with the same CuS content. (d) Photograph of the PVA/CuS composite films. The CuS content in all composite films was 1 wt%.

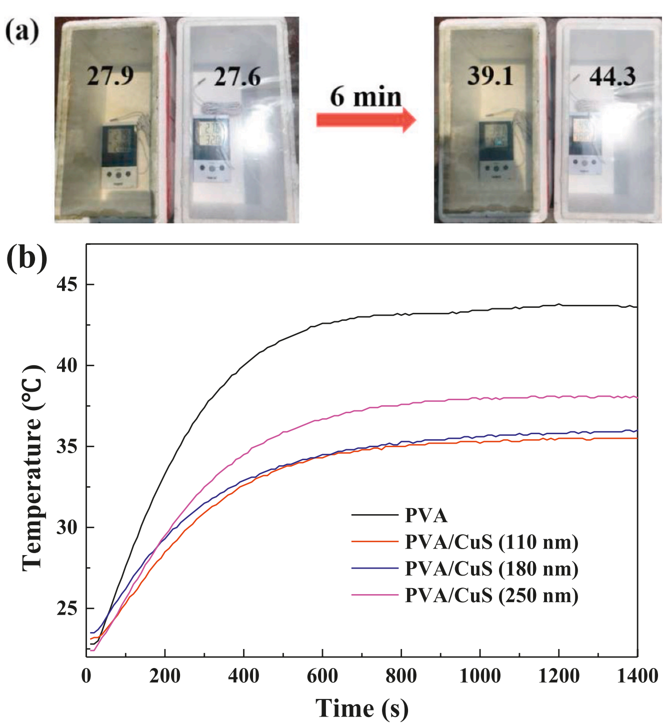

Fig. 4. (a) Monitoring of in situ temperature change of the composite film coated on a sealed box as the window. The light source is the real sun. (b) Changes of the interior air temperature of the box under light irradiation of a xenon lamp. CuS content was 1 wt%.

(Fig. 5 a'). Unfortunately, the thicker the PDA layer, the worse the UV and NIR shielding properties of the composite film. This is because the thick PDA layer hinders the absorption capacity of CuS in the UV and NIR regions (Fig. 5 b'). What's more, the thicker PDA layer makes CuS easier to agglomerate, which leads to the decrease of thermal shielding performance and a poor dispersion in water (Fig. 5 d). The interior air temperature of the box protected by PVA/CuS-PDA-20 composite film was 4.6 °C higher than that of protected by PVA/CuS-PDA-5 composite film (Fig. 5 c). Table 1 summarizes previously reported UV and NIR shielding polymer composites. The reported polymer composites either exhibited a single light shielding properties [9,15,16,27], or hard to maintain the transparency of the composites while showed an outstanding UV and NIR shielding performance [17,25,26]. As a result, it can be seen from Table 1 that our work is comparable or superior to some other previously reported polymeric optical composites.

4. Conclusion

In summary, multifunctional PVA composite films containing CuS were successfully fabricated, which possesses, simultaneously, UV-shielding and NIR shielding properties. The influences of the CuS nanoplate size and the thickness of polymer composite films on the optical properties were further studied. It was found that PVA/CuS composite film with a thickness of 30 μm exhibit efficient UV-shielding and NIR shielding properties, as well as a relatively high visible transmittance, when CuS content was 1 wt %. Furthermore, direct attachment of the PVA/CuS composite film on a sealed box as the window under the irradiation of simulated solar light shows a lower interior air temperature when compared with pure PVA film (ΔT = 7.9 °C). What's more, CuS was surface coated by PDA to further improve its UV-shielding performance. Therefore, PVA/CuS-PDA composite films have great potential in the field of cost-efficient energy-saving and photo-protective materials.

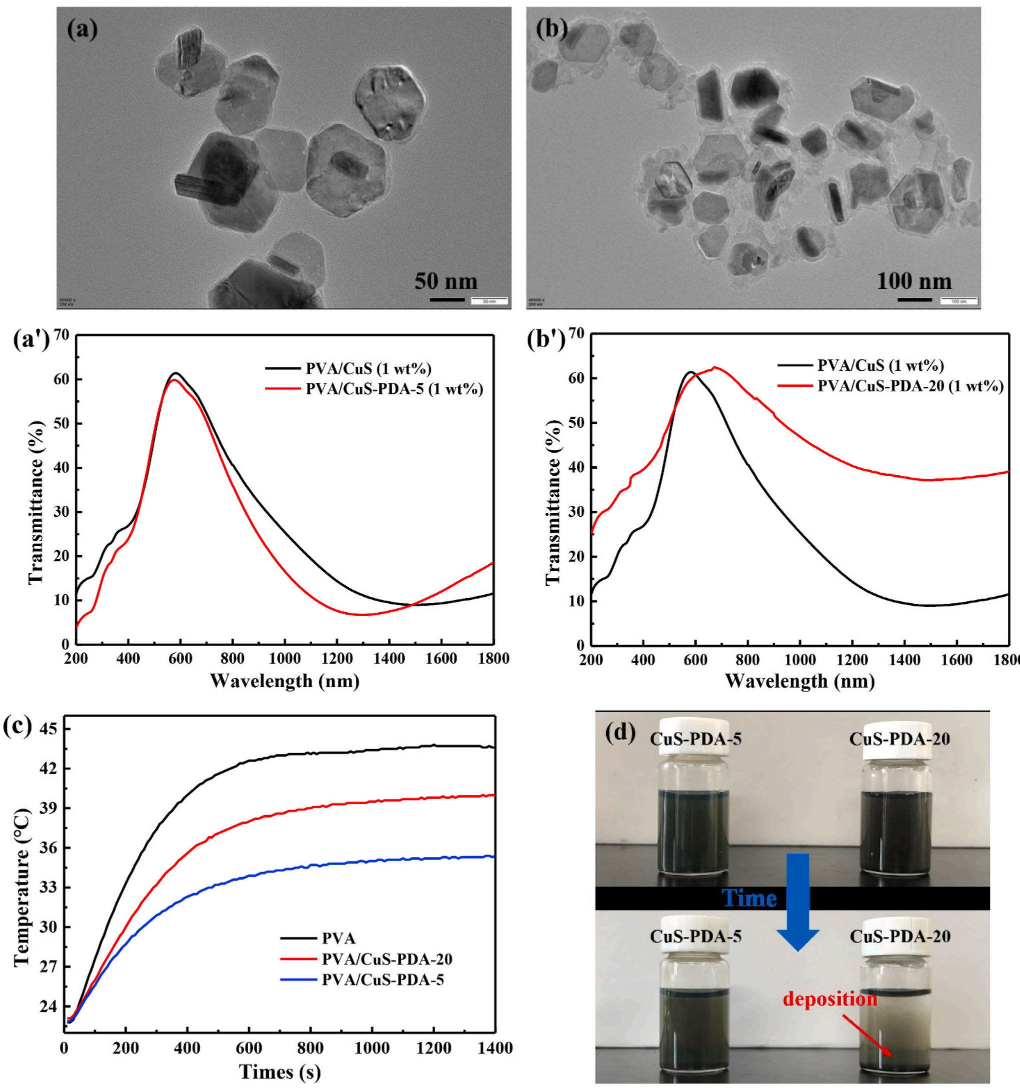

Fig. 5. (a, a') TEM images of CuS-PDA nanoplates with different PDA layer thickness. (b, b') UV-vis transmittance of the PVA composite films composed of CuS-PDA. (c) Changes of the interior air temperature of the box protected by PVA composite films composed of CuS-PDA under light irradiation of a xenon lamp. (d) Photograph of the CuS-PDA-5 and CuS-PDA-20 aqueous solution.

Table 1
Comparison of UV (T_{UV}), visible light (T_{Vis}) and NIR (T_{NIR}) transmittance of our composites with other reported composites.

Sample	T_{UV} (%)	T_{Vis} (%)	T_{NIR} (%)	Reference
Cs_xWO_3	/	~45.3%	~3.8%	27
PPy	20.6%	36.2%	14.4%	25
Pt- $KxWO_3$	~15%	~55%	~5%	17
ATO	~10%	< 50%	~4	26
Sb-PATOs	~40%	55.3%	58.2%	13
ZnO	~1%	~86%	/	9
VO_2	/	< 40%	19.45%	15
$Na_xCs_yWO_z$	/	64%	10.6%	16
CuS-PDA	14%	63.4%	13%	This work

CRediT authorship contribution statement

Hao Yuan: Investigation, Methodology, Writing - original draft. **Ting Li:** Conceptualization, Project administration. **Yang Wang:** Methodology. **Piming Ma:** Resources. **Mingliang Du:** Conceptualization. **Tianxi Liu:** Resources, Writing - review & editing. **Yangyang Yan:** Data curation, Software. **Huiyu Bai:** Formal analysis. **Mingqing Chen:** Supervision. **Weifu Dong:** Conceptualization, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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