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Core-shell structured Cs_xWO_3@ZnO with excellent stability and high performance on near-infrared shielding

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ABSTRACT

Cesium-doped tungsten bronze Cs_xWO_3 (CWO) is a promising candidate for near-infrared (NIR) shielding materials on windows of buildings and automobiles. However, the NIR shielding ability of CWO easily deteriorates in hot humid and alkaline environments, which hinders further applications of CWO. In this paper, we firstly reported a novel core-shell structure of CWO@ZnO, which exhibited high NIR shielding performance with excellent stability. In hot humid environment, CWO@ZnO nanoparticles kept their outstanding NIR shielding ability after 150 days while uncoated CWO nanoparticles showed an evident deterioration in just 1 day. Moreover, the CWO@ZnO core-shell structure also exhibits excellent stability in alkaline environment. The good protection of the uniform, continuous and compact ZnO shells played an important role on enhancing the stabilities of CWO nanoparticles. This study provides a novel route for promoting the practical applications of CWO NIR shielding materials.

1. Introduction

In recent years, worldwide attention has been attracted on decreasing the energy consumption of air conditioning by applying near-infrared (NIR, wavelength of 780–2500 nm) light (heat rays) shielding materials on windows of buildings and automobiles such as noble metals (Au, Ag, etc.) [1–5], black compounds (ruthenium-, rhodium-, and iridium-containing oxides) [6,7], semiconductor oxides (FTO, AZO, ITO) [8–12], and rare-earth hexaborides (PrB_6, NdB_6, LaB_6, etc.) [13–15]. These materials have the ability of blocking NIR through localized surface plasma resonances (LSPRs, collective oscillations between lights and free carriers restricted to the surfaces of nanoparticles) [16–21]. However, there are some disadvantages have hindered their further applications. Noble metals and black compounds show low transmittances in visible lights. Rare-earth hexaborides shield only certain wavelengths of NIR lights, and their high hardness leads to more energy consumption in the process of preparing nanoparticles by milling. FTO and ITO only effectively insulate NIR lights of wavelengths $\lambda > 1500$ nm.

Tungsten bronzes (doped tungsten trioxides), especially alkali-doped tungsten trioxides, show a promising prospect as solar filters, because they can combine two features of outstanding NIR blocking ability and high visible light transmittance which are required for excellent solar filter materials on windows [22–27]. WO_3 does not have any absorption of NIR and visible lights due to its wide band gap of 2.62 eV and lack of free carriers [28]. With the insertion of doped ions, such as NH_4^+, Li^+, Na^+, K^+, Rb^+, Cs^+, etc., part of tungsten atoms in WO_3 are reduced from + 6 to + 5, which leads to more electrons [29–32]. These electrons occupy conduction band (free electrons) and localized states in band gap (trapped electrons). As a result, the doped tungsten trioxides (tungsten bronzes) acquire the ability of blocking NIR in almost whole wave range ($\lambda > 1100$ nm) by absorbing NIR whose photon energy is lower than 0.7 eV through LSPRs and insulating NIR whose photon energy is near 1.4 eV through a small polaron mechanism [33,34]. And with doping, the color of WO_3 also transforms from light yellow to deep blue.

In contrast to the obvious merits mentioned above, the serious problems about the instabilities of tungsten bronzes in weathering evaluations cast a shadow on the prospect of commercial application. A bleaching phenomenon accompanied with the deterioration of NIR

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shielding property also appeared when tungsten bronzes were oxidized in humid environment [35]. Moreover, tungsten bronzes will be corroded inevitably in alkaline environment. However, few researches have been conducted on solving these problems.

Zinc oxide is an important semiconductor material with a band gap of 3.4 eV. It has various attractive properties including transparency, high refractive index, low-cost and biocompatibility [36]. It also has a better stability in alkaline media than tungsten bronzes. Based on these merits, ZnO was commonly used in antireflective and protective layers on windows [37–40].

In this study, we successfully synthesized Cs_xWO_3@ZnO (CWO@ZnO) nanoparticles with high performance on NIR shielding and enhanced stabilities for the first time. CWO nanoparticles were prepared by the thermal reduction method. And then these nanoparticles were coated with a thin layer of ZnO. The obtained CWO@ZnO nanoparticles showed high performance in shielding NIR and excellent stabilities in hot humid environment and alkaline media. This work has definitely played a positive role on the way to commercial applications of tungsten bronzes.

2. Experimental section

2.1. Materials

Tungsten trioxide (WO_3) nanoparticles, cesium carbonate (Cs_2CO_3), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), Hexamethylenetetramine (HMT), polyvinyl butyral (PVB) resin were purchased from Aladdin. All the chemicals above were used without further purification. ANTI-TERRA-U (solution of a salt of unsaturated polyamine amides and low-molecular acidic polyesters) used as dispersant was purchased from the ALTANA specialty chemicals.

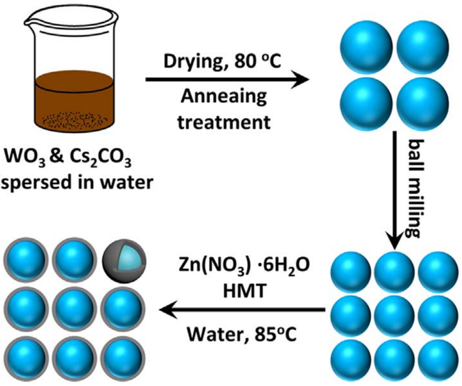
2.2. Preparation of Cs_xWO_3 (CWO) aqueous dispersion

Based on our previous study [41], CWO was synthesized by the thermal reduction method. At the first step, WO_3 nanoparticles were mixed well with aqueous solution of cesium carbonate at a predetermined molar ratio of Cs/W ($\approx$ 0.33). The mixed suspension was stirred at 80 °C overnight for drying. After drying, the mixture of WO_3 and Cs_2CO_3 were annealed at 600 °C for 1 h in a tubular furnace with a reductive atmosphere of 5% H_2/N_2. Then, the blue CWO particles were obtained.

In order to prepare CWO aqueous dispersion, the CWO particles were added into deionized water with certain amount of dispersant. The mass ratio of CWO to water was 5% and the mass ratio of the dispersant to the whole aqueous dispersion was 1%. Bead mill with 0.3 mm zirconia beads was used to mix the dispersion well and diminish the dimensions of CWO particles. After bead milling, the CWO aqueous dispersion was kept for the next experiment.

2.3. Synthesis of CWO@ZnO nanoparticles

2 g CWO dispersion was added into 80 ml deionized water and stirred for 15 min. Then, 0.3 g zinc nitrate hexahydrate and 0.15 g Hexamethylenetetramine (HMT) were dissolved in the suspension. After that, the suspension was kept at 85 °C for 8 h with vigorous stirring to form ZnO shells on CWO particles. When the reaction was finished, the suspension was centrifuged at 9000 rpm for 5 min to collect CWO@ZnO nanoparticles. The obtained nanoparticles were washed by deionized water and ethanol 3 times each and then dried at 80 °C in the air. The whole process for the synthesis of CWO@ZnO nanoparticles is illustrated in Scheme 1.



Scheme 1. Experimental flow chart for the synthesis of CWO@ZnO nanoparticles.

2.4. Characterization

To characterize the optical performances of CWO@ZnO nanoparticles, CWO@ZnO coatings on glasses were made. First, 0.1 g as-synthesized CWO@ZnO nanoparticles were dispersed in 10 ml ethanol with the help of ultrasound. Then 3 g polyvinyl butyral (PVB) resin was added into the dispersion. Strong magnetic stirring was used to mix the dispersion and resin well. Afterward, CWO@ZnO coatings were prepared through spin-coating. The spin speed was 1000 rpm and the spin time was 30 s. Following the spin-coating, the coated glasses were kept at 60 °C for 1 h to remove the residual liquid. After drying, the synthesis of CWO@ZnO coatings was finished and the optical properties of the coatings were measured by a UV-prism spectrometer (HITACHI, U-3010). The optical performances of pure CWO nanoparticles were measured by the same steps.

Based on the measurement of the optical performances of CWO@ZnO nanoparticles, the NIR shielding ability was assessed quantitatively by calculating the solar energy transmittance selectivity (SETS) [41]. SETS was obtained through Eq. (1):

$$\mathrm{SETS} = \frac{1}{2}\left(1 + \frac{\int_{\mathrm{UV}}^{\mathrm{Vis}} E(\lambda)T(\lambda)d\lambda}{\int_{\mathrm{UV}}^{\mathrm{Vis}} E(\lambda)d\lambda} - \frac{\int_{\mathrm{Vis}}^{\mathrm{NIR}} E(\lambda)T(\lambda)d\lambda}{\int_{\mathrm{Vis}}^{\mathrm{NIR}} E(\lambda)d\lambda}\right) \tag{1}$$

In this equation, $E(\lambda)$ is the solar irradiance spectrum for air mass 1.5 corresponding to the sun standing 37° above the horizon. And $T(\lambda)$ is the transmittance spectrum. SETS represents the solar energy transmittance deviation. The range of SETS vales is 0–1. The higher the SETS value is, the more NIR lights are blocked and simultaneously the more visible lights go through, which means the material that the SETS value is belonged to is more suitable for use in NIR blocking films on windows.

To characterize the stabilities of CWO@ZnO nanoparticles in hot humid environment, the CWO@ZnO coatings were kept at 60 °C with 90% humidity in a constant temperature-humidity chamber. The changes of the optical properties of CWO@ZnO coatings were monitored by the UV-prism spectrometer (HITACHI, U-3010). To make a contrast, the stability of pure CWO coatings was also measured by following the same steps.

To characterize the stability of CWO@ZnO nanoparticles in alkaline environment, equal amounts of pure CWO and CWO@ZnO nanoparticles were added into a sodium hydroxide aqueous solution (pH = 10) separately at room temperature. The pH value of 10 was chosen to accelerate the erosion for easier observation. The absorption spectra of the suspensions were measured after different durations. The stabilities of the nanoparticles could be reflected by the changes of the absorption spectra.

The crystal structures of nanoparticles were characterized by an X-ray diffraction (XRD) machine with a Cu-Kα radiation of 1.541 Å wavelength and settings pf 40 kV and 40 mA. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and energy dispersive spectrometer (EDS) were used to characterize the morphologies and compositions of the nanoparticles through a field emission transmission electron microscopy (TEM, JEOL2010) with an EDS attachment.