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Preparation, structural and optical properties of $ZnWO_4$ and $CdWO_4$ nanofilms

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Abstract For the first time, a novel route for preparing AWO_4 (A=Zn, Cd) nanofilm on a glass substrate is proposed through the combination of reverse micelle system with dip-coating technology. Here collodion is used as a dispersant and film-forming agent to obtain nanofilm with a good quality and property. SEM and XRD results indicate $ZnWO_4$ and $CdWO_4$ nanoparticles with monoclinic system and wolframite structure are well dispersed on the substrate. The nanofilm's photoluminescent(PL) bands obviously blue shift compared with bulk materials whereas red shift compared with nanoparticles, which should be due to quantum size effect and film-forming effect. FTIR absorption bands between 400 and 900 cm^{-1} prove the presence of $ZnWO_4$ or $CdWO_4$ nanoparticles on the substrate.

Introduction

Because of its intriguing luminescence and structure properties, oxytungstate with second group metal ion such as $ZnWO_4$ and $CdWO_4$ is an attractive scintillating material and has received much intense research interest [1–3]. However, its more extensive applications are often limited by comparatively low quantum efficiency and strong dependence of their characteristics on the growth conditions as well as by insufficient radiation [4]. Many efforts are thus devoted to increase their light yield by doping [4], nano-scale [5, 6] and film-forming [7] in order to extend their application.

It is well known that thin film materials because of their inherent small size and less transverse scattering have more superior photoelectrical, magnetic and catalytic properties than their powder materials. And nanofilms are more attractive than those of commonly thin films, because that they have some prominent properties, such as giant conductance, giant magnetic resistance, giant Hall effect, and visible light emission and so on [8]. Many scientists thus have been made towards preparation technologies and properties of nanofilms in recent years [9, 10]. So far, less investigation has been focused on oxytungstate bulk films [11–14], much less $ZnWO_4$ and $CdWO_4$ films [15–17]. Nevertheless, no attempts for nanofilms of oxytungstates with second group metal ion have been reported.

Collodion is a comb-like polymer and mainly consists of nitrocellulose, ethanol and ether. It has a good stability and disparity, and is commonly used in medicine and industry fields [18]. Recently, it has been used as an additive in sol-gel system to prepare MgO thin films [19]. Herein, we bring forward a simple technique to prepare $ZnWO_4$ and $CdWO_4$ nanofilms, with collodion as a dispersant and film-forming agent to keep nanofilm with good quality and property. The results indicate either advantage of preparation method or quality and property of nanofilm is satisfying. We hope this can enable us to prepare more nanofilms.

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Experimental details

Synthesis of $ZnWO_4$ and $CdWO_4$ nanoparticles

In this study, reverse micelle system is used to prepare $ZnWO_4$ and $CdWO_4$ nanoparticles, consisting of Tween-80 as a surfactant, *n*-pentanol as a cosurfactant, hexamethylene as continuous oil phase, and either zinc (or cadmium) sulfate or sodium tungstate precursor solution as dispersed aqueous phase.

As a typical synthesis, put 28 mL hexamethylene into a conical flask, and then add 3 mL Tween-80 and 1 mL 0.4 M zinc (or cadmium) sulfate solution into conical flask in turn. When injecting *n*-pentanol into it, solution is stirred strongly at a speed of 3,000 rpm for about 15 min until the reverse micelle solution become transparent. The other reverse micelle solution is obtained, when 1 mL 0.4 M zinc (or cadmium) sulfate solution is taken the place of 1 mL 0.4 M sodium tungstate solution. Thereafter, the above two reverse micelle solutions are mixed quickly. The resulting solutions are aged with stirring at room temperature for 5 min. After 12 h of reaction, add acetone into the mixed solution. A white product is collected by centrifugation, washed by ethanol, acetone and distilled water in turn, that is $ZnWO_4$ or $CdWO_4$ nanoparticles.

Film preparation

The above as-prepared $ZnWO_4$ (or $CdWO_4$) nanoparticles solutions after extracting the above ethanol liquid are stirred at room temperature for 30 min. Then 2 mL collodion is added into the solution and stirred for at least 1 h, which is served as coating material.

Glass slides as substrates are cleaned through ultrasonic treatment with concentrated acid, ethanol and distilled water for 20 min, respectively. Then they are dipped into coating material and pulled at a speed of 35 mm/min, and dried in air at room temperature. The as-prepared samples are white-color and homogeneous. The films are then heated at 200 °C for 30 min and annealed at 500 °C for 1 h, and slowly cooled to room temperature.

Physical measurement

The phase and crystallinity of nanoparticles and films annealed at 500 °C are carried out on a Rigaku D/max2550 X-ray diffractometer (XRD) with CuK_α radiation ($\lambda = 0.15418$ nm) (Japan). A Field-Emission Environmental Scanning Electron Microscope FEI/Phillips XL30 ESEM-FEG (SEM, Holand) is used for observing the surface morphologies of films. All FTIR and Photoluminescence (PL) measurements are made with a Nicolet NEXUS870 FTIR spectrometer (USA) and a Perkin–Elmer luminescence spectrophotometer (LS-55, USA), respectively.

Results and discussion

Optimization of preparation conditions

The introduction of collodion hardly obviously affects the structures of nanofilms, but strongly affects their quality. It is noted from Fig. 1 that uniform nanofilms can be obtained with 2 mL of collodion. And the nanofilms show homogeneous surface morphology without large cavity in this work. Hence 2 mL collodion is used as the optimal amount in this work. Sphere-like $ZnWO_4$ nanoparticles with the average size of 90 nm whereas spindle-like $CdWO_4$ nanoparticles with the length of 250 nm and the diameter of 150 nm (length-diameter ratio: 1.6:1) are distributed equably on the glass substrate, respectively, as shown in Fig. 1a and b.

However, an uneven surface morphology with holes of $ZnWO_4$ nanofilm is observed without collodion

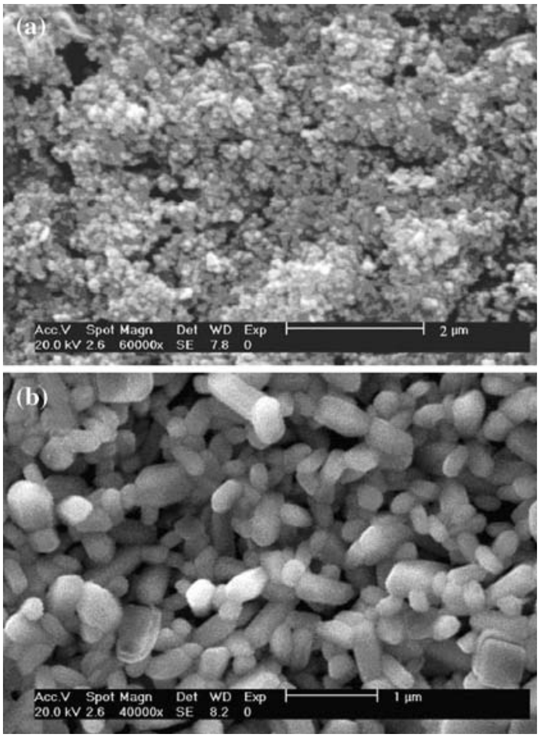


Fig. 1 SEM images of the as-prepared nanofilms: (**a**) $ZnWO_4$ and (**b**) $CdWO_4$

introduced (Fig. 2), and $ZnWO_4$ nanoparticles cannot be well distributed on the substrate.

It is clear that heating temperature and time have some effects on nanofilms. With too low heating temperature and too short heating time, collodion in nanofilms cannot be burned out entirely. On the contrary, with too high heating temperature and too long heating time, the size of nanoparticles will increase beyond nano-scale. So, in this work, the nanofilms are heated with the average rate of 5 °C/min and kept at 200 °C for 30 min to make sure collodion burn out entirely. They are then heated at the same rate and kept at 500 °C for 1 h to crystallization. Finally, they are cooled with the rate of 10 °C/min to room temperature.

X-ray diffraction patterns

Figure 3 presents XRD patterns of the as-prepared films. As shown in Fig. 3a and b, both of $ZnWO_4$ and $CdWO_4$ are sanmartinite with monoclinic system and wolframite structure in terms of JCPDS Card Files: 88-0251 and 14-0676, respectively. It is also seen that an obvious phenomenon of wider diffraction peaks appears, which might be attributed to little dimension of grain. And the crystallinity of nanofilms is slightly better than that of nanoparticles.

Photoluminescence analysis

Figure 4 shows PL spectra of as-prepared bulk materials, nanoparticles and nanofilms. In Fig. 4a, it can be seen that the emission peak of bulk $ZnWO_4$ locates at 460 nm (2.70 eV), which is originated from its wolframite structures with WO_6^{6-} group [20], whereas that of $ZnWO_4$ nanofilm is at 430 nm (2.88 eV). This indicates that band gap of $ZnWO_4$ nanofilm is much wider than that of bulk $ZnWO_4$. So, nanofilm can absorb higher energies to emit light than corresponding bulk material, and an obvious blue-shift about 30 nm appears which should be attributed to both quantum size effect and film-forming effect. According to the definition of quantum size effect [21], the phenomenon that band-gap become wider is the characteristic of nanomaterials. Moreover, Zhao and Mou reported that quantum size effect in direct-gap semiconductors is responsible for the shift of optical absorption edge to higher energies with decreasing size [22], and this phenomenon can also explain PL blue-shift as shown in Fig. 4a. Additionally, the as-prepared $ZnWO_4$ nanoparticles have the widest band gap (3.04 eV, emit at 408 nm) in them, and its PL band shifts obviously to short wavelength region compared with that of $ZnWO_4$ nanofilm. Due to the size of $ZnWO_4$ nanoparticles, which calcined at 500 °C on the substrate to prepare nanofilms, increase and high temperature make them crystallize better (Fig. 4a). Similar results are obtained from $CdWO_4$, as illustrated in Fig. 4b.

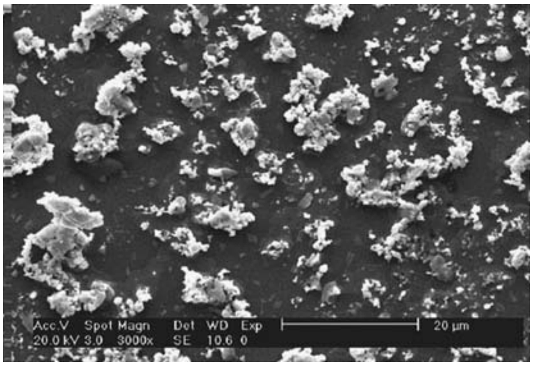


Fig. 2 SEM image of the as-prepared $ZnWO_4$ nanofilm without collodion

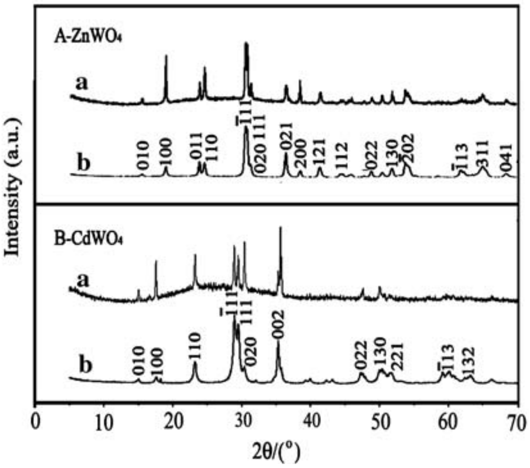


Fig. 3 XRD patterns of the as-prepared nanofilms (**a**) and nanoparticles (**b**)

Film-forming effect on optical properties

To further explore film-forming on optical properties, PL spectra of the as-prepared AWO_4 (A=Zn, Cd) nanoparticles and nanofilms are shown in Fig. 5. It is clear from that emission peaks of $ZnWO_4$ and $CdWO_4$ nanoparticles are at 408 and 403 nm, respectively (Fig. 5a) (proportion of wavelength: 1:0.99), whereas those of $ZnWO_4$ and $CdWO_4$ nanofilms are at 430 and 447 nm, respectively (Fig. 5b) (proportion of wavelength: 1:1.04). This indicates that relative sequences and proportion of peak position

Fig. 4 PL spectra (ex=290 nm) of the as-prepared AWO_4 (A=Zn, Cd): nanoparticles (**a**); nanofilms (**b**); bulk materials (**c**)

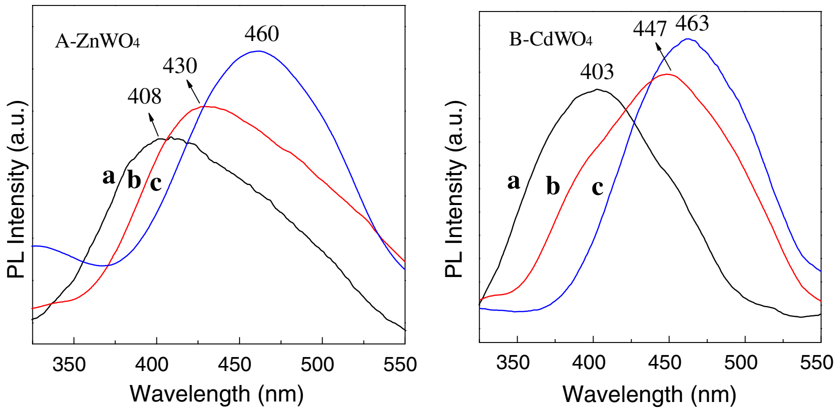
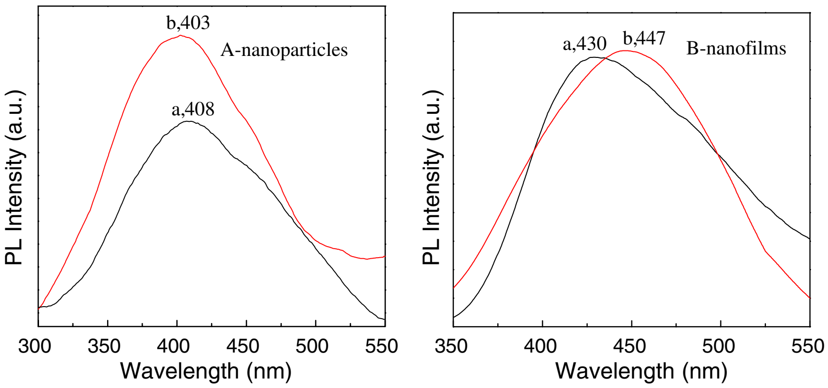


Fig. 5 PL spectra of the as-prepared nanoparticles and nanofilms: (**a**) $ZnWO_4$ and (**b**) $CdWO_4$



are changed. Moreover, nanofilms obviously shift to long wavelength region compared with nanoparticles, which can be due to film-forming effect and increased size of nanoparticles. Additionally, proportional relationships of position-shifts are also changed. Since these nanofilms have the same film-forming condition and process, and proportion relationships of position-shifts should not change. Hence, the causes might be that nanofilms have different morphology and structure (Figs. 1 and 3). It shows that either sphere-like $ZnWO_4$ or spindle-like $CdWO_4$ nanoparticles are interlaced and implanted to form nanofilms. So, we can deduce that position-shifts may be caused by not film-forming but morphology and construction of nanofilms' surface based on the above mentioned. Therefore, morphologies have some effects on optical properties.

FTIR analysis

Figure 6 presented FTIR spectra of bulk materials and nanofilms. The presence of $ZnWO_4$ on nanofilm is proved by the lattice vibration bands between 400 and 900 cm^{-1} (Fig. 6a): the absorption peaks locate at 472 and 532 cm^{-1} are ascribed to bending and stretching vibrations of Zn–O; the absorption peaks at 835 and 874 cm^{-1} are originated from bending and stretching vibrations of Zn–O–W; the absorption peaks at 629 and 695 cm^{-1} are originated from bending and stretching vibrations of W–O. Our results are in good agreement with published data [23]. Similar results for $CdWO_4$ are obtained as shown in Fig. 6b.

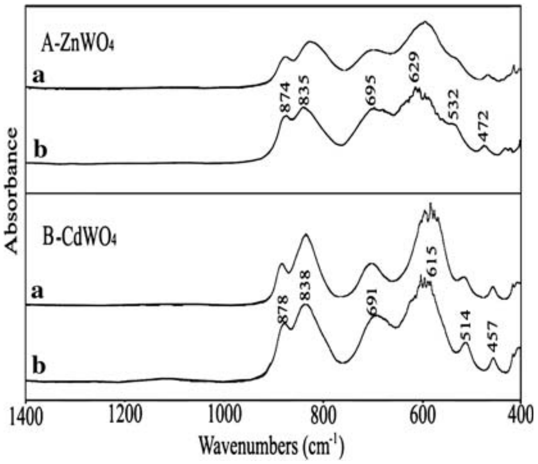


Fig. 6 FTIR spectra of the as-prepared bulk materials (**a**) and nanofilms (**b**)

Conclusion

(1) Collodion as a dispersant and film-forming agent is used to ensure the quality and compactness of film. The proposed technology could not only very expediently fabricate nanofilm but also make organic constituents burn out easily.

(2) PL bands of nanofilms have obvious blue-shifted compared with bulk materials, which should be attributed to quantum size effect.

(3) Due to increased size of nanoparticles and film-forming effect, the PL bands of nanofilms obviously shift to long wavelength region compared with nanoparticles.

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