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Preparation, structures and photoluminescent enhancement of $CdWO_4$–TiO_2 composite nanofilms

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Abstract

For the first time, Cadmium tungstate ($CdWO_4$)–TiO_2 composite nanofilms on a glass substrate were prepared by means of the dip-coating technique, in which collodion was used as a dispersant and film-forming agent. The films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), thermo gravimetric and thermal analyses (TG/DTA), FTIR and photoluminescence (PL) methods, respectively. SEM and XRD characterization of these films indicated that $CdWO_4$ particles crystallized in a monoclinic wolframite-type structure whereas TiO_2 particles were Anatase phase; and both of them were well distributed in the nanofilms. FTIR spectra proved the presence of $CdWO_4$ on the nanofilms. Photoluminescent results showed that the emitting peak of $CdWO_4$ films blue shifted slightly relative to that of $CdWO_4$ crystal. Moreover, the PL intensity of $CdWO_4$–TiO_2 composite nanofilm was much higher than that of $CdWO_4$ nanofilm. We ascribed that the introduction of TiO_2 should be responsible for the PL enhancement.

Keywords: Nanofilms; Composite films; $CdWO_4$; TiO_2; Photoluminescent enhancement

1. Introduction

Because of its intriguing luminescence and structure properties, oxytungstate with second group metal ion is an attractive material and has received much intense research interest [1]. Cadmium tungstate ($CdWO_4$) crystals with a monoclinic wolframite structure are considered to be highly functional materials because of their high average refractive index, low radiation damage, low afterglow to luminescence and high X-ray absorption coefficient [2,3]. $CdWO_4$ shows specific luminescence in the blue–green region suitable for the Si photodetector and as a result it has been used as one of the scintillators for the X-ray inspection system such as X-ray CT [4]. Recently, because of its potential use as an advanced medical X-ray detector in computerized tomography, it has attracted special interest [5]. However, $CdWO_4$ crystals as well as other tungstates are unstable because of their different faults and their effects on the spectral-kinetic and scintillation characteristics [6]. Although various preparation methods have been developed to synthesize tungstates, such as a high temperature solid-state reaction for powders [7], a flux method for whisker growth [8], the Czochralski method for single-crystal growth [9], pulsed laser ablation for growth of thin films of $CdWO_4$ using photoluminescence (PL) less targets [10] and hydrothermal method for $CdWO_4$ nanorod [11]. Nevertheless, new routes for obtaining stable luminescence $CdWO_4$ remain an interesting subject. Additionally, TiO_2 nanoparticle is famous for its good electro-optic and photocatalytic characteristics [12], and novel cooperation effect might occur in the case of the composite of TiO_2 and scintillating tungstates.

It is known that thin film materials have more superior photoelectrical, magnetic and catalytic properties than their powder materials, whereas nanofilms are the optimal candidates because of their prominent properties, such as giant conductance, giant magnetic resistance, giant Hall effect, and visible light emission and so on [13]. The composite nanofilms will further improve their properties. Hence, some researchers devoted themselves to composite nanofilms several years ago [14,15]. Up to now, less investigation focused on tungstate films

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[16–18], and only few studies made towards $CdWO_4$ thin films [19,20]. Nevertheless, there is no report on the tungstate nanofilms, say anything of tungstate composite nanofilms.

The present study represented the first known attempt to prepare tungstate composite nanofilms, in which collodion was used as a dispersant and film-forming agent to make sure the film have a good quality and property. Our approach herein is to prepare the nanoparticles first, and then regulate their ratios, and then disperse to prepare the film. The advantages are that the morphology, size, ratio and uniformity of the films can be handily controlled, and their quality and properties can be further improved. In this work, $CdWO_4$–TiO_2 composite nanofilms were successfully prepared; and the results indicated that the proposed approach is satisfying either in the advantage of this approach or in the quality and property of the film. We hope the proposed technology can help us to prepare more composite nanofilms deposited by different kinds of compounds.

2. Experimental

2.1. Synthesis of nanoparticles

In this study, the reverse micelle system was used to prepare $CdWO_4$ nanoparticles, consisting of Tween-80 as a surfactant, *n*-pentanol as a cosurfactant, hexamethylene as the continuous oil phase, and either cadmium sulfate or sodium tungstate precursor solution as the 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 cadmium sulfate solution into the conical flask in turn. When injecting *n*-pentanol into it, the solution was stirred strongly at the speed of 3000 rpm for about 15 min until the reverse micelle solution became transparent. The other reverse micelle solution was obtained, when 1 mL 0.4 M cadmium sulfate solution was taken the place of 1 mL 0.4 M sodium tungstate solution. Afterwards, the above two reverse micelle solutions were mixed quickly. The resulting solutions were aged with stirring at room temperature for 5 min. After 12 h of reaction, add acetone into the mixed solution. A white precipitate collected was washed by absolute ethanol, acetone and distilled water in an ultrasonic bath in turn for three times. The solid was preserved in absolute ethanol, which is $CdWO_4$ nanoparticle.

The TiO_2 nanoparticles was synthesized according to Ref. [21], and then dissolved in ethanol.

2.2. Film preparation

The above as-prepared $CdWO_4$ and TiO_2 solutions after extracting the above ethanol liquid were mixed or not and stirred at room temperature for 30 min. Then 2 mL collodion was added into the resulted white solution and stirred for at least 1 h, which served as the coating material.

The films were obtained by a dip-coating procedure. Standard glass slide were used as substrates. Before use, supersonic cleaning of the glass slide has been employed for 20 min in concentrated nitric acid and acetone and ethanol, respectively, and washed thoroughly with distilled water each time.

Films deposition were carried out by dipping a hydrophilic glass substrate in the above coating solution with a controlled withdrawal speed of 35 mm/min and kept in air for 20 min at room temperature. The as-prepared samples resulted homogeneous; well-adherent solution to the substrates and white colored. Then the films were heated to 200 °C for 30 min and then annealed at 500 °C for 1 h, and then they were allowed to cool to room temperature naturally.

2.3. Physical measurement

The power X-ray diffraction (XRD) was performed with a Rigaku D/max2550 X-ray diffractometer (Japan) with Cu Kα radiation ($\lambda = 0.15418$ nm) (Japan). Surface morphology and nanostructure were observed by a field-emission environmental scanning electron microscope FEI/Phillps XL30 ESEM-FEG (SEM, Holland). Simultaneous recorded thermogravimetric and thermal analyses (thermogravimetry (TG)/DTA) using SDT Q600 (USA) of the films were carried out in air at a heating rate of 5 °C/min. Absorption spectra of the films were recorded by a Nicolet NEXUS870 FT-IR spectrometer (USA). PL spectra were obtained by a Perkin-Elmer luminescence spectrophotometer (LS-55, USA).

3. Results and discussion

3.1. Thermal analysis

Fig. 1 showed the DTA and TG curves in thermal decomposition/combustion during heating the above as-prepared mixture. The weight loss combined with a sharp exotherm (∼200 °C) implies the combustion of Collodion. After that, there is no significant weight loss was observed (seen Fig. 1A), however, an endothermal effect above 550 °C was observed (seen Fig. 1B), indicating that the TiO_2 crystal phase begins to transform from Anatase to Rutile after heat-treatment at temperature above 550 °C, which is consistent to the report of Ref. [22].

3.2. Morphology and structure

Fig. 2 showed the SEM images of the as-prepared nanofilms. From Fig. 2, it was clear that all of the films possess homogeneous surface morphology and without cracks. As shown in Fig. 2a and c, pillar-like $CdWO_4$ quasi-nanoparticles with the diameter and length in the range of 100–190 nm and 210–300 nm and TiO_2 nanoparticles with the average size of 30 nm were distributed equably on the glass substrate, and both of them have no evidence of a granular structure. Additionally, the surface of $CdWO_4$–TiO_2 films was rougher than $CdWO_4$ film (see Fig. 2a and b). We inferred that the formation of granular structure on the surface of film should be responsible for the increase of roughness, because that there is a slight agglomeration by mixtures of both $CdWO_4$ and TiO_2 particles when TiO_2 nanoparticles were introduced.

Fig. 3 shows the XRD patterns of the as-prepared products. As seen in curve a of Fig. 3, TiO_2 nanoparticles were Anatase