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Template synthesis, structure, optical and catalytic properties derived from novel cadmium tungstates

Jintai Lin [a], Jinglian Yang [b], Jinwei Gao [c], Qianming Wang [a,b,*]

[a] Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, PR China
[b] Guangzhou Key Laboratory of Materials for Energy Conversion and Storage, Guangzhou 510006, PR China
[c] Institute for Advanced Materials, Academy of Advanced Optoelectronics, South China Normal University, Guangzhou 510006, PR China

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ABSTRACT

Two simple templates, ethylenediamine (EDA) and ethylene diamine tetraacetic acid (EDTA), were used as precursors to synthesize $CdWO_4:Eu^{3+}$ with a regular shape based on a hydrothermal method. The derived materials were characterized by X-ray powder diffraction, scanning electronic microscopy and photoluminescence spectra. The images revealed that $CdWO_4:Eu^{3+}$ nanorods with diameters of 30–50 nm and lengths up to 200–300 nm were achieved with the assistance of EDTA. The photoluminescence studies indicated that the fluorescence intensity was significantly improved in the presence of this reagent. The red phosphors exhibited high photocatalytic activities for the degradation of different organic dyes (methyl orange, rhodamine B and methylene blue). The catalyst prepared with EDTA as a precursor gave the best results. The particle size, fluorescence, catalysis and $CdWO_4:Eu^{3+}$ with different microstructures have been discussed.

1. Introduction

Due to their special luminescence and structure, metal tungstates have attracted particular attention in recent years [1]. Among the metal tungstates, $CdWO_4$, with a monoclinic wolframite structure, has been extensively studied because of its unique physical, chemical and structural characteristics. These features could be widely used in various applications, such as X-ray scintillators, advanced medical X-ray detectors in computerized tomography, laser crystals and photocatalysts [2–5]. As far as the photocatalytic properties are concerned, the band-gap of the $CdWO_4$ is as broad as 3.8 eV, which is larger than the value of 3.2 eV for TiO_2. It has been established that with a broader band-gap it is highly possible to obtain stronger redox capabilities, which in turn allow a higher photocatalytic performance [6,7]. According to a previous study [8], $CdWO_4$ was considered to be a good candidate for potential photocatalysis, exhibiting compatible activity in the degradation of organic compounds to that of the known semiconductors $ZnWO_4$ and TiO_2. Additionally, it is well known that the photocatalytic activity of semiconductors is strongly determined by several microstructural factors, such as particle size, surface chemistry, morphology and crystallinity. Therefore, we anticipated to obtain nanosized $CdWO_4$ with high crystallinity for the degradation of organic pollutants. It is well accepted that low-dimensional nanoscale materials exhibit a wide range of optical and electric applications which depend immediately on both size and morphology [9]. Therefore, the corresponding nanoparticles [10], nanofibers [11], nanorods [12] and elongated nanosheets [13] have been fabricated in previous research.

As for the luminescence, trivalent lanthanide ions exhibit narrow band emissions, long excited lifetimes and have large Stokes shifts. Especially, Eu^{3+} has tremendous applications in phosphors because of its high luminescent efficiency [14]. Tungstates, with high crystallographic anisotropy and prominent thermal stabilities, are good candidates as host materials for red phosphors [15]. However, reports on rare earth ion doped cadmium tungstate nanomaterials are very limited [16].

In the crystal growth process, the growth of inorganic nanocrystals can be assembled to the predicted microstructure in the presence of some low molecular weight templates. A few simple organic molecules, such as ethylenediamine (EDA) [17], citric acid (CA) [18] and ethylene diamine tetra acetic acid (EDTA) [19,20], have been used as "morphology control agents" to determine the final product morphology. In the current study, we have successfully prepared luminescent $CdWO_4:Eu^{3+}$ with controlled particle size (rod-like structure) using the very simple complexants EDA

* Corresponding author at: Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, PR China. Tel.: +86 20 39310258; fax: +86 20 39310187.

E-mail address: qmwang@scnu.edu.cn (Q. Wang).

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and EDTA as precursors. The effects of adding precursors on the crystallization, morphology, optical properties and photocatalytic activity of $CdWO_4:Eu^{3+}$ were extensively investigated. Using simple precursors to construct $CdWO_4:Eu^{3+}$ nano rods from micron rods has never been studied.

2. Experimental section

2.1. Materials

All the starting materials were obtained from commercial suppliers and used as received without further purification. Eu_2O_3 (99.9%) was purchased from Aladdin Chemistry Co. Ltd. All the other reagents were analytically pure. The rare earth oxides were dissolved in excess amounts of concentrated nitric acid to convert them completely to their nitrates.

2.2. Synthesis of $CdWO_4:Eu^{3+}$ by the hydrothermal method

$Cd(NO_3)_2{\cdot}4H_2O$ (1 mmol), $Eu(NO_3)_3{\cdot}6H_2O$ (0.03 mmol) and various amounts of complexant EDTA/EDA were dissolved in deionized water (20 ml). The molar ratios of complexant and cadmium used were 1:1, 2:1 and 5:1. After vigorous stirring for 10 min, a 10 ml solution containing 1 mmol $Na_2WO_4{\cdot}2H_2O$ was added into the above solution dropwise under continuous stirring. The pH value was adjusted to 7 by the addition of ammonia. After stirring for another 20 min, the mixture was transferred to a 50 ml Teflon-lined stainless steel autoclave and filled with deionized water up to 80% filling capacity of the total volume. The autoclave was sealed and maintained at 160 °C for 20 h and then cooled down to room temperature. After the aforementioned hydrothermal treatment, the final product was centrifuged and washed with deionized water three times. The precipitate was then dried at 80 °C for 4 h and collected for characterization. The sample with a molar ratio complexant: cadmium of 1:1 was selected for XRD, photoluminescence and photocatalysis tests.

2.3. Catalyst testing

The photocatalytic experiment was carried out in a photochemical reaction instrument produced by Shanghai Bilon Instruments Company, China (BL-GHX). The concentration of the organic dye solution was 5 mg/L and the dosage of catalyst was 1 mg/ml. A 300 W high pressure mercury lamp (dominant wavelength 365 nm) was used as the light source. In a typical photocatalytic experiment, the sample (50 mg) was added into 50 ml methylene blue aqueous solution. The suspension was stirred for 30 min without a light source in order to reach adsorption balance. After that, the mercury lamp was opened. The supernatant was collected at designed time intervals for UV–Vis measurement after centrifugation (5000 rpm, 5 min) at room temperature under visible light irradiation. By monitoring the change of the UV–Vis absorption, the photocatalytic performance of different samples was assessed. The percentage of photodegradation is regarded as C/C_0, where C is the maximum peak derived from the absorption spectra of the organic dyes for each irradiated time interval and C_0 is the absorption of the starting concentration when the adsorption/desorption equilibrium was achieved. The visible light irradiated photodegradation experiments were performed in a photocatalytic reactor (QQ250, Perfect Light company, Beijing) and a 50 W LED lamp was used as the visible light source. The distance between the lamp and solution was fixed to 6 cm. All the other time dependent treatments were similar to the above catalysis experiment.

2.4. Catalyst characterizations

The X-ray powder diffraction (XRD) was investigated at the Y-2000 of Dandong Aolong company, PR China. Photoluminescence spectra (PL) were measured on an Edinburgh FLS920 spectrometer. Scanning electronic microscopy (SEM) was measured with a JSM-6360LV. The photocatalytic activities for the dye degradation were determined by measuring the concentration of the dyes through an ultra-violet and visible spectrophotometer (Shimadzu UV-2550) during constant photo-irradiation treatment.

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the X-ray powder diffraction (XRD) patterns of $CdWO_4:Eu^{3+}$ prepared with different precursors. All the diffraction peaks located at 2θ values of 10–70° can be readily indexed to the monoclinic phase $CdWO_4$ (JCPDS card No. 14-0676). The results verified that the as-prepared $CdWO_4:Eu^{3+}$ products are phase pure and well crystallized. No traces of additional peaks from other phases can be observed in the XRD patterns, suggesting that Eu^{3+} has been uniformly incorporated into the host lattice of $CdWO_4$. Additionally, the diffraction signals of $CdWO_4:Eu^{3+}$ synthesized with EDA as a precursor (Fig. 1c) exhibited a significant increase in intensity for certain diffraction peaks ((100), (110), (020) and (200)). This fact might be due to the orientation growth of crystals [21]. It is estimated that EDA can effectively reduce the energy of some specific crystal planes and finally lead to the orientation growth of $CdWO_4$. These changes have been confirmed in SEM tests as well.

Fig. S1 shows the IR spectrum of $CdWO_4:Eu^{3+}$ measured in the wavenumber region of 400–4000 cm^{-1}. The observed bands at 565, 658 and 806 cm^{-1} are assigned to the in-plane deformation of the WO_4^{2-} group. The strong absorption bands in the 3430 cm^{-1} region are attributed to OH stretching vibrations and the bands located at 1655, 1565 and 1410 cm^{-1} correspond to H–O–H bending vibrations. The IR spectra of the products prepared with different precursors are similar to the above results (figures not given).

SEM images of the as-prepared $CdWO_4:Eu^{3+}$ are shown in Fig. 2. The $CdWO_4:Eu^{3+}$ materials show different rod-like structures with

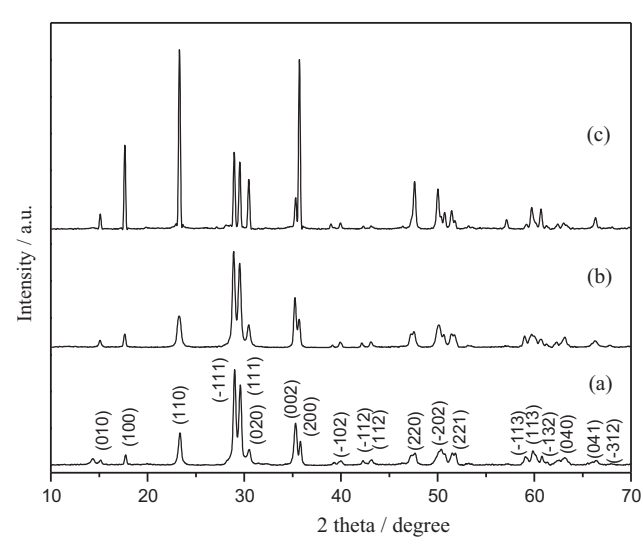

Fig. 1. XRD patterns of $CdWO_4:Eu^{3+}$ prepared with different precursors ((a) without any precursor, (b) EDTA as the precursor ($EDTA/Cd^{2+}$ = 1/1), (c) EDA as the precursor (EDA/Cd^{2+} = 1/1)).