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Controllable synthesis and characterization of cadmium molybdate octahedral nanocrystals by coprecipitation method

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ABSTRACT

Cadmium molybdate ($CdMoO_4$) nanocrystals have been successfully synthesized via coprecipitation method by using $Cd(Sal)_2$ (Sal = salicylidene) and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ as starting materials in water as solvent. Effects of temperature, reaction time, solvent, surfactant and cadmium source were investigated to reach optimum condition. It was found that particle size, morphology and phase of the final products could be greatly influenced via these parameters. The products were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectra, photoluminescence (PL) spectroscopy, energy dispersive X-ray microanalysis (EDX), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

1. Introduction

In recent years, metal molybdates ($MMoO_4$, M = Ca, Sr, Ba, Cd, etc.) have attracted considerable interest, due to their promising technological importance in a wide range of applications, including photoluminescence, industrial catalysts, sensors, optical fibers, electrode materials, photoelectric devices, photonic crystals, photocatalysts and scintillators [1–3]. Among them, $CdMoO_4$ is an interesting material owning to its excellent optical and chemical properties and electronic structure [4,5] such as electronic excitation with UV synchrotron radiation [5], pressure-induced phase transformations [6] and ^{111}Cd and ^{113}Cd spin-lattice relaxation [7]. It is a wide band gap semiconductor (E_g = 3.25 eV) [8], is isostructural to $CaMoO_4$ and $PbMoO_4$ and has a so-called scheelite structure in which the molybdenum atom adopts tetrahedral coordination, where its emission spectrum is mainly attributed to the charge-transfer transitions within the $[MoO_4^{2-}]$ complex [9].

Much effort has been devoted to the synthesis of $CdMoO_4$ with various techniques and methods. The hydrothermal synthesis [8], sacrificial template route [10], microwave [11], microemulsion-mediated route [12] and Ostwald ripening process [13] have been reported to prepare $CdMoO_4$.

According to the electronic structures of $CdMoO_4$ reported by Abraham et al. [4], this material may possess excellent photocatalytic activity and photoluminescence properties due to its electronic versatility, reactivity, and stability [13]. Therefore, the development of a facile and effective route for synthesizing nanostructured $CdMoO_4$ with complex morphology is of great importance to the potential studies of its physical and chemical properties. It is good to know that properties of powders depend on their particle size and morphology [14–19]. Therefore, exploring appropriate methods to synthesize cadmium molybdates and controlling their particle morphology and size is significant. Herein, we develop the coprecipitation method to prepare $CdMoO_4$ nanocrystals. The coprecipitation method is a good synthesis process for synthesis of many inorganic powders. This method is simple, convenient and cost effective synthetic procedure and provides an effective way to the synthesis of uniform nanocrystals. In this method, crystallization procedure is performed at low temperature and design of reaction condition is very flexible. To the best of our knowledge, it is the first time that $Cd(Sal)_2$ is used as Cd source for the synthesis of $CdMoO_4$ and effects of different parameters on the morphology, size and crystallization of cadmium molybdates via a coprecipitation method are investigated.

2. Experimental

2.1. Materials and experiments

All the chemicals used in our experiments were of analytical grade, were purchased from Merck and used as received without further purification. The XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Kα radiation.

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SEM images were obtained on Philips XL-30ESEM equipped with an energy dispersive X-ray spectroscopy. TEM images were obtained on a JEM-2100 transmission electron microscope with an accelerating voltage of 200 kV. Fourier transform infrared spectroscopy (FT-IR) was recorded with Shimadzu Varian 4300 spectrophotometer in KBr pellets. EDS analysis was obtained on Philips EM208. Room temperature photoluminescence (PL) was studied on a Perkin Elmer (LS 55) fluorescence spectrophotometer.

2.2. Synthesis of $Cd(Sal)_2$ complex

$[Cd(Sal)_2]$ was synthesized as follows: cadmium(II) acetate $[Cd(CH_3COO)_2{\cdot}2H_2O]$, 2 mmol, was dissolved in 40 ml distilled water, a solution of salicylaldehyde, 4 mmol, dissolved in the same volume of methanol was dropwise added to the above solution under magnetic stirring. After addition of all reagents, the mixture was refluxed for about 3 h.

2.3. Synthesis of $CdMoO_4$ nanocrystals

$CdMoO_4$ nanocrystals were prepared by simple coprecipitation method. In a typical procedure, an aqueous solution of $Cd(Sal)_2$ in the presence of different surfactants, such as polyethylene glycol (PEG600), polyvinylpyrrolidone (PVP), sodium dodecyl sulfate (SDS) and cetyltrimethyl ammonium bromide (CTAB), was mixed with $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ aqueous solution and solution heated up to 70 °C for 2 h. The white precipitate was centrifuged, washed out with distilled water and methanol for three times and dried under vacuum at 60 °C. For investigating the effect of capping agent, a blank test was carried out in the absent of capping agent. The effects of temperature, reaction time, solvent, surfactant and cadmium source on the morphology, the particle sizes and the phase of $CdMoO_4$ samples were investigated and the results listed in Table 1.

3. Results and discussion

The crystal structure and composition of the as-prepared products were determined by XRD. The XRD patterns of the $[Cd(Sal)_2]$ and cadmium molybdates (sample Nos. 3, 6, 8, 11) obtained under different conditions (time, surfactant, solvent) have been shown in Fig. 1. All peaks in Fig. 1b–e, correspond to the reflections of tetragonal phase $CdMoO_4$. No remarkable diffractions of other phases can be found in the figure, indicating that a pure $CdMoO_4$ phase has been formed. According to this figure, with decrease at the reaction time from 2 h (sample No. 3) to 1 h (sample No. 6), the crystallinity of the as-prepared $CdMoO_4$ nanocrystals is increased and with adding SDS or change at the solvent from water to methanol, crystallinity decreased.

EDX analysis measurement was employed to investigate the chemical composition and purity of as-synthesized $CdMoO_4$ structures. The EDX pattern of $CdMoO_4$ (sample No. 3) in Fig. 2 shows that there exist only elements Cd, Mo, and O. No peak of any impurity is observed, indicating the high purity of the product.

Fig. 3 shows FT-IR spectra of $Cd(Sal)_2$ precursor and $CdMoO_4$ nanocrystals. In the case $[Cd(Sal)_2]$ (Fig. 3a), the peaks at 1420 and 1580 cm^{-1} are attributed to the C–O stretching vibrations (ν_{C-O}) and the peak at 1345 cm^{-1} is attributed to C–C stretching vibrations (ν_{C-C}) of the salicylaldehyde. In free salicylaldehyde ν_{C-O} appears at 1680 and 1660 cm^{-1}, and ν_{C-C} appears at 1490 and 1380 cm^{-1}. Upon complex formation, these stretching vibrations shift to lower regions. The broad absorption band around 3440 cm^{-1} in Fig. 3a, is assigned to the stretching vibrations of absorption water. Absorption peaks at 500–650 cm^{-1} are due to Cd–O bond, there are no absorption bands around this range in salicylaldehyde. Fig. 3b and c shows FT-IR spectra of $CdMoO_4$ nanocrystals obtained in water (samples No. 3) and ethylene glycol, EG, (samples No. 12), respectively. In this figure, strong transmittance mode specified as Mo–O anti-symmetric stretching vibration of $[MoO_4]^{2-}$ tetrahedrons is detected at 740–890 cm^{-1}

Table 1
The reaction conditions for synthesis of $CdMoO_4$ via a coprecipitation method.

Sample No.	Precursors	pH	Temperature (°C)	Solvent	Surfactant	Time	SEM
1	$Cd(Sal)_2$,$(NH_4)_6Mo_7O_{24}$	5–6	30	Water	–	2 h	
2	$Cd(Sal)_2$,$(NH_4)_6Mo_7O_{24}$	5–6	50	Water	–	2 h	
3	$Cd(Sal)_2$,$(NH_4)_6Mo_7O_{24}$	5–6	70	Water	–	2 h	
4	$Cd(Sal)_2$,$(NH_4)_6Mo_7O_{24}$	5–6	90	Water	–	2 h	
5	$Cd(Sal)_2$,$(NH_4)_6Mo_7O_{24}$	5–6	70	Water	–	0 h	
6	$Cd(Sal)_2$,$(NH_4)_6Mo_7O_{24}$	5–6	70	Water	–	1 h	
7	$Cd(Sal)_2$,$(NH_4)_6Mo_7O_{24}$	5–6	70	Water	CTAB	2 h	
8	$Cd(Sal)_2$,$(NH_4)_6Mo_7O_{24}$	5–6	70	Water	SDS	2 h	
9	$Cd(Sal)_2$,$(NH_4)_6Mo_7O_{24}$	5–6	70	Water	PVP	2 h	
10	$Cd(Sal)_2$,$(NH_4)_6Mo_7O_{24}$	5–6	70	Water	PEG600	2 h	
11	$Cd(Sal)_2$,$(NH_4)_6Mo_7O_{24}$	5–6	70	Methanol	–	2 h	
12	$Cd(Sal)_2$,$(NH_4)_6Mo_7O_{24}$	5–6	70	EG	–	2 h	
13	$Cd(Sal)_2$,$(NH_4)_6Mo_7O_{24}$	5–6	70	PG	–	2 h	
14	$Cd(CH_3COO)_2$,$(NH_4)_6Mo_7O_{24}$	5–6	70	Water	–	2 h	
15	$Cd(Sal)_2$,Na_2MoO_4		90	Water	–	2 h	