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Short communication

Low-temperature synthesis of $CdWO_4$ nanorods via a hydrothermal method

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Abstract

Cadmium tungstate ($CdWO_4$) nanorods were successfully synthesized via a hydrothermal process and characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and photoluminescent spectra techniques (PL). A pure monoclinic phase of well-crystallized $CdWO_4$ nanorods, with lengths of 250–400 nm and widths of 30–60 nm, could be readily synthesized at as low temperature as 70 °C.The $CdWO_4$ nanorods showed a PL emissions peak at 435 nm.

Keywords: Hydrothermal method; $CdWO_4$ nanorods; Low temperature

1. Introduction

Tungstates have being attracted particular attention because of their special luminescence and structure [1]. Cadmium tungstate ($CdWO_4$) with a monoclinic wolframite structure is deemed to be a highly functional material due to its low radiation damage, low aftergrow to luminescence, high average refractive index and high X-ray absorption coefficient [2]. $CdWO_4$ has been used as a popular X-ray scintillator [3] with such exceptional advantages as high efficiency, high chemical stability, high stopping power and short decay time, and has also a promising application as an advanced medical X-ray detector in computerized tomography [4].

It is well known that nanometer-sized inorganic low-dimensional systems exhibit a wide range of optical and electric properties [5] that rely sensitively on both size and morphology [6,7]. The fabrication of nanocrystals such as nanoparticles, nanorods, nanofibers, and nanotubes, recently has been subjected to especially intense research because of their promising applications in various fields of technology with respect to their collective optical, magnetic and electronic properties [8–12]. $CdWO_4$ nanorods and nanofibers have been prepared by the hydrothermal method [13–15], but these works show that a holding temperature of >130 °C and adding organic surfactants were still necessary.

In this paper, we present a simple hydrothermal process to synthesize $CdWO_4$ nanorods at 70 °C for 10 h in the absence of any organic surfactants.

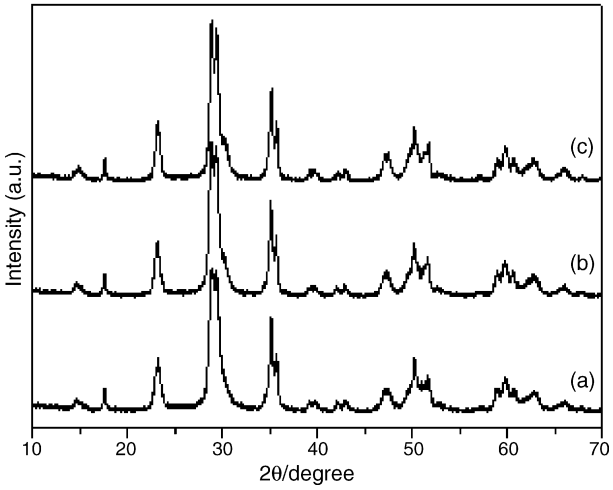

Fig. 1. XRD patterns of the as-prepared samples obtained by the hydrothermal process at: (a) 70 °C; (b) 90 °C and (c) 110 °C for 10 h, respectively.

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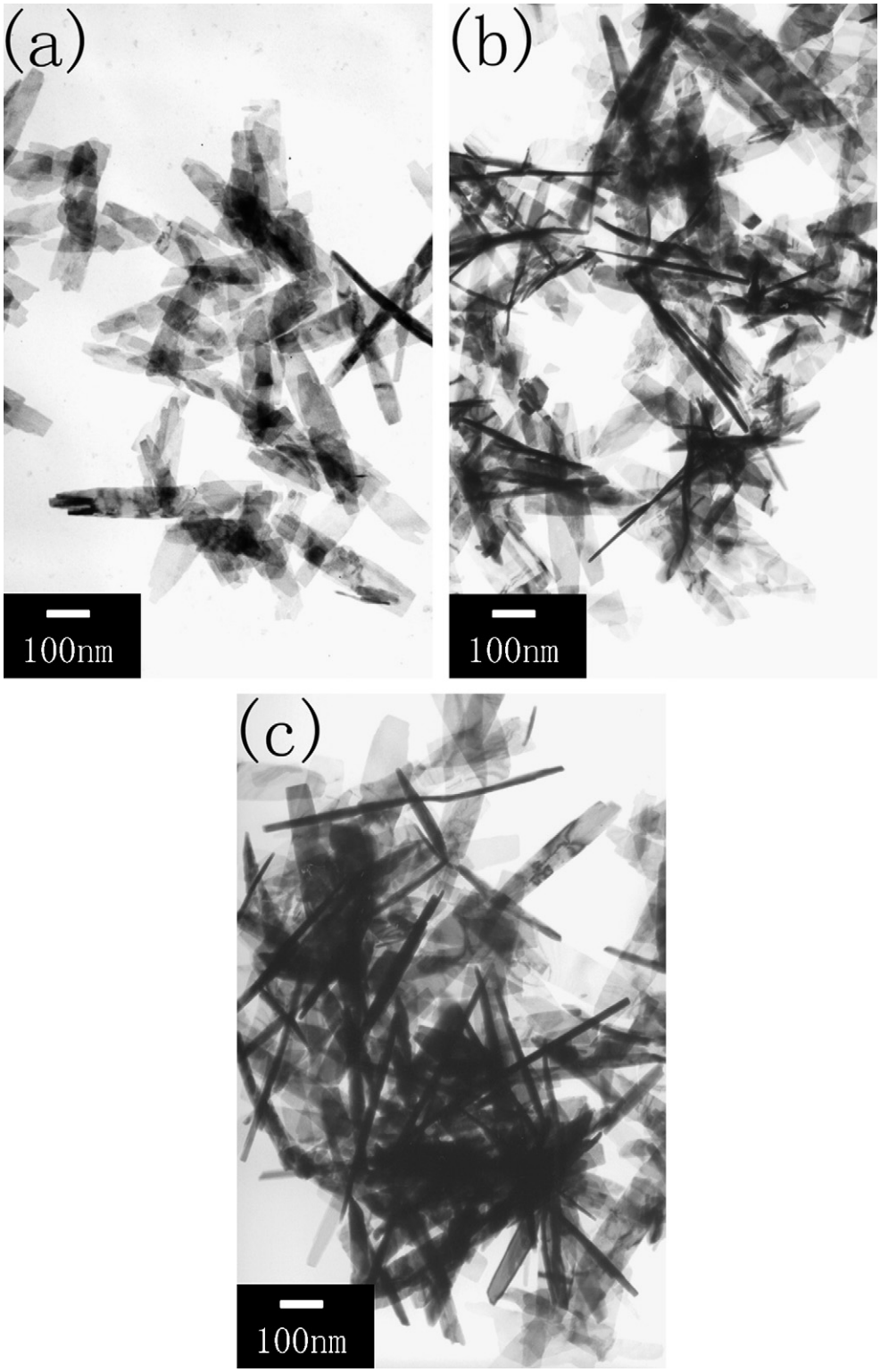

Fig. 2. TEM images of the as-prepared samples obtained by the hydrothermal process at: (a) 70 °C; (b) 90 °C and (c) 110 °C for 10 h, respectively.

2. Experimental procedure

Analytical grade sodium tungstate ($Na_2WO_4{\cdot}2H_2O$) and cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$) were used as the starting materials. Appropriate amounts of $Na_2WO_4{\cdot}2H_2O$ and $Cd(NO_3)_2{\cdot}4H_2O$ were dissolved in distilled water to form aqueous solutions, separately; and then mixed together with strongly magnetic stirring at room temperature. The suspension solution was poured into a 1000 ml stainless steel autoclave to about 50% of its capacity. The autoclave was sealed and maintained at 70, 90 and 110 °C for 10 h, respectively, and then cooled to room temperature naturally. After the above

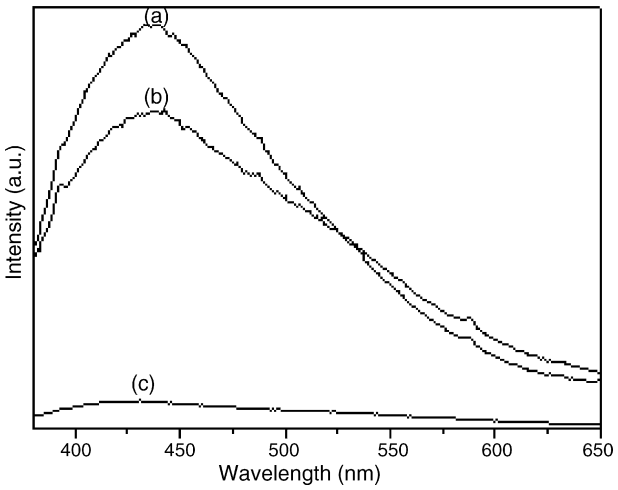

Fig. 3. PL spectra (with the excitation wavelength 320 nm) of the as-prepared samples obtained by the hydrothermal process at: (a) 70 °C; (b) 90 °C and (c) 110 °C for 10 h, respectively.

hydrothermal treatment, the products were filtered, washed with distilled water and absolute ethanol for several times to remove any impurities, and then dried in vacuum at 50 °C for 4 h. X-ray powder diffractometer (XRD) patterns of the samples were recorded on an X-ray powder diffractometer (D/max, Japan) using Cu Kα radiation. All TEM images were taken with a transmission electron microscope (TEM, JEM-1200EX, Japan), operating at 60 KV. The room temperature photoluminescent spectra were performed on a spectrofluorometer (PL, Fluorolog-3, USA).

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples prepared by the hydrothermal process at different holding temperatures of 70, 90 and 110 °C for 10 h, respectively. All XRD patterns can be indexed to a pure monoclinic phase of well-crystallized $CdWO_4$ with a wolframite structure, well consistent with the reported data (JCPDS: 14–676). Nevertheless, an increase in the reaction temperature from 70 to 110 °C made few differences in XRD intensity in Fig. 1, which implies that a higher reaction temperature in our experimental range of temperature would not bring about significant changes in the crystallization of the $CdWO_4$ phase.

TEM micrographs of the $CdWO_4$ samples prepared under different hydrothermal conditions are shown in Fig. 2. The $CdWO_4$ samples prepared at 70 °C for 10 h, display only a rodlike morphology with lengths of 250–400 nm and widths of 30–60 nm (Fig. 2a). However, a small quantity of nanofibers began to appear when increasing the temperature to 90 °C and more were obtained at the temperature of 110 °C. Increasing the reaction temperature in the present hydrothermal process would promote the evolution and growth of the $CdWO_4$ nanofibers. No significant orientation can be seen from the XRD patterns due to the random arrangement of different small crystals. Furthermore, according to the literature [16–20], it is also reasonable that samples with different morphologies have similar XRD patterns.

Room temperature PL properties of the as-prepared $CdWO_4$ samples were also investigated. As shown in Fig. 3, the three samples exhibit the same emission peak position at 435 nm in the PL spectrum, with the excitation wavelength 320 nm. Apparently, raising the reaction temperature of the hydrothermal process would lower the luminescent intensity of the as-prepared $CdWO_4$ nanocrystallites. The luminescent intensity of the sample with a smaller amount of nanofibers is obviously weaker than that of the sample with pure nanorods, meanwhile, the sample with larger amounts of nanofibers, exhibits the weakest luminescent intensity. It implied that $CdWO_4$ nanorods should have a better luminescent intensity than $CdWO_4$ nanofibers. Compared to the PL emission (460 nm) of a single crystal of $CdWO_4$ at room temperature, these $CdWO_4$ nanorods in the emission peak position have a blue shifting by 25 nm. Though Polak et al. [21] reported that the PL emission is only caused by the $^1A1 \rightarrow {}^3T1$ transitions within the WO_6^{6-} complex, we assume that the PL property of $CdWO_4$ is also strongly dependent on its morphology and size.

4. Conclusions

We here reported a hydrothermal method for synthesizing a pure monoclinic phase of well-crystallized $CdWO_4$ nanorods with lengths of 250–400 nm and widths of 30–60 nm at as low temperature as 70 °C. The $CdWO_4$ nanorods show a better luminescence with a PL peak at 435 nm, corresponding to the excitation wavelength 320 nm.

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