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Effect of pH on the synthesis of $In(OH)_3$ and $In(OH)_3:Ce^{3+}/Dy^{3+}$ nanocrystals by a fast, mild microwave method

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ABSTRACT

Indium hydroxide nanocrystals were synthesized through a microwave reaction. It is a fast, simple and mild process to get the uniform and monodisperse $In(OH)_3$ nanomaterials without the aid of any surfactants or templates. Size and morphology of the $In(OH)_3$ nanomaterials could be controllably adjusted through the pH value of the reaction mixtures. The formation mechanisms of the nanostructures have been investigated on the basis of a series of SEM studies of the samples obtained at different reaction durations. Ce^{3+}, Dy^{3+} or Ce^{3+}/Dy^{3+} doped $In(OH)_3$ were also synthesized by the microwave reaction and optical properties of these materials were evaluated.

1. Introduction

Nanoscale materials have been extensively studied for the last decades because materials in nano-size usually exhibited more excellent properties compared to their bulk counterparts [1,2]. Nano-sized indium compounds such as indium hydroxide ($In(OH)_3$), indium oxyhydroxide (InOOH), and indium oxide (In_2O_3) have been investigated intensively for the last decade, because of their special semiconducting and optical properties with potential applications in industrial catalyst and additive of alkaline battery [3–8]. For example, M.-C. Hsieh et al. synthesized nanocomposites of tantalum-based pyrochlore and indium hydroxide which showed high and stable photocatalytic activities for overall water splitting and carbon dioxide reduction [9].

Studies indicated that properties of nano-sized $In(OH)_3$ depended sensitively on its size and morphology [10–19], so that much research efforts have been made on the size and morphology controlled preparation methods of $In(OH)_3$ powders. $In(OH)_3$ nanoparticles have been prepared by several methods such as the sol–gel technique [10], the hydrolysis of indium nitrate [11], thermal decomposition [12], spray pyrolysis [13], hydrothermal/solvothermal routes [14–16] and microwave-assisted hydrothermal [17–19] method. However, these methods usually require high temperatures, tedious and time-consuming process. Sometimes, even templates and/or organic solvents are required to prepare the nano-sized and crystalline indium hydroxide. Microwave-assisted hydrothermal method has recently been used as a fast and mild method for the preparation of nano-sized $In(OH)_3$ under 100–140 °C in 1–3 h treatment [17–20]. Herein, we found that microwave irradiation itself could produce uniform single-crystalline indium hydroxide nanostructures under milder condition at 80 °C and reaction within 5–20 min. It is a rapid and template-free method. Size and morphology of the $In(OH)_3$ nanomaterials could be controllably adjusted through the pH value of the reaction mixtures. The formation mechanisms of the nanostructures have been investigated on the basis of a series of SEM studies of the samples obtained at different reaction durations. Nanocrystals of Ce^{3+}/Dy^{3+} co-doped indium hydroxide were also prepared by the microwave method and their photoluminescent properties were evaluated, and the results indicated that the optimum concentration of Ce^{3+} and Dy^{3+} was $In(OH)_3$:10%Ce/0.5Dy%.

2. Experimental section

2.1. Characterization

The X-ray diffraction (XRD) pattern was collected on an X-ray diffractometer (Bruker Axs D2 PHASER diffractometer) with Cu K*a* radiation (λ = 1.5405 Å). X-ray photoelectron spectroscopy (XPS) analysis was performed by a Microlab 310FX spectrometer. Scanning electron microscopy (SEM, JSM-5601) was used to characterize the morphology of the as-synthesized products. (HR)TEM images were recorded on transmission electron microscopy (FEI TF20 USA). The luminescent spectra were recorded on a PL3-211-P spectrometer (HORIBA Jobin Yvon, America) and a 450 W xenon lamp was used as the excitation source. Luminescent quantum efficient (Φ) was obtained by using $BaSO_4$ as reference.

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2.2. Method

1 mmol (0.390 g) $In(NO_3)_3·5H_2O$ was added into 15 mL 10 wt% NH_4Cl (0.15 g) aqueous solution (pH = 5) under magnetic stirring to form a colorless transparent solution. The solution was reacted in a microwave machine (UWave-1000 Shanghai Sineo Microwave Chemistry Science and Technology Co. Ltd., 50 Hz, 2000 W) for 5 min. The products were washed three times with distilled water and centrifuged for 6 min at 8000 rpm. The quantitative yields of the products obtained after drying are about 45%. The $In(OH)_3$ products prepared in pH = 5 were labeled as **nanocrystal 1**.

Diluted ammonia water was added to 15 mL 10 wt% NH_4Cl (0.15 g) aqueous solution until the pH value was 7. 1 mmol (0.390 g) $In(NO_3)_3·5H_2O$ was added into the pH = 7 aqueous solution to get a transparent solution. The solution was reacted in a microwave machine for 10 min. The products were washed three times with distilled water and centrifuged for 6 min at 8000 rpm. The $In(OH)_3$:Ce, Dy, Ce/Dy^{3+} were synthesized in pH = 7 solution by the same process expect that an extra certain proportion of $Ce(NO_3)_3·5H_2O$ and/or $Dy(NO_3)_3·5H_2O$ were added to the reaction solution at the initial stage. The quantitative yields of the products obtained after drying are about 56%. The $In(OH)_3$ products prepared in pH = 7 were labeled as **nanocrystal 2**.

Diluted ammonia water was added to 15 mL 10 wt% NH_4Cl (0.15 g) aqueous solution until the pH value was 9. 1 mmol (0.390 g) $In(NO_3)_3·5H_2O$ was added into the pH = 9 aqueous solution. The suspension was reacted in a microwave machine for 20 min. The products were washed three times with distilled water and centrifuged for 6 min at 8000 rpm. The quantitative yields of the products obtained after drying are about 58%. The $In(OH)_3$ products prepared in pH = 9 were labeled as **nanocrystal 3**.

3. Result and discussions

3.1. Synthesis and structure

The uniform nanomaterials of indium hydroxide were synthesized through a microwave method. NH_4Cl and $In(NO_3)_3$ were placed in microwave reactor for 5–20 min at 80 °C with water as reaction medium. The pH value of the reaction mixture was tuned by diluted ammonia. Microwave played important role in promoting the reaction and getting monodisperse uniform $In(OH)_3$ nanomaterials. We have tried other methods at the same condition such as hydrothermal, solvothermal, sonication and high-temperature solvent method with varied reaction time and temperature but only heterogeneous bulk materials were obtained.

The composition and phase purity of as-prepared $In(OH)_3$ and $In(OH)_3$:Dy^{3+} were examined through powder XRD measurements. Fig. 1 shows the XRD patterns of $In(OH)_3$ with different pH value and $In(OH)_3$:Dy^{3+}. All the XRD patterns could be easily indexed to the cubic phase of $In(OH)_3$ [JCPDS: 73–1810, Im-3 (204)] indicated the as-obtained nanomaterials were phase pure and the Dy^{3+} were well doped in the $In(OH)_3$ host.

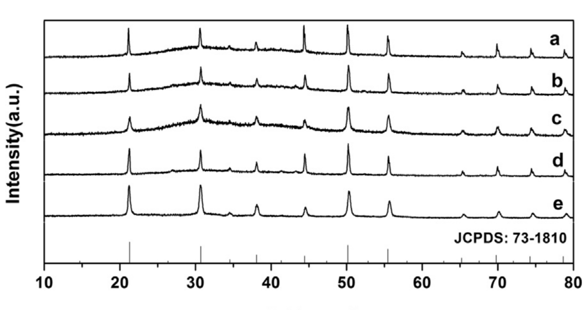

Fig. 1. XRD patterns for $In(OH)_3$: pH = 5 (a), pH = 7 (final product in 10 min reaction) (b), pH = 7 (intermediate product in 5 min reaction) (c), pH = 7 $In(OH)_3$:0.5%Dy (d), pH = 9 (e).

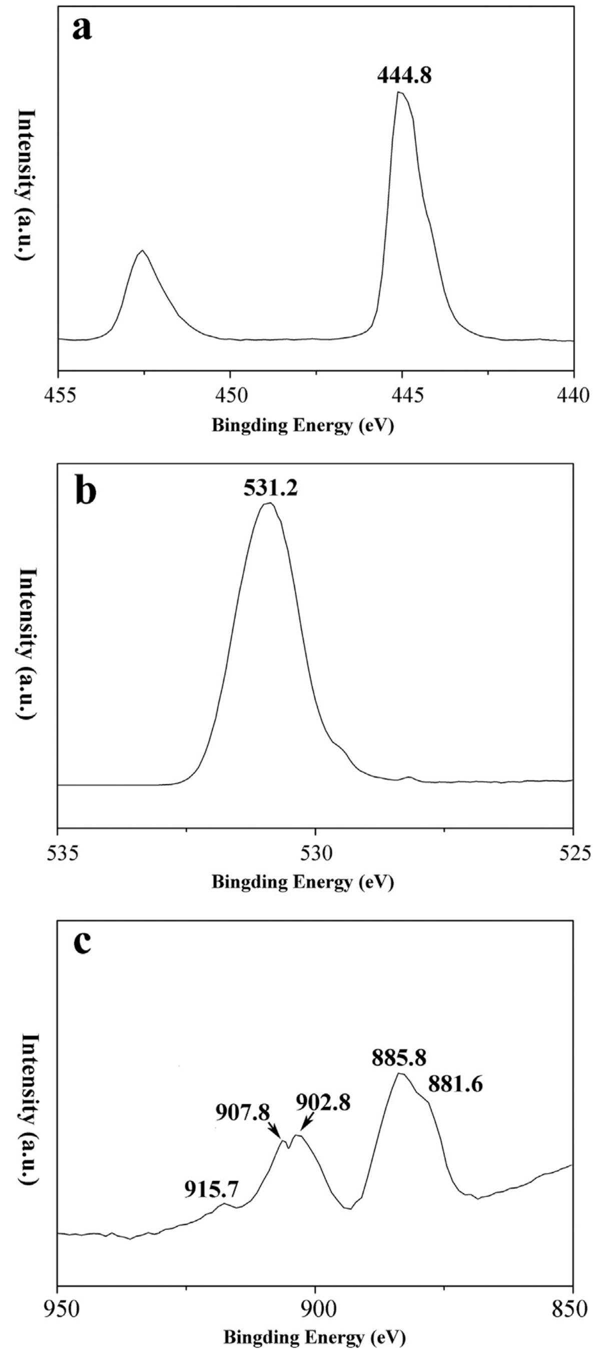

Fig. 2. XPS spectra of the as-prepared $In(OH)_3$:10%Ce^{3+}/1%Dy^{3+}: In $3d_{5/2}$ peak (a); O 1s peak (b); Ce 3d peaks (c).

X-ray photoelectron spectroscopy (XPS) was used to analyze the as-prepared $In(OH)_3$:10%Ce^{3+}/1%Dy^{3+}, which is shown in Fig. 2. The In $3d_{5/2}$ peak with the binding energy of 444.8 eV (Fig. 2a) confirms that the surface of the material is composed of $In(OH)_3$ [21]. Symmetrical O 1 s peak with binding energy of 531.2 eV can be clearly seen in Fig. 2b [22]. Five XPS peaks for Ce 3d were observed in Fig. 2c. Ce 3d peaks at 881.6, 907.8 and 915.7 eV are attributed to primary photoionization from Ce^{4+}, and the binding energy at 885.8 and 902.8 eV can be attributed to Ce^{3+} characteristic peaks, according to previously reported [23]. The results indicated the coexistence of Ce^{3+} and Ce^{4+} on the surface of the nanomaterials. While, no obviously peaks of Dy^{3+} was detected in XPS perhaps because the low doping concentration.