Letter

Controlling growth of single-crystalline indium hydroxide nanocuboids with enhanced sharp cathodoluminescence peak

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ABSTRACT

Indium hydroxide nanocuboids have been grown on the silicon substrate by a hydrothermal method at lower reaction temperature. The concentration of hexamethylenetetramine plays a crucial role for controlling the growth direction and morphology of Indium hydroxide nanostructures. Indium hydroxide nanocuboids exhibit very prominent blue emission in the cathodoluminescence spectrum. The enhancement in optical properties shall be advantageous in applications for nanoscale light-emitting devices.

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1. Introduction

Indium compounds such as indium hydroxide $In(OH)_3$, indium oxyhydroxide (InOOH), and indium oxide (In_2O_3) were investigated intensively for the last decade, because of their novel optical and electrical properties with potential applications in various fields [1,2]. $In(OH)_3$ is an important semiconductor with a wide band gap ($E_g = 5.15$ eV) and has promising application as photocatalyst [3,4]. In_2O_3 is also a good n-type semiconductor with band gap at 3.55–3.75 eV and has been widely used for nonlinear optic research, nanoelectronics, gas sensors, biosensors, and solar cells [5–8]. The thermal decomposition of $In(OH)_3$ is facilitated the phase transfer from cubic $In(OH)_3$ to cubic In_2O_3 [9,10]. Recently, the $In(OH)_3$ structures have been synthesized by hydrolysis [11], hydrothermal [9,10], microwave irradiation [12], and solvothermal routes [13,14]. However, those reaction routes as mention above could not be accomplished without high temperature process (i.e., 130 °C or even above). In addition, some surfactants or organic ligands are required in the fabrication approaches [10,13,14]. The surfactants or organic ligands have a remarkable ability to control the shapes of $In(OH)_3$ nanostructures. However, many reagents pollute the environment and are detrimental to human health.

The ability to adopt non-toxic and bio-friendly reagents for controlling and integrating nanostructures as functional Materials is an important challenge for scientists have faced to develop

biotechnology and environment [15,16]. Hexamethylenetetramine (HMTA) is not only extensively used to synthesize semiconductor nanomaterials, but it is also used as a food additive for preservation [17–19]. The present study uses an appropriate concentration of HMAT in conjunction with a hydrothermal process to produce $In(OH)_3$ nanocuboids at lower reaction temperature. In addition, HMTA was used to control the morphology of $In(OH)_3$ nanostructures for the first time. The $In(OH)_3$ nanocuboids exhibited a significantly strong and sharp blue emission at room temperature. The enhancement in blue emissions shall be advantageous in applications for nanoscale light-emitting devices.

2. Experimental procedure

$In(OH)_3$ structures were grown by a hydrothermal method in 20 mL aqueous solution containing 10 mM indium(III) chloride tetrahydrate (97%, Aldrich) and different concentration of hexamethylenetetramine (99%, Aldrich) (HMTA). The silicon substrates were cleaned in a boiling piranha solution (H_2O_2:concentrated H_2SO_4, 3:7, v/v) for 10 min, and then rinsed with de-ionized water and ethanol. The cleaned silicon substrates were placed at the bottom of sealed bottles containing the above solution. Then, the bottles were putted into an oven and maintained at 90 °C for 3 h. Finally, the product substrates were washed with deionized water and ethanol, and dried under a N_2 purge.

The morphology of $In(OH)_3$ structures was examined with a field emission scanning electron microscope (FESEM) using a JEOL JSM-6500F SEM operating at 10 kV accelerating voltage. A JEOL-2010 transmission electron microscope (TEM) operating at 200 kV was used to examine the microstructures. The crystalline phase of the $In(OH)_3$ structures was determined using the X-ray powder diffraction method (Shimadzu XRD-6000, Cu Kα_1 radiation ($\lambda = 0.1505$ nm)). The cathodoluminescence (CL) spectra were acquired with an electron probe microanalyzer (Shimadzu EPMA-1500) attached to a SEM. CL spectra were accumulated in a single shot mode within an exposure rate of 1 nm/s. All the CL spectra were taken at room temperature.

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3. Results and discussion
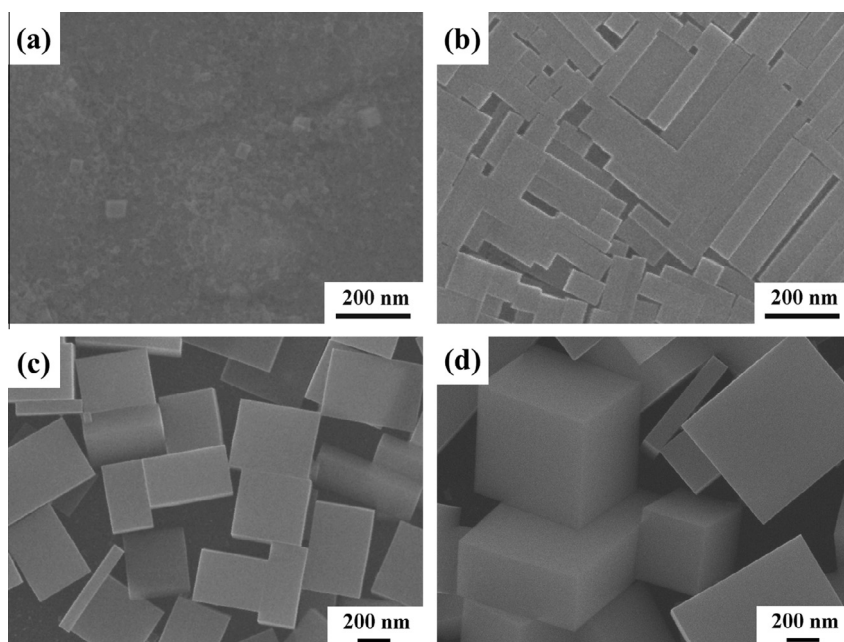
To understand the different concentration of HMTA shall be impacted In(OH)$_3$ structures at 10 mM indium(III) chloride. The concentration-dependent morphological evolution process was examined by FESEM. Fig. 1a shows a top-view SEM image of In(OH)$_3$ nanoparticles and small nanocubics were grown with 10 mM HMTA on the silicon substrate. The morphology of In(OH)$_3$ nanocuboids were grown with 6 mM HMTA on the silicon substrate, as shown in Fig. 1b. The lengths and widths of In(OH)$_3$ nanocuboids are 100–500 nm and 50–150 nm, respectively. The thicknesses of In(OH)$_3$ nanocuboids are lower than 100 nm. Fig. 1c shows a SEM image depicting the randomly oriented of In(OH)$_3$ submicrocubics and submicrocuboids were grown with 2 mM HMTA. In addition, the bigger submicrocubics and submicrocuboids were formed at no HMTA, as shown in Fig. 1d. The lengths and widths of submicrocubics and submicrocuboids were varied a great deal. The phenomenon is attributed to the lower concentration of HMTA being unable to provide for the confinement of morphology. On the other hand, appropriate amounts of HMTA led to the growth of In(OH)$_3$ nanocuboids.

In previous work, HMTA has been widely used as a reaction precursor to synthesize one-dimension (1D) ZnO nanostructures [16]. HMTA acts as a weak base and pH buffer. HMTA can provide the hydroxide ions (OH$^-$) and the ammonia molecules (NH$_3$) in the reaction solution to control growth of ZnO nanostructures [20]. Herein, HMTA exhibits similar characteristics to grow In(OH)$_3$ structures. Fig. 2 shows the XRD patterns of the silicon substrate fabricated with different In(OH)$_3$ structures. All of the reflections of the XRD pattern could be indexed to body-centered cubic In(OH)$_3$ with a lattice constant a = 0.797 nm, which are consistent with reported data (JCPDS Card No. 85-1338). No peaks of impurities were observed, indicating that the product is a pure phase compound. Fig. 2a reveals the XRD pattern of In(OH)$_3$ nanocuboids grown on the silicon substrate. A strong and sharp diffraction peak corresponding to the (200) crystal phase of In(OH)$_3$ indicates that the preferred growth direction of the In(OH)$_3$ nanocuboids is in the [100] direction. When the concentration of HMTA was decreased, the XRD pattern exhibited additional four peaks, as shown in Fig. 2b. The four peaks are [220], [222], [420], and [422], respectively. In addition, XRD pattern of In(OH)$_3$ nanoparticles and small nanocubics (Fig. 1a) exhibit amorphous phase. The results indicated that HMTA could greatly change the growth direction of In(OH)$_3$.

Fig. 3a shows a TEM image of a In(OH)$_3$ nanocuboid with a width of 100 nm and a length of 380 nm. The corresponding selected area electron diffraction (SAED) pattern is shown in Fig. 3b. The SAED pattern exhibits the In(OH)$_3$ nanocuboid is single crystal. The square symmetrical SAED pattern records on the individual In(OH)$_3$ nanocuboid can be attributed to ⟨001⟩ zone axis diffraction of bcc In(OH)$_3$. Both TEM image and diffraction pattern indicate that the In(OH)$_3$ nanocuboid is grown in [100] direction. Fig. 3c and d shows a TEM image and a SAED pattern of a In(OH)$_3$ submicrocubic. The widths of In(OH)$_3$ submicrocubic are 307 nm and 305 nm, respectively. Both TEM image and diffraction pattern can also indicate that the In(OH)$_3$ submicrocubic is also single crystal and grown in [100] direction.

Cathodoluminescence is a useful technique for characterizing the optical properties of nanostructures [15,21,22]. Since CL uses an electron beam for excitation, it is feasible to excite only a single or a small group of nanostructures. All the CL spectra were taken at room temperature for the area of 10 μm × 10 μm. The growth of In(OH)$_3$ nanoparticles and small nanocubics with 10 mM HMTA on the silicon substrate cannot exhibit any CL peak, as shown in Fig. 4a. This phenomenon is the same with nanorod bundles and spheres of In(OH)$_3$ did not exhibit any luminescence under UV light excitation [23]. The CL spectrum of the In(OH)$_3$ nanocuboids grown with 6 mM HMTA on the silicon substrate is shown in Fig. 4b. The strong and sharp blue emission is at 430 nm (2.88 eV) and the FWHM is 0.70 eV. This emission peak is different from band gap emission of In(OH)$_3$ at 241 nm (5.15 eV). This result may be similar to oxide semiconductors (e.g. In$_2$O$_3$, ZnO, and SnO$_2$) consistent with the currently accepted model that the emission arises from the recombination between holes trapped at the surface defects and electrons trapped at the oxygen vacancy [9,21,24,25]. In(OH)$_3$ submicrocubics and submicrocuboids grown

Fig. 1. Top-view SEM images of the In(OH)$_3$ structures grown on the silicon substrate at the different concentration of HMTA. The concentrations of HMTA are (a) 10 mM, (b) 6 mM, (c) 2 mM, and (d) 0 mM, respectively.