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Monodisperse In_2O_3 nanoparticles synthesized by a novel solvothermal method with $In(OH)_3$ as precursors

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ABSTRACT

A novel solvothermal method has been developed for monodisperse In_2O_3 nanoparticles (NPs) with ~5 nm particle size, $In(OH)_3$ as precursors and free of any surfactant and template. The NPs were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), energy-dispersive X-ray spectrum (EDS) and Fourier transform infrared spectrum (FT-IR). The temperature, the concentration of precursors and washing conditions dramatically affected the structure, morphology and size of NPs. The possible growth mechanism was elucidated as well, which was delayed burst nucleation. A weak quantum confinement effect of In_2O_3 NPs resulting from the small particle size was observed in UV spectrum and one photoluminescence emission peak occurring in the visible region was detected as well.

1. Introduction

Indium oxide is a versatile semiconductor material that has achieved considerable attentions in a variety of applications such as photocatalysts [1], luminescent lanthanide-doped inorganic nanoprobes [2], transparent thin-film transistors [3], field-emission devices [4], ultraviolet sensors [5], and antireflection layers for Si solar cells [6]. The importance of In_2O_3 primarily originates from its wide band gap (direct band gap around 3.6 eV) and high transparency to visible light. As other *n*-type transparency semiconductors, it can adjust its electrical conductance when exposure to various gases [7], which is suitable for designs of ultrasensitive gas sensors in the detection of O_3 [8], CO, H_2 [9], NO_2 [10], and Cl_2 [11]. It is noteworthy that, for many applications particle size has a tremendous effect on the mechanical, electronic, magnetic, and optical properties and thus, plays a fundamental role in determining the performance of a material. For example, the gas-sensing performance of In_2O_3 has been shown to be improved significantly while decreasing its particle size [12]. Therefore, fabrication of monodisperse In_2O_3 with ultrafine size, especially for size smaller than 10 nm, becomes a topic of scientific and technological importance.

In general, ultrafine In_2O_3 NPs were synthesized by thermal decomposition method [13]. However, this route suffered from several drawbacks, including harsh experimental conditions (high temperature, inert gas protection), high-cost organometallic precursors, surfactant-requirement and toxic solvent. Comparing to thermal decomposition method, solvothermal method exhibits some advantages, such as moderate experimental conditions, readily available precursors. Although significant progress has been made in the preparation of In_2O_3 NPs with solvothermal method [14], the fine control of the size, especially for size smaller than 10 nm, remains a challenge.

Two factors maybe major obstacles to the synthesis of small size In_2O_3 NPs with solvothermal method. Firstly, the content of water dramatically affects the formation of NPs. Current solvothermal syntheses of In_2O_3 NPs are always performed at excess water [14(a),(c),15]. However, Chen's group proved that addition of a small amount of water was crucial for the oriented aggregation of Co_3O_4 NPs in *n*-hexanol [16], because water could act as a binder to control the nanocrystal aggregation. Therefore, excess water does not favor the synthesis of monodisperse NPs. Secondly, the added or residual inorganic anions, such as NO_3^- or Cl^- in the organic molecule-based synthesis systems, have a dramatical influence on morphology and size of as-synthesized nanostructures [17]. For example, Qian et al. [18] reported that adding sodium nitrate could affect the morphology of $NaYF_4$ obtained through aggregation from smaller NPs. Therefore, inorganic anions, such as NO_3^- or Cl^-, should be avoided being introduced into the synthesis of monodisperse NPs. Indium-organometallic precursors, such as indium(III) acetylacetonate [19], and indium oleate [20] had been

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used to synthesize disperse In_2O_3 NPs. However, organometallic precursors always lead to cost-consuming and labor-intensive.

A combination of judicious control of the amount of water and choosing a suitable precursor could favor the synthesis of monodisperse In_2O_3 NPs by a more convenient and effective solvothermal method, as discussed above. However, there is no report about readily available precursors and surfactant-free synthesis of monodisperse In_2O_3 NPs with size smaller than 10 nm by solvothermal method as far as our knowledge. In this article, we firstly report our synthesis of monodisperse In_2O_3 NPs with ~5 nm size by a novel solvothermal route in ethylene glycol (EG)-medium, $In(OH)_3$ as precursors and without any surfactant and template. Furthermore, we also investigate the influences of the temperature, the concentration of precursors and washing condition on the formation of In_2O_3 and its morphology and size, as well as the optical observation from these NPs.

2. Experimental

2.1. Chemicals

Indium(III) nitrate hydrate ($In(NO_3)_3·4.5H_2O$, AR) was purchased from Sinopharm Chemical Reagent Co., Ltd., China, ammonia solution ($NH_3·H_2O$, AR) and ethylene glycol ($HOCH_2$-CH_2OH, AR) were from Guangzhou Chemical Reagent Factory. The reagents and solvents were used directly without further purification.

2.2. Synthesis of $In(OH)_3$ precursors

$In(OH)_3$ precursors were obtained by hydrolysis of corresponding nitrate. $In(NO_3)_3·4.5H_2O$ (2, 4 or 6 mmol) was dissolved into deionized water (10 mL), then the pH of the solution was adjusted to 7.0 with ammonia solution (1.0 mol L^{-1}). The mixture was continuously stirred for 1 h to form a white suspension, and then was centrifuged and washed with ethanol and ethylene glycol (EG) one time respectively to obtain $In(OH)_3$ precursors (2, 4 or 6 mmol).

2.3. Synthesis of In_2O_3 NPs

The precursors were dispersed into EG (40 mL), charged into a 50 mL Teflon-lined stainless autoclave and then aged at 220 °C for 8 h. Finally, In_2O_3 NPs were isolated by cooling the reaction mixture to room temperature, centrifuged and washed three times with ethanol and finally dried in atmosphere at 80 °C for 24 h. The detailed experimental parameters are listed in Table 1, and the products are denoted as S-1, S-2, and S-3.

2.4. Characterization

A Rigaku, D/max-rB analysis (Cu Ka radiation operated at 36 kV and 20 mA, $\lambda = 1.5406$ Å, scanning speed 4°/min) was used to determine the structure and phase purity of the as-prepared NPs. The NPs' morphology was investigated by transmission electron microscopy (TEM). Additionally, high-resolution TEM (HRTEM) and energy-dispersive X-ray spectrum (EDS) were taken to determine the NPs' structure and elements, respectively. The samples for TEM measurements were prepared by placing a drop of In_2O_3 NPs on a copper grid. The measurements were performed with a Philip Tecnai-10 electron microscope. A Bruker, Nicolet 6700 spectrophotometer was used to perform fourier transform infrared (FT-IR) spectrum. UV–vis absorption spectrum were measured by a Varian, Cary 5000 spectrophotometer and fluorescence spectrum were performed by a Hitachi, F-4500 fluorospectrometer with a 150 W Xenon lamp at room temperature.

Table 1
Summary of the experimental conditions and the corresponding denotations for the final samples.

Samples	$n(In(OH)_3$ (mmol)	V(EG) (mL)	$c(In(OH)_3$ (mol/L)[a]	Temp. (°C)	Time (h)
S-1	2	40	0.05	220	8
S-2	4	40	0.10	220	8
S-3	6	40	0.15	220	8
S-4	4	40	0.10	220	12

[a] $c(In(OH)_3) = n(In(OH)_3)/V(EG)$.

3. Results and discussion

3.1. Characterization of In_2O_3 NPs

3.1.1. Phase

The structure and phase purity of precursors and In_2O_3 NPs were investigated by powder XRD. The XRD pattern of precursors is shown in Fig. 1A. All diffraction peaks could be readily indexed to a hexagonal lattice of pure $In(OH)_3$ according to the Joint Committee on Powder Diffraction Standards (JCPDS) data card no. 85-1338 with no other secondary crystalline phases. The relative intensities of diffraction peaks were gradually reduced with raising the amount of $In(NO_3)_3$. Fig. 1B shows the XRD pattern of as-formed solvothermal products of S-1, S-2, and S-3 (from bottom to top). Typically, diffraction peaks of S-3 could be readily indexed as (2 1 1), (2 2 2), (4 0 0), (3 3 2) and (1 3 4) planes of a cubic lattice [space group: *Ia*3 (No. 206)] of pure In_2O_3 according to the JCPDS data card no. 89-4595. No additional peaks of other phases were found. Moreover, the peaks were broadened, indicating the nanocrystalline nature of the resulting In_2O_3 NPs. Compared with S-3, distinct crystalline peaks were not found while only broad halopeaks were observed for S-1, which suggested the formation of an amorphous phase. While the concentration of precursors was 0.10 mol/L, a weak peak corresponding to (2 2 2) reflection was observed for S-2 and indicated that In_2O_3 predominantly formed. The general increase in relative intensities of diffraction peaks suggested a raise of crystallinity of In_2O_3 with the concentration of $In(OH)_3$ from 0.05 to 0.15 mol/L. The crystalline size of S-3 is estimated from the Debye–Scherrer's equation, $D = K\lambda/(\beta \cos\theta)$, where D is average grain size, K is a constant (0.90), λ is X-ray wavelength (0.15406 nm), and β and θ are the full-width at half-maximum (fwhm, in radian) and diffraction angle of an observed peak (2 2 2). The estimated average crystallite size is about 5 nm, with a good agreement with TEM shown in Fig. 2. The calculated lattice constant using Jade 5.0, $a = 10.1228 \pm 0.0009$ Å for S-2 and $a = 10.0820 \pm 0.0021$ Å for S-3, are well compatible with the literature value of $a = 10.11$ Å (JCPDS 89-4595).

3.1.2. Morphology

Information about the crystal structure and morphology of In_2O_3 NPs was provided by TEM measurements. Fig. 2A–C shows a low resolution TEM images of S-1, S-2, and S-3. It is clear that the concentration of precursors plays critical roles in the formation of In_2O_3 NPs with different morphology and size distribution. When the concentration of $In(OH)_3$ was 0.05 mol/L, TEM image (Fig. 2A) presented massive amorphous produce, completely different from NPs synthesized with 0.10 and 0.15 mol/L $In(OH)_3$. The samples of S-2 included most of spherical as well as club-shaped NPs (Fig. 2B) while the morphology of S-3 was essentially spherical shape (Fig. 2C). The observed lattice fringes of S-2 in the HRTEM image (inset in Fig. 2B) were calculated to be around 2.92 Å corresponding to the (2 2 2) plane of cubic In_2O_3 phase, which indicated that In_2O_3 predominantly formed. The average diameter of S-3, ~5 nm, calculated from TEM images by taking into account 100 particles, is