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Shape- and phase-controlled synthesis of In_2O_3 with various morphologies and their gas-sensing properties

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ABSTRACT

Hexagonal In_2O_3 microspheres, cubic In_2O_3 porous nanoparticles, and cubic In_2O_3 porous nanorectangles were fabricated by calcining precursors at 450 °C, respectively. The precursors InOOH microspheres, $In(OH)_3$ nanoparticles, and $In(OH)_3$ nanorectangles were solvothermally synthesized by adjusting the volume ratios of ethylenediamine and distilled water in autoclave at 160 °C. Gas-sensing properties determination of ethanol, formaldehyde, and ammonia gases show that the cubic In_2O_3 porous nanoparticles have a higher response than the hexagonal In_2O_3 microspheres.

1. Introduction

In_2O_3 is an important n-type semiconductor with a wide band gap (E_g = 3.6 eV) [1], and has potential application in optoelectronic devices, such as solar cell, UV lasers, and detectors [2]. In recent years, the gas-sensing properties of In_2O_3 materials on NH_3 [3], C_2H_5OH [4], HCHO [5], CO [6], O_3 [7], and H_2S [8] gases were investigated. It has been demonstrated that a decrease in the size of the In_2O_3 crystallites in the sensing layer can considerably enhance the response [9]. It is well known that nanomaterials with larger surface area have more chances to adsorb and desorb target gases molecules, which lead to a higher response [10]. By preparing porous structures is one of important methods to increase surface area of nanomaterials and then to improve their gas-sensing properties.

In_2O_3 has two phases: cubic In_2O_3 (c-In_2O_3) and hexagonal In_2O_3 (h-In_2O_3). For various morphologies of c-In_2O_3 nanomaterials, several approaches, such as physical evaporation technique [11], chemical vapor deposition [12], thermal oxidation [13], laser ablation technique [14], sol–gel method [15], and solution-phase growth [16], have been reported. Recently, a route by calcining precursors to synthesize c-In_2O_3 nanomaterials attracts more and more attention. Several synthetic routes, such as solution reaction [17], hydrothermal [1], and solvothermal methods [18], were used to prepare precursor $In(OH)_3$ materials. And c-In_2O_3 lotus-root-like nanostructures [17], nanorod bundles and spheres [1], and hollow microspheres [18] could be obtained by calcining their precursor. Similarly, these methods to fabricate precursor $In(OH)_3$ can also be applied to synthesize precursor InOOH materials. And by thermally treating them, h-In_2O_3 nanofibers [19], nanotubes [20], nanocubes [21], and multipods [22] can be obtained.

In this study, precursors with different phases and morphologies were obtained by adjusting the volume ratios of ethylenediamine and distilled water via a solvothermal route. Then by calcining the precursors at 450 °C, h-In_2O_3 microspheres, c-In_2O_3 porous nanoparticles, and c-In_2O_3 porous nanorectangles were fabricated, these morphologies were all rarely reported. The gas-sensing properties determination of ethanol, formaldehyde, and ammonia gases showed that the c-In_2O_3 porous nanoparticles had a higher response than the h-In_2O_3 microspheres. And all of the sensors made by In_2O_3 micro/nanoparticles were more responsive to C_2H_5OH gas.

2. Experimental

All the reagents were analytically pure, purchased from Shanghai Chemical Company, and were used without further purification. Distilled water was used in our experiments.

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Table 1
The influence of different reaction conditions on the phases and morphologies of the products.

Sample	Method, V_{EN}:V_{DW}/temperature (°C)	Phase	Morphology, average size (nm)
S1	Solvothermal, 35:5	Orthorhombic InOOH	Microspheres, 500
S2	Solvothermal, 25:15	Cubic $In(OH)_3$	Nanoparticles, 50
S3	Solvothermal, 0:40	Cubic $In(OH)_3$	Nanorectangles, 110 in width and 200 in length
S4	Calcination (S1), 450	Hexagonal In_2O_3	Microspheres, 500
S5	Calcination (S2), 450	Cubic In_2O_3	Porous nanoparticles, 50
S6	Calcination (S3), 450	Cubic In_2O_3	Porous nanorectangles, 110 in width and 200 in length

2.1. Synthesis of precursors

The precursors InOOH and $In(OH)_3$ were prepared via a simple solvothermal method. In a typical procedure, 0.5 mmol of $InCl_3{\cdot}4H_2O$ and 4 mmol of hexamethylenetetramine (HMTA) were added to a mixed solution of ethylenediamine (EN) and distilled water (DW) with different volume ratios to form a homogeneous solution by constantly stirring for 30 min. The resulting mixture was transferred into a Teflon-lined stainless-steel autoclave (60 mL capacity) that was then sealed and maintained at 160 °C for 12 h; then cooled to room temperature naturally. The final products were washed with distilled water and anhydrous ethanol several times. Finally, the products were dried in a vacuum chamber at 50 °C for 6 h. The detailed volume ratios of solvents are shown in Table 1.

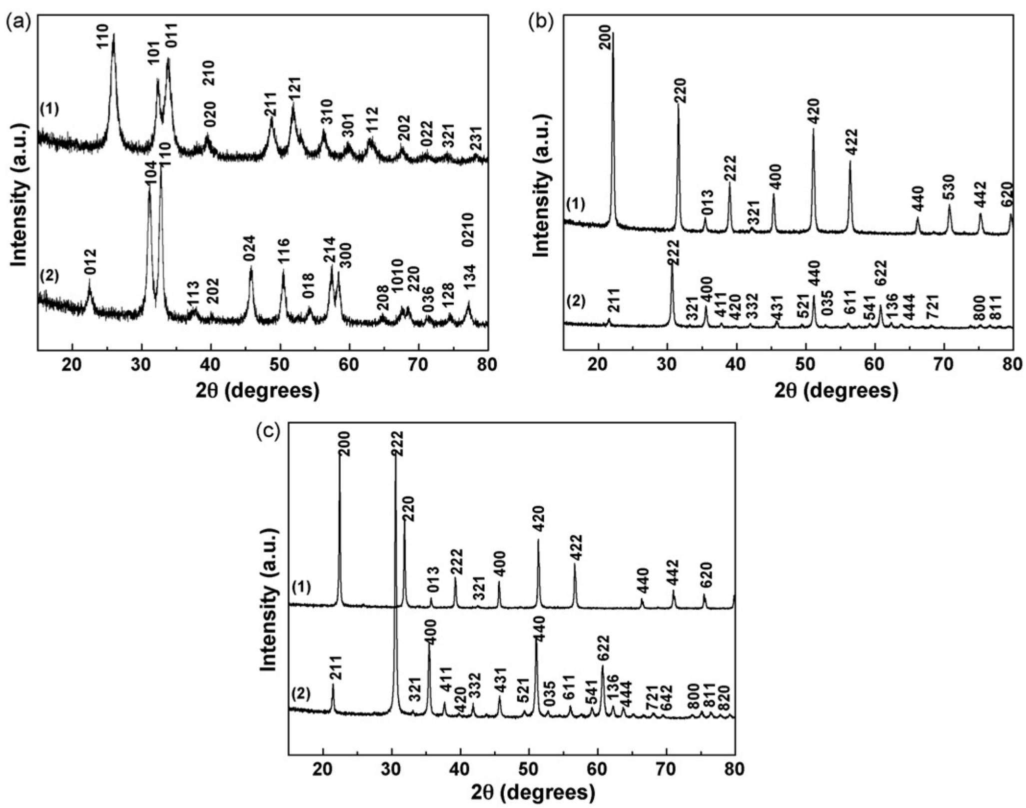

Fig. 1. XRD patterns of the as-prepared samples (a_1) InOOH microspheres, (a_2) h-In_2O_3 microspheres, (b_1 and c_1) $In(OH)_3$ nanoparticles, and (b_2 and c_2) c-In_2O_3 nanoparticles.

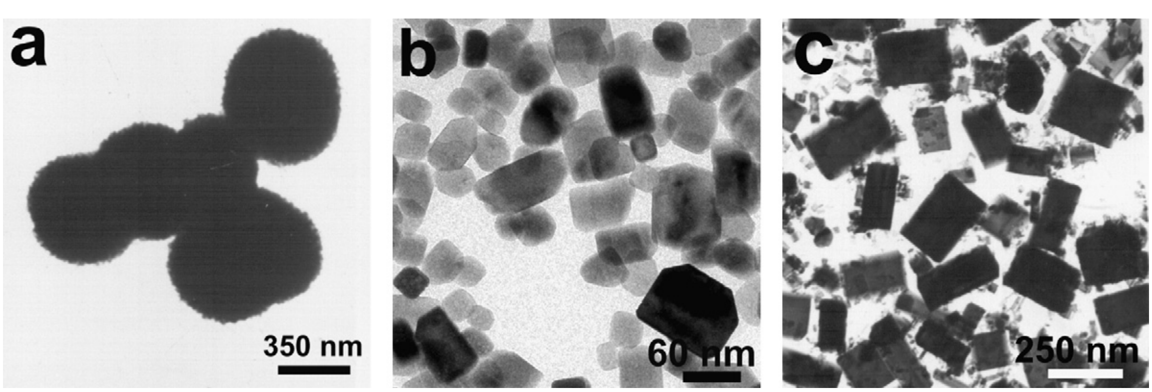

Fig. 2. TEM images of the as-obtained samples via solvothermal process with different volume ratios of EN/DW: (a) 35:5, (b) 25:15, and (c) 0:40.