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SHORT COMMUNICATION

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Rapid preparation of uniform colloidal indium hydroxide by the controlled double-jet precipitation

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Abstract The synthesis of uniform colloidal rod-like $In(OH)_3$ particles from relatively concentrated solutions of $InCl_3$ ($0.1\,mol\,dm^{-3}$) in short reaction time (<15 min) by the controlled double-jet precipitation (CDJP) technique is described. The effects of the molar ratio of $[NH_4OH]/[InCl_3]$, temperature, concentration of the reactants, and reaction time on the size and shape of the final products are investigated. It is found that such $In(OH)_3$ particles are formed by aggregation of nanosize subunits.

Key words Indium hydroxide, colloidal – indium hydroxide, rod-like – controlled double-jet precipitation – monodispersed indium hydroxide – precipitation of indium hydroxide

Introduction

Most of the precipitation procedures described in the literature, that yield monodispersed colloids, require low reactant concentrations and long reaction times. Since the advantages of such materials in various applications have now been widely recognized, it has become necessary to develop production techniques that will use larger amounts of reactants and require relatively short processing times. Recently, several such rapid methods have been introduced [1, 2], among which the controlled double-jet precipitation (CDJP) process has been especially useful in generating uniform fine particles in larger quantities [3–7].

This study describes the use of the CDJP technique in a rapid synthesis of uniform rod-like indium hydroxide particles at reasonably high concentrations of reactants. The previously reported precipitation methods for the preparation of this compound employed, as a rule, dilute solutions ($<10^{-2}\,mol\,dm^{-3}$) and long reaction times (>2 h) [8–10]. The effects of various parameters on the size and shape of the final particles as well as the mechanism of the particle formation are discussed.

Experimental

Materials

Indium chloride (99.99%, Aldrich) and reagent grade ammonium hydroxide were used without further purification.

Stable stock solutions of $InCl_3$ (0.4 or $1.0\,mol\,dm^{-3}$) were prepared in $0.1\,mol\,dm^{-3}$ hydrochloric acid. No formation of particles could be detected at room temperature even after several weeks of storage or on heating at 90 °C for a limited period of time. These solutions were diluted with deionized water when needed.

All stock solutions were filtered through 0.2 μm pore size membranes before use in order to remove any possible particulate contaminants.

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Preparation of particles

The experimental set-up for the controlled double-jet precipitation (CDJP) has been described elsewhere [3, 5]. In a "standard" run, 50 cm^3 of 0.4 mol dm^{-3} $InCl_3$ solution and 50 cm^3 of a 0.8 mol dm^{-3} NH_4OH solution were simultaneously introduced by peristaltic pumps at a flow rate of 5 cm^3 min^{-1}, under stirring, into the reactor containing 100 cm^3 of deionized water kept at 90 °C, followed by aging at the same temperature for 5 min. Before mixing, the $InCl_3$ and NH_4OH solutions were preheated to 90 °C. The volume of the resulting dispersion was 200 cm^3, yielding the final $InCl_3$ concentration of 0.1 mol dm^{-3}. On completion of the aging, the resulting dispersion was immediately quenched to room temperature in cold water, and then the pH was measured. The solids were separated from the mother liquid by centrifugation, repeatedly washed with deionized water, and then dried at 80 °C overnight to obtain the powder.

To investigate the effects of the molar ratio of $[NH_4OH]/[InCl_3]$, reaction temperature, concentration of $InCl_3$, and the flow rate of the reactants on the properties of the resulting particles, separate experiments were carried out by varying one parameter while keeping the others constant as in the "standard" run.

Characterization

The morphology and the size of the particles were examined by scanning (SEM) and transmission (TEM) electron microscopy. The crystal structure was analyzed by the X-ray powder diffraction (XRD) using a CuKα source. The electrophoretic mobilities were measured with the DELSA 440 instrument. The changes on heating of the solids were followed by differential thermal (DTA) and thermal gravimetric (TGA) analyses at a heating rate of 10 °C min^{-1} in air flow.

Results

Uniform rod-like particles (Fig. 1a), obtained by the CDJP process under the "standard" conditions described in the experimental section, had an average length of 320 nm and the width of 80 nm, as evaluated from SEM micrographs. Table 1 lists the effects of additional experimental conditions on the size and shape of the resulting particles.

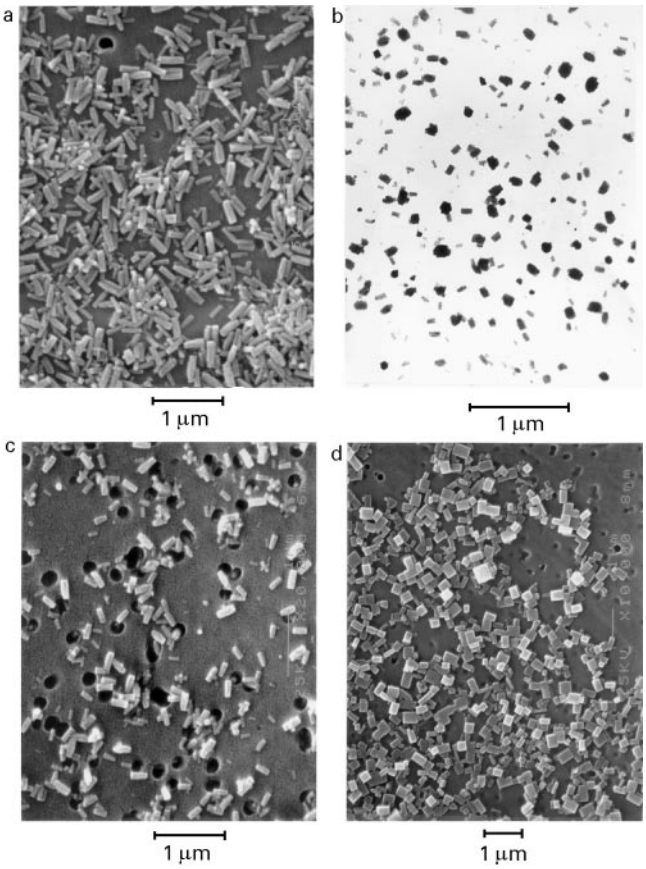

Fig. 1 Electron micrographs of $In(OH)_3$ particles produced by the controlled double-jet precipitation (CDJP) technique using the conditions described in Table 1: (a) sample 2 (standard run); (b) sample 6; (c) sample 10; and (d) sample 13 and aging at 90 °C for 24 h

Effect of the molar ratio $[NH_4OH]/[InCl_3]$

The molar ratio $[NH_4OH]/[InCl_3]$ was found to greatly influence the final pH (Table 1, samples 1–5); above this ratio of ~3.5, the pH increased considerably, and the shape and the size of the resulting particles also changed. These effects appear to be correlated; thus, at $[NH_4OH]/[InCl_3] < 3.5$ well-defined rods were obtained, while at > 3.5 the particles were irregular and aggregated.

Effect of the reaction temperature

Table 1 shows that at the fixed molar ratio of $[NH_4OH]/[InCl_3] = 2$ (samples 2 and 6–8), the particles became appreciably smaller with decreasing reaction temperature; at 70 °C the average size of rods was 120 nm (sample 6, Fig. 1b), as compared to 320 nm at 90 °C (sample 2,

Table 1 Experimental conditions for the preparation of $In(OH)_3$ by the CDJP process

No.	Temp. [°C]	$[InCl_3]_{stock}$ [mol dm^{-3}]	Ratio $[NH_4OH]/[InCl_3]$	Flow rate [cm^3 min^{-1}]	pH_f	Morphology**	Mean size [μm***]	Figure
1	90	0.4	1.0	5	2.9	R	0.33	
2*	90	0.4	2.0	5	3.1	R	0.32	1a
3	90	0.4	3.0	5	3.4	R	0.30	
4	90	0.4	3.5	5	7.5	I/A	~0.25	
5	90	0.4	5.0	5	9.5	A		
6	70	0.4	2.0	5	3.2	R	0.12	1b
7	50	0.4	2.0	5	3.3	R	0.05	
8	25	0.4	2.0	5	4.4	S	0.03	
9	90	0.6	2.0	5	3.2	I/A	~0.3	
10	90	0.2	2.0	5	3.2	R	0.30	1c
11	90	0.1	2.0	5	3.0	R	0.30	
12	90	0.05	2.0	5	2.9	R + C	0.3/0.4	
13****	90	0.025	2.0	5	2.8	R + C	0.3/0.4	1d
14	90	0.4	2.0	10	3.2	R	0.25	
15	90	0.4	2.0	25	3.1	R	0.13	
16	90	0.4	2.0	50	2.9	I/A	~0.1	

* Standard conditions, reaction time 5 min.
** R, rod-like; S, spheres; A, aggregates; C, cubes; I, irregular.
*** Length for rod-like particles; diameter for spehrical particles.
**** Aged for 24 h at 90 °C.

Fig. 1a), while at 25 °C (sample 8), nanosize spheroids of ~30 nm were formed.

Effects of the concentration of $InCl_3$ and aging time

The concentration of $InCl_3$ can affect both the shape and the uniformity of the resulting particles: in acidic media >0.4 mol dm^{-3} $InCl_3$ irregular particles were obtained (sample 9), between 0.4 mol dm^{-3} and 0.1 mol dm^{-3} uniform rod-like particles were formed (samples 2, 10 and 11, Figs. 1a and c), while at <0.1 mol dm^{-3} $InCl_3$, cubes appeared in the resulting dispersions (samples 12 and 13, Fig. 1d). The amount of the latter increased with the aging time.

Effect of the flow rate of reactants

It was established that uniform-rod like indium hydroxide particles could be generated at flow rates as high as 25 cm^3 min^{-1} (sample 15), but their size decreased with the flow rate, from 320 nm at 5 cm^3 min^{-1} to 130 nm at 25 cm^3 min^{-1} (samples 2 and 15). Above 50 cm^3 min^{-1} (sample 16), the resulting particles were irregular and aggregated.

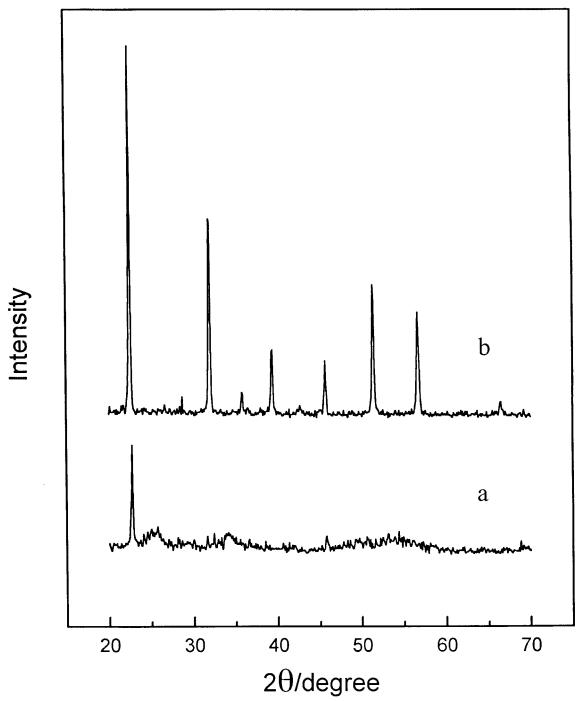

Fig. 2 The XRD pattern of the particles displayed (a) in Fig. 1a, and (b) in Fig. 1d

Particle properties

The XRD pattern of the solid illustrated in Fig. 1a shows that the rod-like particles were poorly crystallized (Fig. 2, a), while the cubic particles displayed in Fig. 1d were well crystallized (Fig. 2, b). The TGA trace of the rod-like particles gave a weight loss of 18% on heating to 400 °C, corresponding to the transformation of $In(OH)_3$

into In_2O_3. The DTA curve of the same sample indicates a single endothermic change due to dehydration over the same temperature range as the weight loss. The i.e.p. of the rod-like particles determined from their electrokinetic mobilities was at pH 7.6.

Discussion

The experimental results presented above offer another example of the advantages of the controlled double-jet precipitation (CDJP) technique for the preparation of uniform particles. In contrast to the batch precipitation methods, the mixing of the reactants in this process prevents internal inhomogeneities in their concentrations, thus, facilitating the formation of uniform colloids in more concentrated media.

In order to elucidate the mechanism of the formation of rod-like $In(OH)_3$, the system prepared under the "standard" conditions (Table 1, sample 2) was quenched in an ice/water bath after 4 min of mixing. Figure 3 shows that the submicron particles consist of aggregates of nanosize precursors.

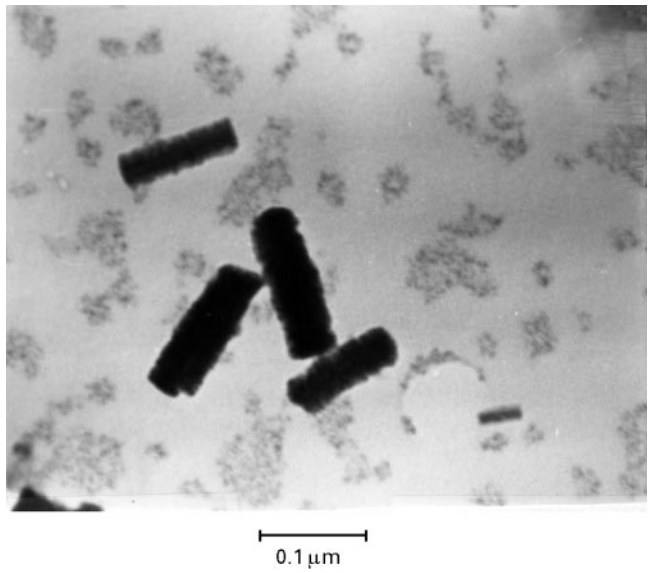

Fig. 3 TEM of the particles prepared by the CDJP technique using the "standard" conditions (sample 2), after mixing for 4 min

The aggregation mechanism has been demonstrated in a large number of monodispersed colloids obtained by precipitation from homogeneous solutions, both with particles of spherical and other shapes, such as CeO_2 [11], SnO_2 [12], CuO [13], or Fe_2O_3 [14, 15]. It was also demonstrated with CuO that the crystallites in the final particles were essentially of the same size as the precursors from which they were built up [13]. In the case of $In(OH)_3$, the aggregation process took place at a pH value below the i.e.p., which means that the subunits were still positively charged. However, the repulsion force was reduced by the high ionic strength of the system, allowing for aggregation to proceed. The elevated temperatures promoted the latter process.

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