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Concomitant synthesis of highly crystalline Zn–Al layered double hydroxide and ZnO: Phase interconversion and enhanced photocatalytic activity

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ABSTRACT

Metal oxide/hydroxide with hierarchical nanostructures has emerged as one of the most promising materials for their unique, attractive properties and feasibility of applications in various fields. In this report, a concomitant synthesis of crystalline zinc aluminum layered double hydroxide (ZnAl-LDH) nanostructure and ZnO is presented using Al substrate as template. Studies on interconversion of ZnO to LDH phase in bulk solution under hydrothermal conditions produced Al-doped ZnO (AZO) in one case, and in other, it improves the crystallinity of LDH film templated on Al substrate. In presence of Al salt, the self-limiting growth nature of plate LDH turned to non-self-limiting. Materials obtained during phase transition, AZO in bulk solution and crystalline porous ZnAl-LDH on substrate, have been demonstrated as effective photocatalysts for decomposition of congo red in aqueous medium.

1. Introduction

Over the past few years, nanostructural architectures with both one-dimensional (1D) and two-dimensional (2D) morphologies have been successfully generated as a densely packed film on solid substrates, which give rise to various technical applications in electronics, optics, biology, medicine, and chemical transformations [1]. These hierarchical complex structures have attracted a lot of interest, as textured design of such spatially oriented inorganic crystalline materials possess both macro- and nanometer level building blocks that tend to exhibit unique exploitable characteristics such as mechanical robustness and multifunctional catalytic properties often derived from anisotropic morphology, compactness, and high surface area in comparison with their bulk analogs [2–4].

One of the materials of interest for organized deposition on substrates is layered double hydroxides (LDH), also called hydrotalcites. LDHs have flat two-dimensional layered structure consisting of positively charged octahedral layers of mixed metal hydroxides $[(M^{II},M^{III})(OH)_x]$ similar to brucite structure of $Mg(OH)_2$ with interlayer galleries occupied by A^{n-} anions and water molecules that bind the layers together [5–8]. Chemical composition of LDH may be described by the general formula $[M^{II}_{1-x}\,M^{III}_x\,(OH)_2]^{x+}\,(A^{n-})_{x/n}\cdot mH_2O$ (M^{II} = divalent metals like Zn, Mg, Fe, CO, Ni; M^{III} = trivalent metals like Al, Cr, Ga; A^{n-} = anions like CO_3^{2-}, SO_4^{2-}, NO_3^-, Cl^-). Hierarchically grown LDH nanostructures have drawn significant interest for applications in biology and catalysis owing to their high surface area and effective adsorption capability of reactant molecules onto the active surface-directed catalytic centers [9,10].

A number of recent studies have reported fabrication of LDH/hydrotalcite-like phases [11,12], $ZnAlCO_3$ [13] or $ZnAl_2O_4$ films [14] on different substrates. For example, Liu et al. has fabricated Zn–Al LDH film on both zinc and aluminum metal substrates with different crystallinity, and calcined product of such coating producing $ZnO/ZnAl_2O_4$ film has been employed as anode material for Li–ion batteries [12]. They also reported secondary growth of ZnO, on LDH grown on Al plate. In another approach, Duan and his group synthesized Mg–Al LDH film on anodized aluminum oxide substrate and the calcined, rehydrated film has been utilized as an immobilized catalyst for aldol condensation of acetone [9]. Gao and coworkers reported formation of porous LDH film on Al surface [11]. However, none of the previously reported studies have specifically enlightened the concurrent synthesis of both crystalline ZnAl–NO_3 LDH and ZnO in one step without using any Al salt solution. Although some morphological and architectural studies have been reported on LDH materials, its use as a photocatalyst has not been addressed well in literature. In this report, hierarchical substrate grown nano LDH as well as the interconversion of one phase to another giving rise to potential photo-responsive material at both ends is presented.

Zinc oxide (ZnO) and its doped counterpart, Al-doped ZnO (AZO), have also been attracting attention because of its variety of applications as blue-violet lasing at room temperature, high conductivity, photocatalytic activity, transparent transistors, and optoelectronic devices [15–18]. Among the various physical techniques, aqueous chemical growth (ACG) for ZnO synthesis has certain

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advantages being cheap, energy-efficient, and "green", as it is devoid of using organic medium, surfactants, or polymer templates [19–21]. By virtue of the hydrothermal ACG method, AZO particles were successfully produced in solution and its photocatalytic efficiency had been exploited.

In the present study, we have developed a facile single-step hydrothermal method to generate porous interconnecting pure and highly crystalline Zn–Al LDH structured on Al plate and rod-like wurtzite ZnO in bulk solution. We have proposed a mechanism for substrate mediated self-limiting growth of LDH and ZnO in the same solution exhibiting different compositions and morphologies. The growth nature of substrate LDH phase changes to non-self-limiting in presence of Al salt. We also report conditions under which the *pure* ZnO phase in bulk solution transforms completely to *pure* LDH phase while improving the crystallinity of the Al-surface deposited LDH phase further. The photocatalytic properties of porous, crystalline LDH and AZO particles obtained during interconversion process have also been reported.

2. Experimental section

2.1. Materials

All of the reagents used in this work were of analytical grade and were used without further purification. Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, AR Grade, Purity: $\geqslant$99.0%) and aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$, AR Grade, Purity: $\geqslant$98%) were purchased from Merck, India. Hexamethylenetetramine (HMTA, $C_6H_{12}N_4$, Purity: $\geqslant$99.0%), aluminum plates (Purity: 99.99%, Thickness: 0.25 mm), and congo red ($C_{32}H_{22}N_6Na_2O_6S_2$, Dye content, $\geqslant$85%) dye were procured from Sigma–Aldrich. Distilled water used in all experimental processes had the following characteristics: pH 7.2, electrical conductance 2×10^{-6} S cm^{-1}, total dissolved salt <0.5 mg/L and turbidity <0.1 NTU.

2.2. Simultaneous synthesis of crystalline LDH and ZnO

Three batches of 100 mL aqueous solutions were made using 50 mL of $Zn(NO_3)_2{\cdot}6H_2O$ (1.49 g, 0.1 M) and 50 mL of HMTA (0.70 g, 0.1 M) at room temperature with a molar ratio of 1:1. The pH of the three solutions were adjusted to 7.5, 10, and 5 by addition of dilute NH_3 ($NH_3{\cdot}H_2O$, 5 mol/L) and dilute HNO_3 (1 mol/L), as required. These were termed as experiment 1 (pH 7.5), 2 (pH 10), and 3 (pH 5), respectively. The resulting solution was transferred to a 250 mL hydrothermal bottle. A clean aluminum plate ($\sim 2 \times 2$ cm^2, 0.25 mm thickness) was then suspended in the solution horizontally by a Teflon thread. The downward face of the plate was analyzed for deposition study in all cases. The bottle was sealed and placed in a laboratory air oven maintained at 90 °C for 24 h.

From the resulting solution, the plate was taken out after the hydrothermal treatment and washed with distilled water for several times followed by rinsing with a copious amount of acetone to facilitate the drying process, after which it was dried at 70 °C for 12 h in air oven. The deposits on the Al plate facing the bottom of the bottle were studied and characterized to be LDH. The solution remaining in the bottle was centrifuged, washed with distilled water for several times, and dried in an air oven at 70 °C for 12 h. These were characterized as ZnO, *vide infra*.

2.3. Conversion of bulk ZnO phase to pure LDH phase

To study the effect of additional Al^{3+} in bulk solution on the nature of deposits on Al plate as well as the particles formed in bulk solution, several batches of 100 mL aqueous solutions was prepared using 50 mL $Zn(NO_3)_2{\cdot}6H_2O$ (1.49 g, 0.1 M) and 50 mL of HMTA (0.70 g, 0.1 M). To these, different amounts of $Al(NO_3)_3{\cdot}9H_2O$ were dissolved so as to maintain Zn:Al molar ratios in the final solution in the range 18:1–2:1, experiment 4 (0.11 g); experiment 5 (0.21 g); experiment 6 (0.31 g); experiment 7 (0.63 g); and experiment 8 (0.94 g). The pH of each solution was adjusted to 7.5 with $NH_3{\cdot}H_2O$ (5 M). The resulting solution was transferred to a 250 mL hydrothermal bottle, and a clean Al plate was suspended horizontally in the solution by a Teflon thread. The bottles were sealed and kept in an air oven at 90 °C for 24 h. The experimental conditions and procedures of experiment 4, 5, 6, 7, and 8 were identical to experiment 1, except that additional different quantities of $Al(NO_3)_3{\cdot}9H_2O$ were added to the latter experiments. The details of all experiments are summarized in Table 1.

2.4. Photocatalytic activity

The photocatalytic activities of both crystalline LDH (grown on Al plate as well as in bulk solution, as mentioned in Results and Discussion) and ZnO (pure and Al-doped) were evaluated by photocatalytic degradation of congo red [(sodium 3,3′-(1E,1′E)-biphenyl-4,4′-diylbis(diazene-2,1-diyl)bis(4-aminonaphthalene-1-sulfonate)] dye in aqueous solution. First, a 100 mL 4×10^{-4} M dye solution was placed in a photocatalytic reactor, to which 5 mg of photocatalyst was added and stirred for 45 min at 400 rpm and 22 °C under dark to establish adsorption–desorption equilibrium between the dye and catalyst surface. After 45 min, the suspension was irradiated with UV light produced from a mercury lamp (60 W, 365 nm) under stirring condition (at 400 rpm, 22 °C). During irradiation, at given time intervals, the samples were taken out and centrifuged, and their absorbances were recorded at 498 nm using a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrometer. Blank dye degradation was also carried out under similar condition without adding the catalyst.

Table 1
Experimental conditions for concurrent synthesis of LDH and ZnO phase in same solution by hydrothermal hydrolysis method.

Exp. no	Amount of $Zn(NO_3)_2{\cdot}6H_2O$/HMTA (g)	Amount of $Al(NO_3)_3{\cdot}9H_2O$ (g)	Zn:Al ratio	Initial pH	Final pH
1	1.49/0.7	×	–	7.5	8.1
2	1.49/0.7	×	–	5	5.6
3	1.49/0.7	×	–	10	10.7
4	1.49/0.7	0.11	18:1	7.5	7.6
5	1.49/0.7	0.21	9:1	7.5	7.6
6	1.49/0.7	0.31	6:1	7.5	7.8
7	1.49/0.7	0.63	3:1	7.5	7.9
8	1.49/0.7	0.94	2:1	7.5	8.0

[a] For all experiments substrate taken = Al plate, temperature = 90 °C, time = 24 h.