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Fabrication of porous microspheres and network arrays of Zn–Al hydrotalcite-like compounds on Al substrate via facile hydrothermal method

Ruixia Shi, Ping Yang*, Yunyu Yin, Xiaobin Dong, Jia Li

School of Materials Science and Engineering, University of Jinan, 250022 Jinan, PR China

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Abstract

The porous microspheres and network arrays of Zn–Al hydrotalcite-like compounds were synthesized on Al substrate using sodium oxalate via a facile one-step hydrothermal approach at low temperature (70 °C). The Zn–Al hydrotalcite-like microspheres assembled by numerous interlaced curved nanoplates with thickness of about 50 nm were generated when the concentration of sodium oxalate is 0.21 M. The XRD pattern indicates that the product was of good quality in terms of phase purity and crystallinity. The morphology of Zn–Al hydrotalcite-like compounds and the thickness of nanoplates varied with the concentration of sodium oxalate, which should be attributed to the different nucleation density and growth rate. When the concentration of Zn^{2+} and sodium oxalate was proportionally reduced the low nucleation density and growth caused the formation of porous network arrays. The reaction temperature directly affected the diffusion rates of ions and thus the density of the nucleation and growth is responsible for the morphology change when the reaction temperature is varied. Additionally, the Zn–Al hydrotalcite-like microspheres transformed into porous network arrays when the sodium oxalate was substituted by the equivalent sodium acetate, which should be attributed to the low alkalinity of sodium acetate. The density and thickness of nanoplates composed of the porous network arrays can be effectively tailored by adjusting the concentration of sodium acetate. On the basis of experimental results, the growth mechanism was proposed and discussed.

Keywords: Zn–Al hydrotalcite-like compounds; Porous microspheres; Network arrays; Al substrate; Sodium oxalate

1. Introduction

Extended and oriented nanostructures are desirable for many applications, but direct fabrication of complex nanostructures with controlled crystalline morphology, orientation and surface architectures remains a significant challenge [1]. For the past few years, much effort has been directed to the study of one dimension nanomaterials. Recently, two-dimensional nanostructures have attracted more and more attention due to their exceptional properties and potential applications. Up to date, the synthesis of two-dimensional and three-dimensional nanomaterials and the investigation of their properties have been an important field [2].

Layered double hydroxides (LDH), which are referred to as hydrotalcite-like compounds (HT) or as anionic clays [3], are a family of layered inorganic materials with structurally positively charged layers and interlayer balancing anions. The structure of LDH consists of positively charged mixed metal hydroxide layers separated by charge-balancing anions and water molecules. The general chemical formula of these lamellar solids can be written as $(M^{2+}_{1-x}M^{3+}_{x}(OH)_2)(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent cations, respectively. The interesting properties of these materials result from their brucite-like structures. They consist of metal cations octahedrally coordinated to OH^- and an interlayer region containing water and anions which compensate the positive charge of the brucite-like sheets [3].

One of the most important properties of LDH is the high anionic exchange capacity that allows the exchange of their original anions with those present in an aqueous solution. Their other interesting properties are "memory effect" [4,5], high surface area, basic properties, homogeneous interdispersion, synergetic effects [5]. Therefore, LDH is considered as promising materials [6] and they have been used in various practical applications in ion exchangers [7,8], anion adsorbents

*Corresponding author. Tel.: +86 531 89736225; fax: +86 531 87974453.
E-mail address: mse_yangp@ujn.edu.cn (P. Yang).

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[9–11], catalysts or catalyst supports [12–14], electroactive materials [15], and nanocomposites [16,17].

The formula of a naturally occurring hydrotalcite is $Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$. As hydrotalcite-like compounds are scarcely found in nature they are conventionally synthesized through coprecipitation methods [18]. Nevertheless, this process suffers from a product with a low crystallinity, extreme long aging time to improve the product quality and extensive washing to remove the salt byproduct. Therefore, widespread use of the material is still limited due to its complex production process [19]. Hydrothermal synthesis is an alternative process to make hydrotalcite-like compounds. In this simple process, slurries of magnesium oxide and aluminum trihydroxide in water are hydrothermally treated. Compared to the conventional precipitation process the hydrothermal process consists of less processing steps and produces no waste [19]. Staminirova suggested that the synthesis mechanism proceeds via a solution mediated dissolution-precipitation process. However, this conversion normally proceeds slowly [19,20].

A large amount of hydrotalcite-like compounds have been prepared by modifying both the layer composition and the anionic interlayer species, so it is possible to control the chemical composition and properties of the material and to prepare tailored materials for specific applications [21], such as $Mg–Al–CO_3$ hydrotalcite-like compounds [21], Co–Al hydrotalcite-like compounds [22] and $(Mg_{1-x}Ga_x(OH)_2)(CO_3)_{x/2}\cdot mH_2O$ hydrotalcite-like compounds[23], tetraborate-pillared hydrotalcite [24] and hydrotalcite-like anionic clays containing Zr^{4+} [25]. Additionally, the direct formation of layered hydrotalcite-like compounds has been reported to be possible on M^{2+}/Al_2O_3 interfaces at a broad pH range, where M refers to metals, such as Co, Ni, Zn, and Mg [26–29].

As a member of the layered double hydroxides family of inorganic layered materials zinc aluminum layered double hydroxide (Zn–Al LDH) were synthesized by various method. Liu et al. synthesized Zn–Al layered double hydrotalcite nanoplatelet at 60 °C via a facile solution phase process [30]. Paulhiac and Clause reported the surface coprecipitation of Co^{2+}, Ni^{2+}, or Zn^{2+} with Al^{3+} ions during impregnation of alumina at neutral pH ($6.5 < pH < 8.5$) and the generation of an Zn–Al hydrotalcite-like compound [23]. Gao et al. have successfully deposited a Zn–Al porous hydrotalcite film on an Al-bearing glass substrate based on an interface reaction between an Al layer and a zinc aqueous solution by a coprecipitation method [31]. Cho and coworkers synthesized hexagonal zinc aluminum hydroxide on Si substrate deposited by Zn via microwave irradiation method [33]. Koh and coworkers fabricated sheet-like and plate-like $ZnAlCO_3$ hydrotalcite on Si substrate precoated with a thin film of aluminum via hydrothermal method at 100 °C [32].

In the present study, the porous microspheres and network arrays of Zn–Al hydrotalcite-like compounds on Al substrate were synthesized via a facile one-step hydrothermal approach at 70 °C. The influences of the concentration of sodium oxalate and reaction temperature on the morphology and growth of Zn–Al LDH were discussed in some detail. Additionally, the effects of proportional reducing the concentrations of Zn^{2+} and sodium oxalate on the morphology of Zn–Al LDH were also investigated. Furthermore, the effects of sodium acetate and its concentration on the morphology of Zn–Al LDH were studied. Using an Al substrate as the interface to the deposition of hydrotalcite-like compounds with high porosity makes it easy to employ various substrates with different shapes and properties and may be important for achieving practical and special applications. The method can be also extended to the production of other hydrotalcite-like compounds.

2. Experimental

All chemicals were of analytical grade and used as purchased without further purification. Aluminum foils (purity: 99.99%, thickness: 0.25 mm) were used as substrates. In a typical procedure to synthesize porous spherical Zn–Al hydrotalcite-like compounds, 30 ml aqueous solution of zinc acetate dihydrate ($Zn(CH_3COO)_2\cdot 2H_2O$, 0.035 M) and sodium oxalate ($Na_2C_2O_4$, 0.21 M) were prepared with stirring for 15 min. Then, the mixture precursor solution was added to a 50 ml Teflon-lined stainless steel autoclave. A piece of aluminum foil (1 cm × 1 cm) washed with diluted hydrochloric acid and deionized water was then put into the precursor solution before sealing. The autoclave was kept at 70 °C for 24 h. Finally, the aluminum foil was taken out of the solution, rinsed with ethanol and distilled water and dried in air.

The products were characterized using X-ray diffraction (Germany Bruker D8 Advance, Cu K_α radiation; $\lambda = 1.5418$ Å) for the crystallization identification. The morphology of the products was examined using scanning electron microscopy (FESEM, QUANTA FEG 250) equipped with an energy dispersive X-ray spectrometer (X-MAX50, Oxford). N_2 adsorption–desorption isotherms were obtained at 77 K using a multi-function adsorption instrument r(MFA-140 of Beijing Builde company). Before measurement, the samples were degassed under vacuum for 2 h at 110 °C. Specific surface area was calculated by Brunaur–Emmett–Teller (BET) method. Pore size distribution was derived from desorption branch by the BJH method.

3. Results and discussion

3.1. Effects of sodium oxalate

Fig. 1 shows the typical SEM images of Zn–Al LDH prepared using 0.035 M zinc acetate and 0.21 M sodium oxalate ($Zn^{2+}/Na_2C_2O_4 = 1{:}6$) on Al substrates. As a result, large quantities of spherical products with diameter of about 1 μm dispersed on the Al substrate (Fig. 1a). The enlarged SEM image in Fig. 1b shows that the microspheres are assembled by numerous interlaced curved nanoplates with thickness of about 50 nm. The EDS analysis reveals that these microspheres are composed of O, Zn and Al elements as suggested by Fig. 2b and c. The XRD pattern of the sample as shown in Fig. 3 indicates that all diffraction peaks can be indexed to $Zn_{0.71}Al_{0.29}(OH)_2(CO_3)_{0.145}\cdot xH_2O$ (PDF2 00-048-1021; space groups R3m, $a = 3.080$ Å, $c = 22.850$ Å) except