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Facile synthesis of ZnAl-layered double hydroxide microspheres with core–shell structure and their enhanced adsorption capability

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ABSTRACT

We have developed a simple solution route for the synthesis of hierarchical ZnAl-layered double hydroxide (ZnAl-LDH) microspheres with core–shell structure, which have great practical application as the efficient adsorbent for wastewater purification. The evolution of the morphology with time suggests that the hierarchical ZnAl-LDH microspheres formed by a stepwise growth mechanism. The results demonstrate that the as-prepared ZnAl-LDH microspheres exhibit more excellent adsorption capacity (523 mg/g) towards methyl orange in aqueous solutions as compared with the LDH microspheres previously reported, result of which is attributed to their enhanced surface area and suitable mesopore distribution. This work provides a promising approach for the synthesis of hierarchical porous materials with excellent adsorption capacity, which can be potentially used in wastewater treatment.

1. Introduction

Water pollution has become one of most serious problems with the rapid development of industrial field. It is desirable to develop an effective method to deal with wastewater purification. Nowadays, wastewater purification methods have drawn enormous interest, such as chemical techniques, biological process, adsorption and oxidation process [1–4]. Among these methods, adsorption takes advantages of low operating cost, high efficiency and low energy consumption, generally considered as the promising method for wastewater purification [5,6]. To date, different conventional adsorbents such as activated carbon [7], gel [8], metal oxides [9], clay [10], etc. have been studied extensively and systematically. The key problem for fundamental and practical applications of adsorption, however, is low adsorption capability for most of conventional adsorbents. Therefore, developing a new adsorbent with higher adsorption capability is a current issue for both foundational research and practical application.

Very recently, layered double hydroxides (LDHs), a class of anionic clays, have been reported as promising adsorbent materials for wastewater treatment due to its layered structure, high porosity, high surface area, and interlayer anion mobility [11–14]. Some easily prepared LDHs for the removal of dyes, such as MgAl-LDH [11], MgFe-LDH [12], and CaAl-LDH [15] were studied in detail. Meanwhile, LDH microspheres with porous structures have attracted much attention for their excellent surface area and structural stability, which have exhibited their promising application in the adsorption. For example, Li et al. synthesized the sphere-like ZnAl-LDHs by a hydrothermal method [6]. Sasaki et al. used polystyrene beads as a template for synthesizing MgAl-LDH hollow spheres [16]. Nevertheless, several problems still remain unresolved. Many surfactants, known as the toxic organic compounds, were used in the procedures. Also, the obtained LDHs with a hollow structure provided less effective diffusion pathways of porous networks, largely influenced the enhancement of adsorption capacity of LDH microspheres.

It has been believed that the nucleation could be affected by the concentration of urea [17]. And controlling the stirring speed is a simple route to adjust the decomposition of urea. Herein, we first report an efficient method for the synthesis of ZnAl-LDH microspheres with core–shell structure. By adjusting the stirring speed and controlling the reaction time, the structure of the resulted products can be tailored from 2D lamellar structure to 3D hierarchical microspheres. The influence of reaction time on the morphology and structure of the microspheres has been investigated. Then the adsorption capabilities of the microspheres, and their abilities to remove methyl orange (MO) from wastewater, were evaluated. This work provides a facile approach for synthesizing the LDH microspheres with high adsorption capacity and enlarges the application of new adsorbents for wastewater purification.

2. Experimental

Synthesis of ZnAl-LDH microspheres: typically, the desired amounts of $ZnCl_2$, $AlCl_3$ and urea were dissolved into 1 dm^3 of DI

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water to yield a mixed solution containing up 7 mM $ZnCl_2$, 3 mM $AlCl_3$ and 48 mM urea. For preparing the LDH precursors, the mixed solution was stirred with 300 r min^{-1} for 4 h at the refluxing temperature (100 °C). Then the mixtures were kept under 50 r min^{-1} for 9 h. The obtained products were washed with DI water and ethanol several times, and dried at 80 °C for 12 h.

Characterization: field emission scanning electron microscopy (FESEM) was conducted on a Nova NANOSEM 430 scanning electron microscope. High resolution transmission electron microscopic (HRTEM) images were received from a JEOL2100 microscope. X-ray diffraction (XRD) analysis were performed on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ=0.1542 nm). The surface area was evaluated by a multipoint Brunauer-Emmett-Teller (BET) method, and the pore size distribution was determined by the Barrett-Joyner-Halenda (BJH) method, performed using a Quantachrome NOVA 2200e analyzer. Adsorption experiments were carried out by the method previously reported [6]. Absorbance was performed using a UV–visible spectrophotometer at 466 nm. The equilibrium adsorption capacity (q_e) and the adsorption efficiency (R) were evaluated.

3. Results and discussion

FESEM and HRTEM were firstly employed to investigate the formation process of ZnAl-LDH microspheres with core–shell structure. As seen in Fig. 1a, the typical disk-like LDH sheets, as the as-prepared precursors, were obtained with 300 r min^{-1} after 4 h. Then, the stirring speed was adjusted to 50 r min^{-1}. As the reaction time was extended to 3 h, those LDH precursors were regarded as the cores, and the numerous nanoflakes ceaselessly grew on the edge and surface of LDH precursors through the self-assembly of the nanoplates. The HRTEM observations (Fig. 1b(II) and c(III)) also indicates that nanoflakes began to form on the edge of LDH precursors. For a longer reaction time (5 h), many nanoflakes completely covered on the surfaces of LDH sheets to form a flat template with core–shell structure, which coincided with the HRTEM results (Fig. 1d(V)). When the reaction time was increasing to 7 h, the nanoflakes further grew on these flat templates, forming the irregular microspheres. With a further reaction to 9 h, the hierarchical microspheres with diameters of 12 μm can be clearly observed, shown in Fig. 1f and Fig. 1f(VI). Moreover, the nanoplates clearly intercrossed and penetrated reciprocally. Therefore, the evolution of the morphology with time suggests that the hierarchical ZnAl-LDH microspheres with core–shell structure formed by a stepwise growth mechanism.

The XRD patterns of these ZnAl-LDH samples are illustrated in Fig. 2a. A series of sharp and intense symmetric peaks appear at low 2θ values and clear (110) reflections are located at high 2θ values, indicating characteristic basal reflections of hydrotalcite-like LDH materials [18]. And the peaks at (003), (006), (101), (012), (009), (015), (018), (1010), (0111), (110) and (113) planes are observed, ascribed to the characteristic peaks of ZnAl-LDHs [6,19]. Moreover, other characteristic peaks are not detected. Such results demonstrate the precursors and the regenerated nanoflakes are typically ZnAl-LDH compounds.

According to the above observations, the formation process of LDH microspheres with core–shell structure can be roughly described as follows (Scheme 1). First, the nanoparticles constantly form through nucleation and growth, and then oriented attachment into the large-sized LDH precursors. Secondly, under the low stirring condition, the nanoparticles tend to the formation of some nanoplates. These nanoplates further assemble together in the edge and surface of the LDH precursors to form the flat templates and microspheres structures. Particularly, the electrostatic and hydrogen bonds might be the driving force for the self-assembly process due to the existence of OH^- groups [20]. Hence, the oriented attachment of adjacent nanoplates and a high density of

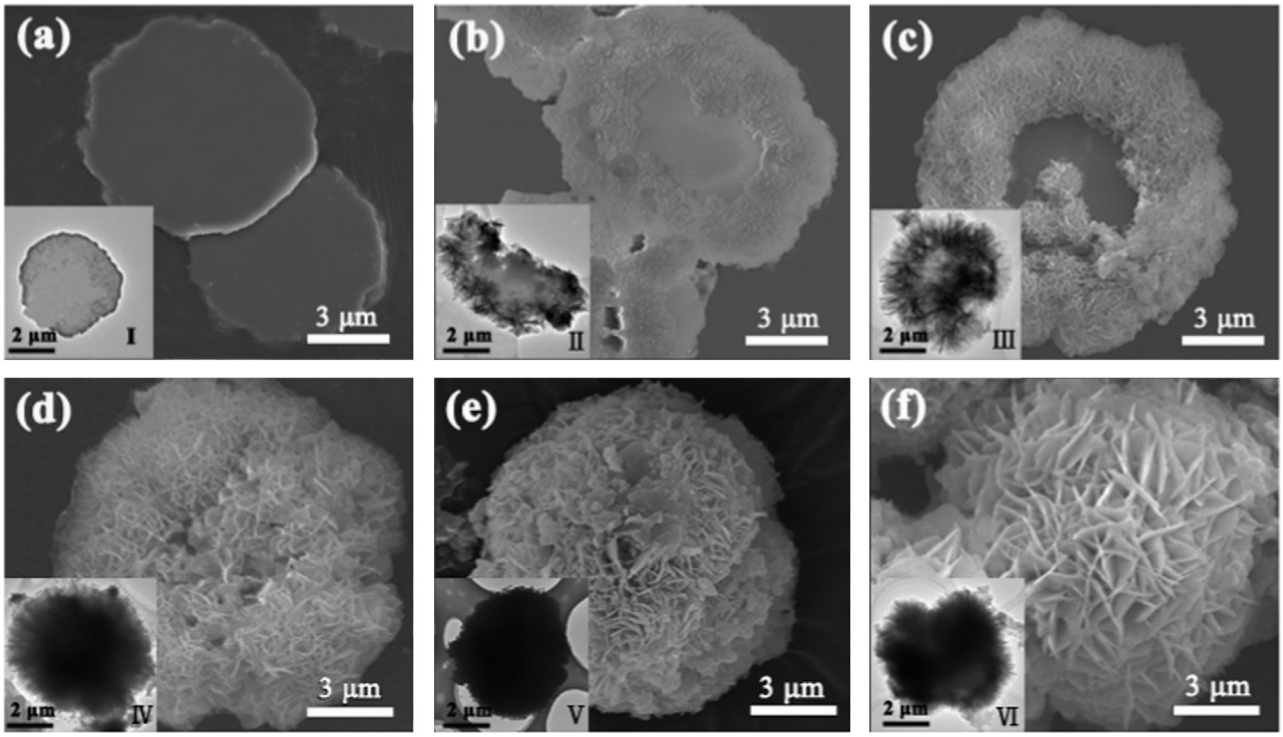

Fig. 1. FESEM and HRTEM images of the ZnAl-LDH samples synthesized with different reaction times: (a) precursors; (b) 1 h; (c) 3 h; (d) 5 h; (e) 7 h; (f) 9 h.