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Hierarchically nanostructured shuttle-like aragonite mesocrystals: Preparation, characterization, growth mechanism, and removal ability to La(III)

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ABSTRACT

Hierarchically nanostructured Shuttle-like aragonite mesocrystals have been successfully achieved in a water/ethylene glycol (EG) binary solvent system by a facile microwave-assisted method without using any other organic additives. The synthesized products were characterized by a wide range of techniques including X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and nitrogen physisorption analysis. The effects of the ratio of EG to water, and calcium sources on the formation of the special structured aragonite were studied systematically. The results indicate that the cooperation of EG and acetate ions are indispensable to the formation of shuttle-like aragonite mesocrystals, and a plausible oriented attachment formation mechanism is proposed. Moreover, the removal ability of the hierarchical aragonite mesocrystals for La(III) was also tested. Batch experiments reveal that the aragonite possesses excellent removal efficiency to La(III), suggesting that the shuttle-like aragonite mesocrystals can be potentially applied in the removal of rare earth elements (REEs) entering the water environment.

1. Introduction

Calcium carbonate ($CaCO_3$), occurring geologically as main mineral constituents of sedimentary rocks and biologically as inorganic components in the skeletons of many mineralizing organisms, is one of the most abundant minerals, and widely used in the areas of plastics, rubbers, papermaking, biomedical implant, drug delivery and wastewater treatment [1–5]. It has three anhydrous crystalline polymorphs: rhombohedral calcite, orthorhombic aragonite, and hexagonal vaterite [6]. The basic differences among the three crystalline polymorphs lie in the disposition of the carbonate ions with respect to the central Ca^{2+} ions in their respective unit cells [7]. Under ambient conditions, calcite is the most stable and thus abundant in nature, aragonite is metastable, while vaterite is the least thermodynamically stable. Aragonite and vaterite can rapidly transform into calcite or aragonite in aqueous solution [8]. Aragonite was often found as a natural component present in fish otoliths, human brain stones, gallstones, and the nacreous layer of mollusc shells, and the sustained interest in aragonite is increasing [9,10]. The applications of $CaCO_3$ are usually decided by a number of strictly defined parameters, such as morphology, structure, size, specific surface area, brightness, chemical purity and so on, which depends on the method of preparation [11]. Compared to conventional morphologies, the inorganic materials with hierarchical structures based on the construction of nanounits (nanowires, nanosheets, nanoneedles, nanobelts or nanotubes) usually have much greater importance in basic scientific research and potential technological applications [12–14]. Moreover, the morphology control of $CaCO_3$ is also an important issue in biomineralization and biomimetic mineralization [15,16]. Thus, the fabrication of $CaCO_3$ crystals with complex structures has received much attention in recent years [17–20].

Crystallization of calcium carbonate in biological systems is known to produce minerals with specific morphologies, hierarchically organized structures and remarkable mechanical

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properties [21]. Inspired by the biomineralization, hierarchically structured $CaCO_3$ with specific morphologies has been usually produced by means of various biomimetic pathways [22–25]. For example, films of calcium carbonate have been obtained in vitro with the coexistence of poly(acrylic acid) and a specific substrate [23–25]. Huang and Zhang reported that aragonite nanorod aggregates with unusual morphologies were produced with the help of natural fibrous proteins [26]. Kotachi et al. prepared planar crystals of aragonite-type carbonates on an insoluble polyalcohol substrate with silicate anions [27]. Wang et al. fabricated the vaterite mesocrystals with a hexagonal prism structure in the presence of sodium citrate and sodium dodecyl benzenesulfonate [28]. Other methods including the CO_2 bubbling method [29], additive-mediated crystallization method in reverse microemulsions [30], surfactant- or template-assisted method [31], and bacteria-mediated route [32], have also been reported to prepare hierarchical structured $CaCO_3$ with special morphologies. Noteworthily, our group first reported the synthesis of aragonite mesocrystals in the absence of organic templates and/or additives via a 3D oriented attachment of aragonite microrods [19]. However, seeking facile, fast and environment friendly method to fabricate $CaCO_3$ with complex morphologies and structures is still a challenge and fascinate many researchers.

Since 1986 the microwave-assisted chemical synthesis was first reported [33,34], Microwave (MW) synthetic method has been demonstrated to be straightforward, fast, efficient, and environmental friendly preparation method [35,36]. With the assistance of microwave-irradiation, our group has successfully synthesized hierarchical nanospheres of ZnS, flower-like β-FeSe microstructures, various hierarchical nanostructures of copper sulfide, monodisperse pyrite microspherolites [37–40]. Recently, vaterite with various morphologies and architectures has also been prepared by microwave-assisted method, and the microwave radiation was found to play key roles in controlling the crystal polymorphs and morphologies of $CaCO_3$ in the precipitation process [20,41]. Generally speaking, the microwave power, heating frequency, and on/off irradiation cycles are the main heating parameters of a microwave reactor, and each of them may have a great effect on the structure and properties of the products [20,41]. In addition, many investigations have revealed that ethylene glycol (EG) is an effective reaction medium due to its special physical and chemical properties [42]. In particular, polyol solvents are very suitable for microwave-assisted reactions because of their relatively high dipole moment [40]. Therefore, microwave-assisted polyol method can be potentially applied to synthesis of metastable aragonite with hierarchical structures.

Moreover, in recent decades, as the rapid increase in the exploitation of rare earth elements (REEs) resources and its wide application to modern industry and daily life, vast REEs enter the environments [43]. The REEs entering the environments are known to accumulate in the human body when inhaled or digested from food chain, and cause adverse health effect [44]. For instance, trivalent ions, such as La(III) and Gd(III), can interfere with calcium channels in human and animal cells [45]. Therefore, the recovery and separation of rare earth elements become more and more important and attract great concern [46–49]. Lanthanum is one of the most abundant REEs, and is practically used as metal, catalytic, and fluorescent materials [47]. The chemical behavior of lanthanum has been considered typical of REEs and some trivalent actinides as well [49]. Techniques, including reduction and precipitation, solvent extraction, ion exchange, and sorption have been proposed and reported for the removal of heavy metals. Among these methods, sorption has been suggested as the most facile and efficient method to remove heavy metals [50–52]. Many studies also demonstrated that calcium carbonate minerals could be a potential cost-effective replacement for activated carbons, due to their omnipresence in nature and high sorption affinity to most heavy metals [5,53]. Moreover, aragonite is a powerful sorbent for cadmium and lead in aqueous environments, and shows much higher sorption capacities than calcite, due to its higher solubility and dissolution rate [53,54].

Herein, we report the preparation of shuttle-like aragonite mesocrystals in EG/water system without any organic additives or templates by a facile microwave-assisted reflux method. The effects of the ratio of EG to water, different calcium resources, and heating methods on the formation of the special structured aragonite are studied systematically. Moreover, the removal ability to La(III) of the aragonite is also evaluated.

2. Experimental methods

2.1. Materials and chemicals

All chemical reagents were of analytical grade and used as received without any further purification. Calcium acetate monohydrate ($Ca(CH_3COO)_2{\cdot}H_2O$), Calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$), Calcium dichloride dehydrate ($CaCl_2{\cdot}2H_2O$), sodium carbonate (Na_2CO_3), ethylene glycol (EG), $La(NO_3)_3$ (mw = 324.9), and commercial calcite were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used in all preparations. A microwave-reflux synthesis system (WBFY-201, Yuhua, China), with cycle period of 22 s, output power of 800 W, working frequency of 2.45×10^9 Hz, was used for the preparation of samples. The microwave reactor could operate at 10%, 30%, 50%, 80%, and 100% of full power by changing the on/off duration of the microwave irradiation on cycle model.

2.2. Synthesis of shuttle-like aragonite with hierarchical structure

In a typical synthetic process, 0.35 g (2 mmol) of $Ca(CH_3COO)_2{\cdot}H_2O$ was dissolved in 20 mL of ethylene glycol (EG) in a 100 mL round-bottomed flask by ultrasonication to form solution A. Then, 0.21 g (2 mmol) of Na_2CO_3 was dissolved in 2 mL of deionized water to form solution B. Solution B was introduced into solution A, leading to a volume ratio (R) of EG to water 10/1 (i.e., R = 10). Meanwhile the mixed solution quickly became turbid, indicating the formation of $CaCO_3$. The round-bottomed flask was then equipped on the microwave reactor, irradiated for 10 min at 50% of the full power. After cooling to room temperature, the precipitates were collected and washed by alcohol several times, and finally dried at 40 °C overnight in a vacuum oven. Moreover, the reaction media with different R values were achieved by varying the volumes of the polyol and water after keeping total volume constant.

2.3. Characterizations

Several analytical techniques were used to characterize the synthesized products. The powder X-ray diffraction (XRD) patterns of as-synthesized samples were recorded with a Japan MapAHF X-ray diffractometer equipped with graphite-monochromatized Cu Kα irradiation (λ = 0.154056 nm). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer at room temperature. The morphology and microstructure of the samples were observed with a JEOL JSM-2010 field-emission scanning electron microscope (FESEM). Before the FESEM observation, the samples were loaded on a copper foil, and then sprayed by platinum (Pt). Energy-dispersive X-ray spectroscopy (EDX) analyses were obtained with an EDAX detector installed on the same FESEM. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed on a JEOL-2010 (JSM) microscope at an accelerating