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Facile synthesis and characterization of hydrophobic vaterite $CaCO_3$ with novel spike-like morphology via a solution route

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ABSTRACT

Hydrophobic spike-like vaterite $CaCO_3$ composed of nanoparticles with an average size of 100 nm has been successfully synthesized via a simple synthetic method. The crystallization of vaterite $CaCO_3$ was fabricated by the reaction of $CaCl_2$ with Na_2CO_3 in ethanol–water solvents in the presence of oleic acid. The as-prepared products were characterized by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and contact angle analysis. The characterization results revealed that oleic acid played an important role in determining the phase and morphology of the sample. In addition, the surface properties of the vaterite $CaCO_3$ changed from hydrophilic to hydrophobic. The contact angle of the modified $CaCO_3$ reached 95.8°.

1. Introduction

Calcium carbonate is an important biological material that has widespread potential applicability in the fields of rubber, paper, plastic and ink industries. Calcium carbonate ($CaCO_3$) can crystallize as calcite, aragonite, and vaterite. Vaterite, a least stable polymorph, will transform into thermodynamically stable forms when in contact with water. Therefore, only a trace amount of vaterite exists in nature as a natural mineral. However, vaterite is expected to have potential applications for various purposes because it has unique properties such as high solubility, high dispersion, high specific surface area and lower specific gravity compared with the other two crystalline forms [1,2]. Over the past years, several methods have been developed for controlling the growth of vaterite, including slow gas diffusion techniques [3–6], microemulsion [7] and microwave-assisted methods [8]. In addition, the shapes of $CaCO_3$ nanoparticles influence their potential application [9,10]. For example, cubic $CaCO_3$ nanoparticles have been applied as fillers and reinforcing materials [11,12]. Currently, controlled morphology studies on vaterite $CaCO_3$ have received much attention in recent years. Sub-micron-sized vaterite tubes could be formed through nanobubble-templated crystal growth [13]. Vaterite nanowires were reported through the interaction of a polyelectrolyte with a self-assembled organic monolayer [14]. Nanorods of vaterite have been synthesized for the first time by the microemulsion method using CTAB as cationic surfactants [7]. Dagger-like vaterite particles have been prepared by a fast microwave-assisted method [8]. Unfortunately, the methods mentioned above are not suitable for producing various morphologies of vaterite $CaCO_3$ that can be dispersed easily in certain solvents. Surface modification of $CaCO_3$ with hydrophobic species would lead to a great expansion in its applications. Thus, it is desirable to develop a single synthetic approach to provide hydrophobic, shaped-controlled vaterite $CaCO_3$ nanoparticles under mild conditions for practical large-scale production.

In this paper, we report a solution route, that is, a chemical co-precipitation method, for the synthesis of hydrophobic spike-like vaterite $CaCO_3$ for the first time. Oleic acid was used as crystal growth modifier.

2. Experimental

All chemicals used were of analytical grade and purchased from the commercial market without further purification. Hydrophobic spike-like vaterite $CaCO_3$ was prepared by a chemical co-precipitation method. $CaCl_2$ (0.5550 g, 5 mmol), oleic acid (0.2824 g, 1 mmol) and 100 mL absolute ethanol were placed in a flask and the mixture was vigorously stirred to give an optically clear solution. A freshly prepared aqueous solution (100 mL, 0.05 M) of Na_2CO_3 was carried out dropwise (approximately one drop per second) to the flask under strong stirring. Subsequently, an obviously turbid solution was obtained, indicating the formation of $CaCO_3$. The system was stirred at room temperature for 2 h for the growth of $CaCO_3$ nanoparticles. Then 100 mL petroleum ether was added and the mixture stirred for

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1 h, allowing the oleic acid-capped $CaCO_3$ nanoparticles to be transferred into the petroleum ether layer. The upper phase of transparent white petroleum ether was collected and mixed with an excess amount of acetone to precipitate the formed $CaCO_3$ nanoparticles from the resulting solution. Then the precipitate white products were collected by centrifugation, washed with absolute ethanol and finally dried in a vacuum oven at 60 °C for 12 h.

The phase of the products was characterized by X-ray powder diffraction (XRD, RigaKu D/max-RB, Japan, Cu Kα radiation, $\lambda = 1.54056$ Å) and Fourier transform infrared spectroscopy (FT-IR, IFS66V/S, Germany). Field emission scanning electron microscopy (FESEM, JSM-6701F type) and transmission electron microscopy (TEM, JEOL JEM 1200, accelerating voltage = 100 kV) were used to characterize the size and morphology of the products. In order to study the surface characteristic, the contact angle of water on the products was measured by the sessile drop technique with a DSA100 (Germany) contact angle analyzer. The powdery samples were prepared under 14 MPa of pressure by compressing, under controlled conditions, 200 mg of $CaCO_3$ in a typical IR die. Then the pellets were dried in a vacuum oven at 100 °C for 24 h.

3. Results and discussion

The phase of the synthesized $CaCO_3$ was identified by XRD characterization. Fig. 1a and b shows the XRD patterns of the $CaCO_3$ obtained in the absence and presence of oleic acid, respectively. Fig. 1a can be indexed as a mixture of vaterite and calcite by comparison with their respective standard JCPDS files (vaterite, 33-0268; calcite, 83-0578). Fig. 1b can be indexed as pure vaterite with a hexagonal structure (JCPDS 33-0268). The phase of the product is further confirmed by FT-IR in Fig. 1c and d. Fig. 1c shows that the characteristic peak of vaterite is at 745 cm^{-1} and those of calcite are at 713 cm^{-1} and 1082 cm^{-1} [15]. It can be concluded that a mixture of calcite and vaterite crystals was obtained in the absence of oleic acid. Fig. 1d shows a strong band at 745 and 877 cm^{-1}, which indicates pure vaterite formation in the presence of oleic acid. The results of XRD and FT-IR show that oleic acid can be used as additives to stabilize vaterite.

The morphology and size of the products were examined by FESEM. It can be seen from Fig. 2a that monodisperse rhombohedra calcite and irregular vaterite particles were produced in the absence of oleic acid. Fig. 2b presents a typical SEM image of the product obtained in the presence of oleic acid. It can be seen that the product is a spike-like structure with excellent dispersibility. The average length and diameter of the spike-like structures are found to be ~2 μm and ~420 nm, respectively, though some even larger and smaller spike-like structures are occasionally found. High-magnification FESEM in Fig. 2c shows that spike-like vaterite $CaCO_3$ is composed of many irregular nanoparticles with an average size of 100 nm. FESEM results indicate that oleic acid plays an important role in determining the morphology of $CaCO_3$. In our opinion, oleic acid polar groups act as active sites for $CaCO_3$ nucleation because of their electrostatic interaction with Ca^{2+}. Then, the electrostatic localization of Ca^{2+} caused the increase in CO_3^{2-} local concentration around the oleic acid aggregates. That is, the local concentration of Ca^{2+} and CO_3^{2-} around the aggregates is much higher than in bulk solution. Therefore, nucleation occurs at a much faster rate on the oleic acid aggregates than in bulk solution. In addition, the polarization of ethanol and water may facilitate anisotropic growth of $CaCO_3$ [16]. On the other

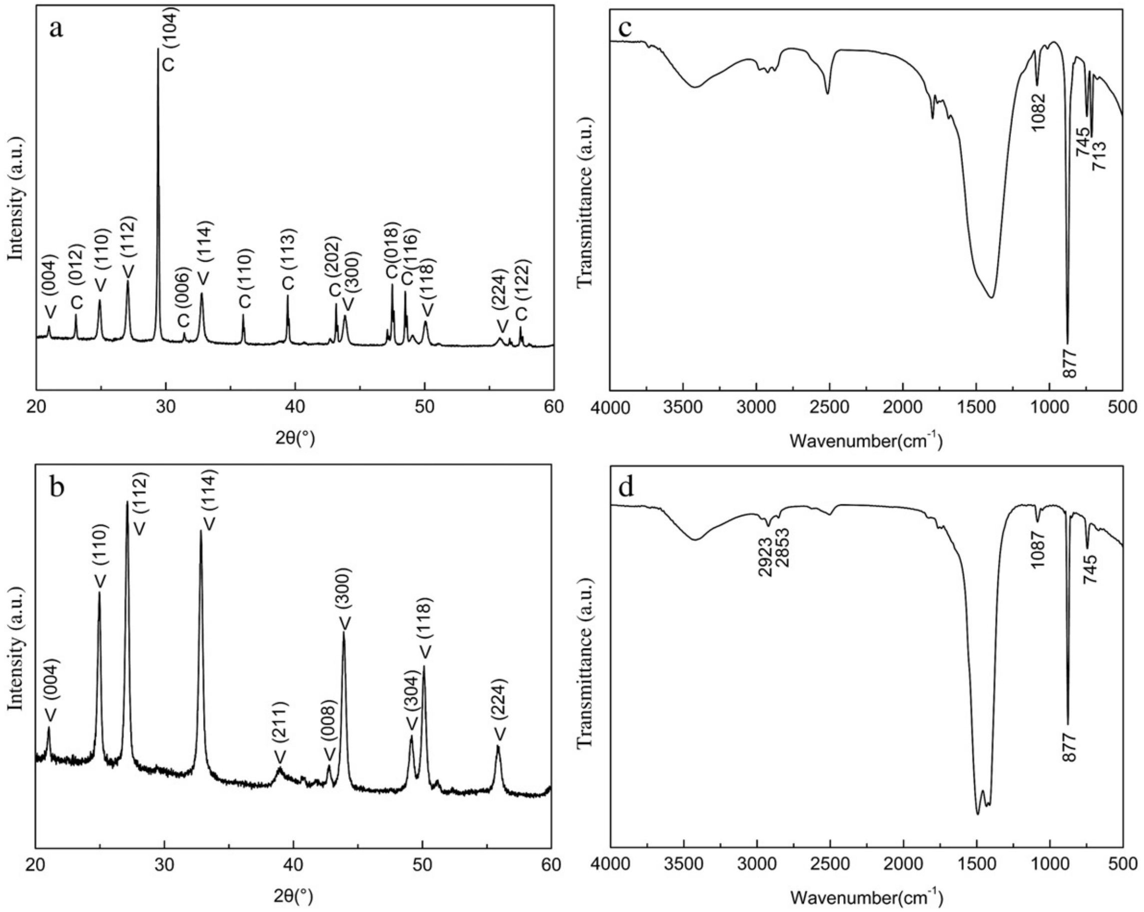

Fig. 1. XRD patterns (left) and FT-IR spectra (right) of $CaCO_3$ obtained (a, c) in the absence of oleic acid and (b, d) in the presence of oleic acid. C: calcite; V: vaterite.