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Effects of polyacrylic acid additive on barium sulfate particle morphology

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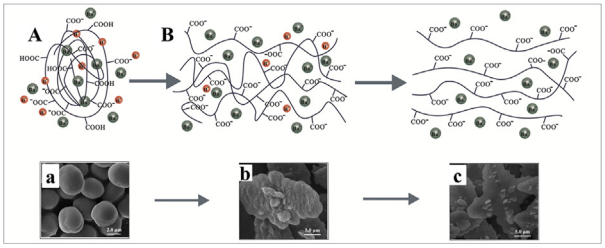
HIGHLIGHTS

- Polyacrylic acid (PAA) was used as a growth modifier to control micron-sized $BaSO_4$ particles.
- The PAA/$BaSO_4$ particles were exhibited various morphologies.
- Provide a preliminary understanding of the formation mechanism of $BaSO_4$ particles.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, polyacrylic acid (PAA) was used as a growth modifier to control micron-sized barium sulfate particles via a simple precipitation reaction between sodium sulfate and barium chloride at ambient temperature. The barium sulfate particles were exhibited various morphologies, such as monodisperse spheres, ellipsoids, rose-like aggregates, etc. To better understand the formation mechanisms of the various morphologies of these particles, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and thermo-gravimetric analysis (TGA) were employed. It was found that the PAA concentration, pH, and Ba^{2+} and SO_4^{2-} ions concentrations were the most important parameters controlling the morphology of the $BaSO_4$ particles. These parameters affected the $BaSO_4$ morphology by influencing the interactions between the PAA carboxyl groups and inorganic ions and the conformation change of the PAA molecular chains. Moreover, this work attempts to provide a preliminary understanding of the formation of the spherical $BaSO_4$ particles with the randomly coiled conformation of the polymer.

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1. Introduction

Currently, inorganic materials are widely used in various technological fields, such as catalysis [1,2], medicine [3,4], electronics [5,6], ceramics [7], pigments [8,9], cosmetics [10], papermaking [11] etc. The ability to control the size and morphological structure of synthetic materials is a key factor in their application [12]. In the

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synthesis materials, organic matrices, such as proteins and polysaccharides, play an important role in controlling the orientation, polymorphism, composition, and morphology of the mineral phase [13–17]. Inspired by the exquisite control that biological systems exert over the nucleation and growth of biominerals, the biological environment in these syntheses is used to regulate the mineral crystallization and growth [18,19]. In recent years, many organic additives have been used to induce crystal growth and control the morphological structure and crystallization of inorganic crystals [20,21].

Barium sulfate ($BaSO_4$) has been widely used as a model system for investigating inorganic precipitation reactions and crystallization because it crystallizes in a single phase [22]. $BaSO_4$ can be obtained in various unusual and well-defined morphologies via controlled crystallization [23–26]. Different organic additives have been used to control $BaSO_4$ crystallization to obtain $BaSO_4$ crystals of various sizes and morphological structures [27–29]. Very recently, we found that the presence of polyacrylic acid (PAA) during the crystallization of calcium carbonate [30–32] and calcium oxalate [33] particles strongly influenced their morphologies and crystal structures. Ouhenia et al. [34] obtained $CaCO_3$ particles with various morphologies, such as rhombohedral, spherical, cauliflower, and needle- and sponge-like morphologies, in the presence of PAA at different temperatures. Cölfen et al. [35,36] obtained $BaSO_4$ fiber in the presence of sodium polyacrylate (PAANa). Donners et al. [37] have reported that the small disturbance of the secondary structure of the polymeric template resulting from a change in the chirality of the polymer will have a great effect in crystalline morphology of $CaCO_3$.

In this paper, PAA was used as a growth modifier to control micron-sized barium sulfate particles of various morphologies via a simple precipitation reaction between sodium sulfate and barium chloride at ambient temperature. The effects of the experimental conditions, including the PAA concentration, pH, and Ba^{2+} and SO_4^{2-} ion concentrations, on the $BaSO_4$ morphology and crystallization were investigated and are discussed in the following sections. These parameters affect the $BaSO_4$ morphology by influencing the interactions between the PAA carboxyl (−COOH) groups and inorganic ions and the conformation change of the PAA molecular chains. Moreover, this work attempts to provide a preliminary understanding of the formation of the spherical $BaSO_4$ particles with the randomly coiled conformation of the polymer.

2. Material and methods

2.1. Chemicals and $BaSO_4$ synthesis

Analytical grade anhydrous barium chloride, sodium sulfate, ethanol, sodium hydroxide, and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Polyacrylic acid (average molecular weight ~240,000, 25 wt.% aqueous solution) was obtained from Sigma–Aldrich. Aqueous solutions of $BaCl_2$ (>96.0%), Na_2SO_4 (>99.8%) and NaOH (>96.0%) were prepared immediately before use. Deionized water with a relative resistivity greater than 18.2 MΩ cm at 25 °C was used in the experiments (Milli-Q Plus system, Millipore). All chemicals were used without further purification.

2.2. Preparation

In a typical synthesis, 64 mg of 25 wt.% PAA and a $BaCl_2$ aqueous solution (5 mM, 40 mL) were mixed according to methods reported in the literature [38] and stirred at 500 rpm for 10 min. The solution pH was adjusted with 0.1 M NaOH. Then, an Na_2SO_4 aqueous solution (Ba^{2+} and SO_4^{2-} were mixed in a 1:1 ratio during this step) was slowly added dropwise (30 drops per minute) to the $BaCl_2$/PAA solution under stirring at 500 rpm, and the resulting mixture was then maintained under static conditions for 1 h. The mixture was washed by repeated centrifugation, first with distilled water and then with absolute ethanol, and dried at 40 °C under vacuum for 24 h. In these experiments, the PAA concentration varied from 0.04 to 0.8 mg mL^{-1}, and the other experimental parameters, e.g., the pH, were also systematically adjusted. Control experiments in which the $BaSO_4$ precipitates were prepared in the absence of PAA under the same conditions were also performed. All experiments were conducted at room temperature.

2.3. Characterization

The samples were coated with Au before examining them with a QUANTA 200 scanning electron microscope (SEM) at an accelerating voltage of 15 kV. X-ray diffraction (XRD) patterns were obtained on a Rigaku TTR-III powder X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm, 40 kV, 120 mA). The crystal structure was analyzed in the 2θ range of 15–50° using a step size of 0.02°. The samples were placed on carbon mesh grids (200 mesh) for transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) (JEM-2200FS) experiments at an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) of the samples was performed using a TQ50 TGA analyzer purged with nitrogen gas.

3. Results and discussion

Fig. 1 shows the SEM images of pure $BaSO_4$ and PAA/$BaSO_4$ particles obtained at ambient temperature. The SEM image (Fig. 1a) of the pure $BaSO_4$ particles (5 mM $BaSO_4$) revealed blossom-like particles approximately 10–15 μm in size. The $BaSO_4$ crystal surfaces had multiple protruding areas (Fig. 1b). When the $BaSO_4$ particles were synthesized in the presence of 0.2 mg mL^{-1} PAA, they had a monodisperse spherical or ellipsoidal morphology. In addition, the particle size was reduced to approximately 2–4 μm, and the $BaSO_4$ crystal surfaces were smooth (Fig. 1c and d).

To further characterize the crystalline structure, the samples were characterized by bright-field TEM and the corresponding selected area electron diffraction (SAED) experiments (Fig. 2). The TEM image of the pure $BaSO_4$ crystals (Fig. 2a) revealed irregular, square blocks. The SAED pattern of these crystals (Fig. 2b) indicates that they were polycrystalline, and the SAED diffraction spots were indexed as the (200), (211), (221) and (212) reflections of the $BaSO_4$ crystal. The HRTEM image of the crystals provides further insight into their nanostructure, as shown in Fig. 2c. The distance between the lattice fringes of the nanoparticles was approximately 4.34 Å, which corresponds to the d spacing of the (101) planes of the $BaSO_4$ crystal and confirms the formation of $BaSO_4$. This result is consistent with the XRD results (Fig. SI-2). The TEM image of the PAA/$BaSO_4$ particles (Fig. 2d) shows ellipsoidal morphology. The SAED pattern of the PAA/$BaSO_4$ crystals (Fig. 2e) exhibited a polycrystalline concentric ring structure, and the SAED diffraction spots were indexed as the (211), (121), (002) and (212) reflections of the $BaSO_4$ crystal. The distance between the lattice fringes of the PAA/$BaSO_4$ particles was approximately 3.10 Å, which corresponds to the d spacing of the (121) planes of the $BaSO_4$ crystal [27] and confirms the formation of $BaSO_4$. This result is consistent with the XRD results (Fig. 4).

3.1. Effect of the PAA concentration

At a $BaSO_4$ concentration of 5 mM and pH 3, the morphology and size of the $BaSO_4$ crystals were effectively controlled by the PAA

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