Microemulsion Synthesis of Nanosized Calcium Sulfate Hemihydrate and Its Morphology Control by Different Surfactants

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Supporting Information

ABSTRACT: Calcium sulfate hemihydrate with different structures and morphologies has a broad scope of applications. Herein, we reported a strategy for nanosized calcium sulfate through room-temperature microemulsion by using calcium carbonate and sulfuric acid. After characterizations, it was indicated that the morphology of calcium sulfate products fabricated could be changed and controlled using different surfactants TritonX-114, SDBS, and CTAB by the microemulsion method. The method demonstrated in this work would be a benefit for the synthesis of nanomaterials with special structures in the future.

INTRODUCTION

Calcium sulfate as a common mineral salt has been widely used in molding, the construction industry, sewage purification, and drug delivery due to its excellent workability, high strength, biocompatibility, and biodegradability.1–5 As nanoscience and nanotechnology prosper today, many chemists, materials scientists, and engineers have put in tremendous efforts to understand new phenomena and develop technologies in nanomaterials.6,7 Major contributions to the development of nanomaterials have been made by chemists working primarily on the theme of their nanostructures and functionalization using both room-temperature solution-based routes and thermodynamics methods.8,9 Calcium sulfate with various morphologies and sizes has been gradually studied in recent years.10–14 Kong et al.15 fabricated α-calcium sulfate hemihydrate nanowires in reverse microemulsions, while α-calcium sulfate hemihydrate nanowhiskers were reported by Hou and his partners.16 Zhang et al.17 reported a method for α-calcium sulfate hemihydrate with a low aspect ratio using high-gravity reactive precipitation combined with a salt solution method at atmospheric pressure. Except for high-temperature or pressurized solution-based routes, calcium sulfate nanomaterials fabricated via room-temperature methods have still been challenges.

Microemulsion-based synthesis is a potential method without expensive or specialized instruments, in contrast to several physical methods such as plasma synthesis, ball milling, and chemical vapor deposition.18,19 Moreover, the microemulsion method is one kind of room-temperature route that is exploited to tailor and remodel nanoparticles. Microemulsion in solution acts as a dynamically stable phase, which mostly benefits from different surfactants and external controllable driving fields such as a mechanical or thermodynamic field.20,21 Microemulsions can be found in most surfactant systems in which both oil and water diffusions are uninhibited and only moderately reduced compared to that in single liquids. The knowledge of factors for microemulsions enables one to choose surfactants for desired applications especially in the synthesis of nanomaterials with controlled sizes and shapes. From recent studies, different types of surfactants have been used in microemulsion formation, which include anionic, cationic, and nonionic surfactants.22,23 On the other hand, the room-temperature microemulsion method for nanomaterials has potential because of the confinement during the formation process of particles. Crystal growth in microemulsions is also a complex process that involves the interplay of crystal growth kinetics and thermodynamics in the multiphase system.

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Herein, calcium sulfate has been successfully synthesized through a room-temperature microemulsion method. During the synthesis of nanosized calcium sulfate, three different types of surfactants have also been studied in this work such as TritonX-114, SDBS, and CTAB, shown in Scheme 1. This work deepens the strategies for nanosized calcium sulfate and presents interesting applications in the future.

**RESULTS AND DISCUSSION**

Surfactants play a crucial role in stabilizing the immiscible oil/water phase by lowering the interfacial tension to form microemulsions. A variety of surfactants categorized as cationic, anionic, nonionic, and zwitterionic depending on the type of charge on their head group is known. During the synthesis of nanosized calcium sulfate, cyclohexane and water work as a microemulsion system with surfactants at room temperature. The formation and growth of calcium sulfate through different surfactant-supported microemulsions are shown in the TEM images in Figure 1. In TritonX-114-supported microemulsion, calcium sulfate nanoparticles rapidly formed as nanocrystals with a size smaller than 5 nm, and the nanoparticles finally grew into a nanorod cluster with a diameter of more than 100 nm as shown in Figure 1a,b. Because of the nonionic nature of TritonX-114, the microemulsion played a role like nanoreactors, which restricted the growth of calcium sulfate. Meanwhile, in the SDBS-supported microemulsion process, calcium sulfate formed as nanowires, and then into clusters, and finally into whiskers, as shown in Figure 1c,d, mainly because of the anionic nature and functional groups of SDBS. In CTAB-supported microemulsion, calcium sulfate formed a quasi-spherical structure and increased in size as the particles grew. From the EDX spectra of those final products after drying in a vacuum oven, all those products were calcium sulfate with different surfactants on the final particles, shown in Figures S1 and S2. Combined with these TEM images, they indicated that different surfactants might control the final morphology of calcium sulfate in a room-temperature microemulsion-based method.

During synthesis, TritonX-114 acted as a nonionic surfactant in the microemulsion system, which could form and stabilize the partial environment during the reactions inside the microemulsion droplets, while SDBS acted as an anionic surfactant, and CTAB acted as a cationic surfactant. To gain information on the interactions between surfactants and particles, FT-IR spectra of final products were measured as shown in Figure 2. From Figure 2a, the bands at 3615, 3555, and 3398 cm$^{-1}$ could be assigned to O−H stretching of the −OH groups of TritonX-114 and crystal water segments of calcium sulfate. The bands at 1656 and 1620 cm$^{-1}$ could be assigned to C−H stretching, which indicated the presence of the TritonX-114 surfactant on the surface of particles. The band at 1141 cm$^{-1}$ could be assigned to $\nu_3$ SO$_4^{2-}$ stretching, and the bands at 666 and 595 cm$^{-1}$ could be assigned to $\nu_4$ SO$_4^{2-}$ stretching. Compared with Figure 2a, Figure 2b shows the bands at 3550 and 3416 cm$^{-1}$, which are assigned to O−H stretching of crystal water segments of calcium sulfate. The bands at other peaks are attributed to the same groups as those in Figure 2a.
The band at 1141, 666, and 595 cm$^{-1}$ could be assigned to O–H stretching and SO$_4^{2−}$ stretching. All those FT-IR data confirmed that the phases of the final products were calcium sulfate hemihydrate, which matched the recent report. The rigidity of the surfactant played a crucial role in the morphology of the product formed as well as the surfactant packing parameters and charge. It indicated that the interactions between surfactants and calcium sulfate largely depended on the nature of surfactants not only in the synthesis process of calcium sulfate but also in the final particles.

The XRD pattern of samples shown in Figure 3 confirmed the formation of calcium sulfate according to the pure calcium sulfate hemihydrate phase (JCPDS 041-0244) with the characteristic diffraction peaks at $2\theta = 25.45, 31.27, 32.11, 38.67, 41.40, 43.45, 49.28, 52.27, 55.75,$ and $62.31^\circ$, which could be indexed to (020), (204), (402), (024), (422), (033), (424), (040), (240), and (244), respectively. It indicated that room-temperature microemulsion synthesis of calcium sulfate gave a final product in the calcium sulfate hemihydrate phase. Composed of water and cyclohexane and surfactants, the microemulsion controls the growth of calcium sulfate especially in a lattice structure.

The TG pattern in Figure 4 showed a weight loss when samples were heated to 200 °C, which was assigned to the escape of crystal water after being dried at 60 °C for 4 h. Figure 4 a–c shows weight losses of 7.45, 8.46, and 9.44 wt %, respectively, which were assigned to the crystal water content of calcium sulfate hemihydrate. It was noted that this value was different from the crystal water content of 6.2 wt % in the pure calcium sulfate hemihydrate phase. Combining this with XRD patterns and TEM images, calcium sulfate through a room-temperature microemulsion method resulted in different morphologies but was of the same phase as calcium sulfate hemihydrate. It indicated that the room-temperature microemulsion method was successfully used in fabricating calcium sulfate hemihydrate, and the surfactants might work in the morphology control of calcium sulfate.

The DSC pattern of samples presented one typical hemihydrate crystal-water removal profile, the weight loss starting with an endothermic reaction with a peak temperature at 160.4 °C followed by an exothermic reaction with a peak at 168 °C, shown in Figure 5c, which is a little different to those in Figure 5a,b. It indicated the calcium sulfate the surfactants present on the surface of calcium sulfate might affect the DSC pattern.
pattern indirectly, which exothermic reaction peak did not exist. Combining this with the XRD and TG pattern of the samples, those samples were all found to be calcium sulfate hemihydrate.

To evaluate the water solubility of calcium sulfates by different surfactants, 0.3 g of calcium sulfates was dissolved in 50 mL of deionized water, and the electrical conductance was recorded immediately as shown in Figure 6. At the first step of dissolution, the electrical conductance of all calcium sulfate samples was linear with $R^2 \approx 1$ in the first 400 s. It indicated that during the synthesis of calcium sulfate, surfactants might affect the crystallization structure, which resulted in water dissolution according to the electrical conductance data.

### CONCLUSIONS

In this work, nanosized calcium sulfate hemihydrate has been successfully fabricated through a room-temperature microemulsion method using calcium carbonate and sulfuric acid. Compared with different surfactants, TritonX-114, SDBS, and CTAB had taken advantage of the microemulsion method as well as the microenvironment during the reactions which finally fabricated nanosized calcium sulfate hemihydrate but with different morphologies. The control strategy provided an efficient and stable way of fabricating nanosized calcium sulfate hemihydrate and may be used for the synthesis of nanomaterials with a special structure in the future.

### MATERIALS AND METHOD

**Materials.** Analytical reagent-grade calcium carbonate (CaCO$_3$, 99.7%), sodium dodecylbenzene sulfonate (SDBS, 99.7%), polyoxyethylene mono-tert-octyl phenyl ether (TritonX-114, 99.7%), and cetyltrimethyl ammonium bromide (CTAB, 99.7%) were purchased from Sigma-Aldrich. Cyclohexane (99.5%), sulfuric acid (H$_2$SO$_4$, 99.5%), and anhydrous ethanol (99.5%) were purchased from Sinopharm Chemical Reagent. All reagents were used as received without further treatments. Deionized water was distilled with a Milli-Q water purification system.

**Preparation of Nanosized Calcium Sulfate by Surfactant TritonX-114.** Following recent reports, 18,27 nanosized calcium sulfate was prepared. First, 3 mL of 5 wt % TritonX-114 was dissolved in 20 mL of cyclohexane and stirred for 30 min, and 10 mL of 30 wt % H$_2$SO$_4$ aqueous solution was added into the mixture and continuously stirred for 3 h. Then, 0.3 g of CaCO$_3$ was added and continuously stirred for another 30 min. The suspension was centrifuged and washed immediately with anhydrous ethanol three times. The solid products were collected after being dried at 60 °C in a vacuum oven for 4 h, which were named CS-T.

**Morphology Control of Nanosized Calcium Sulfate by Surfactants SDBS and CTAB.** During this step, the process was the same as the preparation of nanosized calcium sulfate by surfactant TritonX-114; however, SDBS or CTAB was individually used as the surfactant instead of TritonX-114. The final solid products finally collected were named CS-S or CS-C.

**Characterization.** For transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images, the samples were recorded on a field-emission transmission electron microscope (JoelJEM-2001F) to measure the size and size distribution of particles by depositing them on carbon-coated copper grids (holey carbon, 200 mesh Cu) and leaving them to dry at room temperature. Powder X-ray diffraction (XRD) patterns were acquired on a D/MaxIIIA (Rigaku) diffractometer using Cu Kα radiation ($\lambda = 1.54 \text{ Å}$) in a 2θ range from 5 to 80° at a scan rate of 0.02° per step. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a simultaneous thermal analyzer (STA 499C, Netzsch) at a heating rate of 10 °C·min$^{-1}$ in a flowing nitrogen atmosphere from room temperature to 800 °C. Fourier transform infrared (FT-IR) spectra were obtained on an FT-IR spectrometer (Nicolet iS50) using KBr pellets. The electrical conductance (EC) was recorded on an EC meter (DDSJ-308F).

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00797.

EDX spectra of samples (a) CS-T, (b) CS-S, and (c) CS-C and their elemental content table from EDX spectra (PDF)

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**Notes**

The authors declare no competing financial interest.

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