Effect of EDTA and Phosphate on Particle Size during Precipitation of Nanosized $BaSO_4$ Particles

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Barium sulfate particles with average size of 16 nm and 203 nm were successfully synthesized by precipitation method at 25 °C. The characterization of $BaSO_4$ particles were performed by X-ray diffraction (XRD), transmission electron microscopy (TEM). It was found that the selected reaction conditions played an important role in controlling the size of particles. The difference in morphology of $BaSO_4$ particles mainly depends on the different additives during the precipitation process.

Barium sulfate is an important chemical industrial material which has extensive applications. For example, barium sulfate serves as filler in pigment, papermaking, and printing, rubber, dyestuff, and plastics to improve their functions.[1] Barium sulfate powder is added to pigment, which can enhance hardness and abradability of pigment.[2] The conventional method for preparing barium sulfate in industry is direct precipitation method. However, barium sulfate powder obtained is several micrometers in size and nonuniform by the above conventional method and has some defects in application. For example, in pigment, the outflow readily occurred.[3] In recent years, it is of great medical interest to synthesize uniform and ultrafine barium sulfate powder for X-ray gastrointestinal series requirement.[4] Barium sulfate particles with the diameter less than 200 nm have wonderful optical characteristics and flow behavior.[5]

In synthesis of nanosized inorganic particles. The liquid-phase method is the most popular since it is easy to control size and morphology of particles.[5] However, the aggregation of particles is a crucial question met in controlling particle size in liquid-phase method.[6] The additives have influence on both the nucleation and growth rates.[7] In the synthesis of nanosized particles, the size and morphology of particles are controlled usually by additives. Chen et al. synthesized spherical $BaSO_4$ nanoparticles using membrane dispersion precipitation.[5] Barium sulfate nanoparticles were synthesized also by reverse micelles and microemulsions.[8–10] However, these methods required complex process and long reaction time. In addition, a lot of surfactants were added to the reaction system. It was very difficult that they were separated from particles.

In this work, spherical barium sulfate nanoparticles were obtained by percipitation method with EDTA at 25 °C. The EDTA consumption was very small in synthesis process and consumed low energy. The submicronsized $BaSO_4$ particles were obtained in the presence of sodium hexametaphosphate. In addition, this research discussed the possible mechanism of formation of small sized barium sulfate particles.

Sodium sulfate of analytical grade purity was used without further purification. Barium sulfide (BaS) of industrial grade was purified before use. EDTA (99.0%) was purchased from Beijing Chemical Reagent Co. Sodium hexametaphosphate ($(NaPO_3)_6$) came from Shanghai Chemical Reagent Co. Ethanol of analytical grade purity was obtained from Tianjin Medicament Co. Water used in all experiments was distilled water.

After the optimization of experimental conditions, $BaSO_4$ particles were synthesized as following: On a water bath at 25 °C, 0.38 g of EDTA (or 0.1 g of $(NaPO_3)_6$) used as an additive was added to 80 cm^3 of 0.15 $mol \cdot dm^{-3}$ BaS solution under stirring to form transparent solution, then 60 cm^3 of 0.2 $mol \cdot dm^{-3}$ Na_2SO_4 solution was added without stirring, during which white precipitation appeared. The precipitation was filtered off under vacuum, then it was rinsed several times by water and ethanol, respectively. Finally, we obtained barium sulfate particles after drying the precipitation at 60 °C for 2 h under vacuum.

The phase structure and purity of particles were identified by X-ray diffraction (Y-4Q876909* 3KVX, Dandong, China) using Cu Kα ($\lambda = 1.54178$ Å) radiation at a scan rate of 0.03° $2\theta\,s^{-1}$. The accelerating voltage and applied current were 40 kV and 20 mA, respectively. The morphology and size of particles were characterized by transmission electron microscopy (H-600, Hitachi, Japan).

Figure 1 shows the XRD pattern of $BaSO_4$ particles obtained when using EDTA as an additive. All the sharp diffraction peaks can be indexed in the unit cell of barium sulfate (JCPDS 24-1035). These data implied $BaSO_4$ nanoparticles obtained had good crystallinity and had no obvious impurity. The XRD pattern indicated that orthorhombic crystal had been successfully synthesized.

The morphology and size of $BaSO_4$ particles obtained were characterized by TEM. Figure 2 shows the TEM photograph of $BaSO_4$ nanoparticles obtained with EDTA at the optimum reaction conditions. We can know it is sphere in morphology and the average diameter of the particles is about 16 nm.

In precipitation reaction, when reaction system reaches supersaturation, crystal nuclei are formed immediately. Crystalline grain grow gradually and form big cluster.[11] The definite

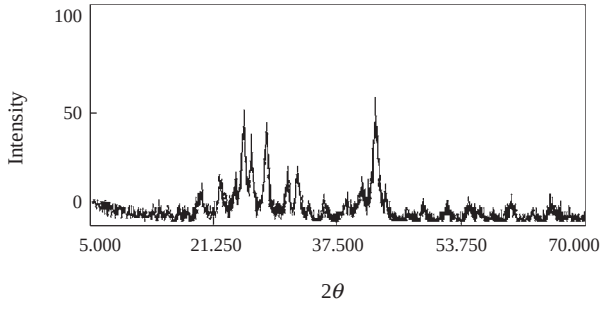

Figure 1. The XRD pattern of samples obtained with EDTA under optimum reaction conditions.

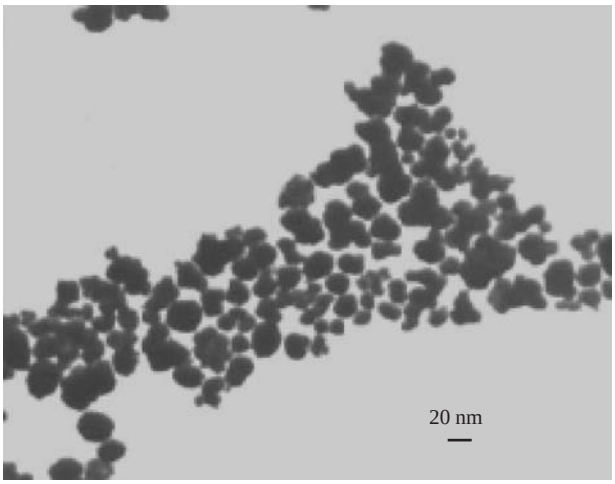

Figure 2. The TEM photograph of sample obtained with EDTA at optimum reaction conditions.

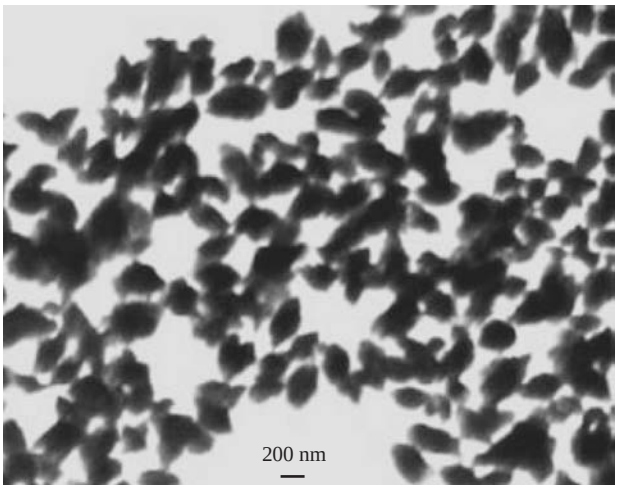

Figure 3. The TEM photograph of sample obtained in the presence of sodium hexametaphosphate.

separation of nucleation from growth stages is the primary requirement for uniform particles formation.[12] Addition of EDTA may favor the separation between the two stages.[13] EDTA is a strong chelator for many metal ions and reacts with M^{n+} (metal ions) to form stable M–EDTA complexes. In $BaSO_4$ precipitation reaction, EDTA was first added to BaS solution and formed Ba–EDTA complex, then Na_2SO_4 was added to the above BaS solution, causing $BaSO_4$ precipitation (with K_{sp} of 1.08×10^{-10} at 25 °C[14]). The complex of Ba^{2+} with EDTA reduces both in the nucleation process and in the nuclei growth[15–17] and has influence on the size and morphology of $BaSO_4$ particles.[7] Therefore, the addition of EDTA results in small particles size. From above discussion, it is easy to understand why uniform spherical barium sulfate nanoparticles were obtained using EDTA as an additive.

The additives can affect the nucleation and growth of particles and subsequently change particle morphology and size during precipitation process.[2,18] In this work, sodium hexametaphosphate served as another additive was investigated in barium sulfate precipitation process. The size and shape of particles are different from these of sample obtained in the presence of EDTA. The different shape implies the change tendency of morphology of $BaSO_4$ particles. Sodium hexametaphosphate may have weak influence on morphology of $BaSO_4$ particles.[7] It makes free growth of $BaSO_4$ particles. The TEM photograph of $BaSO_4$ particles obtained in the presence of sodium hexametaphosphate is shown in Figure 3. The shorter axis diameter was about 203 nm. The XRD pattern of $BaSO_4$ particles obtained in the presence of $(NaPO_3)_6$ was the same as Figure 1.

In summary, we successfully synthesized nano- and submicronsized $BaSO_4$ particles by liquid-phase precipitation method at 25 °C in the presence of EDTA and $(NaPO_3)_6$, respectively. The size and morphology of $BaSO_4$ particles can be controlled by addition of specific additives in the precipitation process. EDTA has stronger influence than $(NaPO_3)_6$ on size and morphology of barium sulfate particles. Therefore, the spherical $BaSO_4$ nanoparticles were obtained in the presence of EDTA.

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