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Technical note

Radiolytic synthesis of $BaSO_4$ microspheres

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Abstract

The solid $BaSO_4$ microspheres, mainly consisting of quasi-spherical nanoparticles, were successfully synthesized by precipitating Ba^{2+} ions with SO_4^{2-} ions, which were generated from the reduction of $K_2S_2O_8$ in the presence of EDTA under N_2 atmosphere by γ-irradiation. It was found that the controlled release of SO_4^{2-} played an important role in the formation of the microspheres.
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Keywords: Barium sulfate; γ-Irradiation; Controlled release; EDTA

1. Introduction

Barium sulfate ($BaSO_4$), commonly known as barite, has been widely used in many areas such as a filler and additive in polymers and paints (Qi et al., 1996; Qu et al., 2005), medicaments (Qi et al., 1996), catalyst carriers (Li and Yuan, 2006) and reflector material of optical devices (Heinrichs et al., 2002). Among the numerous $BaSO_4$ materials, $BaSO_4$ microspheres have attracted much attention (Qi et al., 2000; Yu et al., 2005). In addition, as one of the relatively simple inorganic materials, $BaSO_4$ has been used extensively for investigating the precipitation and crystallization processes (Coveney et al., 2000; Jones et al., 2006).

In general, $BaSO_4$ is synthesized by adding SO_4^{2-} ions directly into the solution containing Ba^{2+} or the complex of Ba^{2+} (Takiyama, 1958; Coveney et al., 2000; Qi et al., 2000, 2001; Uchida et al., 2000; Yu et al., 2005; Jones et al., 2006; Zhao and Liu, 2006). In addition, SO_4^{2-} ions can be added indirectly through the hydrolysis of dimethyl sulfate (Li and Yuan, 2006) and the reaction between $(NH_4)_2S_2O_8$ and $Na_2S_2O_3$ (Takiyama, 1959). So far, for controlling the size and morphology of $BaSO_4$ particles, surfactants (Li and Yuan, 2006), amino-carboxylate additives (Takiyama, 1958; Uchida et al., 2000; Zhao and Liu, 2006), phosphonate/phosphate inhibitors (Jones et al., 2006; Zhao and Liu, 2006), sodium polymethacrylate (Qi et al., 2000) and double-hydrophilic block copolymers (Qi et al., 2000, 2001) were used, as well as microemulsions (Qi et al., 1996; Hopwood and Mann, 1997). However, to the best of our knowledge, there is no report on the synthesis of $BaSO_4$ particles by ionizing radiation, which is an important method in the syntheses of nanoparticles (Belloni et al., 1998).

In our previous work, Ag and Cu nanoparticles (He et al., 2004; Chen et al., 2007a), octahedron Cu_2O nanocrystal (He et al., 2005), solid and hollow Cu_2O nanocubes (Chen et al., 2007b) in water-in-oil microemulsions and Ag-poly(4-vinylpyridine) hybrid microgels (Chen et al., 2006) in surfactant-free aqueous solution were successfully synthesized by γ-irradiation. Herein, we report the synthesis of solid $BaSO_4$ microspheres, mainly composed of quasi-spherical nanoparticles, in aqueous solution by γ-irradiation.

2. Experimental

An aqueous solution containing 4.0 mmol/L $Ba(NO_3)_2$, 4.0 mmol/L $K_2S_2O_8$ and 8.0 mmol/L disodium ethylenediaminetetraacetate (EDTA) was prepared. The pH value

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of the solution was measured to be 4.51. After bubbling with high-purity N_2 under anaerobic conditions for 20 min, the solution was irradiated in the field of a ^{60}Co γ-ray source. The dose rate was 20 Gy/min and the absorbed dose was 6 kGy unless otherwise stated.

After irradiation, white precipitates were obtained and washed with water, and then dispersed in water. The obtained dispersion was dropped onto a Formvar-covered copper grid placed on a filter paper. After the solvent was evaporated at room temperature, the transmission electron microscopy (TEM) images were conducted on a JEOL JEM-200CX microscope operated at 160 kV, and the scanning electron microscopy (SEM) images were obtained via a Hitachi S-4800 scanning electron microscope operated at 0.3 kV. The range of particle sizes was determined by measuring the dimensions of more than 100 particles on the micrographs. In addition, after the dispersed sample was deposited on a piece of glass, the powder X-ray diffraction (XRD) pattern was recorded on an X' Pert PRO MPD diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm) and the X-ray photoelectron spectrum (XPS) was collected on a Kratos Axis Ultra spectrometer with monochromatized Al Kα radiation.

3. Results and discussion

Fig. 1 presents the SEM images of the obtained sample. As shown in Fig. 1a, the product is composed of microspheres, with the diameter of 2–3 μm, besides the existence of a few fragments. From SEM image of a microsphere's cross-section (see the arrowhead in Fig. 1a) and the related SEM image in a higher resolution (Fig. 1b), it can be clearly seen that the microspheres are solid. The related XPS analysis (Fig. 2A) shows that the binding energies of Ba 3d, S 2p and O 1s are 779.51, 168.16 and 531.11 eV, respectively, close to the values of $BaSO_4$ reported in the literature (Moulder et al., 1992). Furthermore, the analysis result also exhibits the presence of Ba, S and O in the ratio of 1.0:0.9:4.0, close to the stoichiometry of $BaSO_4$ within experimental error. Thus, it can be deduced that $BaSO_4$ was generated.

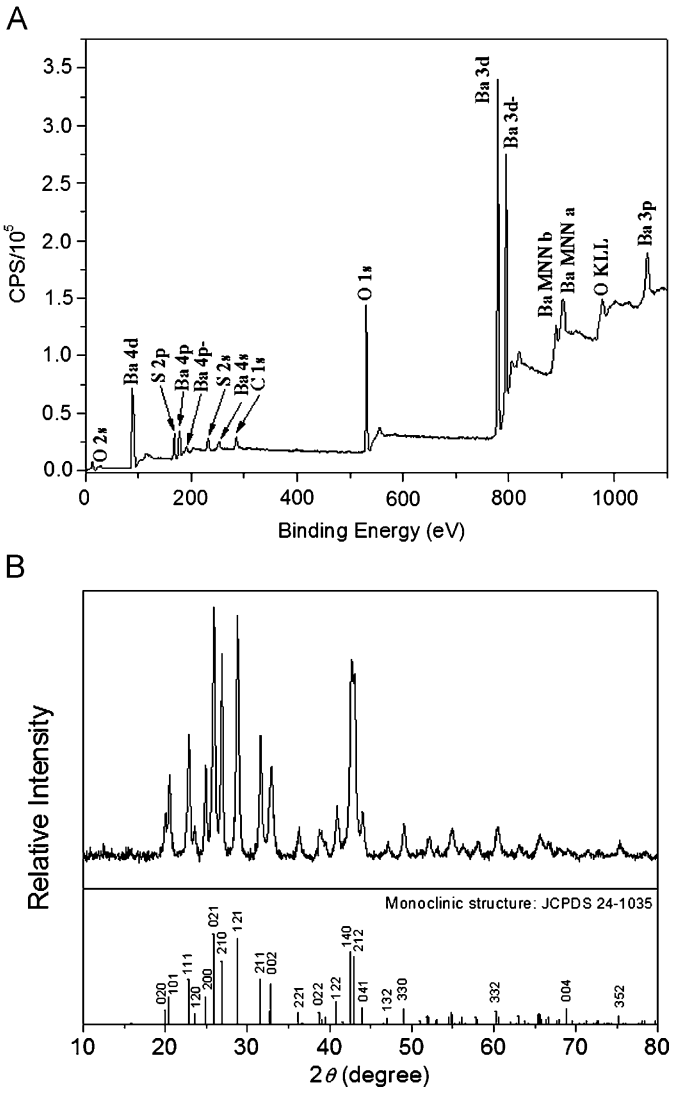

Fig. 2. X-ray photoelectron spectrum (A) and XRD pattern (B) of the same sample studied in Fig. 1.

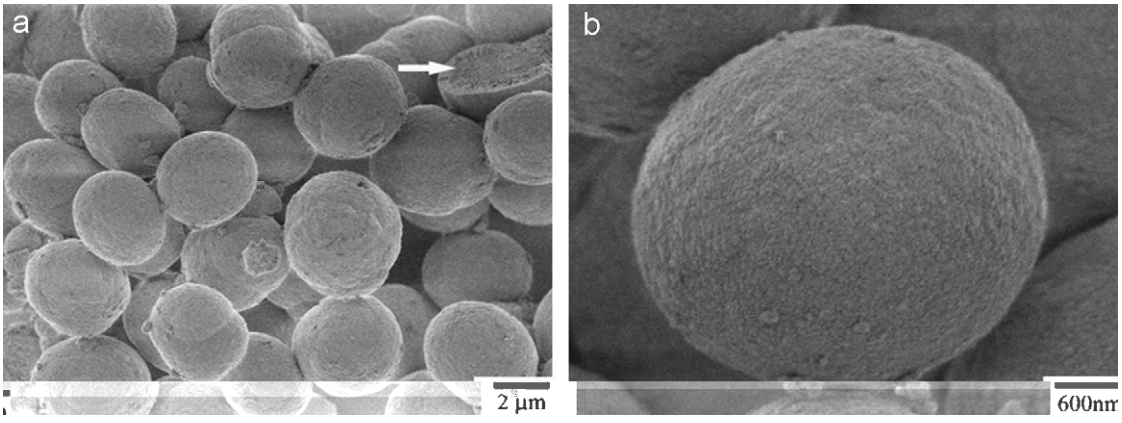

Fig. 1. SEM images of the sample synthesized by the irradiation of the mixed solution of 4 mmol/L $Ba(NO_3)_2$, 4 mmol/L $K_2S_2O_8$ and 8 mmol/L EDTA: (a) at 6000×, (b) at 25,000× magnifications.

The corresponding XRD pattern (Fig. 2B) that is consistent with the monoclinic $BaSO_4$ structure, further demonstrates the generation of $BaSO_4$. Moreover, it can be seen in Fig. 2B that the diffraction peaks are broadened to some extent, suggesting that the $BaSO_4$ microspheres consist of nanoparticles. To verify this deduction, the obtained sample was dispersed in water, and then sonicated at room temperature for 1 h to obtain the sample for TEM characterization. The TEM image presented in Fig. 3 clearly shows that some microspheres were disassembled to fragments constructed by a lot of quasi-spherical nanoparticles and a few irregular nanorods. This result confirms our speculation.

In our experiment, when the solution was irradiated by γ-rays, the water molecules absorbed the irradiation energy and generated many reactive species, such as hydrated electrons (e_{aq}^-), H and $^{\bullet}OH$ (Buxton et al., 1988)

$$H_2O \xrightarrow{\text{irradiated}} e_{aq}^-, H, {}^{\bullet}OH, {}^{\bullet\bullet\bullet}. \quad (1)$$

Then, $^{\bullet}OH$ was eliminated by EDTA (Sahul, 1987; Buxton et al., 1988), with a rate constant of $4.0 \times 10^8\ L\ mol^{-1}\ s^{-1}$ (Buxton et al., 1988), and the reducing species, especially e_{aq}^-, reduced $S_2O_8^{2-}$ ions to SO_4^{2-} ions, with a rate constant of $1.2 \times 10^{10}\ L\ mol^{-1}\ s^{-1}$ (Buxton et al., 1988)

$$S_2O_8^{2-} + e_{aq}^- \rightarrow SO_4^{2-} + SO_4^{-\bullet}. \quad (2)$$

Thus, the controlled release of SO_4^{2-} and the following generation of $BaSO_4$ could be realized. It may be the controlled release of SO_4^{2-} the controlled release of Ba^{2+} through the dissociation of Ba–EDTA complex as well as the adsorption of EDTA on the surface of $BaSO_4$ nuclei that retard the formation and growth of $BaSO_4$ nuclei, leading to the generation of nanoparticles (Zhao and Liu, 2006) and the following aggregations.

To investigate the effect of the controlled release of SO_4^{2-} on the formation of $BaSO_4$ microspheres, a control experiment was performed, in which the mixed solution of 4 mmol/L $K_2S_2O_8$ and 8 mmol/L EDTA was irradiated under N_2 atmosphere. Then, 4 mmol/L $Ba(NO_3)_2$ solution was added into the solution and mixed rapidly. The mixture was left to stand under static conditions away from light at room temperature for 300 min to obtain the sample for SEM characterization. The SEM image (Fig. 4) shows that the obtained product is composed of the aggregations of some ellipsoids with different aspect ratio, similar to the morphology of the product obtained in a similar condition except that the pH value was different (Takiyama, 1958). It is also seen from Fig. 4 that the morphologies of these aggregations are obviously different and the distribution of their sizes is large. Thus, it can be concluded that the controlled release of SO_4^{2-} is important to the formation of $BaSO_4$ microspheres.

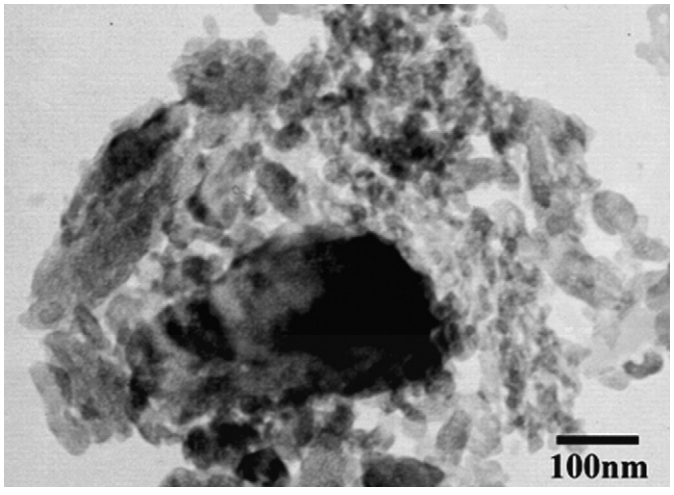

Fig. 3. TEM image of the fragments in the sonicated $BaSO_4$ microspheres sample.

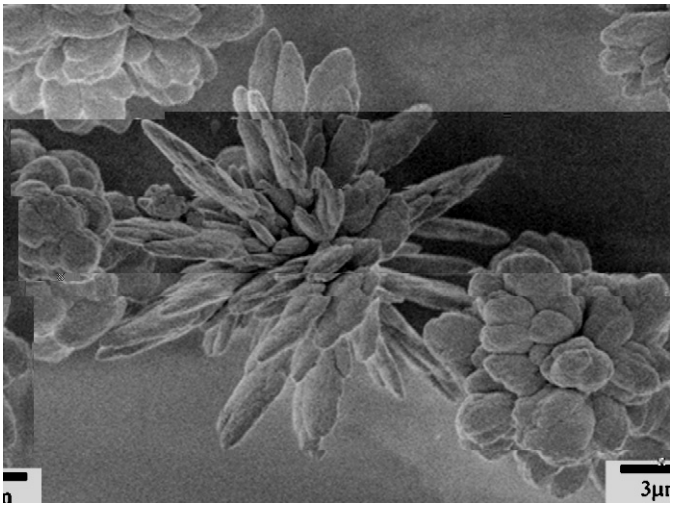

Fig. 4. SEM image of the sample synthesized by the addition of 4 mmol/L $Ba(NO_3)_2$ into the irradiated mixed solution of 8 mmol/L EDTA and 4 mmol/L $K_2S_2O_8$.

4. Conclusions

The solid $BaSO_4$ microspheres, mainly consisting of quasi-spherical nanoparticles, were successfully synthesized by precipitating Ba^{2+} ions with SO_4^{2-} ions, which were generated from the reduction of $K_2S_2O_8$ in the presence of EDTA under N_2 atmosphere by γ-irradiation. It was found that the controlled release of SO_4^{2-} played an important role in the formation of the microspheres. Moreover, it is believed that the result reported herein will not only contribute in a new way to the syntheses of insoluble sulfate nanoparticles, but also extend the application of ionizing radiation in the nanotechnology.

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