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Technical note

Radiolytic synthesis of $BaSO_4$ microspheres

Qingde Chen[a,b], Huaying Bao[a,*], Xinghai Shen[b,**]

[a]College of Chemistry, Beijing Normal University, Beijing 100875, PR China
[b]Beijing National Laboratory for Molecular Sciences, Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

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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.

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

*Corresponding author. Tel.: +86 10 58806845; fax: +86 10 58806048.
**Also for correspondence. Tel.: +86 10 62765915; fax: +86 10 62759191.
E-mail addresses: hybao@bnu.edu.cn (H. Bao), xshen@pku.edu.cn (X. Shen).

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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.

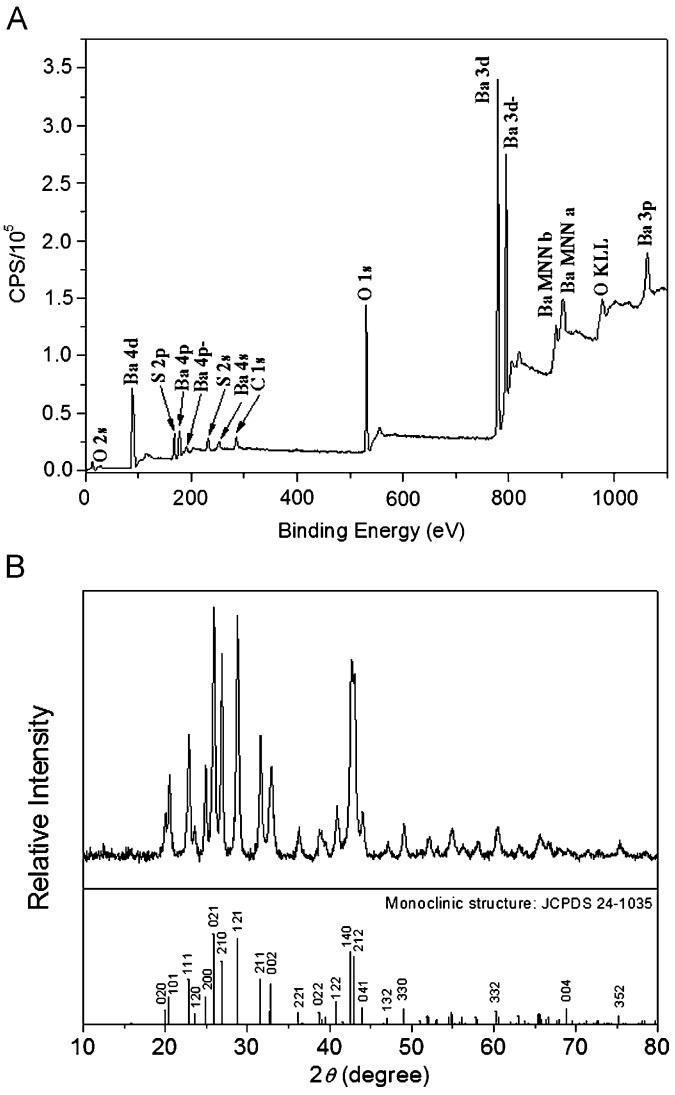

Fig. 2. X-ray photoelectron spectrum (A) and XRD pattern (B) of the same sample studied in Fig. 1.

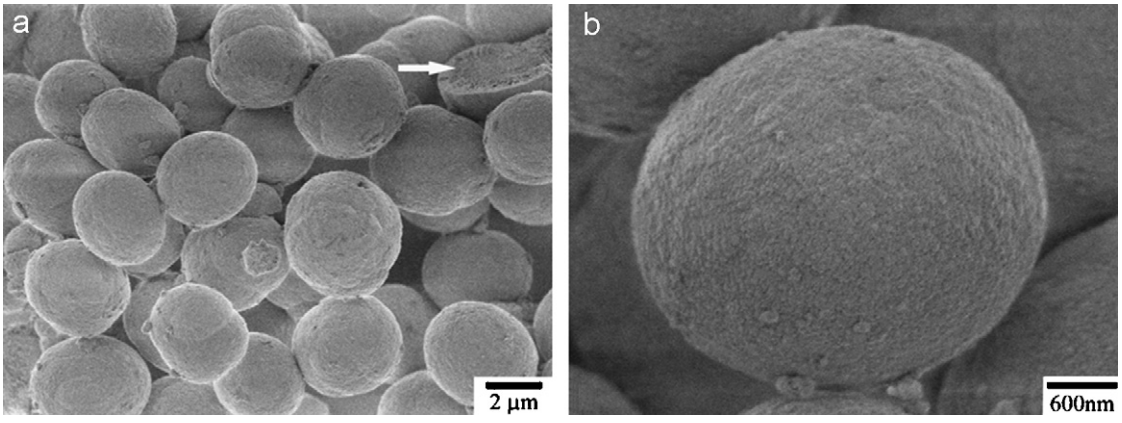

Fig. 1. SEM images of the sample synthesized by the irradiation of the mixed solution of 4 mmol/L $Ba(NO_3)_2$, 4 mmol/L $K_2S_2O_8$ and 8 mmol/L EDTA: (a) at 6000×, (b) at 25,000× magnifications.