

Green Synthesis of Barium Sulfate Particles Using Plant Extracts

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Abstract. The biological molecules in the extracts of four fruits or vegetables: kiwifruit, oranges, tomato and carrot, were used as templates to synthesize barium sulfate (BaSO_4) particles. The products were characterized by scanning electron microscopy, Fourier transform infrared spectroscopy and X-ray power diffractometry. The results showed that, leaf-shaped barite BaSO_4 crystals with toothed edge were obtained with kiwifruit extracts; thorn spherical barium sulfate crystals with diameter of 2-4 micrometers were produced with tomato extracts; rod-like or quasi-spherical BaSO_4 crystals with size of several hundred nanometers to several micrometers were gained with orange extracts; while quasi-spherical BaSO_4 nano-crystals were obtained with carrot extracts. The formation mechanism of BaSO_4 is also discussed, showing that the proteins, carbohydrates, vitamins and organic acids in above four kinds of fruits or vegetables may provide nucleation sites, controlling the growth of BaSO_4 crystals with different morphologies.

1 Introduction

Barium sulphate (BaSO_4) is generally white or colorless, chemically inert, insoluble in water, with high density, and the main source of barium[1]. It is widely used as a shading material for the x-ray photography, a gamma-ray absorber, a white pigment and etc because it is non-harmful to humans. BaSO_4 is also one of the most important fillers used in the plastics, rubber and paint industries, and is also used in pharmaceutical formulations[2]. It can be used for X-ray attenuation instead of shielding made from lead when incorporated into polymeric materials to form composite [3].

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In recent years, more attention has been paid on synthesis of BaSO₄ nanoparticles for their multiple applications in the oil industry, electronics, TV screen, glass, car filters, paint industry, ceramics and medicine, etc. Many approaches have been chosen to control the size and morphology of BaSO₄ particles. These methods could be classified as direct precipitation, microemulsion, membrane separation and organic modification [1]. M. Ismaiel et al have synthesized BaSO₄ nanoparticles by precipitation method using polycarboxylate as a modifier[4]. D. Adityawarman have obtained BaSO₄ nanoparticles in a non-ionic microemulsion[5]. G. Wu et al have precipitated BaSO₄ nanoparticles through impinging streams[6]. A. Gupta have prepared BaSO₄ nanoparticles using sodium hexa metaphosphate as a stabilizer[7]. Very recently, the synthesis of BaSO₄ nanoparticles by a chemical precipitation route without polymer stabilizers has been reported[1].

In this paper, we have synthesized BaSO₄ particles by a very simple and green method. The BaSO₄ particles especially nanoparticles obtained may be used as filler in plastics. The possible formation mechanism of the BaSO₄ particles directed by biomolecules of the fruits or vegetables including kiwifruit, oranges, tomato and carrot is discussed. This report may be very significant for biomineralization research and green synthesis of functional inorganic materials.

2 Experimental

2.1 Materials and Instruments

Barium chloride dihydrate (BaCl₂·2H₂O), anhydrous sodium sulfate (Na₂SO₄), and ethanol were purchased from reagent plant of Shanghai (Shanghai, China), and were analytically pure. They were used without further purification. Four kinds of fruits or vegetables: kiwifruit, oranges, tomato and carrot were purchased from a local farmer. Double-distilled water was used in all experiments.

The samples were characterized by Fourier transform infrared spectroscopy (Nicolet 870, America) using KBr pellets over the wave number range of 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹ and X-ray diffractometer (D8 ADVANCE, Germany) using CuK α radiation at a scan rate of 0.06° 2 θ ·S⁻¹. The morphologies of the samples were observed by scanning electron microscopy (SEM) (KYKY-EM3200, China) with an accelerating voltage of 20 kV.

2.2 Methods

First, 80g of each fruit or vegetable were washed carefully, and then crushed to extract juice, and the juice was mixed proper amount of double-distilled water, obtaining 90 mL of the fruit or vegetable extracts aqueous solution. After that, 20 mL of each solution was mixed with 40 mL of 0.05 mol/L BaCl₂, completely, obtaining 60 mL of mixed solution

containing fruit or vegetable extracts and 0.0333 mol/L BaCl₂. Then each of the mixed solution was blended with 40 mL of 0.05 mol/L Na₂SO₄ very slowly. The white precipitates produced in the mixed systems. The control experiment was also performed without adding of fruit or vegetable extracts. The above five reaction systems were placed at room temperature for 24 hours.

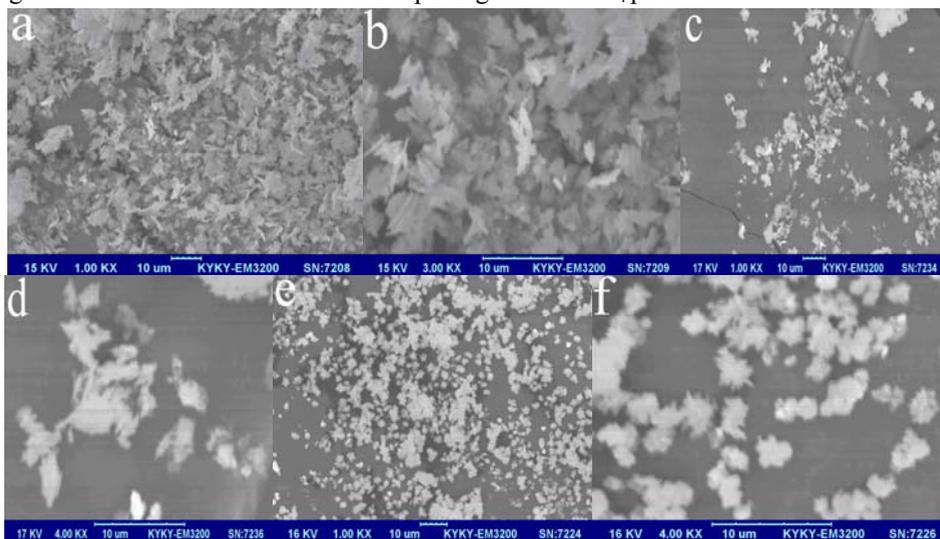
The white precipitates produced in the reaction solutions were separated by centrifugation (centrifugating rate, 4000 rpm), washed three times with double-distilled water and ethanol, respectively, and then vacuum dried for further determination.

The sizes and morphologies of the precipitates were examined by scanning electron microscopy (SEM), while their crystal phases were determined by Fourier transform infrared spectroscopy (FT-IR) or X-ray powder diffractometry (XRD).

3 Results and discussion

Fig.1 indicates SEM images of BaSO₄ particles obtained in different systems. From Fig.1a and b, it can be seen that the particles obtained without any extracts are leaf-shaped with toothed edge. The size of each “leaf” is about 4-8 μm. Fig. 1c and d shows that the particles obtained with kiwifruit extracts are also leaf-shaped, but the sizes of them become slightly smaller. When in the presence of tomato extracts, many thorn spheres with diameters of 2-4 μm are produced (Fig. 1e and f). While with orange extracts, quasi-spherical or rod-like BaSO₄ particles with sizes of several hundred nanometers are gained (Fig. 1g and h). At last, it can be seen from Fig. 1i and j, uniform BaSO₄ quasi-spheres with diameter of several hundred nanometers are obtained in the presence of carrot extracts .

From the results above, it can be concluded that the extracts of the fruits or vegetables have an influence on the morphologies of BaSO₄ particles.



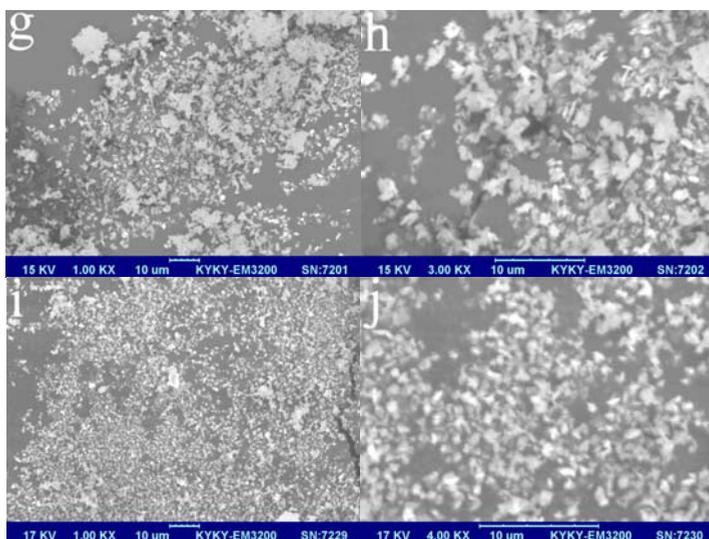


Fig. 1 SEM images of the products obtained in different systems.

(a, b: without any extracts; c, d: with kiwifruit extracts; e, f: with tomato extracts; g, h: with orange extracts; i, j: with carrot extracts;
b, d, f, h and j are the magnified images of a, c, e, g and i, respectively.)

In order to confirm the component of the products, FT-IR spectra of them obtained in different systems were measured. Fig. 2 shows the related FT-IR spectra, it can be seen that the characteristic peaks of the products are located at $1190\text{-}1070$, 984 and 849 cm^{-1} assigned to out of plane bending vibrations of SO_4^{2-} . This suggests that the products obtained in different conditions are BaSO_4 particles. The absorption peaks at about 1635 and 1550 cm^{-1} may be assigned to amide I ($\nu_{\text{C=O}}$) and II ($\delta_{\text{N-H}}$) absorptions of protein(s), respectively. This implies that the biomolecules such as proteins in the extracts of the fruits or vegetables might finally exist in the products.

Fig. 3 shows XRD patterns of BaSO_4 crystals obtained in different systems. From Fig. 3a, it can be seen that the XRD pattern of the BaSO_4 crystals obtained without any extracts displays the following diffraction peaks (2θ [$^\circ$]): 19.95° , 22.45° , 22.80° , 24.87° , 25.85° , 26.84° , 28.75° , 31.53° , 32.80° and 42.60° , which can be correlated to the (hkl) indices (020), (101), (111), (200), (021), (210), (121), (211), (002) and (140), of barite (JCPDS card number 83-1718). This suggests that the products are BaSO_4 crystals. Fig. 3b-e indicate almost the same XRD results, revealing that the products gained with the four kinds of extracts are both barite crystals.

If seen clearly, the intensity of crystal face (020) in Fig. 3a is stronger than that of it in Fig. 3b-e. It may be speculated that the extracts of the fruits or vegetables are able to inhibit the (020) face growth of BaSO_4 crystals.

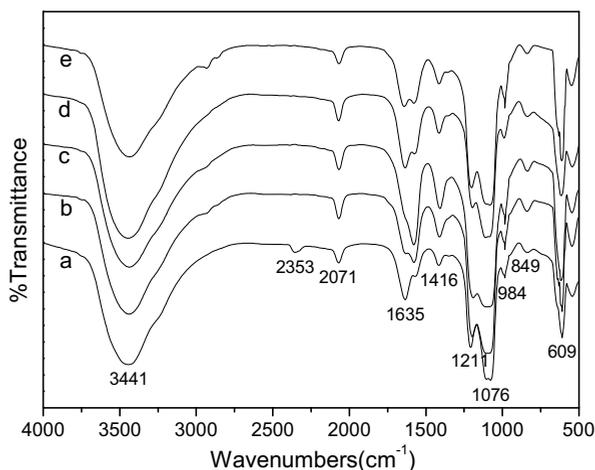


Fig. 2 FT-IR spectra of the products obtained in different systems.

(a: without any extracts; b: with kiwifruit extracts; c: with tomato extracts; d: with orange extracts; e: with carrot extracts)

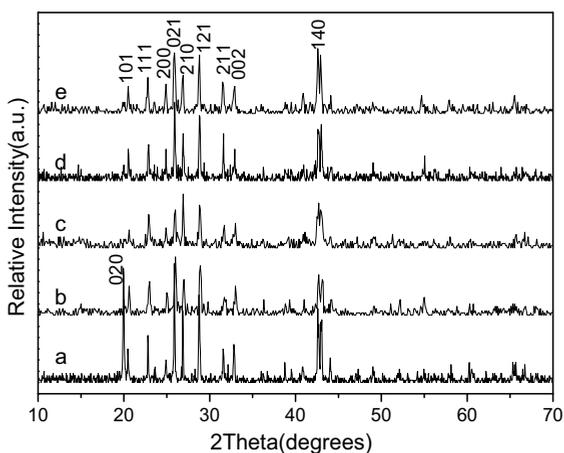


Fig. 3 XRD patterns of the products obtained in different systems.

(a: without any extracts; b: with kiwifruit extracts; c: with tomato extracts; d: with orange extracts; e: with carrot extracts)

The extracts of fruits and vegetables including kiwifruit, tomato, orange and carrot contain many kinds of organic macromolecules such as proteins, carbohydrates, vitamins and some organic acids. In previous reports, it is accepted that the soluble biomacromolecules such as acidic proteins, glycoproteins and polysaccharides in biological systems act as nucleators, growth modifiers, and anchoring units in the mineral formation [8]. Here, we speculate that Ba²⁺ ions may complex with the soluble biomolecules in the fruits and vegetables and form stable aggregates in solution firstly. Then the entrapped Ba²⁺ ions react with SO₄²⁻ ions forming BaSO₄ nuclei. At last, biomolecule aggregates adsorb onto faces of BaSO₄ crystals, controlling the formation of BaSO₄ particles with different

morphologies.

4 Summary

Green synthesis of BaSO₄ particles using the extracts of four fruits or vegetables including kiwifruit, oranges, tomato and carrot was performed. leaf-shaped barite BaSO₄ crystals with toothed edge were obtained in kiwifruit juice; thorn spherical barium sulfate crystals with diameter of 2-4 micrometers were produced in tomato juice; rod-like or quasi-spherical BaSO₄ crystals with size of several hundred nanometers to several micrometers were gained in orange juice; while quasi-spherical BaSO₄ nano-crystals were obtained in carrot juice. The formation mechanism of BaSO₄ was also discussed, showing that proteins, carbohydrates, vitamins and organic acids in above four kinds of fruits or vegetables can provide nucleation sites, controlling the formation of BaSO₄ particles with different morphologies.

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References

1. B. Sifontes, E. Cañizales, J. Toro-Mendoza, E. Ávila, P. Hernández, B. A. Delgado, G. B. Gutiérrez, Y. Díaz, E. Cruz-Barrios, Obtaining highly crystalline barium sulphate nanoparticles via chemical precipitation and quenching in absence of polymer stabilizers, *Journal of Nanomaterials* (2015) Article ID 510376.
2. H. C. Kim, Y. S. Chung, Preparation and radiopaque properties of chitosan/BaSO₄ composite fibers, *Fibers and Polymers* 14(2013) 292-297.
3. J. Unsworth, B. A. Lunn, P. C. Innis, M. Mapson, X-ray attenuation properties of electrically insulating barytes/epoxy composites. *Journal of Materials Science Letters*, 12(1993) 132-134.
4. M. Ismaiel, I. Mostafa, Synthesis of BaSO₄ nanoparticles by precipitation method using polycarboxylate as a modifier, *American Journal of Nanotechnology* 2(2011) 106-111.
5. D. Adityawarman, A. Voigt, P. Veit, K. Sundmacher, Precipitation of BaSO₄ nanoparticles in a non-ionic microemulsion: identification of suitable control

parameters, *Chemical Engineering Science* 60(2005) 3373-3381.

6. G. Wu, H. Zhou, S. Zhu, Precipitation of barium sulfate nanoparticles via impinging streams, *Materials Letters* 61(2007) 168-170.
7. A. Gupta, P. Singh, C. Shivakumara, Synthesis of BaSO₄ nanoparticles by precipitation method using sodium hexa metaphosphate as a stabilizer, *Solid State Communications* 150 (2010) 386–388.
8. A. Berman, J. Hanson, L. Leiserowitz, T. F. Koetzle, S. Weiner, L. Addadi, Biological control of crystal texture: a widespread strategy for adapting crystal properties to, *Science* 259 (1993) 776-779.