Controlled formation of barium fluoride nanocrystals by electric-assisted phase separation and precipitation

Wei Song, Kuo Liu, Lei Feng, Qing Shen*

State Key Laboratory for Modification of Chemical Fiber and Polymer Materials,

Polymer Department of Donghua University,

2999 N. Renmin Rd.,Songjiang, 201620 Shanghai, P. R. China

ABSTRACT

This work demonstrated that the barium fluoride, BaF_2, nanocrystals can be controllably formed by electric-assisted phase separation and precipitation, EAPSP, method in water/ethanol mixture. Experimentally, we employed an electrostatic generator to provide various voltages to reduce the surface tension of water/ethanol mixture to cause the phase separation rapidly occurred then the BaF_2 nanocrystals subsequently formed and precipitated under controlling. Results showed that the average diameter of those formed BaF_2 nanocrystales was reduced with the voltage increase, e.g. the 0V sample at about 70 nm, 500V sample at 50 nm and 1000V sample at 30 nm, respectively. The conductivity of these nanocrystals was found to increase with the size reduce.

Keywords: barium fluoride; nanocrystals; water/ethanol mixture; electric-assisted phase separation and precipitation.

*Corresponding author: sqing@dhu.edu.cn (Q. Shen), Tel & Fax: 86-21-62822096.

1. Introduction

Barium fluoride, BaF_2, is one of the dielectric fluorides having a wide range of potential applications in microelectronic and optoelectronic devices, such as wide-gap insulating overlayers, gate dielectrics, insulators and buffer layers in semiconductor-on-insulator structures, and more advanced three dimensional structure devices.[1-9] Recently studies have showed that the BaF_2 doped with rare-earth ions can display unique luminescent properties to fit the application in the X-ray storage phosphors, scintillators, up-to-down conversion and ionic conductivity materials.[3] According to literature, the BaF_2 particles can be prepared in various shapes, e.g. in nanowhiskers *via* a microemulsion-mediated hydrothermal method,[3] in nanocubes by arching flake-like dendrites grown *via* reverse micelles[4] or by hydrothermal precipitation at certain pH environments,[5] in cubic-phase and orthorhombic-phase *via* the liquid–solid–solution approach[6] and in hollow nest-like nanostructure *via* ultrasound-assisted self-assembly.[7]

The use of water/ethanol mixing solvents to precipitate BaF_2 nanoparticles has been reported by Lv et al.,[8] and according to them, the size of BaF_2 nanoparticles precipitated in water/ethanol was at about 50 nm smaller than in pure water, e.g. at about 70 nm.[8] The reason on water/ethanol mixture has advantages than that of water is for formation of nanosize is ascribed to the addition of low dielectric medium in aqueous solution in the precipitation process altering the thermodynamics of reaction system and nucleation kinetics thus induced reduction of the particle size and size distribution of resulting particles.[10] As observed that the water/alcohol mixed solution has been also applied as a media to form other nanoparticles[11-16] and found this mixture can enhance the reaction rate to reduce the precipitation time.[8,10-16] It is truly that the mixed solvent has been now applied as a new approach for synthesizing novel materials because it can not only change the dielectric property of the mixed solvent to affect the solubility of the inorganic salt molecules, but also influence the colloidal interaction between solid particles.[10]

In this work, we report a case for controlled formation of BaF_2 nanocrystales in water/ethanol mixing solvent by using an electric-assisted phase separation and precipitation, EAPSP, method. Experimentally, an electrostatic generator was employed to provide adjustable voltages to control the surface tension of water/ethanol mixture to cause the phase separation and precipitation rapidly and under control.

2. Experimental section

2.1 Materials

The $Ba(NO_3)_2$ with a purity of 99.5 % and NH_4F with a purity of 99.5 % both in analytic grade were obtained from local chemical store at Shanghai and directly used without furthermore purification.

Ethanol (99.7 %) was also purchased as above mentioned without furthermore treatment before use.

The lab-made distilled water was always used through the whole work.

2.2 Controlled formation of BaF_2 nanocrystals in water/ethanol mixture by electric-assisted phase separation and precipitation method

Initially, a 20 ml water/ethanol mixing solvent was prepared by taking them each at 10 ml to mix under magnetic condition for 30 min. Then, 0.8 g $Ba(NO_3)_2$ powder was dissolved in this water/ethanol mixing solvent to form a Ba^{2+} solution by stirring 1 h at 25 ℃. Meanwhile, a F^--solution was prepared by dissolution of 16 g NH_4F powder in water/ethanol mixing solvent (20 ml/20 ml) under the same stirring condition as above. To keep the stirring condition, the F^--solution was then rapidly added into the Ba^{2+}-solution to form the final mixing solution and stirred of 1 h at 25℃.[8,9]

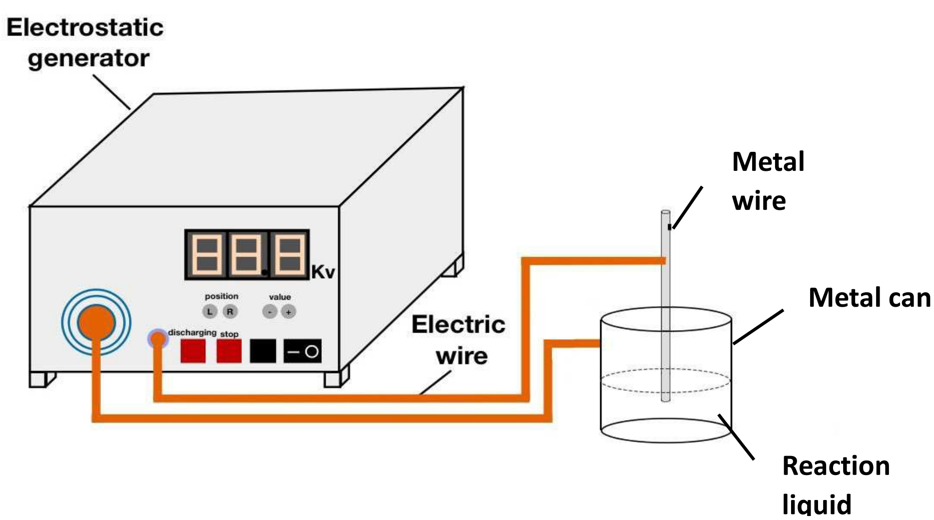

Figure 1. Scheme on the application of the electric-assisted phase separation and precipitation method to form nanocrystals.

The above prepared mixed solution was moved into a metal can where two electrodes from the electrostatic generator were linked to either the mixing solution or the metal can wall as Figure 1 described to form electric cycle. Under this electric field condition, the phase separation would be controllably occurred because the surface tension of the solvent would be gradually reduced with the voltage increase as below discussed to benefit the particles precipitation under control. The whole process was performed at 2 h, and the final precipitated product was filtered and oven dried 24 h at 100 ℃.

2.3 Measurement and characterization

The surface tension of water/ethanol mixing solvent was measured using an electric-assisted Wilhelmy plate method, where an electrostatic generator was applied by taking its two electrodes respectively linked to both the solvent and the Wilhelmy plate under varied voltages from zero to 3 kV. During the measurement process, the platinum plate was initially winded some Cu wires to increase its weight to avoid the effect from voltage increase induced swing then be hung on above the solvent container. The measurement was started by raising the liquid-based container up to contact the bottom of plate to form contact angle which was meanwhile measured automatically by the tensiometer and appeared in computer to show the surface tension directly. Each presented value was averaged by three independence measurements and the related standard deviation was about 2%. All measurements were performed at 25 ℃.

The field emission scanning electron microscopy (FESEM) image was prepared by drop-casting an aqueous dispersion (~1 g/L) of the doped substituted sample onto a silicon wafer. A JEOL JSM-6700-F field emission SEM microscope was employed.

The Fourier transform infrared, FTIR, spectrum was recorded using the NEXUS 8700 (Nicolet, UK) in the range of 400-4000 cm^{-1} with the resolution of 4 cm^{-1}. The KBr pellet technique was adopted to prepare all samples.

The X-ray diffraction, XRD, pattern was recorded by the Rigaku D/Max-2550 PC instrument (Rigaku, USA) at 40 kV, 30 mA, by the Cu-Ka monochromatic radiation with a wavelength of 1.5406 A˚, after scanning in the 2θ range of 10-90° at intervals of 0.02.

The particle size was measured using a Malvern Zetasizer nanosizer at 25 □.

The electrical conductivity was measured using SDY-4 Four-Point Probe Meter at ambient temperature. The pellets were obtained by subjecting the powder samples to a pressure of 30 MPa. The measurement reproducibility was checked by measuring the resistance three times for each pellet.

3. Results and discussions

FESEM images and particle size distribution of three prepared BaF_2 nanocrystals in relation to applied voltage at 0, 500 and 1000V were combined showed in Figure 2. In terms of the FESEM images, these nanocrystals all showed cubic morphology and uniform size in good agreement with literature.[1-9] This was strongly supported by the presented particle size distribution plot because where three samples each showed a unique peak to give quantitatively size values corresponding to three applied voltages, respectively. Thus, it is clearly that the use of this novel EAPSP method one can controllably fabricate uniform inorganic nanostructures with controlled size.

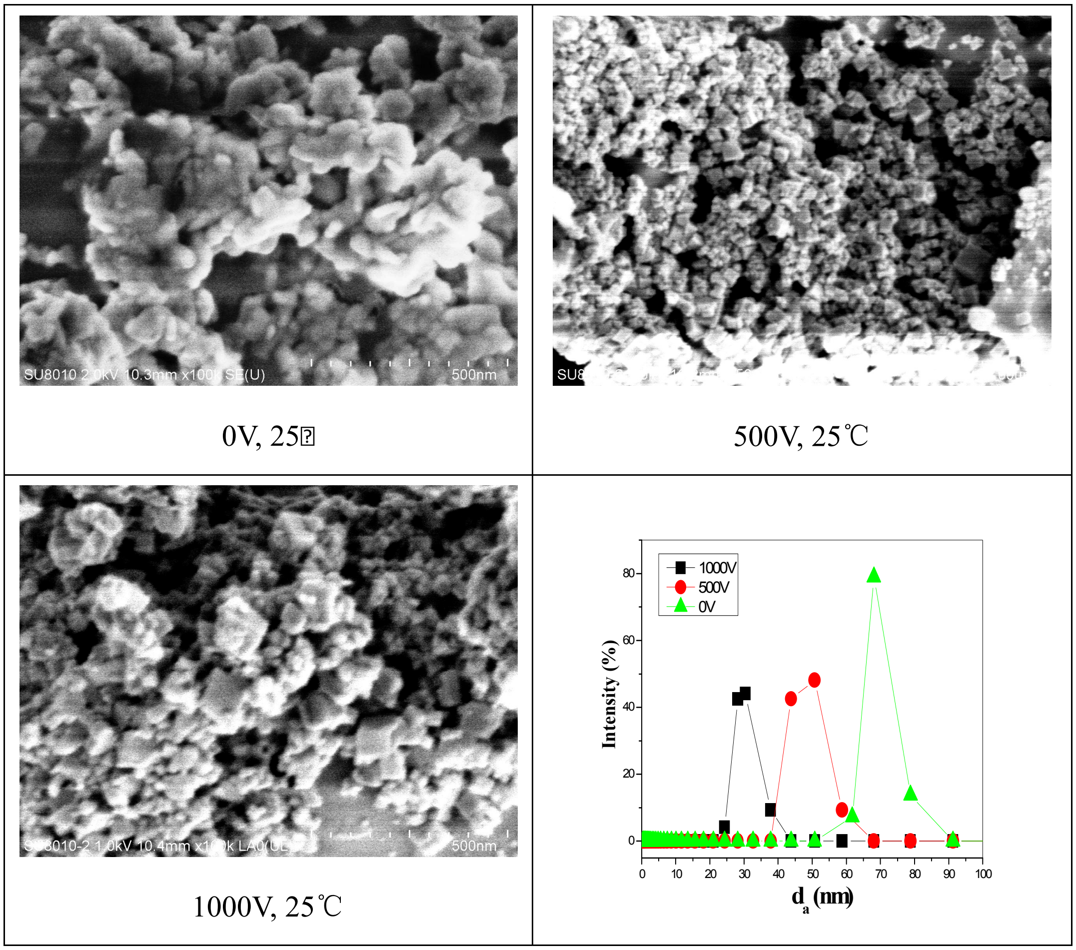

Figure 2. FESEM images and particle size distribution of BaF_2 nanocrystales formed by electric-assisted phase separation and precipitation in water/ethanol mixture.

Since Figure 2 (bottom right) showed that the BaF_2 nanocrystales prepared at 1000V has an average size at about 30nm which is smaller not only in this work, but also comparable with other methods prepared samples as summarized in Table 1.[1-9,17,18] Though literature has reported some cases on formation of BaF_2 nanocrystals,[8,18] it seems to be truly that the sample formed by EAPSP method is uniformly as can be seen in Figure 2 by used SEM and particle size measurement.

Table 1. BaF_2 nanocrystales prepared in this work or reported in literature.

Samples	Voltage (V)	d_a (nm)	Media	Refs
BaF_2	0	70	Water/ethanol (1/1)	This work
BaF_2	500	50	Water/ethanol (1/1)	This work
BaF_2	1000	30	Water/ethanol (1/1)	This work
BaF_2	0	55	pH 2 solution	(5)
BaF_2	0	200	pH 4 solution	(5)
BaF_2	0	1000	pH 6 solution	(5)
BaF_2	0	1000	pH 7 solution	(5)
BaF_2	0	800-900	Surfactant-based solution	(7)
BaF_2	0	70	Water	(8)
BaF_2	0	50	Water/Ethanol (1/1)	(8)
BaF_2	0	61	Water/ethanol (3/1)	(8)
BaF_2	0	43	Water/ethanol (3/5)	(8)
BaF_2	0	34	Water/ethanol (1/4)	(8)
BaF_2	0	10-70	Microemulsion	(9)
BaF_2	0	40	Microemulsion	(17)
BaF_2	0	34	Solution	(18)

The XRD patterns of three EAPSP formed BaF_2 nanocrystals were presented and compared in Figure 3. As seen in Figure 3, all three samples appeared intense and consistent peaks well indexed to the phase-pure crystalline BaF_2 in cubic structure with the face-centered lattice (space group *Fm*3*m*) and the lattice constant *a*=6.20Å in good agreement with literature (JCPDS Card No. 85-1342).[1-9]

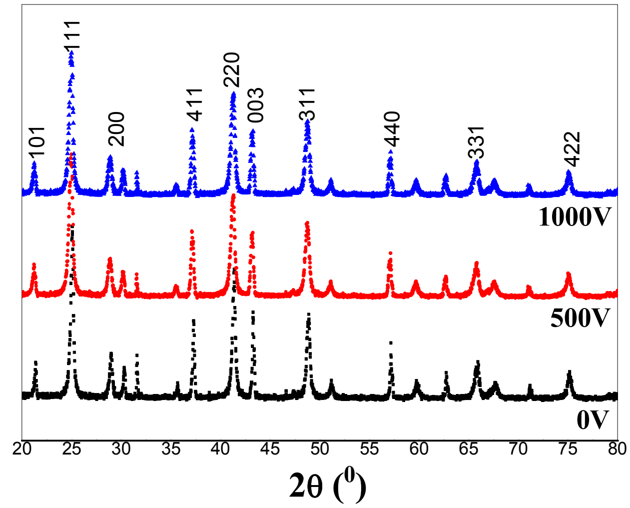

Figure 3. XRD patterns of BaF_2 nanocrystals prepared by electric-assisted phase separation and precipitation.

In terms of Figure 3 presented XRD patterns, the BaF_2 nanocrystal is growth mainly along the 111 and 220 planes.[5,7,19,20] Since the presented intensity is the highest for 1000 V sample and smallest for 0 V sample (Figure 3), this indicated that the formed nanocrystal size is reduced with the voltage increase to support the SEM results (Figure 2) as above mentioned. This again implied that the pure BaF_2 nanocrystal can be better formed in electric field condition.

The FTIR spectra of three EAPSP formed BaF_2 nanocrystals corresponding to the applied voltage at 0, 500 and 1000 V were presented in Figure 4, respectively. It was found that the 0 V sample showed visible bands at 3341, 3136, 3041, 2095, 1531, 1428, 1259, 1040, 732, 556 and 483 cm^{-1} in agreement with literature.[21] Since a comparison found that the 500 and 1000V formed samples both disappeared two peaks at 2095 and 1259 cm^{-1} corresponding to the remove of NH_4^+ and one peak shifted upward from 1531 to 1626 cm^{-1} corresponding to the remove of water, this indicated that the use of EAPSP formed purified BaF_2 nanocrystals as that of the normal 0 V sample. This is reasonable because the EAPSP process would reduce the surface tension of solvent as Figure 5 presented, therefore benefit the used mixed solvent to easy evaporation.

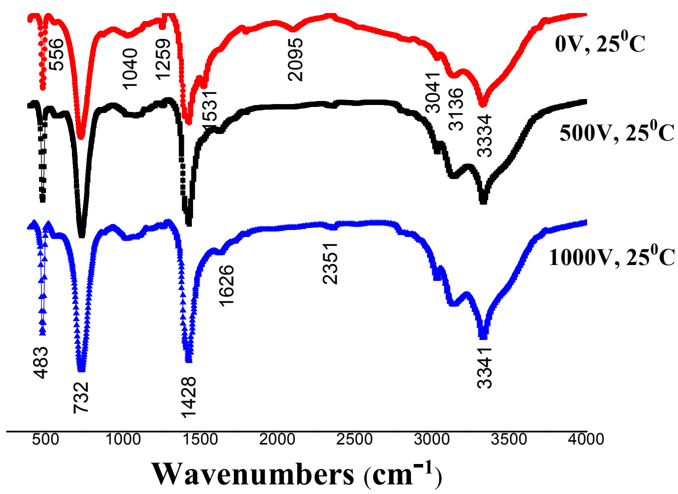

Figure 4. FTIR spectra of BaF_2 nanocrystals prepared by electric-assisted phase separation and precipitation method.

It clearly showed that the surface tensions of either the pure water and ethanol or their mixture all were reduced with the voltage increase. This result is in good agreement with our recently reports.[22-24] In terms of the Figure 5, the water/ethanol mixture showed a low surface tension similar to the pure ethanol. Therefore, this low surface tension-based water/ethanol mixing solvent should play interesting role during the EAPSP process that the pure water and ethanol unable. This was good supported by Chen and Chang[10] because they have applied several water/alcohol mixtures to form cerium dioxide nanocrystals and found that the smallest size could be formed by the lowest surface tension-based mixture.

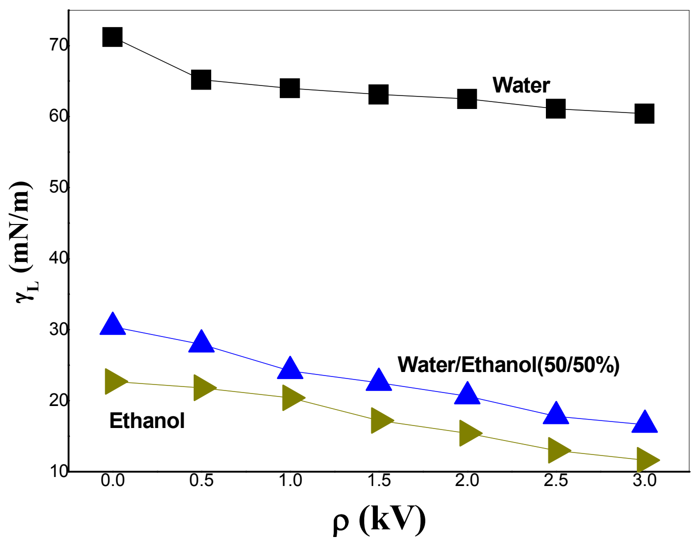

Figure 5. Effect of applied voltages on the surface tension of water/ethanol mixtures.

Hence, the binding between the Ba^{2+} and F^- ions to be enhanced for EAPSP formed samples.

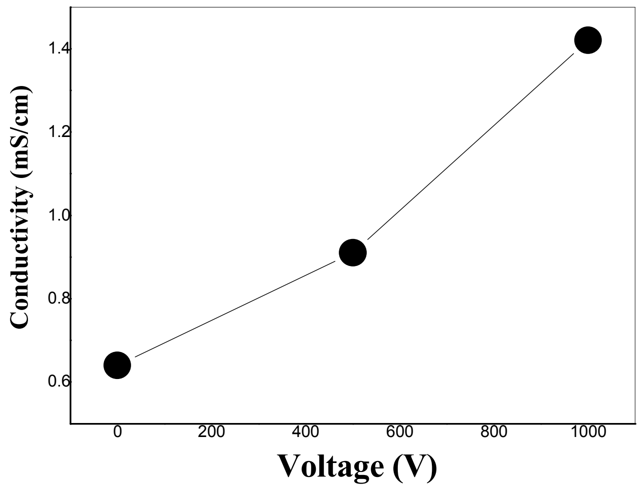

Figure 5. Effect of applied voltages on the conductivity of BaF_2 nanocrystals prepared by electric-assisted phase separation and precipitation.

The conductivity of BaF_2 nanocrystals has been focused by researchers due to this property strongly affecting the application.[20, 25,26] Figure 6 presented a plot where the conductivity of those BaF_2 samples was found to increase with the applied voltages increase. This importantly implied that the use of this novel EAPSP method can controllably form BaF_2 nanocrystals with required electric properties.

Noted the conductivity values presented in Figure 6 are greater as compared with literature reported values for BaF_2 nanocrystals.[20,26] For example, Ruprecht et al.[20] have applied a high-energy ball milling method to prepare nanocrystalline BaF_2:CaF_2 composites and found the conductivity at about 0.1 mS/cm at 450K. In fact, our samples presented greater conductivities as measured at 295K as compared with literature reported values measured at 450K.[20]

According to above discussion, a related mechanism on formation of BaF_2

nanocrystals in water/ethanol mixture *via* this novel EAPSP process was known. Because the presence of electric field leading to reduce the surface tension of this particles/mixing solvent system and the evaporation of ethanol and water enhanced with the voltage increase, this thus lead the phase separation occurred and enhanced to benefit the particles collision to finally lead the BaF_2 nanocrystales precipitated.

4. Conclusion

In summary, the BaF_2 nanocrystals can be successfully prepared with controlled size and property by using a novel electro-assisted phase separation and precipitation method in water/ethanol mixing solvent. This work has proven that the voltage increase can reduce the surface tension of the mixing solvent to form uniform BaF_2 nanocrystals.

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