Formation of BaF₂ Microcrystals as Superhydrophobic Materials via a Hydrothermal Method

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Research Article

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Abstract

Controllable BaF_2 microcrystals with super-hydrophobic property have been successfully synthesized via a facile hydrothermal process. XRD, SEM and CA are used to study the structure, morphology and the hydrophobic properties of the BaF_2 materials. The effects of reaction time, surfactants and pH are also detailed investigated in order to get a series of accurate reaction conditions for the preparation of BaF_2 material. The results show that uniform BaF_2 tetragonal phase structure was fabricated when the reaction temperature was controlled at 180 °C for 24 h. In addition, the BaF_2 materials showed excellent super-hydrophobic properties. The results about the influence of time and substrates exhibit that the sample can maintain the stable super-hydrophobic property for over 10 days. As a promising super hydrophobic materials, the studies of BaF_2 reported in this paper is quite practical and it has a certain guiding meaning for the future study about super hydrophobic materials.

1 Introduction

Superhydrophobicity occurs by combining micro-nanoscale rough structures with low surface energy materials to produce a water-repelling surface ^[1]. Recently, superhydrophobic surfaces have attracted much attention for applications in various fields such as self-cleaning ^[2], drag reduction ^[3–6], oil-water separation ^[7–9] and so on. MX_2 type (M = Be, Mg, Ca, Sr, Ba; X = F, Cl, Br, I) micro-nanoparticles are used in various industries because of their unique advantages such as narrow particle size, But in the superhydrophobic industry is a new research field. Among MX_2 micro-nanoparticles, BaF_2 , as a classical dielectric alkaline earth fluoride material, has attracted a large number of experimental and theoretical studies in the past decades due to its exceptional properties such as excellent luminescence and absorption properties, lattice kinetic properties, high density and non-hygroscopic properties ^[10–12]. It has a wide range of potential applications in microelectronics, optoelectronic and thin film materials. However, the synthesis method of BaF_2 materials is relatively single, the synthesized materials are not uniform enough, without high dispersion and crystallinity, and can not show excellent superhydrophobic properties. Therefore, further regulation is still needed in synthesis to improve superhydrophobic properties.

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So far, numerous methods were used to synthesize the BaF_2 Crystals in previous reports, such as chemical precipitation, flame process, microemulsion, hydrothermal method, liquid–solid–solution method, thermal decomposition of trifluoroacetates, and so on ^[13–21]. Hu and Zang et al. reported that the BaF_2 materials synthesized successfully by the CTAB/2-octanol/water microemulsion method ^[16]. Glazunova and Boltalin et al. used the thermal decomposition of trifluoroacetate complexes, then

annealed the fluoride materials in an oxygen flow at 500 ° C for the preparation of barium fluoride^[18]. Among these preparation method, hydrothermal method was successful for the synthesis of unique condensed functional materials and it can provide a stable and gentle reaction conditions^[22, 23]. Jia and Zhang et al. prepared barium rare earth fluorides for all the typical rare earth ions via a modified hydrothermal system to and the result samples have high purity^[24].

Inspired by the aforementioned considerations, in this study we chose a simple hydrothermal method and controlled the synthesis of BaF₂ materials by adjusting temperature, pH, reaction time and adding surfactants. Obtained BaF₂ materials with high monodispersity and crystallinity. We grind the product evenly on the glass surface to form a superhydrophobic coating, and further study its superhydrophobic properties. As a result, the BaF₂ material can be used as a new type of superhydrophobic material with the increasing requirements in related fields.

2 Experimental Sections

2.1 Synthesis of Materials

To synthesize the BaF₂ materials, barium chloride (BaCl₂·2H₂O, analytical grade), ammonium fluoride (NH₄F, analytical grade) were employed as barium and fluoride sources. All the other chemicals used in the experiments were also of analytic reagent grade without further purification.

The BaF₂ materials were synthesized by a facile hydrothermal method. Firstly, 8mL BaCl₂ solution (0.4M) was added in 100mL beaker. Then, 16mL NH₄F solution (0.4M) was dropwise added to the BaCl₂ solution under stirring vigorously. Finally, the milky turbid solution was transferred into a 20 mL Teflon-lined stainless steel autoclave, then the autoclave was sealed, heated under autogenous pressure at 160 °C for 6 h, 12 h, 24 h, 48 h, (four kinds of compounds have been named as 160-TM6, 160-TM12, 160-TM24, and 160-TM48, which correspond to reaction time of 6 h, 12 h, 24 h and 48 h, respectively.) and followed by cooling down to room temperature. The obtained purple precipitates were filtrated and washed three times with absolute ethanol and deionized water, finally dried at 60 °C in vacuum for 12 h.

For comparison, the samples which were prepared at 160 °C for 24h with different pH values such as 3, 6, 9 and 12 (the pH value of the mixed solution was adjusted by the dripping of 0.5 mol/L NaOH/HCl solution.) have been also synthesized, the samples were named as p3-TM24, p6-TM24, p9-TM24 and p12-TM24, which correspond to pH value of 3, 6, 9 and 12, respectively. Moreover, another series samples were carried out to study the effect of surfactants, the samples which were prepared at 160 °C for 24h with 0.1g EDTA, 0.1g CTAB and 0.1g PEG added, the as-prepared samples were named as S-EDTA, S-CTAB and S-PEG, which correspond to the three reactions, respectively.

2.2 Characterization

The crystal structure of samples were characterized by X-ray diffraction (XRD) on a Rigaku D/MAX-2500 powder diffractometer at 40 kV and 10 mA using Cu-K α radiation ($k = 0.15418\text{nm}$) operated with a scan rate of 4° min^{-1} in the 2θ range of 10° - 70° . The morphologies of the samples were investigated by a JEOL JSM-6610LV scanning electron microscope. The TGA analysis were carried out by HTG-1. Water contact angle (CA) and sliding angle measurements were carried out at ambient temperature by an optical contact angle meter (Ramé-hart Model p/n 250-F1). Water droplets ($5 \mu\text{L}$) were carefully dropped onto the surfaces, and an average value of five measurements obtained at different positions in the samples was used as the final contact angle.

2.3 Preparation of super-hydrophobic surfaces

The surface of a glass substrate was steeped with concentrated sulphuric acid to remove any pollutants, and then cleaned with ethanol in ultrasonic washer for 3 h. The super-hydrophobic surface was prepared via a facile dip-coating method: firstly, a glass surface was modified by slowly evaporation of the BaF₂ (0.2g)-ethanol solution dispersion, then dried at room temperature. In the second step, the films on glass substrates was dried at 120°C for 1 h.

3 Result And Discussion

The X ray diffraction (XRD) patterns of the samples prepared at different reaction times are shown in Fig. 1. The XRD peaks at angles of 24.8 , 28.8 , 41.2 , 48.7 , 51 , 59.6 , 65.6 , and 67.5° were indexed to (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1) and (4 2 0) planes of BaF₂, respectively (JCPDS card No.85-1341)^[25]. Its lattice parameters are $a = b = 0.6189\text{nm}$, $c = 0.6200\text{nm}$, indicating that the synthesized sample belongs to tetragonal BaF₂. The diffraction peaks of all the products are very complete and sharp, denoting the high crystallinities of the samples prepared in the hydrothermal method. The reaction time of 6 h, the diffraction peak of the sample 160-TM6 is obviously weak, indicating that the BaF₂ can not be fully synthesized and has low crystallinity. The reaction time is 48 h, some unknown diffraction peaks appear in the sample 160- TM48, which means that some impurities are formed due to the re-dissolution of the crystal nucleus during the longer reaction time, but BaF₂ microcrystals still occupy the main body of the product. While both the samples 160- TM12 and 160-TM24 showed rather sharp diffraction peaks without other impurities, indicating that the optimum time for synthetic BaF₂ was between 12–24 h.

To compare the effect of surfactants on materials, three surfactants were added during the reaction. Figure 2 is the XRD of BaF₂ obtained by hydrothermal reaction at 160°C for 24 h with 0.1 g of different surfactants. It can be clearly found from the figure that the crystallinity of the samples S-CTAB and S-PEG is the highest, and the crystallinity of the sample S-EDTA is slightly worse. This may be because EDTA forms a complex with Ba²⁺ in the system and cannot combine with F⁻ ions in the system to form a nucleus in time^[26]. CTAB and PEG played a role in accelerating and speeding up the reaction process, so a product with better crystallinity was obtained. The three kinds of surfactants with and without surfactants basically have no impurity peaks, which are in good agreement with the standard card peaks,

indicating that the addition of surfactants can greatly improve the performance of the material, which is an important factor in the preparation of BaF_2 .

Figure 3 shows the XRD pattern of the samples prepared at different pH values. As shown in Fig. 3, when $\text{pH} = 6$, the diffraction peaks of sample (p9-TM24) are much sharper than others, means impurities and when the pH value drops to 3, the diffraction peaks become much weaker. The most noteworthy is when the pH value is controlled to 9, the diffraction peaks become much sharp obviously. But when the pH value rises to 12, some diffraction peaks of impurities were observed obviously. The results indicate that BaF_2 materials have the higher crystallinity when the pH value controlled to 9.

Figure 4 shows the SEM of all samples prepared with different surfactants. The typical surfaces and morphologies of the materials prepared with the addition of different surfactants are also measured by SEM. As shown in Fig. 4, Fig. 4(a) shows that the BaF_2 micron particles (S-CTAB) obtained with CTAB added are square morphology. Moreover, the shape of its particles is regular and the size is homogeneous with $\sim 3.4 \mu\text{m}$ in length and $\sim 2.3 \mu\text{m}$ in width, the water CA value is 151° . The samples S-EDTA, S-PEG are shown in Fig. 4(b) and Fig. 4(c), respectively. Both of the two samples show the clearly square morphology with $\sim 4.3 \mu\text{m}$ in length and $\sim 2.4 \mu\text{m}$ in width. But as shown in Fig. 4(d), the size of sample 160-TM24 is much smaller than others and its morphology is not as homogeneous as the samples with surfactants added. Above all, the addition of surfactants can improve the morphology of BaF_2 particles and this agrees well with the results of Fig. 2.

Meanwhile, the reaction mechanism is also concluded based on the related research results. It is well known that the reaction time, surfactants and pH values of reaction system have a great effect on the formation of BaF_2 . Figure 5 shows that the reaction process: $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and NH_4F become ionic state in deionized water, then Ba^{2+} and F^- ions begin to react with stirring. The BaF_2 particles get close to each other under the effect of Van der Waals force which leads to a result of gather. When the surfactants are added, the products is self-assembly under the effects of surfactants and then the squares BaF_2 are formed with time going. All of the factors have influences on the reaction together and also improve products performance. In our experiments, the reaction temperature at 160°C for 24 h with the $\text{pH} = 6$ and the addition of CTAB or PEG can lead to the best result in terms of the formation of BaF_2 .

To investigate the super hydrophobic properties of the synthesized BaF_2 materials, a contrast experiment is firstly carried out to compare the influence of modification with TMFS. As shown in Fig. 6, It can be obviously found that the curves of the contact angles of the modified surfaces with TMFS show the same regularity. No matter the surface modified or unmodified, the sample p9-TM24 all show the highest contact angle and the contact angle is between 169° and 150° . It is clear seen that the TMFS modified has enormous effect on the contact angle, and $\text{pH} = 9$ is the best condition to synthesis the BaF_2 materials with super- hydrophobic property.

The BaF_2 particles are dip-coated on the three substrates (glass, copper and aluminum) to measure the water contact angles. Figure 7 shows the water contact angles of the modified surface on the different

substrates, the results show that all the surfaces coated on the three kinds of substrates exhibit an excellent super-hydrophobic property. Especially, the contact angle of BaF₂ surface coated on copper reaches to 156°, but the glass surface is just 155° and the aluminum is just 147°. The result shows that BaF₂ surface coated on copper have excellent super-hydrophobic property.

Furthermore, the effect of placement time on the super-hydrophobic properties of BaF₂ was studied, the results are collected under three drops of water with pH value 3, 6 and 9 on the glass as a substrate. As shown in Fig. 8, the water at pH = 9 have the highest contact angle than water at pH = 3, 6 in the first day. In addition, the water at pH = 9 contact angle reaches around 156° after 10 days and its contact angle maintains above 150° in 40 days, these results shows that the BaF₂ materials have an excellent super-hydrophobic properties which can keep stable for a long time.

Thermogravimetric analysis was also carried out to study the stability of the samples. The thermogravimetric analysis of BaF₂ crystals was under the protection of N₂ atmosphere, heated from 20°C to 900°C, and the heating rate was 5°C /min. The results are shown in Fig. 9. Obviously, at a temperature of 394.5°C, there is only a 3% weight loss ^[27], which is most likely due to the combination of unreacted PEG and a small amount of water molecules in the sample. In addition, the weight loss of the sample with increasing temperature is not obvious, losing 3.2% at 697.4°C and 4% at 900°C. This strongly proves the excellent stability of BaF₂ material.

4 Conclusions

In summary, the BaF₂ micron materials were successfully synthesized by a facile hydrothermal method. The results show that the BaF₂ materials exhibit well-defined cubic structure at reaction temperature of 160°C for 24 h. The particle size is ~ 2µm and the particles are uniform and unbroken. In addition, the samples showed excellent super-hydrophobic properties when water pH value = 9. The results about the influence of time and substrates exhibit that the sample can maintain the stable super-hydrophobic property for over 10 days. Therefore, this excellent performance of the as-prepared BaF₂ material can probably possess enormous application prospect to replace conventional engineering materials.

Declarations

Conflicts of interest

There are no conflicts to declare.

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Figures

Figure 1

XRD diffraction patterns of the samples 160-TM6, 160-TM12, 160-TM24 and 160-TM48.

Figure 2

XRD diffraction patterns of the samples 160-TM24, S-EDTA, S-CTAB and S-PFG.

Figure 3

XRD diffraction patterns of the samples p3-TM24, p6-TM24, p9-TM24 and p12-TM24.

Figure 4

SEM images of the (a) S-CTAB, (b) S-EDTA, (c) S-PEG, and (d) 160-TM24.

Figure 5

The reaction mechanism of BaF2.

Figure 6

Water contact angles of the un-modified and modified resulting surface according to the pH of the water (a, Modified before; b, Modified).

Figure 7

Water contact angles of the modified resulting surface according to the pH of the water with different substrates ((a) glass, (b) copper, (c) aluminum)

Figure 8

Water contact angles of the modified resulting surface according to the time of the water with different pH value.

Figure 9

TGA analysis of 160-TM24.