Formation of BaF₂ microcrystals as superhydrophobic materials via a hydrothermal method

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Abstract
Controllable BaF₂ microcrystals with super-hydrophobic property have been successfully synthesized via a facile hydrothermal process. XRD, SEM and CA were used to study the structure, morphology and the hydrophobic properties of the BaF₂ materials. The effects of reaction time, surfactants and pH were investigated in order to get a series of accurate reaction conditions for the preparation of BaF₂ material. The results showed that uniform BaF₂ cubic phase structure was fabricated when the reaction temperature was controlled at 160 °C for 24 h. In addition, the BaF₂ materials showed excellent super-hydrophobic properties. The results of the influence of time and substrates exhibited that the sample could maintain the stable super-hydrophobic property for over 10 days. As a promising super hydrophobic material, the studies of BaF₂ reported in this paper has potential application prospect and has a certain guiding meaning for the future study about super hydrophobic materials.

Keywords BaF₂; Microcrystals; Superhydrophobic; Hydrothermal

1 Introduction
Superhydrophobicity occurs by combining micro-nanoscale rough structures with low surface energy materials to produce a water-repelling surface (Sam et al. 2019). Recently, superhydrophobic surfaces have attracted much attention for applications in various fields such as self-cleaning (Langmuir et al. 2009), drag reduction (Daniello et al. 2009; Shircilffe et al. 2009; Mchale et al. 2010; Wang et al. 2018), oil-water separation (Xue et al. 2015; Gao et al. 2016; Bay et al. 2016) and so on. MX₂ type (M=Be, Mg, Ca, Sr, Ba; X=F, Cl, Br, I) micro-nanoparticles are used in various fields because of their unique advantages such as narrow particle size. However, in the superhydrophobic industry is a new research field. Among MX₂ micro-nanoparticles, BaF₂, 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-hygrosopic properties (Wu et al. 2015; Wang et al. 2016; Cao et al. 2003). It has a wide range of potential applications in microelectronics, optoelectronic and thin film materials. However, the synthesis method of BaF₂ materials is relatively single and the synthesized materials are not uniform enough without high dispersion and crystallinity, which cannot show excellent superhydrophobic properties. Therefore, further efforts are still needed in synthesis to improve superhydrophobic properties.

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So far, numerous methods were used to synthesize BaF₂ crystals in previous reports, such as chemical precipitation, flame process, microemulsion, hydrothermal method, liquid–solid–solution method, thermal decomposition of trifluoroacetates, and so on (Bender et al. 1983; Yoshikawa et al. 1984; Kolar et al. 1984; Hua et al. 2003; Lian et al. 2004; Glazunova et al. 2006; Xie et al. 2009; Zhang et al. 2008; Zhang et al. 2013). Hu and Zang et al. reported that the BaF₂ materials synthesized successfully by the CTAB/2-octanol/water microemulsion method (Hua et al. 2003). Glazunova and Boltalin et al. used the thermal decomposition of trifluoroacetate complexes, and then annealed the fluoride materials in an oxygen flow at 500 °C for the preparation of barium fluoride (Glazunova et al. 2006). Among these preparation methods, hydrothermal method was successful for the synthesis of unique condensed functional materials and it can provide stable and mild reaction conditions (Peng et al. 2012; Sun et al. 2014). 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 (Jia et al. 2014).

Inspired by the above mentioned reports, in this study we chose a simple hydrothermal method and achieved controllable the synthesis of BaF₂ materials by adjusting temperature, pH, reaction time and adding surfactants. Obtained BaF₂ materials had high monodispersed and crystallinity. A facile drop-casting method was used to form a superhydrophobic coating on the glass surface, and its superhydrophobic properties were investigated. In summary, the BaF₂ material could 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 BaF$_2$ materials, barium chloride (BaCl$_2$•2H$_2$O, analytical grade), ammonium fluoride (NH$_4$F, 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 BaF$_2$ materials were synthesized by a facile hydrothermal method. Firstly, 8 mL BaCl$_2$ solution (0.4 M) was added in 100 mL beaker. Then, 16 mL NH$_4$F solution (0.4 M) was dropwise added to the BaCl$_2$ 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 and 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-TM6, and 160-TM6, 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 was 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 24 h 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 were prepared at 160°C for 24 h 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-Kα radiation (λ = 0.15418nm) 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 was 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 µL) 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 was cleaned with ethanol in ultrasonic washer for 3 h. The super-hydrophobic surface was prepared via a facile drop-casting method: firstly, a glass surface was modified by slowly evaporation of the BaF$_2$ (0.2 g) ethanol solution dispersion, then dried at room temperature. In the second step, the films on glass substrates were 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 figure 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 BaF$_2$, respectively (JCPDS card No.C4-452) (Sharma et al. 2019). Its lattice parameters are a=b=c=0.6196 nm, indicating that the synthesized sample belongs to cubic BaF$_2$. The diffraction peaks of all the products are very complete and sharp, denoting the high crystallinities of the samples prepared in the hydrothermal method. When the reaction time is 6 h, the diffraction peak of the sample 160-TM6 is obviously weak, indicating that the BaF$_2$ cannot be fully synthesized and has low crystallinity. The reaction time is 48 h, some unknown diffraction peaks appear in the sample 160-TM48 can be attributed to BaClF (JCPDS No. 84-0631), which means that Barium chloride fluoride microcrystals are formed due to the re-dissolution of the crystal nucleus during the longer reaction time, but BaF$_2$ microcrystals still occupy the main phase 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 BaF$_2$ was between 12-24 h.
To compare the effect of surfactants, three surfactants were added into the reaction system. 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 to form a nucleus in time (Bender et al. 2000). 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 advantage factor in the preparation of BaF₂.

Figure 3 shows the SEM of all samples prepared with different surfactants. The typical surfaces and morphologies of the materials prepared with different surfactants were also measured by SEM. Fig. 4(a) shows that the BaF₂ micron particles (S-CTAB) obtained with CTAB added are square morphology. Moreover, the shape of the particles is regular and the size is homogeneous with ~3.4 μm in length and ~2.3μm in width. The water CA value is 151°, when the S-CTAB sample was used to construct the surface on glass. 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 ~4.3μm in length and ~2.4μm in width. However, 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. In summary, the addition of surfactants can improve the morphology of BaF₂ particles which agrees well with the results of XRD.

Fig. 2 XRD patterns of 160-TM24, S-EDTA, S-CTAB and S-PFG, respectively.

Fig. 3 XRD patterns of p3-TM24, p6-TM24, p9-TM24 and p12-TM24, respectively.

Fig. 4 SEM images of the (a) S-CTAB, (b) S-EDTA, (c) S-PEG.
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$_2$. Fig. 5 shows that the reaction process: BaCl$_2$·2H$_2$O and NH$_4$F 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 not only have influences on the reaction system and also improve products performance. In the obtained experimental data, the reaction temperature at 160 °C for 24 h with the pH = 6 and the addition of CTAB or PEG can lead to the best performance in terms of the formation of BaF$_2$.

To investigate the superhydrophobic properties of the synthesized BaF$_2$ materials, a contrast experiment was 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 trend. No matter the surface modified or unmodified, the sample p9-TM24 both showed the highest contact angle and the contact angle is 169° and 150°, respectively. It is clear seen that the TMFS modified has enormous effect on the contact angle, and pH = 9 is the best condition to synthesis the BaF$_2$ materials with super-hydrophobic property.

Further more, the durability and stability of the superhydrophobic coating of BaF$_2$ 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 the 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, which indicated that the BaF₂ materials have an excellent super-hydrophobic properties.

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 Figure 9. Obviously, at a temperature of 394.5°C, there is only a 3% weight loss (Salinas et al. 2008), 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 conclusion, the BaF₂ micron materials were successfully synthesized by a facile hydrothermal method. The results showed that the BaF₂ materials exhibited 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 indicated that the samples can maintain the stable super-hydrophobic property for over 10 days. Therefore, these excellent performances of the as-prepared BaF₂ material can probably possess enormous application prospect to replace conventional engineering materials.

Conflicts of interest
There are no conflicts to declare.

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