Formation of BaF_2 microcrystals as superhydrophobic materials via a hydrothermal method

Jinxiu Ma[1], Gaoyu Ou[1], Taohai Li[1, 2], Feng Li[1,2]*

Abstract

Controllable BaF_2 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 BaF_2 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 BaF_2 material. The results showed that uniform BaF_2 cubic phase structure was fabricated when the reaction temperature was controlled at 160 ºC for 24 h. In addition, the BaF_2 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 BaF_2 reported in this paper has potential application prospect and has a certain guiding meaning for the future study about super hydrophobic materials.

Keywords BaF_2; 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; Shirtcliffe 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. MX_2 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 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 (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 BaF_2 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.

1 College of Chemistry, Xiangtan University and Key Lab of Environment Friendly Chemistry and Application in Ministry of Education, Hunan, Xiangtan, 411105, China.

2 Nano and Molecular Systems Research Unit, University of Oulu, P.O. Box 3000, FIN-90014, Finland

So far, numerous methods were used to synthesize 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 (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 BaF_2 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 BaF_2 materials by adjusting temperature, pH, reaction time and adding surfactants. Obtained BaF_2 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 BaF_2 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 ($BaCl_2$•$2H_2O$, analytical grade), ammonium fluoride (NH_4F, 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_4F 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 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 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-Ka radiation (k = 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 1h.

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.

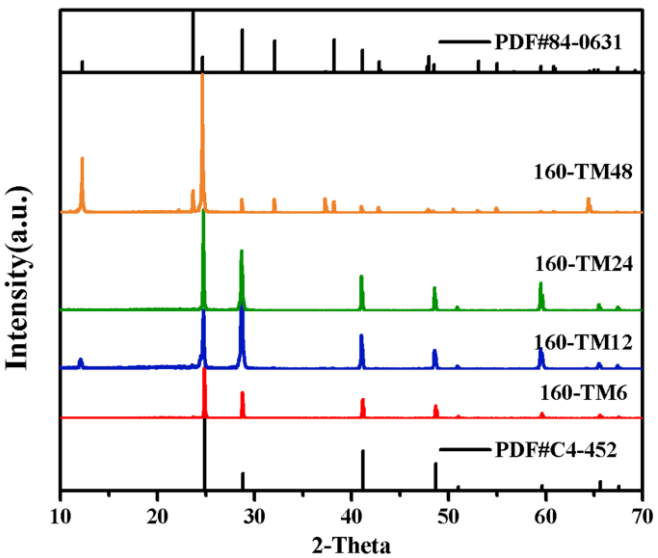

Fig.1 XRD patterns of 160-TM6, 160-TM12, 160-TM24 and 160-TM48, respectively.

To compare the effect of surfactants, three surfactants were added into the reaction system. Figure 2 is the XRD of BaF_2 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 Ba^{2+} 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 BaF_2.

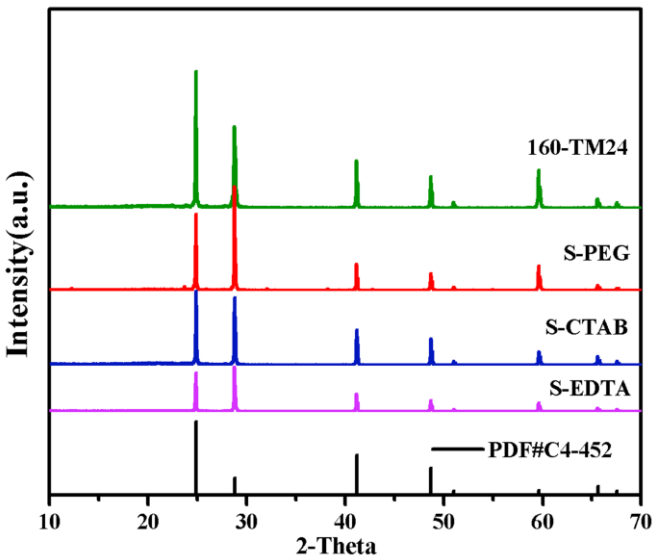

Fig.2 XRD patterns of 160-TM24, S-EDTA, S-CTAB and S-PFG, respectively

Fig. 3 shows the XRD pattern of the samples prepared at different pH values. As shown in Fig. 3, when pH = 6, the diffraction peaks of sample (p6-TM24) are much sharper than others, which means the sample has high crystallinity. When the pH value drops to 3, the diffraction peaks become much weaker. The most noteworthy is that the diffraction peaks become much sharp obviously, when the pH value is controlled to 9. However, some diffraction peaks of impurities are observed obviously, when the pH value rises to 12. The results indicate that BaF_2 materials have the higher crystallinity when the pH value was controlled to 9.

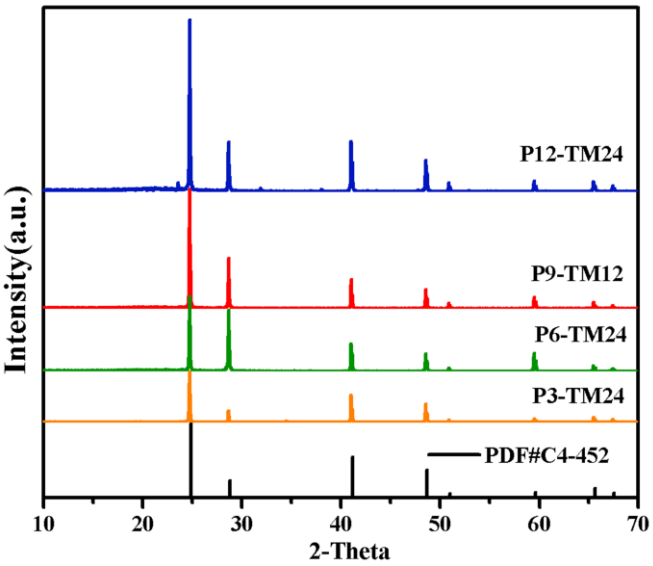

Fig.3 XRD patterns of p3-TM24, p6-TM24, p9-TM24 and p12-TM24, respectively.

Figure 4 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 BaF_2 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 BaF_2 particles which agrees well with the results of XRD.

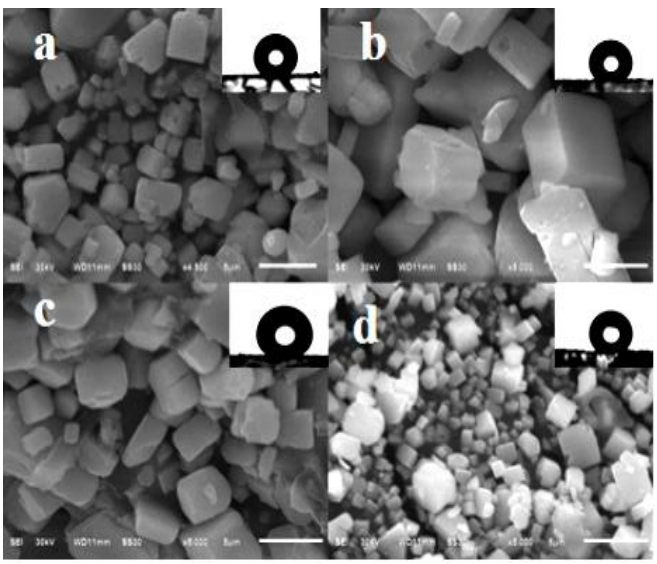

Fig.4 SEM images of the (a) S-CTAB, (b) S-EDTA, (c) S-PEG,

and (d) 160-TM24.

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: $BaCl_2 \cdot 2H_2O$ 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 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.

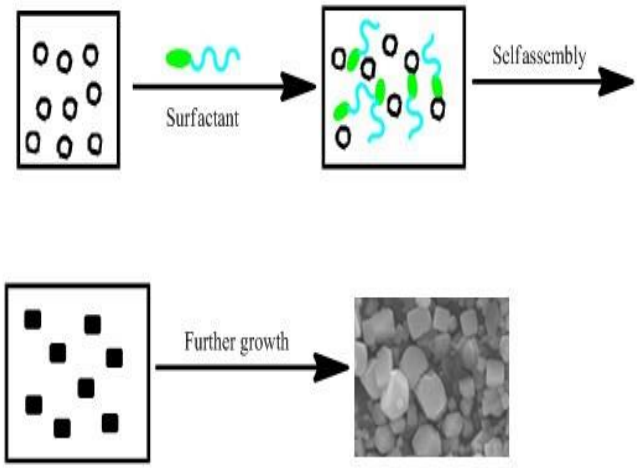

Fig.5 The reaction mechanism of BaF_2.

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.

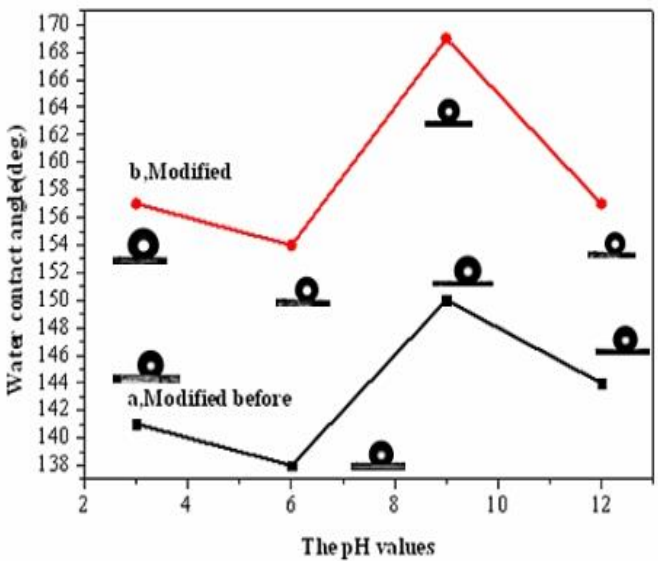

Fig.6 Water contact angles of the un-modified and modified resulting surface according to the pH of the water (a) modified before; (b) modified.

The BaF_2 particles are coated on the three substrates (glass, copper and aluminum) by drop-casing to measure the water contact angles. Fig. 7 shows the water contact angles of the modified surface on the different substrates. The results show that all the surfaces exhibit an excellent super-hydrophobic property. Especially, the contact angle of BaF_2 surface coated on copper reaches to 156°. The glass surface is just 155° and the aluminum is just 147°. The result shows that BaF_2 surface coated on copper have excellent super-hydrophobic performance.

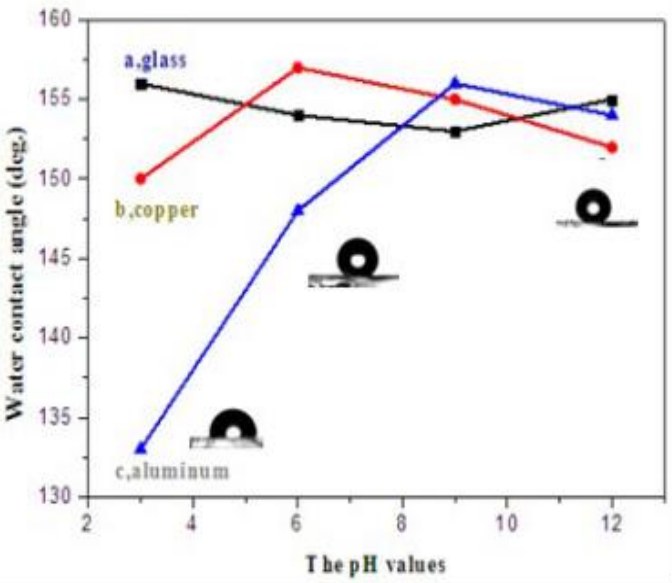

Fig.7 Water contact angles of the modified resulting surface according to the pH of the water with different substrates (a) glass, (b) copper, (c) aluminum.

Furthermore, the durability and stability of the super-hydrophobic 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 156º after 10 days and its contact angle maintains above 150 º in 40 days, which indicated that the BaF_2 materials have an excellent super-hydrophobic properties

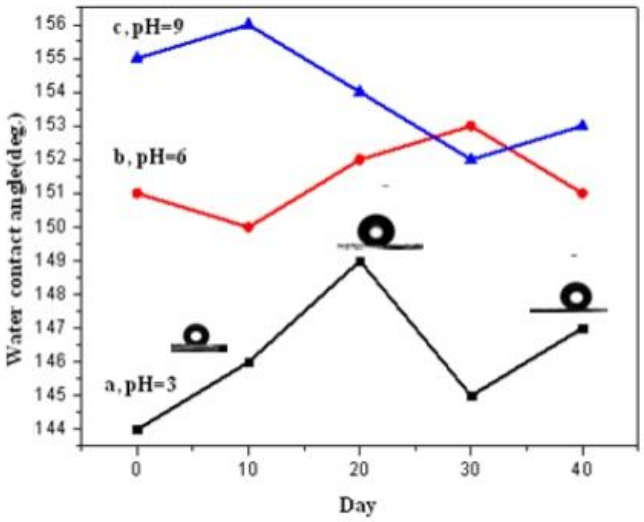

Fig.8 Water contact angles of the modified resulting surface according to the time of the water with different pH value.

Thermogravimetric analysis was also carried out to study the stability of the samples. The thermogravimetric analysis of BaF_2 crystals was under the protection of N_2 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 394.5ºC, 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 BaF_2 material.

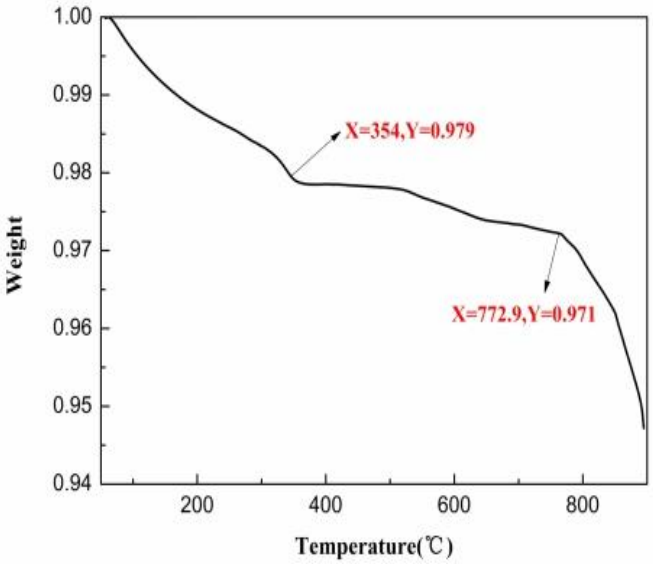

Fig.9 TGA analysis of 160-TM24.

4 Conclusions

In conclusion, the BaF_2 micron materials were successfully synthesized by a facile hydrothermal method. The results showed that the BaF_2 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 BaF_2 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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