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# Low-temperature synthesis of $BaTiO_3$ powders by the sol–gel-hydrothermal method

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## Abstract

$BaTiO_3$ powders were successfully prepared by a novel sol–gel-hydrothermal method using tetrabutyl titanate and barium acetate as the main raw materials. The phase composition and microstructure of the powders were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The results indicate that $BaTiO_3$ powders with well-developed crystallinity and good morphology could be synthesized at 120 °C (12 h) comparatively lower than the normal sol–gel route. The crystallinity and morphology were less affected by further increasing the reaction temperature and time. However, the KOH concentration had a great impact on the crystallinity and particles size of the powders that were all cubic phase with perovskite structure.

*Keywords:* Synthesis; Sol–gel-hydrothermal; $BaTiO_3$; Powders

## 1. Introduction

As a kind of typical electronic ceramic materials, barium titanate ($BaTiO_3$) is widely utilized in fabricating multilayer ceramic capacitors (MLCCs), positive temperature coefficient of resistivity (PTCR) thermistors, dynamic random access memory (DRAM) and piezoelectric sensors due to its excellent properties, such as high permittivity, outstanding ferroelectric and piezoelectric properties, etc. [1–3].

Generally, the preparation technology of ceramics powders has an important effect on the microstructure, which affects the performance of ceramics significantly. In order to improve the property of $BaTiO_3$ ceramics, the application of a new preparation method of $BaTiO_3$ powders has become a hotspot in electroceramics field. Conventionally, $BaTiO_3$ is prepared by solid-state reaction using $TiO_2$ and $BaCO_3$ as raw materials under high temperature above 900 °C [4], whereas as-prepared $BaTiO_3$ powders are agglomerated easily and distributed widely with low purity as well as uncontrolled morphologies, leading to poor electrical properties of the sintered body [5]. The wet-chemistry synthesis techniques mainly include hydrothermal method [6], solvothermal method [7], sol–gel processing [8,9], chemical coprecipitation [10], microwave heating [11], etc. Recently, much attention has been focused on the preparation of $BaTiO_3$ powders by the sol–gel technique because of their mild reaction conditions and the outstanding performance of as-obtained powders such as high purity, excellent particles distribution, compositional control and homogeneity.

However, the sol–gel process is regarded as a solid state method rather than a solution process because the high-temperature calcinations in air are inevitable for the formation of crystalline materials [12]. In view of the crystallizing process, the hydrothermal method is considered as a good candidate due to its low temperature and the well-crystallized products [13,14]. As a result, a novel route called the sol–gel-hydrothermal method (SGHM) which combines hydrothermal and sol–gel methods has been reported in many literatures [15–18]. Because of combining the advantages of both hydrothermal and sol–gel synthesis, the SGHM can provide high crystallinity, high purity, narrow particle size distribution, and

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well-controlled morphology of the powders, and has become a focus in the last decade in the field of ceramics powders preparation [19,20].

In this paper, the SGHM technique has been successfully used as a novel route to produce $BaTiO_3$ powders at low temperature (120 °C). The as-prepared powders were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The effects of the experimental parameters, including hydrothermal temperature, time and KOH concentration were investigated in detail.

## 2. Experimental

### 2.1. Materials

Tetrabutyl titanate ($Ti(C_4H_9O)_4$) (Aladdin reagent, China), and barium acetate ($Ba(CH_3COO)_2$) (Sinopharm Chemical Reagent Co. Ltd., China) were used as the raw materials. Acetic acid ($CH_3COOH$) (Sinopharm Chemical Reagent Co. Ltd., China) and absolute ethanol (Sinopharm Chemical Reagent Co. Ltd., China) were used as the solvent. Potassium hydroxide (KOH) was used as a mineralizer. Distilled water was used as an additional agent during the hydrothermal process and for the aqueous solutions and washing. The chemicals in the experiment were all analytical grade reagents and were used without further treatment.

### 2.2. Synthesis procedure

0.02 mol $Ba(CH_3COO)_2$ and 0.02 mol $Ti(C_4H_9O)_4$ were dissolved in 20 ml acetic acid and 10 ml absolute ethanol under continuous stirring for 30 min, respectively. Then the absolute ethanol containing $Ti(C_4H_9O)_4$ was added dropwise into the solution of acetic acid containing $Ba(CH_3COO)_2$, maintaining a Ba:Ti mole ratio of 1:1. After stirring vigorously for 3 h, a homogenous, transparent sol was obtained. A clear wet dry was formed after allowing the sol to sit undisturbed for 3 h at room temperature. The clear gel was then treated at 80 °C for 12 h by vacuum drying to produce a dry gel which was used as the precursor of the hydrothermal process. The obtained gel precursor was introduced to a KOH aquasolution to form a suspension. The initial concentration of the KOH solution varied as 0.5 M, 1.0 M, 2.0 M, 4.0 M or 8.0 M. The as-prepared mixture was put into a Teflon-lined stainless steel-autoclave (80 ml) with a filling volume of 80%. The hydrothermal treatment was conducted at different temperatures (from 80 to 180 °C) for various time (from 3 to 48 h) allowing the autoclave to cool to ambient temperature naturally. The deposition was finally filtered, washed with acetic acid, distilled water and absolute ethanol for several times to remove $BaCO_3$ as well as other impurities and dried in a vacuum oven at 70 °C for 12 h. Finally the $BaTiO_3$ powders were obtained.

### 2.3. Characterization

The as-prepared $BaTiO_3$ powders were characterized by XRD, SEM, and FTIR spectra. The phase purity and crystalline structure of $BaTiO_3$ were determined using a X-ray diffraction diffractometer (XRD, Bruker D8 Advance) with Cu $K_\alpha$ radiation. The morphologies and size of the synthesized $BaTiO_3$ particles were observed by a scanning electron microscope (SEM, JEOL, JSM 840, Japan) employing an accelerating voltage of 20 kV. Fourier transform infrared spectra of the products were recorded on a spectrometer (FTIR, Bruker Optics, TENSOR 27, German) using the KBr pellet method in the frequency range of 400–4000 $cm^{-1}$. The size distribution histograms of $BaTiO_3$ powders were obtained using nanomeasure software and the size distribution was estimated by averaging a certain number of typical particles from the scanning electron microscope image.

## 3. Results and discussion

### 3.1. Influence of hydrothermal reaction temperature on crystallinity and morphology

Fig. 1 shows the XRD patterns of $BaTiO_3$ powders synthesized at different temperatures. As shown in the XRD patterns of the product prepared at 80 °C, the peaks of $BaTiO_3$ had begun to appear, implying that the crystallized $BaTiO_3$ powders have formed, while the crystallinity of the powders was still low due to the relatively weak peaks. As the temperature was raised over 120 °C, the well-crystalline $BaTiO_3$ powders were obtained and all the peaks of the XRD patterns could match well with the standard pattern of $BaTiO_3$ (JCPDS card: 31-0174) with cubic perovskite structure. No split of the {200} peaks (around $2\theta \approx 45^o$) and characteristics of $BaCO_3$ byproduct and other phases could be observed in the XRD patterns, indicating that as-prepared $BaTiO_3$ powders have relatively high purity and can be stabilized in the cubic form at ambient temperature [21].

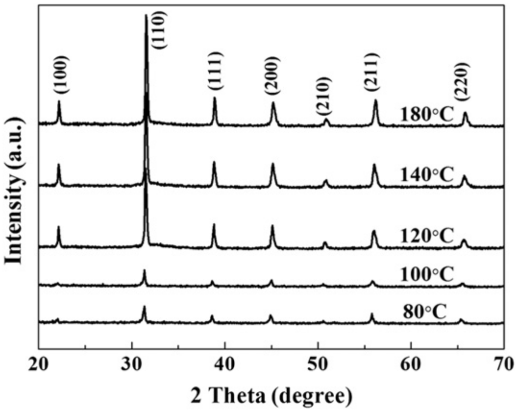

Fig. 1. XRD patterns of $BaTiO_3$ powders synthesized from 80 to 180 °C for 12 h with a KOH concentration of 2.0 M.

Theoretically, compared to the high-temperature calcinations (800–1000 °C) of the conventional sol–gel route [22], the sol–gel-hydrothermal method can decrease the synthesis temperature of $BaTiO_3$ largely. The main reason for the synthesis of $BaTiO_3$ powders at 120 °C can be attributed to the dry gel precursor obtained in the sol–gel process. During the sol–gel reaction, the barium and titanium sources can be homogenously mixed at the molecular level. The three-dimensional network structure can be obtained possibly by hydrolysis and polycondensation reaction, and initial crystallization also occurs at the same time. All of the above lead to the effective reduction of the phase transformation energy barrier for the subsequent hydrothermal treatment [23].

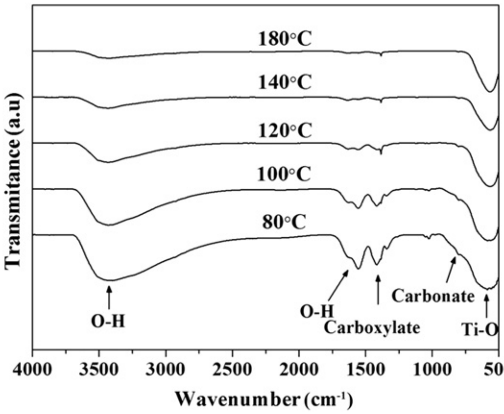

Fig. 2. FTIR spectra of $BaTiO_3$ powders synthesized from 80 to 180 °C for 12 h with a KOH concentration of 2.0 M.

In order to study the purity of the samples, the FTIR spectra of $BaTiO_3$ powders synthesized at different temperatures are shown in Fig. 2. According to the reported literatures, $BaCO_3$ is the main impurity of the $BaTiO_3$ powders prepared by the hydrothermal method, but there were no apparent absorption peaks attributed to $BaCO_3$ at around 1430 and 850 $cm^{-1}$, which indicates that $BaCO_3$ barely existed [24]. With the increase of treated temperature, the Ti–O absorption peaks increased gradually, and the absorption peaks at $3600-3000\ cm^{-1}$ (the symmetric and asymmetric stretching vibrations of O–H), 1640 $cm^{-1}$ (the bending vibration of H–O–H) [22,25] and 1420 $cm^{-1}$ (the symmetric stretching of carboxylic groups) disappeared gradually, which indicates that the crystallinity of $BaTiO_3$ powders is enhanced and highly pure $BaTiO_3$ can be obtained by hydrothermal treatment over 120 °C.

Fig. 3 shows the SEM photographs of $BaTiO_3$ prepared hydrothermally at various temperatures. For the sample synthesized at 80 °C (Fig. 3a), the powders were constructed with a number of agglomerated spherical particles. This indicates that $BaTiO_3$ particles were deficient in growth and immature when the hydrothermal temperature was only 80 °C. As the temperature increased, uniform $BaTiO_3$ particles with spherical shape gradually formed (Fig. 3b–d). However, different from the obvious growth of $BaTiO_3$ particles under traditional hydrothermal conditions, the size of $BaTiO_3$ particles prepared by SGHM does not increase apparently with the rise of treated temperature, and the average particles sizes were about 170, 190 and 210 nm for the samples treated under 120 °C, 140 °C, and 180 °C, respectively (Fig. 4). This may result from the

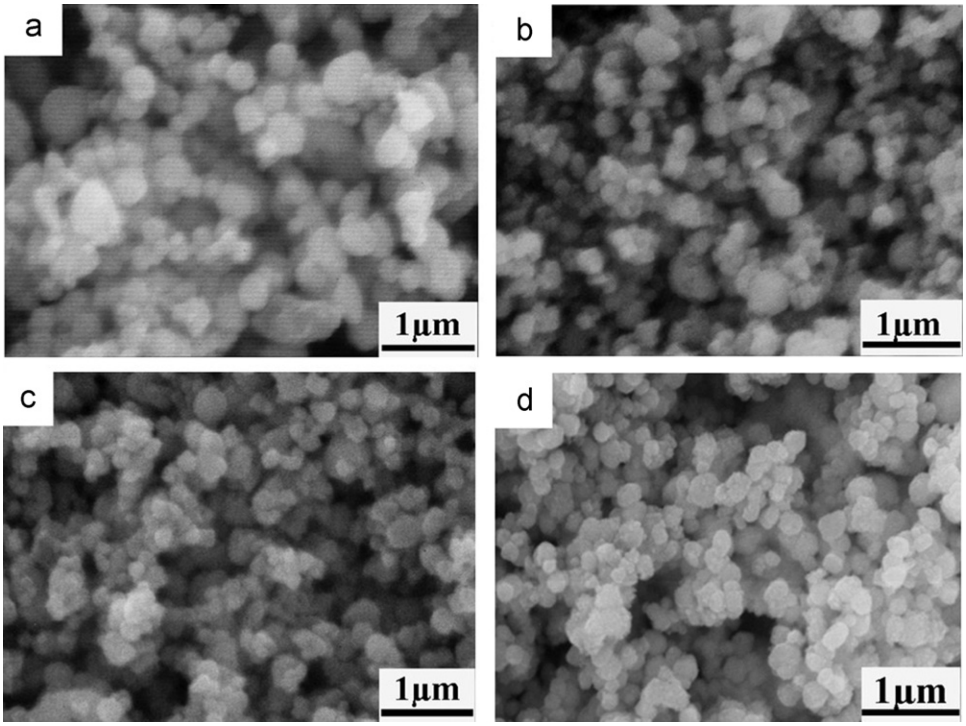

Fig. 3. SEM photographs of $BaTiO_3$ powders synthesized at different temperatures for 12 h with a KOH concentration of 2.0 M: (a) 80 °C; (b) 120 °C; (c) 140 °C; and (d) 180 °C.

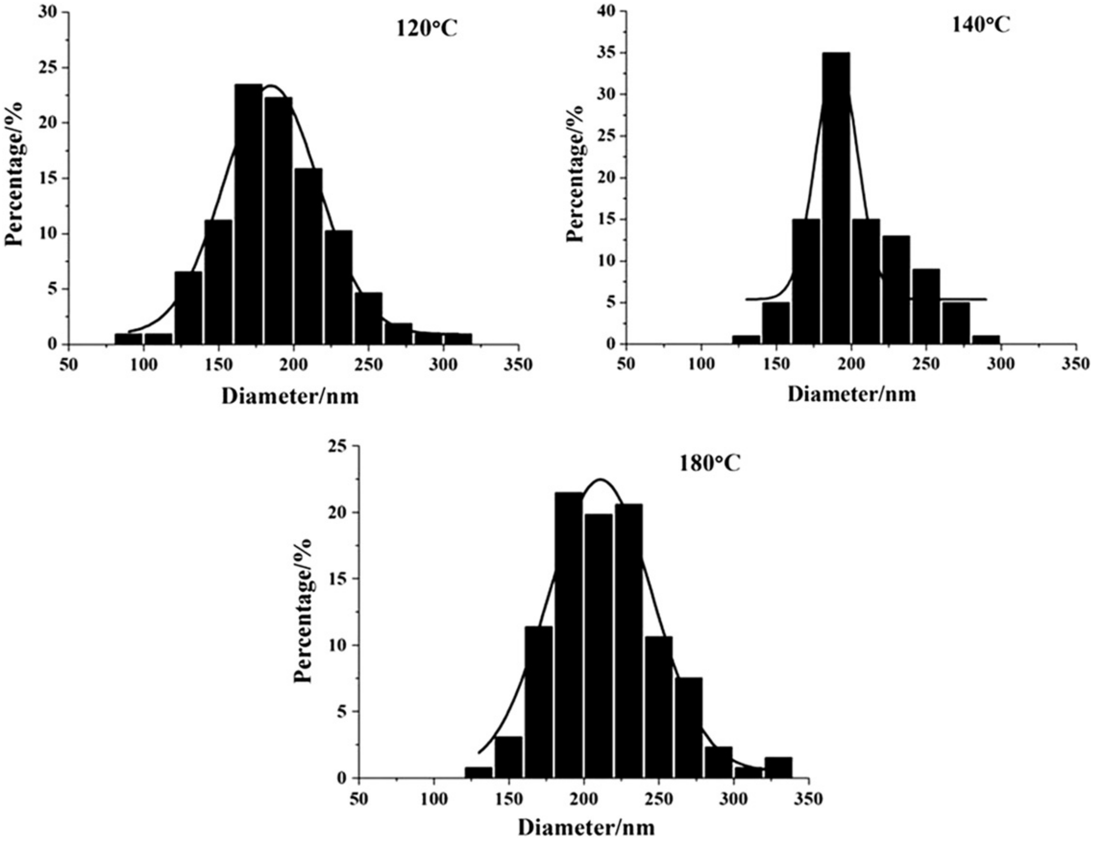

Fig. 4. The size distribution histograms of $BaTiO_3$ powders synthesized at different temperatures for 12 h with a KOH concentration of 2.0 M.

well-controlled growth of gel precursors. Therefore, the SGHM is a promising way to produce the high-crystalline uniform $BaTiO_3$ powders with small particle size under low-temperature conditions.

### 3.2. *Influence of hydrothermal reaction time on crystallinity and morphology*

Fig. 5 shows the XRD patterns of $BaTiO_3$ powders synthesized at various reaction time. As the time was only 3 h, peaks corresponding to perovskite $BaTiO_3$ had appeared and the intensity of the peaks was relatively strong. However, it was observed that the intensity of the $BaTiO_3$ peaks did not change obviously with the further extension of the reaction time. This indicates that the crystalline $BaTiO_3$ had formed after treating at 120 °C for 3 h and when the reaction time is longer than 3 h, the crystallinity is independent of reaction time according to Fig. 5.

Fig. 6 shows SEM photographs of $BaTiO_3$ powders synthesized at 120 °C for different reaction time. The $BaTiO_3$ particles obtained for 6 h presented large agglomerated materials consisting of nano-sized grains due to the deficiency in growth (Fig. 6a). When the hydrothermal reaction time was prolonged from 12 to 48 h, the crystallization of samples was improved, however, the change of crystallinity and morphology was not obvious. Therefore, considering the energy cost and the crystallinity, we chose 12 h as the optimum time in our experiment.

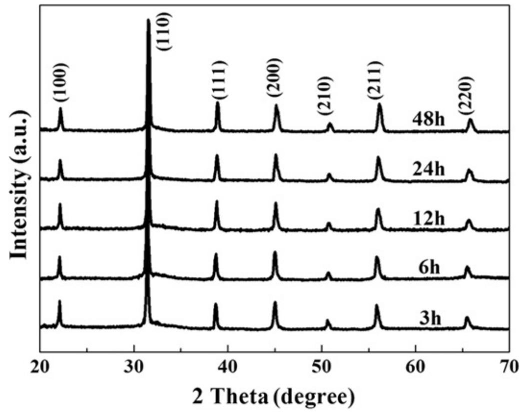

Fig. 5. XRD patterns of $BaTiO_3$ powders synthesized at 120 °C for different reaction time from 3 to 48 h with a KOH concentration of 2.0 M.

### 3.3. *Influence of KOH concentration on crystallinity and morphology*

Fig. 7 displays the XRD patterns of $BaTiO_3$ powders synthesized with KOH concentration from 0.5 to 8.0 M. When KOH concentration was 0.5 M, the diffraction peaks of $BaTiO_3$ appeared, but the intensity of the peaks was weak indicating the low crystallinity of the powders. In 1.0 M KOH,

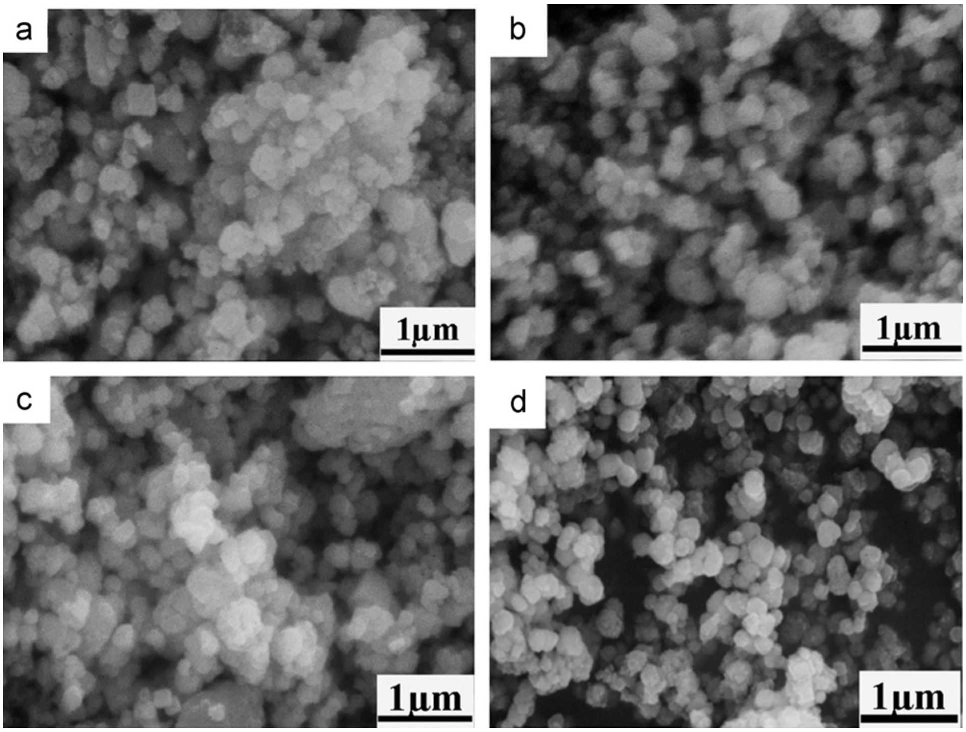

Fig. 6. SEM photographs of $BaTiO_3$ powders synthesized at 120 °C with a KOH concentration of 2.0 M for different reaction time: (a) 6 h; (b) 12 h; (c) 24 h; and (d) 48 h.

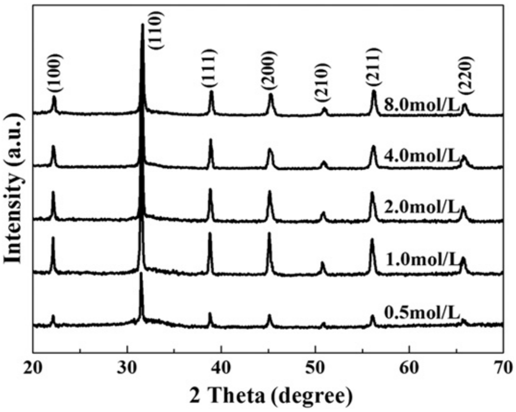

Fig. 7. XRD patterns of $BaTiO_3$ powders synthesized at 120 °C for 12 h with KOH concentrations from 0.5 to 8.0 M.

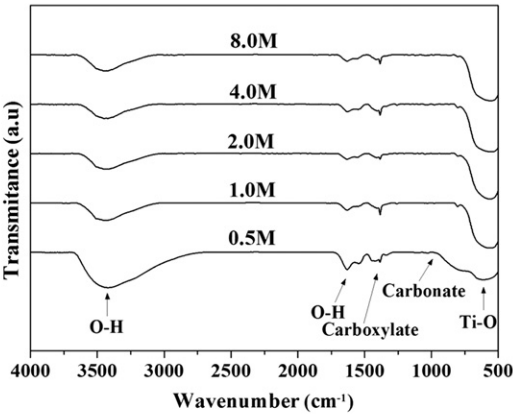

Fig. 8. FTIR spectra of $BaTiO_3$ powders synthesized at 120 °C for 12 h with KOH concentrations from 0.5 to 8.0 M.

the diffraction peaks were enhanced obviously. However, as KOH concentration increased over 1.0 M, the intensity of the peaks gradually decreased. A similar phenomenon had also been reported by Hwang et al. [22]. As-obtained $BaTiO_3$ powders were of cubic perovskite structure because all the XRD patterns match well with the standard pattern of $BaTiO_3$ (JCPDS card: 31-0174), and no split at {200} peak can be observed. Thus it can be concluded that the optimum KOH concentration in preparing $BaTiO_3$ via SGHM is 1.0 M.

Fig. 8 shows the FTIR spectra of $BaTiO_3$ powders with different KOH concentrations. No obvious absorption peaks attributed to $BaCO_3$ at around 1430 and 850 $cm^{-1}$ could be noted as the KOH concentration increased, which shows that no $BaCO_3$ is produced with the change of KOH concentration. In 0.5 M KOH, the Ti–O absorption peak was relatively weak and the absorption bands corresponding to the O–H stretching vibration were apparent, which suggests the low crystallinity of $BaTiO_3$ powders. With the increase of KOH concentration, the intensity of Ti–O absorption peaks enhanced strongly, while the peaks of O–H and the carboxylic groups became very low. This indicates that the purity of as-obtained powders cannot be influenced obviously by the KOH concentration.

Fig. 9 illustrates SEM photographs of $BaTiO_3$ powders synthesized with different KOH concentrations. In 0.5 M KOH, it could be observed that the product was composed

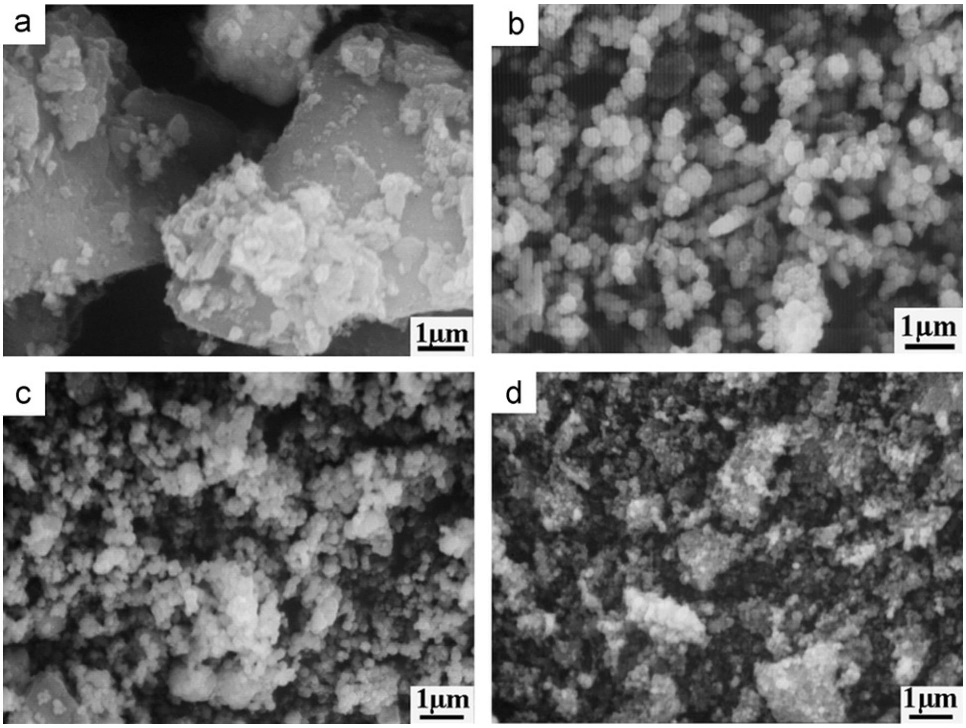

Fig. 9. SEM photographs of $BaTiO_3$ powders synthesized at 120 °C for 12 h with different KOH concentrations: (a) 0.5 M; (b) 1.0 M; (c) 4.0 M; and (d) 8.0 M.

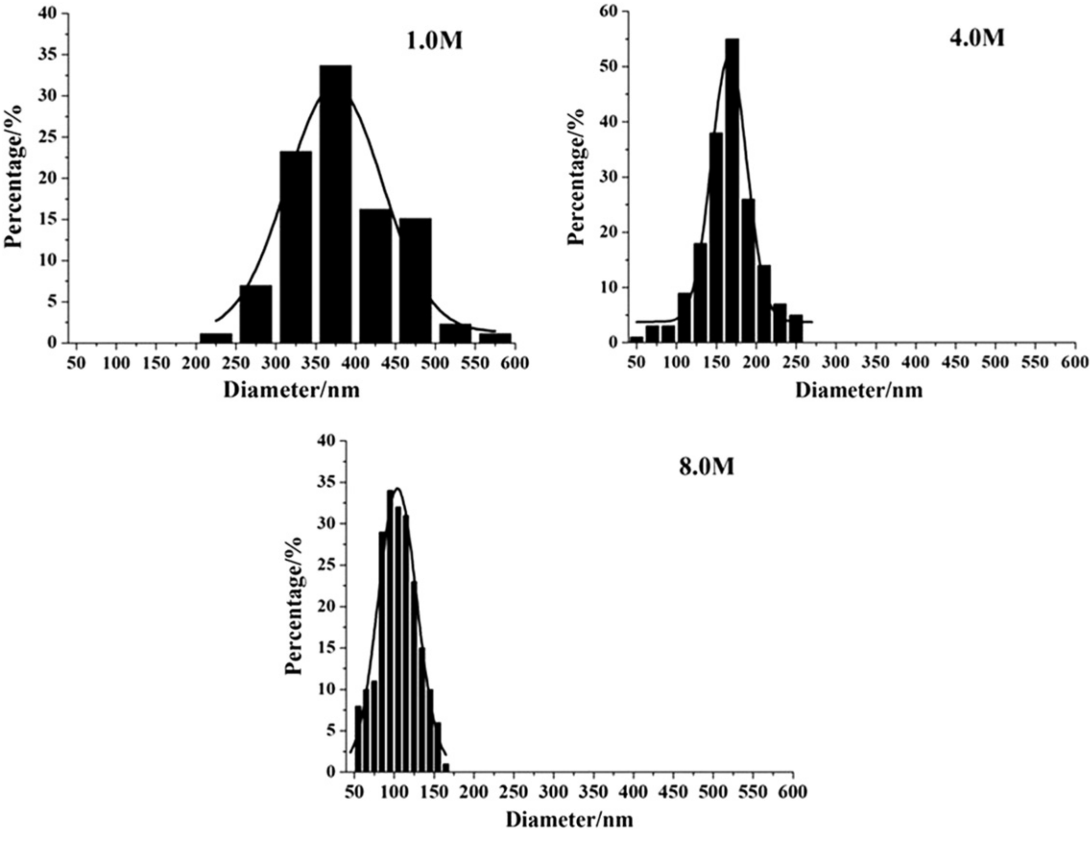

Fig. 10. The size distribution histograms of $BaTiO_3$ powders synthesized at 120 °C for 12 h with different KOH concentrations.

of unfeatured conglomeration without obvious separate particles as shown in Fig. 9(a). Considering the results of XRD and FTIR, it can be concluded that these particles cannot grow well and part of them are still non-crystalline under the condition of low KOH concentration. However, as shown in Fig. 9(b–d), well-developed spherical $BaTiO_3$ particles could be generated when the KOH concentration was just over 1.0 M, suggesting that KOH concentration plays an important role in the formation of $BaTiO_3$, and the necessary value is 1.0 M. Interestingly, KOH concentration could affect the particle size greatly. The average particles size of $BaTiO_3$ could decrease from 370 nm to 100 nm as the concentration of KOH changed from 1.0 M to 8.0 M (Fig. 10). The phenomenon may be explained by the surface chemistry of $BaTiO_3$. The surface of $BaTiO_3$ is negatively charged in the solutions with $pH > 10$. Based on this, the surface of $BaTiO_3$ particles is inclined to be negatively charged and repel each other when the amount of hydroxyl group increases with the increase in KOH concentration. The particles size becomes smaller as a result of the decrease in the collision frequency [22].

## 4. Conclusions

A novel sol–gel-hydrothermal method has been carried out to prepare $BaTiO_3$ powders successfully. Well-crystallized, pure $BaTiO_3$ particles with cubic structure have been obtained at only 120 °C for 12 h as the KOH concentration was over 1.0 M. Although the crystallinity and morphology are less affected by further increase in the reaction temperature and time, the KOH concentration has an important effect on the crystallinity and particles size of samples. The average size of $BaTiO_3$ particles varies from 370 nm to 100 nm when the KOH concentration increases from 1.0 M to 8.0 M. Being a gentle environment method, the sol–gel-hydrothermal method provides a simple route to produce the highly pure and uniform $BaTiO_3$ powders products, and exhibits a wide application prospect.

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