Controlled synthesis of flower-like CaTiO$_3$ and effects of morphology on its photocatalytic activities

Weixia DONG,$^{*,**}$ Qifu BAO,$^*$ Xingyong GU$^*$ and Gaoling ZHAO$^{**}$

$^*$Department of material Science and Engineering, Jingdezhen Ceramic Institute, Jingdezhen, 333001, P. R. China
$^{**}$State Key Lab of Silicon Material & Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China

CaTiO$_3$ structure with flower-like morphology was prepared by a template-free and surfactant-free solvothermal process in an ethanol-H$_2$O mixed solvent. The possible growth of flower-like structure was discussed based on the experimental results. During this process, PVP and NaOH affected drastically the kinetics of crystal growth and morphology of CaTiO$_3$. NaOH played a crucial role in the formation of CaTiO$_3$ flower-like structure without surfactant. A diffusion-limited and etching growth mechanism was proposed to elucidate the formation of CaTiO$_3$ flower-like structure. Experiment results indicated that the as-synthesized flower-like morphology exhibited higher photocatalytic activities for RhB evolution than those of the “cubic” cubic and prism-like structures, which was attributed to the special flower-like structure morphology. The electrochemical property of flower-like morphology was investigated through the cyclic voltammogram (CV) measurement.

Key-words : Flower-like CaTiO$_3$, Solvothermal method, Controlled synthesis, Photocatalytic activities

1. Introduction

In the recent years, the fabrication of complex inorganic material with controlled structure, composition, and tailored properties have attracted significant consideration due to their novel properties and potentially numerous applications in optics, catalysis, electronics, biology, lightweight filler materials and chemical reactors. Recently, lots of hierarchical morphogenesis, such as dendrite-like, snowflake-like, dandelion-like, dumbbell structures and sheaf-like structure have been synthesized using the various methods. Among these methods, the surfactant- and/or template-assistant method is used to control the morphology of the products. However, the use of surfactants and templates make the process complicated and expensive which restrict the popularization of the surfactant- and/or template-assistant techniques in practical applications. Thus, it is great significance to develop facile and effective surfactant- and/or template-free methods for the controllable synthesis of hierarchical structures.

As an important group of compounds with perovskite-type structure, calcium titanate (CaTiO$_3$) has began to attract wide attention because of their potential applications such as semiconductors, luminaire, and optoelectronics. Due to its potential application, CaTiO$_3$ was initially synthesized by the conventional solid-state reaction. However, the method presented several problems such as high treatment temperature, inhomogeneity and contamination by impurities. To avoid these problems, chemical vapor deposition (CVD), coprecipitation method, sol–gel and organic-inorganic solution technique have been employed to synthesize CaTiO$_3$ with desired stoichiometry. However, these methods need the assisted additive to synthesize CaTiO$_3$ which not only increases the production cost but also makes it difficult for scale up production. In addition to these methods, one-step hydrothermal method is a promising option for the preparation of well-crystallized CaTiO$_3$ due to its simple, fast and less expensive virtues. Although many researches have been done on the formation of flower-like hierarchical structure of inorganic material, such as oxides, chalcogenides, selenium compounds, sulfide and so on, to the best of our knowledge, only few 3D hierarchical nanostructures, especially the flower-like nanostructure have been reported for CaTiO$_3$.

Here, we report a facile surfactant-free and template-free hydrothermal route to the control synthesize CaTiO$_3$ flower-like structure. The effects of the temperature, NaOH and PVP contents are investigated in detail on the formation of the CaTiO$_3$ products. The photocatalytic and electrochemical properties are studied.

2. Experimental section

In a typical procedure, 0.01 mol CaCl$_2$ was put into 36 ml of water under vigorous stirring. Subsequently, a certain amount of NaOH was added into the above solution under continuous stirring. Then the mixture of 0.01 mol titanium n-butoxide [Ti(OC$_4$H$_9$)$_4$] and 5 ml of ethanol was dropwise added into the above solution under continuous stirring. After being stirred for 20 min, the total solution was transferred into a 100 ml Teflon-lined stainless steel autoclave and maintained at 180°C for 24 h, followed by natural cooling to room temperature. Afterward, the products were centrifuged and washed with distilled water several times. The final products were dried under a vacuum at 90°C for 12 h. Other experiment were also carried out in order to investigate the effects of different parameters including the temperature, the amount of PVP and NaOH on morphologies of as-prepared samples while keeping other conditions unchanged.

The working electrode was prepared by mixing 80 wt% of the as-prepared CaTiO$_3$, 10 wt% of acetylene black and 10 wt% of poly(tetrafluoroethylene), and pressing (10 MPa) the mixture onto a nickel grid (1.5 cm$^2$).

$^*$ Corresponding author: W. Dong; E-mail: weixia.dong@sina.com

©2015 The Ceramic Society of Japan. All rights reserved.

DOI: http://dx.doi.org/10.2109/jcersj2.123.643
2.1 Characterization

The morphologies and compositions of the powders were investigated by field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan) equipped with an energy-dispersive X-ray spectroscopy (EDS). The crystal phases of the products were characterized by X-ray diffraction (XRD, PANalytical X’Pert Pro, Holland), in a 2θ range from 10 to 80°, using Cu-Kα radiation (λ = 0.15405 nm) at V = 50 kV and I = 40 mA at a scan rate of 0.04° s⁻¹. The microstructures of the products were analyzed using transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F-30, Holland) operating at an accelerating voltage of 200 kV. N₂ adsorption/desorption was determined by Brunauer–Emmett–Teller (BET) measurements using a Micromeritics TriStar ii 3020 analyzer. Cyclic voltammograms (CV) and chronopotentiometry (CP) were measured by a CHI660B electrochemical workstation in a three-compartment cell with a working electrode, a platinum plate counter electrode and a saturated calomel electrode (SCE) reference electrode. The electrolyte was a 6 M KOH aqueous solution. The SCS of the composites were calculated from the CP curves based on Eq. (1):

\[ C = \frac{I \Delta t}{m \Delta ν} \]  

where I, m, Δt, Δν and C are the discharge current, the mass of the composite, the potential window during discharging, the total discharge time and the specific capacitance, respectively. Galvanostatic charge-discharge was carried out by LAND CT2001A test system.

2.2 Measurements of the photocatalytic properties

The photocatalytic activities of CaTiO₃ products were evaluated by degradation of rhodamine B (RhB) under the irradiation of UV light. An aqueous CaTiO₃ dispersion was prepared by adding 0.025 g of CaTiO₃ powder into 10.0 ml of RhB solution (1 × 10⁻⁵ M). The solution was magnetically stirred and irradiated by UV light (254 nm, 11 W). After irradiation for a designated time, the suspension was centrifuged to separate the CaTiO₃ particles, and the RhB concentration of the filtrate was determined using the TU-1901 spectrophotometer equipped with a reflectance attachment.

3. Results and discussion

3.1 Morphology and structure of CaTiO₃ flowerlike structure without surfactant

Figure 1(a) shows the XRD pattern of the CaTiO₃ sample with typical flower-like morphology, the main identified peaks are in good agreement with those of CaTiO₃ (JCPDS: 42-0423), confirming that the as-prepared sample has good crystallinity. Meanwhile, two tiny diffraction peaks of Ti₂O₅ are detected. Figure 1(b) shows that FESEM image of the as-prepared sample. The sample is composed of flowerlike structure with a little trace of imperfect flower-like structure. A typical TEM of the flower-like structure [Fig. 1(c)] exhibits good and uniformity of shape and size. The total length of the flowerlike structure is approximately 500–600 nm. Furthermore, the corresponding EDS spectrum shown in Fig. 1(d) reveals that the flowerlike structure consists of Ca and Ti with a ratio of about 1:1, which is close to the stoichiometry of CaTiO₃.

To provide further insight into flowerlike structure, TEM, SAED and HRTEM images are shown in Fig. 2. Figure 2(a) shows that the SAED pattern in the low-magnification TEM image of the flowerlike structure, indicating a single crystal structure. Figure 2(b) shows that HRTEM images in 1 marked in Fig. 2(a). The observed lattice fringe distances are 0.383 nm, which is in good agreement with the (101) spacing of CaTiO₃. The FFT of the HRTEM image [inset of Fig. 2(b)] gives the preferential growth direction of [101]. Figure 2(c) shows that the d spacing of the circle marked with 2 in Fig. 2(a) is also 0.382 nm, which agrees well with the lattice spacing of (101) of orthorhombic CaTiO₃. Figure 2(d) also shows that the circle marked with 3 in Fig. 2(a) is also 0.382 in accord with lattice spacing of (101). It seems that the CaTiO₃ crystals grows along [101] directions to form the flower-like dendrites.
3.2 Influences of reaction parameters on the formation of CaTiO$_3$ with various morphologies

The morphologies of the CaTiO$_3$ products can be affected by many factors such as the reaction temperature, NaOH concentration and PVP, which are systematically investigated. Figure 3 shows FESEM images of the samples synthesized at the various temperature with all other reaction conditions unchanged. When the reaction temperature is reduced to 140°C, the sample is composed of many tiny nanosheets [Fig. 3(a)] and the corresponding sample is not CaTiO$_3$ phase. When the temperature is increased to 220°C, the polyhedron is observed as shown in Fig. 3(b). These observations suggest that the formation of CaTiO$_3$ flower-like morphology is subject to an appropriate temperature at 180°C (Fig. 1).

In the experiments, the formation of the CaTiO$_3$ flower-like structure is found to strongly depend on NaOH concentration. Figure 4 shows the FESEM images of the samples obtained at various NaOH concentrations from 2 to 8 M at 180°C and keeping other experimental conditions unchanged. When NaOH concentration is 2 M, the cubic structure is observed [Fig. 4(a)]. Further increasing NaOH concentration to 8 M leads to the formation of the “cross” cubic structure as shown in Fig. 4(d).

Surfactants can also play an obvious role in the morphology of the products. Figure 5 shows that the FESEM images of the as-prepared product in 3 M NaOH at 180°C for 24 h without any surfactant is 0.04 g, the imperfect flower-like structure with pits is obtained as Fig. 5(a). When PVP is 0.1 g, the prism-like structures with the etching pits are shown in Fig. 5(b). When PVP increases to 0.16 g, the prism-like morphology with smooth surface is obtained as shown in Fig. 5(c). Further increasing PVP to 0.28 g, the dendrites are obtained as shown in Fig. 5(d).

3.3 Conversion mechanisms of CaTiO$_3$ crystals

On the basis of the above experimental results, it is possible to control and tune the shape of CaTiO$_3$ crystals by controlling the appropriate experiment parameters. To shed light on how the experimental conditions result in the as synthesized samples with various morphologies, the summary of morphology evolution for the samples is shown in Table 1. It indicates that changing the experimental parameters (e.g., NaOH, PVP, and temperature etc.) may lead to the formation of CaTiO$_3$ crystals with diverse shapes and tunable sizes. When the reaction temperature is lower (140°C), low energy can not afford a number of CaTiO$_3$ nuclei and growth at the initial stage of the reaction. When the reaction temperature was improved (i.e. 180 and 220°C), the speed of CaTiO$_3$ nucleation and growth is greatly accelerated, the mechanism of CaTiO$_3$ flower-like structure (i.e. 180°C) would be discussed later. It is well known that the {111} surface intrinsically possesses a higher surface energy than those of the {100} or {110} faces for fcc structure, so the {111} facets can easily be stabilized.21) When the reaction temperature is relatively high (220°C), more Ti$^{4+}$ ions selectively adsorbed on the {111} facets could stabilize the {111} facets, and thus the growth rates along the {111} directions were confined. The {100} and {101} facets were remained because of their lower growth rates, which might result in the formation of polyhedron shape [Fig. 3(b)]. In the present work, NaOH is used as a coordination agent, and the concentration of OH$^-$ ions affects the concentration of Ti$^{4+}$ ions, thus, and affects the reaction rate, which can influence the final shapes.22) As is well known, the formation of crystals involves two steps: nucleation and growth. When NaOH concentration is below 4 M, due to the lower amounts of active OH$^-$ ions, Ti$^{4+}$ concentration is relatively low around the CaTiO$_3$ nucleus and also low in the regions far from the nucleation centers. Thus, Ti$^{4+}$ ions will diffuse only slowly into the CaTiO$_3$ nucleation regions, which limit the crystal growth rate. According to the Berg effect, the concentration of reaction ions over the corners, edge, and side face is supposed to decrease in sequence.22) Ti$^{4+}$ ions may not only
growth results in OH− similar with those at lower NaOH concentration (2.75, 3.5 and 4 M). Meanwhile, the etching of OH− ions can be seen in Figs. 1 and 4(a)−4(c). These results indicate slow diffusion-limited growth results in OH− etching processes, which are responsible for the flower-like and dendritic shapes. Some similar OH− etching mechanisms have been reported in the synthesis of PbS cubes structure.23) When NaOH concentration further increases to 8 M, the crystal morphology depends on the competition between nucleation and growth that can be adjusted through controlling the reaction rate.22) Enough high NaOH concentration provides the enhanced surface recrystallization but also facilitates self-oriented aggregation and consequent crystal growth. The reaction rate is excessively fast, CaTiO3 particles addition would be faster than the dissolution of atoms caused by etching. The crystal growth cannot perform the preference growth caused by OH− etching at such a fast reaction rate. In this case, there are enough growth units to make CaTiO3 cubes grow from the solution. Moreover, in our experiment, abundant water is added in the reaction system. It not only enhances the surface recrystallization but also facilitates self-adjustment of the orientations of the particles. So instead it is beneficial for the formation of the “cubic” cubic shapes. When PVP was added in the system, PVP as capping molecules can adsorb onto the surfaces of crystals via ligand coordination, and the adsorption of PVP on different crystal faces may direct the growth of particles.23) When PVP is 0.04 g, under the competition between PVP and the etching of OH−, as well as the competition between the recrystallization of CaTiO3 and the etching of OH−. It has been reported that PVP may attach to the 100 planes of CaTiO3 and slow the rate of 100 planes.21) Owing to the slow diffusion-limited process, the etching of OH− dominate in the hydrothermal process, OH− is apt to attack the 100 planes of CaTiO3 crystals, and induce the surface energy rearrangement of CaTiO3 nuclei, which results in the formation of flower-like morphology with solid hierarchical structure [Fig. 5(a)]. And the flower-like structure with a lot of pits shown in Fig. 5(a), also gave cogent support to the above etching process in the presence of PVP. Introducing 0.1 g PVP [Fig. 5(b)] could intrinsically change the growth mechanism, and a fast growth process dominated by PVP could be appropriate for the formation of CaTiO3 prism-like morphology. The imperfect prisms with a lot of the etching pits are obtained, which suggests that PVP molecules adhere to the surfaces of the prisms and act as a protective layer to confine the free etching of NaOH. However, the unprotected areas are besieged by OH− ions, which lead to the etching and the etching pits occurring as shown in Fig. 5(b). When PVP increases to 0.16 g, the adsorption of lots of PVP molecules on the crystal CaTiO3 surface enhances a better oriented aggregation and confines the free etching of NaOH, therefore, the intact prisms are obtained. Similar phenomenon has been reported when using PVP as surfactant to effectively control the anisotropy growth of nano-crystals in the preparation of Fe2O4 dendrite.24) Further increasing PVP to 0.28 g, the related mechanism may have been drastically changed. The polar face of the CaTiO3 could be terminated with PVP molecules, which may prevent the growth along these faces and induces the anisotropy growth guided by PVP as a soft template.25)

### Table 1. Summarized morphologies and their corresponding experimental conditions

<table>
<thead>
<tr>
<th>sample</th>
<th>morphology</th>
<th>orientation</th>
<th>PVP (g)</th>
<th>NaOH (M)</th>
<th>Reaction time (h)</th>
<th>Reaction temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>flower-like</td>
<td>best</td>
<td>0</td>
<td>3</td>
<td>24</td>
<td>180</td>
</tr>
<tr>
<td>B</td>
<td>nanosheets</td>
<td>worst</td>
<td>0</td>
<td>3</td>
<td>24</td>
<td>140</td>
</tr>
<tr>
<td>C</td>
<td>polyhedron</td>
<td>better</td>
<td>0</td>
<td>3</td>
<td>24</td>
<td>220</td>
</tr>
<tr>
<td>D</td>
<td>flower-like</td>
<td>better</td>
<td>0.04</td>
<td>3</td>
<td>24</td>
<td>180</td>
</tr>
<tr>
<td>E</td>
<td>prism-like with pits</td>
<td>general</td>
<td>0.1</td>
<td>3</td>
<td>24</td>
<td>180</td>
</tr>
<tr>
<td>F</td>
<td>prism-like</td>
<td>best</td>
<td>0.16</td>
<td>3</td>
<td>24</td>
<td>180</td>
</tr>
<tr>
<td>G</td>
<td>dendrites</td>
<td>general</td>
<td>0.28</td>
<td>3</td>
<td>24</td>
<td>180</td>
</tr>
<tr>
<td>H</td>
<td>flower-like</td>
<td>better</td>
<td>0</td>
<td>2.75</td>
<td>24</td>
<td>180</td>
</tr>
<tr>
<td>I</td>
<td>flower-like</td>
<td>better</td>
<td>0</td>
<td>3.5</td>
<td>24</td>
<td>180</td>
</tr>
<tr>
<td>J</td>
<td>dendrites</td>
<td>better</td>
<td>0</td>
<td>4</td>
<td>24</td>
<td>180</td>
</tr>
<tr>
<td>K</td>
<td>“cross” cubic</td>
<td>best</td>
<td>0</td>
<td>8</td>
<td>24</td>
<td>180</td>
</tr>
</tbody>
</table>

#### 3.4 Optical properties of CaTiO3 structure

The optical properties of CaTiO3 were studied by UV−visible optical absorbance spectra as shown in Fig. 6. From Fig. 6, it is obvious that the samples exhibit a strong absorption below 400 nm. The inset of Fig. 6 shows the plot of (ahν)2 versus photon energy (hν) for the sample A (flower-like morphology), sample F (prism-like morphology) and sample K (“cross” cubic morphology). The optical absorption near the band edge follows the equation \(\alpha h\nu = A(h\nu-E_g)^{n/2}\), where \(\alpha\), \(h\nu\), \(E_g\), and \(A\) are the absorption coefficient, light frequency, band gap, and constant, respectively.26) According to this equation, the value \(n\) for the present samples was 4 using the data in Fig. 6 (inset). The band gap value \(E_g\) can be calculated by extending the linear part...
of the curve to zero absorption. The band gap values of the CaTiO$_3$ flower-like morphology and “cross” cubic morphology are similar: 3.45 and 3.42 eV, respectively, which is in good agreement with literature values. For the CaTiO$_3$ prism-like morphology, the band gap values shifted to 3.23 eV, which is lower than that of the CaTiO$_3$ flower-like and “cross” cubic morphologies. It is attributed to the generation of the CaTiO$_3$ prism-like containing PVP in the sample.

3.5 BET Test

A nitrogen adsorption–desorption measurement was measured to gain the information about the BET surface area and pore sizes. As shown in Fig. 7, the isotherm can be categorized as type IV, with a distinct hysteresis loop observed in the range of 0.5–1.0 $P/P_0$. CaTiO$_3$ flower-like morphology has a BET surface area of 10.81 m$^2$ g$^{-1}$. The corresponding Barrett–Joyner–Halenda (BJH) analyses (Inset in Fig. 7) show that the CaTiO$_3$ flower-like structures possesses small pore size distribution of 2 and 5 nm, which may be formed by the etching of OH$^-$. The surface area of the flower-like CaTiO$_3$ is much higher than those of “cross” cubic morphology (6.96 m$^2$ g$^{-1}$) and prism-like morphology (BET: 3.61 m$^2$ g$^{-1}$). The comparative high surface area and porous structure of the flower-like CaTiO$_3$ structure could reduce transport limitation in catalysis, resulting in enhanced photocatalytic performance.

3.6 Photocatalytic properties

RhB is not degraded under illumination in the absence of photocatalyst, nor in the dark in the presence of the photocatalyst. Figure 8(a) shows the evolution of the RhB absorption spectra of the sample A with flower-like structures. From Fig. 8(a), the concentration of RhB decreased rapidly with the time increasing. To compare the photocatalytic effects, prism-like structure, the “cross” cubic shapes and home-made CaTiO$_3$ nanoparticles are used as a reference to evaluate the photocatalytic property of the flower-like structure. Figure 8(b) shows the photocatalytic activity of CaTiO$_3$ with the various morphologies. It can be seen clearly from Fig. 8(b) that all CaTiO$_3$ samples show photocatalytic properties in the degradation of RhB, regardless of the morphologies. The catalytic performances of the four CaTiO$_3$ samples possess the sequence of flower-like structure (BET: 10.81 m$^2$ g$^{-1}$) > the “cross” cubic structure (BET: 6.96 m$^2$ g$^{-1}$) > prism-like structure (BET: 3.61 m$^2$ g$^{-1}$), which is agreement with the sequence that the surface areas of the samples decrease. The increase of the BET surface areas could improve the photocatalytic performance. As is well known, the catalytic process is mainly dependent on the adsorption and desorption on the surface of the catalyst. When the specific surface area of the crystals is higher, the more unsaturated coordination sites are exposed to the reactants. At the same time, more reactant molecules are stored in the interconnected hollow pores of the catalyst. Therefore, it is reasonable that catalytic activities with high surface are enhanced.

3.7 Electrochemical properties

Figure 9(a) shows the typical CV of the flower-like structure in 6 M KOH electrolyte at a high scan rate of 200 mV s$^{-1}$. The CV curve exhibits mirror-image characteristics, which indicate high reversibility. The shapes of CV curves are similar at all other scan rate. The stabilities of the flower-like structure is examined by carrying out large number of charge/discharge cycles as shown in Fig. 9(b), the specific-capacitance increases from 27 to 50 F g$^{-1}$, which may cause by the activated material not fully used at the initial stage. After hundreds of cycles (e.g. 2000 cycles), the electrochemical active sites inside the nickel foam electrode are fully exposed and keep constant 50 F g$^{-1}$, which provides the composite’s excellent long-term electrochemical stability. The experiment indicates that the repetitive cycling does not induce noticeable degradation of the microstructure.

4. Conclusion

In conclusion, a facile and low-cost hydrothermal method was developed for fabricating CaTiO$_3$ flower-like structure without any surfactants or templates. An etching of OH$^-$ and diffusion-limited growth mechanism can be used to explain the formation of the CaTiO$_3$ flower-like structure. NaOH concentration is key.
factor for the formation of CaTiO3 flower-like structure without surfactant. Moreover, the as-synthesized CaTiO3 flower-like structure exhibited higher photocatalytic activity for the photocatalytic degradation of RhB aqueous solution under the ultraviolet illumination than those of “cubic” cubic and prisms-like CaTiO3 structure, due to the distinctive structural morphology. The as-prepared CaTiO3 flower-like structure has the potential applications in various fields, such as catalysis, and carriers.

Acknowledgements We would like to express our gratitude for financial support from the National Natural Science Foundation (Grant No. 51462016) Major natural science foundation of Jiangxi Province (No. 20152ACB21022), Jingdezhen technology bureau (Grant No. 51462016) Major natural science foundation of Jiangxi financial support from the National Natural Science Foundation.

References
7) W. Dong, G. Zhao, B. Song, G. Xu, J. Zou and G. Han, CrystEngComm, 14, 6990–6997 (2012).