Effects of morphologies on the photocatalytic properties of CaTiO_3 nano/microstructures

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Without surfactants or templates, CaTiO_3 with various morphologies had been synthesized via a simple hydrothermal route. Effects of optical properties and photocatalytic activities of the CaTiO_3 nanostructures with various morphologies were investigated. The results found that the optical reflectance, absorption and photocatalytic properties of the samples were found to be significantly dependent on their morphologies. Three-dimensional CaTiO_3 butterfly-like structures with nanoflakes showed lower reflectance, more efficient light harvesting, higher surface area and higher photocatalytic activities compared with that of other dendrites and prism. It can be ascribed to the unique butterfly-like structure in which the interspace between ordered nanoflake units acts as a light-transfer path for introducing incident light into the inner surface of CaTiO_3 . This allows UV light waves to penetrate deep inside the CaTiO_3 . The nanoflake units also offer multiple reflective and scattering effects of UV light, preventing the incident waves from bouncing back to the free space. Due to microstructure with nanometer-scale unit, they are much easier to store and be separated from the solution as photocatalysts compared with traditional nanometer-scale powders, which might offer opportunities for fundamental study and industrial applications to explore CaTiO_3 nano-structure under effective morphology control.

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1. Introduction

It is well-known that the size and morphology of the materials greatly affect their properties as well their further applications. Therefore, shape, size and structure of inorganic nano/micro-crystals have attracted broad interest for modern materials chemistry.¹⁾ CaTiO_3 has been one of the best known and widely used materials, due to its excellent dielectric, photocatalysis, and biocompatibility.^{2–4)} In the previous report, we presented a simple solvothermal preparation of CaTiO_3 nanostructures with various morphologies.^{5,6)} Recently, T. Kimijima reported that calcium titanate fine particles were synthesized by an optimized hydrothermal method, and CaTiO_3 showed a high photocatalytic activity for H_2 evolution from the methanolic aqueous solution and the decomposition of acetic acid in water.⁷⁾ To our knowledge, however, our prepared CaTiO_3 with different morphologies and surface crystal plane on the photocatalytic activity for RhB dyes has not been reported. Herein, to compare their photocatalytic properties, we chose some kinds of typical CaTiO_3 samples with ordered-structure morphology at various hydrothermal conditions, and the final morphology and photocatalytic properties are analyzed as shown.

2. Experiment section

All the chemical reagents are in analytical-grade. In a typical procedure, 0.01 mol $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in water-ethanol solution in a Teflon flask, named solution A. 0.01 mol titanium *n*-butoxide (TBOT) was dissolved in 5 ml ethanol, named solution B. Solution B was added dropwise into the solution A under

vigorous stirring for 5 min. Then pH was controlled to 10 by adding NaOH aqueous solution. The molar ratio of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$:TBOT:water:ethanol was 1:1:50–400:10–15. Subsequently, the autoclave was sealed and maintained at 180°C for 24–36 h, followed by natural cooling to room temperature. The obtained solutions were centrifuged and washed with distilled water several times to get white powders. Finally, the powders were dried under a vacuum oven at 90°C for 12 h to obtain the samples.

3. Characterization

The crystal phases of the samples were characterized by X-ray diffraction (XRD, PANalytical X'Pert Pro, Holland), in a 2θ range from 10 to 80°, using Cu-K α radiation ($\lambda = 1.542 \text{ \AA}$), operating at 50 kV and 40 mA. The morphologies of the powders were investigated by a field emission scanning electron microscopy (FESEM Hitachi S-4800, Japan) operating at an accelerating voltage of 5.0 kV. The optical absorption spectra were performed on a UV-visible (UV-vis) spectrophotometer (TU-1901, China) using an integrating sphere with an incident angle of 8° and all the samples were powder samples. The Brunauer–Emmett–Teller (BET) of the powder samples were determined by nitrogen adsorption-desorption isotherm measurement at 77 K on a Micromeritics TriStar II 3020 nitrogen adsorption apparatus.

4. Photocatalysis experiments

CaTiO_3 powders were used as the photocatalysts to degrade rhodamine B (RhB) methyl orange and methylene blue in an aqueous suspension with an initial concentration of 10^{-5} M , respectively. Firstly, 10 milligram of the CaTiO_3 powder samples were separately put in 50 ml different dye aqueous solution for

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24 h in the dark to establish the adsorption equilibrium. The suspension was then exposed to UV light (254 nm, 11 W). Light irradiation time was 20, 40, 60, 80 and 100 min, respectively. The photocatalytic activity was characterized by the apparent first-order rate constant k as equation $k = \ln(A_0/A)/t$, where A_0 was the absorbance of the initial methyl orange, methylene blue and RhB solution at 460, 662, 553 nm, and A was the absorbance of methyl orange, methylene blue and RhB at 460, 662, 553 nm.

5. Results and discussion

Figure 1 shows XRD patterns of CaTiO₃ with different morphology synthesized under various conditions. From XRD patterns, it can be seen that all the samples are composed of CaTiO₃ as main phase and the intensities of CaTiO₃ are the almost same, indicating the similar crystalline of all the samples. The crystallinity (X) of each sample is calculated from XRD data by using the following equation: $X = (I_d/I_t) \times 100\%$, where X is the average of the crystallinity (calculated from XRD curve), I_d is intensity of (1 0 1), (1 1 1), (2 0 0), (1 2 1), (1 1 2), (1 3 1), (2 2 0), (1 2 3), (4 0 0) and (2 0 4) diffraction peaks, and I_t is the sum of the intensities of the sample.⁸⁾ The crystallinity and average crystalline size are summarized in **Table 1**. It can be seen that the crystallinity of the samples is around 86%, and doesn't change obviously with various morphologies. The crystalline size decreases with the increase of x , which is due to CaTiO₃ with various morphologies.

Fig. 1. XRD patterns of CaTiO₃ with different morphology synthesized under various conditions: (a) CaTiO_{3(I)} (b) CaTiO_{3(II)} (c) CaTiO_{3(III)} (d) CaTiO_{3(IV)} (e) CaTiO_{3(V)} (f) CaTiO_{3(VI)}.

Figure 2 shows FESEM images of CaTiO₃ with different morphology synthesized under various conditions. CaTiO₃ with different morphology synthesized under various conditions are concluded in **Table 2**.

Figure 3 shows the optical absorbance and reflectance spectra of the samples with various morphologies. It can be seen that the reflectance spectra of all the samples are noticeably suppressed in the 300–800 nm range. Since CaTiO₃ is a wide band gap semiconductor, the antireflection characteristics are related to the structural properties instead of the band gap absorption, especially, the surface morphology. For the butterfly-like dendrites, CaTiO_{3(I)} shows the lowest reflectance primarily due to its interspace between ordered nanoflake units. For ordered nanoflake, they act as a light-transfer path for introducing incident light into the inner surface of CaTiO₃. This allows UV light waves to penetrate deep inside the CaTiO₃. The nanoflake units also offer multiple reflective and scattering effects of UV light, preventing the incident waves from bouncing back to the free space and prolongs the optical path between the nanoflakes, resulting in the light trapping effect.⁹⁾ For CaTiO_{3(II)} and CaTiO_{3(III)}, the nanoflakes are randomly oriented and developed surface, resulting in weakened light refraction and scattering. For CaTiO_{3(IV)}, CaTiO_{3(V)} and CaTiO_{3(VI)}, a flat surface is favourable for reflection properties due to dense structure and large units. Moreover, the scattering effect is negligible on a densely packed surface. So the probability of the incident light reflecting back to the outside space is greatly increased. From Fig. 3(b), it was obvious that all the samples exhibit a strong absorption below 400 nm. CaTiO_{3(I)} exhibits higher absorbance in the visible region compared with other samples due to the favorable surface geometry for effective light trapping and efficient absorption of incident photons. The abrupt increase below 400 nm was due to

Table 1. The crystallinity and crystalline size of CaTiO₃ samples with various morphologies

CaTiO ₃ samples with various morphologies	Crystallinity (%), X	Crystalline size (nm)
CaTiO _{3(I)}	85.93	93.10
CaTiO _{3(II)}	85.87	93.52
CaTiO _{3(III)}	85.92	105.01
CaTiO _{3(IV)}	85.89	123.40
CaTiO _{3(V)}	85.34	143.52
CaTiO _{3(VI)}	85.72	153.33

Fig. 2. FESEM images of CaTiO₃ with different morphology synthesized under various conditions: (a) CaTiO_{3(I)} (b) CaTiO_{3(II)} (c) CaTiO_{3(III)} (d) CaTiO_{3(IV)} (e) CaTiO_{3(V)} (f) CaTiO_{3(VI)}.

Table 2. Morphology of the samples synthesized at various experimental conditions

Samples	Ca:Ti:water:ethanol (mol.)	NaOH (M)	time (h)	temperature (°C)	morphology	orientation
CaTiO ₃ (I)	1:1:400:15	3 (pH = 10.0, 3 ml)	36	180	Butterfly-like dendrites	best
CaTiO ₃ (II)	1:1:400:15	3 (pH = 12.1, 9 ml)	36	180	butterfly-like dendrites	better
CaTiO ₃ (III)	1:1: 50:10	3 (pH = 12.1, 9 ml)	36	180	dendrites	general
CaTiO ₃ (IV)	1:1:200:10	7 (pH = 12.1, 4 ml)	24	180	“cross” cubic shape	best
CaTiO ₃ (V)	1:1:200:10	7 (pH = 12.1, 4 ml)	36	180	“cross” cubic shape	better
CaTiO ₃ (VI)	1:1:200:10	7 (pH = 13.2, 5 ml)	36	180	Prism-like shape	general

Fig. 3. (a) Optical diffuse reflection spectra and (b) absorption spectra of CaTiO₃ with different morphology synthesized under various conditions.

Fig. 4. Plots of photocatalytic degradation of the sample A with butterfly-like dendrite under different dyes: (a) methyl orange (b) methylene blue (c) Rhodamine B.

the absorption of light caused by the excitation of electrons from the valence band to the conduction band of CaTiO₃.

Figure 4 shows plots of photocatalytic degradation of CaTiO₃(I) with butterfly-like dendrite under different dyes. Before light irradiation, the concentration of three kinds of dye is normalized for 10⁻⁵ M. It was noteworthy that the photocatalytic decolorization of methyl orange, methylene blue and rhodamine B was not achieved under ultraviolet illumination in the absence of CaTiO₃ samples, respectively. To evaluate the morphology effect of the samples, the adsorption properties of these samples after dark condition experiment should be exam-

ined. It is found that the three kinds of dyes color don't obviously change, which indicates no adsorption properties for the samples with various morphologies. It can be seen that the photocatalytic degradation of the sample A under methyl orange, methylene blue and Rhodamine B is 0.437, 0.762, 2.069 min⁻¹, respectively. From the degradation rate K, Rhodamine B dyes is the most susceptible to degradation, followed by methylene blue dye, and the most difficult to degrade for methyl orange dye. It is well known that the photocatalytic degradation rate is not only related to the surface morphology of the sample, and the dye structure, dye adsorption in CaTiO₃ surface and utilization of light etc. The dye rhodamine B not only exists in the positively charged electron center, but also an additional terminal carboxyl groups [Fig. 5(a)], which can anchorage dyes on the surface CaTiO₃. And at the same mass concentration of the dyes, rhodamine B has higher light utilization than that of methyl blue due to the lighter color of rhodamine B than that of methyl blue, which is more easily through the light, thus high photocatalytic activity is improved due to high light efficient. It can be seen that the degradation rate of CaTiO₃ for methylene blue dye is better than that of methyl orange. There are three reasons as follows. First of all, methylene blue belongs to singlet oxygen sensitizer [Fig. 5(b)]. Superoxide anion free radicals could be produced from electron transfer due to the reaction with oxygen at the light. The combination of hydroxyl radicals and superoxide anion free radicals make methylene blue photodegrade. Second, related literature research¹⁰⁾ show that hydroxyl (OH), amino (NH₂), amino N ≡ (–) groups promote dyes decolorizing, which can improve the light degradability. Methoxy (–OCH₃), sulfonic group (SO₃), nitro (NO₂), methyl (CH₃) and carboxyl (–COOH) group can

Fig. 5. Diagrammatic sketch of different dyes structure: (a) Rhodamine B, (b) methylene blue, (c) methyl orange.

Fig. 6. (a) BET surface areas and (b) plots of photocatalytic degradation of RhB using CaTiO₃ with various morphologies.

inhibit dye degradation. When the aromatic ring has promoting and inhibiting reactive group, dyes decolorizing effect depends on them. Methyl orange with inhibiting group sulfonic group (SO₃) [Fig. 5(c)], it blocks the oxidant dual ligand (–NH–N≡) attack. Finally, methylene blue belongs to the branched chain dye molecules, which is more easily absorbed than that of methyl orange with straight-chain type dye molecules.

Figure 6 shows BET surface areas and plots of photocatalytic degradation of RhB using CaTiO₃ with various morphologies. It can be seen that without illumination, the RhB absorbance remains almost unchanged. This assures that the reduction of RhB adsorption comes from the photocatalytic effect of the CaTiO₃ samples rather than powder adsorption. Figure 6(a) shows the BET of the samples with various morphologies. It can be seen that the sample CaTiO₃(II) has the highest specific surface areas, then CaTiO₃(I), CaTiO₃(III) and CaTiO₃(IV), then CaTiO₃(V) and CaTiO₃(VI) have small specific surface areas. High specific surface areas of the samples promote the contact between photocatalysts and dyes. According, the photocatalytic properties of the sample CaTiO₃(I), CaTiO₃(II), CaTiO₃(III) and CaTiO₃(IV) were superior to CaTiO₃(V) and CaTiO₃(VI). Compared with CaTiO₃(II), the specific surface area of CaTiO₃(I) decreased to 8.9 m² g⁻¹ [Fig. 6(a)]. However, the photocatalytic properties of the sample increase dramatically [Fig. 6(b)]. It is well-known that photocatalytic activity is relevant to the size, shape and the exposed plane of the particles. As photocatalytic reaction mainly occurs on the surface of catalyst, the surface morphology would have an important effect on the efficiency. Dendrites have an ordered nanoflakes and developed surface, and thus many of their active sites are accessible for the RhB molecules.¹¹⁾ On the other hand, it is commonly accepted that a larger band gap corresponds

to a more powerful redox ability.⁸⁾ The increase in band gap results in an enhanced oxidation–reduction potential (See Fig. 3). The proper selection of the particle shape, outer surface is one of the key factors for the photocatalytic activity.⁷⁾ In our experiments, it may be assumed that the butterfly-like dendrites is expected to selectively occur on the more reactive surfaces than those of others samples, which shows a higher oxidative reaction than the other samples. To clarify the mechanism better, the related structures are under way. At the same time, deferent crystal size is considered a very important factor for photocatalytic properties, small crystalline size is facilitating for suppressing the recombination of carrier and hole.¹²⁾ The decrease in crystalline size results in a shorter electron transfer distance (See Table 1). In addition, the high light trapping efficient also contributes to the enhanced activity of the samples with dendritic structure. Therefore, the dendritic samples provide much higher photocatalytic activities than that of the samples with various morphologies such as prism-like shape and “cross” cubic shape. Due to microstructure with nanometer-scale unit, they are much easier to store and be separated from the solution as photocatalysts compared with traditional nanometer-scale powders.

6. Conclusions

CaTiO₃ with various have been successfully prepared by hydrothermal route. The surface morphologies, especially butterfly-like dendrites were found to be crucial to photocatalytic properties of the CaTiO₃. Photocatalytic degradation of RhB using CaTiO₃ butterfly-like dendrites is superior to those of methylene blue and methyl orange. Butterfly-like dendrites with order nanoflakes and vertical alignment exhibit the highest optical absorption intensity and photocatalytic properties. This enhanced photocatalytic

properties can be attributed to ordered nanoflake units, and vertical alignment of CaTiO_3 nanoflakes, which acts as a light-transfer path for introducing incident light into the inner surface of CaTiO_3 . The significant improvement in the optical and photocatalytic properties for the butterfly-like dendrites together with the simple and low-cost fabrication procedures suggests that CaTiO_3 has a promising application in photocatalytic fields.

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