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Effects of pH on morphosynthesis and photocatalytic activity of calcium titanium oxides via a facile aqueous strategy



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1. Introduction

Due to its widespread potential applications in a lot of fields, calcium titanium oxides have been considered as one of the most important inorganic materials. For example, CaTiO₃ has received much attention due to its important industrial applications, such as electric engineering [1–3], catalyst control techniques [4], and even biotechnology [5]. Various chemical methods, e.g. sol-gel [6-8], solid reaction [9], co-precipitation [10] and mechanochemical methods have been employed to fabricate CaTiO₃ [11,12]. CaTi₂O₅ is often observed as a metastable phase during the preparation of CaTiO₃ materials. Due to its metastable nature, pure CaTi₂O₅ is not easy to obtain. CaTi₂O₄(OH)₂ was firstly found in Union of Soviet Socialist Republics (USSR) around 1965. It is a layered metal hydroxide structure [13]. More recently, CaTi₂O₄(OH)₂ was obtained during the preparation of CaTiO₃ by Huang et al. via a hydrothermal reaction method under a nitrogen atmosphere [14], and our work found that CaTi₂O₄(OH)₂ may have electrochemical properties [15,16].

It is known that the sample's microstructure, such as size, crystalline phase and shape, greatly effects their chemical and physical properties, as well its further applications [17]. As an eco-friendly aqueous process, hydrothermal methods are attractive in

ABSTRACT

By controlling pH values, calcium titanium oxides with various morphologies had been synthesized via a simple hydrothermal route. No surfactants or templates were involved in the shaping process. The results found that pH values had a crucial effect on the crystal phase and shape evolution of the samples. With increasing pH values, the obtained sample changed from one-dimension (1D) CaTi₂O₅ rod or shuttle-like shape to two-dimension (2D) CaTi₂O₄(OH)₂ nanosheets, and then to three-dimension (3D) CaTiO₃ aggregated prisms, butterfly-like dendrites and cross cubic shapes. The formation mechanism was proposed for the evolution of phase and morphology. 3D CaTiO₃ butterfly-like sample showed good photocatalytic activity due to unique morphology, enhanced light harvesting and large surface area. (© 2013 Elsevier Ltd. All rights reserved.

fabricating materials with well-controlled stoichiometry, precisely-tailored morphology and high crystallinity [18]. Due to wide application in the biomedical area, many studies have reported surface properties and biological activity of hydrothermally obtained nanostructured CaTiO₃ layer in various Ti substrates, because it can improve the adhesion between apatite and substrates. Compared to the former, there are few reports for structure and photocatalytic properties of nanostructured CaTiO₃ powders without any surfacatant or additives by hydrothermal method. Recently, some papers have reported that the hydrothermally synthesized CaTiO₃ powders exhibit various morphologies, e.g. cubic, dendritic, butterfly-like and prism-like, depending on the reaction conditions, e.g. reaction temperature and time, template, solvent, reactant concentrations, mineralizer, etc. [14,19–21]. Among these reaction conditions, pH plays a critical role in the final product since pH determines the chemical nature of the aqueous species. Namely, the pH values are responsible for shape and phase determination of crystals [22]. In previous researches, perovskite oxides (e.g. PbTiO₃ and BaTiO₃, etc.) with different microstructure had been synthesized by controlling pH values via the hydrothermal method [14,23-25].

In this paper, by controlling pH values, calcium titanium oxides with a series of novel morphologies have been fabricated through a simple "one-pot" hydrothermal method without any surfactant or template. A wide range of solution pH values has been employed. Effects of pH on crystal phase, morphology, optical and photocatalytic properties are discussed.

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2. Experiment section

All the chemicals are analytical grade. In a typical procedure, calcium chloride dehydrate (CaCl₂·2H₂O) was added in water– ethanol solution in a Teflon flask, then the mixture of titanium nbutoxide (TBOT) and ethanol was added dropwise into the solution under vigorous stirring for 5 min. Afterwards, concentrated nitric acid (65–68%) was added to control the solution at pH = 5, then adding NaOH (3 M) aqueous solution to the above solution and pH was controlled to a certain value, which is 6, 8, 9, 10, 12 and 13. The molar ratio of CaCl₂·2H₂O: TBOT: water: ethanol was 1:1:400:15. Subsequently, the autoclave was sealed and maintained at 180 °C for 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-Ka radiation ($\lambda = 1.542$ Å), 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. Infrared spectra of the samples were obtained using a Nicolet Nexus 470 Fourier transform infrared (FT-IR) spectrometer in the 400–4000 cm⁻¹ region by KBr pellet. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were carried out on a Philips C200 Transmission electron microscopy operating at 160 kV. The microstructures of the samples were further analyzed using a high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F-30, Holland) operating at an accelerating voltage of 200 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.

3.1. Photocatalysis experiments

CaTiO₃ powders were used as the photocatalysts to degrade rhodamine B (RhB) in an aqueous suspension with an initial concentration of 10^{-5} M. Firstly, 10 mg of the CaTiO₃ powder samples were seperately put in 10 ml RhB aqueous solution for 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 min and 100 min, respectively. The photocatalytic activity was characterized by the apparent firstorder rate constant *k* as equation $k = \ln(A_o/A)/t$, where A_o was the absorbance of the initial RhB solution at 553 nm, and *A* was the absorbance of RhB at 553 nm.

4. Results

Fig. 1 shows the XRD patterns of the samples synthesized at various pH values. When pH is 5, the sample is pure $CaTi_2O_5$ phase (JCPDS card 25-1450). When pH increases to 6, the sample is composed of $CaTi_2O_5$ phase and a little of $CaTi_2O_4(OH)_2$ (JCPDS card 39-0357). When pH is 8, the sample is pure $CaTi_2O_4(OH)_2$. When pH is \geq 9, pure $CaTiO_3$ (JCPDS card 42-0423) is obtained. Further increasing pH to 13 increases the peak intensity.



Fig. 1. XRD patterns of the samples synthesized at various pH values: (a) 5, (b) 6, (c) 8, (d) 9, (e) 10, (f) 12 and (g) 13.

Fig. 2 shows FT-IR spectra in the range of $400-4000 \text{ cm}^{-1}$ of the samples synthesized at various pH. All the samples exhibit the absorption bands centered at 1400 cm⁻¹, 410 cm⁻¹, 425 cm⁻¹ and 450 cm^{-1} . The peaks at 1400 cm^{-1} can be attributed to the N–O stretching vibrations of NO_3^- [26]. The absorption bands below 500 cm^{-1} , i.e. bands centered at 410, 425 and 450 cm⁻¹ can be ascribed to Ca–Ti–O bending vibrations [27]. When pH is <6, the peak at 1634 cm^{-1} may be assigned to the bending mode of the OH⁻ vibration [28,29]. When pH is 8, there are absorption peaks at 3200 cm^{-1} and 1538 cm^{-1} , which cannot be observed from the spectra of other samples. The broad absorption band observed at 3200 cm⁻¹ is originated from the presence of hydroxyl groups of water [30]. The absorption peak at 1538 cm⁻¹ attributes to H–O–H bending of the lattice water [27]. A band centered at 750 cm⁻¹, which is attributed to isolated tetrahedron TiO₄ stretching vibrations, appears only for the sample synthesized at pH = 8[31]. When pH value is \geq 9, there are strong absorption peaks at 3450 cm⁻¹ and 3643 cm⁻¹ in the FT-IR spectrum, which corresponds to the OH⁻ stretching vibration [30,31]. As the pH increases, intensity of the absorption peak at 3450 cm⁻¹ increases. A sharp absorption peak is observed at 3643 cm⁻¹ for the sample synthesized at pH = 10.

Fig. 3 shows typical FESEM and TEM images of the samples synthesized at various pH. When pH is 5, the aggregate particles are obtained (Fig. 3(a)). When pH is 6, 1D shuttle-like sample is



Fig. 2. FT-IR spectra in the range of $400-4000 \text{ cm}^{-1}$ of samples synthesized at various pH values: (a) 5, (b) 6, (c) 8, (d) 9, (e) 10, (f) 12 and (g) 13.





Fig. 3. Typical FESEM of the samples synthesized at various pH values: (a) 5, (b) 6, (c) 8, (d) 9, (e) 10, (f) 12 and (g) 13.

obtained (Fig. 3(b)). When pH is 8, 2D irregular nanosheets are obtained (Fig. 3(c)). When pH increases to 9, 3D aggregated prisms are obtained with size of about 5.20 μ m in length and 1.70 μ m in width, and these prisms bond each other (Fig. 3(d)). When pH is 10,

the sample is mainly composed of 3D butterfly-like dendrites (Fig. 3(e)). From the top view, there is a long central trunk and four branches extending from the central trunk, the four-fold symmetry of the structure can be identified. When pH is 12, 3D cross cubic

sample with an edge length about 4.5 μ m is obtained (Fig. 3(f)). When pH further increases to 13, 3D cross cubic sample with an edge length about 5 μ m is formed (Fig. 3(g)).

Fig. 4 shows TEM and the corresponding SAED pattern, and HRTEM investigations of the selected samples at various pH. Fig. 4(a) and (b) give TEM and the corresponding SAED pattern (inset), and HRTEM images of the sample synthesized at pH = 5. Fig. 4(a) reveals that the aggregated particles in Fig. 3(a) are composed of 1D nanorods. Inset of Fig. 4(a) indicates the sample is polycrystalline. Fig. 4(b) reveals that the lattice spacing of the nanorod is 0.273 nm, which corresponds to the (1 3 3) plane of $CaTi_2O_5$ crystal. Fig. 4(c) shows that the sample exhibits an irregular and ovelapped 2D nanosheets synthesized at pH = 8. The corresponding SAED pattern (inset of Fig. 4(c)) reveals the sample is a polycrystalline structure. The lattice parameters of the nanosheets are also confirmed by HRTEM as shown in Fig. 4(d). The spacing of the lattice fringes is about 0.370 nm, corresponding to the (1 5 1) plane of $CaTi_2O_4(OH)_2$. Fig. 4(e) shows typical TEM image of a butterfly-like dendrite synthesized at pH = 10, which reveals that the 3D butterfly-like dendrite structure forms. Inset of Fig. 4(e) shows the dendrite is a single-crystalline structure. The HRTEM image shown in Fig. 4(f) is caught from the joint section of the branch and trunk (marked in white circle). The *d* spacings in Fig. 4(f) are 0.143 and 0.256 nm, which agree well with the lattice spacings of $(3 \ 3 \ 1)$ and $(2 \ 1 \ 0)$ of orthorhombic CaTiO₃.

Fig. 5 shows optical absorption spectra of CaTiO₃ samples synthesized at pH of 9, 10, 12 and 13. All the samples exhibit a strong absorption below 400 nm. When pH is 10, the sample is more effective in absorbing UV light than those of pH 9, 12 and 13. The optical absorption near the band edge follows the equation $\alpha h \upsilon = A(h \upsilon - E_g)^{n/2}$, where *a*, υ , E_g , and *A* are the absorption coefficient, light frequency, band gap, and constant, respectively. Among them, *n* decides the characteristics of the transition in a semiconductor. In our experiment, the value *n* for the present samples is 4 [32]. After the determination of these parameters, the relationship of $(\alpha h \upsilon)^{1/2}$ vs $h \upsilon$ is plotted to obtain the band gap. The band gap value (E_g) can be calculated by extending the linear part of the curve to zero absorption as shown in Table 1, which is in good agreement with those of CaTiO₃ materials reported in the literature values (3.5 eV) [33,34].

Fig. 6 shows the plots of photocatalytic degradation of RhB using $CaTiO_3$ samples synthesized at pH of 9, 10, 12 and 13. In order

Fig. 4. Typical microstructure of the samples synthesized at various pH values: (a, b) 5, (c, d) 8, (e, f) 10. (a), (c) and (e) are TEM images and the corresponding SAED pattern (inset). (b) and (d) are HRTEM images, and (f) is HRTEM image from the junction of the trunk and branch as marked in Fig. 4(e).





Fig. 5. Optical absorption spectra of CaTiO₃ synthesized at various pH.

to eliminate the influence of adsorption, the typical plot of photocatalytic degradation of RhB without illumination of the CaTiO₃/RhB solution is also showed in Fig. 6. The RhB absorptance remains almost unchanged without illumination. The k values for the degradation of RhB are presented in Table 1. The k value of the sample synthesized at pH of 10 is relatively higher than those of the samples synthesized at pH of 9, 12 and 13.

5. Discussion

5.1. Effects of pH on the crystal phase of the samples

Based on the experimental results, it is obvious that morphology and phase of the samples are strongly dependent on pH values. In this work, because present system contains water and TBOT, and the molar ratio of water and TBOT is large (400:1), it is reasonable that titanium hydroxides exist in the reaction system [35,36]. Under hydrothermal conditions, dissolution of calcium and titanium hydroxides would occur [19,20,22]. Titanium hydroxides are quickly formed at the initial stage of reaction. Titanium hydroxides firstly transform into titanium dioxides by the dehydrating condensation, then titanium dioxides would dissolve and release Ti⁴⁺ ions gradually, which depend on the concentration of OH^{-} [19]. When pH is <6, owing to the small solubility of titanium dioxide in the acid conditions, CaTi₂O₅ forms (Fig. 1(a) and (b)) following Eq. (1). When pH increases to 8, as revealed by FT-IR spectrum (Fig. 2(c)), isolated tetrahedron TiO₄ stretching vibrations appears, indicating titanium dioxide dissolve partly. Therefore, it can be suggested Ti⁴⁺ ions are released to the solution. Moreover, H–O–H bending of the lattice water (Fig. 2(c)) indicates water is formed in this structure. Considering pH = 8, it can be known that the amount of active of OH⁻ is relatively small. Therefore, Eq. (2) is suggeted, and CaTi₂O₄(OH)₂ forms (Fig. 1(c)). When pH is \geq 9, more OH⁻ ions help the dissolution of titanium

 Table 1

 Morphology, BET surface area, the band gap value and rate constant of the samples synthesized at various pH.

рН	Morphology	$E_{g} (eV)$	BET (m ² /g)	Rate constant $k \ (\min^{-1})$
9	Aggregated prisms	3.46	0.48	0.0050
10	Butterfly-like dendrites	3.49	8.14	0.0207
12	Cross cubic shape	3.44	0.14	0.0040
13	Cross cubic shape	3.45	0.13	0.0039



Fig. 6. Plots of photocatalytic degradation of RhB using $CaTiO_3$ synthesized at various pH.

dioxides, and thus more Ti^{4+} ions are released. Ca^{2+} and Ti^{4+} ions react with OH⁻, forming CaTiO₃ (Fig. 1(d)–(g)). The reaction at pH \geq 9 is suggested as Eq. (3).

$$Ca^{2+} + 2TiO_2 + H_2O \rightarrow CaTi_2O_5 + 2H^+ \quad pH = 5-6 \tag{1}$$

$$Ca^{2+} + Ti^{4+} + TiO_2 + 6OH^- \rightarrow CaTi_2O_4(OH)_2 + 2H_2O \quad pH = 8 \quad (2)$$

$$Ca^{2+} + Ti^{4+} + 60H^{-} \rightarrow CaTiO_3 + 3H_2O \quad pH = 9-13$$
 (3)

5.2. Effects of pH on the morphology of the samples

Based on FESEM images experiment results (Fig. 3), the samples synthesized at various pH have different morphology. Firstly, the different crystalline phases synthesized at various pH have various crystal structures [37]. Secondly, the morphology depends upon the competition between nucleation and crystal growth. Thirdly, in a way, the adsorption behavior of crystal planes is dependent on the pH of the solution. Moreover, the crystal growth is controlled by the adsorption of the species to the certain crystal facets, which inhibits the growth of some crystal planes and leads to different growth rates of different crystal planes. Therefore, different morphology forms at various pH.

Based on XRD patterns, acidic condition favors the formation of CaTi₂O₅ crystallites, which determine the crystal growth behavior. Meanwhile, the adsorption of OH⁻ also plays an important role in the shape of CaTi₂O₅. When pH is 5, as revealed by FT-IR spectra (Fig. 2(a) and (b)), OH⁻ ions present in CaTi₂O₅ sample, indicating OH⁻ ions might be adsorbed on the surface of CaTi₂O₅. Combining with FT-IR, FESEM and TEM results, it can be found the adsorption of OH⁻ blocks the lateral growth of the (1 3 3) plane of CaTi₂O₅ sample, and 1D anisotropic growth is predominant, resulting in the formation of nanorods (Fig. 4(a)). With the addition of NaOH (aqueous), the solution pH value increases to 6. FT-IR spectrum (Fig. 2(b)) reveals that the absorption peak of OH⁻ ions becomes relatively weak as compared to curve a of Fig. 2, indicating the weak specific interactions of nuclei and OH⁻. Therefore, blocking of the crystals growth becomes less efficient. Consequently, the shuttle-like CaTi₂O₅ is obtained. The formation of 1D nanorods and shuttle-like shapes are shown in Fig. 7(a). When solution pH value increases to 8, from XRD, FESEM and FT-IR spectrum results, it can be concluded that OH⁻ might be absorbed on the (151) plane of particles and lead CaTi₂O₄(OH)₂ particles to grow into nanosheets based on its growth habit. The formation of CaTi₂O₄(OH)₂ nanosheets are illustrated in Fig. 7(b). When pH values further



Fig. 7. Schematic representation for the formation mechanism of the samples: (a) nanorods and shuttle-like samples at pH = 5 and pH = 6, respectively, (b) nanosheets at pH = 8, and (c) aggregated prisms at pH = 9, butterfly-like dendrites at pH = 10 and cross cubic shape at pH = 12, 13.

increase to \geq 9, CaTiO₃ forms (Fig. 1(d)–(g)). As has discussed above, the released speed of Ti⁴⁺ ions could be adjusted by OH⁻ concentration. Therefore, OH⁻ concentration is responsible for the shape evolution of CaTiO₃. FT-IR spectrum (Fig. 2 (d)–(g)) reveals that OH⁻ stretching vibration appears in all sample for pH \geq 9, indicating OH⁻ was absorbed on the surface of CaTiO₃ nuclei. When pH is 9 and 10, the amount of OH⁻ is relatively low and thus the released speed of Ti⁴⁺ is slow, which leads to a low monomer concentration (as shown in Eq. (3)). The process slows down the nucleation and subsequent crystal growth of CaTiO₃. At this stage, amphiphile bilayer presented in the ethanol-water mixture becomes the dominant factor [31]. Therefore, it is proposed that the amphiphile bilayer capped outside the particle acts as a microreactor and soft temple for crystal growth. As for the orthogonal structure of CaTiO₃, the charge density of {1 0 0} should be much lower than that of {1 1 1}, which makes {1 0 0} having precedence over {1 1 1}, and thus being the most preferential bonding planes [30,32]. Thus, these planes would be free for bonding by the interaction between OH⁻ and nuclei, and aggregated prisms were obtained (Fig. 3(d)). When pH increases to 10, as revealed by FT-IR spectrum (Fig. 2(e)), OH⁻ was relatively strong as compared with that of pH = 9, indicating that the interaction between OH⁻ and nuclei would be relatively strong. Therefore, we proposed that OH⁻ ions were selectively adsorb on (3 3 1) and (2 1 0) planes of CaTiO₃ particles based on the FT-IR, FESEM and TEM results, which blocked (3 3 1) and (2 1 0) planes growth of the crystals. Eventually, the symmetry branch grows along the normal vector of (3 3 1) and (2 1 0) planes to form dendrites (Fig. 3(e) and Fig. 4(e)). Further increasing pH to 12 and 13, excess [OH⁻] markedly accelerated the releasing speed of Ti⁴⁺ ions from titanium hydroxides. Thus, the mass transport rate of ions that feed the growing crystals was much improved as compared with pH of 9 and 10. A variety of crystal surfaces have opportunity to grow due to the relatively larger rate of mass transportation of ions. OH⁻ ions might be strongly adsorbed on the lowest energy {1 0 0} surface of CaTiO₃ and slows down the Oswald ripening growth rate, and thus enhances the oriented assembly, which conceals the difference of the surface energies of {1 0 0}[31,35]. Therefore, cross cubic CaTiO₃ forms (Fig. 3(f) and (g)). The mechanism for the formation of aggregated prisms, butterfly-like dendrites and cross cubic sample is illustrated in Fig. 7(c).

5.3. Effects of pH on optical absorption spectra of $CaTiO_3$ micro/nano structure

Based on the optical absorption spectra results (Fig. 5), the abrupt increase below 400 nm is due to the absorption of light caused by the excitation of electrons from the valence band to the conduction band of CaTiO₃. Compared to the samples with prismlike (pH = 9) and cross cubic shape (pH = 12 and 13), the butterflylike sample (pH = 10) exhibits more effective in absorbing UV light. This can be ascribed to the unique butterfly-like structure in which the interspace between ordered nanoflake units acts as a lighttransfer 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 [38]. Both of these give rise to more efficient light harvesting. The decrease in UV light absorbance for prism-like and cross cubic sample can be due to the densely arranged flat tops [38].

5.4. Effects of pH on the photocatalytic activity of $CaTiO_3$ micro/nano structure

Higher value of k indicates better photocatalytic activity. It is noteworthy that the photocatalytic decolorization of RhB is not achieved under ultraviolet illumination in the absence of CaTiO₃ samples. The photodegradation results show without illumination, the RhB absorptance remains almost unchanged. This assures that the reduction of RhB absorptance comes from the photocatalytic effect of the CaTiO₃ samples rather than powder adsorption. It is commonly accepted that larger surface area provides more active adsorption sites, which can improve the photocatalytic activity. It can be expected that high photonic efficiency can promote the ratio of the surface carrier transfer rate to the electron-hole recombination rate. Additionally, the augment of the band gap energy can enhance the redox potentials of photogenerated electrons and holes; consequently, the photocatalytic activity can be improved [39]. Compared with the sample synthesized at pH of 9, 12 and 13, respectively, the butterfly-like sample at pH of 10 displays larger surface area and band gap energy (Table 1). That is why the sample synthesized at pH of 10 shows a greater photocatalytic activity than those of pH at 9, 12 and 13. It should be noted that the surface area is relatively low because of the samples with micron-sized mophorology (see SEM image in Fig. 3), which is characteristic of a relatively low surface area.

6. Conclusions

 $CaTi_2O_5$, $CaTi_2O_4(OH)_2$ and $CaTiO_3$ had been obtained via a hydrothermal method by controlling pH values. When pH was less

than 6, the morphology of CaTi₂O₅ was composed of 1D nanorods or shuttle-like shapes. Increasing pH to 8, 2D CaTi₂O₄(OH)₂ nanosheets formed. When pH was higher than 9, 3D CaTiO₃ nano/ micro structures with various morphologies, such as aggregated prism-like, butterfly-like and cross cubic shapes were observed. Fourier transform infrared spectroscopy (FT-IR) also revealed that the interaction controls crystal growth rates of different crytstalline faces in a certain way by adsorption on the calcium titanium surface in various pH aqueous solutions. Compared with the samples synthesized at pH of 9, 12 and 13, CaTiO₃ sample synthesized at pH of 10 possessed hierarchical structures exhibited higher light harvesting since the ordered units provided a lighttransfer path for incident light and multiple reflective and scattering effects. And CaTiO₃ sample synthesized at pH of 10 showed good photocatalytic activity due to this unique structure and optical properties.

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References

- [1] C.L. Huang, C.L. Pan, S.J. Shium, Mater. Chem. Phys. 78 (2003) 111-115.
- [2] S. Kucheiko, J.W. Choi, H.J. Kim, H.J. Jung, J. Am. Ceram. Soc. 79 (1996) 2739–2743.
- [3] T. Bak, J. Nowotny, C.C. Sorrell, M.F. Zhou, E.R. Vance, J. Mater. Sci.: Mater. Electron. 15 (2004) 645–650.
- [4] H. Mizoguchi, K. Ueda, M. Orita, S. Moon, K. Kajihara, M. Hirano, H. Hosono, Mater. Res. Bull. 37 (2002) 2401–2406.
- [5] N. Ohtsu, K. Sato, A. Yanagawa, K. Saito, Y. Imai, T. Kohgo, A. Yokoyama, K. Asami, T. Hanawa, J. Biomed. Mater. Res. A 82 (2007) 304–315.
- [6] S.K. Manik, S.K. Pradhan, M. Pal, Phys. E: Low-Dimension. Syst. Nanostruct. 25 (2005) 421–424.
- [7] S.J. Lee, Y.C. Kim, J.H. wang, J. Ceram. Process Res. 5 (2004) 223-226.
- [8] G. Pfaff, Chem. Mater. 6 (1994) 58-62.
- [9] L.S. Cavalcate, V.S. Marques, J.C. Szczancoski, M.T. Escote, M.R. Joya, J.A. Varela, M.M. Santos, P.S. Pizani, E. Longo, Chem. Eng. J. 143 (2008) 299–307.
- [10] X.M. Zhang, J.H. Zhang, X.G. Ren, X.J. Wang, J. Solid State Chem. 181 (2008) 393-398.
- [11] G. Brankovic, V. Vukotic, Z. Brankovic, J.A. Varela, J. Eur. Ceram. Soc. 27 (2007) 729–732.
- [12] K. Wieczorek-Ciurowa, P. Dulian, A. Nosaland, J. Domagała, J. Therm. Anal. Calorim. 101 (2010) 471–477.
- [13] G.S. Peter, R.B. Peter, Am. Mineral. 76 (1991) 283-287.
- [14] Y.J. Huang, M.C. Tsai, H.T. Chiu, H.S. Sheu, C.Y. Lee, Cryst. Growth Des. 10 (2010) 1221–1225.
- [15] W.X. Dong, B. Song, G.L. Zhao, G.R. Han, Ceram. Int. 39 (2013) 6795-6803.
- [16] W.X. Dong, B. Song, G.L. Zhao, G.R. Han, Int. J. Electrochem. Sci. 8 (2013) 4551– 4559.
- [17] H. Hosono, Y. Mishima, H. Takezoe, KJ.D. MacKenzie, Nanomaterials: From Research to Applications, Elsevier Ltd, Oxford, 2006p. 206.
- [18] Y.W. Juna, J.W. Seoa, S.J. Ohb, J. Cheon, Coordin. Chem. Rev. 249 (2005) 1766– 1775
- [19] Y.J. Huang, H.T. Chiu, C.Y. Lee, CrystEngComm 11 (2009) 1904–1909.
- [20] W.X. Dong, G.L. Zhao, B. Song, X. Gang, J. Zhou, G.R. Han, CrystEngComm 14 (2012) 6990–6997.
- [21] X. Yang, J. Fu, C. Jin, J. Chen, C.L. Liang, M.M. Wu, W.Z. Zhou, J. Am. Chem. Soc. 132 (2010) 14279–14287.
- [22] M.M. Lencka, R.E. Riman, Chem. Mater. 7 (1995) 18-25.
- [23] C. Li, J. Yang, Z. Quan, P. Yang, D. Kong, J. Lin, Chem. Mater. 19 (2007) 4933-4942.
- [24] J. Jang, S. Kim, H. Choi, J. Kim, W. Jung, Mater. Chem. Phys. 1 (2009) 389–394.
- [25] X.Y. Chen, H.S. Huh, S.W. Lee, Nanotechnology 28 (2007) 5608.
- [26] F. Cot, A. Larbot, G. Nabias, L. Cot, J. Eur. Ceram. Soc. 18 (1998) 2175–2181.
- [27] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fifth ed., Wiley, Toronto, 1997, pp. 67–78.
- [28] M. Ma, Y. Zhu, J. Chang, J. Phys. Chem. B 110 (2006) 14226–14230.
- [29] S.W. Cao, Y.J. Zhu, J. Wu, K.W. Wang, Q.L. Tang, Nanoscale Res. Lett. 5 (2010) 781–785.
- [30] G.M. Duffy, S.C. Pillai, D.E. McCormack, J. Mater. Chem. 17 (2007) 181–184.
- [31] S. Music, M. Gotic, M. Ivanda, S. Popovic, A. Turkovic, R. Trojko, A. Sekulic, Mater. Sci. Eng. B 47 (1997) 33–40.
- [32] M. Butler, J. Appl. Phys. 48 (1977) 1914-1920.
- [33] H. Mizoguchi, K. Ueda, M. Orita, S.C. Moon, K. Kajihara, M. Hirano, H. Hosono, Mater. Res. Bull. 37 (2002) 2401–2406.

- [34] L.S. Cavalcante, V.S. Marques, J.C. Sczancoskia, M.T. Escote, M.R. Joya, J.A. Varela, M.C. Santos, P.S. Pizania, E. Longo, Chem. Eng. J. 143 (2008) 299–307.
 [35] Z. chen, G. Zhao, H. Li, G. Han, B. Song, J. Am. Ceram. Soc. 92 (2009) 1024–1029.
- [36] B.E. Yoldas, J. Mater. Sci. 21 (1986) 1087–1092.

- [37] Z.P. Liu, J.B. Liang, S. Li, S. Peng, Y.T. Qian, Chem. Eur. J. 10 (2004) 634–640.
 [38] L.K. Yeh, K.Y. Lai, G.J. Lin, P.H. Fu, H.C. Chang, C.A. Lin, J.H. He, Adv. Energy Mater. 1 (2011) 506-510.
- [39] L.X. Cao, F.J. Spiess, A. Huang, S.L. Suib, T.N. Obee, S.O. Hayn, J.D. Freihaut, J. Phys. Chem. B 103 (1999) 2912.