Research Article

Photocatalytic Degradation of 2,4-Dichlorophenol Using Nanosized $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ Heterostructure Particles

Zicong Jian,^{1,2} Shaobin Huang,^{1,2,3,4} and Yongqing Zhang^{1,2}

¹ College of Environment and Energy, South China University of Technology, Guangzhou 510006, China

² Guangdong Provincial Key Laboratory of Atmospheric Environment and Pollution Control, Guangzhou 510006, China

³ State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510006, China

⁴ The Key Laboratory of Environmental Protection and Eco-Remediation of Guangdong Regular Higher Education Institutions, Guangzhou 510006, China

Correspondence should be addressed to Shaobin Huang; chshuang@scut.edu.cn

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$\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ composite particles were synthesized through the hydrolyzation of tetrabutyl titanate in a reverse microemulsion and characterized by thermogravimetry and differential scanning calorimetry (TG-DSC), X-ray diffraction (XRD), and scanning electron microscope (SEM). The photocatalytic property of $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ was evaluated by degradation of 2,4-dichlorophenol (2,4-DCP) under 40 W ultraviolet lamp ($\lambda = 365$ nm) irradiation and compared with commercial P25- TiO_2 in the same condition. The results showed that the synthesized nanobelts $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ heterostructures had typical width from 80 to 100 nm, with thickness less than 40 nm and length up to 5 μm . Such $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ nanosized particles exhibited better photocatalytic activity than that of P25- TiO_2 , and the degradation rate of 2,4-DCP with initial concentration of 0.02 g/L reached 99.4% at the end of 50 min.

1. Introduction

Chlorophenols, as significantly harmful environmental pollutants [1–3], are of high toxicity, recalcitrance, bioaccumulation, and persistence in the environment. These compounds, which have been widely used as insecticides, bactericides, herbicides, fungicides, and wood preservative, are difficult to be biodegraded [4, 5]; thus, they are environmental residue. Chlorophenols are considered to be harmful for human health [6, 7] and have been listed as priority pollutants by the US EPA and the EU. Conventional processes [8–10], such as physical, chemical, and biological methods, are used to remove chlorophenols. These techniques, however, are difficult to degrade such refractory biodegradation organic pollutants completely. In recent years, several advanced oxidation processes (AOPs) are put forward for the degradation of chlorophenols [11, 12], including electrochemical anodic oxidation [13, 14], Fenton oxidation [15, 16], and photocatalytic oxidation [17, 18]. Such AOPs generate free radicals, which have strong oxidation capability; thus, the organic

pollutants can be destructed easily. Photocatalytic oxidation is one of the AOPs widely used to degrade organic pollutants into harmless final products.

The present researches focusing on the materials of photocatalytic oxidation are semiconductors included oxides [19, 20], sulfides [21], nitrides [22], and oxynitrides [23]. These semiconductors provide a promising strategy for environmental pollutants control or hydrogen generation. One of the most important photocatalysts is titanium dioxide (TiO_2) [24, 25], which has been known as the most preferable photocatalyst due to its stability, nontoxicity, and low cost. However, there are disadvantages, such as low separation rate of the photoexcited electrons and holes, which lead to the limited quantum efficiency of TiO_2 . Therefore, many scholars have been devoted to prepare a TiO_2 photocatalyst that is capable of efficient generation and separation of photo-induced electron-hole pairs. These investigations include doping with cation or anion ions, coupling TiO_2 with other semiconductors [26], depositing precious metal, and so on. For example, Yu et al. synthesized novel carbon self-doped

TiO₂ sheets with exposed {001} facets, which exhibited an excellent absorption in the whole visible-light region, due to the exposed {001} facets which were much more reactive than the thermodynamically more stable {101} surface [27].

It was reported [28, 29] that alkali titanates, general formula as A₂O-*n*TiO₂ ($3 \leq n \leq 8$, A = Li, Na, K), exhibited good photocatalytic activity and ion conductivity. According to Billik et al. [30], Na₂Ti₆O₁₃ could be prepared by mechanochemical reaction of the TiC₁₄-Na₂SO₄·10H₂O-Na₂CO₃ mixture followed by a molten salt synthesis.

The present work is based on the idea that heterostructures of Na₂Ti₆O₁₃ coupling with TiO₂ would perform outstanding photocatalytic properties. To our knowledge, Na₂Ti₆O₁₃ is hard to be obtained at the temperature lower than 800°C. Since the costs are high and the process of crystallization is difficult to control, we proposed a simple and rapid method to obtain such heterostructures. In this paper, *x*-Na₂Ti₆O₁₃/TiO₂ ($x = 0, 1.0, 1.5, 2.5$) composite particles were synthesized in reverse microemulsions system at room temperature and ambient pressure followed by heat treatments from 500°C to 800°C. The photocatalytic activity of these samples was evaluated and compared with the commercial P25-TiO₂ on the degradation of 2,4-DCP in aqueous solution under ultraviolet light irradiation. The forming conditions of Na₂Ti₆O₁₃/TiO₂ heterostructures and their photocatalytic property were discussed based on characterization results.

2. Materials and Methods

2.1. Preparation of Na₂Ti₆O₁₃/TiO₂ Composite Particles. The nanostructured Na₂Ti₆O₁₃/TiO₂ photocatalyst was synthesized by a microemulsion approach. The *n*-hexanol (chemically pure, CP) was considered as both the oil phase and the cosurfactant, and cetyltrimethylammonium bromide (CTAB) (CP) was chosen as the surfactant. Sodium hydroxide (CP) solution with specific molar concentration of 0, 1.0, 1.5, and 2.5 mol/L, respectively, acted as the water phase.

Stock solutions of *n*-hexanol and CTAB with a quality ratio of 2:1 were mixed under stirring. Sodium hydroxide solution was added drop-wise to the glass vial containing the mixtures aforementioned, and the mass of sodium hydroxide solution was 10% of the bulk quality. After stirring for 60 min, a steady microemulsion was obtained. A desired amount of Ti(OBut)₄ (CP) was injected into the microemulsion. The resultant suspension was stirred for 120 min until it became milk white. In the system, the quality ratio of CTAB to Ti(OBut)₄ was 2.5:1. The solid products were separated in a centrifuge at 4000 r min⁻¹ and washed with anhydrous ethanol (AP) to remove the organic compounds and surfactants from the particles and dried in an oven at 105°C for 12 h. The obtained precursors were calcined for 3 h at 500, 600, 700, and 800°C, respectively. The final products were milled before characterization. Samples were labeled as *x*-Na₂Ti₆O₁₃/TiO₂, where $x = 0, 1.0, 1.5$, and 2.5 mol/L was the molar concentration of NaOH. All the products were synthesized at room temperature and ambient pressure without thermal treatment, if not otherwise stated.

2.2. Characterization of Na₂Ti₆O₁₃/TiO₂ Composite Particles. X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm) at a high voltage of 40 kV with a step of 0.02°. The particle size and morphology were observed on a field emission scanning electron microscope (FESEM, LEO 1530 VP, Germany). The TG analysis of precursors was measured by an STA449c/1/41G thermal analyzer (Netzsch, Germany).

2.3. Photocatalytic Studies. The photocatalytic reaction was conducted in a 200 mL cylindrical glass vessel fixed in the XPA photochemical reactor (Nanjing Xujiang Machine-electronic Plant). The XPA reactor consists of a magnetic stirrer, quartz cool trap, and a condenser to keep the reaction temperature steady and to prevent the evaporation of water. A 40 W Hg lamp (365 nm) was used as the UV light source. 2,4-Dichlorophenol (2,4-DCP) with certain concentration (0.02 g/L) was used as reactant.

Prior to illumination, various quantities of photocatalyst powder were dispersed in 200 mL reaction solution and stirred in the dark for 30 min in order to obtain an optimally dispersed system and to ensure complete adsorption/desorption equilibration. Subsequently, the Hg lamp was turned on, and the catalysts began to decompose 2,4-DCP.

During the course of illumination, 1.0 mL of suspensions was withdrawn periodically from the reactor and filtered (Millipore Millex25 0.45 mm membrane filter) previously to HPLC measurements.

The concentrations of 2,4-DCP were monitored with a high performance liquid chromatography (HPLC, Shimadzu, Japan) equipped with a UV detector (SPD-10AV) and a Symmetry C18 column (250 mm × 4.6 mm). Mobile phase: methanol (HPLC grade) and water (80:20, volume); flow rate: 1.0 mL/min; injection volume: 20 μL; absorbance detection: 284 nm. The concentration of the remaining 2,4-DCP was measured by its area of characteristic peak (*A*). The degradation ratio (*X*) of the reactant was calculated using $X(\%) = 100(A_0 - A_t)/A_0$.

3. Results and Discussion

3.1. Characterization of Na₂Ti₆O₁₃/TiO₂ Composite Particles. The TG-DSC curves for 1.5-Na₂Ti₆O₁₃/TiO₂ precursor are shown in Figure 1. The TG results indicate that the sample lost weight slowly from 25 to 80°C, which could be attributed to the volatilization of physically absorbed oil phase and water. There is a sharp weight loss from 80 to 270°C due to the evaporation of water and the desorption of hexanol (boiling point 156°C), and this is supported by the exothermic peak at 119°C in the DSC curve. As the temperature increases from 270 to 320°C, the sample exhibits further and faster weight loss, which corresponds to the burning of residual surfactant, and this could be explained well by an exothermic peak detected in the DSC curve at 272°C. Beyond 320°C, the curve becomes almost flat, implying that the weight of the precursor has little changed. Combining with the DSC curve, phase transition may be the mainly occurring at this process.

FIGURE 1: TG-DSC curves of 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ precursor.

The DSC curve of the precursor shows two main exothermic peaks: one of which is the evaporation of water and oil phase, and the other is the decomposition of surfactant as discussed earlier. Three endothermic peaks appear at 341, 406, and 566°C, which could be ascribed to the crystallization of TiO_2 from amorphous to anatase, and from anatase to rutile, and the crystallization of $\text{Na}_2\text{Ti}_6\text{O}_{13}$, respectively.

The typical SEM images of 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ are presented in Figure 2. As can be seen in Figure 2(a), the 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ precursor without heat treatment is amorphous and bonding loosely, appearing to be large and bubbles-like, which might reflect the situation of the water droplet in the microemulsion. While the precursors were calcined at 500 or 600°C, the loose bubbles-like structures break into small particles, and the diameter was less than 100 nm. Comparing with Figures 2(b) and 2(c), particles calcined at 600°C dispersed better than that at 500°C. Subcircular and well-crystallized particles with diameter of around 50 nm were obtained in Figure 2(c). Combining with XRD pattern, it can be known that the precursors were dehydrated and they would be transformed into the crystalline anatase and $\text{Na}_2\text{Ti}_6\text{O}_{13}$, under calcinations at 500 and 600°C, respectively.

The SEM micrographs of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ powders calcined at 700 and 800°C are shown in Figures 2(d) and 2(e). The belt-like morphology of the product calcined at 700°C is well documented in the SEM image shown in Figure 2(d). $\text{Na}_2\text{Ti}_6\text{O}_{13}$ nanobelts have typical width from 80 to 100 nm, thickness less than 40 nm, and length up to 5 μm . The phase of the obtained sample was supported by XRD. It is also found that the nanobelts were fractured under calcination at 800°C, though the fragments have higher degree of crystallinity, as shown obviously in Figure 2(e).

Figure 3 shows the XRD patterns of 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ precursor and the composite particles which were calcined for 3 h at 500, 600, 700, and 800°C, respectively. As can be seen, no characteristic diffraction peaks are observed from the pattern of precursor, indicating that the precursor is amorphous. The XRD pattern of 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ calcined at 500°C shows a strong peak at $2\theta = 25.34^\circ$ and a

weak one at $2\theta = 27.50^\circ$, implying that TiO_2 is crystallized as the anatase and rutile phase coexistence after calcined at 500°C. Curves of 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ calcined at 600–800°C show that $\text{Na}_2\text{Ti}_6\text{O}_{13}$ could be obtained by calcining the microemulsion-resulted precursor at relatively low temperature ($<800^\circ\text{C}$). The pattern of 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ calcined at 600°C shows the characteristic diffraction peak of both rutile and $\text{Na}_2\text{Ti}_6\text{O}_{13}$; however, the samples calcined at 700, and 800°C have no characteristic diffraction peak of TiO_2 .

Although the formation mechanisms of the titanate nanobelts are still under debate, we believe that the formation of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ nanobelts may be affected by the crystallite size or chemical activity of the precursor and the condition of crystallization. In our work, the precursor is considered to be $\text{Ti}(\text{OH})_4$. Under heat treatment, $-\text{OH}$ from the surface of $\text{Ti}(\text{OH})_4$ combined with each other to produce H_2O and $-\text{O}-\text{Ti}-\text{bond}$. With the calcined temperature increase and the existence of Na^+ , more $-\text{OH}$ were removed and $\text{Na}-\text{O}-\text{Ti}-\text{bonds}$ were formed, which means that $\text{Na}_2\text{Ti}_6\text{O}_{13}$ were formed. As it was supported by SEM and XRD, at the temperature of 600°C, the crystallization of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ which are the prerequisites for the nanobelts formation was obtained. According to Dominko et al. [31], $\text{Na}_2\text{Ti}_6\text{O}_{13}$ crystallizes in a monoclinic crystalline structure with continuous tunnel channels along c axis (Figure 4). Such tunnel channels suppressed the possible delamination into sheets or nanotubes [30].

In a word, the amorphous precursor forms anatase and rutile phase at 500°C, and the anatase phase transits into rutile phase at 600°C; meanwhile, $\text{Na}_2\text{Ti}_6\text{O}_{13}$ crystal formed. However, when the temperature is higher than 600°C, no TiO_2 exists. Thus, the optimum temperature for heterostructure particles is 600°C.

3.2. Degradation Activities of $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$. In this investigation, 2,4-dichlorophenol (2,4-DCP) was chosen as a representative model pollutant ($C_0 = 20 \text{ mg/L}$, 200 mL) to study the adsorption and photocatalytic activity of the $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ composite particles (10 mg) under UV-light (40 W Hg lamp) irradiation and the results can be seen in Figure 5. The degradation efficiency of 2,4-DCP increased with time. After 50 min UV-light irradiation, the degradation rate reached 99.4%, 96.0%, 83%, and 56.2%, by the photocatalyst synthesized in 1.5, 1.0, 0, and 2.5 mol/L sodium hydroxide solution, respectively, while the commercial P25 has the degradation rate of 76.9%, and the degradation rate of 11.5% was obtained without any photocatalysts.

The different molar ratios of $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ have significant differences in photoactivity. While the ratio raises from 0 to 1.5, the degradation rate raises obviously; however, the 2.5 sample has the weakest activity. The sample of 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ has the best efficiency for decomposing 2,4-DCP, which is about 1.3 times higher than commercial P25. Thus, 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ was chosen as the standard photocatalyst.

Figure 6 shows the photoactivity of 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ calcined at different temperatures. After 50 min UV-light irradiation, the degradation rate reached 99.4%, 83.8%, 56.3%, and 37.2%, by the photocatalyst calcined at 600, 500,

FIGURE 2: SEM image of $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ composite particles. (a) $1.5\text{-Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ precursor; (b) $1.5\text{-Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ calcined at 500°C ; (c) $1.5\text{-Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ calcined at 600°C ; (d) $1.5\text{-Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ calcined at 700°C ; (e) $1.5\text{-Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ calcined at 800°C .

700°C , and 800°C , respectively. The commercial P25 has the degradation rate of 76.9%, and the blank experiment showed the degradation rate of 11.5%.

Combining with SEM and XRD characterization, the temperature of calcinations determines the crystal line, the morphology, and the components of the photocatalyst. At 500°C the component of the photocatalyst mainly is TiO_2 . Such photocatalyst formed by anatase and rutile exhibits a general photoactivity. At 600°C $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ heterostructure formed and the particles were well crystalline. These microstructures improve the separation efficiency of photogenerated electrons and holes, increase the contact area,

and allow more efficient transport for the reactant molecules to get to the active sites on the framework walls, enhance the adsorption of light, and reduce the reflection of light. Therefore, the photocatalytic activity was enhanced.

In order to observe the photo degradation process of 2,4-DCP, the concentrations of possible intermediates, such as phenol, 4-CP, and 2-CP, were measured with HPLC. Figure 7 represents these three intermediates generation from the system. It is clear that 2,4-DCP was not completely mineralized and was residue as phenol and chlorophenol; meanwhile, the concentration of phenol is much higher than 4-CP and 2-CP. After 40 min photoreaction, the concentration

FIGURE 3: XRD pattern of 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ composite particles: (a) 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ precursor; (b) 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ calcined at 500°C ; (c) 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ calcined at 600°C ; (d) 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ calcined at 700°C ; (e) 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ calcined at 800°C .

FIGURE 4: Schematic representation of the crystal structure of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ along a -axis [31] (octahedral: $\text{Ti}-\text{O}_6$; spheres: Na).

of these three intermediates reduced obviously, indicating that $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ heterostructure is capable of degrading phenol and chlorophenol.

4. Conclusions

Nanobelts $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ heterostructure particles were synthesized in an n -hexanol/CTAB/sodium hydroxide solution reverse microemulsion. The samples were investigated by TG-DSC, XRD, and SEM. The results show that such belt-like photocatalyst has typical width from 80 to 100 nm, thickness of less than 40 nm, and length up to $5\ \mu\text{m}$. The photocatalytic activity of photocatalysts synthesized by 1.5 mol/L sodium hydroxide solution and calcined at 600°C for 3 h gave the greatest degradation rate towards 2,4-DCP. In summary, it

FIGURE 5: Effects of ratio of $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ calcined at 600°C : (a) 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$; (b) 1.0- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$; (c) 0- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$; (d) commercial P25; (e) 2.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$; (f) blank.

FIGURE 6: Effects of calcined temperature of 1.5- $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$: (a) 600°C ; (b) 500°C ; (c) commercial P25; (d) 700°C ; (e) 800°C ; (f) blank.

FIGURE 7: Variation of (a) phenol; (b) 4-CP; (c) 2-CP concentration during the photo degradation.

was proved that the heterostructure particles had higher photocatalytic activity than the common TiO_2 .

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