Bi$_4$Ti$_3$O$_{12}$ synthesized by high temperature solid phase method and it’s visible catalytic activity

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Abstract

Oxides containing bismuth with layer structures are well known for their unique properties and high visible catalytic activity. In this paper, Bi$_2$O$_3$ and TiO$_2$ were used as raw materials to synthesize Bi$_4$Ti$_3$O$_{12}$ by high temperature solid phase method. The shape and crystal structure of Bi$_4$Ti$_3$O$_{12}$ were characterized via X-Ray Diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Scanning electron microscope (SEM), Transmission electron microscopy (TEM), High resolution TEM (HRTEM), and Selected area electron diffraction (SAED). The photochemical characteristics of products were measured by UV-Vis absorption. We focused on the environmental application of the prepared nanoparticles for the destructions of chlorine phenol (4-CP) and microcystin-RR (MC-RR) under visible light irradiation ($>420$ nm). The results demonstrated that nearly all of 4-CP and MC-RR were degraded by Bi$_4$Ti$_3$O$_{12}$ which showed superior photocatalytic activity. At the same time, transient oxidative species generated during photocatalysis were tracked by Electron spin resonance (EPR), which indicated that the major oxidative species in the system were hydroxyl radical (OH) and superoxide radical (O$_2^-$).

Keywords: bismuth titanate; Bi$_4$Ti$_3$O$_{12}$; photocatalysis; visible light

1. Introduction

Bismuth oxides, such as Bi$_2$O$_3$ [1-3], bismuth oxyhalides BiOX (X = Cl, Br, I) [4-5], bismuth titanate (Bi$_4$Ti$_3$O$_{12}$, Bi$_2$Ti$_2$O$_7$, Bi$_2$Ti$_4$O$_{11}$, Bi$_{12}$Ti$_2$O$_{20}$, Bi$_{20}$TiO$_{32}$) [6-8], Bi$_2$WO$_6$ [9-11], BiVO$_4$ [12-14] and so on, all have unique layered structures characterized by [Bi$_2$O$_3$] slabs interleaved by slabs of inorganic atoms.

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Their photocatalytic activity can be attributed to the special electronic structure and the well dispersive electrons of Bi<sub>6</sub>S, which can form the wide valence band and increase the mobility of electric charges.

Bismuth titanate compounds have various crystal structures and electronic structures, and may also possess band structures which can be stimulated by visible light and high movability of h<sup>+</sup>-e<sup>-</sup> pairs, which turn them into a kind of the potential industrialization photocatalysts. Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> [15-17] is one of the most simple bismuth titanate compounds and a perovskite oxide compound with layer structure composited by Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> [18], and its unusual structures depends on the crystal and electronic structure. There are TiO<sub>6</sub> octagonal or TiO<sub>4</sub> tetrahedron in its structure, and the connection BiO<sub>n</sub> polyhedron containing stereo-active Bi<sup>3+</sup> because it owns 6s<sup>2</sup> lone pair electrons, so Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> shows good catalytic activity. At present, the reported preparation methods of titanate bismuth mainly contain chemical solvents decomposition method (CSD) [19-20] and hydrothermal method [21]. However, the operational complexity and difficult control of CSD method and hydrothermal method limit their application fields. While high temperature solid phase method is a familiar catalyst preparation methods with simple operation and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> prepared via this method is rarely reported so far. Herein, Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> were served as raw materials to prepare Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> through high temperature solid phase method in the paper.

The other aim of this paper is to focus on the application of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> in the destruction of environmental contaminants of worldwide concern. So far, dyes such as methyl orange (MO) [20] was usually used to investigated the photocatalytic activity of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> in previous research. Nevertheless, colorless small molecules 4-CP and macromolecular toxic microcystins-LR, more toxic and harmful than dyes, are never regarded as degrade gelatins to discuss the practical application of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> in water treatment field. 4-CP is a kind of chlorophenol pollutants and has high toxicity even at low concentration, and their treatment is of considerable importance in environmental protection [22-23]. Meanwhile, microcystins (MCs) are the most widespread and poisonous cyanotoxins found in potable water, a large family of cyclic heptapeptides. As we all know, microcystins regard the liver as target organ and inhibit the activity of protein phosphatase, and then induce cancer and other pathological changes. Consequently, microcystins are implicated as one of the key risk factors for an unusually high occurrence of primary liver cancer in the world [24-26]. Microcystins-LR (MC-LR) and Microcystins-RR (MC-LR) are the most toxics and have been used as the standard variant in various experiments [27]. It is worth to note that sometimes the content of MC-RR is more universal and higher than that of MC-LR in our country. Hence, the removal of MC-RR in source water is more significant to remit water pollution in our country.

In this study, the destruction of 4-CP and MC-RR with Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> were discussed under visible light irradiation to test the visible-light photocatalytic active of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>. Besides, the photocatalytic mechanism of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> was discussed via detecting the reactive oxygen species produced during the reaction.

2. Experimental Section

2.1. Preparation and Characterization of Materials

Bismuth nitride (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O), Hexadecyl trimethyl ammonium chloride (CTAC) were of A.R. grade from the Beijing Chemical Factory (China). Titanium dioxide (TiO<sub>2</sub>) was p.a. 99% commercially available from Carlo Erba; Chlorine phenol (4-CP) was purchased from Beijing Ouhe Chemical Factory (China); Microcystin-RR was purchased from Express Technology Company; anhydrous ethanol (CH<sub>3</sub>CH<sub>2</sub>OH); Other chemicals were of reagent grade and used without further purification. Deionized and doubly distilled water was used throughout the investigation.

JEM-2010 transmission electron microscopy (TEM) (Japan, JEOL); S-4300 scanning electron field emission microscope (Japan, Hitachi); N/C 2100 TOC analyzer (Germany, Jena); Lambda25 UV-visible
All the chemicals were received from Beijing Chemical Co. (Beijing, China) and used without further purification. In a typical procedure, Bi$_2$O$_3$ was prepared according to the literature [28]. Then the prepared Bi$_2$O$_3$ and TiO$_2$ were used as raw material according to a certain stoichiometric proportion and mixed to react 24 h in 700 °C after ultrasound.

X-ray diffraction (XRD) patterns were conducted on a D8ADVANCE X-ray diffraction equipped with a Cu Ka radiation at a scanning speed of 5°/min ranging from 5 to 80°. The accelerating voltage and applied current were 40 kV and 100 mA respectively. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopic (EDX) measurements were performed using a Hitachi S-4300 scanning electron field emission microscope operating at 15kV. Transmission electron microscopy (TEM), high resolution TEM (HRTEM), and selected area electron diffraction (SAED) patterns were performed on a JEOL JEM-2010 electron microscope with a field emission gun operating at 200kV. X-ray photoelectron spectroscopy (XPS) was acquired by an VG Multilab 2000 (VG Inc.) photoelectron spectrometer by using monochromatic Al KR radiation under vacuum at 2 × 10⁻⁶ Pa. The spectra of the films were collected and corrected by referencing the binding energy to carbon (C1s, 284.6 eV). The UV-vis spectroscopy was recorded at room temperature on a Hitachi U-3010 spectrophotometer from 200 to 800 nm. N$_2$ adsorption-desorption isotherms were performed with a Quanta chrome Autosorb1-C system at 196 °C; the data were analyzed by employing the BET method.

2.2. Degrading 4-CP under visible light

The light source was a 500-W halogen lamp positioned in a XPA series photochemical reactions instrument. A cut off filter was placed outside the Pyrex jacket to eliminate any radiation at wavelength below 420 nm to ensure illumination by visible light only. 20 mL 4-CP containing 10 mg Bi$_4$Ti$_3$O$_{12}$ with different initial concentration was put into a cylindrical glass bottle and the solutions pH was adjusted. First, the above solutions were placed in dark 15 h to achieve the adsorption and desorption-balance and then sampled in different time intervals with Ep tube in the visible light (λ> 420 nm). Samples were centrifuged and analyzed with high performance liquid chromatography analysis. Chromatographic conditions: C$_{18}$ reversed-phase chromatography column, mobile phase was methanol: water=8:2, the velocity was 0.7 mL/min.

2.3. Degrading Microcystin-RR under visible light

2.0 mg/L 5 mL MCs (Express Technology Co., China) and 2 mg of Bi$_4$Ti$_3$O$_{12}$ were placed in the Pyrex reaction vessel. To ensure the establishment of an adsorption/desorption equilibrium, the suspensions were magnetically stirred in the dark for approximately 2 h prior to the irradiation. In a certain time intervals, 300 μL samples were collected, centrifuged, and then filtered through a Milli porefilter (poresize 0.22 μm) to remove the solid catalyst particles. The solution pH was not adjusted. High-performance liquid chromatography (HPLC) analysis was performed with a Waters 600 HPLC (USA, Waters) with a Waters 2998 photodiodearray (PDA) detector and a C$_{18}$ reverse-phase column (4.6 mm i.d. × 150 mm, Kromasil). The mobile phase was water containing 0.05% TFA (v/v) and methanol, and the ratio is 35:65. The injection volume of the sample is 20 μL and the flow rate was 0.6 mL/min. The wavelength of the UV absorbance detector was λ≤388 nm. The detection limit for microcystin-RR was 0.15 μg/L.
2.4. Determination of active radicals

The oxidative active radicals produced in the process of reaction were measured with the ESR method [29]. In order to reduce the experimental errors, the same root quartz capillary was used in the whole process of measuring ESR. DMPO was put in the reacting systems to capture the ·OH or O$_2^-$ radicals produced in the reacting process.

2.5. LC-MS analysis

A LC/MS instrument (LC/MSD Trap1100, Agilent) was used to monitor the reaction intermediates by full scanning from m/z 300 to 1200 in the positive ion mode. An LC/MSD Trap software work station was used for the LC-MS instrument control, data analysis and quantitative results. The mobile phase was a gradient elution of formic acid (pH=2.6) and acetonitrile. Gradient elution was programmed as 0-20% acetonitrile (10 min) followed by an increase to 35% (10 min), 60% (15 min), and 80% (10 min). Thermo Orion 3-Star Dissolved Oxygen Analyzer (US) was used to detect the oxygen consumption during the photodegradation MC-RR by Bi$_4$Ti$_3$O$_{12}$.

2.6. TOC Analyses

The TOC changes in different reaction time during in degrading 4-CP were analyzed by N/C 2100 TOC.

3. Results and discussion

3.1. Characterization analysis

To investigate the chemical state and the surface compositions of Bi$_4$Ti$_3$O$_{12}$, X-ray Photoelectron Spectroscopy(XPS) characterization was employed. It can be observed that the spin orbit splitting peaks of Bi$_{4f}$ level is split into two peaks(Fig. 1a), and the peaks were centered at 164.5 and 159.2 eV in the Bi$_4$Ti$_3$O$_{12}$ samples corresponding to the binding energy of Bi$_{4f5/2}$ and Bi$_{4f7/2}$, which were corresponded to Bi(III) according to the literatures [30]. The O1s region contains one peak as shown in Fig. 1b. The binding energy peak at around 529.8 eV was attributed to bridging oxygen atoms from Bi-O bond and Ti-O bond since it is seen at the same position as that of O$_{is}$ peak of BiOX [31] and TiO$_2$ surfaces [32], while the minor peak at around 530.6 eV was due to the hydroxyl group adsorbed on the surface. From the Ti$_{2p}$ region in Fig. 1c, the spectrum contain speaks at 465.9eV and 457.9 eV were attributed to the binding energies of the Ti 2p 3/2 and Ti 2p 1/2 , respectively. It was agreed with the literature reported by Jovalekić [33] and suggested that Bi$_4$Ti$_3$O$_{12}$ is composed of Ti$^{4+}$ ions.

The X-ray diffraction(XRD) pattern (Fig. 2) of product was well indexed as Bi$_4$Ti$_3$O$_{12}$ with a space group of C***(65)/nmn and lattice constants of $a$=5.49(9), $b$=32.81(5) and $c$=5.41(0)Å (JCPDS No.36-1486), corresponding to (111), (002), (202), and (113) diffractions around $\theta$=23.34°, 32.98°, 43.34°, and 53.42°. The intense and narrow diffraction peaks reveal the good crystallinity of the Bi$_4$Ti$_3$O$_{12}$ samples.

The Scanning electron microscopy (SEM) examination revealed that Bi$_4$Ti$_3$O$_{12}$ was smooth-faced nano-sheet with 200-300 μm in width and 20-50 nm in thickness (Fig. 3a). Transmission electron microscopy (TEM) image (Fig. 3b) further confirmed its perfect and regular sheet-shaped structures. The corresponding selected-area electron diffraction (SAED) pattern (Fig. 3c) showed speckled form, which indicated the single-crystalline characteristic of Bi$_4$Ti$_3$O$_{12}$. The high-resolution TEM (HRTEM) (Fig. 3d) revealed the highly crystalline nature of the nanosheets and the clear lattice fringes with an interplanar
lattice spacing of 0.18 nm. The EDS analysis (Fig. 3e) indicated that only Bi, Ti, and O peaks were observed in the spectrum, which was agreeing with the XPS result.

Fig. 1. High-resolution XPS spectra of Bi4f(a), O1s(b) and Ti2p(c) of Bi4Ti3O12.

Fig. 2. X-Ray Diffraction pattern of Bi4Ti3O12.

Fig. 3. SEM image (a), TEM pattern (b), SEAD (c), THRTEM(d) and EDS(e) of Bi4Ti3O12.
The specific surface area of the Bi$_4$Ti$_3$O$_{12}$ was investigated by using nitrogen adsorption and desorption isotherms. The BET specific surface area of the sample was calculated from N$_2$ isotherms and was found to be as much as $3.462 \, \text{m}^2/\text{g}$.

The character of light absorption of Bi$_4$Ti$_3$O$_{12}$ was analyzed by UV-Vis diffuse reflection. The linear relationship between the bandgap of Bi$_4$Ti$_3$O$_{12}$ structure and $(\alpha\text{Ephoton})^{1/2}$ was shown in the Fig. 4 (which the $\alpha$ and Ephoton respectively were absorption coefficient and discrete photon energy). The extrapolation values of Ephoton when $\alpha=0$ (the intersection of straight line and X axis) gave the energy absorption, and the corresponding forbidden band width was $E_g = 2.92 \, \text{eV}$.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig4}
\caption{UV-Vis diffuse reflectance curve of Bi$_4$Ti$_3$O$_{12}$.}
\end{figure}

3.2. The photodegradation of 4-CP

3.2.1. The degradation curve of 4-CP

Chlorine phenol (4-CP) is a colorless small molecular pollutant and has no absorption in visible area, so it is often regarded as degradation object to detect the visible catalytic activity of catalysts. In visible light, the degradation of 4-CP with Bi$_4$Ti$_3$O$_{12}$ can be seen in fig. 5. 4-CP in visible light happened a little photodecomposition and about 17% of 4-CP photolyzed after reacting 8 h to reach balance basically(curve b). Besides, 4-CP had little adsorption on the catalyst in the dark (curve a). However, Bi$_4$Ti$_3$O$_{12}$ could degrade 93% 4-CP after illuminating 20 h (curve c) and showed a certain visible catalytic activity.

3.2.2. The effect of initial concentration of 4-CP on photodegradation

The kinetic curves of Bi$_4$Ti$_3$O$_{12}$ degrading 4-CP with different initial concentration were seen in Fig. 6. Bi$_4$Ti$_3$O$_{12}$ had a little adsorption of 4-CP in the dark, and the adsorption quantity increased slightly with the concentration aggrandizing (curve a, b, c). Under visible light, Bi$_4$Ti$_3$O$_{12}$ could degrade different concentration of 4-CP (curve e, f, g) with different reaction speed. In addition, the degradation reaction was faster when the initial concentration of 4-CP was lower. When $c_0 = 1.25 \times 10^{-5} \, \text{mol/L}$, Bi$_4$Ti$_3$O$_{12}$ degraded 4-CP above 90% after 20 h.
3.2.3. The effect of pH

4-CP was degraded respectively in acidic, neutral and alkaline conditions by Bi$_4$Ti$_3$O$_{12}$ and the results showed in Fig. 7. 4-CP is degraded faster in acidic solution than that in alkaline and neutral solution. When pH=3.56, the degradation reaction was the fastest. With pH increasing, the degradation rate decreased, and the rates in pH=7.32 and pH=10.68 had a little difference, which attribute to 4-CP ionizing with negative charges at alkaline and neutral conditions and becoming more water-soluble. However, 4-CP remained in molecular form with more hydrophobic property at acidic condition [34]. Thus, large amount of 4-CP would absorb onto the surface of Bi$_4$Ti$_3$O$_{12}$, which was beneficial to its degradation.

3.2.4. The measurements of free radicals

The free radicals were measured in the process of Bi$_4$Ti$_3$O$_{12}$ degrading dyes through the electronic spin technology, as seen in Fig. 8. The ESR signal in picture a showed obvious 1:2:2:1 four peaks which was the feature signal peaks of DMPO-OH adducts; In addition, the picture b showed 1:1:1:1 four peaks which was the feature signal peaks of DMPO-O$_2^-$ adducts. We can conclude that there could produce ‘OH
and \(O_2^-\) in the process of \(Bi_4Ti_3O_12\) catalytic degradation, and the mechanism of degradation involves the ‘OH and \(O_2^-\) oxidation mechanism.

![Fig. 8. ESR signals of the DMPO-•OH adducts(a) and DMPO-O2.- adducts(b).](image)

### 3.2.5. TOC analysis

Fig. 9 showed the mineralization of \(Bi_4Ti_3O_12\) degrading 4-CP. The TOC value had no significant change in dark; Under visible irradiation, 4-CP solution was mineralized, and the mineralization rate reached 80% after reacting 25 h, which indicated that \(Bi_4Ti_3O_12\) could not only degraded 4-CP in visible, but also continue to mineralize 4-CP into \(CO_2\), \(H_2O\) and other small molecules.

### 3.3. The kinetic curve of degrading MC-RR

\(Bi_4Ti_3O_12\) was used to degrade MC-RR under visible light, as can be seen in Fig. 10. The photolysis of MC-RR was extremely slow under visible light illumination without a photocatalyst, and MC-RR concentration decreased by only 5% after 18 h with a photocatalyst in the absence of light. However, when \(Bi_4Ti_3O_12\) was used as the photocatalyst, nearly 100% of MC-RR was degraded after 18 h under visible light irradiation, which indicated \(Bi_4Ti_3O_12\) had a good application prospect in water treatment of cyanotoxins.

![Fig. 9. Changes of TOC during the degradation process of 4-CP.](image)

![Fig. 10. The photodegradation of MC-RR by \(Bi_4Ti_3O_12\).](image)
3.4. The photocatalytic mechanism of Bi$_4$Ti$_3$O$_{12}$ under visible light

3.4.1. The band structure of Bi$_4$Ti$_3$O$_{12}$

The DOS calculations confirmed that the valence band (VB) of Bi$_4$Ti$_3$O$_{12}$ is defined mainly by the O2p and Ti3d orbitals and conduct band (CB) by the Bi6p orbital [34-35]. The band gap of Bi$_4$Ti$_3$O$_{12}$ was 2.92 eV calculated via UV-Vis diffuse reflectance, and the active species produced during photocatalytic process were ‘OH and O$_2^\cdot$ measured by ESR method. Therefore, we can infer the photocatalytic mechanism of Bi$_4$Ti$_3$O$_{12}$(Fig. 11). When Bi$_4$Ti$_3$O$_{12}$ is stimulated by visible light, the electrons in the VB can be aroused to the CB and produce electronic-hole pairs which migrate to the surface of the catalyst and react with water and oxygen to generate free radicals ‘OH and O$_2^\cdot$ respectively [36]. The active species show the high oxidizability and are able to oxidate pollutants and even mineralize the substrates to CO$_2$ and H$_2$O.

3.4.2. The photocatalytic mechanism of Bi$_4$Ti$_3$O$_{12}$ degrading MC-RR

Upon analysis of the LC-MS data, the initially main products of MC-RR by Bi$_4$Ti$_3$O$_{12}$ were respectively with m/z 1055.5(a), m/z 905.5(b) and m/z 839.5(c), which all were come from ‘OH radicals attacking on the aromatic ring on the Adda chain. The main products MS were seen in Fig. 12. Product a was the single hydroxyl substitution of the aromatic ring, which made the Adda chain activated and generate produce b, then reacted further to give a aldehyde product c (m/z 839.5). This observation was consistent with TiO$_2$ photocatalysis and sulfate radical oxidation in which the primary pathway of hydroxyl radical attacks when degraded MC-LR [37-38]. The results also further corroborated free radicals ‘OH was the main active specie to oxidate pollutants.

![Diagram](image)

Fig. 11. The mechanism of Bi$_4$Ti$_3$O$_{12}$ under visible light.
Fig. 12. Hydroxylation products of MC-RR by Bi$_4$Ti$_3$O$_12$ photocatalysis.
4. Conclusions

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was synthesized via high temperature solid phase method by using $\text{Bi}_2\text{O}_3$ and $\text{TiO}_2$ as raw materials. 4-CP and MC-RR were regarded as objective pollutant to test the visible photocatalytic activity. The results showed 4-CP was degraded in visible light, and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ showed the best photocatalytic efficient when the concentration of 4-CP was $1.25 \times 10^{-5}$ mol/L and the solution was acidic. In addition, the main active species during the degradation process were ‘$\text{OH}$ and $\text{O}_2$‘, which indicated the degradation mechanism involved the ‘$\text{OH}$ and $\text{O}_2$‘ oxidation mechanism. In the meantime, the efficient degradation rate of MC-RR revealed that $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ could be used in the practical water treatment.

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