

Facile fabrication of plate-like Bi₃O₄Cl for visible-light-driven photocatalytic degradation of tetracycline hydrochloride

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Novel visible (vis)-light-driven Bi₃O₄Cl plates were first prepared via a facile method. The structure, morphology, and photo absorption properties of as-prepared Bi₃O₄Cl were characterised by multiple physicochemical techniques. Tetracycline hydrochloride (TC-HCl), a famous broad-spectrum antibiotic, was used to evaluate the photocatalytic activity of the as-prepared samples. Compared to the BiOCl and solid-state reaction synthesised Bi₃O₄Cl, the plate-like Bi₃O₄Cl exhibited highly improved vis-light-driven photoreactivity toward TC-HCl degradation under aqueous solution. Moreover, the Bi₃O₄Cl plates also displayed excellent photochemical stability even after four times photocatalytic recycling tests. This work provides a simple approach to fabricate the novel Bi-based semiconductor for potential application in treatment of antibiotic pollutant.

1. Introduction: Photocatalytic degradation of organic pollutant from wastewater based on the sustainable solar light as driving force is a promising technology for solving the serious environmental issues [1, 2]. In the past years, the traditional photocatalysts such as TiO₂ and BiOCl were widely emerged for environmental remediation [3–5]. However, both of them cannot be active under visible (vis)-light irradiation because of their bandgap higher than 3.0 eV. In addition, the ultraviolet (UV) light only accounts a small proportion (4%) in the sunlight. Thus, developing vis-light-driven photocatalyst with stable and high-performance activity for efficient using solar light energy is the research focus in the area of photocatalysis.

Recently, Bi₃O₄Cl, a novel Bi-based oxychloride, has received much attention in photocatalysis due to its open crystalline structure, uniquely layered architecture, and high chemical stability [5–9]. What is more, Bi₃O₄Cl possesses a narrower bandgap than the BiOCl, which can be considered as a promising candidate for pollutant degradation. The Bi₃O₄Cl belongs to a typical Sillén-related oxide and its unique crystalline structure can make itself with the self-built internal static electric fields for accelerating the charge separation, which is useful for the photocatalytic reactions [8, 10]. It has been experimentally shown that Bi₃O₄Cl usually can prepare by the traditional solid-state reaction [9–11], but the photocatalytic activity is limited because of its very large bulky size resulting in difficult separation of charge carries. Here, we reported a simple solvothermal methodology following a calcination approach to prepare the novel Bi₃O₄Cl. The as-prepared Bi₃O₄Cl has plate-like structure and possesses a narrow bandgap (2.62 eV). Compared to the BiOCl and solid-state reaction synthesised Bi₃O₄Cl, the Bi₃O₄Cl plates exhibited much superior photoreactivity for tetracycline hydrochloride (TC-HCl) degradation. Moreover, the Bi₃O₄Cl plates had good photochemical stability for removal of TC-HCl even undergoing four times recycling tests. Furthermore, the photocatalytic mechanism of the plate-like Bi₃O₄Cl for photodegradation of TC-HCl was studied.

2. Experimental results: Bi(NO₃)₃•5H₂O, NH₄Cl, Bi₂O₃, ethylene glycol, and ethanol were analytical grade agents and used without further purification. Typically, 0.4851 g of Bi(NO₃)₃•5H₂O was completely dissolved in 10 ml of ethylene glycol through string and ultrasonic dispersion to form a clear solution A. About 0.1765 g of NH₄Cl was dissolved in 20 ml of deionised water by stirring for 10 min to form a clear

solution B. Then, the above solution A was slowly added into solution B and the white suspension immediately appeared. After vigorously stirring for 30 min, the mixture was transferred to a 50 ml teflon-lined autoclave and heated at 160°C for reaction 12 h. After cooled to the room temperature naturally, the resulting precipitation was washed with water and ethanol three times to remove the residual ions, and then collected by drying in vacuum at 80°C. At last, the obtained powders were headed in a muffle furnace at 500°C for reaction 4 h with a heating rate of 2°C/min under air atmosphere. Additionally, the traditional BiOCl was synthesised by solvothermal reaction with 1 mmol of Bi(NO₃)₃•5H₂O and 1 mmol of NH₄Cl, but without the calcination process. For comparison, the Bi₃O₄Cl powders were also prepared by a solid-state reaction with 0.1 mmol of comical Bi₂O₃ and 0.1 mmol of as-obtained BiOCl [11].

The crystal structures were determined by powder X-ray diffraction (XRD, D/MAX-2500 diffractometer, Rigaku, Japan) using copper K-alpha (K α) radiation ($\lambda = 1.54178 \text{ \AA}$). The morphology and microstructure were observed by using field emission scanning electronic microscopy (SEM, Hitachi, Japan), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM, JEM-2100F, Japan). The X-ray photoelectron spectroscopy (XPS) was obtained by a Thermo ESCALAB 250 \times (America) electron spectrometer using 150 W aluminium K α X-ray sources. The UV–vis diffused reflectance spectra were performed on a Shimadzu UV-2450 spectrophotometer using BaSO₄ as the reference.

The photocatalytic activity was evaluated by the photodegradation of TC-HCl in aqueous solution. The light source is using a 250 W xenon lamp equipment with an optical filter ($\lambda > 420 \text{ nm}$). Briefly, the photochemical reactor contains 100 mg of catalysts and 100 ml of 10 mg/l TC-HCl aqueous solution. Before the light irradiation, the suspension was stirred in the dark for 30 min to achieve the adsorption–desorption equilibrium. Then, the 5 ml of the suspension was taken out at an interval and centrifuged to remove the catalyst before measurement. Subsequently, the photochemical reactor system was kept at 25°C by introducing the jacket to cool the solution. The peak absorbency of TC-HCl at 357 nm was used to determine its concentration by a TU-1810 UV–vis spectrophotometer. Then, the triethanolamine (TEOA), 1,4-benzoquinone (BQ), and isopropanol (IPA) (1 mM) were selected as the scavengers for trapping of the superoxide radical ($\bullet\text{O}_2^-$), hydroxyl radicals ($\bullet\text{OH}$), and holes (h^+), respectively [12]. The active species experiments are similar to the photocatalytic procedure.

3. Results and discussion: Fig. 1a displays the XRD diffractograms of the as-synthesised Bi₃O₄Cl. It is found that the sample can be readily indexed to the monoclinic phase structure (JCPDS Card No. 86-2221), and the sharp peaks elucidated that the product was well crystallised. Moreover, there is no other impurity phases observed, suggesting the product was composed of the single-phase Bi₃O₄Cl [13]. In addition, the compositions and chemical states of as-obtained Bi₃O₄Cl were investigated by XPS. As illustrated in Fig. 1b, the high-resolution Bi 4f peaks at 164.5 and 159.2 eV are assigned to the Bi 4f_{5/2} and Bi 4f_{7/2} levels, which are assigned to Bi³⁺ in the Bi₃O₄Cl [14]. The high-resolution O 1s spectrum is deconvoluted into two peaks at 531.5 and 529.7 eV (Fig. 1c), which are, respectively, ascribed from the Bi–O bond and surface hydroxyl groups (Bi–O–H) in the sample [14, 15]. In the high-resolution Cl 2p spectrum (Fig. 1d), the Cl 2p peaks at 199.8 and 198.3 eV are referred to the Cl 2p_{1/2} and Cl 2p_{3/2} levels, which correspond to the monovalent oxidation state Cl [5].

The morphology and microstructure of as-prepared Bi₃O₄Cl were recorded by SEM and TEM. As shown in Figs. 2a and b, SEM images depicted that the obtained Bi₃O₄Cl exhibited the plate-like structure and some nanocrystals were observed on its surface. Moreover, TEM image also showed that the sample displayed the

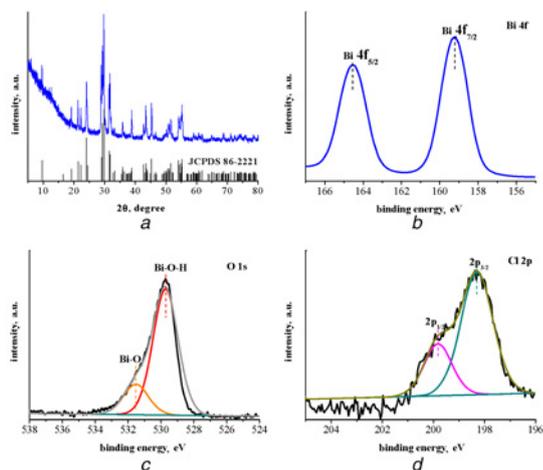


Fig. 1 XRD diffractograms
a XRD pattern and XPS spectra of as-prepared sample
b Bi 4f
c O 1s
d Cl 2p

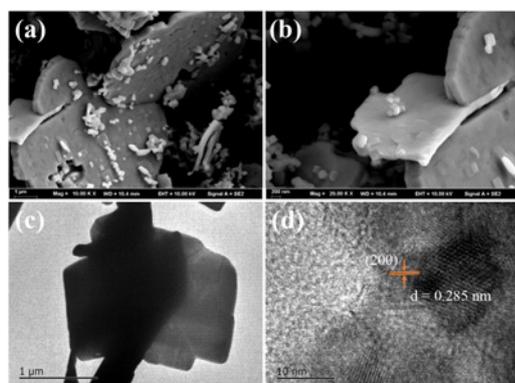


Fig. 2 SEM images
a, b SEM images of as-prepared sample
c TEM
d HRTEM images of as-prepared sample

plate-like architecture (Fig. 2c). As presented in Fig. 2d, the HRTEM image clearly depicted that the lattice space of the sample is 0.285 nm, which can correspond to the (200) plane of the monoclinic Bi₃O₄Cl. The results are in good agreement with the above XRD analysis, indicating the Bi₃O₄Cl with plate-like structure had been successfully prepared.

The UV–vis diffuse reflection spectra of the as-prepared BiOCl and Bi₃O₄Cl plates were displayed in Fig. 3a. The BiOCl exhibited a sharp absorption edge rising at around 370 nm, suggesting it can only absorb the UV light. However, the as-synthesised Bi₃O₄Cl plates showed a broad absorption ranges at about 500 nm, revealing the sample possessed good vis-light response ability. From their Tauc plots in Fig. 3b, the bandgap energies of BiOCl and Bi₃O₄Cl were, respectively, calculated to be 3.31 and 2.62 eV. The valence band (VB) position of Bi₃O₄Cl is determined to be 1.88 eV by VB-XPS (Fig. 3c), the conduction band (CB) position is calculated to be –0.74 eV. The result indicates that the as-obtained Bi₃O₄Cl plates had a narrower bandgap for effective absorption of the vis light.

TC-HCl, a famous broad-spectrum antibiotic, has been widely used to evaluate the semiconductor material's photoactivity. Meanwhile, the colourless TC-HCl molecules also can avoid the photosensitisation effect in comparison with the traditional dyes [16]. Fig. 4a showed the photocatalytic activity of as-prepared samples for degradation of TC-HCl in aqueous solution. The photolysis test for TC-HCl degradation can be negligible, suggesting that the TC-HCl molecules cannot be degraded under light irradiation. In addition, both of the BiOCl and solid-state reaction obtained Bi₃O₄Cl exhibited low photocatalytic activity, which only 22.3 and 40.6% TC-HCl degradation ratios were achieved. Interestingly, the as-synthesised Bi₃O₄Cl plates displayed much high photocatalytic activity for TC-HCl degradation (73.4%), which is about 1.8 and 3.3 times higher than the BiOCl and solid-state reaction synthesised Bi₃O₄Cl, respectively. The higher photocatalytic activity of the Bi₃O₄Cl plates can be explained by their unique 2D plate-like architecture in comparison with the several micrometres bulky structure of solid-state reaction obtained Bi₃O₄Cl. Moreover, it can be found that the calcination temperature of the prepared Bi₃O₄Cl at 500°C showed much higher-performance than that of 400 and 600°C, revealing that the

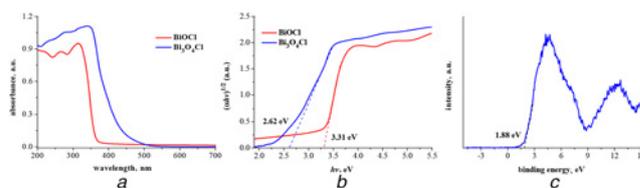


Fig. 3 UV–vis diffuse reflection spectra
a UV–vis diffuse reflection spectra
b Tauc plots of as-prepared samples
c VB-XPS spectra of the as-prepared Bi₃O₄Cl

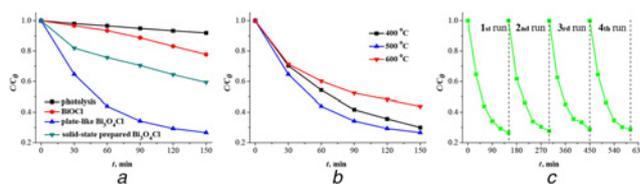


Fig. 4 Photocatalytic activity
a Photocatalytic degradation of TC-HCl over the as-prepared samples as a function of light irradiation time
b Photocatalytic degradation of TC-HCl over the as-prepared Bi₃O₄Cl with different calcination temperature
c Recycling tests of the as-prepared Bi₃O₄Cl plates

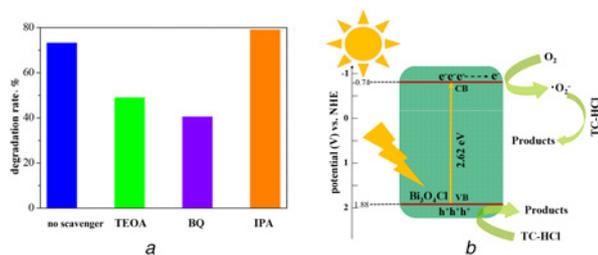


Fig. 5 Degradation rates
 a Addition of different radical scavengers over the $\text{Bi}_3\text{O}_4\text{Cl}$ for degradation of TC-HCl
 b Schematic illustrations of the possible charge transfer in the $\text{Bi}_3\text{O}_4\text{Cl}$ photocatalyst for TC-HCl photodegradation

calcination temperature can affect the photocatalytic activity (Fig. 4b). Additionally, the plate-like $\text{Bi}_3\text{O}_4\text{Cl}$ also displayed excellent stability even after tests run four times (Fig. 4c). The results demonstrate that the as-prepared $\text{Bi}_3\text{O}_4\text{Cl}$ plates exhibited better vis-light-driven photoactivity for efficient removal of TC-HCl antibiotic pollutant.

Fig. 5a exhibited the degradation rates (DRs) of the $\text{Bi}_3\text{O}_4\text{Cl}$ over different radical scavengers for degradation of TC-HCl. It can be found that the DRs were significantly inhibited by the addition of TEOA and BQ, whereas the DR increased slightly when IPA was added. The results imply that the main active species for TC-HCl degradation were h^+ and $\bullet\text{O}_2^-$ radicals. Thus, a possible photocatalytic mechanism of the plate-like $\text{Bi}_3\text{O}_4\text{Cl}$ for TC-HCl degradation was proposed. As illustrated in Fig. 5b, the $\text{Bi}_3\text{O}_4\text{Cl}$ plates can be excited to create the photoinduced e^- - h^+ pairs under vis-light irradiation ($\lambda > 420$ nm). Then, the e^- on the CB can react with oxygen (O_2) to produce the $\bullet\text{O}_2^-$ because the position of CB of $\text{Bi}_3\text{O}_4\text{Cl}$ is negative than the potential of $\text{O}_2/\bullet\text{O}_2^-$ (-0.33 V versus Normal Hydrogen Electrode (NHE)) [17]. However, the VB potential of $\text{Bi}_3\text{O}_4\text{Cl}$ is lower than the redox potentials of $\text{H}_2\text{O}/\bullet\text{OH}$, (2.72 V versus NHE) [18], suggesting h^+ cannot oxidize the H_2O to generate $\bullet\text{OH}$ radicals. Therefore, both of the $\bullet\text{O}_2^-$ and h^+ can break down the pollutant into small molecules, which are the powerfully oxidative species for the photo-oxidation reaction.

4. Conclusion: In summary, narrow bandgap $\text{Bi}_3\text{O}_4\text{Cl}$ plates were first synthesised by a facile solvothermal methodology following a calcination approach. Compared to the traditional BiOCl and solid-state reaction prepared $\text{Bi}_3\text{O}_4\text{Cl}$, the obtained plate-like $\text{Bi}_3\text{O}_4\text{Cl}$ exhibited excellent vis-light-driven photocatalytic activity for degradation of TC-HCl. Furthermore, the $\text{Bi}_3\text{O}_4\text{Cl}$ photocatalyst also displayed good stability and the photocatalytic mechanism was proposed.

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