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Intimate contacted two-dimensional/zero-dimensional composite of bismuth titanate nanosheets supported ultrafine bismuth oxychloride nanoparticles for enhanced antibiotic residue degradation

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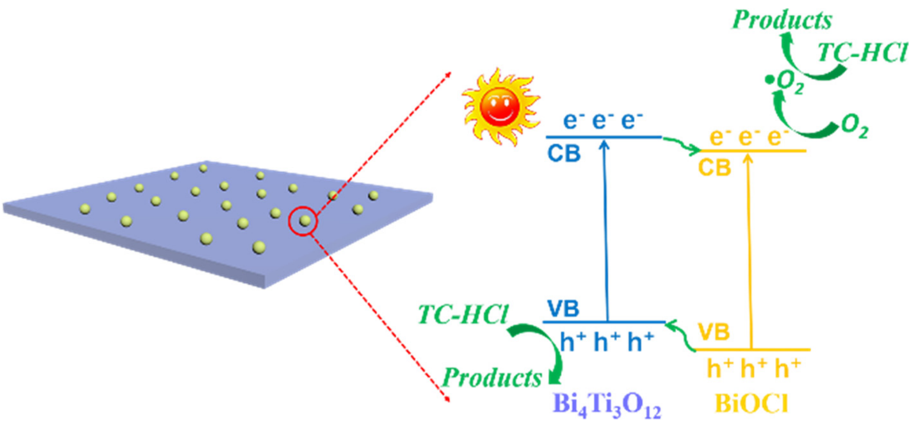
GRAPHICAL ABSTRACT



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ABSTRACT

Constructing a two-dimensional/zero-dimensional (2D/0D) composite with matched crystal structure, suitable energy band structure as well as intimate contact interface is an effective way to improve carriers separation for achieving highly photocatalytic performance. In this work, a novel bismuth titanate/bismuth oxychloride ($Bi_4Ti_3O_{12}$/BiOCl) composite consisting of 2D $Bi_4Ti_3O_{12}$ nanosheets and 0D BiOCl nanoparticles was constructed for the first time. Germinating ultrafine BiOCl nanoparticles on $Bi_4Ti_3O_{12}$ nanosheets can provide abundant contact interface and shorten migration distance of photoinduced carriers via two-step synthesis contained molten salt process and facile chemical transformation process. The obtained $Bi_4Ti_3O_{12}$/BiOCl 2D/0D composites exhibited enhanced photocatalytic performance for antibiotic tetracycline hydrochloride degradation. The rate constant of optimal $Bi_4Ti_3O_{12}$/BiOCl composite was about 4.4 times higher than that of bare $Bi_4Ti_3O_{12}$ although $Bi_4Ti_3O_{12}$/BiOCl composite appeared lesser photoabsorption. The enhanced photocatalytic performance can be mainly ascribed to matched crystal structure, suitable energy band structure and intimate contact interface between $Bi_4Ti_3O_{12}$ nanosheets and ultrafine BiOCl nanoparticles as well as unique 2D/0D composite structure. Besides, a probable degradation mechanism on the basis of active species trapping experiments, electrochemical impedance spectroscopy, photocurrent responses and energy band structures was proposed. This work may be stretched to other 2D/0D composite photocatalysts construction, which is inspiring for antibiotic residue treatment.

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1. Introduction

Over the past years, dozens of antibiotics have been discharged into the aquatic environment and recognized as a new kind of pollutants because of their continuous input and detrimental effects on living ecosystems even at low concentrations [1,2]. As a representative antibiotic, tetracyclines (TCs) have been extensively used in aquaculture, human and livestock medicine. However, TCs residues can induce severe problems, for instance, antibiotic resistance to bacteria and potential threats to human health through convoluted food chain [3–5]. Therefore, there is an urgent need to establish efficient and green treatment technologies to remedy these residual pollutants. Several remediation techniques have been adopted to handle these residues, such as biological degradation, physical adsorption, ozonation, Fenton reagent oxidation and semiconductor photocatalysis [1,6–8]. Among these techniques, semiconductor based photocatalytic oxidation technique may be a promising and efficient strategy for treating antibiotic residues by the highly oxidizing radicals generated after the photoexcitation of semiconductor.

As a member of Aurivillius family compounds, $Bi_4Ti_3O_{12}$ (BTO) composed of pseudoperovskite $(Bi_2Ti_3O_{10})^{2-}$ layer sandwiched by double bismuth oxygen $(Bi_2O_2)^{2+}$ layers, is a very attractive photocatalyst thanks to its unique crystal and electron structures and has been widely explored in the field of organic pollutants degradation [9,10]. As expected, the photocatalytic efficiency of bare BTO is inferior due to the ubiquitous recombination of electron-hole pairs. It has been reported that constructing composite may promote separation and transfer of photoinduced electron-hole pairs and suppress their recombination [11–14]. To date, lots of composites via the combination of BTO with other materials have been developed, such as BTO/TiO_2, BTO/g-C_3N_4, BTO/Bi_2S_3, BTO/CeO_2, and so forth [15–18]. However, it is worth noting that only the composite with matched crystal structure, suitable energy band structure and intimate contact interface can improve the separation efficiency of photoinduced carriers, thus enhancing the photocatalytic performance of BTO. Bismuth oxychloride (BOC), another member of Aurivillius family compounds, possesses the same layered crystal structure consisting of $[Bi_2O_2]^{2+}$ layers interleaved with two slabs of Cl^- with BTO [19,20]. They may facilely grow together to create a composite satisfied with the above mentioned characteristics through a convenient chemical transformation process. As a result, the combination of BTO and BOC may be an ideal candidate to construct BTO/BOC composite.

In general, the morphology of composite also has significant effect on separation efficiency of photoinduced carriers. However, constructing a BTO based composite simultaneous consideration of morphology, crystal structure and energy band structure was seldom reported in previous studies. Recently, two-dimensional/zero-dimensional (2D/0D) composite has attracted attention owing to its distinctive characters [21–23]. 2D nanosheets can be applied as substrate to offer large contact areas while 0D nanoparticles have the merit of short migration distance of photoinduced carriers [24,25]. Therefore, it is highly wistful that constructing BTO nanosheets/BOC nanoparticles 2D/0D composite to achieve matched crystal structure, suitable energy band structure, intimate contact interface and more efficient separation of photoinduced carriers simultaneously.

In this study, BTO nanosheets/BOC nanoparticles 2D/0D composites were prepared by two-step approach containing molten salt process and facile chemical transformation process. Compared to the previous reports [16,26–28], more factors including crystal structure and energy band structure as well as morphology affected separation and transfer of photoinduced carriers were considered simultaneously. Moreover, the photocatalytic performance of prepared BTO/BOC photocatalysts was evaluated by photodegradation of antibiotic residue tetracycline hydrochloride (TC-HCl). To the best of our knowledge, this is the first report about BTO/BOC 2D/0D composites structure for antibiotic photodegradation. The BTO/BOC 2D/0D composites exhibit much higher photocatalytic efficiency than the bare BTO nanosheets although the light absorption is slightly weak. In addition, the detail photodegradation mechanism of TC-HCl over the BTO/BOC 2D/0D composites was also investigated.

2. Experimental section

2.1. Materials

Bismuth oxide (Bi_2O_3), sodium chloride (NaCl), potassium chloride (KCl), ethylene glycol as well as hydrochloric acid (HCl) were purchased from Sinopharm Chemical Reagent Co., Ltd. All these materials were of analytical reagent and used directly without further purification. Titanium dioxide (TiO_2, 99.8%) and TC-HCl (USP grade) were purchased from Aladdin Chemistry Co., Ltd. Ultrapure water was used to prepare all solutions.

2.2. Synthesis of BTO nanosheets and BTO/BOC composites

BTO nanosheets were obtained via a molten salt synthesis strategy [29]. Bi_2O_3 and TiO_2 were used as bismuth source and titanium source, respectively. NaCl and KCl were used to provide a highly reactive medium. Typically, the same mole ratio (2 mmol) of Bi_2O_3 and TiO_2 were evenly mixed with the same mole ratio (0.1 mol) of NaCl and KCl. After sustainably grinding for an hour in a mortar, the remnant mixture was put into a corundum crucible with a lid, which was heated at 800 °C for 2 h in a muffle furnace with a ramp rate of 5 °C min^{-1}. Afterwards, the final product was centrifuged and washed using water and ethyl alcohol to remove the residual inorganic salt, and dried at 60 °C to obtain the BTO nanosheets.

A facile in-situ chemical transformation strategy was adopted here to synthesize BTO/BOC composites using BTO nanosheets as substrate and HCl as chlorine source [27]. First, 0.2 g of as-synthesized BTO nanosheets were dissolved in 100 mL of HCl aqueous solution with vigorous stirring to form a homogeneous suspension. After that, the suspension was stirred drastically for 12 h at room temperature. Last, the product was collected by centrifugation and washed, drying at 60 °C in an oven. The different concentrations of HCl (0.025, 0.05, 0.1 and 0.2 mol L^{-1}) were prepared to control the different weight ratios of BTO/BOC composites and the obtained samples were termed as BTO/BOC-1, BTO/BOC-2, BTO/BOC-3 and BTO/BOC-4, respectively.

2.3. Characterization of catalyst

X-ray diffraction (XRD) patterns were recorded by D/max 2550 X-ray diffractometer (Rigaku Corporation). Fourier transform infrared spectra (FT-IR) were collected on Nicolet 6700 spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on Thermo Escalab 250 X-ray photoelectron spectrometer. Scanning electron microscopy (SEM) was obtained on Nova Nano 230 (FEI Co., Ltd). Transmission electron microscopy (TEM) was observed on JEM-2100F (Japanese electronics Co., Ltd). Surface areas were measured by QuadrasorbSI-3MP surface area analyzer. The actual amount of Bi in samples was measured by Spectro Blue Sop inductively coupled plasma optical emission spectrometry (ICP-OES). The UV–Vis diffuse reflectance spectra (DRS) were operated on Evolution 220 UV–Vis spectrometer.