



Research Paper

Oxygen vacancy-rich 2D/2D BiOCl-g-C₃N₄ ultrathin heterostructure nanosheets for enhanced visible-light-driven photocatalytic activity in environmental remediation



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ABSTRACT

Photocatalytic degradation has been unearthed as a promising strategy for environmental remediation, and the calling is endless for more efficient photocatalytic system. In this study, a novel oxygen vacancy-rich two-dimensional/two-dimensional (2D/2D) BiOCl-g-C₃N₄ ultrathin heterostructure nanosheet (CN-BC) is successfully prepared by a facile solvothermal method for degradation of non-dye organic contaminants. HRTEM observes the formation of heterojunction, while ESR and XPS unveil the distinct oxygen vacancy concentrations. Density functional calculations reveal that the introduction of oxygen vacancies (OVs) brings a new defect level, resulting in the increased photoabsorption. Under visible light irradiation, the OVs-rich optimum ratio of CN-BC (50CN-50BC) exhibits 95% removal efficiency of 4-chlorophenol within 2 h, which is about 12.5, 5.3 and 3.4 times as that of pure BiOCl, g-C₃N₄ and OVs-poor heterostructure, respectively. The photocatalytic mechanism of OVs-rich 50CN-50BC is also revealed, suggesting that the synergistic effect between 2D/2D heterojunction and oxygen vacancies greatly promotes visible-light photoabsorption and photoinduced carrier separation efficiency with a prolonged lifetime, which is confirmed by multiple optical and electrochemical analyses, including DRS, steady-state photoluminescence spectra, electrochemical impedance spectroscopy, photocurrent response and time-resolved fluorescence spectra. This study could bring new opportunities for the rational design of highly efficient photocatalysts by combining 2D/2D heterojunctions with oxygen vacancies in environmental remediation.

1. Introduction

Semiconductor photocatalysis technology has been considered to be a green and benign method to eliminate most environmental contaminations [1]. Thus, exploiting high-efficient and environment-friendly visible-light-driven photocatalysts has attracted explosive attention due to their potential application in solar energy conversion [2–4]. Among various photocatalysts investigated, triggered by the great success of graphene, two-dimensional (2D) nanosheets have emerged as a new class of photocatalysts, which benefit from their large specific surface areas and unique structural feature of ultimate two-dimensional anisotropy with small thickness. These characters can increase intimate surface to contact with reactants, shorten the transmission path of the photoinduced charges and realize the effective separation of electron-hole pairs [5,6]. When the thickness of the bulk materials is reduced to nanometer and even subnanometer scale, the

surface atomic structures such as coordination number, bond length, and degree of atom disorder will vary [7]. The ultrathin nanosheets will lead to a large fraction of exposed interior atoms and inevitably induce the formation of various defects with structure disorder on the surface, which can enhance the optical absorption and serve as highly active sites for photocatalytic reactions, inducing a nonnegligible enhancement on the photocatalytic activity [7–9]. Thus, ultrathin 2D nanosheets have been regarded as a new opportunity to synthesize highly efficient photocatalysts.

Bismuth oxychloride (BiOCl), a new type of promising layered materials for photocatalytic environmental remediation, has been intensively investigated due to its stabilized chemical property, non-toxicity, corrosion resistance, indirect-transition band gap and open crystalline structure [10–12]. The indirect-transition band gap of BiOCl forces the excited electron to travel a certain k-space distance to the valence band (VB), which reduces the recombination probability of the

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excited electron and the hole [13]. On the other hand, BiOCl has an open layered structure consisting of $[\text{Bi}_2\text{O}_2]^{2+}$ layers sandwiched between two slabs of halogen ions, which provides a large space to polarize the related atoms and orbitals, and then enhances the separation of the photoinduced electron-hole pairs [14]. However, despite these excellent advantages, BiOCl is limited by its wide band gap, making it useful only under UV irradiation, which results in its poor visible-light photocatalytic performance. Up to now, many strategies have been employed to regulate and modify BiOCl, such as morphological control [15,16], exposure of specific crystal faces [11,17], and heterologous hybridization [18], however, the acquired visible-light photoactivity is generally active in dye photosensitization degradation, and the photocatalytic performance is unsatisfactory [17,19]. Recently, Xie et al. [20] has synthesized triple-vacancy BiOCl ultrathin nanosheets, which had highly photocatalytic efficiency for Rhodamine B photosensitization degradation under visible light irradiation, while its visible-light photoactivity for colorless non-dye organic contaminant was still moderate. Therefore, it is urgently desirable to design an ideal architecture of 2D ultrathin hybrid nanosheets between BiOCl and other narrow band gap semiconductors, aiming to further imbue BiOCl with higher visible-light photocatalytic activity to non-dye organic contaminants.

Graphitic carbon nitrides ($g\text{-C}_3\text{N}_4$) has attracted extensive attention as a potential layered-structure photocatalyst with excellent visible-light response due to its narrow band gap of 2.7 eV [21,22]. Since Wang et al. [23] firstly reported that $g\text{-C}_3\text{N}_4$ could be used for hydrogen production from water under visible light irradiation, many followed reports have been booming. However, the photocatalytic performance of bulk $g\text{-C}_3\text{N}_4$ is far from optimum because of its poor mass diffusion and fast charge recombination [24]. Fortunately, these short-comings have been overcome through exfoliating bulk $g\text{-C}_3\text{N}_4$ into $g\text{-C}_3\text{N}_4$ ultrathin nanosheet, which can increase specific surface area, improved electron transport ability along the in-plane direction, and prolong lifetime of photoexcited charge carriers [6,25]. More importantly, it has been reported that when $g\text{-C}_3\text{N}_4$ ultrathin nanosheets were fabricated into 2D/2D heterostructures with other layered semiconductors, its face-to-face contact would form a large interface region, and consequently an enhanced photocatalytic performance would be achieved [26–28]. Nonetheless, to the best of our knowledge, in 2D/2D heterostructures, the insightful understanding of the impact of vacancies on photocatalytic activity is still missing.

Herein, inspired by the above considerations, in this work we have rational designed an oxygen vacancy (OV)-rich ultrathin $g\text{-C}_3\text{N}_4\text{-BiOCl}$ heterostructure nanosheet with a high visible-light-driven photocatalytic activity via a facile solvothermal method. The visible photocatalytic activity of as-prepared ultrathin $g\text{-C}_3\text{N}_4\text{-BiOCl}$ nanosheets was evaluated by the degradation of 4-chlorophenol (4-CP), and several endocrine disruptors (bisphenol A (BPA), bisphenol S (BPS) and bisphenol F (BPF)). Multiple optical and photoelectrochemical experiments were employed to study the degradation mechanism in this system. The enhanced optical absorption and separation efficiency led to the superior visible-light photocatalytic activity, which were originated from the synergistic effect between oxygen vacancies (OVs) and heterojunction in ultrathin hybrid $g\text{-C}_3\text{N}_4\text{-BiOCl}$ nanosheets. The construction of oxygen vacancy-rich ultrathin 2D/2D heterostructures could bring new opportunities for rational design highly active visible light photocatalysts for environmental remediation and other applications.

2. Experimental section

2.1. Materials

All chemical reagents used in this work were analytical reagent grade and without further purification. Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), sodium chloride (NaCl), urea, polyvinylpyrrolidone (PVP, K-30), glycerol, 4-chlorophenol (4-CP), bisphenol A (BPA),

bisphenol S (BPS), bisphenol F (BPF) and ethanol were all obtained from Sinopharm Chemical Reagent Co. Ltd. Deionized water was used throughout the experiments.

2.2. Catalysts preparation

2.2.1. Synthesis of graphite carbon nitrogen ($g\text{-C}_3\text{N}_4$) nanosheets

Bulk $g\text{-C}_3\text{N}_4$ was synthesized by annealing urea at 550 °C for 3 h with the heating rate of 5 °C min^{-1} [29]. The $g\text{-C}_3\text{N}_4$ nanosheets were obtained by liquid exfoliating of as-prepared bulk $g\text{-C}_3\text{N}_4$ in water according to the previous reports with a small modification [30]. In detail, 200 mg bulk $g\text{-C}_3\text{N}_4$ powder dispersed in 100 mL water, and then ultrasound for about 4 h. The initial formed suspension was centrifuged at 5000 rpm to remove the residual unexfoliated $g\text{-C}_3\text{N}_4$ nanoparticles and the supernatant was dried at 60 °C for further study. The prepared $g\text{-C}_3\text{N}_4$ nanosheets were denoted as CN.

2.2.2. Synthesis of oxygen vacancy-rich ultrathin $g\text{-C}_3\text{N}_4\text{-BiOCl}$ (CN-BC) nanosheets

In a typical procedure, 0.260 $g\text{-C}_3\text{N}_4$ nanosheets were added in 25 mL water, and then ultrasound for 30 min, yielding a uniform yellow suspension. 0.486 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 0.400 g PVP and 25 mL glycerol were dissolved into this suspension at room temperature with vigorous stirring for 1 h. Then, 5 mL saturated NaCl solution was dropwise added into the above mixture. After another 1 h of agitation, the mixture solution was transferred into a 100 mL Teflon-lined stainless steel autoclave. The autoclave was heated at 160 °C for 6 h under autogenous pressure, and then cooled to room temperature naturally. Finally, the resulting product was gathered by centrifugation, washed with water thoroughly and dried at 60 °C, and the obtained powder was ultrathin $g\text{-C}_3\text{N}_4\text{-BiOCl}$ nanosheets with a $g\text{-C}_3\text{N}_4$ loading of 50 wt%. Thereby, a series of $g\text{-C}_3\text{N}_4\text{-BiOCl}$ heterojunction nanosheets with different mass ratios were prepared by adjusting the addition of $g\text{-C}_3\text{N}_4$. The prepared samples were denoted as xCN-(100-x)BC, where x refers to the percentage of $g\text{-C}_3\text{N}_4$ ($x = 0, 10, 30, 50, 70, 90$), which could be abbreviated as BC, 10CN-90BC, 30CN-70BC, 50CN-50BC, 70CN-30BC, and 90CN-10BC.

2.2.3. Synthesis of oxygen vacancy-poor $g\text{-C}_3\text{N}_4\text{-BiOCl}$ nanoplates

As a control sample with poor oxygen vacancies, the $g\text{-C}_3\text{N}_4\text{-BiOCl}$ nanoplates with a $g\text{-C}_3\text{N}_4$ loading of 50 wt% were prepared in a similar way without adding PVP, and denoted as 50CN-50BC-P.

2.3. Characterization

The micro-morphologies of the samples were observed by using the Quanta 200FEG SEM, FEI Tecnai G2 F30 TEM and JEOL JEM-1400 TEM. XRD patterns were collected by using a Bruker D8 X-ray diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm). The thickness of the samples was determined by atomic force microscopy (AFM, Bioscope system, USA). The BET surface area measurements were performed by using an ASAP2020 instrument. The FTIR spectra were recorded on a Perkin-Elmer Spectrum One B spectrometer. X-ray photoelectron spectroscopy measurements were taken on a Thermo ESCALAB 250 with Al K α X-ray ($h\nu = 1486.6$ eV) radiation. Electron spin resonance (ESR) spectroscopy (Bruker A200 spectrometer, Germany) was applied for investigation of the existence of oxygen vacancies and the generation of reactive radicals. The UV-vis diffuse reflectance spectra (DRS) of samples were achieved by a spectrophotometer (Shimadzu, UV2550), using the BaSO_4 as the reflectance sample. The steady-state photoluminescence (PL) spectra were obtained using a Hitachi F-4600 fluorescence spectrophotometer with excitation at 315 nm. Total organic carbon (TOC) was analyzed by TOC measuring instrument (Shimadzu TOC-5000). The time-resolved fluorescence emission decay spectra were recorded on an ISS ChronosBH time-domain fluorescence spectrophotometer, and the decay curves were recorded with excitation at 460 nm.

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