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Atomic scale g-C_3N_4/Bi_2WO_6 2D/2D heterojunction with enhanced photocatalytic degradation of ibuprofen under visible light irradiation

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ABSTRACT

Although photocatalytic degradation is an ideal strategy for cleaning environmental pollution, it remains challenging to construct a highly efficient photocatalytic system by steering the charge flow in a precise manner. In this study, a novel atomic scale g-C_3N_4/Bi_2WO_6 heterojunction (UTCB) constructed by ultrathin g-C_3N_4 nanosheets (ug-CN) and monolayer Bi_2WO_6 nanosheets (m-BWO) was successfully prepared by hydrothermal reaction. The UTCB heterojunctions were characterized by various techniques including XRD, TEM, AFM, BET measurements, UV–vis spectrometry, and XPS. The results indicated that UTCB heterojunctions were assembly of m-BWO on ug-CN and presented high separation efficiency of photogenerated carriers. Under visible light irradiation, the optimum molar ratio of ug-CN/m-BWO (1:4, UTCB-25) reached almost 96.1% removal efficiency of IBF within 1 h, which was about 2.7 times as that of pure m-BWO. The photocatalytic mechanisms of UTCB-25 were revealed, suggesting that the synergistic effect of UTCB-25 heterojunction with strong interfacial interaction promoted the photoinduced charge separation. According to the LC–MS/MS, five photodegradation pathways of IBF under visible light irradiation were proposed. This study could open new opportunities for the rational design and a better understanding of atomic scale two dimensions/two dimensions (2D/2D) heterojunctions in environmental or other applications.

1. Introduction

With the development of industry and population, energy crisis and environmental pollution have aroused people's concern [1–3]. It is widely accepted that photocatalysts are significant materials for achieving a future sustainable society with graceful environment [4–6]. However, developing photocatalyst materials that can efficiently utilize solar energy for practical application is of great technical challenge due to the limitation of photon absorption, charge separation, and charge utilization [7,8].

Recent progress in graphene studies are provoking tremendous interest in exfoliation-based fabrication of 2D single-layered nanosheets [9]. The as-exfoliated 2D monolayers with atomic thicknesses offer opportunities to the atomic-level understanding of charge separation [10–12]. Such monolayers enable atomic level control over architectures and electronic structures, thus manipulating the charge flow from the electron–hole separation sites to their surface in a desired route [13]. However, individual semiconductor monolayers still encounter substantial charge recombination for photocatalytic degradation, because they lack sufficient active sites to manipulate the fates of these surface reaching electrons [14,15]. To address this issue and also to realize the charge flow at the atomic level, it is highly desirable constructing atomic scale 2D/2D heterostructures, because its face-to-face contact might form the larger interface region as compared to the point-to-face contact in the 0D/2D heterojunction and the line-to-face contact in the 1D/2D heterojunction [16,17]. 2D/2D heterostructures have been proven to be an effective way for photodegradation of contaminants with successful cases such as SnS_2/g-C_3N_4, g-C_3N_4/$K^+Ca_2Nb_3O_{10}^-$, rGO/Bi_2WO_6, CdS/MoS_2, and $BiOIO_3$/BiOI [16,18–22]. Bi_2WO_6, with a narrow band gap about 2.7 eV, is a more promising photocatalyst, due to its stable physical and chemical properties, low cost, and non-toxicity. Bi_2WO_6 also

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consists of alternate stacking of $[Bi_2O_2]$ layers and perovskite-type layers with oxygen atoms shared between layers. It has been widely used in environmental remediation such as PPCPs removal [23,24], treatment of VOCs indoor [25], and reduction of carbon dioxide to the fuels [26]. Recently, Zhou et al. fabricated monolayer Bi_2WO_6 nanosheets (m-BWO) [27], in which holes are directly generated on the active surfaces and electrons in the middle layer on irradiation, leading to ultrafast charge separation. Notably, graphite-like carbon nitride (g-C_3N_4), a rising star of metal-free photocatalyst, has attracted worldwide attention due to its low cost, polymeric p-conjugated structure, and remarkable physical and chemical properties [28,29]. A large amount of ultrathin g-C_3N_4 nanosheets (ug-CN) based heterostructured photocatalysts such as $NaNbO_3$/g-C_3N_4, graphene/g-C_3N_4, Bi/g-C_3N_4 [6,30,31] has been constructed, and they exhibited a remarkably high photoactivity towards water splitting, disinfection, and NO reduction.

Motivated by the above studies, this work is to initially integrate ug-CN and m-BWO into an atomic scale 2D/2D heterostructure as an efficient visible light driven photocatalyst. We can successfully steer the charge separation, transportation and consumption all at the atomic level to construct a highly active photodegradation system. In such a system, electrons originating from visible light-irradiated ug-CN transfer to the middle $[WO_4]^{2-}$ layers, and holes photogenerated from $[BiO]^+$ layers directly transfer to intimate ug-CN nanosheets. What's more, the large specific surface area of ug-CN can increase the specific surface area of the photocatalysts, thus providing more active sites. Ibuprofen (IBF) is selected as the target PPCPs for photocatalytic removal with the as-prepared UTCB heterojunctions. As a widely used anti-inflammatory drug, IBF has been detected in surface water and wastewater in a range from ng/L^{-1} to mg/L^{-1} levels, and its stability of non-photolysis and non-biodegradation makes it accumulate in aquatic environment and sediments [32–36]. What arouses public concern is that IBF was reported to inhibit the postembryonic development of anuran species in freshwater [37].

In the present study, an atomic scale g-C_3N_4/Bi_2WO_6 2D-2D heterostructure was successfully constructed by ultrathin g-C_3N_4 nanosheets and monolayer Bi_2WO_6 nanosheets (donated as UTCB). Such atomic scale 2D-2D heterostructure provided a large contact area for fast interfacial charge separation as well as a large specific surface area. The photocatalytic performance of UTCB heterostructures was investigated by degradation of IBF under visible light irradiation. The results suggested that UTCB heterojunctions displayed much higher photocatalytic activity under visible light irradiation than bare ug-CN and m-BWO nanosheets. The possible visible light driven degradation pathway of IBF removal was investigated. The construction of atomic scale 2D-2D heterostructures with intimate contact opens new opportunities for rational design highly active visible light photocatalysts for environmental applications and other applications.

2. Materials and methods

2.1. Materials

Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$, Aladdin, Shanghai, 99.5%), sodium tungstate dihydrate ($Na_2WO_4{\cdot}2H_2O$, Aladdin, Shanghai, 99.5%), melamine ($C_3H_6N_6$, Damao chemical reagent factory, Tianjin, 99.0%), cetyltrimethyl ammonium bromide (CTAB, $C_{19}H_{42}BrN$, Damao chemical reagent factory, Tianjin, 90.0%) were used. Scavenger stock solution used to quench reactive species were 10 mM ethylenediamine tetra acetic acid disodium salt (EDTA-Na_2) (Aladdin, Shanghai) for photogenerated-holes (h^+), 10 mM isopropanol (Aladdin, Shanghai) for hydroxyl radicals ($^{\bullet}OH$), 2 mM benzoquinone (BQ, Sigma, USA) for superoxide radical ($^{\bullet}O_2^-$). Tap water samples were collected from the Changsha water group (Changsha, China) and stored at 4 °C. River wastewater samples were collected from Xiangjiang River and stored at 4 °C. All other reagents were of analytical grade and used without further purification.

2.2. Synthesis of UTCB heterojunctions

The detailed synthesis procedure of UTCB heterojunctions was prepared by hydrothermal reaction. Firstly, the ultrathin g-C_3N_4 nanosheets were prepared according to the previously reported method [15]. Melamine was calcined at 520 °C for 4 h with the heating rate of 2.3 °C min^{-1}. After calcination, the bulk g-C_3N_4 was milled into powder and heated at 500 °C for 2 h with the heating rate of 5 °C min^{-1}. A light yellow powder of g-C_3N_4 nanosheets was finally obtained. Secondly, the ultrathin g-C_3N_4/Bi_2WO_6 heterojunction was prepared by a bottom-up approach [27]. A certain amount of as-prepared ultrathin g-C_3N_4 nanosheets, 50 mg CTAB, 1 mmol $Na_2WO_4{\cdot}2H_2O$, and 2 mmol $Bi(NO_3)_3{\cdot}5H_2O$ were added in 80 mL deionized water. After 30 min stirring, the mixed solution was transferred to a 100 mL Teflon-lined autoclave. Then the autoclave was treated at 120 °C for 24 h. Finally, the product was collected and washed several times with deionized water and dried at 60 °C in air for 10 h. The different mass ratio of ug-CN/m-BWO at 0.05:1, 0.1:1, 0.25:1, and 0.5:1 were prepared and signed as UTCB-5, UTCB-10, UTCB-25, and UTCB-50, respectively. In contrast, pure m-BWO was prepared in the same procedure without adding ug-CN.

2.3. Characterization

The phase and composition of the as prepared samples were identified by powder X-ray diffraction (XRD, Rigaku, Japan). The morphologies and microstructures of the as-prepared samples were investigated by Transmission Electron Microscopy (TEM, JEOLJEM-2100F, accelerating voltage 200 kV). UV−vis diffuse reflectance spectra of the samples were recorded on a UV–vis diffuse reflection spectrophotometer (DRS, Cary 300, USA) with $BaSO_4$ used as a reference. The surface elemental composition of the samples was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, UK). The thickness of the samples was determined by atomic force microscopic (AFM, Bioscope system, USA).

2.4. Photocatalytic degradation procedure

The as-prepared UTCB heterojunctions were utilized for photodegradation of IBF under visible light irradiation of a 300 W xenon lamp (CEL-HXF300, Beijing AuLight) with the 420 nm cutoff filter. The light spectrum and light intensity of the compacted fluorescent lamps were determined by a light monitor (International light, RPS900-R, USA), which consisted of visible light with average intensity of 326 mW cm^{-2}, and no UVA determined. Generally, 10 mg of UTCB heterojunctions and 2.5 mL of IBF solution (500 μM), were added to 50 mL of deionized water in a beaker under stirring at 400 rpm throughout the test. Before photocatalytic reaction, the suspension was stirred in the dark for 30 min to reach the adsorption/desorption equilibrium. At given time intervals, 1 mL of the suspension was collected and then filtered through 0.45 μm membrane filters for analysis. The experiments were conducted in triplicate. The concentration of IBF was analyzed by high performance liquid chromatography (HPLC, Angilent) equipped with a UV detector (SPD-10AV) and C18 column (250 mm × 4.6 mm). The mobile phase was a mixture of 80/20 (v/v) methyl alcohol-water