Applied Catalysis B: Environmental 222 (2018) 115–123

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Research Paper

0D/2D interface engineering of carbon quantum dots modified Bi_2WO_6 ultrathin nanosheets with enhanced photoactivity for full spectrum light utilization and mechanism insight

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ARTICLE INFO

Keywords:
Carbon quantum dots
Bi_2WO_6
0D/2D heterojunction
Full spectrum light
Interface engineering
Density functional theory

ABSTRACT

A novel full spectrum light driven carbon quantum dots (CQDs)/Bi_2WO_6 (CBW) hybrid materials were synthesized via a facile hydrothermal method. Multiple techniques including XRD, TEM, XPS, BET, UV–vis, XPS, PL and TRPL, were employed to investigate the structures, morphology, optical and electronic properties and photocatalytic performance of as-prepared samples. The results indicated that CBW heterojunctions were assembly of CQDs on m-BWO and presented high separation efficiency of photo-generated carriers and full light spectrum absorption. The photocatalytic mechanism of CBW hybrid materials was revealed, suggesting that the excellent photocatalytic activity towards organic pollutants was ascribed to the up converted photoluminescence (PL) and electron reservoir properties of CQDs. Density functional theory calculations indicated that complementary conduction and valence band-edge hybridization between CQDs and m-BWO could apparently increase separation efficiency of electron-hole pairs of CBW hybrid materials. According to ESR measurement and quenching experiments, the $O_2\cdot^-$, ·OH and h^+ were the main active species during the photocatalytic process. This study could shed light on 0D/2D interface engineering of carbon quantum dots based heterojunctions with enhanced photoactivity for full spectrum light utilization in pollutant degradation and energy conversion.

1. Introduction

Inspired by the discovery of graphene in 2004, two-dimensional (2D) nanosheets with atomic thickness have attracted increasing interest due to their unique electronic structures and broad applications, particularly in catalysis [1–3]. As is known, ultrathin 2D nanosheets are considered as superior junction that could combine the microscopic structural features with outstanding macroscopic properties, realizing the maximum functionality with a minimized size [4,5]. Particularly, ultrathin 2D nanosheets have ultra-large specific surface area and unique surface structures and can be applied in series of research fields, such as catalysis, sensing, energy conversion, etc. For photocatalytic application, ultrathin 2D nanosheet materials enable the photo-generated carrier transfer from their inside to the surface, which results in high photoactivity [6]. Meanwhile, the ultrathin 2D nanosheets with large fraction of uncoordinated surface atoms could harvest more ultraviolet-visible light [7]. Therefore, it is desirable to fabricate ultrathin 2D nanosheets with a suitable band gap and apply them in photocatalysis.

Bismuth tungstate (Bi_2WO_6), one of the most simple aurivillius oxides, has aroused much interest because of its low cost, high stability, nontoxicity and high photoactivity [8–10]. Bi_2WO_6 also consists of alternate stacking of $[Bi_2O_2]$ layers and perovskite-type layers with oxygen atoms shared between layers [11–13]. Up to now, many strategies have been employed in order to acquire Bi_2WO_6 materials with high photocatalytic activity, such as morphology control [14,15], surface modification [16–18], and coupling with other photocatalysts [19,20]. Among them, the controllable preparation of atomic scale nanosheets may be an effective strategy. Recently, Zhou et al. fabricated monolayer Bi_2WO_6 nanosheets (m-BWO) with outstanding performance in solar energy conversion [21]. The ultrathin Bi_2WO_6 nanosheets could display improved separation efficiency of electron–hole pairs. However, the photo-activity of the pure Bi_2WO_6 materials is still not satisfactory due to its narrow photo-absorption from UV light to visible light regions which is shorter than 450 nm and the fast photo-generated electron-carriers recombination of single photocatalyst

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http://dx.doi.org/10.1016/j.apcatb.2017.10.014
Received 31 May 2017; Received in revised form 27 August 2017; Accepted 6 October 2017
Available online 08 October 2017
0926-3373/

semiconductor.

Carbon quantum dots (CQDs), as new class of 0D dimension carbon nanomaterials with size below 10 nm, can be amorphous or nanocrystalline with sp^2 carbon clusters and may fused with some sp^3 carbons with diamond-like structure [22,23]. Due to its unique properties, CQDs have shown tremendous potential as versatile nanomaterials utilized in bio-sensing, bio-imaging, chemical-sensing, drug-delivery, photodynamic therapy and electro-catalysis [24–26]. Recently, CQDs have been also introduced to photocatalytic applications due to the superior electron transfer ability. Notably, they possess both up and down-converted photoluminescence (PL), and electron-accepting and transport properties, which makes CQDs-based NIR light sensitive hybrid photocatalysts become promising agents for harvesting NIR light [27,28]. Several photocatalytic systems based on the CQDs have also been studied, such as CQDs/$BiVO_4$ [29,30], CQDs/TiO_2 [31,32], CQDs/g-C_3N_4 [33,34], CQDs/Cu_2O [35]. However, the relationships between 0D/2D interface engineering and photoactivity have not been systematically studied, and the insightful mechanism of photocatalysis by ultra-small CQDs based hybrid materials still needs to be further investigated. Considering the advantages of m-BWO and CQDs, the interface mismatch between the CQDs and m-BWO ultrathin nanosheets can be reduced, and nanoscale composites with intimate contacts can be constructed. This unique nanostructure are expected to have some advantages: a) the accessible area between the CQDs and m-BWO planar interface and the channels of bulk-to-surface for the electrons can be well structured; b) the enhanced utilization of the full spectrum of solar energy can be obtained; c) the ultra-small nanostructure can efficiently contact with contaminants, thus accelerating the interfacial charge transfer process; d) sp^2 carbon clusters of carbon quantum dots facilitate the adsorption capacity of nanostructure for organic pollutants, especially the hydrophobic pollutants. Inspired from the mentioned concepts, it is favorable to construct the architecture of ultrathin 2D nanosheets modified by CQDs to achieve efficient photocatalytic application for pollutant degradation and energy conversion.

In this work, a novel CQDs modified monolayer Bi_2WO_6 nanosheets (CBW) hybrid material was prepared via a hydrothermal method. The structures, morphologies, optical properties and photocatalytic properties were investigated in detail. Density functional theory (DFT) calculations were employed to reveal a strong interface interaction between CQDs and m-BWO. The photocatalytic activities of the as-prepared heterostructures were evaluated by the degradation of methylene orange (MO) and bisphenol A (BPA) which are toxic to human health under visible and near-infrared (IR) light irradiation [36,37]. It was demonstrated that CQDs modification was an effective approach to improve the photocatalytic performance. The present work could provide further insights into the effects of CQDs modifying m-BWO as well as the design of CQDs based heterojunctions with highly efficient full spectrum light driven activity for environmental applications.

2. Experimental

2.1. Synthesis of the photocatalysts

All the reagents were of analytical grade and were used without any further purification. The CQDs solid was fabricated according to Yang et al.'s previous work followed by the freeze-drying [38]. In general, a 5 mmol portion of citric acid was dissolved in 10 mL of deionized water and the 335 μL ethylenediamine was added. The above solution was transferred into 25 mL Teflon-lined autoclave and heated at 200 °C for 5 h. After cooling to room temperature, the obtained product was subjected to dialysis for 12 h in order to get the purified CQDs solution. Then the CQDs solution was dealing with freeze-drying for 48 h to obtain the CQDs solid.

The CBW hybrid materials were synthesized via hydrothermal reaction. Typically, 1 mmol $Na_2WO_4 \cdot 2H_2O$, and 2 mmol $Bi(NO_3)_3 \cdot 5H_2O$ and 0.05 g cetyltrimethylammonium bromide (CTAB) were added in 80 mL deionized water. After the mixture became clear, a certain amount of CQDs solid was added, and a brown solution appeared immediately. After magnetically stirring for 1 h, the mixed solution was transferred to a 100 mL Teflon-lined autoclave, and then sealed into a steel tank and heated to 120 °C for 24 h. Finally, the product was centrifugalized and washed several times with deionized water and vacuum dried at 60 °C for 12 h. The different mass ratio of CQDs/m-BWO at 1 wt%, 3 wt%, 5 wt%, and 7 wt% were prepared and were signed as CBW-1, CBW-3, CBW-5, and CBW-7, respectively. In contrast, pure m-BWO was prepared by the same procedure without adding CQDs.

2.2. Characterization

A Bruker XRD-D500 X-ray diffractometer (Cu Kα source) was employed to record X-ray powder diffraction (XRD) patterns in the range from 5° to 80° at a scan rate of 8°/min. Transmission electron microscopy (TEM) images were obtained from a JEOL JEM-2100F transmission electron microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurement was performed on a VG Multi Lab 2000 system with a monochromatic Mg- Kα source operated at 20 kV. FT-IR spectrum was performed on a Shimadzu FTIR spectrophotometer (IRAffinity-1) using KBr disks at room temperature. UV–vis diffuse reflection spectroscopy (DRS) was performed on a Cary 300 spectrophotometer using $BaSO_4$ as the reference. The nitrogen adsorption–desorption isotherms at 77 K were investigated using a Nova 2200 e Surface Area and Porosity Analyzer (Quantum, USA). The Raman spectrum of as-obtained sample was recorded on a Labram-010 Laser confocal Raman spectrometer at ambient temperature (about 25 °C). The photoluminescence (PL) measurements were carried out on fluorescence spectrophotometer (FluroMax-4) at room temperature. Time-resolved photoluminescence (TRPL) decay spectra were measured on a FLS920 fluorescence spectrometer (Edinburgh Instrument). The electron spin resonance (ESR) signals of radicals spin-trapped by spin-trap reagent DMPO (Sigma Chemical Co.) in water were examined on a Bruker model ESR JES-FA200 spectrometer.

2.3. DFT calculations

All electronic structure calculations were performed within the framework of DFT by using the "Vienna ab initio simulation package" (VASP). The exchange-correlation interactions were treated within the spin-polarized generalized gradient approximation (GGA) by Predew-Burke-Ernzerhof (PBE). The interaction between the ions and electrons was described using the projected augmented wave (PAW) formalism. For the 2D heterostructure, a vacuum layer thicker than 18 Å along the direction perpendicular to the surface was added to avoid the interactions between adjacent images. To get accurate results, the energy cutoff was set to 500 eV until the force on each atom was less than 0.01 eV/Å. A Gaussian smearing was used with a smearing width of 0.2 eV. The electronic structures were calculated with a basis set, consisting of the atomic orbitals of C, Bi, W, and O atoms with a $3 \times 3 \times 1$ k-mesh.

2.4. Photo-electrochemical measurements

CHI 660C electrochemical analyzer (CHI-660C, China) was used to measure the photo-electrochemical responses of the samples in a three-electrode cell. FTO electrodes deposited with samples served as the working electrode. A platinum foil served as counter and Ag/AgCl (3 M KCl) served as the reference electrodes. 0.1 M Na_2SO_4 was used as electrolyte solution. All the samples were analyzed without bias potential. The photo-responses of the samples as visible light switched on and off were measured at 0.0 V. A 300 W Xe lamp was chosen as a visible light and IR light source. All of the electrochemical measurements were carried out at room temperature.