Applied Catalysis B: Environmental 209 (2017) 253–264

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Carbon nanodots/WO_3 nanorods Z-scheme composites: Remarkably enhanced photocatalytic performance under broad spectrum

Jun Zhang[a], Yue Ma[a], Yilin Du[a], Huizhong Jiang[a], Dandan Zhou[b], Shuangshi Dong[a,*]

[a] Key Laboratory of Groundwater Resources and Environment, Ministry of Education, Jilin University, Changchun, 130021, Jilin, China
[b] School of Environment, Northeast Normal University, Changchun 1l30117, Jilin, China

ARTICLE INFO

Article history:
Received 7 January 2017
Received in revised form 28 February 2017
Accepted 2 March 2017
Available online 6 March 2017

Keywords:
Carbon nanodots/WO_3 nanorods
Photocatalytic
UV–vis–NIR light
Interfacial charge transfer
Z-scheme

ABSTRACT

The search for low-cost, earth-abundant and environmentally friendly photocatalysts that can efficiently function over the entire UV–vis–NIR spectrum remains one of the most pressing challenges in the photocatalytic elimination of pollutants from water. Herein, we accurately designed and fabricated a direct Z-scheme carbon nanodots/WO_3 nanorods composite (CDots/WO_3) with highly enhanced photoresponse and broad-spectrum photocatalytic activity. Under ultraviolet, visible, near-infrared (UV, Vis, NIR) irradiation, respectively, the removal efficiencies of rhodamine B (RhB) always decreased in the order CDots/WO_3 (97.1, 99.1, 61.2%) > prepared WO_3 nanorods (66.6, 69.1, 22.4%) > commercial WO_3 nanoparticles (22.1, 11.6, ~0%). Additionally, reaction rate constants of 0.4030 and 0.2889 h^{-1} were achieved by the CDots/WO_3 nanocomposites when photo-oxidizing tetracycline hydrochloride (TCH) and phenol, respectively, both of which were ~2.9 times higher than those for WO_3 nanorods. This excellent photocatalytic performance was ascribed to synergistic effects, including the highly dispersed carbon nanodots on the surface of the WO_3 nanorods and efficient charge separation induced by the heterostructure formed between carbon nanodots and WO_3 nanorods. Accordingly, a mechanism was proposed to account for the photocatalytic reaction process. The prepared catalyst showed no obvious change in its photocatalytic performance or other chemical properties after 5 cycles of use. Therefore, the carbon nanodots/WO_3 nanocomposites may represent a new strategy for the full-spectrum utilization of solar light, providing an invaluable methodology for the remediation of current water-pollution issues.

1. Introduction

Efficient semiconductor photocatalysis is a promising and effective strategy for purifying water contaminated by various environmental pollutants [1]. To date, a wide variety of semiconductor materials have been developed, including ZnO, TiO_2, C_3N_4, Bi_2WO_6, CdS and Ag_2O, among others [2–6]. However, two key factors seriously restrict the further application of these photocatalysts, namely, the low solar-light utilization efficiency and rapid electron–hole recombination [7]. Therefore, numerous efforts have been made to solve these problems.

Regarding solar-energy utilization, the preparation of semiconductor photocatalysts that can harvest the entire spectrum of solar light, from ultraviolet (UV) to near-infrared (NIR) wavelengths, while achieving efficient solar-energy conversion, remains one of the most important challenges [6,8]. Recently, several UV–vis–NIR-active catalysts have been reported, including CdS, Ag_2O, BiOI and carbon nanodots (CDots) [4,6,9–11]. Among them, CDots, a new member of the carbon family consisting of particles with sizes below 10 nm, have attracted increasing interest because of unique properties including their large two-photon absorption cross sections, up-conversion ability, low toxicity, high biocompatibility and excellent electron-transfer and electron-reservoir properties [12,13]. Accordingly, CDots can be employed as a co-catalyst to build surface separation centers for electrons and reduce the recombination rate of charge carriers. It has been reported that CDots/TiO_2 nanotube arrays [14], CDots/Ag_3PO_4 [15], CDots/H-γ-TaON [8], CDots/BiOX (X = Cl, Br and I) [16], CDots/Bi_2WO_6 [5] and CDots/g-C_3N_4 [12] composites as well as CDots/CdS [17] heterostructures exhibit enhanced photocatalytic activity and structural stability, compared with single-species catalysts, for the photo-decomposition of organic compounds, evolution of hydrogen by water splitting or solar-light-driven conversion of CO_2 to methanol. The conjugated π structure of the CDots in these composites plays an important role in their improved photocatalytic activities [8]. Therefore, CDots could potentially function as a co-

---

* Corresponding author.
E-mail address: dongshuangshi@gmail.com (S. Dong).

http://dx.doi.org/10.1016/j.apcatb.2017.03.017
0926-3373/© 2017 Elsevier B.V. All rights reserved.

catalyst, capable of harnessing a broader range of visible or NIR light to enhance the performance of the main photocatalysts.

Recently, one-dimensionally (1-D) nanostructured semiconductor photocatalysts have received extensive attention, and are considered to be ideal photocatalytic materials because their reduced grain boundaries can shorten the transmission path of the photo-generated charges and realize the effective separation of electron–hole pairs [18–21]. Their high crystallinity and abundance of surface active sites are conducive to photo-absorption and redox reactions, and allow them to efficiently gather organic pollutants in wastewater [20,22]. Considering the above-mentioned properties and previous reports regarding 1-D nanomaterials, it is likely that they have the potential to achieve higher photocatalytic activity than nanoparticles.

Among the wide range of 1-D nanostructured semiconductors, tungsten oxide (WO_3) nanorods have been regarded as particularly suitable candidates because of their stable physicochemical properties, resilience to photo-corrosion effects, relatively narrow band-gap energy (2.4–2.8 eV) and the high oxidative power of their valence band (VB) holes [20,23]. In addition, in contrast with WO_3 nanoparticles, WO_3 nanorods, with their high specific surface area, provide more active sites and attachment points, which is conducive to the formation of composite photocatalysts. In spite of these advantages, the photocatalytic activity of WO_3 nanorods alone is still limited by several critical drawbacks. First, their intrinsic band-gap energy (2.4–2.8 eV) severely limits their solar-light utilization efficiency [23]. Second, they usually suffer from a high recombination rate of the charge carriers at the surface, which are slow to participate in interface redox reactions [20]. Last, their relatively low conduction band (CB) level does not provide a sufficient potential to react with strong electron acceptors, which directly results in fast recombination and thus lower photocatalytic activity. Therefore, considerable efforts have been devoted to the development of a novel WO_3 nanorods-based photocatalyst that can efficiently utilize a wide spectrum of solar-light irradiation.

It has already been confirmed that CDots can efficiently enhance the photocatalytic and photo-electrochemical performance of WO_3 under visible-light irradiation [24,25]. Shi et al. [24] showed that a CDots/WO_3 electrode had a higher photo-current and photo-electric conversion efficiency than the corresponding WO_3 electrode. Yang et al. used IO_3^-/I^- as a shuttle redox mediator to transfer the photo-generated electrons in the CB of WO_3 to the VB of CDots, and found that this Z-scheme was an effective strategy to improve the photocatalytic performance of WO_3 [25]. Thus, on the basis of these reports, it is plausible that the CDots/WO_3 nanorods Z-scheme heterostructure could be used as an efficient photocatalyst. However, little is known about the photocatalytic activity and mechanism of CDots/WO_3 nanocomposites over the UV–vis–NIR broad spectrum. Is a direct Z-scheme system still present in CDots/WO_3 in the absence of redox mediators such as IO_3^-/I^-? It is desirable to construct direct Z-scheme systems from CDots/WO_3 nanorods composites to enhance the photo-response and broad-spectrum photocatalytic performance of WO_3, and to reveal the corresponding photocatalytic oxidation mechanisms accurately and in detail.

To the best of our knowledge, there is no previous report of simultaneous broad-spectrum light utilization and efficient charge separation by a system comprising CDots coupled with WO_3 nanorods to form an all-solid-state direct Z-scheme heterojunction. Herein, for the first time, we synthesized UV-, visible- and NIR-light-driven CDots/WO_3 nanorods composite photocatalysts, ensuring the fast interior transport, surface separation and effective solar-light absorption of the carriers so as to enhance the photocatalytic activity. The WO_3 nanorods were used as a supporting material, leading to the homogeneous dispersion of the prepared CDots nanoparticles on the nanorod surfaces to form CDots/WO_3 nanorods Z-scheme heterostructures with spectrum-versatile activity, i.e., UV, visible and NIR. The photocatalytic performance of the catalysts was evaluated by decomposing Rhodamine B (RhB), tetracycline hydrochloride (TCH) and phenol in aqueous solutions under UV, visible and NIR irradiation, respectively. The composites exhibited superior photocatalytic activity, which was mainly ascribed to the synergistic effect between WO_3 nanorods and CDots. Subsequently, a possible photocatalytic mechanism for the broad-solar-spectrum activity of the CDots/WO_3 nanorods heterostructures was proposed. Hence, this work may be of interest to both materials scientists and those working in the area of catalyst design.

2. Experimental

2.1. Catalysts preparation

All chemicals were analytical grade without further purification. A common electrochemical method was used to synthesize CDots. WO_3 nanorods was prepared via a simple hydrothermal method that according to previous reports with some modified [26]. The detailed processes can be found in Supplementary materials.

CDots/WO_3 nanorods composites prepared via an oil bath reflux. First, 0.1 g WO_3 nanorods dissolved into 80 mL CDots aqueous solution to form a homogeneous mixture. Then, the mixture was transferred to oil bath pot and run at 90 °C for 3 h and the heterostructure was obtained. Last, the resulted samples were washed with ultrapure water for 3 times and dried at 60 °C. For comparison, a series of CDots/WO_3 nanocomposites were prepared by adding different content of CDots (wt%), which were accordingly denoted as X wt% CDots/WO_3 (X = 0.2, 0.4, 0.8 and 1.2). In this paper, we used CDots/WO_3 instead of 0.8 wt% CDots/WO_3, as it was proved to possess the highest photocatalytic activity and was most intensively studied.

2.2. Characterization

The morphology and crystal structure of prepared samples were investigated via the Scanning Electron Microscopy (SEM, JEOL JSM-7001F), Transmission Electron Microscopy (TEM), and High-Resolution TEM (HRTEM) (via a 200 kV FEI-Tecnai F20, USA) measurements. Accordingly, the corresponding 2D fast Fourier transform (FFT) pattern was obtained via Digital Micrograph. The XRD patterns were acquired with a powder X-ray diffraction (XRD, Bruker D8, Germany) equipped with Cu Kα radiation. X-ray photo-electron spectroscopy (XPS) was conducted via an X-ray photo-electron spectroscopy using an Al Kα (h = 1486.6 eV) radiation excitation source. All of the obtained spectra were calibrated against the C 1s signal at BE = 284.6 eV. The UV–vis–NIR diffuse reflection spectra (DRS) was taken on a Lambda 750 spectrophotometer (Perking Elmer). Raman spectra was obtained by using an HR 800 Raman spectroscope (Horiba Jobin Yvon, France). The Fourier transform infrared (FT-IR) spectrums were investigated by a FT-IR spectrometer (Spectrum One, Perkin Elmer). The photoluminescence (PL) spectra were carried out on a luminescence spectrometer (Cary Eclipse, Varian Medical Systems, USA). The electron spin resonance (ESR) spectra were performed on a Bruker model ESR JES-FA200 spectrometer by using the spin-trap reagent DMPO (5,5-dimethyl-1-pyrroline N-oxide, Sigma Chemical Co.) in water (for hydroxyl radical) and methanol (for superoxide radical).

2.3. Photocatalytic measurements

The light source for photocatalytic reaction was a 150 W Xenon lamp (CEL-HXF 300, Beijing Education Au-light Co., Ltd.). Three