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Fabrication of GO/CDots/BiOI nanocomposites with enhanced photocatalytic 4-chlorophenol degradation and mechanism insight

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ABSTRACT

Non-metallic graphene oxide (GO) and carbon nanodots (CDots) co-doped BiOI ternary system (GO/CDots/BiOI) was successfully synthesized via a simple one-step solvothermal process. The compositional characterization, optical and electrical properties of photocatalysts were investigated in detail. The prepared ternary photocatalysts possessed the excellent visible-light driven photocatalytic 4-chlorophenol (4-CP) degradation. Additionally, the 4-CP removal efficiencies decreased in the order of GO/CDots/BiOI (98.2%) > CDots/BiOI (89.9%) > GO/BiOI (78.5%) > pristine BiOI (41.7%) in 3 h under visible light irradiation. The dissolved organic carbon (DOC) removal and the dechlorination efficiency by the GO/CDots/BiOI were 66.3% and 85.2%, respectively, much higher than pristine BiOI. The co-existence of GO and CDots on the BiOI greatly promoted visible light harvesting and utilizing ability and inhibited the recombination of photogenerated electron/hole pairs. The synergistic effect between GO, CDots and BiOI was expounded, and the photocatalytic reaction mechanism was proposed in detail via the band structure analysis and free radical trapping experiments.

1. Introduction

Photocatalytic techniques had attracted explosive attention since it could utilize the solar energy to degrade the contaminants efficiently, as well as its low cost, innocuous, environment-friendly and easily available nature [1]. The diverse photocatalysts were studied for the degradation of organic pollutants under Ultra Violet (UV) or visible light irradiation such as TiO_2, ZnO, WO_3, g-C_3N_4 $ZnFe_2O_4$ and Bi_2WO_6 [1–5]. Iodine bismuth oxide (BiOI) had unique layered structure built by interlacing $[Bi_2O_2]^{2+}$ slabs with double I atoms, which was benefit to form internal static electric fields between I positive and I negative layer and then enhanced separation of the photo-generated electron/hole pairs [6–8]. Besides, the photo-excited electrons should travel a certain k-space distance to the valence band due to the indirect-transition band-gap of BiOI, leading to the low recombination probability of the electron/hole pairs [9–11]. Nevertheless, the photocatalytic performance of unitary BiOI was still limited owing to the low solar energy utilization efficiency and rapid electron/hole pairs recombination [12–14].

In recent years, carbon nanodots (CDots, a carbon nanomaterial less than 10 nm in diameter) attracted the interests of researchers due to the unique characteristics over conventional semiconductor-based dots including water-soluble, intrinsic low toxicity, good biocompatibility, photostable and nanosized light-harvester [15–17]. The conjugated π structure of the CDots made them excellent electron reservoir and transporter [18]. Simultaneously, the up-conversion properties of CDots enabled the light from the longer wavelength to shorter wavelength, improving the utilization of solar light [16]. These properties endowed CDots as a co-catalyst to decorate many semiconductors to accelerate the separation-transportation process of photo-induced carriers within the semiconductors and improve their interfacial reduction/oxidation reactions [4,16,17]. Besides, some researchers have also tried to couple semiconductors with graphene oxide (GO), a promising carbon material, which possesses high surface area, excellent electrical conductivity, rapid heterogeneous electron transfer and outstanding mechanical properties to enhance its electron conduction and transfer behavior to restrain recombination of photogenerated electron/hole pairs [19–22].

Recently, the ternary photocatalysts with GO and CDots co-dopants have received much attention owing to much higher photocatalytic performance compared to the binary photocatalysts [23]. However, limited work has been done on the mechanism insight to the combined effect of GO and CDots on the surface of semiconductors. In this work, we fabricated the GO/CDots/BiOI ternary photocatalyst to dramatically

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improve the photocatalytic activity compared to the pristine BiOI and the binary system. The crystal structures, morphologies and optical and electrochemical properties were investigated in detail. The photocatalytic activities of the GO/CDots/BiOI microspheres were tested by the degradation of 4-CP. The effect of GO and CDots on the band structure of BiOI microspheres was intensively studied. The synergistic effect between GO, CDots and BiOI was investigated. Accordingly, the photocatalytic mechanism of the separation and transfer of photogenerated charges on the GO/CDots/BiOI ternary system was proposed and elucidated under visible light illumination.

2. Experimental section

2.1. Catalysts preparation

All reagents were used directly without further treatment. The details of the chemicals were listed in Table S1. The CDots was prepared via a typical electrochemical method [17]. The GO/CDots/BiOI were synthesized by a mixed precipitation method according to previous reports [12,24]. In a typical procedure, 4 mmol $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved into a solution contained 36 mL deionized water and 4 mL acetic acid to obtain solution A. 4 mmol IL [C16mim]I, 2 mL CDots (4 mg/L) and 4 mL GO (5 mg/L) aqueous were all dispersed into 40 mL alcohol to obtain solution B. The solution B was added into solution A dropwise under stirring condition and then the mixing solution was stirred for another 1 h. Subsequently, the resultant product was centrifuged and washed adequately with alcohol and deionized water three times. Finally, the resulting precipitates were dried in a vacuum at 60 °C overnight and ground into fine powder before further characterization and using in photocatalytic reactions. For comparison, the pure BiOI, GO/BiOI and CDots/BiOI were also prepared via the same approach by only adding nothing, GO and CDots, respectively.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.seppur.2018.08.027.

2.2. Characterization

The scanning electron microscopy (SEM, JEOL JSM-7001F), transmission electron microscopy (TEM, 200 kV FEI-Tecnai F20) and high-resolution TEM (HRTEM) were used to investigate the morphology and structure of as-prepared catalysts. The chemical composition was investigated via energy-dispersive X-ray spectroscope (EDX). X-ray diffraction (XRD) measurements were conducted on a Bruker D8 powder X-ray diffractometer with Cu Kα (λ = 0.15406 nm) radiation. Fourier transform infrared (FT-IR) spectra were obtained via a VERTEX70 spectrophotometer (Bruker, Germany) using pressed KBr discs. X-ray photoelectron spectroscopy (XPS) was detected via a VG ESCALAB210 (Thermo Fisher Scientific, USA) XPS system using an Al Kα (h = 1486.6 eV) radiation excitation source. All obtained spectra were calibrated against the C 1s signal at 284.6 eV. UV–Vis diffuse reflection

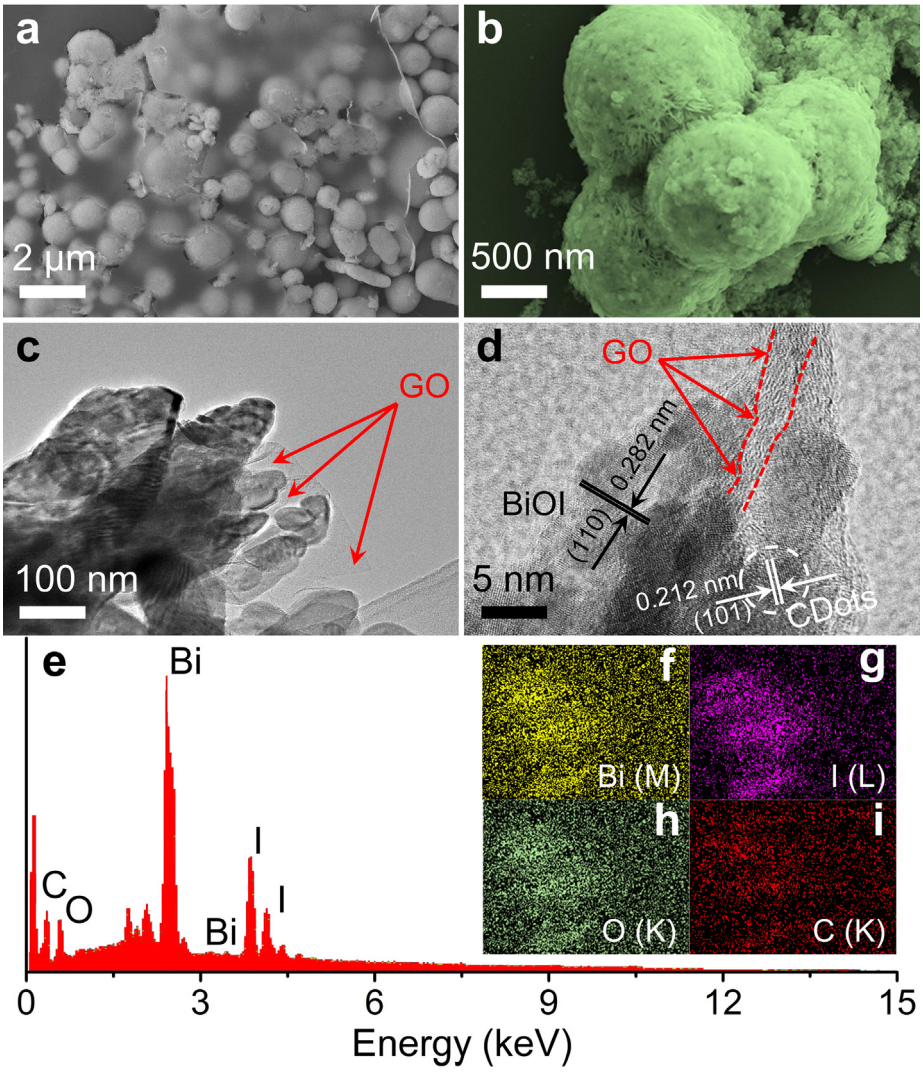

Fig. 1. SEM (a and b), TEM (c) and HRTEM (d) images and EDX mapping (e–i) of the as-prepared GO/CDots/BiOI photocatalysts.