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Regular Article

Ionic liquid-assisted bidirectional regulation strategy for carbon quantum dots (CQDs)/$Bi_4O_5I_2$ nanomaterials and enhanced photocatalytic properties

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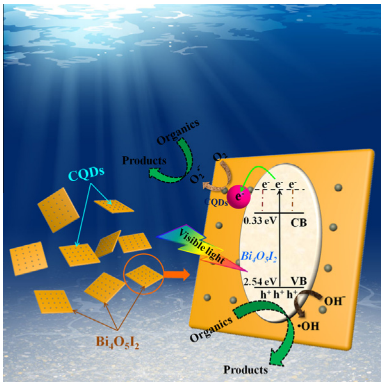
GRAPHICAL ABSTRACT

Novel CQDs/$Bi_4O_5I_2$ materials have been prepared via a reactable ionic liquid assisted bidirectional regulation solvothermal method. This is the first time for the preparation of CQDs/$Bi_4O_5I_2$ material with halogen and CQDs bidirectional regulation at the same time.



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ABSTRACT

In this study, novel visible-light-driven carbon quantum dots (CQDs)/$Bi_4O_5I_2$ material has been prepared via a reactable ionic liquid 1-hexyl-3-methylimidazolium iodide ([Hmim]I) assisted bidirectional regulation solvothermal method. This is the first time for the preparation of CQDs/$Bi_4O_5I_2$ material with halogen and CQDs bidirectional regulation at the same time. With CQDs modified on the surface of $Bi_4O_5I_2$, fast transfer of photogenerated charges and low recombination of photo-induced electron-hole pairs facilitated the enhancement of photodegradation activity. At the same time, the introduction of CQDs made the electrons occupied in high-energy potential on the conduction band of $Bi_4O_5I_2$ transfer to the reaction center CQDs and the molecular oxygen can be thus activated. The enhanced mechanisms for the active species (holes, hydroxyl and superoxide radicals) during the photocatalytic reaction under visible irradiation were analyzed using DRS analysis, electron spin resonance (ESR) technique and free radicals trapping experiments.

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1. Introduction

Solar energy as an essential renewable clean energy has aroused the extensive attention of researchers and how to realize the efficient conversion of solar energy is being explored to achieve a new breakthrough around the world [1–4]. In the last few decades, the semiconductor photocatalysis technology brings us a new discovery of the utilization of sun light, of which anatase phase TiO_2 has been regarded as one of the most effective photocatalysts for its predominant photocatalytic activity, high photoelectric conversion efficiency and at a low cost [5–7]. However, the narrow light absorption region of TiO_2 greatly limits it to extend the applications to the visible light region [8–10]. Hence, the exploration of visible-light response photocatalysts is indispensable for further practical application.

Bismuth oxyhalides (BiOX, X = Cl, Br, I), as a member of the Sillén family, has drawn extensive interests in photocatalytic researches for its unique layered structure and excellent photocatalytic activities under UV or visible light irradiation [11–19]. The BiOX possessed the structure of $[Bi_2O_2]$ slabs interleaved with double slabs of halogen atoms could induce the generation of internal static electric fields so as to realize the effective separation of photogenerated carriers and bring about the remarkable photocatalytic activity [20]. Among these, Bismuth oxyiodide (BiOI) has been widely investigated by right of the stronger optical absorptivity in the visible light range. However, the low separation efficiency of photoinduced charge carriers and high recombination rate of photo-generated electrons and holes greatly limited its industrial applications. On account of this, many strategies have been adopted to enhance the photocatalytic activity of BiOI material, such as the control of crystal growth, the regulation of morphology and structure as well as the introduction of defects. At the same time, many of the hybrid materials have also been successfully prepared, for instance, the mesoporous g-C_3N_4/BiOI [21], AgI/BiOI [22], BiOI/TiO_2 [23], BiOCl/BiOI [24], BiOI/n-$ZnTiO_3$ [25] and $BiVO_4$/BiOI [26]. Very recently, a suitable dehalogenation process has been proved to be a useful strategy to further optimize the photocatalytic activities of the BiOX materials. A series of Bi-rich bismuth oxyhalides have been synthesized by different ways, for example, Bi_3O_4Cl [27], $Bi_4O_5Br_2$ [28], $Bi_7O_9I_3$ [29] Bi_5O_7I [30], and $Bi_4O_5I_2$ [29,31–33] etc., and the enhanced photocatalytic activity can be observed. Therefore, as if a proper way could be adopted by reasonably regulating and controlling the content of I in BiOI material, the improved photocatalytic activity could be expected.

Carbon quantum dots (CQDs), with particle sizes below 10 nm, have been widely known as a fascinating class of zero-dimensional nanocarbons [34]. The unique properties of stabilities, biocompatibility, nontoxicity and the strong fluorescence promise a potential application for the novel water-soluble carbon nanomaterial. In addition, results of previous researches indicate that CQDs modified on semiconductor photocatalysts can enhance the capacity of light absorption to utilize more of the full spectrum of the sunlight and accelerate the transfer of photo-induced electrons to suppress the rapid recombination of the charge carriers that have been transmitted to the surface of the semiconductors [35]. However, it still needs to explore that how to introduce the CQDs to the semiconductor by evenly disperse it on the surface of the semiconductor.

In the current study, ionic liquid 1-hexyl-3-methylimidazolium iodide ([Hmim]I) was employed to act as reactant source and dispersing agent at the same time to synthesize a novel CQDs/$Bi_4O_5I_2$ material via a facial solvothermal method. According to our preliminary researches, the introduction of ionic liquid [Hmim]I could promote the CQDs disperse well on the surface of $Bi_4O_5I_2$ nanosheets so that the fast transfer and efficient separation of the surface charge carriers can be achieved, thus the photocatalytic activity was greatly enhanced [8,36]. In this study, on the one hand, the appropriate removal of halogen atoms in BiOI material could regulate the internal energy band structure of $Bi_4O_5I_2$ material, so as to the value of downward VB potential could be expected to reach the oxidation reduction potential of oxidizing hydroxyl groups to generate the effective active specie hydroxyl free radical ($OH^{\cdot}$) in the photocatalytic reaction. On the other hand, the CQDs surface modified Bi_4O_5-I_2 material could be expected to rapidly transfer the photo-induced charge carriers, effectively inhibit the recombination of electron-hole pairs and highly efficiently transfer the excited high-energy electrons from conduction band (CB) of $Bi_4O_5I_2$ material to the surface of CQDs. The bidirectional regulation strategy of energy band modulation and surface modification for the prepared CQDs/$Bi_4O_5I_2$ material was proposed for the first time. Rhodamine B (RhB) was degraded under visible light irradiation to evaluate the photocatalytic activity of CQDs/$Bi_4O_5I_2$ materials. And a possible mechanism for the photodegradation process was proposed eventually.

2. Experiment section

2.1. Preparation for CQDs/$Bi_4O_5I_2$ materials

Materials used in experiments were analytical purity and used as yet untreated. The ionic liquid1-hexyl-3-methylimidazolium iodide ([Hmim]I) (99%) was purchased from Shanghai Chengjie Chemical Co. Ltd.

CQDs powder was prepared according to the literature with freeze-drying [34]. 1 mmol $Bi(NO_3)_3{\cdot}5H_2O$ and 1 mmol [Hmim]I were dissolved in 10 mL mannitol under magnetic stirring to obtain suspension A and B, respectively. Then solution B was added into the A suspension by drops with steadily stirring. After that, different amount of as-prepared CQDs powder was added into the suspension and the pH of the suspension was adjusted to 10 by 1 mol/L NaOH solution with continuous stirring for 30 min at room temperature. The mixture was poured into a 25 mL Teflon-lined stainless-steel autoclave and heated at 140 °C for 24 h in a drying oven. Subsequently the precipitate was collected from refrigerant autoclave and washed several times with aquadistillate and anhydrous ethanol by centrifugation. The obtained precipitate then was dried at 60 °C for hours. The content of CQDs added in CQDs/$Bi_4O_5I_2$ materials was 0.5 wt%, 1 wt%, 3 wt%, respectively.

2.2. Characterization

Power X-ray diffraction (XRD) spectra for the as-prepared photocatalysts were determined using a Shimadzu XRD-6000 X-ray diffractometer with CuKα radiation ($\lambda = 1.54$ Å). Fourier transform infrared (FT-IR) were measured on a Nicolet Model Nexus 470 FT-IR equipment using KBr pellet technic. UV–vis diffuse refection spectra (DRS) were recorded on an UV–vis spectrophotometer (UV-2450 Shimadzu Corporation, Japan) in the range of 200–800 nm ($BaSO_4$ powder used as the substrate). X-ray photoelectron spectroscopy (XPS) analysis was taken on an ESCALab MKII X-ray photo-electron spectrometer using the MgKα radiation. The electron spin resonance (ESR) spectra were examined on a Bruker model ESR JES-FA200 spectrometer with the spin-trap reagent DMPO (Sigma Chemical Co.) in methanol and water. Transmission electron microscopy (TEM) micrographs were observed on a JEOL-JEM-2010 (JEOL, Japan) operated at 200 kV. The nitrogen adsorption-desorption isotherms at 77 K were researched using a TriStar II 3020 surface area and porosity analyzer (Micromeritics Instrument Corporation, USA).

2.3. Photocatalytic activity measurement

The photocatalytic activity of the as-prepared CQDs/$Bi_4O_5I_2$ materials was evaluated by the degradation of rhodamine B