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Graphene-like boron nitride induced accelerated charge transfer for boosting the photocatalytic behavior of $Bi_4O_5I_2$ towards bisphenol a removal

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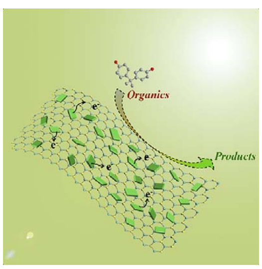
GRAPHICAL ABSTRACT



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ABSTRACT

A novel graphene-like BN/$Bi_4O_5I_2$ 2D-2D stacking has been prepared via a facile ionic liquid 1-hexyl-3-methylimidazolium iodide ([Hmim]I) assisted solvothermal method with the proper pH for the first time. Series of characterizations, such as XRD, XPS, FT-IR, TEM, BET, PL, EIS and ESR have been applied to analyze the composition, morphology, structure, optical and electronic properties of the graphene-like BN/$Bi_4O_5I_2$ composites. The sufficient contact and strong interfacial interaction between the graphene-like BN and $Bi_4O_5I_2$ nanosheets can be effective constructed. Colorless endocrine disrupter bisphenol A (BPA) was chosen as the target pollutant to evaluate the photocatalytic degradation performance of the pure $Bi_4O_5I_2$ nanosheets and graphene-like BN/$Bi_4O_5I_2$ composites under visible light irradiation. The enhanced photocatalytic activity of the graphene-like BN/$Bi_4O_5I_2$ composites could be attributed to the higher electron transfer ability over the graphene-like BN nanosheet and thus the molecular oxygen can be better activated. Superoxide radical and hole were determined to be the main active species during the photodegradation process. This work will provide a new sight into the design of other two-dimensional atomic level material based composites for photocatalysis.

1. Introduction

Environmental pollution, resource shortage and ecological damage are identified as three major global crises in modern society and have aroused great concern in various research areas. In which, water environment pollution has become the nonnegligible issue in China. Bisphenol A (BPA), as an important raw material in organic chemical engineering, has been widely used in plastic bottles, food, medical equipment and so on since the 1960s. However, some research work has demonstrated that the BPA accumulated in the environment could lead to a series of disease, such as endocrine disorders, precocious puberty and embryo teratogenic [1]. So it is urgent to remove the endocrine disrupter BPA in the environment. Photocatalysis technique is recognized as a promising green technology in solving energy shortage

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and environmental restoration [2,3].

Since the appearance of authentic two-dimensional atomic level material graphene, its unique structural, optical, electronic and mechanical properties have brought a hot-spot of research in the last decade [4–6]. At the same time, many other layered materials with the ultrathin even monolayer structure [7], like MoS_2 [8], WO_3 [9], BN [10] and g-C_3N_4 [11] have attracted more and more attention and have been applied in the different research fields, especially for the catalysis. Hexagonal boron nitride (BN) as a member of two-dimensional metal-free layered material, is isostructural to the graphite. Its good chemical stability, thermal conductivity and mechanical properties enable it with considerable research interests in recent years [12–16]. When the bulk BN was exfoliated to atomically thickness, the graphene-like BN could be more electronegative, the negatively charged graphene-like BN could favor the charge separation and transfer [17]. Therefore, it is extremely meaningful to construct graphene-like BN modified semiconductor photocatalyst in order to achieve the high photogenerated charge utilization efficiency to realize the enhanced photocatalytic activity.

As a novel promising material with the wide spectral response, bismuth oxyiodide (BiOI) photocatalyst shows the outstanding photocatalytic performance in environmental remediation and energy conversion [18–23]. As a member of bismuth oxyhalides (BiOX), BiOI material also has the unique layered structure. The structure of $[Bi_2O_2]$ slabs interleaved with double iodine atoms could lead to the generation of the self-built internal static electric fields, thus promoting the photogenerated electron-hole pairs separation along [0 0 1] orientation [24–27]. However, the excessive narrow band gap of the BiOI material (about 1.7 eV) results in the rapid recombination of the photogenerated charge carriers which greatly limits its photocatalytic performance. Several strategies have been employed to overcome this intrinsic deficiency of the pure BiOI material, such as morphology controlling [28], heterojunction constructing [29], element doping [30] and exposed crystal facet tuning [1]. Recently, changing the halogen content in the BiOX family has been considered to be a feasible route to optimize the photocatalytic performance of the pure BiOX material. A series of bismuth-rich bismuth oxyhalides have been prepared, such as Bi_3O_4Cl [31], $Bi_{12}O_{15}Cl_6$ [32], $Bi_4O_5Br_2$ [33], $Bi_{24}O_{31}Br_{10}$ [34], $Bi_7O_9I_3$ [35], Bi_5O_7I [36] and $Bi_4O_5I_2$ etc. Among the bismuth-rich bismuth oxyiodide materials, $Bi_4O_5I_2$ shows the excellent photocatalytic behavior and has a promising prospect in different photocatalysis field, such as the solar water spliting, carbon dioxide conversion and organic pollutants removal [25,33,37–42]. However, based on the previous reports, there are fewer researches on optimizing the photocatalytic performance of the $Bi_4O_5I_2$ material. Therefore, it is significant for fabricating graphene-like BN/$Bi_4O_5I_2$ nanocomposites in order to realize the fast transfer and effective utilization of the photogenerated interfacial charge and thus to further enhance the photocatalytic performance of the pure $Bi_4O_5I_2$.

In this study, the novel graphene-like BN/$Bi_4O_5I_2$ nanocomposites have been prepared via a facile ionic liquid 1-hexyl-3-methylimidazolium iodide ([Hmim]I) assisted solvothermal method. The introduced ionic liquid not only served as the reactant source to participate in the preparation process, but also as the dispersant to construct an optimal contact between the graphene-like BN and $Bi_4O_5I_2$ materials. The endocrine disrupter BPA was chosen as the target pollutant to evaluate the photocatalytic degradation performance of the graphene-like BN/$Bi_4O_5I_2$ composites under visible light irradiation. A possible mechanism for the enhanced photocatalytic performance has been proposed.

2. Experimental

2.1. Preparation of the BN/$Bi_4O_5I_2$ composites

All of the reagents that used in this research were analytical purity and used without further purification. The ionic liquid 1-hexyl-3-methylimidazolium iodide ([Hmim]I) (99%) was purchased from Shanghai Chengjie Chemical Co. Ltd. Two dimensional graphene-like boron nitride (BN) material with ultrathin structure was prepared by calcining the mixture of urea and boric acid at 900 °C for 5 h in nitrogen gas atmosphere [12].

Typically, the synthesis of graphene-like BN/$Bi_4O_5I_2$ composites via a facile ionic liquid-assistant solvothermal method was as follows: firstly, 1 mmol $Bi(NO_3)_3 \cdot 5H_2O$ was poured into 10 mL 0.1 mol/L mannitol aqueous solution until dissolved with continuous stirring, then as-prepared graphene-like BN material was added. The obtained dispersion was named as A solution. Besides, 1 mmol [Hmim]I dissolved in 10 mL 0.1 mol/L mannitol aqueous solution with continuous stirring was named as B solution. Then the obtained B solution was added into above A solution dropwise. The pH of the achieved red suspension was adjusted to 10 by adding 1 mol/L NaOH under stirring for 30 min. Next, the white mixture was poured into a 25 mL Teflon-lined stainless-steel autoclave maintained at 140 °C for 24 h in a drying oven. The yellow products finally were washed with distilled water and ethanol for several times to remove the impurity fully and dried at 60 °C for one day. The obtained samples were named as X wt% BN/$Bi_4O_5I_2$, where X was the BN addition during the synthetic process.

2.2. Characterizations of the BN/$Bi_4O_5I_2$ composites

The crystallinity of the different samples were confirmed by power X-ray diffraction (XRD) on Shimadzu XRD-6000 X-ray diffractometer with Cu-Kα radiation at room temperature. X-ray photoelectron spectroscopy (XPS) was performed on a VG MultiLab 2000 system with a monochromatic Mg-Kα radiation operated at 20 kV. The surface areas of the as-prepared $Bi_4O_5I_2$ and BN/$Bi_4O_5I_2$ samples were determined by the nitrogen adsorption-desorption isotherms using a Micromeritics TriStar II 3020 Surface Area and Porosity Analyzer at 77 K. Transmission electron microscopy (TEM, JEOL JEM 2010, Japan) was used to observe the samples' morphology and the combination of BN and $Bi_4O_5I_2$ material. UV–vis diffuse refection spectra (DRS) were recorded on an UV–vis spectrophotometer (Shimadzu UV-2450) with $BaSO_4$ as the blank correction from 200 to 800 nm. A micro Raman spectrometer (Renishaw Invia) with a 532 nm laser as an excitation source was used to obtain the Raman spectra at room temperature. The electron spin resonance (ESR) signals of spin-trapped radicals were examined on a Bruker model ESR JES-FA200 spectrometer using spin-trap reagent DMPO in water and methanol, respectively. The Agilent high performance liquid chromatography (HPLC) system equipped with an Agilent TC-C (18) column, two Varian ProStar210 pumps and a Varian ProStar325 UV–Vis detector was used to evaluate the photocatalytic removal of BPA. The mobile phase was a mixture of 75% methanol and 25% purity water of the volume. The flow rate of the mobile phase was 1.0 mL min^{-1} and the detection wavelength was 230 nm.

2.3. Photocatalytic experiments of the as-prepared composites

The photocatalytic activities of the as-prepared $Bi_4O_5I_2$ nanosheets and BN/$Bi_4O_5I_2$ composites were evaluated by the degradation of 10 mg/L bisphenol A (BPA) and 10 mg/L rhodamine B (RhB) under visible light irradiation. 20 or 50 mg as-prepared samples was transferred into a Pyrex photocatalytic reactor with 100 mL RhB or BPA target pollutant and the reactor was placed in a box with a 300 W Xe lamp as the light source and an air pump as the constant supply of oxygen, respectively. A 400 nm cut-off filter was used to ensure the visible light irradiation during the reaction process and the reaction temperature was maintained at 30 °C by a circulating water system. The mixture solution was stirred for 30 min under the dark to achieve the adsorption-desorption equilibrium between the pollutant and catalyst and then the light on. After irradiation for each specific time, 4 mL