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Regular Article

Enhanced photocatalytic performance of Ag/TiO_2 nanohybrid sensitized by black phosphorus nanosheets in visible and near-infrared light

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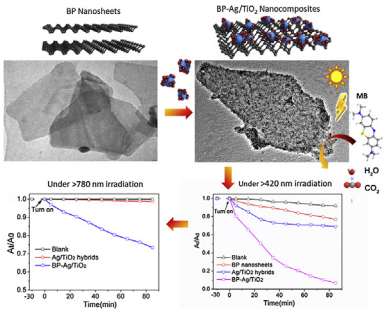
HIGHLIGHTS

- BP-Ag/TiO_2 nanocomposite was successfully prepared.
- TiO_2 maintained smaller Ag clusters and incorporated to BP nanosheets.
- Enhanced photocatalytic activity was observed in visible and NIR light.
- Photocatalytic activity of Ag/TiO_2 was sensitized by BP nanosheets.

GRAPHICAL ABSTRACT



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ABSTRACT

The efficient utilization of solar energy for environmental cleaning has attracted great attention, where the key is to efficiently harvest the visible and near-infrared (NIR) light which occupies approximately 95% of the solar light energy. Recently, black phosphorus (BP), as a new staring 2D material, has been extensively studied as photocatalytic materials due to its broad light absorption and tunable bandgap. Herein, we report a novel ternary nanocomposite, BP-Ag/TiO_2, prepared through controlled deposition of Ag clusters on the surface of TiO_2 nanocrystals and then incorporated to BP nanosheets. The BP-Ag/TiO_2 nanocomposite has shown excellent photocatalytic activity towards the degradation of methylene blue (MB) under visible and NIR light irradiation. About 100% and even 25% of MB was degraded in 85 min under >420 nm and >780 nm irradiation, respectively. The enhanced photocatalytic activity of BP-Ag/TiO_2 nanocomposite was mainly ascribed to the sensitization of BP nanosheets by fully harvest of solar light and high electron-hole separation efficiency. We believe that the BP-Ag/TiO_2 nanocomposite will be an effective photofunctional material in full-spectrum solar energy conversion and opens up a new door for the development of solar light driven photocatalysts for the remediation of environmental pollution.

1. Introduction

Energy and environmental issues are of great significance in social and economic developments, where many researchers

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devoted to the utilization of renewable energy for environmental remediation [1–4]. Solar energy, as a green and inexhaustible resource, has been considered as one of the most promising renewable sources of energy. For example, utilizing solar light in an efficient approach to degrade harmful and toxic dyes through photocatalysis has been of great concern and extensively investigated [5–8]. However, most of the previously reported photocatalysts, such as TiO_2, have a wide band gap (>3.2 eV), which means that only UV light could be used to activate their photocatalytic activities [4,9]. It is also known that in the solar spectrum, UV light contributes to <5% of the energy, while the most part lies in the visible range (<45%) and the near-infrared (NIR) range (about 50%). As a result, to increase the efficiency of solar-energy utilization, efforts to extend the light response of the photocatalysts from UV to visible and NIR range have been made [10]. Over the past few decades, a series of visible light and NIR light driven photocatalysts such as RGO/Ag_2S/TiO_2 nanohybrids, WS_2, up-conversion nanoparticles, Ag/AgCl@ZIF8 heterostructures and Ag/AgCl@MIL-101 nanohybrids have been developed [8,11–14]. Unfortunately, most of them either display low photo-energy harvesting efficiency or are difficult to synthesize. It still remains a challenge to design photocatalysts capable of harvesting sunlight covering the visible and the NIR regions.

Ultra-thin black phosphorus (BP), as a rapidly rising star in the materials field, has been intensively investigated since early 2014. It has a 2D layered structure with tunable band gap in the range of 0.3–2.0 eV, which enables its broad light absorption from the visible to NIR region [15–17]. Recently, Sa et al. investigated the potential application of BP in photocatalytic hydrogen production from water splitting based on density functional theory calculations [18]. Liu et al. have reported a novel Ag/BP plasmonic nanohybrid with experimental studies as well as numerical simulations, where the as-prepared Ag/BP nanohybrid showed enhanced photocatalytic activity for the degradation of RhB [19]. The Majima group developed a novel BP-Au/LTO nanostructure, which was used as an efficient and stable visible and NIR light-driven photocatalyst for H_2 production [20].

Herein, a ternary BP-sensitized Ag/TiO_2 (BP-Ag/TiO_2) nanostructure was synthesized for the first time and used as an efficient and stable visible and NIR light-driven photocatalyst for the photocatalytic degradation of MB. The as-obtained BP-Ag/TiO_2 nanocomposite was characterized using UV–vis absorption spectroscopy, atomic force microscopy (AFM), Raman microscopy, transmission electron microscopy (TEM), ultra-high resolution scanning electron microscopy (Ultra-HRSEM), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS) and so on. The results demonstrate that the Ag/TiO_2 nanocomposite can be effectively sensitized by BP nanosheets to obtain an enhanced photocatalytic activity towards the degradation of MB under visible and NIR light irradiation with a 300 W xenon lamp equipped with a 420 nm and 780 nm long-pass cut-off filter. This enhanced photocatalytic activity of degradation of MB is ascribed to the sensitization of BP nanosheets, which serve as a novel semiconductor to fully harvest visible and NIR light.

2. Experimental

2.1. Preparation of the TiO_2 nanocrystals

The synthesis of TiO_2 nanocrystals has been previously reported using a two-phase solvothermal method. In this synthesis, about 3 mL of *tert*-butylamine was added to 300 mL of water and the mixing solution was transferred to a 1 L Teflon-lined stainless-steel autoclave. Subsequently, 30 mL of oleic acid, 5 mL of *n*-butyltitanate and 300 mL of toluene were added to the autoclave, respectively. Then, the sealed autoclave was heated to 180 °C and held at this temperature for 720 min, and then allowed to cool to room temperature naturally. The obtained crude solution was centrifuged at 6000 rpm/min to remove the solid impurities and the upper supernatant solution containing the TiO_2 nanocrystals was precipitated upon the addition of ethanol and further isolated using centrifugation. The purified TiO_2 nanocrystals were re-dispersed in toluene for further use.

2.2. Synthesis of the Ag/TiO_2 nanocomposite

In this synthesis, firstly, 0.34 g of $AgNO_3$ and 1 g of 1-dodecylamine were added to 20 mL of a mixed solution comprised of toluene and ethanol (volume ratio = 3:1) under vigorous stirring to form a stock solution of silver-dodecylamine complexes (silver precursor). Then, a certain amount of silver precursor solution and 100 mg of TiO_2 nanocrystals solution were added to 30 mL of toluene in a 100 mL round bottom flask at 50 °C. Subsequently, a certain amount of acetaldehyde/toluene solution (about 8 mol/L, 0.25 mL) was added to initiate the reduction. During the reduction, 0.25 mL of the sample solution was taken and diluted with 3 mL toluene for characterization using UV–vis spectroscopy. The resultant solution was precipitated upon the addition of ethanol and submitted to a cycle of centrifugation, re-dispersion and precipitation. This procedure was repeated three times to remove the oleic acid absorbed on the Ag/TiO_2 nanocomposite (Scheme 1a).

2.3. Preparation of the BP nanosheets

The BP nanosheets were obtained using an *N*-methyl-2-pyrrolidone (NMP) solvent exfoliation process. 20 mg of bulk BP was added into 20 mL of NMP. The dispersion was sonicated for 2 h using a tip sonicator (Misonix XL-2000) at a power output of 10 W with cooling in an ice-water bath. The dispersion was centrifuged at 2000 rpm for 20 min to remove the non-exfoliated bulk BP, the remaining filtrate was further sonicated in bath for 2 h and centrifuged at 7000 rpm for 20 min to remove BP quantum dots dispersion solution, resulting in the BP nanosheets product.

2.4. Preparation of the BP-Ag/TiO_2 nanocomposite

The BP-Ag/TiO_2 nanocomposite was prepared by adding 12 mg of Ag/TiO_2 into 10 mL of NMP with sonication to form a homogeneous dispersion. Afterwards, 15 mL of the as-prepared BP NMP dispersion was added into the Ag/TiO_2 dispersion with sonication for 2 h. The resulting mixture was stirred overnight. The powders were collected using high-speed centrifugation, thoroughly washed with ethanol and then dried in an oven at 40 °C for 0.5 h to give the BP-Ag/TiO_2 nanocomposite (Scheme 1b). For comparison, Ag/TiO_2 deposited on Graphene oxide (GO) for BP-Ag/TiO_2 nanocomposite was also synthesized by replacing BP nanosheets with GO.

2.5. Characterization

UV–vis spectra were recorded in the range from 200 to 800 nm using a Shimadzu UV-1780 spectrometer. AFM measurements were carried out using a BRUKER-MultiMode 8 microscope. Raman Microscopy was performed using a Renishaw INVIA REFLEX HR Evolution confocal Raman spectrometer equipped with a microscope and an automated XYZ–table (excitation wavelengths 457 nm) with a laser spot size of ~1 μm. TEM images were recorded on a Philips Tecnai G2 Spirit microscope operating at an accelerating voltage of 120 kV, HRTEM image was obtained using a FEI Tecnai G2 F30 Spirit microscope operated at 300 kV accelerating voltage, and the samples were prepared by dropping a diluted dispersion of the sample onto a 200 mesh carbon-coated copper grid. Ultra-HRSEM images were