



Black phosphorus: A promising two dimensional visible and near-infrared-activated photocatalyst for hydrogen evolution



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ABSTRACT

The search for active photocatalysts that directly split water to hydrogen (H_2) under visible and near-infrared (NIR) light irradiation remains one of the most challenging tasks for solar energy utilization. Here we report that two dimensional (2D) black phosphorus (BP) nanoflakes can harness visible and NIR light for H_2 evolution. In the presence of reduced graphene oxide and Pt nanoparticles, ca. 5.13 and 1.26 $\mu\text{mol } H_2$ were obtained after excited BP nanoflakes under $>420 \text{ nm}$ and $>780 \text{ nm}$ irradiation for 4 h, respectively. The apparent quantum efficiencies (AQEs) were as high as approximately 8.7% at $420 \pm 5 \text{ nm}$ (visible) and 1.5% at $780 \pm 5 \text{ nm}$ (NIR), respectively. These results indicate that 2D BP can be used as visible- and NIR-activated elemental photocatalyst in artificial photosynthesis and renewable energy conversion.

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1. Introduction

Solar energy, as a free, clean, green, and inexhaustible resource, has long been considered as one of the most promising renewable sources of energy [1–3]. The search for semiconductor photocatalysts in splitting the water to hydrogen (H_2) has attracted considerable attention since the first discovery of water splitting on a TiO_2 electrode under ultraviolet (UV) light irradiation in 1972 [3–8]. Up to now, great efforts have been made in developing diversified semiconductor photocatalysts for efficient splitting of water [4–6]. However, most of the traditional semiconductors such as TiO_2 have a wide bandgap ($>3.2 \text{ eV}$), which means that UV light is necessary to activate their photocatalytic activities [4–6]. In our incoming solar spectrum, the UV light only accounts for 5%, while the visible light ($\sim 48\%$) and the near-infrared (NIR) light ($\sim 44\%$) account for more than 90% not to be utilized to activate the traditional semiconductor photocatalysts [4,9].

A great deal of time and efforts have been dedicated to achieve a novel photocatalyst that can harvest the broad range of solar light, especially in NIR region, over the past few decades. However, the search for such NIR-light-driven photocatalysts has focused mainly on photosensitization, upconversion materials, and a few of NIR photocatalysts, such as carbon quantum dots, $Cu_2(OH)PO_4$, and Bi_2WO_6/TiO_2 heterostructures [9–14]. Seriously, the above find-

ings bear either low photocatalytic efficiency based on narrow absorption or synthetic difficulty. To search for a photocatalyst with broadband solar absorption especially covering the NIR range still remains a formidable challenge.

Since the first report on field-effect transistors in 2014, ultrathin black phosphorus (BP), as a new two dimensional (2D) material, grabs a big triumph in electronics, optoelectronics, and sensors, and becomes a rapidly rising star in material science [15–21]. As one of the most infusive properties, the direct bandgap of BP can be tuned sufficiently for photon absorption in the UV and visible region, and also NIR region [21–25], indicating that BP is suitable to be an efficient photocatalyst with broadband solar absorption [25–31]. Recently, Sa et al. [26] demonstrated the potential of BP as a water splitting photocatalyst for H_2 evolution based on density functional theory calculations. Qiao's group [27] had critically reviewed the fundamental electronic, optical and chemical properties of BP and also assessed its suitability and stability as a future water splitting photocatalyst.

Here we demonstrate 2D BP nanoflakes can be worked as a broad spectrum photocatalyst, which can harness visible and NIR light for photocatalytic H_2 evolution. In the presence of reduced graphene oxide (RGO) and Pt nanoparticles, the optimum H_2 evolution activities are ca. 5.13 and 1.26 μmol with rate of 3.4 and 0.84 $\text{mmol g}^{-1} \text{ h}^{-1}$ under $>420 \text{ nm}$ and $>780 \text{ nm}$ irradiation, respectively. The efficient electrons transfer from excited BP nanoflakes and Pt/RGO contribute to NIR light driven photocatalytic H_2 evolution, which was proved by photoelectrochemical measurements and transient absorption. Our findings render 2D BP to be a broad

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spectrum photofunctional material and grab an attractive potential application in solar energy conversion.

2. Results and discussion

The ultrathin BP nanoflakes were prepared by using a basic N-methyl-2-pyrrolidone (NMP) solvent exfoliation method [32]. To directly visualize the effect of the above ultrasonication exfoliation, the scanning electron microscopy (SEM) images of the original BP powders (Fig. S1a) and the sediments separated after centrifugation (Fig. S1b) were examined. The results show that the raw BP powder consists of bulky plates, while the sediments separated after ultrasonication and centrifugation have much thinner and layers structures. It is suggested that the ultrasonication exfoliates the bulk BP to give BP nanoflakes. After centrifugation, a brownish dispersion was obtained, resulting in BP nanoflakes NMP dispersion (Fig. S2).

To explore the fine morphology and crystallinity of as-exfoliated BP, the above suspension was investigated by means of atomic force microscopy (AFM) and transmission electron microscopy (TEM). The thickness of BP nanoflakes ranging from 2.4 to 5.2 nm was measured by AFM to be close to that of the 4–10 phosphorus atomic layers (Figs. S3 and S4) based on the monolayer thickness of 0.5–0.7 nm [20]. Moreover, ultrathin sheet-like structures with the size of 200 nm ~ 2 μm of BP nanoflakes were revealed from TEM images on randomly place of carbon-coated copper grid, which is used to hold samples (Fig. 1a and Fig. S5). The crystallinity of the as-prepared BP nanoflakes was studied by high-resolution TEM (HRTEM) (Fig. 1b) and selected-area electron diffraction (SAED) (Fig. 1c). Firstly, clear lattice fringes were observed from BP layers and those of 2.18 Å and 1.65 Å correspond to the *x* and *z* directions, respectively [25]. The SAED image suggests the as-prepared BP nanoflakes to be single crystalline with [010] preferential orientation [25], which is consistent with BP lattice parameters. The uniform lattices (Fig. 1b and c) suggest that the nanoflakes produced by solvent-exfoliation retain the original crystalline state.

Raman spectroscopy is an effective technique for the identification of crystallographic orientation and chemical composition of materials. Herein, Raman spectra were measured to study the structural transformation of BP after liquid exfoliation process (Fig. S6). Bulk BP exhibits characteristic peaks at 362.3, 438.7, 466 cm⁻¹, which assigned to A_g¹, B_{2g}, and A_g² phonon modes of vibration originating from in-plane (B_{2g} and A_g²) and out-of-plane (A_g¹) vibrational modes, respectively [25,32]. On the other hand, these peaks for BP nanoflakes slightly shift to 363.7, 439.4, and 466.7 cm⁻¹, respectively, compared to bulk BP. The similar shifts have been found in the previous reports [25], indicating the successful exfoliation process.

The quality of BP nanoflakes was further analyzed by performing energy-dispersive X-ray spectroscopy (EDX) with the spectra on the SEM and mapping on the HAADF-STEM (Figs. S7 and S8), respectively. Firstly, the as-exfoliated sample showed C, O, and P elements clearly (Fig. S7a). The C and O signals were coming from the carbon gel substrate, which was used for supporting samples during the measurements. Compared with blank comparison, only small amount of P was oxidized after as-exfoliated BP samples were stored for one month. Furthermore, the HAADF-STEM image and corresponding EDX elemental mapping of P, C, and O were detected (Fig. S8). The elemental mapping for phosphorus extracted from the spectrum image confirms that the phosphorus signal is strongly correlated with the nanoflake location and other elements detected are those associated with the TEM grid, suggesting that the nanoflakes produced are consistent with their crystalline nature.

X-ray photoelectron spectroscopy (XPS) spectra of bulk BP and BP nanoflakes were measured (Fig. S9) to further confirm the quality of as-prepared BP nanoflakes. Firstly, in the full spectra of bulk BP and BP nanoflakes, there were some contaminate elements observed beside P element. These contaminate elements are probably originated from environment atmospheres. The control experiment for carbon gel was carried out to show same elements for bulk BP and BP nanoflakes except the P element. The high resolution XPS spectra of P 2p in bulk BP and BP nanoflakes display two bands at *ca.* 129.7 and 130.5 eV, corresponding to P 2p_{3/2} and P 2p_{1/2} binding energies, respectively. Besides, a sub-band is apparent at 134.1 eV, corresponding to oxidized phosphorus (i.e., P_xO_y) [20]. The ratio of oxidized phosphorus (P_xO_y) in BP nanoflakes is higher than that in bulk BP, suggesting that the surface of BP nanoflakes was slightly oxidized after exfoliation process. Furthermore, the O 1s peaks of bulk BP and BP nanoflakes were deconvoluted into peaks for O=C=O (530.6 eV), oxygen (531.6 eV), C=O (532.2 eV), C–OH/C–O–C (532.8 eV), H₂O (533.3 eV), and P–O_x (534.1 eV) [33]. The ratio of P–O_x in BP nanoflakes is also higher than that in bulk BP, further showing the slight oxidation of as-synthesized BP nanoflakes.

As the most infusive properties, the broadband solar absorption of BP nanoflakes makes them to be used as an effective visible and NIR optical material [21–24,30]. To observe the broadband solar absorption property of the as-exfoliated BP nanoflakes, the UV-vis-NIR spectra of different concentration BP aqueous dispersions and the corresponding photograph were shown in Fig. S10. The sample displays a brownish color and a very broad absorption from UV to NIR region. This intrinsic feature indicates that as-prepared BP nanoflakes might have potential application possibilities as visible and NIR light-induced photocatalysts.

The photocatalytic H₂ evolution reactions were performed over BP nanoflakes as photocatalyst under visible and NIR light irradiation with ethylenediaminetetraacetic acid (EDTA) as a sacrificial agent. No H₂ evolution was observed when only bare BP nanoflakes were used in the reaction under light irradiation. Generally, an efficient photocatalytic H₂ evolution system usually consists of a sacrificial agent, photosensitizer, electron mediator, and cocatalyst [34,35]. As known, the most efficient H₂ evolution catalyst is Pt nanoparticles, because Pt has a low overpotential for proton reduction to evolve H₂ [34,35]. However, when we mixed the commercial Pt colloids with BP, trace amount of H₂ was observed. This is probably due to poor electron transfer efficiency between BP and Pt nanoparticles without an electron mediator.

Recently, 2D RGO has been confirmed as an excellent electron mediator for storing and shuttling electrons [36,37]. Accordingly, the Pt/RGO nanocomposites were introduced to the above reaction, where RGO served as an electron mediator and Pt nanoparticles worked as a co-catalyst. The morphology of as-prepared Pt/RGO nanocomposite was studied by TEM. As shown in Fig. 2a, the Pt nanoparticles with the average size of 4.2 ± 0.5 nm were uniformly distributed on the wrinkled RGO surface. Furthermore, the ternary BP/Pt/RGO nanocomposite was obtained *via* mixing the as-prepared Pt/RGO and BP nanoflakes under the ultrasonic process. Fig. 2b clearly shows that the sheet-like Pt/RGO nanostructures were assembled on the surface of 2D BP nanoflakes. To further confirm the formation of the hybridization of BP and Pt/RGO, the HRTEM and EDX mapping on the HAADF-STEM of ternary BP/Pt/RGO nanocomposite. Fig. 2c shows that the evident lattice fringes indicating a lattice spacing of *ca.* 0.227 nm and 0.218 nm, which correspond to the (111) facets of Pt and (020) planes of BP, respectively, could be easily observed in the representative HRTEM images. Meanwhile, the lattice fringes of graphene also easily observed from the HRTEM image. The HAADF-STEM image and corresponding EDX elemental mapping of P and Pt (Fig. 2d–f) clearly show the different element distributed on the surface of the

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