Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2018

**Supporting Information** 

# p-Type BP Nanosheet Photocatalyst with AQE of 3.9% in the Absence of a Noble Metal Cocatalyst: Investigation and Elucidation of Photophysical Properties

Mohammad Z. Rahman<sup>a,c</sup>, Munkhbayar Batmunkh<sup>b</sup>, Munkhjargal Bat-Erdene<sup>b</sup>, Joseph G. Shapter<sup>b\*</sup>, and Charles B. Mullins<sup>a\*</sup>

<sup>a</sup>John J. Mcketta Department of Chemical Engineering and Department of Chemistry The University of Texas at Austin, Austin, Texas 78712, USA E-mail: mullins@che.utexas.edu

<sup>b</sup>Australian Institute of Bioengineering and Nanotechnology (AIBN), University of Queensland, St. Lucia, Queensland 4072, Australia

E-mail: j.shapter@uq.edu.au

<sup>c</sup>School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

#### Synthesis

*Synthesis of phosphorene:* The phosphorene was synthesized using a microwave-exfoliation technique. Briefly, 25 mg of bulk BP was dispersed in 5 mL of N-Methyl-2-pyrrolidone (NMP), and exfoliated using two microwaves (MW) of different power ratings. In the first microwave exfoliation, the mixture was heated in a microwave (StartSYNTH Microwave Synthesis Labstation, Milestone s.r.l) operating at 50 °C with 600 W for 8 min. This step was used to weaken the van der Waals interaction between BP layers. The second microwave step was carried out using CEM Discover SP – MW operating at 70 °C with 220 W for 3 min. This step further exfoliates and separates the BP to provide a yellow dispersion. The supernatant (4 mL) was centrifuged at 6000 rpm for 30 min. Top 70 % of the centrifuged solution was then collected for further analysis and application.

<u>Synthesis of carbon nitride</u>: 5 g of dicyandiamide was placed in a crucible and heated in a muffle furnace up to 550 °C at a rate of 2.3 °C min<sup>-1</sup> for 4.5 h. After cooling down the furnace at a rate of 10 °C min<sup>-1</sup>, yellow agglomerate was collected.

<u>Synthesis of carbon dots</u>: 5 g of citric acid was placed in a crucible and heated in a muffle furnace up to 180 °C at a rate of 5 °C for 40 h followed by subsequent heating up to 320 °C at a rate of 5 °C min<sup>-1</sup> for 100 h. After cooling down the furnace at a rate of 10 °C min<sup>-1</sup>, dark brown carbon dots were collected. These carbon dots were stirred with DI water (300 mL) and NaOH (5 M, 10 mL). The solution then filtered to remove the insoluble particles. The filtered solution was freeze-dried to obtain carbon dots.

<u>Synthesis of phosphorene/(carbon nitride, carbon dots, and red-P)</u>: 1 g of carbon nitride, carbon dots, and red-P were separately dispersed in 25 mL of DI water and stirred to make a suspension. 50  $\mu$ L of phosphorene dispersion was then added to each 25 mL solution and

vigorously stirred. The mixtures were freeze-dried and ball-milled. Red-P was purchased and used without any further modification.

#### **Photo-Physical Characterization**

Atomic force microscopy (AFM) was performed in air using a Bruker Dimension FastScan AFM with Nanoscope V controller while operating in Peak Force Tapping mode or standard tapping mode. Peakforce tapping mode images were acquired using Bruker ScanAsyst-air probes (nominal tip diameter and spring constant is 4 nm and 0.4 N/m respectively) and for tapping mode the probes used were silicon HQNSC15/AIBS Mikromasch probes (nominal tip diameter and spring constant is 16 nm and 40 N/m respectively). The AFM topography images have been flattened, and thickness measurements were made using the section analysis tool of Nanoscope Analysis 1.4. For AFM analysis, the samples were prepared by spin coating the asprepared solutions onto cleaned silicon substrates at 3000 rpm for 20 s. Bright-field transmission electron microscopy (TEM) images were acquired using a FEI Titan Themis at 80 kV accelerating voltage. Samples were dispersed by drop-casting onto quantifoil SQR12-200CU grids at 80 °C in air for ~2 mins until dry, and then immediately transferred to high vacuum storage prior to analysis. Raman spectra were acquired using a LabRAM HR Evolution spectrometer (Horiba Jobin Yvon, Japan) at an excitation laser wavelength of 532 nm with a 40x objective (numerical aperture 0.60). The optical absorption of the as-prepared dispersions of phosphorene was analyzed using a UV-vis-NIR spectroscopy (Perkin Elmer Lambda 950) at wavelengths ranging from 200 nm to 2200 nm. An AXIS ultra-spectrometer (Kratos Analytical Ltd., GB) was used to obtain XPS spectra. Auger electron spectroscopy (AES) (including elemental mapping) and simultaneous Secondary Electron Microscopy was performed on a PHI710 Scanning Auger Nanoprobe. The vacuum pressure in the analysis chamber during analysis was maintained at approximately 10<sup>-10</sup> Torr. A 10 kV electron beam with a beam

3

current of 10 nA was used to produce SEM images and AES data. Elemental maps were obtained at either 512 x 512 or 256 x 256 pixel resolution.

#### **Photocatalytic Test**

Two reactor systems were prepared using three-neck Pyrex flasks to test photocatalytic activities of phosphorene. For the first one, 5 mg of phosphorene photocatalyst was dispersed in 50 mL of DI water, while for the second one, 5 mg of photocatalyst was dispersed in 50 mL of I0 vol. % triethanolamine. To test the cocatalyst activities of phosphorene, 100 mg of each phosphorene/carbon nitride, phosphorene/carbon dots, and phosphorene/red-P was dispersed in 80 mL of 10 vol. % triethanolamine. For comparison purposes, 100 mg of carbon nitride, carbon dots and red-P only were dispersed in 80 mL of 10 vol. % triethanolamine. For comparison purposes, 100 mg of carbon nitride, carbon dots and red-P only were dispersed in 80 mL of 10 vol. % triethanolamine. Afterwards, 3 wt. % H<sub>2</sub>PtCl<sub>6</sub> was added as a source of Pt. In all cases, the openings of the flask were sealed with silicone rubber septa. Following degassing in argon flow for 30 min, the reactor was irradiated by a light source (300 W Xenon arc lamp) mounted with a 420 nm cut-off filter. The evolved gas was sampled through an on-line gas chromatograph (Clarus 480, Perkin-Elmer) every hour and the rate of hydrogen production was quantified. The gas chromatograph (GC) consisted of 5 Å molecular sieve column and a built-in thermal conductivity detector. For GC, Ar was used as a carrier gas. The experiment was carried out at RT and atmospheric pressure.

#### **Electrochemical Characterization**

A working electrode was prepared by coating slurry on fluorine-doped tin-oxide glass electrode (2 cm  $\times$  1.5 cm) and drying in an oven under nitrogen flow (350 °C for 30 min). The slurry was made by grinding 0.1 g of photocatalyst with 0.03 g of polyethylene glycol in 0.5 mL of ethanol. The measured film thickness of the electrode was around 10–11 µm. The Mott–

Schottky measurement was performed using an impedance–potential methods where the frequency was set to 1 kHz over the potential range –0.4 to +0.4 V, and 0.2 M Na<sub>2</sub>SO<sub>4</sub> was used as electrolyte. The experiments were carried out in a three-electrode system electrochemical analyzer (CHI 650D instruments). The prepared sample was used as the working electrode with an active area of about 1.35 cm<sup>2</sup>, a Pt wire as the counter electrode, and Ag/AgCl (saturated KCL) as the reference electrode.

#### **Apparent Quantum Efficiency (AQE) Calculation**

Quantum efficiency was computed following the method described by Liu et al.<sup>1</sup> The catalyst solution was irradiated for 1 h by a 300 W Xe arc lamp using a 420, 450, 500 and 550, nm bandpass filters. The average intensity of irradiation was determined AQE was computed using following equation:<sup>2, 3</sup>

$$AQE = \frac{2 \times number \ of \ evolved \ hydrogen \ molecules}{Number \ of \ incident \ photons} \times 100\%$$
(1)

#### **FDTD** simulation

Lumerical FDTD solutions has been employed to carry out the electromagnetic simulations. Perfectly matched layer (PML) boundary conditions in the x-axis and y-axis was used to set the unit cell of the structure as the simulation region. A plane-wave light source irradiated normally to the device was set to be transverse magnetic (TM) polarized. One monitor was placed between the source plane and device surface in order to detect the device absorption. The current density vectors are collocated at the positions of the electric field vectors.

## Supplementary Figures



Figure S1. Height profile measurements using atomic force microscopy.



Figure S2. XRD pattern of few-layer BP nanosheets.



**Figure S3.** a) TEM image of phosphorene nanosheets, scale bar 200 nm. b) High resolution TEM images, and corresponding c) SAED pattern.



**Figure S4.** Chemical composition of BP nanosheets. This image has been reproduced with permission from our previous publication.<sup>4</sup>



**Figure S5.** Absorption spectrum of phosphorene when subjected to illumination from continuous electro-magnetic light source in FDTD simulations.



Figure S6. XRD and XPS spectra of the BP nanosheets before and after photocatalytic reactions.

#### **Supplementary Note 1: Principles of Optical Absorption Calculation**

Following Maxwell's equations are embedded in Lumeric FDTD solutions software to simulate the optical absorption.

$$\nabla . \boldsymbol{D}(t) = \rho(t) \tag{2}$$

$$\nabla \boldsymbol{B}(t) = 0 \tag{3}$$

$$\nabla \cdot \boldsymbol{E}(t) = -\frac{\partial \boldsymbol{B}(t)}{\partial t} \tag{4}$$

$$\nabla \cdot \boldsymbol{H}(t) = \boldsymbol{J}(t) - \frac{\partial \boldsymbol{D}(t)}{\partial t}$$
(5)

Where **D**, **E**, **H**, **B** and **J** represent the electric displacement vector, electric field intensity, magnetic field intensity, magnetic induction, and current density, respectively.

The Poynting vector **S** was calculated as follows:

$$S = \frac{1}{2} Re(\boldsymbol{E} \times \boldsymbol{H}^*)$$
(6)

The divergence of the Poynting vector **P** was calculated as follows:

$$P = -\nabla . S \tag{7}$$

$$P = -\frac{1}{2} \cdot \omega \cdot |\mathbf{E}| \cdot Imag(\epsilon)$$
(8)

Where  $\omega$  is the angular frequency of the light,  $\varepsilon$  is the permittivity which can be calculated from the refractive index **n** and the extinction coefficient **k**:

Real $(\epsilon) = n^2 - \kappa^2$	(9)
$Imag(\epsilon) = 2. n. \kappa$	(10)

#### Supplementary Note 2: BP as a Cocatalyst

In photocatalytic hydrogen production, cocatalysts typically play crucial roles in enhancing the activity of a photocatalyst. Incorporation of a suitable cocatalyst brings three advantageous attributes that favor the overall redox reactions. These attributes include (i) lowering the activation energy for redox reactions, (ii) assisting in separation of electron-hole pairs at the interface, and (ii) suppressing photo-corrosion which increases the stability of the photocatalyst. Therefore over the years many cocatalysts have been developed. Transition metals (Pt, Cu, Ni, Co etc.), and their oxides, hydroxides, and sulfides are most commonly used as cocatalysts.<sup>5</sup> Pt dominates among all cocatalysts because of its low activation energy and fast charge transport abilities. However, these metal based cocatalysts are sometimes not cost-effective for hydrogen production. Clearly, earth abundant metal-free cocatalysts are as important as metal-free photocatalysts for low-cost and sustainable hydrogen production. Here we assess the efficacy of standalone phosphorene as a co-catalyst for proton reduction.

Recently, Ran et al. has demonstrated that phosphorene could lead to an increased reduction/oxidation activity for CB electrons and VB holes, a decrease in electron-hole recombination probability, and production of much more exposed sites with strong electron coupling.<sup>6</sup> These properties are favorable for proton reduction co-catalysts. Indeed, when phosphorene was incorporated in zinc-cadmium-sulfide (ZCS), it significantly augmented the hydrogen quantum yield for this system.

We have extended the use of phosphorene as a cocatalyst for a number of metal-free photocatalysts, such as polymeric carbon nitride (CN), red-P, and carbon dots (CD). We have chosen these metal-free photocatalysts because they showed zero or insignificant hydrogen production in absence of a noble metal-cocatalysts. Carbon nitride and carbon dots are synthesized following procedures described elsewhere, while red-P was purchased and used

10

without any modification.<sup>7, 8</sup> The phosphorene is incorporated in these materials by freezedrying followed by a ball-milling.

The influence of phosphorene as a cocatalyst in photocatalytic hydrogen production is shown in Figure. S7. Noticeably, the addition of phosphorene enhanced the hydrogen production from these materials. For example, carbon nitride showed ~ 4.5 times greater H<sub>2</sub> production, while red-P showed ~6 times greater hydrogen production when phosphorene was added. Standalone carbon dots showed no activity but hydrogen production was observed when incorporated with phosphorene. These results demonstrate the effectiveness of phosphorene as a suitable cocatalyst.



**Figure S7.** Hydrogen production activities of phosphorene cocatalyst when incorporated with carbon nitride (CN), carbon dots (CD) and red phosphorus (red-P) under visible light irradiation (420 nm). Experimental conditions: 100 mg of photocatalyst was dispersed in 10 vol. % triethanolamine-water solution and irradiated by a 300 W Xenon arc lamp for an hour.

The enhancement in hydrogen production on CN, red-P and CDs with phosphorene is partly due to the influence of the heterojunction formed between them. This heterojunction leads to delocalization of electrons, and therefore inhibits the recombination of electrons with holes. It consequently increased the availability of electrons for the proton reduction reaction for evolving hydrogen.<sup>3, 9</sup>

We also compared the efficiency of phosphorene with the widely used Pt cocatalyst. Although, red-P and carbon-dots showed greater hydrogen production with Pt than phosphorene, carbon nitride showed almost comparable performances (see Figure S8 – S10). It is a promising result to use phosphorene as a noble-metal substituted co-catalyst for photocatalytic hydrogen production. More importantly, phosphorene as a co-catalyst showed stable hydrogen production for ~72 h when incorporated with carbon nitride, red-P, and carbon dots, respectively (see Figure S11 and S12). This indicates that phosphorene becomes well passivated in the presence of other materials, and therefore showed strong resistance against degradation agents (i.e. water, light and air).



**Figure S8.** Comparison of hydrogen production rate using carbon nitride alone, with phosphorene and with Pt cocatalyst.



**Figure S9.** Comparison of hydrogen production rate using carbon dot alone, with phosphorene and with Pt cocatalyst.



**Figure S10.** Comparison of hydrogen production rate with red-p alone, with phosphorene and with Pt cocatalyst.



**Figure S11.** Time course of hydrogen production using CN, CDs and red-P in presence of phosphorene under visible light irradiation. The production rate of evolved gas was measured with GC after each hour of irradiation. After 4 h, the reaction system was evacuated under Ar gas flow for 45 min to remove the evolved gas inside the flask for next time course of hydrogen production.



**Figure S12**. The 18<sup>th</sup> time course of hydrogen production in CN, CDs and red-P in presence of phosphorene. Before re-irradiation under visible light, the evolved gas was evacuated under the Ar flow for 45 min after 17<sup>th</sup> time course of hydrogen production.

Photocatalyst	Cocatalyst	Light	HER	AQE	Ref.
		Source/Filter	(µmol h⁻¹)	(%)	
BP-	-	300W/420 nm	17.92	~4	This
nanosheets					work
BP-	-	300W/420 nm	0.37	-	10
nanosheets					
BP-	20 wt.% Pt	300W/420 nm	11.17	~4	10
nanosheets					
Bulk BP	-	300W/420 nm	0.14	-	11
BP-	-	300W/420 nm	2.56	0.47	11
nanosheets					

**Table S1** Comparison of hydrogen production rate and AQE in standalone BP photocatalysts.

### References

- 1. J. Liu, Y. Liu, N. Liu, Y. Han, X. Zhang, H. Huang, Y. Lifshitz, S.-T. Lee, J. Zhong and Z. Kang, *Science*, 2015, **347**, 970-974.
- 2. M. Z. Rahman, Y. Tang and P. Kwong, *Applied Physics Letters*, 2018, **112**, 253902.
- 3. M. Z. Rahman, J. Zhang, Y. Tang, K. Davey and S.-Z. Qiao, *Mater. Chem. Front.*, 2017, **1**, 562-571.
- M. Bat-Erdene, M. Batmunkh, C. J. Shearer, S. A. Tawfik, M. J. Ford, L. Yu, A. J. Sibley, A. D. Slattery, J. S. Quinton, C. T. Gibson and J. G. Shapter, *Small Methods*, 2017, 1, 1700260.
- 5. J. Ran, J. Zhang, J. Yu, M. Jaroniec and S. Z. Qiao, *Chemical Society Reviews*, 2014, **43**, 7787-7812.
- 6. J. Ran, B. Zhu and S. Z. Qiao, *Angew Chem Int Ed Engl*, 2017, **56**, 10373-10377.

- 7. M. Z. Rahman, P. C. Tapping, T. W. Kee, R. Smernik, N. Spooner, J. Moffatt, Y. Tang, K. Davey and S.-Z. Qiao, *Advanced Functional Materials*, 2017, **27**, 1702384.
- 8. B. C. M. Martindale, G. A. M. Hutton, C. A. Caputo, S. Prantl, R. Godin, J. R. Durrant and E. Reisner, *Angewandte Chemie International Edition*, 2017, DOI: 10.1002/anie.201700949.
- 9. M. Zhu, S. Kim, L. Mao, M. Fujitsuka, J. Zhang, X. Wang and T. Majima, *J Am Chem Soc*, 2017, **139**, 13234-13242.
- 10. B. Tian, B. Tian, B. Smith, M. C. Scott, Q. Lei, R. Hua, Y. Tian and Y. Liu, *Proc Natl Acad Sci U S A*, 2018, **115**, 4345-4350.
- 11. X. Zhu, T. Zhang, Z. Sun, H. Chen, J. Guan, X. Chen, H. Ji, P. Du and S. Yang, *Adv Mater*, 2017, **29**.