

Journal of Materials Chemistry A

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COMMUNICATION

A black/red phosphorus heterostructure for efficient visible-light-driven photocatalysis

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

A new single elemental heterostructure of black and red phosphorus was prepared by a simple ball milling method. The product exhibited high visible-light-driven photocatalytic activity comparable to that of CdS.

Designing efficient visible-light-driven (VLD) photocatalysts has been an intensively pursued topic in materials chemistry.¹⁻⁶ An ideal photocatalyst should be environmentally friendly that it would not release toxic materials during its lifetime.⁷ This can be achieved by replacing traditional photocatalysts with nonmetal ones such as silicon,⁸ selenium,⁹ red phosphorus,¹⁰ sulfur^{11,12} and boron¹³. The metal-free elemental photocatalysts have unique advantages of low cost, abundant and easily available, showing great potential for practical applications. However, the study of elemental photocatalysts is still in its infancy, and to achieve a high efficiency is a great challenge.⁸⁻¹³ Black phosphorus is an elemental material that has attracted wide interest in the fields of rechargeable batteries¹¹ and electronic devices¹⁵. The layered black phosphorus (and phosphorene) has greatly excited the scientific world as a novel field-effect transistors (FETs) material.^{16,17} These recent reports reveal that black phosphorus has a tunable band gap, high charge carrier mobility and low toxicity. Such properties are very attractive for photocatalytic applications.

Herein, we report a new single elemental heterostructure composed of black phosphorus and red phosphorus (denoted as “BP-RP”). The in-situ growth of black phosphorus in red phosphorus matrix gave rise to an excellent interfacial contact. Their difference in energy levels and high charge carrier mobility of black phosphorus facilitates charge separation and transfer. Therefore, it exhibits VLD photocatalytic activity comparable to that of CdS but with much lower toxicity. A mechanism for its superior activity is proposed based on experimental results and Density functional theory (DFT) calculations. This work demonstrates the great potential of simple metal free VLD photocatalysts. Moreover, the in-situ formation of elemental heterostructure would be a useful route for improving other metal free elemental photocatalysts.

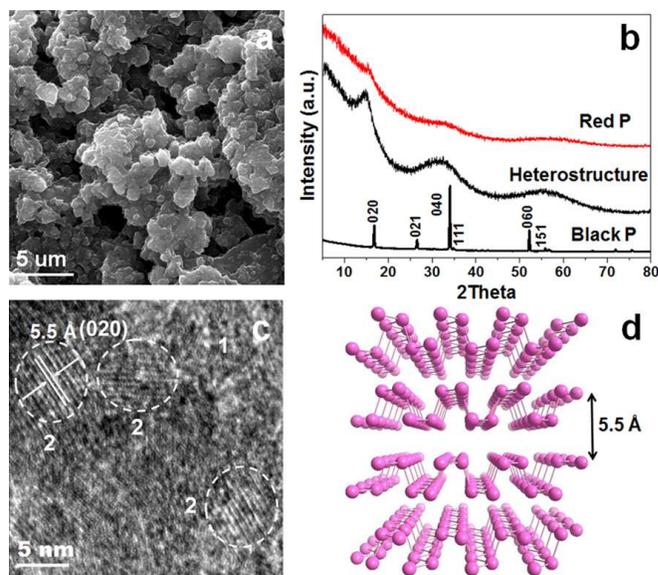


Fig. 1 (a) SEM image, (b) XRD pattern and (c) HRTEM image of BP-RP heterostructure. In (b), the XRD patterns of pure red phosphorus and black phosphorus were shown as the references; in (c) the white circles highlighted the black phosphorus nanoparticles, and 1-amorphous red phosphorus, 2-black phosphorus nanoparticles; (d) layered structure of black phosphorus. “P”: phosphorus.

This BP-RP heterostructure was prepared by a facile mechanical ball milling method using commercial red phosphorus as the precursor (details in ESI). During the milling process, the high pressure and temperature generated by drastically clashing could induce the phase transformation of red phosphorus.¹⁴ By selecting proper rotation speed and time, the black phosphorus could in-situ grow from the red phosphorus. A typical SEM image (Fig. 1a)

shows that the as-prepared BP-RP heterostructure (milling for 2h, 450 rounds/min) was composed of microparticles with the size of ~ 1 μm . Unlike the pure red phosphorus, its XRD pattern (Fig. 1b) displays the main characteristic of pure black phosphorus (JCPDS NO. 73-1358) with three wide and overlapped peaks centered at $\sim 15^\circ$, $\sim 30^\circ$ and 55° . This phenomenon suggests the presence of small crystal size of black phosphorus in the heterostructure according to the Scherer rules, which is further confirmed by its HRTEM image. As shown in Fig. 1c, most of the black phosphorus nanoparticles are less than 10 nm. Some of them display a layered structure with the interlayer spacing of 5.5 Å (*d*-spacing of (020) crystal lattices), which is typical for black phosphorus (Fig. 1d).¹¹⁻¹⁴ The EDX results show that the heterostructure is composed of phosphorus element (ESI, Fig. S1), and only pure amorphous red phosphorus was used as the starting material. It is known that red phosphorus exists in the amorphous phase among the stable allotropes of elemental phosphorus.^{14, 18, 19} Therefore, "Region 1" in Fig. 1c is denoted as the amorphous red phosphorus. Several parts in the low resolution TEM image are also enlarged, and it is found that the small black phosphorus particles are embedded in amorphous red phosphorus (ESI, Fig. S2). Results from TGA measurements show approximately 50 wt% of black phosphorus in the heterostructure (ESI, Fig. S3).

To further study the chemical natures of the BP-RP heterostructure, its FT-IR and XPS spectra were recorded (ESI, Fig. S4 and Fig. S5). As shown in Fig. S4, the heterostructure displays IR characteristics similar to those of pure red and black phosphorus. The broad absorption bands centered at ~ 1000 cm^{-1} and ~ 1200 cm^{-1} can be ascribed to the P-O stretching²⁰ and P-P-O linear stretching modes²¹, while the small peak at ~ 1620 cm^{-1} is assigned to the P=O stretching mode²⁰. The XPS spectrum shows that its surface is mainly composed of P^0 atoms (129.8 eV)²² and a small amount of P^{5+} atoms (134.4 eV)²² (ESI, Fig. S5).

This as-prepared BP-RP heterostructure has a dark grey colour that is very different from the red phosphorus (Fig. 2 inset). The heterostructure exhibits stronger absorption from 600 to 800 nm as compared to red phosphorus (Fig. 2). Results from photocurrent response measurements under visible light irradiation ($\lambda > 420$ nm) show an obvious on-off photocurrent curve (ESI, Fig. S6). This confirms the generation of electrons and holes on the BP-RP heterostructure.

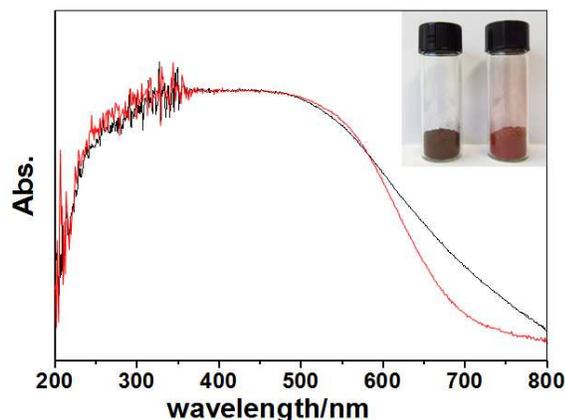


Fig. 2 UV-Vis diffuse reflectance spectra of the BP-RP heterostructure (grey) and pure red phosphorus (red).

The degradation of 10 ppm Rhodamine B (RhB) under visible light irradiation was monitored to evaluate the photocatalytic activity of BP-RP heterostructure (Fig. 3 and ESI, Fig. S7). As shown in Fig. 3a, during the first 30 minutes irradiation, 89 % RhB was degraded over the BP-RP heterostructure, while only 57 % RhB was degraded over the pure red phosphorus. After prolonging the reaction to 120 min, the RhB degradation efficiencies over BP-RP heterostructure and pure red phosphorus were 95 % and 76 %, respectively. The apparent rate constant for the degradation of RhB was calculated by the following equation: $k = \ln(C_0/C)/t$.²³ The BP-RP heterostructure showed nearly 2.87 times apparent reaction rate compared with that of pure red phosphorus (0.069 min^{-1} vs. 0.024 min^{-1}) in the initial 30 minutes of the reaction (ESI, Fig. S8). This suggested that the in-situ formation of black phosphorus nanoparticles in red phosphorus could efficiently improve the photocatalytic activity of the whole heterostructure. In addition, the stability of the BP-RP heterostructure was evaluated, and 85 % activity was maintained after three cycles (Fig. 3b). To further illustrate the strong photocatalytic activity of the BP-RP heterostructure, the degradation of RhB over CdS (known by its high visible-light efficiency²⁴) was also studied for comparison. Results show that the BP-RP heterostructure has higher photocatalytic activity than CdS especially during the first 30 minutes (Fig. 3a, 89% vs. 32%; *k* value, 0.069 min^{-1} vs. 0.0105 min^{-1} , ESI, Fig. S8). Since the phosphorus-based catalyst does not release toxic metals during photocatalysis, it has an obvious advantage over CdS. Therefore, our BP-RP heterostructure should have great potential for efficient environmental remediation.

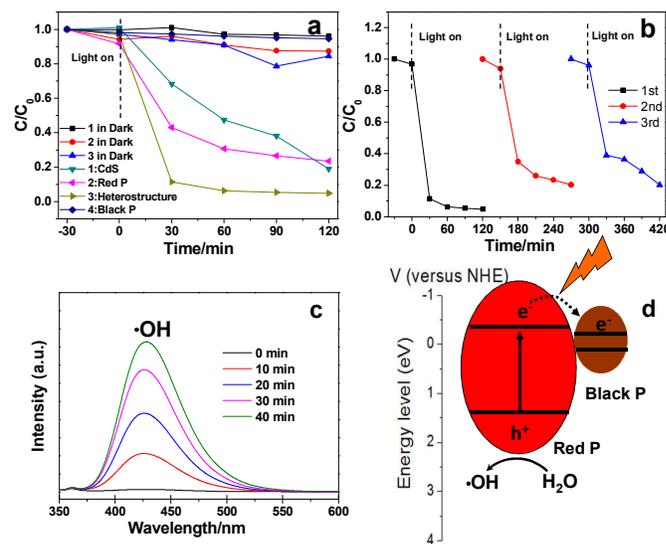


Fig. 3 (a) VLD photocatalytic degradation of RhB over CdS, red phosphorus and BP-RP heterostructure and their dark control curves; (b) recycled photocatalytic degradation of RhB under the irradiation of visible light over BP-RP heterostructure; (c) Time dependent fluorescence spectra for BP-RP heterostructure; (d) schematic illustration showing the mechanism for its enhanced charge separation and transfer. "P": phosphorus.

The photocatalytic performance of pure black phosphorus was also tested, but it showed almost no activity. This further confirmed the role of the heterostructure (Fig. 3a). Moreover, other BP-RP heterostructures were prepared by changing the milling time (45 min: ~ 30 wt % black phosphorus; 12 h: ~ 70 wt% black phosphorus, ESI,

Fig. S9). However, both of them displayed weaker activity than the one described above (~50 wt % black phosphorus, ESI, Fig. S10), which indicated two points: i) only the quantity of black phosphorus was high enough, the heterostructure would exhibit high efficiency; ii) if the quantity of black phosphorus was too high, its possible shield effect for red phosphorus would reduce the activity of heterostructure. With a relatively small amount of black phosphorus (e.g. 30 wt %) in the system, only partial red phosphorus can form heterostructure with it. So the improvement of efficiency is not obvious (61 % degradation of RhB after 30 min, ESI, Fig. S10). If the quantity of black phosphorus becomes too high (e.g. >70 wt %), they will absorb most of the incident light, but they can't efficiently generate light excited charge carriers (Fig. 3a, curve 4). Meanwhile, the light absorption of red phosphorus is not high. So the excited charge carriers on the red phosphorus will decrease, which brings about a reduced efficiency for the heterostructure (62 % degradation of RhB after 30 min, ESI, Fig. S10).

A fluorescence method was used to detect the formation of hydroxyl radicals.¹⁰ The increasing fluorescence intensities confirm the involvement of OH radicals in the photocatalytic pathway (Fig. 3c). Generally, photocatalytic treatment would benefit from an increased adsorption of pollutants, an enhanced light absorption and an efficient charge separation and transfer. While the BP-RP heterostructure shows a slightly enhanced visible light absorption (Fig. 2), its ability to adsorb pollutants is virtually the same as that of pure red phosphorus (Fig. 3a). Therefore, the efficient charge separation and transfer must be the dominant factor for its high activity. In our previous study, the energy band structure of pure red phosphorus was determined to be -0.32 eV (vs. NHE) for conduction band (CB) and 1.38 eV (vs. NHE) for valence band (VB).¹⁰ Herein, the energy band structure of black phosphorus is calculated to be -0.26 eV (vs. NHE) for CB and 0.06 eV (vs. NHE) for VB based on the DFT method (details in ESI, Fig. S11). As the CB is 0.06 eV lower than that of pure red phosphorus, it would facilitate the transfer of excited electrons from CB of red phosphorus to the CB of black phosphorus. Although the difference in their CB is not so large, the high charge carrier mobility of black phosphorus could probably promote this process.^{16, 17} The combined effect of efficient charge separation and transfer makes the BP-RP heterostructure a superior VLD photocatalyst (Fig. 3d).

In summary, a single elemental heterostructure composed of red phosphorus and black phosphorus has been prepared for the first time. The heterostructure exhibits photocatalytic activity comparable to that of CdS under visible light irradiation. This work offered a potential metal free photocatalyst with high efficiency and low toxicity. Moreover, the simple in-situ fabrication method would inspire the study of other elemental heterostructure for photocatalytic applications.

Acknowledgements

This work was partially supported by the Shenzhen Basic Research Scheme (JCYJ20120619151417947) and a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China, under Theme-based Research Scheme through Project No. T23-407/13-N. The authors are grateful for getting the black phosphorus from Prof. Bo Song at Harbin Institute of Technology.

Notes and references

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Electronic Supplementary Information (ESI) available: [Experimental sections and other supporting data.] See DOI: 10.1039/c000000x/

- 1 D. M. Schultz and T. P. Yoon, *Science*, 2014, **343**, 985.
- 2 M. Manikandan, T. Tanabe, P. Li, S. Ueda, G.V. Ramesh, R. Kodiyath, J. J. Wang, T. Hara, A. Dakshnamoorthy, S. Ishihara, K. Ariga, J. H. Ye, N. Umezawa and H. Abe, *ACS Appl. Mater. Interfaces* 2014, **6**, 3790-3793.
- 3 X. Lang, X. D. Chen and J. C. Zhao, *Chem. Soc. Rev.*, 2014, **43**, 473-486.
- 4 Z. F. Hu and J. C. Yu, *J. Mater. Chem. A* 2013, **1**, 12221 – 12228.
- 5 H. G. Kim, D. W. Hwang and J. S. Lee, *J. Am. Chem. Soc.* 2004, **126**, 8912–8913.
- 6 J. C. Yu, W. K. Ho, J. G. Yu, H. Yip, P. K. Wong and J. C. Zhao, *Environ. Sci. Technol.* 2005, **39**, 1175–1179.
- 7 X. C. Wang, K. Maeda, A. Thomas, K. Takanebe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater.*, 2009, **8**, 76-80.
- 8 Z. H. Kang, C. H. A. Tsang, N. B. Wong, Z. D. Zhang and S. T. Lee, *J. Am. Chem. Soc.* 2007, **129**, 12090–12091.
- 9 Y. D. Chiou and Y. J. Hsu, *Appl. Catal. B: Environ.* 2011, **105**, 211–219.
- 10 F. Wang, W. K. H. Ng, J. C. Yu, H. J. Zhu, C. H. Li, L. Zhang, Z. F. Liu and Q. Li, *Appl. Catal. B: Environ.* 2012, **111–112**, 409–414.
- 11 G. Liu, P. Niu, L. C. Yin and H. M. Cheng, *J. Am. Chem. Soc.* 2012, **134**, 9070–9073.
- 12 W. C. Peng and X. Y. Li, *Nano Research* 2013, **6**, 286–292.
- 13 G. Liu, L. C. Yin, P. Niu, W. Jiao and H. M. Cheng, *Angew. Chem. Int. Ed.* 2013, **52**, 6242–6245.
- 14 C. M. Park and H. J. Sohn, *Adv. Mater.* 2007, **19**, 2465–2468.
- 15 J. Dai and X. C. Zeng, *J. Phys. Chem. Lett.* 2014, **5**, 1289–1293.
- 16 L. K. Li, Y. J. Yu, G. J. Ye, Q. Q. Ge, X. D. Ou, H. Wu, D. L. Feng, X. H. Chen and Y. B. Zhang, *Nat. Nano.* 2014, **9**, 372-377.
- 17 H. Liu, T. N. Adam, Z. Zhu, Z. Luo, X. F. Xu, D. Tománek and P. D. Ye, *ACS Nano*, 2014, **8**, 4033–4041.
- 18 W. L. Roth, T. W. Dewitt and A. J. Smith, *J. Am. Chem. Soc.* 1947, **69**, 2881.
- 19 J. A. Young, *J. Chem. Educ.*, 2004, **81**, 945.
- 20 M. Ceppatelli, S. Fanetti and R. Bini, *J. Phys. Chem. C* 2013, **117**, 13129–13135.
- 21 H. B. Qian, P. B. Davies and P. A. Hamilton, *J. Chem. Soc. Faraday Trans.*, 1995, **91**, 2993-2998.
- 22 U. Braun and B. Schartel, *Macromol. Chem. Phys.* 2004, **205**, 2185–2196.
- 23 X. Q. An, J. C. Yu, F. Wang, C. H. Li and Y. C. Li, *Applied Catalysis B: Environ.* 2013, **129**, 80–88.
- 24 Y. Hu, X. H. Gao, L. Yu, Y. R. Wang, J. Q. Ning, S. J. Xu and X. W. D. Lou, *Angew. Chem. Int. Ed.* 2013, **52**, 5636–5639.

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