A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
GDCh
International Edition
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Accepted Article

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201906416
Angew. Chem. 10.1002/ange.201906416

Link to VoR: http://dx.doi.org/10.1002/anie.201906416
http://dx.doi.org/10.1002/ange.201906416

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Angewandte Chemie International Edition 10.1002/anie.201906416

Direct Z-Scheme Hetero-phase Junction of Black/Red Phosphorus for Photocatalytic Water Splitting

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Abstract: Black phosphorus (BP) has recently drawn tremendous attention in photocatalysis for its excellent optical properties. However, limited by the rapid recombination of photogenerated carriers, the use of BP for photocatalytic water splitting still remains a huge challenge. Herein, we fabricate a black/red phosphorus (BP/RP) hetero-phase junction photocatalyst by a wet-chemistry method to successfully promote the interfacial charge separation and thus achieve Z-scheme photocatalytic water splitting without using sacrificial agents. The Z-scheme mechanism was unambiguously confirmed by time-resolved transient absorption spectroscopy. This work provides a novel insight into the interface design of hetero-phase junction with atomic precision.

Solar-to-hydrogen (H_2) conversion has been considered as an attractive and sustainable technique to solve the environmental issues and global energy crisis. Since the pioneer work reported by Fujishima and Honda on photoelectrochemical water splitting using a TiO_2 electrode,[1] various semiconductor photocatalysts have been explored in this field. In particular, metal-free photocatalysts such as graphitic carbon nitride (g-C_3N_4), have attracted increasing attention in recent years, because they are generally earth abundant, low toxic and environmentally friendly.[2] However, the solar-to-hydrogen efficiency of these photocatalysts is still far from the threshold of industrial applications. Therefore, it is highly desired to develop novel metal-free high-performance photocatalysts for water splitting.

Recently, black phosphorus (BP), as an emerging 2D material, has shown promising potential in photocatalytic solar energy conversion owing to its anisotropic layered structure, layer-dependent direct bandgap, and superior carrier migration characteristics.[3] Especially, the adjustable direct-band-gap enables BP as an efficient photocatalyst for water splitting with wide response in the solar light spectrum.[4] However, due to the rapid recombination of photogenerated carriers, the observed H_2 evolution rate by bare BP is very low.[5] To overcome this drawback, BP-based heterostructure systems have been proved to be effective for boosting the separation of photogenerated carriers.[6] Particularly, the construction of Z-scheme systems can not only achieve complementary light absorption and efficient separation of photogenerated carriers, but also reserve their strong photoredox properties for catalytic reactions.[7] However, the construction of Z-scheme based on exfoliated BP nanosheets still suffers from the following issues: 1) the preparation of BP nanosheets from bulk BP is a complicated and time-consuming process; 2) low charge transfer efficiency between the different semiconductors due to poor interface contacts.

Herein, we design and construct a BP/RP hetero-phase junction photocatalyst by a one-step wet-chemistry method. The two semiconductors for hetero-phase junction have the same chemical composition but different crystal lattices, therefore providing an opportunity to build a perfect interface with atomic precision. We note that this strategy has been previously used to promote charge separation in both anatase-rutile TiO_2 and α-β Ga_2O_3 hetero-phase junction.[8] In our current case, the BP/RP photocatalysts are successfully obtained and can be well-dispersed in water to achieve efficient visible light-driven Z-scheme water splitting without using any sacrificial agents. Benefiting from their appropriate band structures with a staggered alignment and high-quality interfacial contacts forming from the in situ growth of BP into the matrix of RP, the efficient separation and transfer of photogenerated electrons and holes can be realized and thus enable the water reduction and oxidation reactions to occur in BP and RP, respectively.

The BP/RP hetero-phase junction was in situ constructed with bulk RP as a feedstock and ethylenediamine as the solvent (Scheme S1, Supporting Information). The detailed experimental procedures and optimal reaction conditions are provided in the Supporting Information (Figure S1 and S2, Table S1). It should be stressed that solvents play a crucial role in the phase transformation process. The RP transformed to BP successfully only in primary diamine solvents (for example, ethylenediamine and diethylenetriamine) but failed in solvents including H_2O, alcohols and other amines. We infer that the polymeric RP chain can be expanded, activated and cleaved by the intercalation effect of diamine solvents.[9] The energy-dispersive X-ray (EDX) results show that the products mainly consist of P element (Figure S3). Further, Raman spectra prove that both RP and BP exist in the hetero-phase junction. As shown in Figure 1a, three characteristic peaks of BP are found at 361.5, 443.4 and 470.2 cm^{-1}, attributed to the A_g^1 (out-of-plane mode), B_{2g} and A_g^2 (in-plane mode) of BP, respectively.[10] And the peaks at 345.7, 385.2-400.8 and 451.3 cm^{-1} can be indexed to the fundamental

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10.1002/anie.201906416

mode (B_1), symmetric stretch modes (A_1) and degenerate mode (E_1) of RP, respectively.[11] Based on thermogravimetric analysis (TGA), the content of BP is estimated to be about 10 wt% (Figure S4).[12] Due to the amorphous nature of RP, X-ray diffraction (XRD) patterns of the as-prepared samples only display the characteristic of orthorhombic (Cmca) crystal structure of BP (JCPDS no. 76-1967) (Figure 1b).[13]

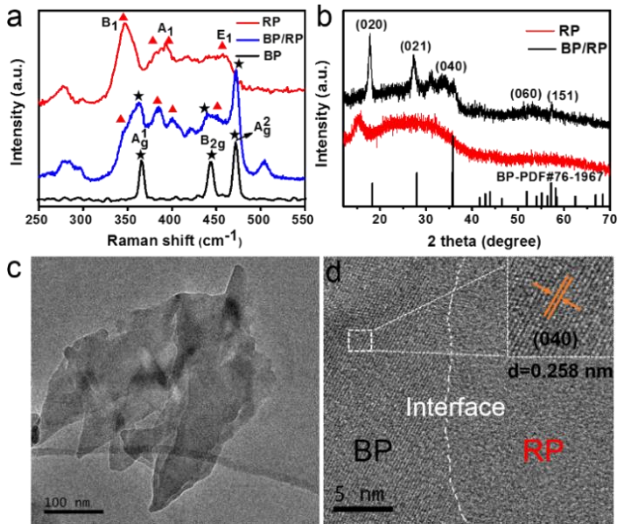

Figure 1. a) XRD patterns, b) Raman spectra, c) TEM image and d) HRTEM image of the BP/RP hetero-phase junction, inset: a high-resolution magnified picture.

The morphologies of the as-prepared BP/RP hetero-phase junction were characterized by transmission electron microscopy (TEM) and atomic force microscopy (AFM). TEM images clearly show an ultrathin sheet-like structure with size ranging from 50 to 200 nm (Figure 1c and S5). AFM images reveal that the samples possess a thickness of about 6 nm (Figure S6). High-resolution TEM analysis gives direct evidence for the formation of hetero-phase junction. The distinct lattice fringes are observed with a d-spacing of 0.258 nm, assigned to (040) planes of BP crystal (Figure 1d).[14] Obviously, high-quality interfacial contacts are formed in BP/RP hetero-phase junction, in which crystallized BP interlaced with amorphous RP. Such phase junction is achieved by covalent bonds at the atomic level rather than van der Waals forces, which can maximize the separation and transfer of photogenerated carriers.

To further determine the chemical composition of the BP/RP hetero-phase junction, we measured its X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR). The XPS survey spectrum affirms the main existence of elemental P in BP/RP (Figure S7a). High-resolution P_{2p} XPS spectra show two narrow peaks located at 129.6 and 130.5 eV, which are assigned to elemental P $2p_{3/2}$ and $2p_{1/2}$ (Figure S7b).[15] A weak and broad sub-band for oxidized phosphorus species (P_xO_y) is apparent at ~133.2 eV, which is also confirmed by the corresponding FT-IR spectra (Figure S8).[5b] These results imply that partial oxidation happened on the surface of BP/RP, in accordance with its low zeta potential value of –39.2 mV (Table S2). Note that the moderate surface oxidation can enhance the hydrophilicity and dispersibility of samples in water (Figure S9).

Then, the light-harvesting capability of the BP/RP hetero-phase junction was investigated by UV-Vis diffuse reflectance spectra (DRS). As shown in Figure 2a, the absorption edge of RP appears at about 680 nm, while BP nanosheets display a very wide absorption from the UV to NIR region with absorption edge located at about 1000 nm. For the BP/RP hetero-phase junction, the absorption edge extends to 900 nm with intense tail absorption in the NIR region. Compared with RP, the absorption edge of BP/RP exhibits an obvious redshift, which reveals a strong interfacial interaction between BP and RP in the BP/RP hetero-phase junction.[6c, 7d]

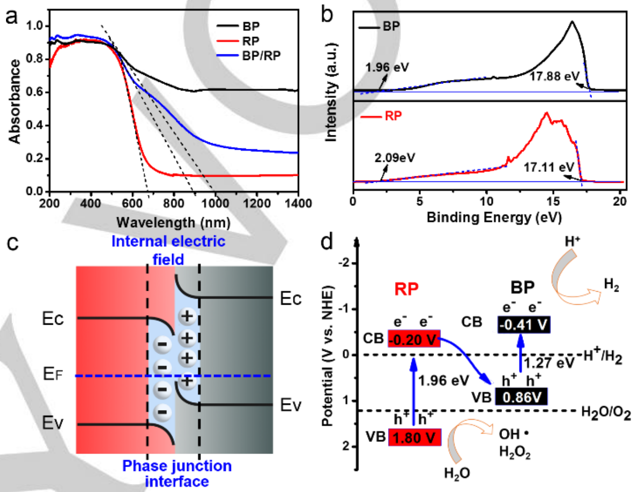

Figure 2. a) UV-vis DRS spectra. b) UPS spectra. c) The energy band offsets diagram and hetero-phase junction interface charge property. d) Schematic illustration of direct Z-scheme charge transfer pathway.

Appropriately aligned band structures are critical to achieve photocatalytic water splitting. We thus take use of Tauc plots and ultraviolet photoelectron spectra (UPS) to determine the band structures of BP and RP. Based on Tauc plot equation: $[(\alpha h\nu)^2 = A(h\nu - E_g)]$, the band gap values ($E_g$) of BP and RP nanosheets are estimated to be about 1.27 and 1.96 eV, respectively (Figure S10). The UPS spectra of BP and RP nanosheets are shown in Figure 2b. According to the linear intersection method, the maximum valence band values (E_{VB}) of BP and RP are determined to be 0.86 and 1.76 V (vs. NHE), respectively (Figure S11).[16] Correspondingly, the conduction band values (E_{CB}) of the BP and RP are –0.41 and –0.20 V (vs.NHE) by formula $E_{CB} = E_{VB} - E_g$.

Meanwhile, the work functions (Φ) of BP and RP are determined to be about 3.34 and 4.11 eV, respectively (Figure S10). Since the charge transfer process at the interface of two semiconductors is dependent on their work functions, the electrons in BP will flow to RP through the hetero-phase junction until their Fermi levels reach an equilibrium,[7c, 17] Hence, the BP layer will remain positive charges, and accordingly, the RP layer will accumulate negative charges (Figure 2c). Consequently, an internal built-in electric field directed from RP to BP at the phase junction interface is formed, which benefits the separation and transfer of photogenerated carriers via the Z-scheme pathway. Adversely, a traditional type II charge transfer pathway requires more energy due to band bending and internal electric field, which is not conducive to continual charge transfer in thermodynamics (Figure S12). The BP/RP hetero-phase junction

10.1002/anie.201906416
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with Z-scheme charge transfer pathway can also be supported by photoelectrochemical measurements (Figure S13).[18] According to the aforementioned results, the energy band alignment of BP can match well with RP to form a valid direct Z-scheme photocatalytic system (Figure 2d). The photogenerated electrons in the CB of RP can readily recombine with the photogenerated holes in the VB of BP at the hetero-phase junction interface. As a result, the strong reducibility of electron in the CB of BP and oxidizability of holes in the VB of RP are retained to drive redox reactions.

To thoroughly clarify the efficient interfacial charge transfer within the hetero-phase junction via a direct Z-scheme pathway, time-resolved transient absorption spectra (TAS) of samples were performed under 400 nm excitation to track the real-time photogenerated carrier dynamics.[6c, 7d, 19] Usually, the surface-trapped electrons peaks of TAS are at 500-1500 nm.[7d, 20] As shown in Figures 3a-c, broad absorption bands centered at 550 nm were observed, the concentration of photogenerated carrier decayed in a multi-exponential manner because of charge recombination.

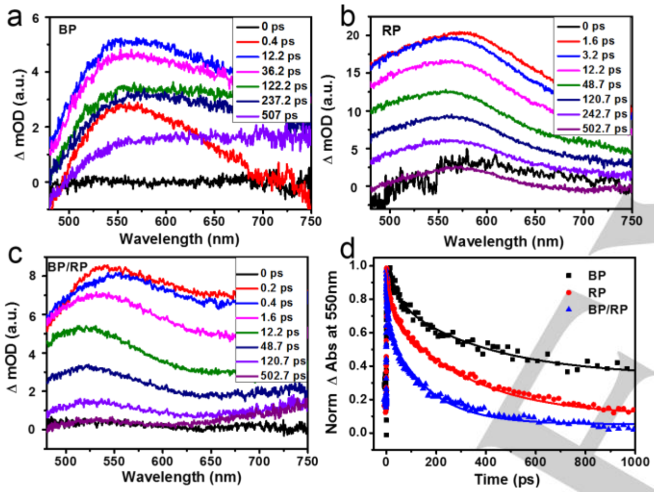

Figure 3. TAS measurements: a) BP, b) RP and c) BP/RP after irradiation with a 400 nm laser flash, d) time profiles of normalized TAS at 550 nm.

To estimate the decay kinetics of photo-generated carrier in the samples, the time profiles of the TAS probed at 550 nm were fitted by a two-exponential function (Figure 3d), and their fitting parameters were summarized in Table S3. Generally, the short lifetime (τ_1) and long lifetime (τ_2) components result from electrons trapped at shallow and deep sites before their recombination.[19c] Considering the main content (90 wt%) of RP in the as-prepared samples, the TAS signals of BP/RP are mainly attributed to excited RP. Compared to pure RP ($\tau_{1:}$ 15.9 ps; $\tau_{2:}$ 315.2 ps), the decay lifetimes of BP/RP hetero-phase junction are largely decreased to 6.5 ps (2%) and 166.2 ps (98%), owing to the existence of an additional channel of interfacial electron transfer from CB of excited RP to the VB of adjacent BP (Figure S14). Similar phenomena have been observed in previous reports.[7d, 19a, 19c] Meantime, the rate of electron transfer from RP into BP is calculated to be 2.9 × 10^9 s^{-1} (Table S3).[19a, 21] Upon decreasing the content of BP, the electron transfer rate is slower (Figure S15). A series of phoelectrochemical (PEC) measurements including photocurrent response, electrochemical impedance spectra (EIS) and open-circuit potential decay curves (OCP), were also carried out to testify the charge separation in the BP/RP hetero-phase junction by Z-scheme pathway (Figure S16–S18, Table S4).

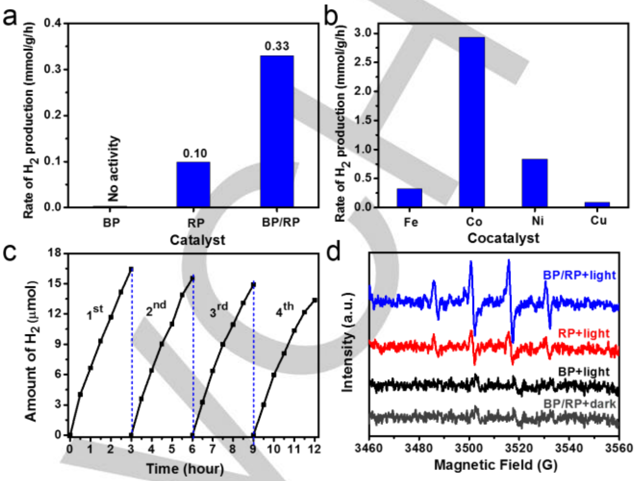

Figure 4. a) Photocatalytic H_2 production over various samples. b) The rate of H_2 production over BP/RP hetero-phase junction with different non-noble metals incorporation. c) Photocatalytic durability test and d) EPR spectra.

The photocatalytic performance of the samples was evaluated in pure water without using any sacrificial agents. As shown in Figure 4a and Figure S19, pristine BP does not show H_2 production activity, while BP/RP hetero-phase junction has excellent H_2 production activity (0.33 mmol g^{-1} h^{-1}), 3.3 and 2.5 times higher than that of RP and the mixture of BP and RP, respectively, indicating the potential of the hetero-phase junction with Z-scheme pathway for achieving high performance of water splitting. Delightedly, when a certain amount of non-noble metals are loaded as cocatalyst, the H_2 evolution activity is improved significantly, and 1.4 wt% Co-incorporated BP/RP hetero-phase junction achieves the maximum activity (2.96 mmol·g^{-1}·h^{-1}) (Figure 4b, S20, S21). Moreover, the apparent quantum efficiency (AQE) reaches up to 1.21% at 420 nm. In addition, the Co-incorporated BP/RP still retains 82% of its initial photocatalytic activity after four cycles (Figure 4c). The Raman spectra of the BP/RP hetero-phase junction after photocatalytic reaction showed no obvious change (Figure S22), demonstrating the good stability of our photocatalytic system.

We then analyzed the oxidation species produced from photogenerated holes during the water splitting reaction. Surprisingly, O_2 was not detected. Instead, oxidized species •OH radicals and H_2O_2 were identified through a series of spectroscopic experiments. The characteristic quartet peaks of DMPO-•OH adducts in the BP/RP suspension were detected through in situ EPR spectra (Figure 4d), suggesting the single-electron oxidation of water to produce •OH by photogenerated holes. Meanwhile, photoluminescence spectrum also proved the appearance of •OH radicals (Figure S23). As the photocatalytic reaction proceeded, a small amount of H_2O_2 was also detected (Figure S24). We tentatively attribute the formation of H_2O_2 to the combination of two •OH.[22] Although the valence band position of the materials is positive enough for the formation of O_2 and H_2O_2, compared to the concerted four-electron process for O_2 evolution, these species formed H_2O_2 via the two-electron process is kinetically more favorable.[23] Additionally, trace amounts of phosphate ions produced by self-photocorrosion were detected by Ion chromatography.

In summary, direct Z-scheme hetero-phase junction of BP/RP is successfully constructed by an in situ wet-chemistry method and unambiguously confirmed by various spectroscopic and electrochemical measurements. Benefiting from their appropriate band structures with a staggered alignment and perfect phase junction interface, the efficient separation and transfer of photogenerated carriers is realized and consequently allow the water reduction and oxidation reactions to occur in BP and RP, respectively. This work not only provides a facile one-step method to synthesize a BP/RP hetero-phase junction, but also demonstrates its promising application for photocatalytic water splitting.

Acknowledgements

This work is supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB17000000), the Natural Science Foundation of China (21773275, 21633015, 11721404) and the Ministry of Science and Technology (2018YFA0208701). Y.C. thanks the financial support from K.C. Wong Education Foundation and CAS-Croucher Funding Scheme for Joint Laboratories.

Keywords: Black Phosphorus • Phase Junction • Z-scheme • Photocatalysis • Water Splitting

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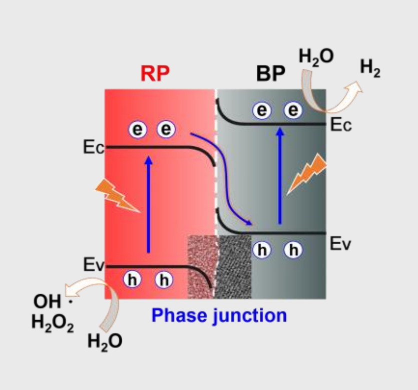

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