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# Stable functionalized phosphorenes with photocatalytic HER activity<sup>†</sup>

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Phosphorene, a mono-elemental 2D material of phosphorus, can catalyze the hydrogen evolution reaction (HER) owing to the suitable position of its conduction band minimum but the ambient instability of phosphorene is the major challenge for its application. We have functionalized phosphorene with indium(III) chloride, tris(penta-fluorophenyl) borane and a benzyl group. The functionalized phosphorenes show stability under ambient conditions as well as good dispersibility in water and exhibit hydrogen yields as high as 6597  $\mu$ mol h<sup>-1</sup> g<sup>-1</sup>. The HER activity of the functionalized phosphorenes is much superior compared to pristine phosphorene and black phosphorus-based catalysts reported earlier.

After the discovery of phosphorene, a 2D monolayer sheet of black phosphorus (BP), there have been studies on BP and its composites.<sup>1-6</sup> The phosphorene sheet is composed of sp<sup>3</sup> hybridized phosphorus atoms, wherein each phosphorus atom is covalently bonded to three neighbouring phosphorus atoms to form a puckered honeycomb structure. The phosphorus atoms contain lone-pair electrons. Owing to the unique structure, phosphorene exhibits excellent charge carrier mobility as well as a thickness tuneable band-gap in the 0.3-2.0 eV range.7-10 The conduction band minimum (CBM) of BP lies above the water reduction potential (0.0 V vs. RHE). These properties suggest that few-layer BP can effectively catalyze the hydrogen (H<sub>2</sub>) evolution reaction.<sup>7,10</sup> Besides, phosphorus is an earth-abundant and environmentally benign non-metal element. Therefore, it is of great interest to exploit the potential of phosphorene as a metal-free photocatalyst for H<sub>2</sub> evolution. It has been reported that the H<sub>2</sub> production activity of semiconducting CdS,<sup>11,12</sup> ZnS,<sup>11,12</sup> and g-C<sub>3</sub>N<sub>4</sub> photocatalysts can be significantly improved by hybridizing with a small amount of BP.13-15 The enhanced photocatalytic activity at an optimum BP

content is attributed to the effective separation of electron–hole pairs in the photocatalysts as well as the availability of more active sites on the catalyst surface. Bare BP nanostructures produce trace amounts of  $H_2$ .<sup>8,11,16</sup> Pt-deposited BP showed improved  $H_2$  evolution from water.<sup>17</sup> But the ambient instability of phosphorene remains a challenge for its applications. In the recent past, a number of efforts have been made to understand the mechanism of phosphorene degradation and its prevention. One strategy to suppress phosphorene degradation is to functionalize its surface with different chemical entities through covalent<sup>18,19</sup> and coordination bonds<sup>20,21</sup> as well as van der Waals interaction.<sup>22</sup> It was our special interest to stabilize phosphorene under ambient conditions by using chemical routes and to study the efficiency of stabilized phosphorene for photochemical  $H_2$  evolution.

We have employed different means for the functionalization of solvent exfoliated few-layer phosphorene (Scheme 1). The first one uses the ability of group-III trivalent molecules with vacant orbitals (v) to form  $\eta$ -v adducts with the lone-pair electrons ( $\eta$ ) of phosphorene as in triphenylphosphine (PPh<sub>3</sub>).<sup>23</sup> For this purpose, we have employed indium trichloride (InCl<sub>3</sub>) and tris(pentafluorophenyl) borane  $(B(C_6F_5)_3)$ . We have also carried out the reaction of few-layer phosphorene nanosheets with benzyl bromide to form phosphonium ylide. Under ambient conditions, the functionalized few-layer phosphorenes show significantly improved stability compared to the pristine phosphorene. They show enhanced water dispersibility as well. We have examined the dye-sensitized photocatalytic HER activity of the stable phosphorenes in visible light. We have used Eosin-Y (EY) as the photosensitizer. The HER activity of these compounds is significantly higher than those reported for bare BP nanostructures as well as the semiconductor-based photocatalysts hybridized with BP.

We will first discuss the features of the  $\eta$ - $\nu$  adducts of phosphorene with InCl<sub>3</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. Few-layer phosphorene nanosheets were prepared by ultrasonic exfoliation of black phosphorus crystals in deaerated anhydrous *N*,*N'*-dimethylformamide (DMF) under an inert atmosphere. The exfoliated

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Scheme 1 (a) Schematic of the preparation of phosphorene nanosheets by exfoliation of black phosphorus. (b) Schematic of functionalization of phosphorene nanosheets with indium(III) chloride, tris(pentafluorophenyl) borane and a benzyl group.

nanosheets separated from the non-exfoliated bulk by centrifugation at 400g. The top 75% of the supernatant containing fewlayer phosphorene was collected and used for characterization using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and <sup>31</sup>P NMR spectroscopy (see Fig. S1-S3, ESI<sup>†</sup> for details of characterization). To carry out functionalization reactions, we removed the DMF solvent from the dispersion by centrifugation and re-dispersed the exfoliated material in tetrahydrofuran (THF). The room temperature reaction of the THF dispersion with InCl<sub>3</sub> yielded the P·InCl<sub>3</sub> adduct which was characterized by SEM, TEM, EDS, XPS, Raman spectroscopy and NMR spectroscopy. Fig. 1a shows the Raman spectra of pristine phosphorene along with that of the P·InCl<sub>3</sub> adduct. Pristine phosphorene shows  $A_g^1$ ,  $B_{2g}$  and  $A_g^2$  Raman bands at 361.7, 438.0 and 465.9 cm<sup>-1</sup>, respectively. While  $P \cdot InCl_3$  exhibits these bands at 360.0, 435.8 and 462.0 cm<sup>-1</sup>, respectively.<sup>3,4</sup> All three bands of P·InCl<sub>3</sub> soften compared to those of pristine phosphorene. The Raman characteristics of functionalized phosphorene suggest that the adduct formation takes place without significantly changing the structure of phosphorene sheets. The chemical composition of P·InCl<sub>3</sub> was examined by EDS (Fig. 1b) which shows the presence of P, In and Cl elements. SEM and TEM images show the layered nature of the material (Fig. 1c and S4, ESI<sup>†</sup>). Fig. 1c shows the TEM image of a P·InCl<sub>3</sub> nanosheet along with the HR-TEM image. The HR-TEM image shows a *d*-spacing of 2.65 nm corresponding to the



Fig. 1 (a) Raman spectra of phosphorene and P·InCl<sub>3</sub>. (b) Energydispersive X-ray spectrum (EDS) of P·InCl<sub>3</sub>. (c) TEM image of a P·InCl<sub>3</sub> nanosheet, the inset shows the HR-TEM image with lattice fringes corresponding to the (004) crystallographic plane of black phosphorus. (d) CP-MAS <sup>31</sup>P NMR spectrum of P·InCl<sub>3</sub>.

(004) crystal plane of black phosphorus. We recorded the crosspolarization magic angle spinning (CP-MAS) <sup>31</sup>P NMR spectrum of P·InCl<sub>3</sub> (Fig. 1d) which shows a <sup>31</sup>P chemical shift of  $\sim$ 95 ppm. The sharp signal with a chemical shift of  $\sim$ 18 ppm is due to the non-coordinated phosphorus.<sup>24</sup> The broad hump around  $\sim 5$  ppm is due to H<sub>3</sub>PO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> formed by autooxidation of phosphorene.25 XPS of P·InCl<sub>3</sub> shows signals due to P, In and Cl elements (Fig. 2a). The P 2p spectrum shows the 2p<sub>3/2</sub> and 2p<sub>1/2</sub> states at 129.8 and 130.7 eV, respectively, due to the bare phosphorene (Fig. 2b). The peak at 133 eV suggests interaction between phosphorus and InCl<sub>3</sub>, consistent with metal-coordinated black phosphorus reported earlier.20,21 Additionally, a peak at 134.3 eV is observed due to oxidized phosphorene  $(P_xO_y)$ .<sup>21</sup> It is possible that during the exfoliation and functionalization reaction, phosphorene is oxidized to some extent. Fig. 2c shows the In 3d spectrum with In  $3d_{5/2}$  and  $3d_{3/2}$ peaks at 446.0 and 453.8 eV, respectively, and the Cl 2p signal at 200 eV (Fig. 2d).26

We synthesized the P·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> adduct from few-layer phosphorene and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> under reaction conditions similar to that for P·InCl<sub>3</sub>. As shown in Fig. 3a, the Raman spectrum of P·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> shows A<sup>1</sup><sub>g</sub>, B<sub>2g</sub> and A<sup>2</sup><sub>g</sub> bands at 360.8, 436.7 and 464.6 cm<sup>-1</sup>, respectively. These Raman bands are softened by ~2 cm<sup>-1</sup> compared to the pristine sample. The layered and crystalline nature of the phosphorene sheets in P·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was confirmed by SEM and TEM images as well as the SAED pattern (Fig. S5a-c, ESI†). The CP-MAS <sup>31</sup>P NMR spectrum of P·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> shows a broad signal around ~85 ppm due to the phosphorus atoms coordinated to B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (Fig. 3b).<sup>27</sup> EDS (Fig. S5d, ESI†) and XPS (Fig. 4 and S6, ESI†) measurements show the presence of B, C, F and P elements in the adduct. The P 2p spectrum (Fig. 4a) shows 2p<sub>3/2</sub> and 2p<sub>1/2</sub> states at 129.9 and 130.8 eV, respectively, due to non-coordinated phosphorus, while the



Fig. 3 Spectral characterization of  $P\cdot B(C_6F_5)_3$  showing (a) Raman and (b) CP-MAS  $^{31}P$  NMR spectra.

broad signal at 133 eV corresponds to phosphorus coordinated to  $B(C_6F_5)_3$  as well as oxidized phosphorus. Fig. 4b-d show the C 1s, F 1s and B 1s peaks at 287.3, 688.0 and 187.8 eV, respectively, due to the coordinated  $B(C_6F_5)_3$ .

Covalent functionalization of BP with an aryl diazonium salt was reported by Hersam *et al.*<sup>18</sup> who found that the functionalization occurs through the formation of a P–C bond between the BP nanosheet and the aryl group. Trivalent phosphorus compounds such as PPh<sub>3</sub> are known to form alkyltriphenylphosphonium ylides with alkyl halides. Phosphonium ylides are important reagents in the Wittig reaction, and are used in the synthesis of olefins from ketones or aldehydes.<sup>28</sup> We have carried out the reaction of few-layer phosphorene with benzyl bromide to synthesize benzylphosphonium ylide P·CH–C<sub>6</sub>H<sub>5</sub> on the phosphorene nanosheets (Fig. 5a). The Raman spectrum of P·CH–C<sub>6</sub>H<sub>5</sub> (Fig. S7a, ESI†) shows A<sup>1</sup><sub>g</sub>, B<sub>2g</sub> and A<sup>2</sup><sub>g</sub> bands at 360.4, 437.0 and 464.7 cm<sup>-1</sup>, respectively. The SEM and TEM images as well as the SAED pattern show the layered morphology as well as the crystallinity of the product



Fig. 2 XPS of the  $P \cdot InCl_3$  adduct: (a) survey spectrum, (b) high resolution P 2p spectrum, (c) high resolution In 3d spectrum and (d) high resolution Cl 2p spectrum.



Fig. 4 XPS of  $P \cdot B(C_6F_5)_3$  showing (a) P 2p (b) C 1s, (c) F 1s and (d) B 1s bands.



Fig. 5 (a) Schematic of the synthesis of benzylphosphonium ylide of phosphorene and its Wittig reaction with benzaldehyde to form stilbene. (b) GC-MS of stilbene formed in the Wittig reaction (molecular mass of stilbene is 180.2).

(Fig. S7b–d, ESI<sup>†</sup>). In the XPS of  $P \cdot CH-C_6H_5$  (Fig. S8, ESI<sup>†</sup>), the P 2p signal is significantly broad and can be deconvoluted into three bands due to P–P, P–C and P–O bonds at 130, 133 and 134 eV, respectively. We treated the isolated  $P \cdot CH-C_6H_5$  solid with *n*-BuLi followed by the reaction with benzaldehyde to prepare stilbene. We confirmed the formation of stilbene by GC-MS (Fig. 5b). This reaction further provides proof that the benzyl group is present in  $P \cdot CH-C_6H_5$  ylide.

The ambient stability of the functionalized samples was assessed by Raman spectroscopy. The samples were deposited on glass slides and kept under ambient conditions. As shown in Fig. 6, we recorded Raman spectra at 0, 5, 10 and 20 days. We find that the intensity of the spectra of the pristine film decreased drastically in 5 days and was completely suppressed in 10 days. Interestingly, the functionalized samples retain their Raman intensity during the experiments. According to a few reports, the  $A_g^1/A_g^2$  intensity ratio in the Raman spectrum is a good parameter to evaluate the degree of phosphorene degradation.<sup>29,30</sup> We analysed the integrated intensities of the Raman spectra after their baseline subtraction. The pristine phosphorene showed a decrease in the  $A_g^1/A_g^2$  intensity ratio from 0.58 (0 days; fresh sample) to 0.42 in 5 days. The intensity ratio in the case of P·InCl<sub>3</sub> showed a small change from 0.48 (fresh sample) to 0.38 in 20 days. The intensity ratio of  $P \cdot B(C_6F_5)_3$  and  $P \cdot CH - C_6H_5$  did not change much on ambient exposure. These results are consistent with the XPS results, where we observed that the oxide  $(P_xO_y)$  peak is much smaller in the case of  $P \cdot B(C_6F_5)_3$  and  $P \cdot CH - C_6H_5$ . In addition, we found water droplets absorbed on pristine phosphorene, while the functionalized samples did not show such droplets (Fig. S9, ESI†). These studies suggest that the functionalized phosphorene samples are stable in humid air. They show good dispersibility in the aqueous medium compared to the pristine one.

We examined the HER activity of pristine and functionalized phosphorenes in visible light. We carried out an Eosin Y (EY) sensitized photocatalytic reaction in an aqueous solution of triethanolamine (TEOA, 20%; v/v). TEOA has been used as an efficient sacrificial electron donor in dye sensitized photocatalysts.<sup>31,32</sup> On visible light irradiation, the photocatalyst (EY + phosphorene + TEOA) showed H<sub>2</sub> evolution which increased steadily with time. A plausible mechanism of the H<sub>2</sub> evolution reaction is shown in Fig. 7a. EY, in the presence of visible light and TEOA, goes through a series of changes to generate a highly reducing species EY<sup>-</sup> which then transfers an electron to catalyze the HER over phosphorene sheets. Fig. 7b shows the amount of H<sub>2</sub> evolved in the four different photocatalyst systems for a period of 6 h. In the presence of EY and TEOA, pristine phosphorene shows an activity of 621  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> which is much less compared to that of the functionalized



Fig. 6 Raman spectra of the samples deposited on glass slides; (a) pristine phosphorene, (b)  $P \cdot InCl_3$  and (c)  $P \cdot CH - C_6H_5$ . The spectra were collected for the fresh sample from 0 day to up to 20 days of exposure to air.



**Fig. 7** Photocatalytic H<sub>2</sub> evolution from water by phosphorene based photocatalysts: (a) schematic of a plausible mechanism of the H<sub>2</sub> evolution reaction, (b) comparison of H<sub>2</sub> evolution activities of different photocatalysts for 6 h, (c) cycling study on P·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> for 36 h (see Fig. S10–S12, ESI† for the cycling study of other photocatalysts) and (d) SEM image of P·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> after the H<sub>2</sub> evolution reaction; the inset shows the corresponding Raman spectrum.

samples. The hydrogen yields of P·InCl<sub>3</sub>, P·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and P·CH-C<sub>6</sub>H<sub>5</sub> are 2058, 6597 and 5691 µmol g<sup>-1</sup> h<sup>-1</sup>, respectively. The P·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> exhibits the highest activity which is nearly 10.6 fold higher than that of the pristine sample. The H<sub>2</sub> yields increase in the pristine phosphorene  $\ll$  P·InCl<sub>3</sub> < P·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> ~ P·CH-C<sub>6</sub>H<sub>5</sub> order which is consistent with the stability order suggested by Raman spectroscopy and XPS. The superior HER activity of P·InCl<sub>3</sub>, P·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and P·CH-C<sub>6</sub>H<sub>5</sub> could be due to their enhanced ambient stability, and dispersibility in water. The surface functional groups also stabilize the few-layer

nanosheets by inhibiting re-stacking which is a common phenomenon in 2D materials.<sup>33</sup> The apparent quantum efficiency (AQE) of pristine phosphorene,  $P \cdot InCl_3$ ,  $P \cdot B(C_6F_5)_3$  and  $P \cdot CH-C_6H_5$  is found to be 0.8, 2.1, 8.4 and 7.3%, respectively. Our control experiments on individual components EY, phosphorene and the starting reagents of the functional groups in the presence of TEOA showed no H<sub>2</sub> evolution (Tables S1 and S2, ESI†). We did not observe H<sub>2</sub> evolution from the catalysts in the dark, indicating that it is a photocatalytic reaction and that the phosphorene sheet is the HER site. To examine the

Table 1A comparison of the photocatalytic $H_2$ yields of various phosphorene based photocatalysts <sup>a</sup>				
Sr. no.	Photocatalysts	Photocatalytic $H_2$ yields (µmol $h^{-1} g^{-1}$ )	AQE (%)	References
1	Few-layer phosphorene	621	0.8	This work
2	Phosphorene · InCl <sub>3</sub>	2058	2.1	This work
3	Phosphorene $\cdot$ B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	6597	8.4	This work
4	Phosphorene · CH–C <sub>6</sub> H <sub>5</sub>	5691	7.3	This work
5	BP nanosheets	64	NA	8
6	BP nanoparticles	45	NA	8
7	BP nanoflakes/g-C <sub>3</sub> N <sub>4</sub>	571 and 427	1.2 and 1.0-3.5	13 and 14
8	BP nanoflakes	138	NA	16
9	BP nanosheet/Pt	138	NA	17
10	BP quantum dots/g-C <sub>3</sub> N <sub>4</sub>	1900 and 271	NA, NA	15 and 35
11	BP nanosheets/CoP	735	5.5	36
12	BP nanosheets/BiVO <sub>4</sub>	160	0.89	37

<sup>*a*</sup> NA: data not available.



Fig. 8 (a) Photoluminescence quenching profile of an aqueous solution of EY (concentration =  $1.4 \times 10^{-7}$  M; excitation wavelength = 490 nm) in the presence of pristine and functionalized phosphorenes (10 µg mL<sup>-1</sup>) and (b) photoluminescence decay curves of aqueous solution of EY in the presence of pristine and functionalized phosphorenes. For lifetime measurements, the samples were excited at 480 nm and the emission was monitored at 535 nm.

stability of the photocatalysts during the HER, we conducted cycling studies. The functionalized phosphorene catalysts retained their HER activities throughout the study (36 h, in that 24 h is the light period and 12 h is the dark period) (Fig. 7c and S10-S12, ESI<sup>†</sup>). In the case of pristine phosphorene, a decrease in the activity was observed in the second cycle. We recovered the catalysts after the HER and assessed their structural stability by SEM and Raman spectroscopy (Fig. 7d, S13 and S14, ESI<sup>†</sup>). Both SEM images and Raman spectra show no observable changes after the reaction, confirming the stability of the catalysts. We have compared our results of dyesensitized photocatalytic activity with those reported for bare few-layer BP and its composites at room temperature (Table 1). Our dye-based photocatalysts show superior HER performance compared to other few-layer BP based photocatalysts. It is noteworthy that the H<sub>2</sub> evolution activity of these photocatalysts is higher than that of BP-loaded semiconductorbased photocatalysts.

Electronic absorption spectra show that the phosphorenes absorb very little in the visible light, while EY shows intense absorption in this region (Fig. S15 and S16, ESI<sup>†</sup>). To understand the photo-excited electron transfer between EY and phosphorene, we measured steady-state and time-resolved photoluminescence (PL) spectra. The aqueous solution of EY shows an emission band at 535 nm which was quenched on the addition of phosphorene (Fig. 8a and S17, ESI†). It is worth mentioning that the functionalized phosphorenes quench the PL more efficiently compared to the pristine phosphorene. Time-resolved photoluminescence spectra (Fig. 8b) suggested that the excited state lifetime of EY decreased significantly in the presence of phosphorenes (Table S3<sup>†</sup>). The decays of EY and EY-phosphorenes show mono- and bi-exponential behaviour, respectively. This suggests a dynamic quenching mechanism with an efficient photoinduced electron transfer process from EY to phosphorenes.<sup>31,34</sup> These electrons eventually facilitate proton reduction on the phosphorene sheet. These results support our HER mechanism shown in Fig. 7a.

In conclusion, we have successfully stabilized phosphorene under ambient conditions by functionalization. For this

purpose we have the advantage of the lone-pair electrons of phosphorus to react phosphorene with indium(m) chloride, tris(pentafluorophenyl) borane and a benzyl group. The functional groups protect the phosphorene sheets from oxidation as well as re-stacking. They show significant photocatalytic HER activity with high hydrogen yields of 2058, 6597 and 5691  $\mu$ mol h<sup>-1</sup> g<sup>-1</sup> and apparent quantum efficiency (AQE) in the 0.8-8.4% range. The high activity of these functionalized phosphorenes arises from their enhanced ambient stability and water dispersibility as well as the efficient sensitization effect of EY. Electron transfer from EY to phosphorene is crucial for the photocatalytic proton reduction on phosphorene nanosheets. Our method of functionalization provides not only metal-free HER photocatalysts with high activity, but also new avenues to work with phosphorene nanomaterials under ambient conditions.

#### Conflicts of interest

The authors declare no conflicts of interest.

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