

Electronic Supporting Information

Stable Functionalized Phosphorenes with Photocatalytic HER Activity

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Experimental Section

Materials. Black phosphorus (BP) crystals were purchased from Smart Elements (99.998 % purity) and stored in a nitrogen-filled glovebox (MBraun) with oxygen and water levels < 1.0 ppm. Tris(pentafluorophenyl) borane, indium(III) chloride and benzyl bromide were purchased from Sigma Aldrich and used as received. *n*-BuLi (1.6 M in hexane) was purchased from Alfa Aesar. Anhydrous *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Spectrochem (India). The solvents were deaerated and stored in the glovebox. Triethanolamine (TEOA, 98 %) was purchased from S. D. Fine Chem. Ltd., India. Eosin Y (EY) was purchased from Sigma Aldrich.

Characterization. Transmission electron microscopy (TEM) images were acquired on a JEOL-3010 and an FEI Tecnai microscopes at the operating accelerating voltage of 300 and 200 kV, respectively. X-ray photoelectron spectroscopy (XPS) data were collected with an Omicron Nanotechnology spectrometer by using Al-K α (1486.6 eV) X-ray radiation. The core level XPS were charge corrected with reference to the C 1s peak at 285 eV. Scanning electron microscopy (SEM) images were obtained with an FEI Nova NanoSEM 600 microscope. Energy dispersive X-ray spectroscopy (EDS) analysis was carried out on an EDAX Genesis instrument attached to the SEM. Raman studies were performed on a LabRAM HR Raman spectrometer (Horiba-Jobin Yvon) with 514.5 nm laser excitation (Ar laser). ^{31}P NMR data were collected on a Bruker 400 MHz spectrometer. The quantitative measurements of the H_2 evolved were carried out on a Perkin Elmer 580 C gas chromatograph equipped with a thermal conductivity detector (TCD).

Preparation of Phosphorene Nanosheets. Probe sonication of black phosphorus crystals was carried out on a Sonics Vibra cell™ VCX 750 (750 W and 20 kHz) ultrasonic processor. DMF was deaerated by nitrogen gas bubbling for 5 h in a Schlenk flask. BP crystals (20 mg) were ground in a mortar-pestle and transferred to a 50 mL oak ridge centrifuge tube (polypropylene, Tarsons, India). To this, de-gassed DMF (20 mL) was added and close with the screw cap. In the center of the screw cap, a hole was created to insert the tapered sonicator microtip (6 mm diameter and 142 mm in length). The tip was immersed in the top half of DMF filled in the tube and sealed the interface with silicon grease, Teflon tape, and Parafilm. The sample was sonicated at ultrasound amplitude of 27% (200 W) in pulse operation mode (4 sec on-phase and 4 sec off-phase) for 8 h. The sample tube was dipped in a water bath, connected to a Julabo recirculating cooler. The temperature of the water bath was maintained below 10 °C by circulating glycol-water mixture. The black dispersion obtained after sonication was collected in an oak ridge centrifuge tube under a nitrogen atmosphere. The dispersion was centrifuged at 400g for half an hour (REMI PR-24, angular R-242 rotor head, REMI Instruments, India). Top 75 % of the supernatants were collected in another oak ridge tube under nitrogen flow and centrifuged it at 14,500g for 1 h. The sediments were collected and used for the functionalization reactions.

Preparation of P-InCl₃. Exfoliated black phosphorus (32 mg) and InCl₃ (110 mg) were taken in anhydrous and de-gassed THF (20 mL) in a Schlenk flask under a nitrogen atmosphere. The mixture was stirred at room temperature for 48 h. After the reaction, the mixture was centrifuged at 14,500g for 1 h. The sediment was collected and purified by washing two times with THF (20 ml). The product was separated by centrifugation at 14,500g for 1 h, dried in a vacuum desiccator and used for the characterization and other studies.

Preparation of P-B(C₆F₅)₃. Phosphorene nanosheets (32 mg) and tris(pentafluorophenyl)borane (275 mg) were mixed in anhydrous and degassed THF (20 mL). The mixture was stirred at room temperature for 48 h and centrifuged at 14,500g for 1 h. The sediment was washed with degassed THF (20 ml x 2), and the product was separated by centrifugation at 14,500g for 1 h. The black product was dried in a vacuum desiccator and used for the characterization.

Preparation of P·CH-C₆H₅ and Wittig reaction. Phosphorene nanosheets (32 mg) and benzyl bromide (85 mg) were taken in anhydrous and degassed THF (20 mL) in a Schlenk flask. The reaction mixture was heated at reflux for 48 h. The black product was separated via centrifugation at 14,500g for 1 h which was washed with THF (20 ml x 2). After each washing, the product was isolated by centrifugation at 14,500g for 1 h and then dried in a vacuum desiccator and used for the characterization. We prepared stilbene by Wittig reaction of the phosphonium ylide of phosphorene with benzaldehyde. The black phosphonium ylide obtained was dispersed in THF in a Schlenk flask under a nitrogen atmosphere. To this, *n*-BuLi (1.0 eq) was added, and the reaction mixture was heated at reflux for 48 h. The product was centrifuged at 14,500g for 1 h and then re-dispersed the solid in THF. After adding benzaldehyde (1.0 eq) to this dispersion, the mixture was stirred for overnight at room temperature. The supernatant was analyzed by GC-MS to ascertain the formation of stilbene.

Determination of Stability of Functionalized Phosphorene in Ambient Condition. Pristine phosphorene, P·InCl₃, P·B(C₆F₅)₃ or P·CH-C₆H₅ were drop-casted on separate glass slides. The samples were kept under ambient conditions where they were exposed to humid air. Raman spectra of these films were recorded over a period of three weeks. Optical images of the films were captured by using the optical camera attached to the Raman spectrometer.

Photocatalytic H₂ Evolution Reaction (HER). The HER experiment was carried out in distilled and deaerated (for 5 h by bubbling nitrogen gas) water. We used triethanolamine (TEOA) and Eosin Y (EY) as the sacrificial and photosensitizing agents, respectively. In a typical experiment, 2.2 mg of the photocatalyst (*i.e.*, pristine phosphorene, P·InCl₃, P·B(C₆F₅)₃ or P·CH-C₆H₅) was dispersed into 25 mL of TEOA (20%; v/v) by sonication for one minute in a vessel, and then EY (14.0 μmol) was added to the mixture. The vessel was closed with a silicon septum and purged with nitrogen gas for 5 minutes. The reaction vessel was irradiated with a 100 W halogen lamp. The gases evolved were taken out intermittently through the septum and analyzed by manual injections.

Control experiments were conducted on individual components EY, phosphorene and the starting reagents of the functional groups in the presence of TEOA which showed no H₂ evolution. We did not observe H₂ evolution from the catalysts in the dark either, indicating that it is a photocatalytic reaction. It means the phosphorene sheet is the site for HER.

Table S1. Control experiments conducted in the visible light.

Catalyst(s)	H₂ evolved
EY alone	No
EY + TEOA	No
Phosphorene + TEOA	No
EY + Functional group + TEOA	No
EY + Phosphorene + TEOA	YES

Table S2. Control experiments conducted in the dark.

Catalyst(s)	H₂ evolved
EY alone	No
EY + TEOA	No
Phosphorene + TEOA	No
EY + Functional group + TEOA	No
EY + Phosphorene + TEOA	No

Calculation of Apparent Quantum Efficiency (AQE). The AQE was calculated by using the following formula.^{S1}

$$n_p = t \times S \times Q$$

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

where n_p is number of photons, t is the irradiation time, S is effective light irradiation area (m^2) and Q is the photon flux of the incident light. The number of photons were calculated by using a thermopile detector and reference solar cell certified by NREL (Oriel instruments, calibrate reference cell and meter).

Optical Properties. UV-visible spectra were recorded in aqueous solution / dispersion with a PerkinElmer UV/VIS/NIR Lambda-750 spectrophotometer. The photoluminescence spectra were recorded on a PerkinElmer LS55 spectrofluorometer. Photoluminescence lifetimes were measured by using a time-correlated single-photon counting (TCSPC) system from IBH. The samples were excited at 480 nm and the emission was monitored at 535 nm. The Full Width at Half Maxima of IRF was 7.304138 ch (189.841 ps). The decays were fitted

to mono-exponential and bi-exponential kinetics by using DAS6 software (HORIBA) as given in the equations below.

Mono-exponential function

$$f(t) = A + B_1 \exp(-t/\tau_1) \quad (1)$$

Bi-exponential function

$$f(t) = A + B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) \quad (2)$$

The average lifetime was calculated by using the method described elsewhere.^{S2}

Table S3. Photoluminescence decay parameters of aqueous solution EY in the presence of pristine and functionalized phosphorenes.

Fluorophore	Lifetime (ns)	Normalized pre-exponential function	Average lifetime τ_{av} (ns)	CHISQ
EY	$\tau = 1.16$	B = 100 %	1.16	1.03
EY-Phosphorene	$\tau_1 = 0.02; \tau_2 = 1.14$	B ₁ = 99%; B ₂ = 1%	0.03	1.07
EY-P.InCl ₃	$\tau_1 = 0.03; \tau_2 = 1.14$	B ₁ = 97%; B ₂ = 3%	0.06	1.09
EY-P.B(C ₆ F ₅) ₃	$\tau_1 = 0.03; \tau_2 = 1.04$	B ₁ = 99%; B ₂ = 1%	0.04	1.02
EY- P.CH-C ₆ H ₅	$\tau_1 = 0.02; \tau_2 = 1.13$	B ₁ = 99%; B ₂ = 1%	0.02	1.00

Characterization of Phosphorene Nanosheets. Fig. S1 shows the SEM and TEM images, Raman spectrum and XP spectrum of phosphorene prepared in DMF by probe sonication followed by centrifugation at 14500g. The SEM image shows the layer feature of the sample, and the TEM images and electron diffraction show crystalline nature. The HR-TEM image shows lattice fringes with *d*-spacings of 2.65 and 4.37 Å correspond to the (004) and (010) crystal planes, respectively. The Raman spectrum of phosphorene shows the characteristics A_g^1 , B_{2g} and A_g^2 bands at 362.0, 439.0 and 467.2 cm⁻¹, respectively. The chemical state of the exfoliated material has been determined by XPS. Fig. S2 shows the P 2p XP spectra of phosphorene as well as the bulk BP. Phosphorene as well as bulk BP exhibit P 2p peaks at the binding energy of ~ 130 eV. This is consistent with previously reported values.^{S3} A singlet signal at 17.5 ppm has been observed in the CP-MAS ³¹P NMR spectrum (Fig. S3) of phosphorene, which is consistent with that obtained for the bulk BP crystals.^{S4} The NMR spectrum does not show the formation of oxides.

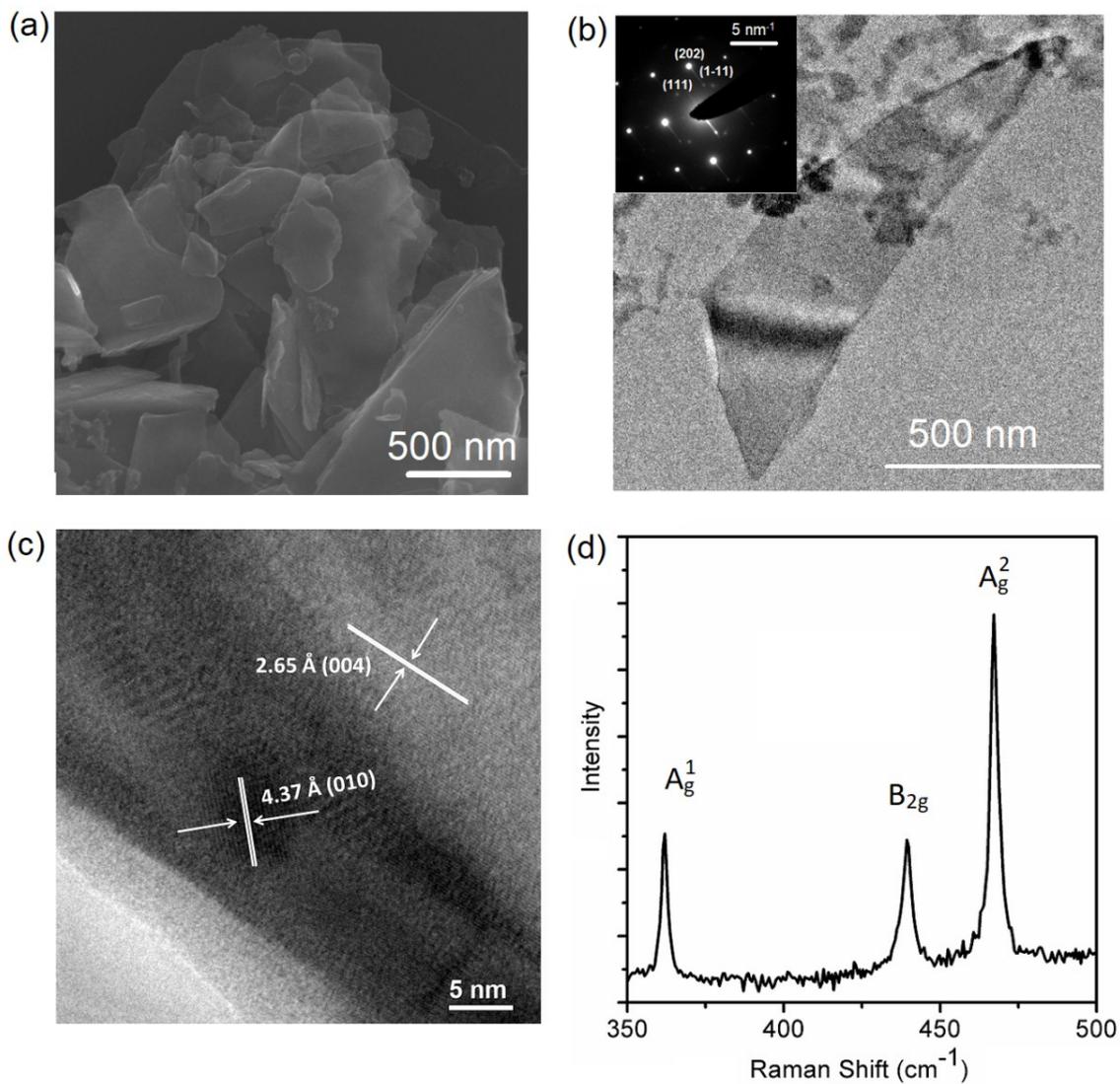


Fig. S1 Characterization of as-exfoliated phosphorene nanosheets; (a) SEM image, (b) low magnification TEM image, the inset shows selected area electron diffraction (SAED) pattern, (c) HR-TEM image and (d) Raman spectrum.

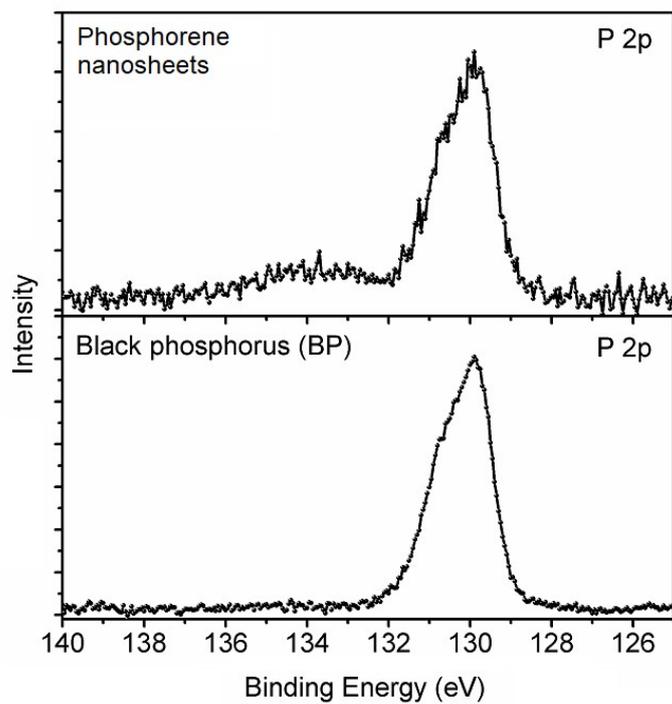


Fig. S2 Core level P 2p of phosphorene nanosheets and black phosphorus.

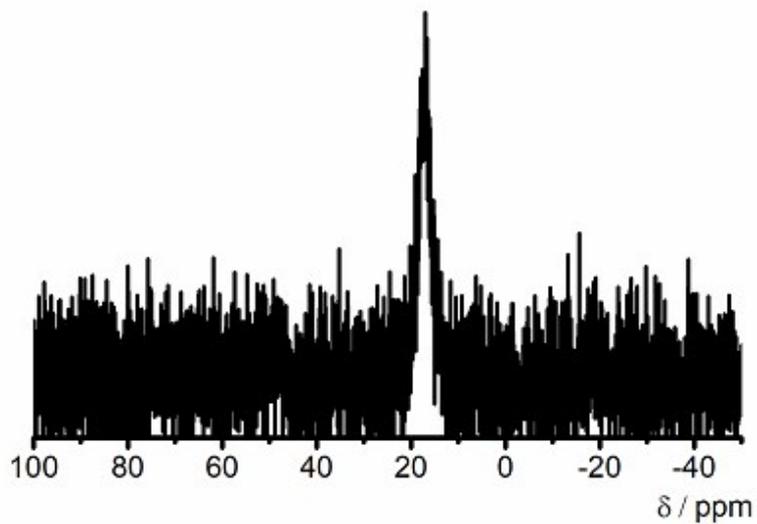


Fig. S3 CP-MAS ^{31}P NMR spectrum of few-layer phosphorene.

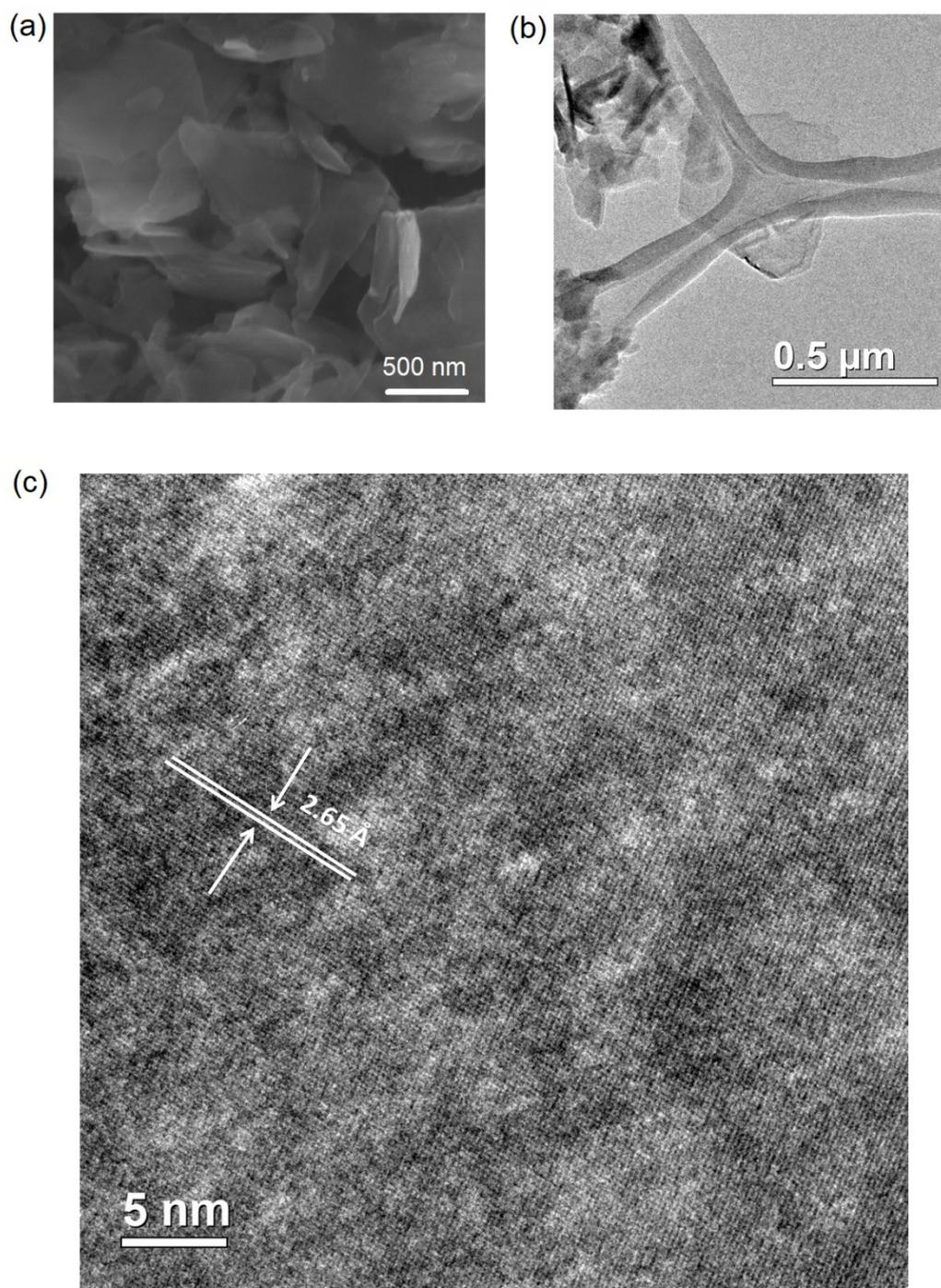


Fig. S4 Microscopic characterization of P-InCl₃; (a) SEM image, (b) low magnification TEM images and (c) HR-TEM showing (004) lattice plane.

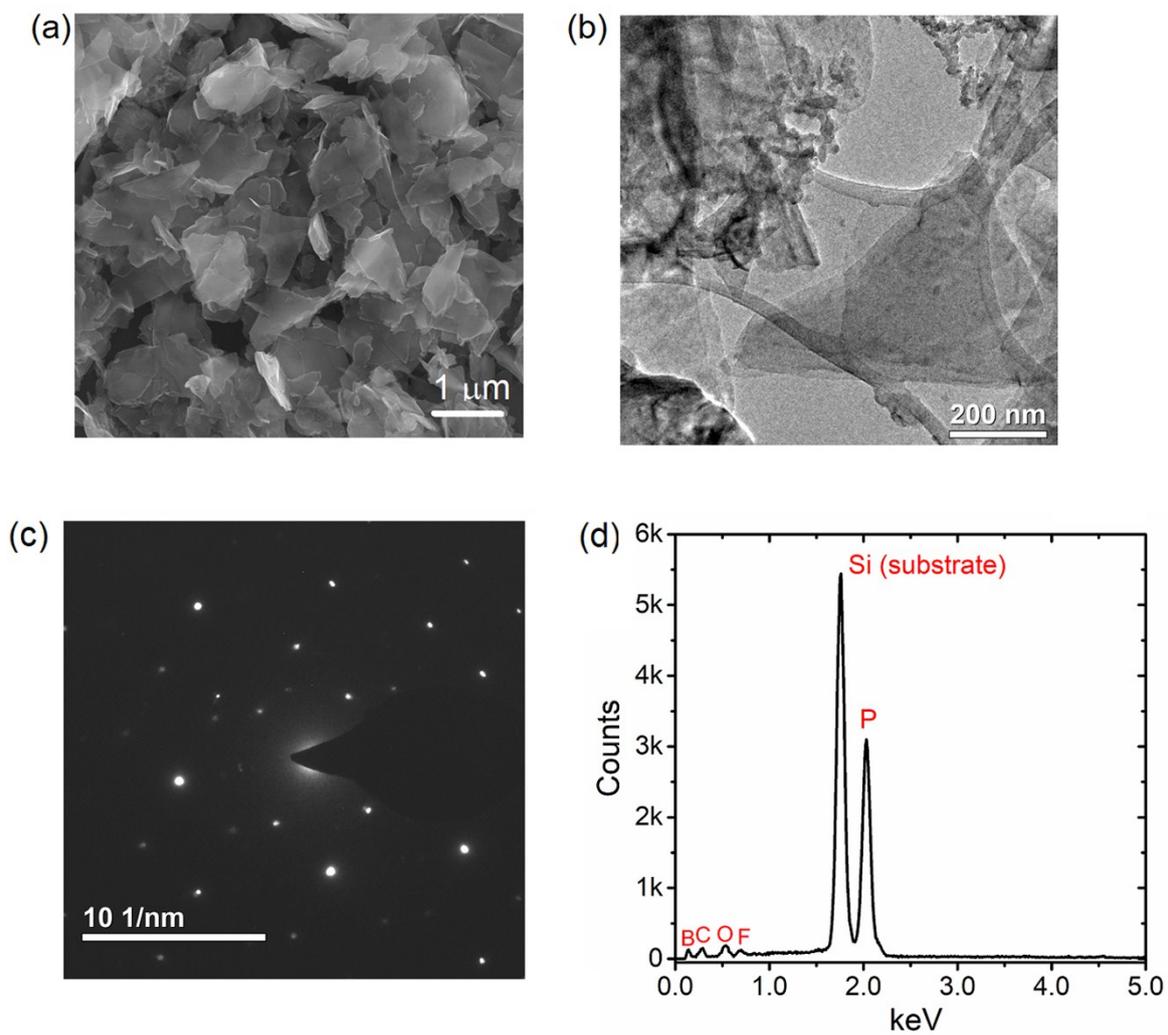


Fig. S5 Microscopic characterization of $P \cdot B(C_6F_5)_3$; (a) SEM image. (b) TEM image, (c) SAED pattern and (d) EDS spectrum.

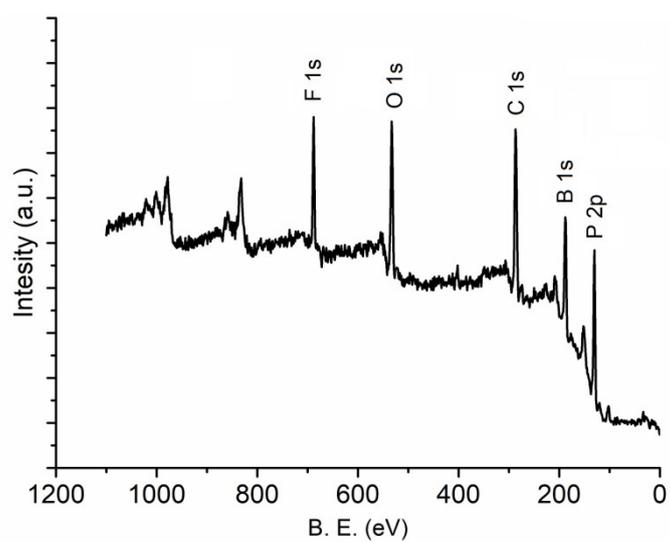


Fig. S6 Survey spectrum of $P \cdot B(C_6F_5)_3$ adduct.

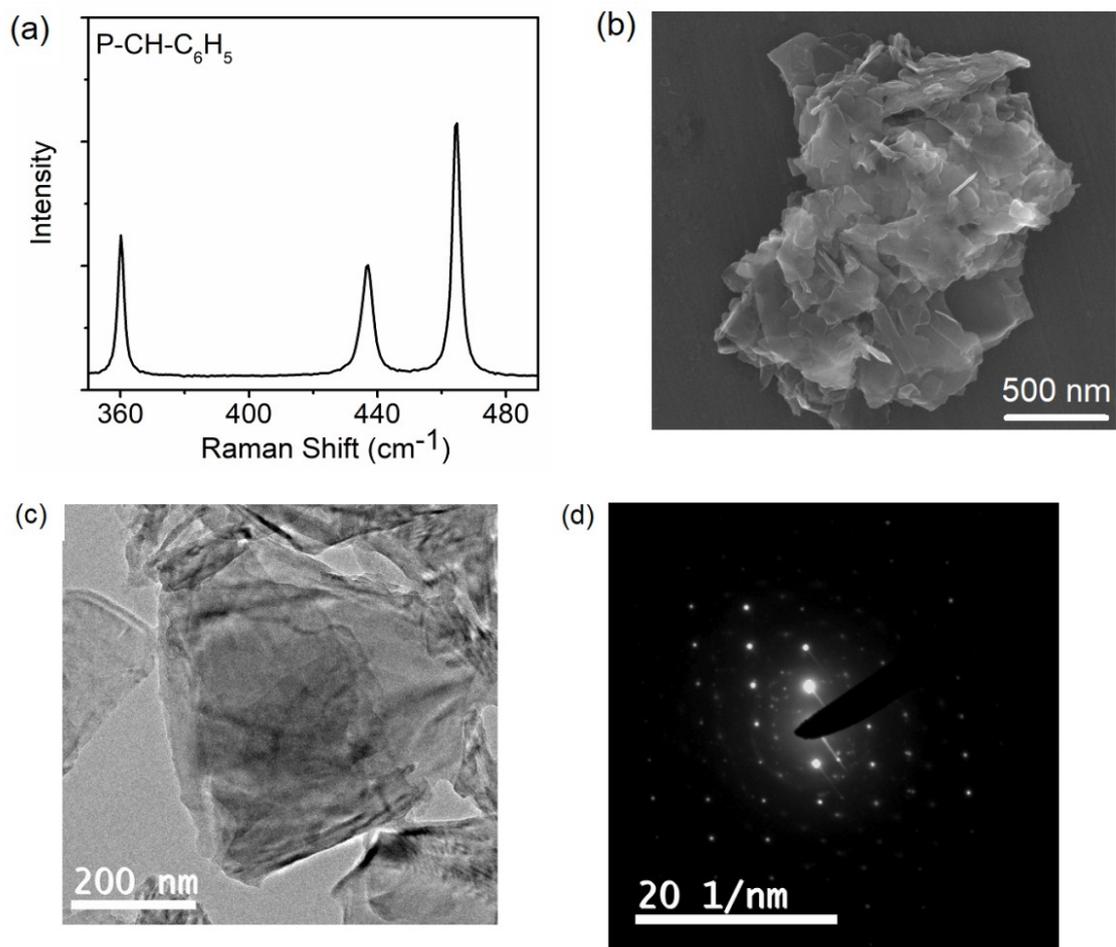


Fig. S7 Characterization of P-CH-C₆H₅; (a) Raman spectrum, (b) SEM image, (c) TEM image and (d) SAED pattern.

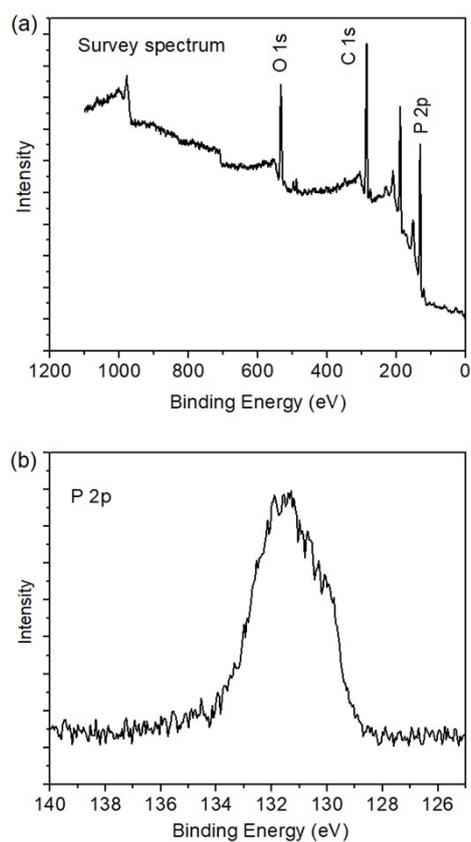


Fig. S8 XPS of P·CH-C₆H₅; (a) survey spectrum and (b) high-resolution P 2p spectrum.

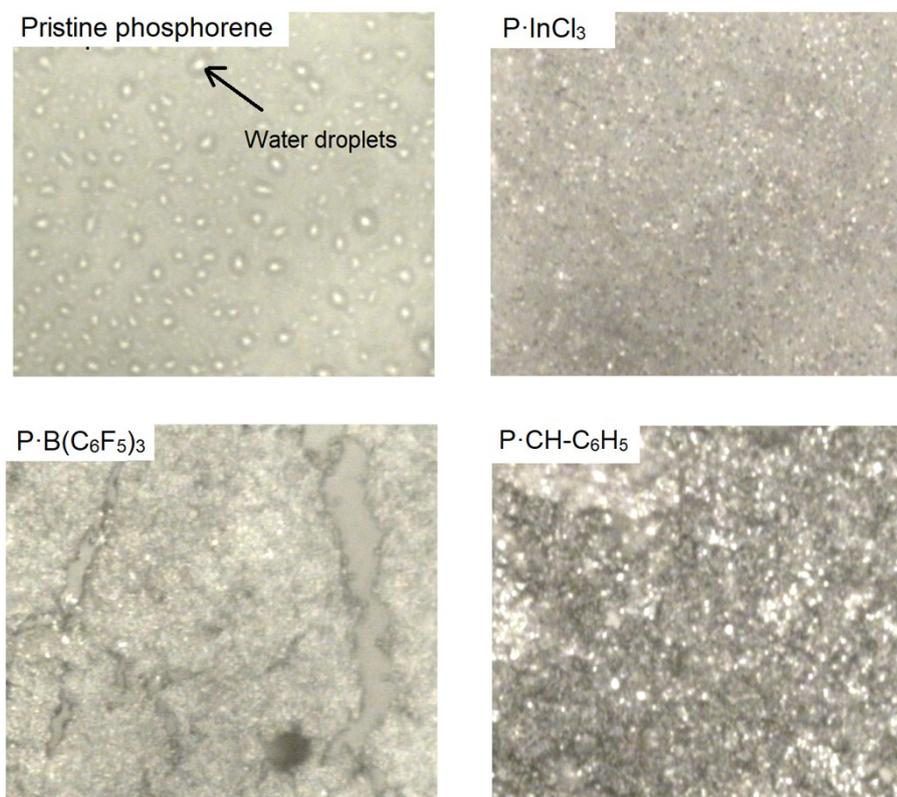


Fig. S9 Optical images of the samples prepared on glass slides for Raman study. The images were taken after exposing the samples to ambient air for 20 days.

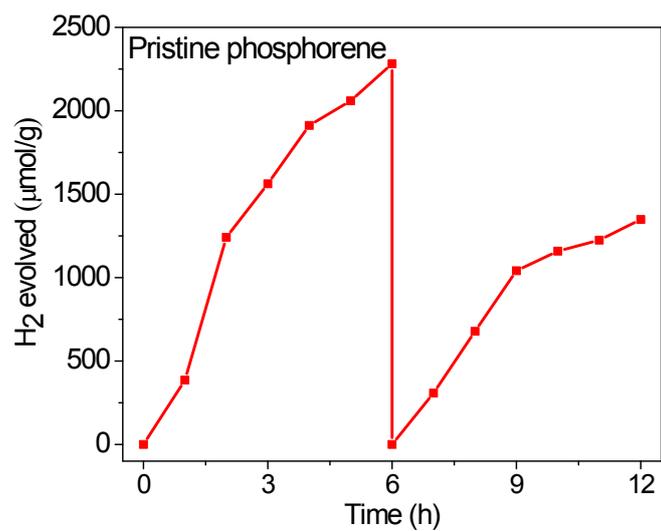


Fig. S10 Cyclic stability study on pristine phosphorene.

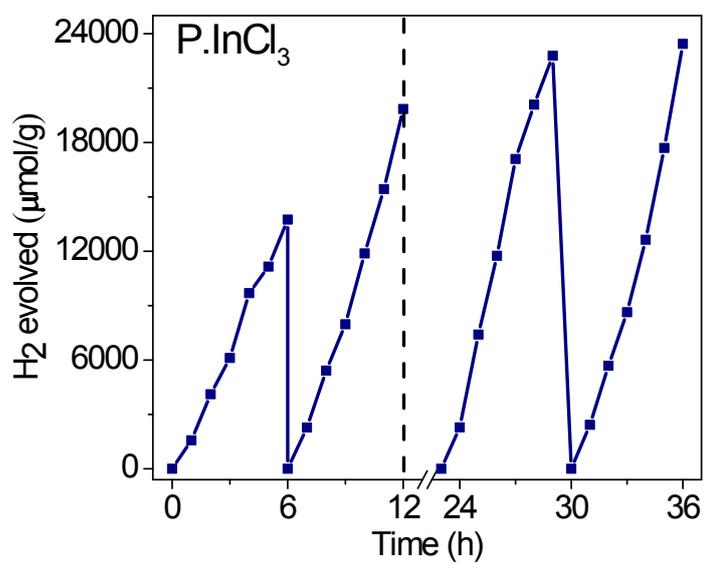


Fig. S11 Cyclic stability study on P·InCl₃ for 36 h.

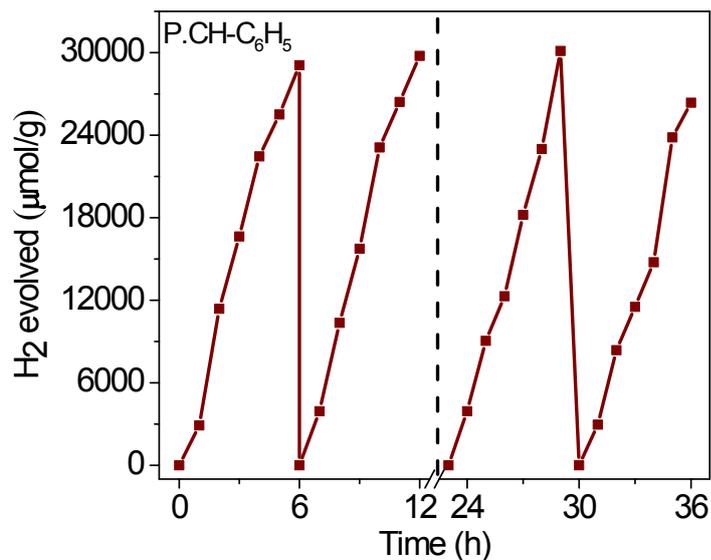


Fig. S12 Cyclic stability study on P·CH-C₆H₅ for 36 h.

Stability of the Photocatalysts after HER Experiments. The H₂ evolution reaction (HER) mixture was centrifuged at 6000 rpm for half an hour, and the photocatalyst (sediment) was collected. The sediment was washed with deaerated water to remove water soluble components, *i.e.* ETOA and EY. The catalysts were characterized by Raman spectroscopy and scanning electron microscopy (SEM). The SEM images (Figure S13) show layered nature of 2D few layer phosphorene sheets. The Raman spectra (Figure S14) show three bands characteristics of phosphorene. These studies suggest that there are no obvious changes in the structure and morphology due to HER. Raman spectra were obtained by drop-casting the aqueous dispersion of the samples on glass slides and the spectra were recorded at arbitrarily selected five different areas. SEM images were obtained by drop-casting the aqueous dispersion of the samples on Si-substrates.

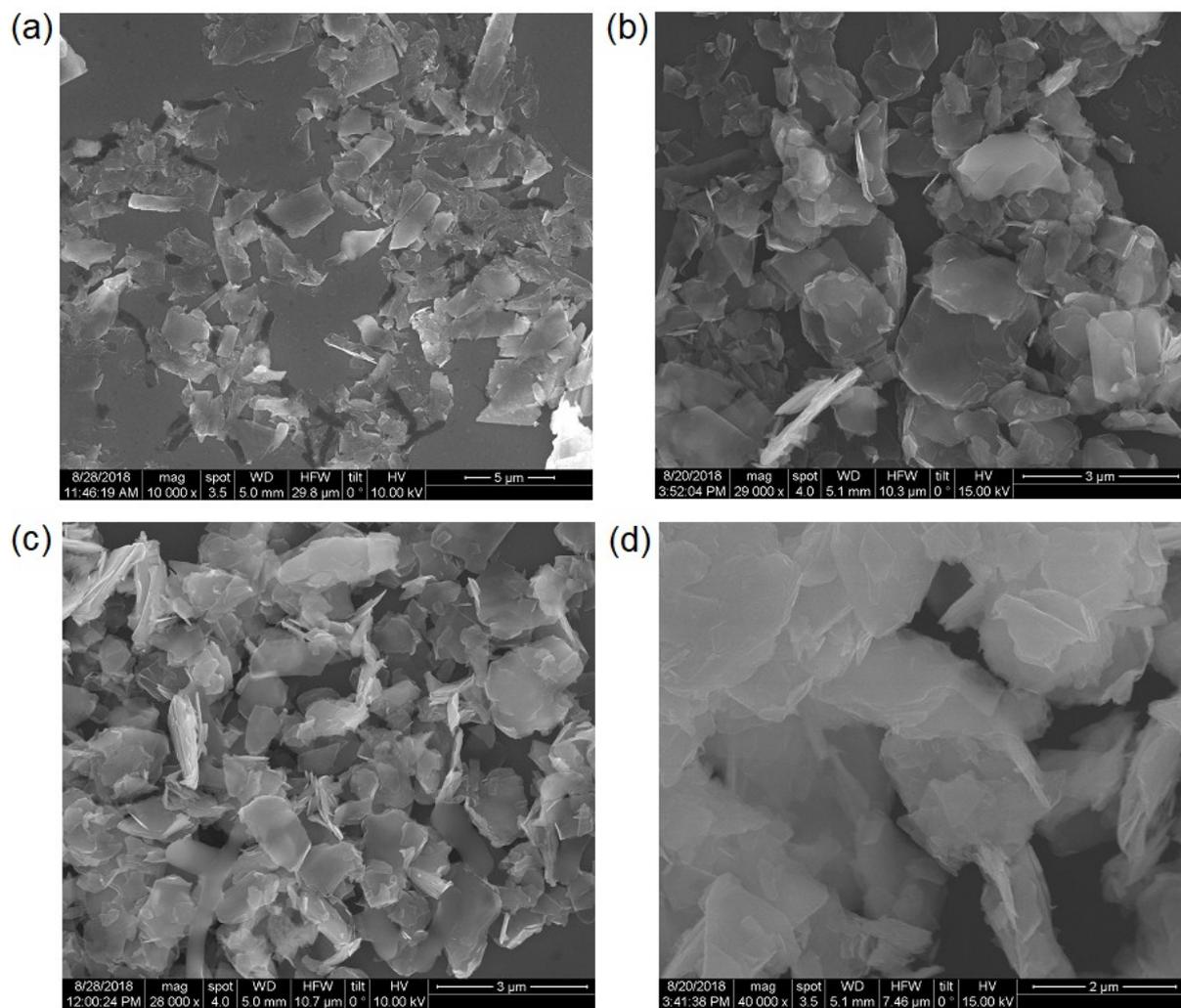


Fig. S13 SEM images of phosphorene photocatalysts, recovered after HER experiments. (a) Pristine phosphorene. (b) $\text{P}\cdot\text{InCl}_3$. (c) $\text{P}\cdot\text{B}(\text{C}_6\text{F}_5)_3$. (d) $\text{P}\cdot\text{CH-C}_6\text{H}_5$.

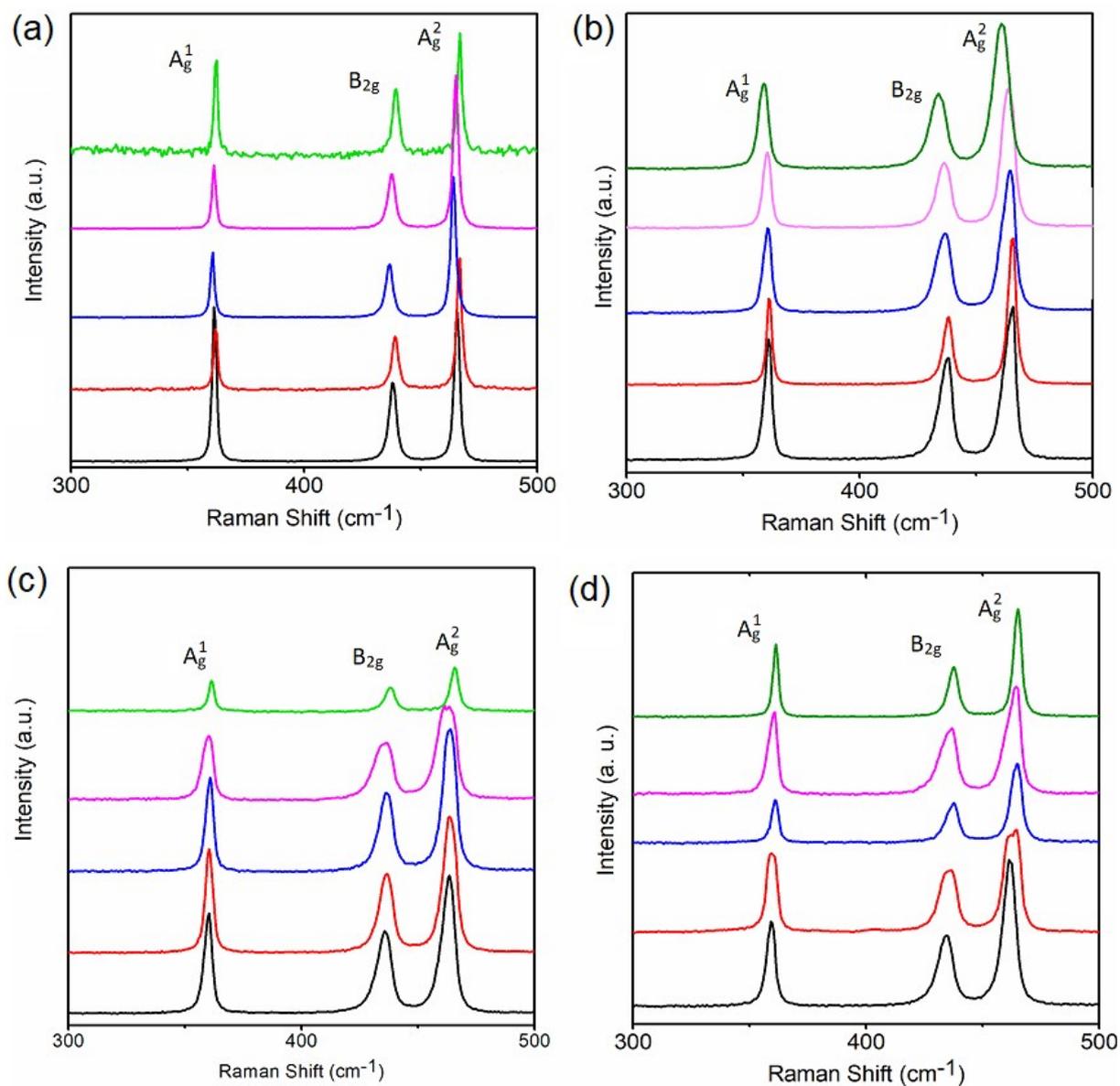


Fig. S14. Raman spectra of phosphorene photocatalysts, recovered after HER experiments; (a) Pristine phosphorene, (b) $\text{P}\cdot\text{InCl}_3$, (c) $\text{P}\cdot\text{B}(\text{C}_6\text{F}_5)_3$ and (d) $\text{P}\cdot\text{CH}\text{-C}_6\text{H}_5$. The Raman spectra are collected at arbitrarily selected five distinct areas of each sample.

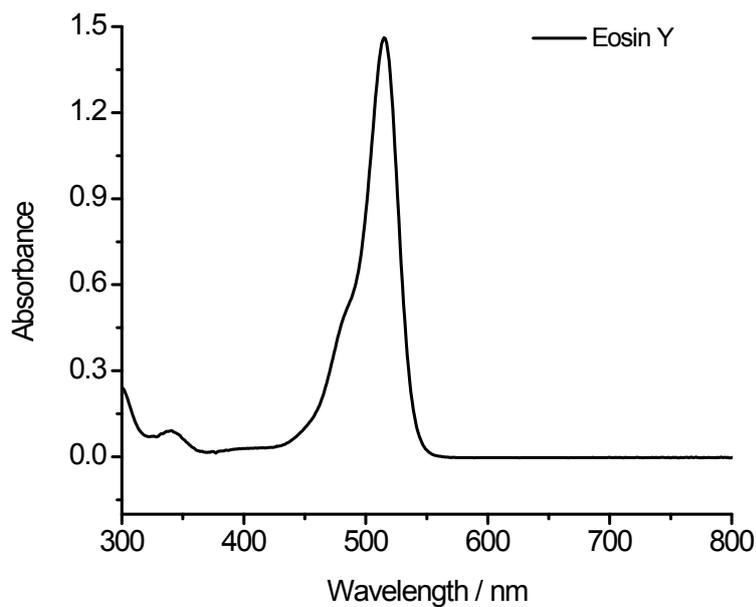


Fig. S15. UV-visible absorption spectrum of an aqueous solution of Eosin Y dye, Concentration 1.7×10^{-5} M.

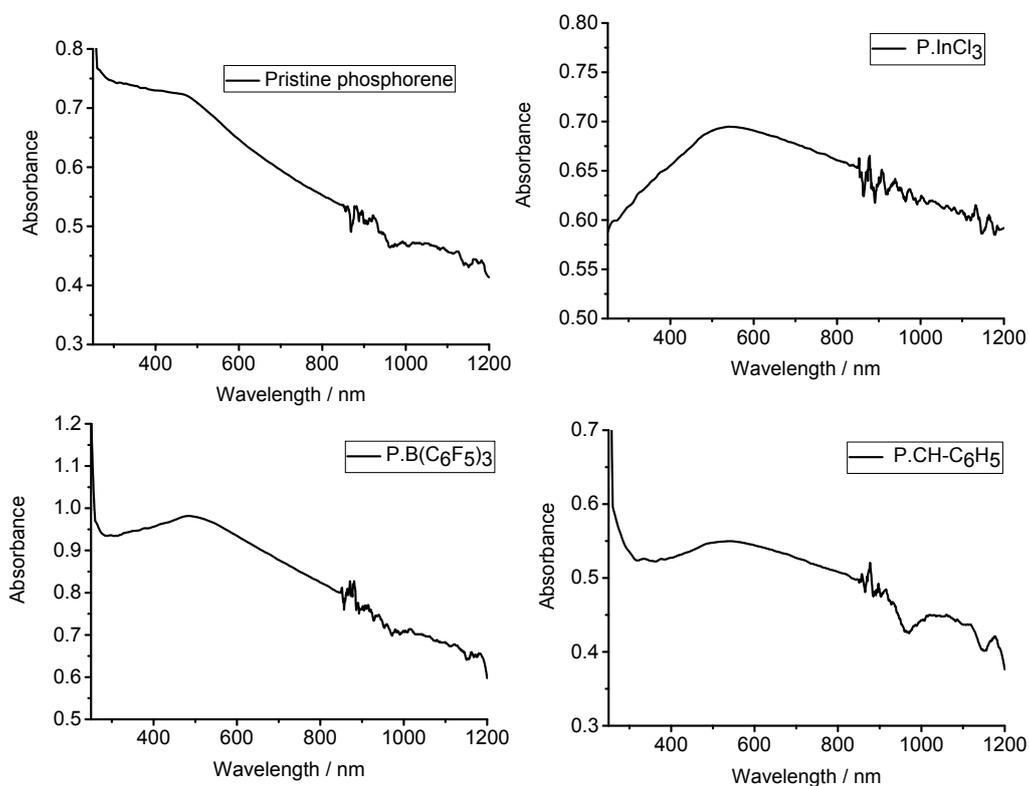


Fig. S16. UV-visible absorption spectra of aqueous dispersions of pristine and functionalized phosphorenes.

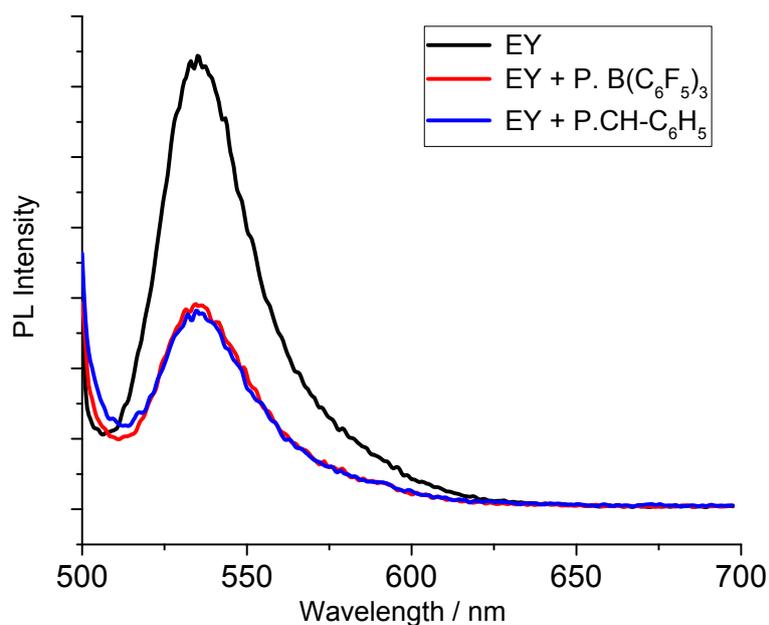


Fig. S17. Photoluminescence quenching profile of aqueous solution of EY (concentration = 1.4×10^{-7} M; excitation wavelength = 490 nm) in the presence of functionalized phosphorenes. The spectra were recorded in aqueous solution of TEOA (10%; v/v).

References

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