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Supporting Information

Evolution of hydrogen by few-layered black phosphorus under visible illumination

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Experimental details:

Exfoliation of black phosphorus nanosheets: High purity black phosphorus crystal pieces (5g in argon filled glass ampoule) were purchased from smart elements, GmbH and stored in Argon filled glove box immediately. Organic solvents like N, N-Methyl Pyrrolidinone (NMP), Isopropyl alcohol (IPA) are obtained from Sigma-Aldrich. Raw BP crystals (~200 mg)) are grounded well into coarse powder with the help of mortar and pestle inside the glove box and transferred to100 ml of organic solvent, NMP immediately. This mixture was probe sonicated with Vibra Cell (VCX-500W, Sonics Inc, USA) for 6 hr with 40% amplitude and duty cycle (5 s on and 5 s off) within the range of 4-8°C using an ice bath. Sonicated dispersion was kept idle for few hours to remove un-exfoliated BP crystals by gravity and the subsequent 90% of the supernatant was transferred to Centrifuge (KUBOTA 4200, AT-508C, fixed angle rotor) and centrifuged at 1000 rpm (150g) for 180 min to remove completely un-exfoliated BP crystals. Top 60% supernatant was collected by micro pipette from the centrifuge tubes without disturbing them. Further, exfoliated BP was subjected to centrifugation at 6000 rpm for 60-80 min, and top 80% supernatant was pipette out to remove broken BP crystals/small nanosheets/ nanoparticles and the sediment was re-dispersed again in fresh NMP for further experiments (Sample A, BP nanosheets). These samples were further centrifuged (Eppendorf 5424, fixed angle rotor) at 14,400 rpm (20238 rcf) for 20 min and sediment was collected (Sample B, BP nanosheets) and the supernatant was discarded. These two sets of samples (Sample A and Sample B, BP nanosheets) were always stored in NMP to protect it from the degradation. The main difference between Sample A and Sample B-BP nanosheets is average lateral size, <L> and the number of layers, <N>. The concentration of exfoliated BP nanosheets (Sample A and Sample B) was calculated using Beer-Lamberts law by following literature coated extinction coefficient (~15 l $g^{-1}cm^{-1}$).

Exfoliation of black phosphorus nanoparticles: The BP nanoparticles were synthesized by following earlier published report[1]. As purchased BP crystals (~5 mg) were added into 1 mL of NMP in a mortar and then ground with pestle for ~30 min inside the Argon filled glove box. Further, 3 mL of NMP was added to the grounded mixture and transferred to a glass vial and bath sonicated in an ice-bath for 5 h at the power of 300 W. The sonicated dispersion was centrifuged at speed of 4000 rpm for 45 min. The top 80% supernatant containing BP nanoparticles was pipette out gently.

Characterization techniques:

UV-Vis absorption spectroscopy: The absorbance spectra was recorded for the exfoliated BP nanosheets and BP nanoparticles in NMP dispersions using UV-Vis-NIR spectrophotometer (UV-3600 SCHIMANDZU) equipped with integrating sphere. Quartz cuvettes (10 mm path length, 3.5 ml total volume) have been used. The concentration of the BP nanosheets was derived by substituting measured absorbance at 465 nm in Beer Lambert's law, absorbance (A) = -log(I/I0) and measured A is correlated by A = εlc where ε is extinction coefficient in m/mg/ml and c is the concentration in mg/ml. We have used literature quoted extinction coefficient which is 15 $lg^{-1}cm^{-1}$ to calculate the concentration[2].

Atomic force microscopy: Exfoliated BP nanosheets in NMP was transferred to IPA after washing 2-3 times and the sample was highly diluted (look transparent to the eye) was drop casted over pre-heated Silicon substrate (120-140°C) and immediately removed from the hotplate to carry out AFM topography measurements. Images were recorded with Veeco AFM under tapping mode and the height profile was analysed with inbuilt software.

Field emission scanning electron microscopy (FE-SEM): FE-SEM imaging was performed using JOEL JSM-7600F Scanning Electron Microscope at 5-10 kV at a working distance of ~8 mm. Here freshly prepared solvent exchanged BP/IPA nanosheets samples are drop casted over preheated substrate and further coated by Platinum layer using sputtering technique (10 nm) to avoid discharge from the samples. The samples were prepared same as for the case of AFM samples.

High resolution transmission electron microscopy (HRTEM): HRTEM imaging was performed by using TEM JEOL 2010 HR instrument at an accelerating voltage of 200 keV. The samples were prepared on holey carbon grids using a drop casting method.

X-ray photoelectron spectroscopy (XPS) and Ultraviolet photoelectron spectroscopy (UPS): XPS is performed with monochromatic Al Kα radiation (hν = 1486.7 eV). UPS is performed with a helium discharge lamp (He I, hν = 21.2eV). The samples are prepared on preheated ITO substrates (~120 °C) by drop casting the BP nanosheets and BP nanoparticles (IPA solvent). The analyser work function is calibrated using Au Fermi level.

Raman spectroscopy: BP/IPA dispersion was drop casted over preheated Si/SiO_2 substrate. Raman spectra were recorded with WITEC Raman (Confocal) with 0.5 s integration time, 488 excitation wave length and 10 accumulations. Spectra were taken at different locations of the sample in order to represent the average value.

Hydrogen evolution Activity Test:

For hydrogen evolution activity test, the BP nanosheets and BP nanoparticles in NMP solvent was transferred to acetonitrile solvent by sedimentation and re-dispersion process. Briefly, the BP was centrifuged at 14,000 rpm to remove NMP and then dispersed in acetonitrile followed by solicitation for 5 min and centrifugation to remove residual NMP solvent. This process was repeated 3 times. H_2 evolution reactions were carried out in a top-window Pyrex reaction cell connected to a closed gas circulation and evacuation system. A 300-W Xe lamp equipped with a 420 nm cut off filter was used as the light source. In a typical run, 10 mL acetonitrile solution containing 2 mg BP (nanosheets/nanoparticles) was mixed with 1.76 mL triethanolamine (TEOA) and 0.5 mL DI water in the reaction cell by constant stirring. Before light irradiation, the reaction system was evacuated and refilled with argon gas several times to remove air inside and finally filled with argon gas to reach a pressure of about 30 Torr. The temperature of the reaction cell was kept at around 20 °C by a water cooling jacket. The H_2 gas generated during the reaction was measured by an online gas chromatography (Shimadzu GC-2014, TCD detector, argon as the carrier gas, molecular sieve 5Å column).

Theoretical calculations:

The structural and optical properties of experimentally synthesized black phosphorous have been investigated based on Density Functional theory (DFT) formalism as implemented in VASP (Vienna Ab-initio Simulation Package) program. Projector augmented wave method (PAW) has been used to describe the core electrons behaviour and the interaction between valence electrons and the ion. The Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation (GGA) has been employed as the exchange-correlation functional to obtain the optimized configuration and consequently the respective optical absorption cross-section. The Brillouin zone has been sampled by 6x4x1 Monkhorst Pack k-points. The valence electrons are described by a plane waves basis set with an energy cut off of 500 eV. After obtaining the optimized structure, we increased the number of bands as double of the initial one so that there will be enough number of unoccupied states for allowed HOMO-LUMO transitions. The structure has been optimized until the calculate Hellman-Feynman forces are smaller than 0.01eV/Å. There is a large vacuum of 15 Å is used to consider the surface periodicity throughout the calculations.

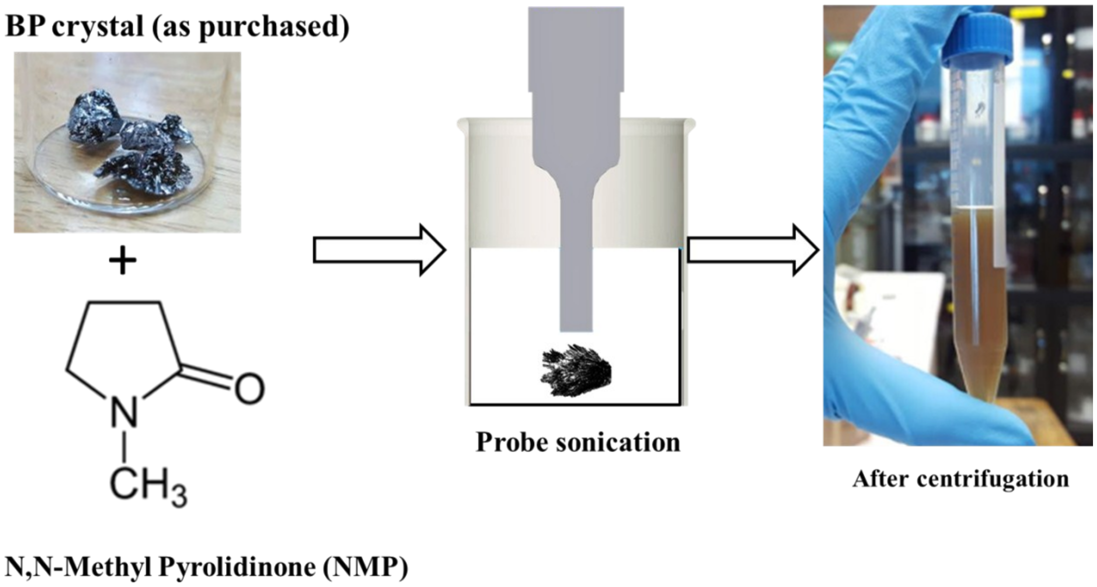
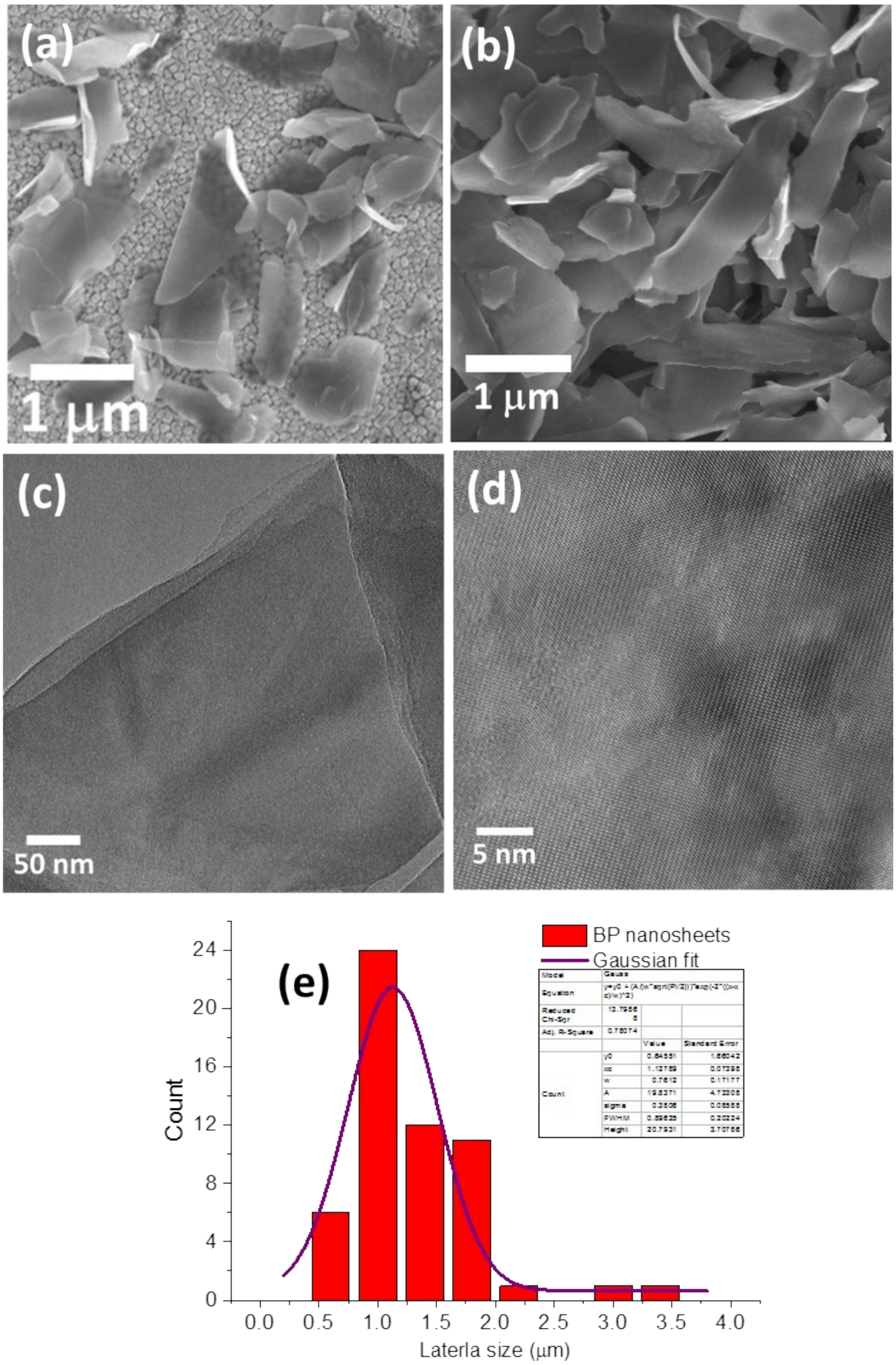


Fig. S1 *Schematic diagram of synthesis procedure of BP nanosheets.*



Model	Gauss		
Equation	y=y0 + (A/(w*sqrt(PI/2)))*exp(-2*((x-xc)/w)^2)		
Reduced Chi-Sqr	13.79665		
Adj. R-Square	0.78074		
		Value	Standard Error
Count	y0	0.84551	1.66042
	xc	1..12769	0.07396
	w	0.7612	0.17177
	A	19.5371	4.73306
	sigma	0.3806	0.08588
	FWHM	0.89625	0.20224
	Height	20.7931	3.70756

Fig. S2 (*a, b) SEM images of BP nanosheets, (c) TEM image and (d) HR-TEM image of BP nanosheet, (e)size histogram.*

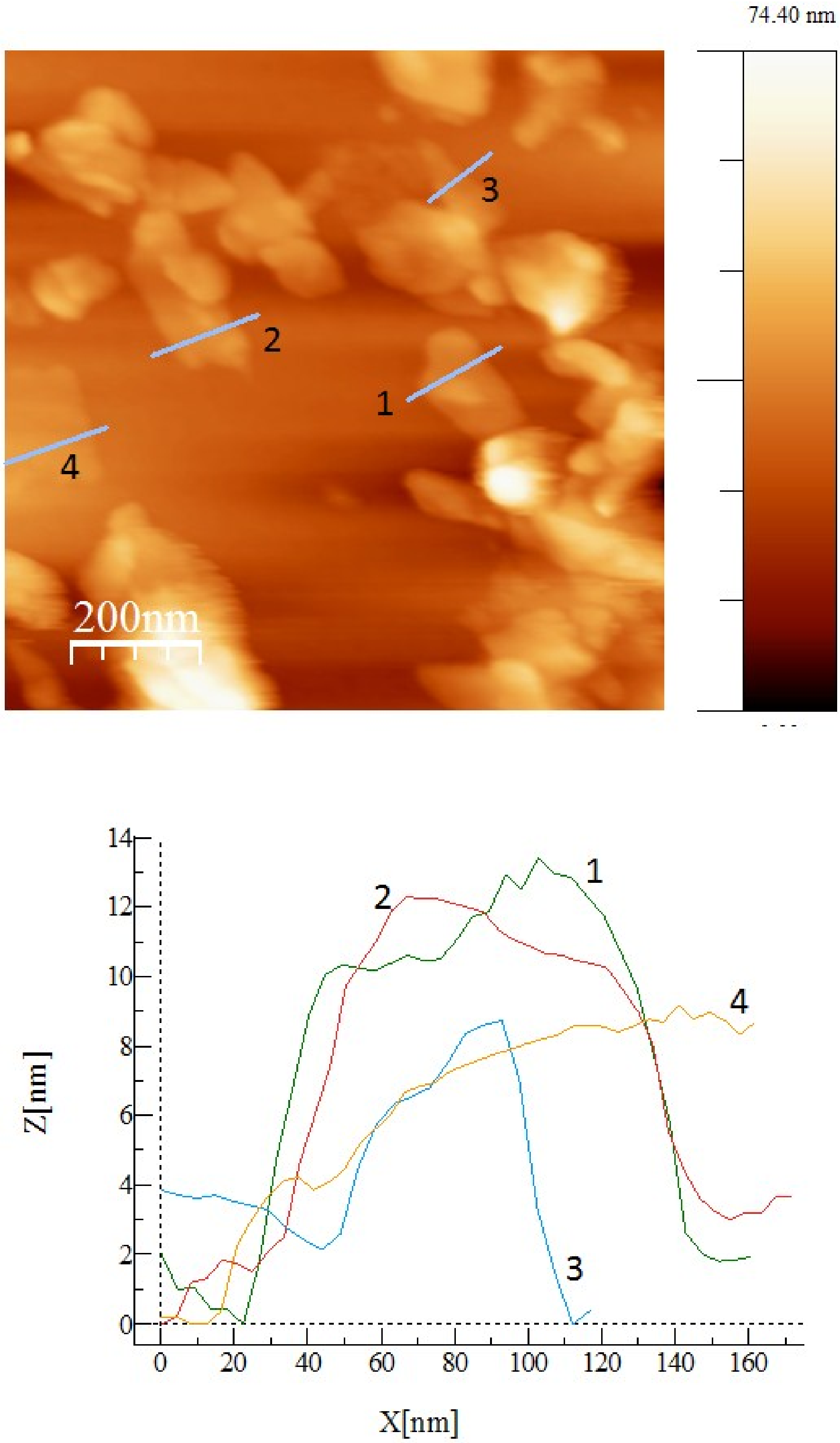


Fig. S3: *Typical AFM image and height profile of exfoliated BP nanosheets.*

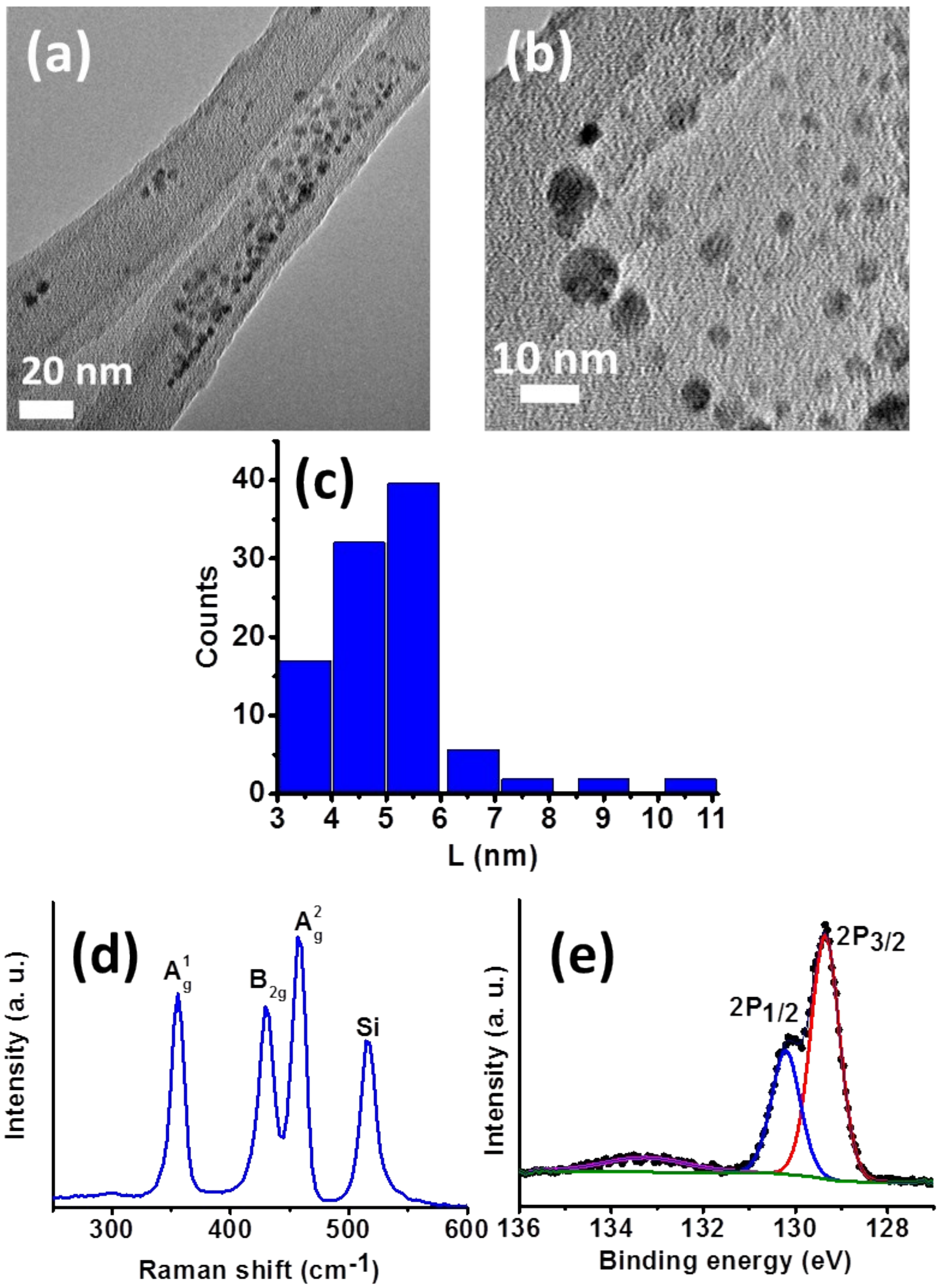


Fig. S4 *(a, b) TEM images of BP nanoparticles, (c)histogram of BP nanoparticles, (d) Raman spectrum of BP nanoparticles and (e) High-resolution XPS spectrum of BP nanoparticles.*

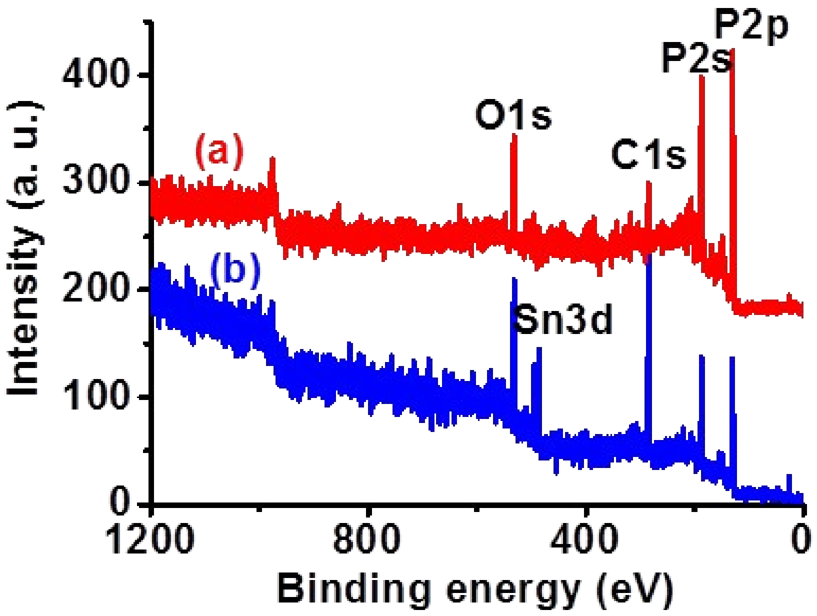
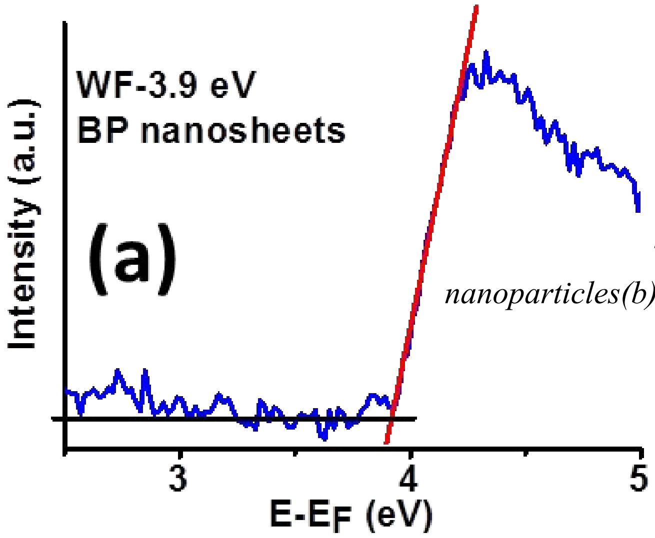
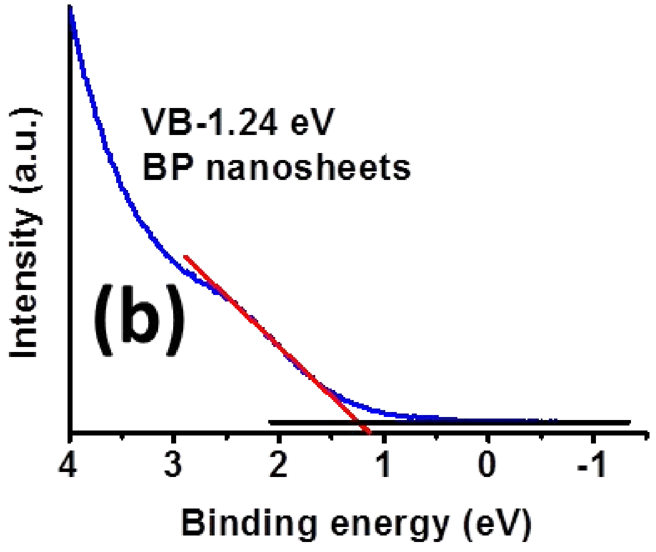


Fig.S5 *Wide-scan XPS survey spectrum of BP nanosheets (a) and BP nanoparticles(b).*





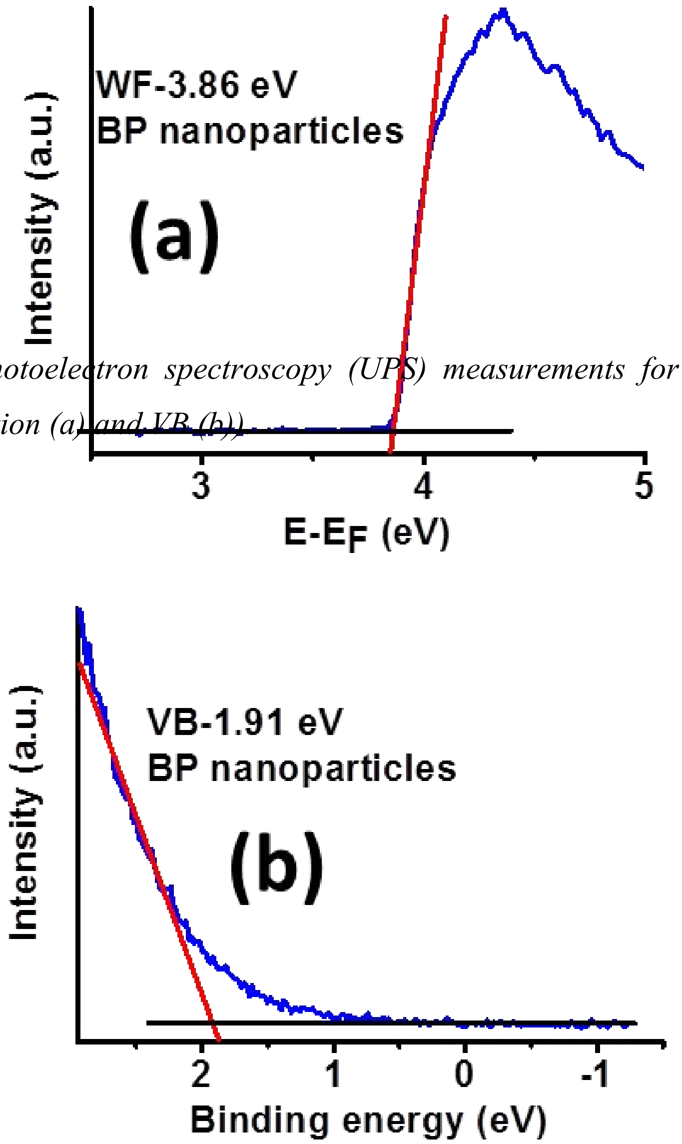


Fig. S6 *Ultraviolet photoelectron spectroscopy (UPS) measurements for the case of BP nanosheets (Work function (a) and VB (b)).*

Fig. S7 *Ultraviolet photoelectron spectroscopy (UPS) measurements for the case of BP nanoparticles (Work function (a) and VB (b)).*

The material's Fermi level is commonly measured by means of the work function measurement in UPS [3]. Work function is the energy difference between Fermi level and vacuum level. The former level is the highest energy where electron can be filled and the latter one is the minimum energy needed to excite a bound electron into a free electron. Without any contact, all materials are naturally vacuum level aligned. However, when two materials are in electrical contact, the Fermi level difference will push the carriers towards the lower Fermi level until two Fermi levels are in equilibrium. The only exception is insulator with all carriers are localized. In UPS measurement, Fermi level is always our naturally zero point and all binding energy refers to Fermi level as zero.

In semiconductors, a forbidden gap is formed right around Fermi level region causing no significant states to exist there. This is why UPS can determine the valence band maximum (VBM). No states or no electron is available above the VBM and this gives a clear cutoff in

UPS spectrum. When estimating the Fermi level (work function) through UPS measurements, we do not directly measure the electrons from the Fermi level. A direct measurement will be very unreliable/ impossible. Instead, work function is determined by comparing sample and analyzer work function using secondary electrons which have been scattered randomly during emission process. When a sample work function is larger than the electron analyzer used, a kinetic energy onset will be present at the lower energy range. To make the onset more obvious and to measure the onset when sample work function is smaller than analyzer work function, a negative bias (-5V in our measurement) is usually applied to sample. After subtracting the bias applied, this onset energy indicates the work function difference between sample and analyzer. Since we can determine the analyzer work function by a standard Au sample which has electrons at the Fermi level, the sample work function can be determined using formula below:

$$\Phi_s = E_{onset} - V + \Phi_a$$

Φ_s is the sample work function and Φ_a is the analyzer work function. E_{onset} is the secondary onset energy measured in UPS and V is the value of the bias applied.

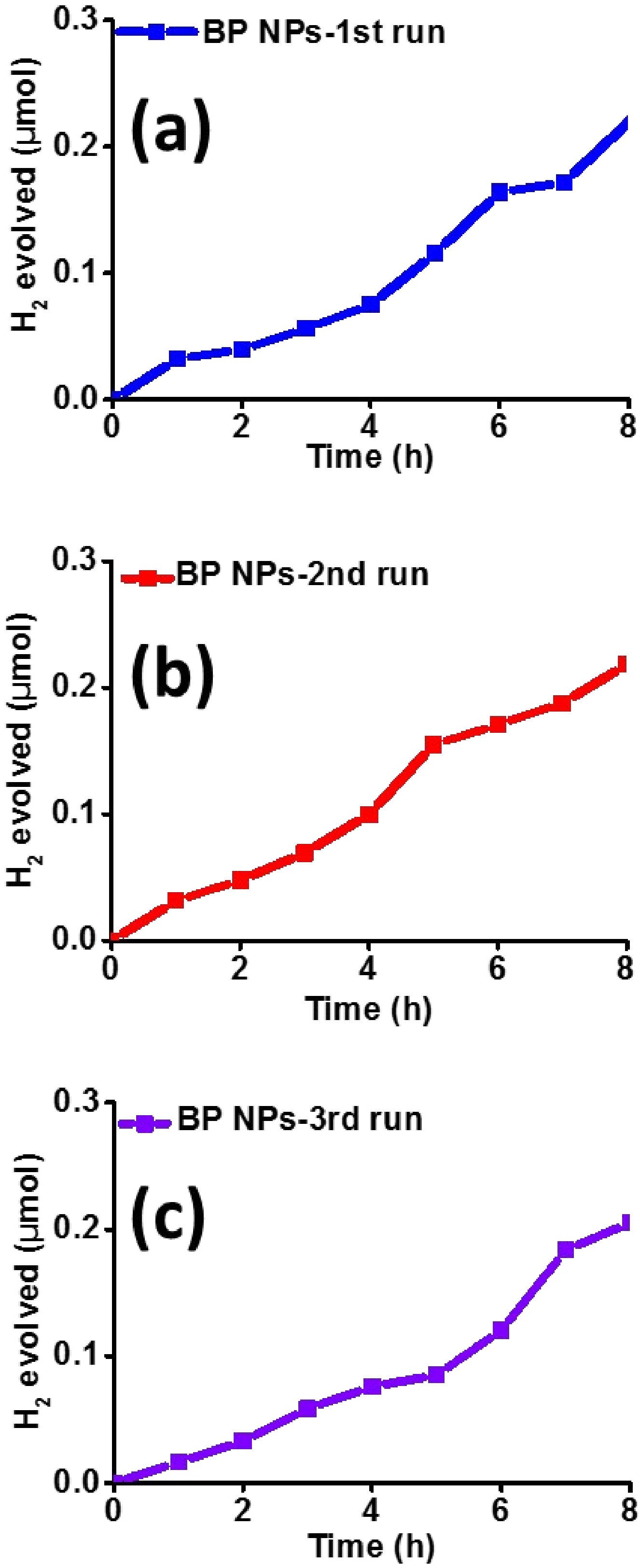


Fig. S8 *H_2 evolution performance of BP nanoparticles (a) 1st run, (b) 2nd run after degassing, and (c) 3rd run after degassing (Conc. 0.8 mg/ml).*

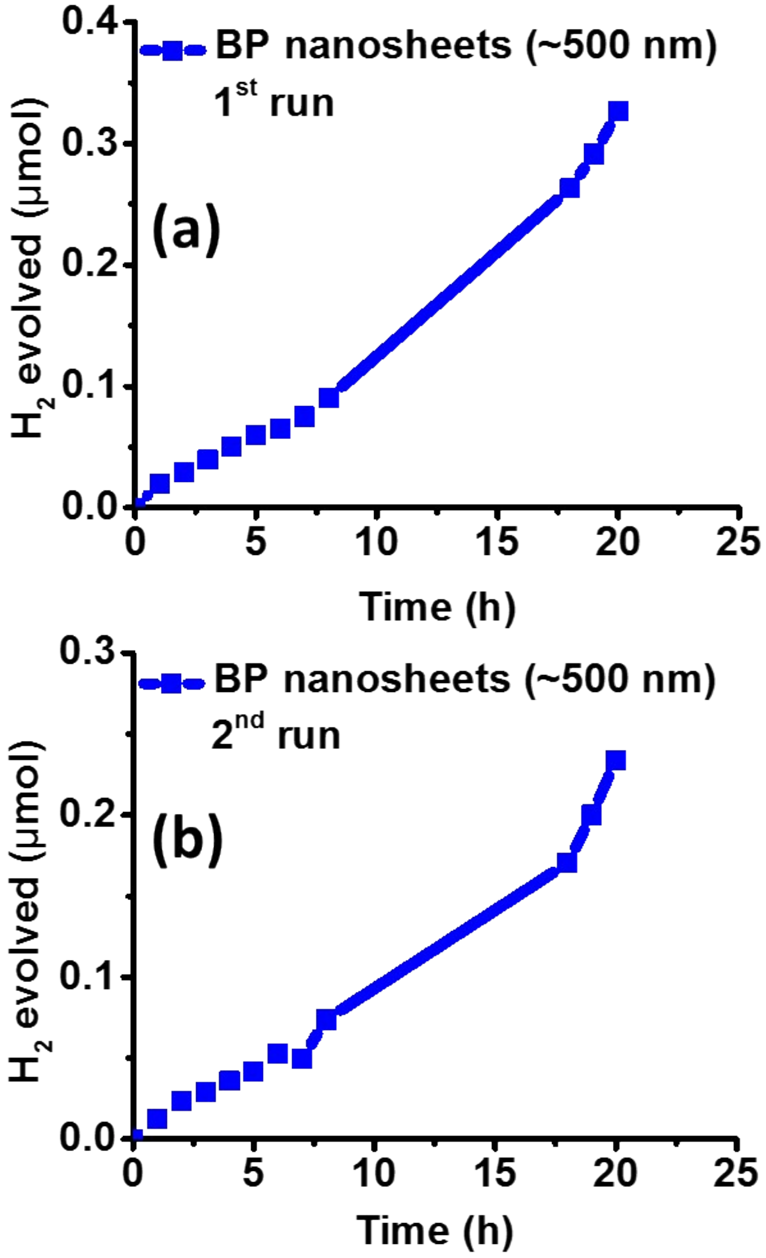


Fig. S9 *H_2 evolution performance of BP nanosheets (sample B, Conc. 0.1 mg/ml, liquid volume, 10 ml) (a) 1st run, (b) 2nd run after degassing.*

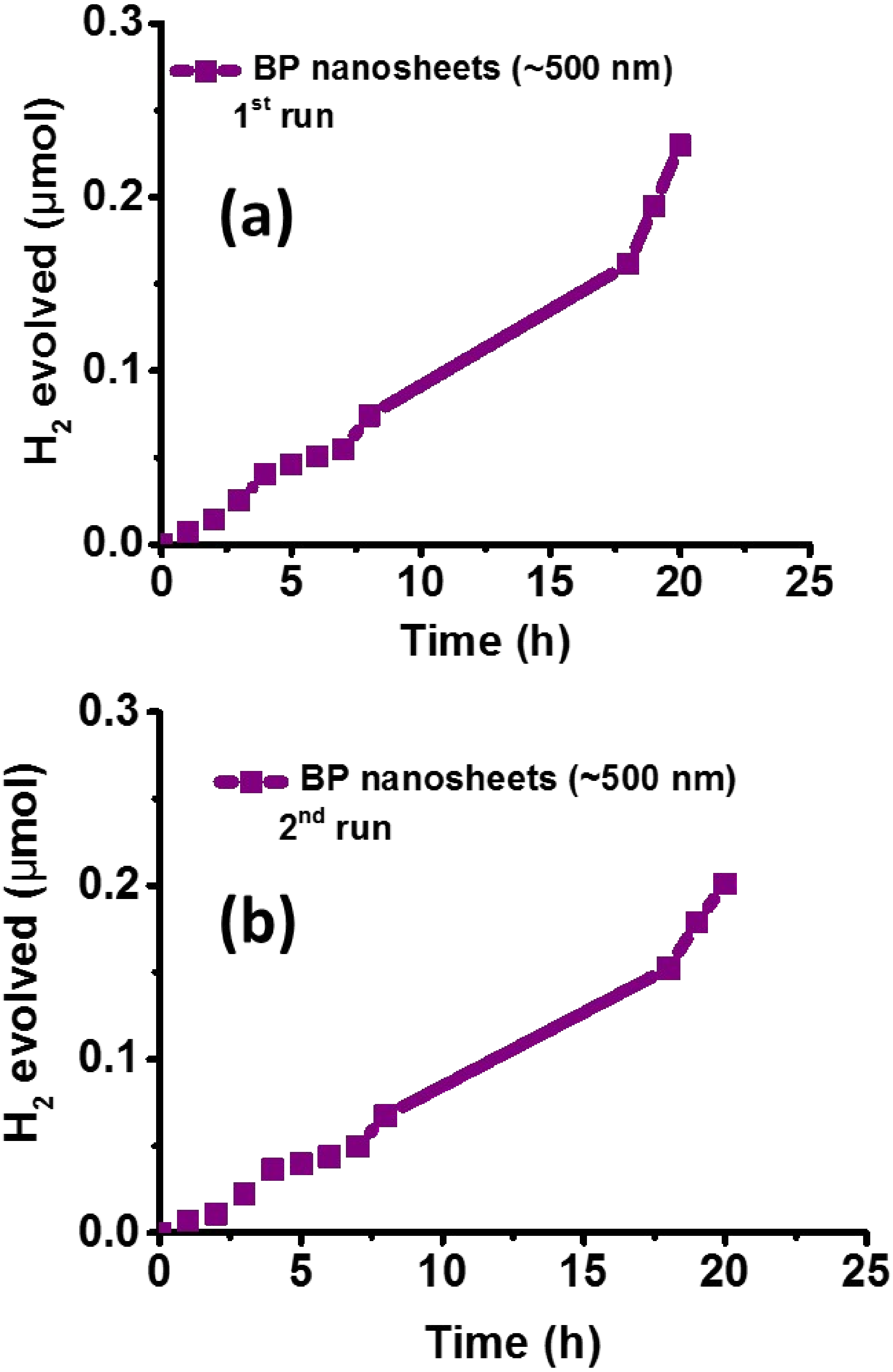


Fig. S10 Concentration dependant *H_2 evolution performance of BP nanosheets (sample B, Conc. 0.13 mg/ml, liquid volume, 45 ml) (a) 1st run, (b) 2nd run after degassing.*

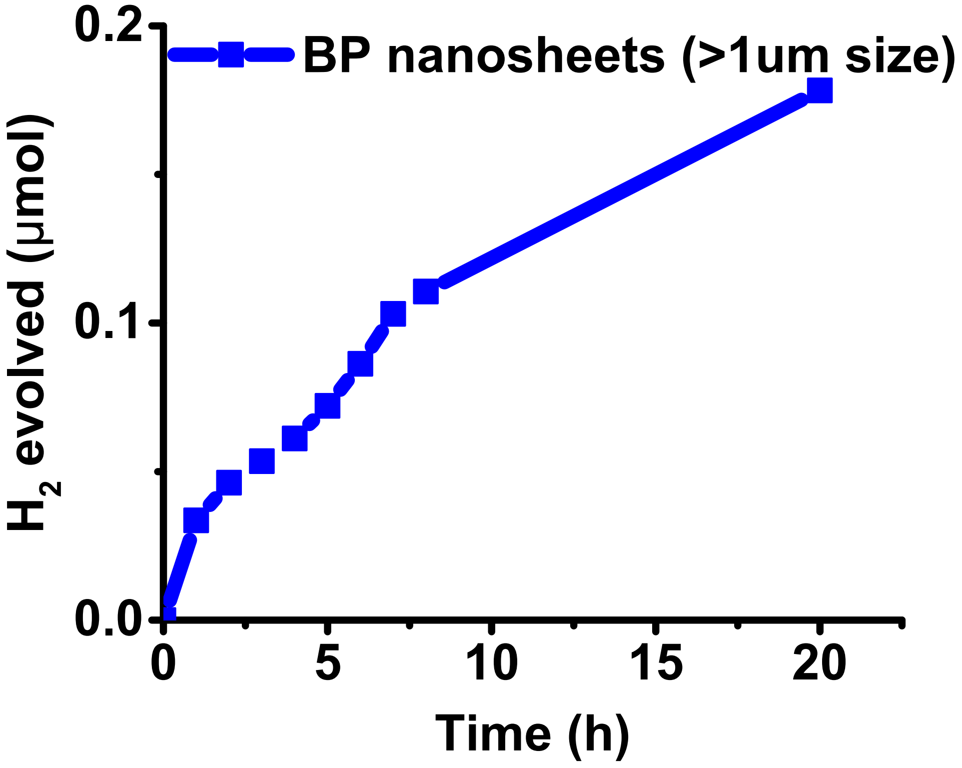


Fig. S11: *H_2 evolution performance of BP nanosheets (sample A, Conc. 0.25 mg/ml, liquid volume, 10 ml).*

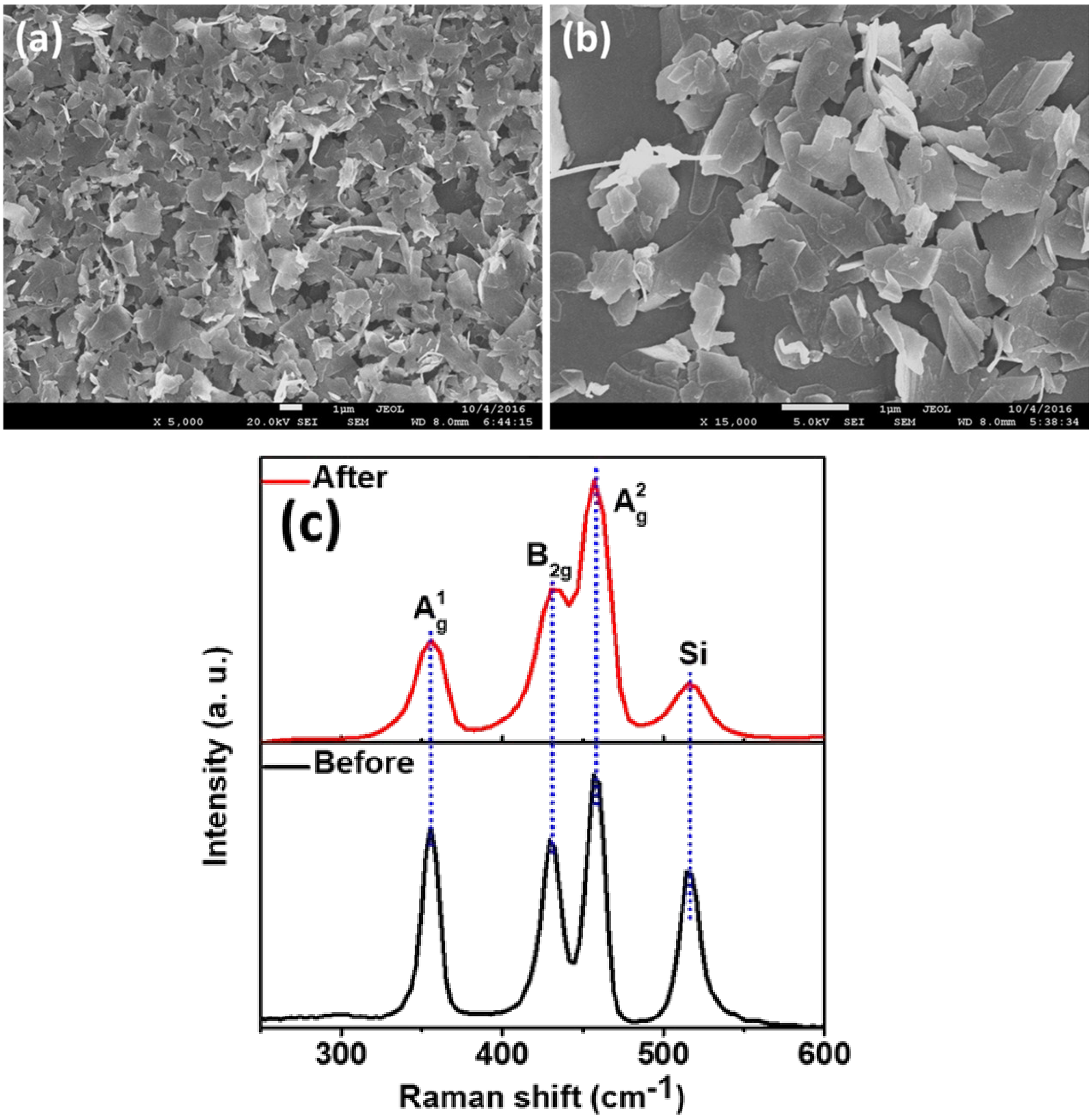


Fig. S12 *Characterization of BP nanosheets before and after* H_2 *evolution measurements (a, b) FE-SEM images and (c) Raman spectra of BP nanosheets.*

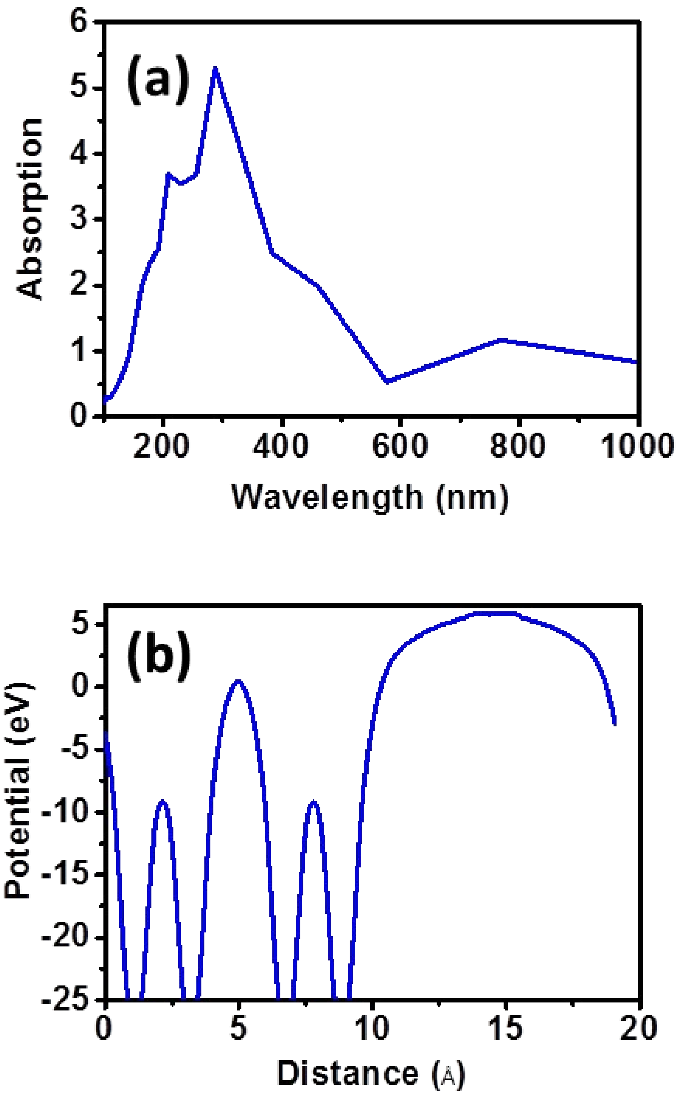


Fig. S13 *DFT calculated absorption spectra (a) and work function (b) of black phosphorous (bilayer).*

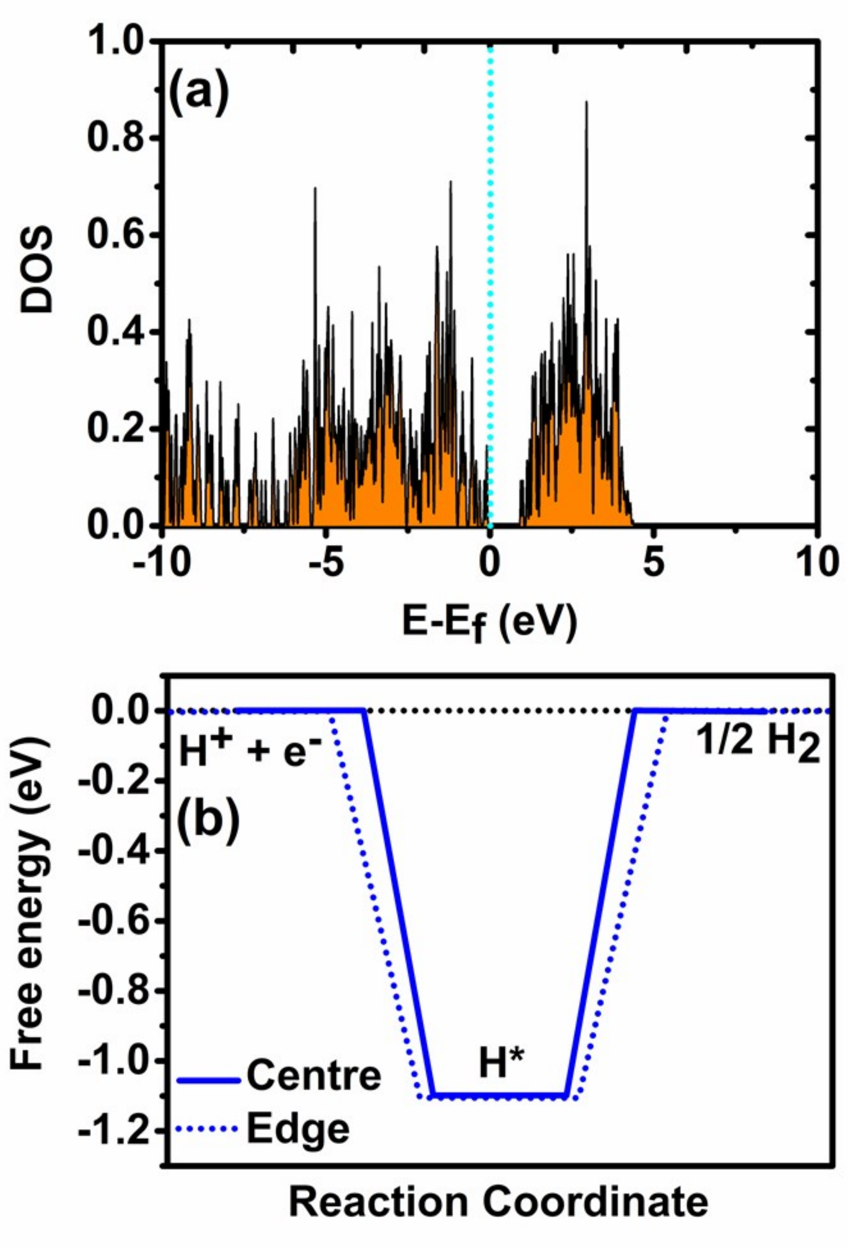


Fig. S14 *(a) density of states* (states/eV) *of black phosphorous (monolayer) and (b) free-energy diagram of HER on the surface of black phosphorous (monolayers)*

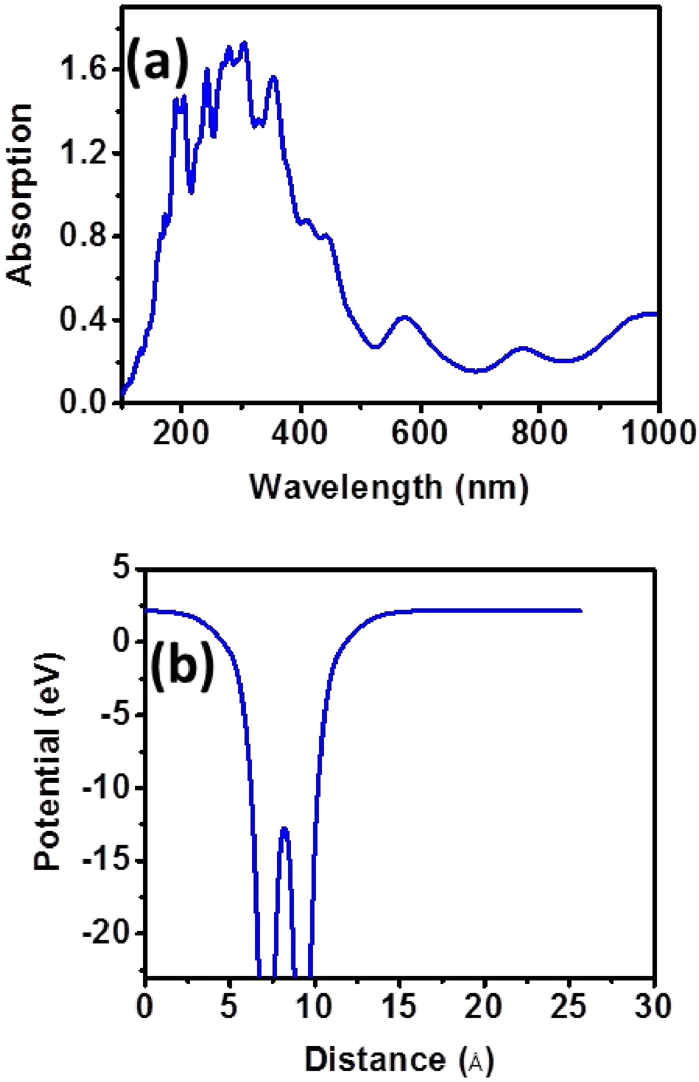


Fig. S15 *DFT calculated absorption spectra (a) and work function (b) of black phosphorous (monolayer)*

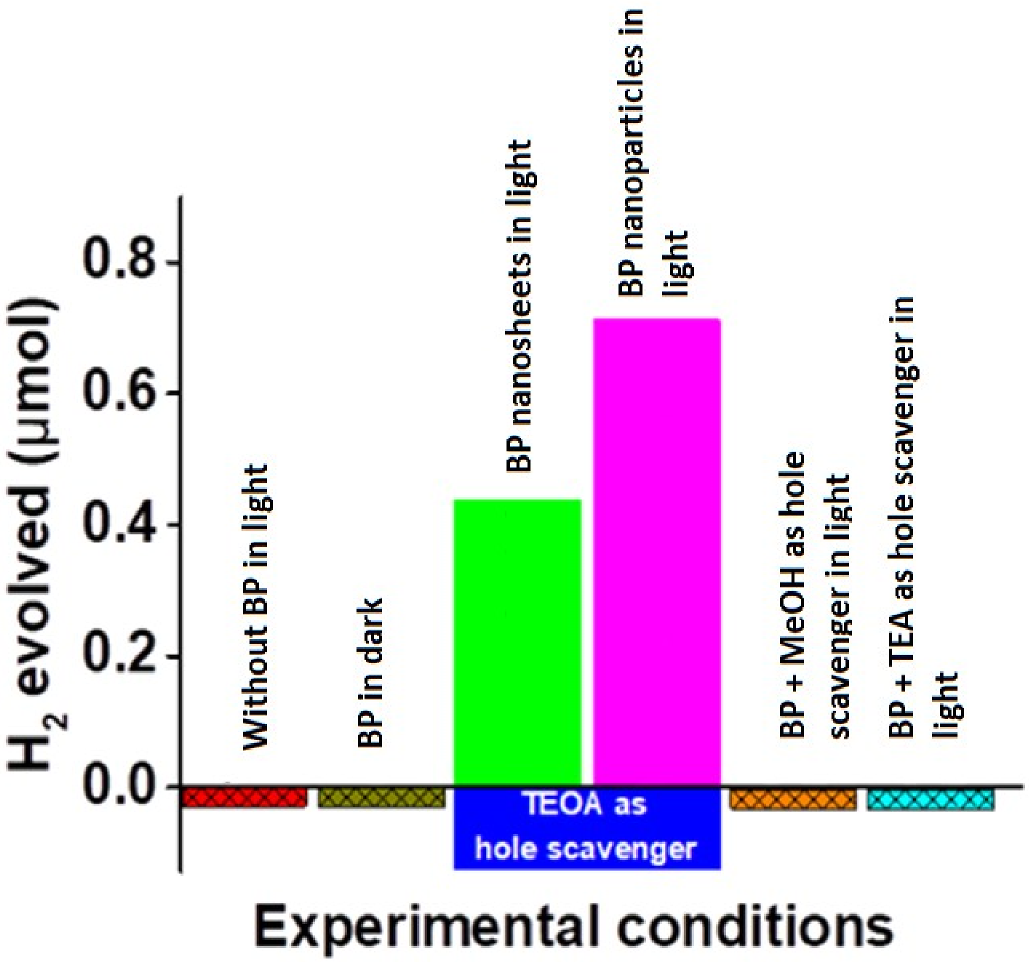


Fig. S16 *Hydrogen evolution activity of BP at different experimental conditions.*

References

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