Electronic Supplementary Information

Facile preparation of NH_2-functionalized black phosphorene for electrocatalytic hydrogen evolution reaction

Lianyi Shao,[a] Hongming Sun,[a] Licheng Miao,[a] Xiang Chen,[a] Mo Han,[a] Jianchao Sun,[a] Shuang Liu,[a] Lin Li,[a] Fangyi Cheng[a,*] and Jun Chen[a,b]

[a] China Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China.
[b] State Key Laboratory of Elemento-Organic Chemistry, Innovative Collaboration Center of Chemical Science and Engineering, Nankai University, Tianjin 200071, China.

Experimental section:

Preparation of NH_2-functionalized BP nanosheets. Bulk BP (>99.998% purity) was purchased from XFNANO. The nanosheets were prepared from exfoliation of bulk BP by a solid-state ball milling method. In a typical synthesis, BP (100 mg) and $CO(NH_2)_2$ (200 mg, 99% purity) were mechanically ball-milled at a rate of 150 rpm for 4 h under Ar atmosphere using a planetary ball-mill machine (Pulverisette 7 Premium Line). The milled samples were washed with oxygen-free water and ethanol several times in an Ar-filled glove box to remove $CO(NH_2)_2$. The collected powders were dispersed in absolute ethanol (200 mL) in a sealed bottle and ultrasonicated at a power of 300 W for 0.5 h in ice water. The resultant suspension was centrifuged at 5000 rpm for 30 min to remove the residual unexfoliated particles. The supernatant was collected after centrifugation at 11000 rpm for 30 min and freeze-dried for further use.

Material characterization. XRD patterns were recorded on Rigaku MiniFlex600 with Cu Kα radiation in the 2θ range of 10–70°. TEM measurements were carried out on Philips Tecnai FEI system operated at 200 kV. Field-emission scanning electron microscopy (SEM) was recorded on JEOL JSM-7500F. Raman spectra were obtained on confocal Raman microscope (DXR, Thermo Fisher Scientific) with excitation at 532 nm from an argon-ion. FTIR measurements were performed with Bruker TENSOR Π. XPS spectra were recorded on Axis Ultra DLD system. Zeta potential of BP suspension was carried out on ZETAPALS/Bl-200SM. The exfoliated BP nanosheets suspension was dropwise afforded onto a 300 nm SiO_2-capped Si substrate surface and dried under vacuum condition for AFM measurement (Bruker Dimension icon).

Electrochemical Measurements. Tests of electrocatalytic HER were performed on a PARSTAT 263A workstation accompanied with a model 636 system at room temperature in a three-electrode system, using a carbon electrode as counter electrode, a saturated calomel as reference electrode and a glass carbon coated with catalyst as working electrode. The preparation of working electrode was described below. A mixture of BP nanosheets (7 mg) and carbon powders (3 mg, Vulcan XC-72) were dispersed in solvent containing 6.65 mL isopropyl alcohol and 0.35 mL neutralized Nafion solution (5 wt%, Sigma-Aldrich). The mixture solution was sonicated for 0.5 h to form a homogeneous ink. 10μL of the ink was pipetted on the glassy carbon electrode (diameter 5.6 mm) and air-dried. The electrolyte was 1 M KOH solution. LSV curves were collected at a scan rate of 5 mV s^{-1}. EIS was recorded on PARSTAT 4000 (AMETEK) electrochemical workstation in the frequency range from 0.1 Hz to 100 kHz. Cyclic voltammetry (CV) and chronopotentiometry were carried out on PARSTAT 4000 (AMETEK) electrochemical workstation. All the potentials

were calibrated to the reversible hydrogen electrode (RHE) scale.

Computational Details. To gain insight into the interaction between $CO(NH_2)_2$ and BP, the dispersion-corrected density functional theory (DFT-D2)[1] calculations, which takes into consideration the long-range van der Waals interaction, were performed by the Vienna Ab-initio Simulation Package (VASP).[2-4] The exchange-correlation function was described within the projector augmented wave (PAW) method[5,6] and generalized gradient approximation with the function of Perdew-Burke-Ernzerhof (GGA-PBE).[7] A 3×3×1 k-point mesh was used for four-layered BP structure optimizations. Vacuum layers of 15 Å were introduced for the sake of minimizing interactions between adjacent layers in a BP supercell of 2×3×1 . For all the calculations, the cutoff energy was 450 eV. The convergence criterion of the total energy and the residual Hellmann-Feynman force were 10^{-5} eV/atom and 0.035 eV/Å, respectively. Adsorption energy is given by

$$E_{ads} = - (E_{BP + urea} - E_{BP} - E_{urea}) \quad (1)$$

where E_{BP} and E_{urea} correspond to total energies of the relaxed four-layered BP and the isolated urea molecule, respectively, and $E_{BP+urea}$ is the energy of the optimized system.

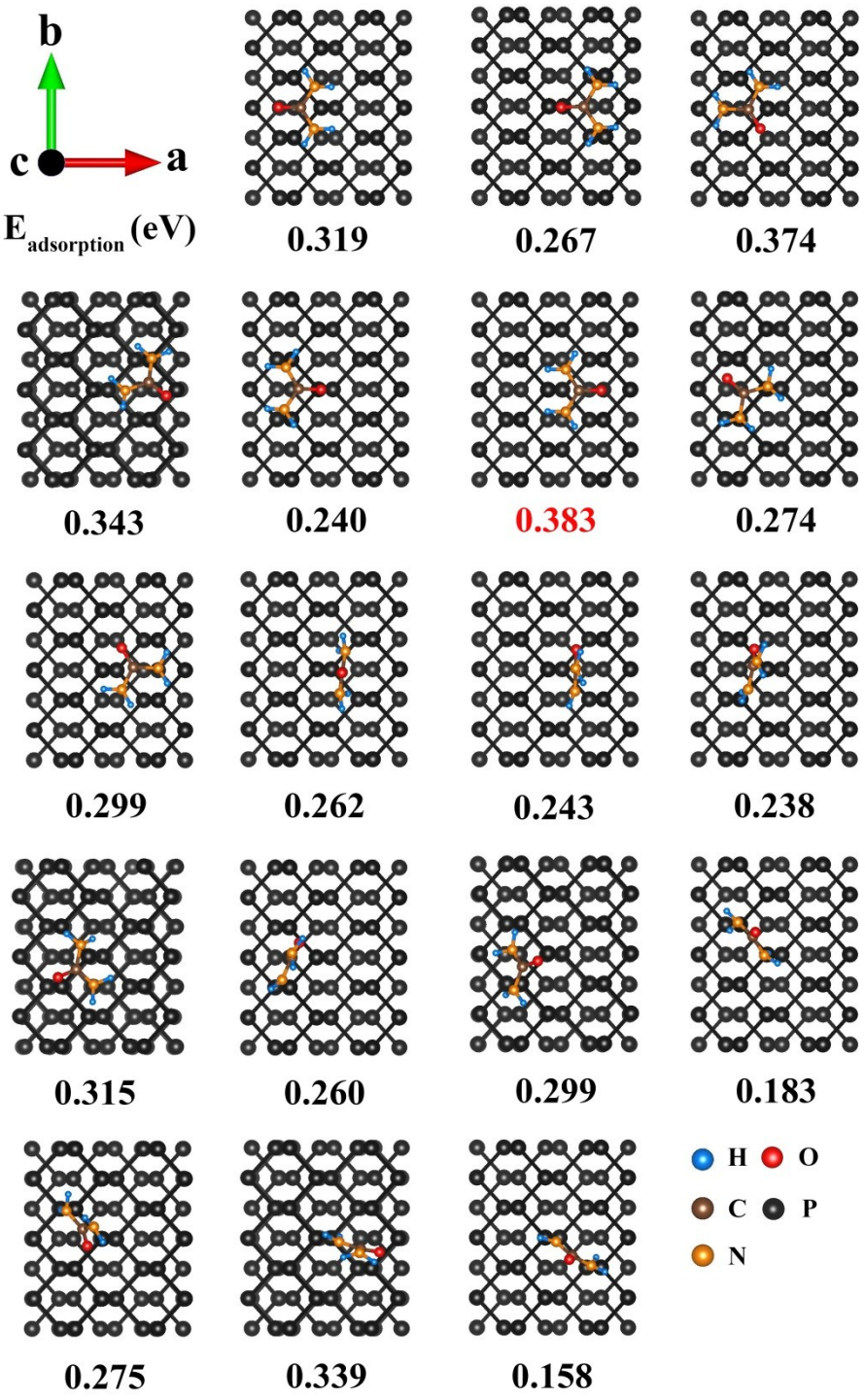

Fig. S1. Top views of 18 adsorption configurations of $CO(NH_2)_2$ adsorbed four-layered BP.

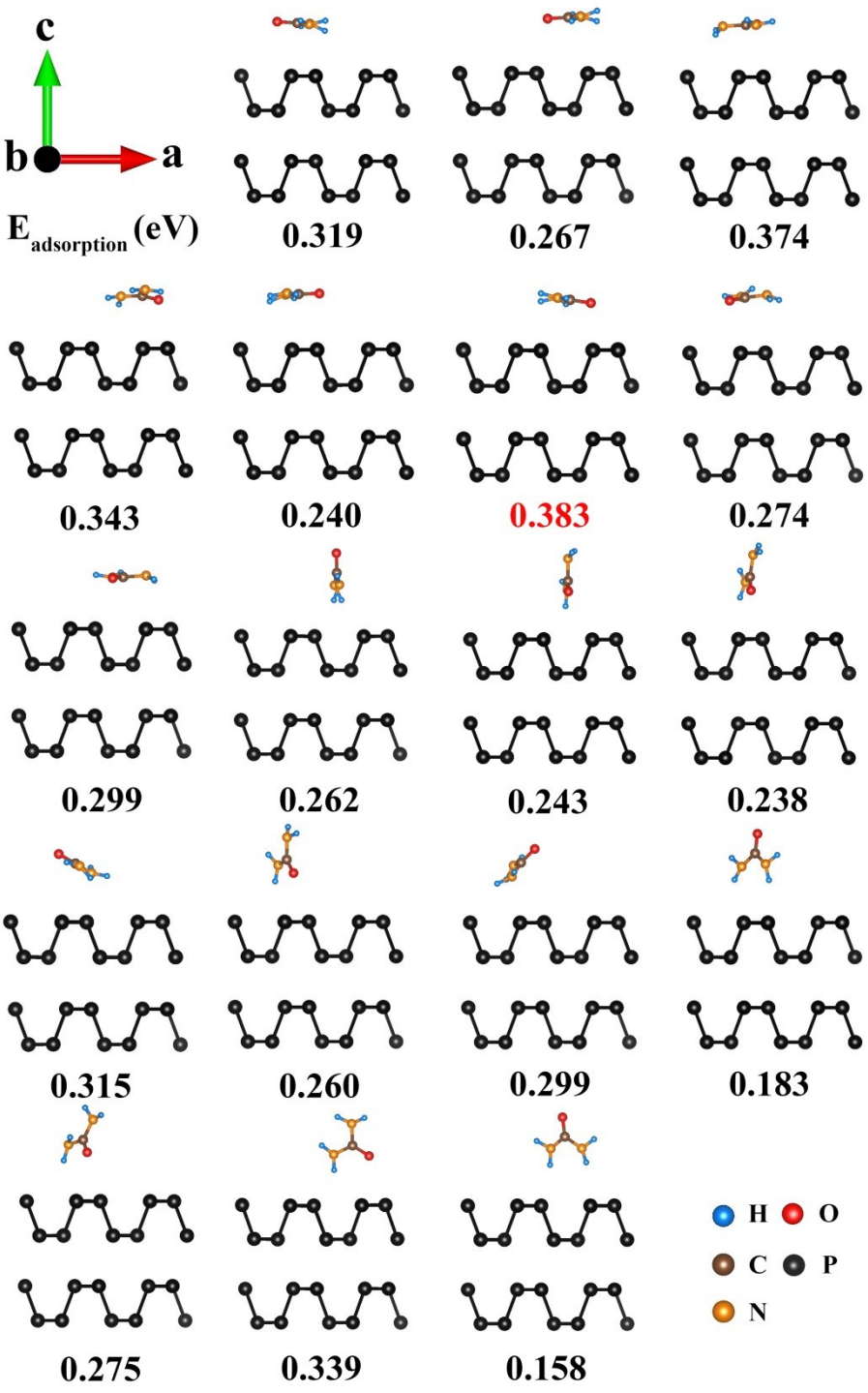

Fig. S2. Side views of 18 adsorption configurations of $CO(NH_2)_2$ adsorbed four-layered BP.

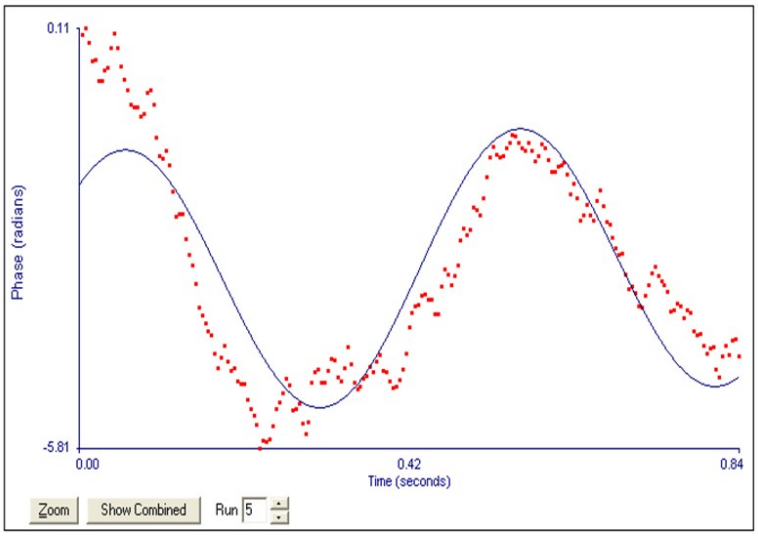

Fig. S3. Zeta potential curve of NH_2-BP nanosheets.

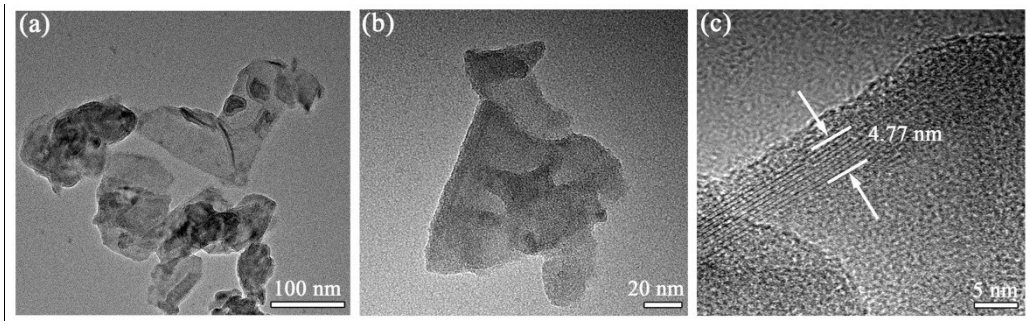

Fig. S4 TEM images of the sample obtained by ball-milling $CO(NH_2)_2$ and BP mixture (a weight ratio of 2/1) ball-milled at 250 rpm for 4 h after washing by water and ethanol.

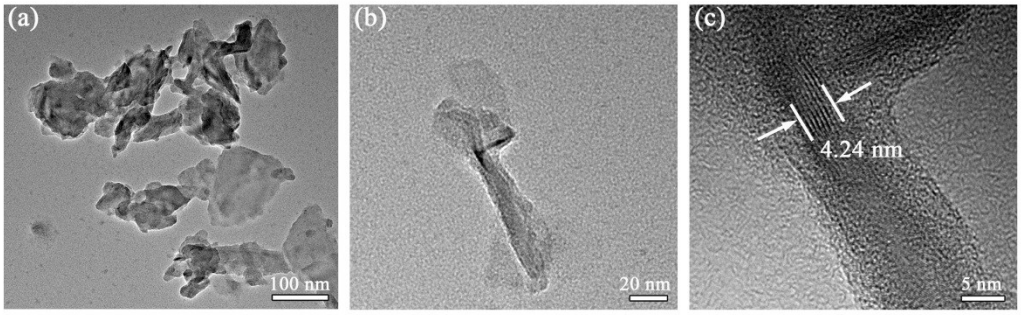

Fig. S5 TEM images of the sample obtained by ball-milling the $CO(NH_2)_2$ and BP mixture (a weight ratio of 2/1) at 350 rpm for 4 h and after washing by water and ethanol.

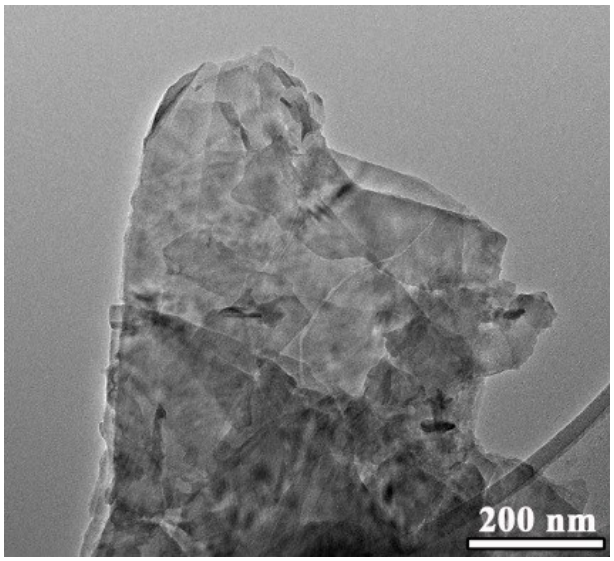

Fig. S6. TEM image of the sample obtained by ball-milling the $C_3N_3(NH_2)_3$ and BP mixture (a weight ratio of 2/1) at 150 rpm for 4 h after washing by water and ethanol.

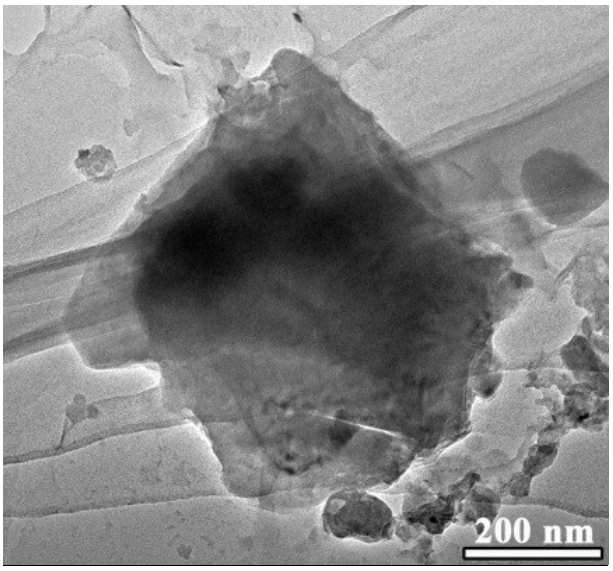

Fig. S7. TEM image of the sample obtained by ball-milling the NH_4Cl and BP mixture (a weight ratio of 2/1) at 150 rpm for 4 h after washing by water and ethanol.

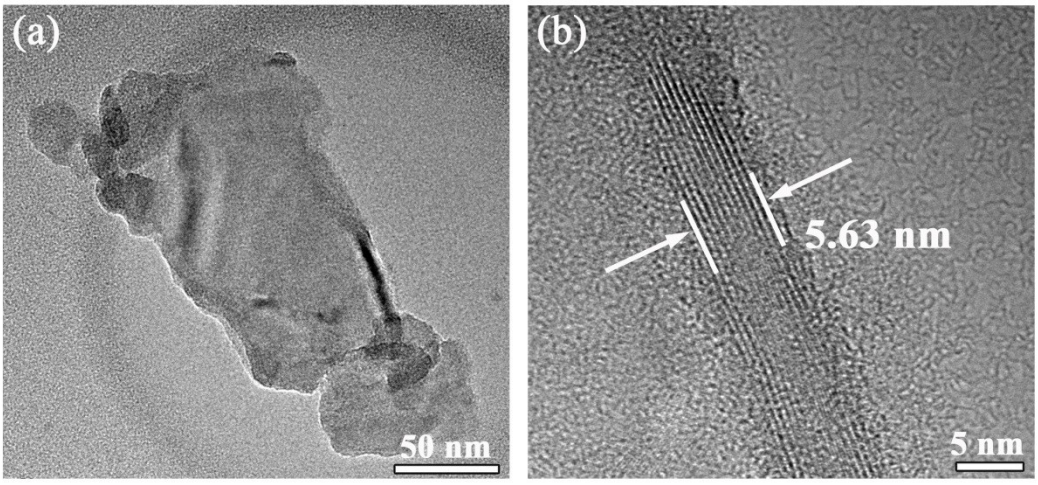

Fig. S8. TEM images of the sample obtained by ball-milling the NH_3BH_3 and BP mixture (a weight ratio of 2/1) at 150 rpm for 4 h after washing by water and ethanol.

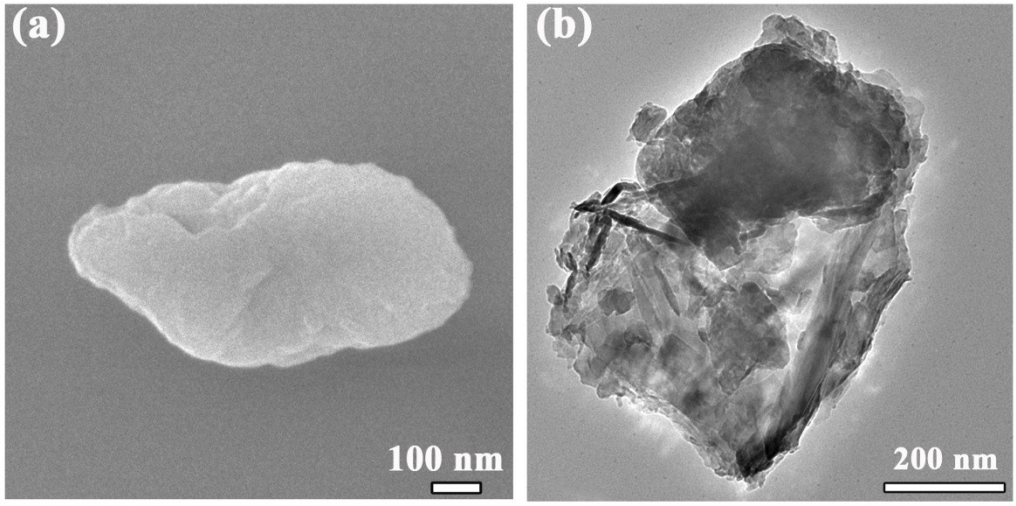

Fig. S9. SEM and TEM images of the ball-milled BP prepared without the use of $CO(NH_2)_2$ at 150 rpm for 4 h.

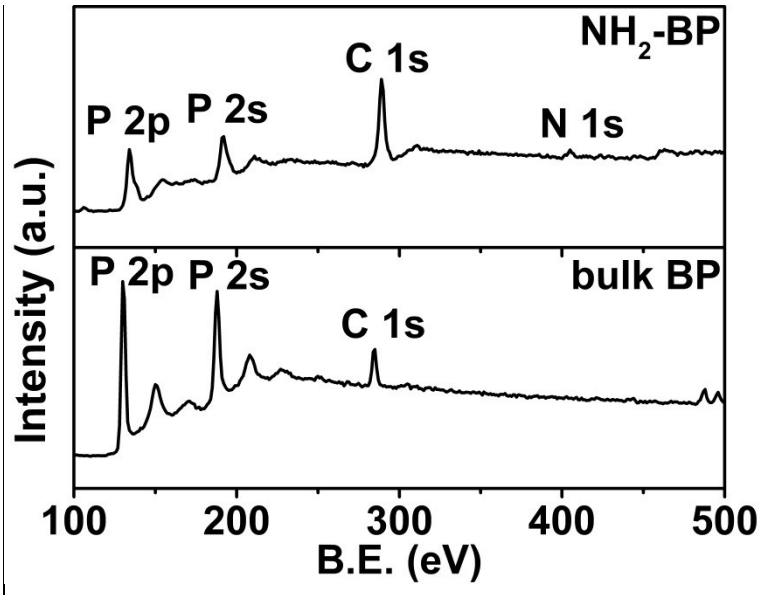

Fig. S10. XPS survey spectra of bulk BP and NH_2-BP nanosheets.

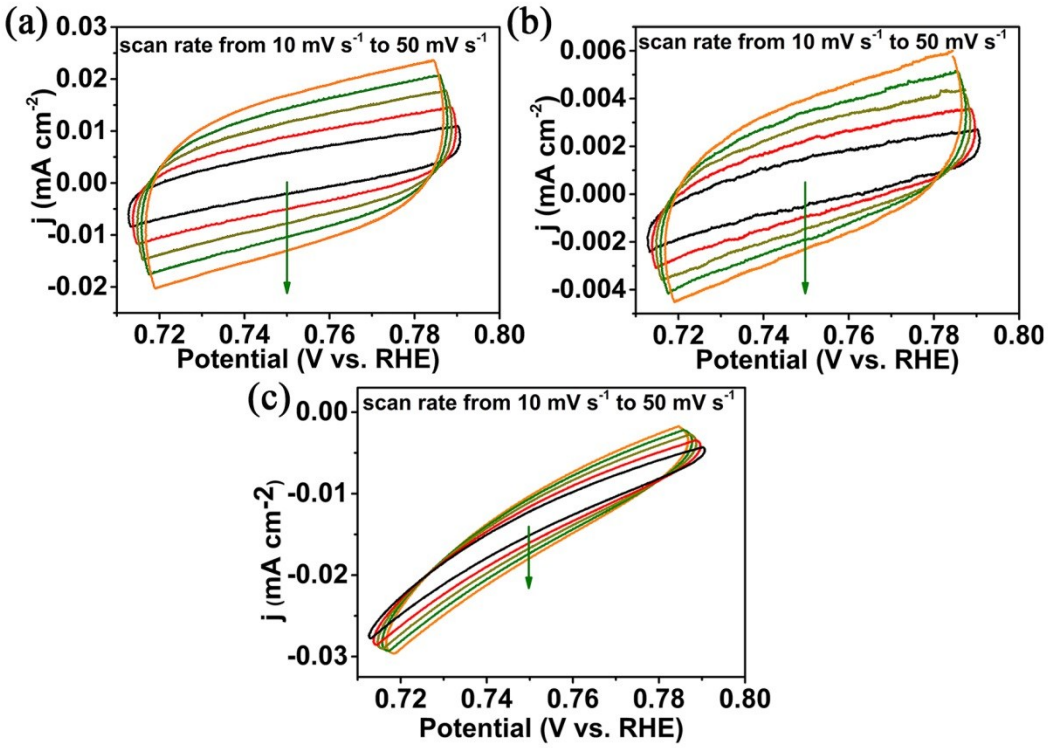

Fig. S11. CV curves of (a) NH_2-BP nanosheets, (b) bulk BP and (c) milled BP at different scan rate from 10 mV s^{-1} to 50 mV s^{-1}.

Electrochemical active surface area

$$A_{ECSA(NH_2\text{-BP nanosheets})} = \frac{\text{total specific capacitance of } NH_2\text{-BP nanosheets}}{\text{specific capacitance per real surface area}} = \frac{0.27\ \text{mF/cm}^2}{40\ \mu\text{F/cm}^2\ \text{per ECSA cm}^2} = 6.75\ \text{cm}^2_{ECSA} \quad (2)$$

$$A_{ECSA(\text{bulk BP})} = \frac{\text{total specific capacitance of bulk BP}}{\text{specific capacitance per real surface area}} = \frac{0.05\ \text{mF/cm}^2}{40\ \mu\text{F/cm}^2\ \text{per ECSA cm}^2} = 1.25\ \text{cm}^2_{ECSA} \quad (3)$$

$$A_{ECSA(\text{milled BP})} = \frac{\text{total specific capacitance of milled BP}}{\text{specific capacitance per real surface area}} = \frac{0.12\ \text{mF/cm}^2}{40\ \mu\text{F/cm}^2\ \text{per ECSA cm}^2} = 3\ \text{cm}^2_{ECSA} \quad (4)$$

$$n_{H_2} = \left(j\frac{\text{mA}}{\text{cm}^2}\right)\left(\frac{1\text{C s}^{-1}}{1000\ \text{mA}}\right)\left(\frac{1\ \text{mol e}^{-1}}{96485.3\ \text{C}}\right)\left(\frac{1\ \text{mol H}_2}{2\ \text{mol e}^{-1}}\right)\left(\frac{6.022\times10^{23}\ \text{molecules H}_2}{1\ \text{mol H}_2}\right)$$

$$= 3.12\times10^{15}\frac{\text{H}_2\ \text{s}^{-1}}{\text{cm}^2}\ \text{per}\ \frac{\text{mA}}{\text{cm}^2} \quad (5)$$

$$n^{\text{surface sites}}_{NH_2\text{-BP nanosheets}} = \left(\frac{12\ \text{atoms per unit cell}}{149.95\ \text{Å}^3\ \text{per unit cell}}\right)^{\frac{2}{3}} = 1.857\times10^{15}\ \text{atoms per real cm}^2 \quad (6)$$

$$n^{\text{surface sites}}_{\text{bulk BP}} = \left(\frac{12\ \text{atoms per unit cell}}{149.95\ \text{Å}^3\ \text{per unit cell}}\right)^{\frac{2}{3}} = 1.857\times10^{15}\ \text{atoms per real cm}^2 \quad (7)$$

$$n^{\text{surface sites}}_{\text{milled BP}} = \left(\frac{12\ \text{atoms per unit cell}}{149.95\ \text{Å}^3\ \text{per unit cell}}\right)^{\frac{2}{3}} = 1.857\times10^{15}\ \text{atoms per real cm}^2 \quad (8)$$

Finally, plot of current density can be converted into a turnover frequency (TOF) plot according to:

$$TOF_{NH_2\text{-BP nanosheets}} = \frac{\left(3.12\times10^{15}\,\frac{H_2\ s^{-1}}{cm^2}\ \text{per}\ \frac{mA}{cm^2}\right)\times\left|j_{NH_2\text{-BP nanosheets}}\right|}{n^{\text{surface sites}}_{NH_2\text{-BP nanosheets}}\times A_{ECSA(NH_2\text{-BP nanosheets})}}$$

$$=0.2489\times\left|j_{NH_2\text{-BP nanosheets}}\right| \quad (9)$$

$$TOF_{\text{bulk BP}} = \frac{\left(3.12\times10^{15}\,\frac{H_2\ s^{-1}}{cm^2}\ \text{per}\ \frac{mA}{cm^2}\right)\times\left|j_{\text{bulk BP}}\right|}{n^{\text{surface sites}}_{\text{bulk BP}}\times A_{ECSA(\text{bulk BP})}}$$

$$=1.3441\times\left|j_{\text{bulk BP}}\right| \quad (10)$$

$$TOF_{\text{milled BP}} = \frac{\left(3.12\times10^{15}\,\frac{H_2\ s^{-1}}{cm^2}\ \text{per}\ \frac{mA}{cm^2}\right)\times\left|j_{\text{milled BP}}\right|}{n^{\text{surface sites}}_{\text{milled BP}}\times A_{ECSA(\text{milled BP})}}$$

$$=0.5600\times\left|j_{\text{milled BP}}\right| \quad (11)$$

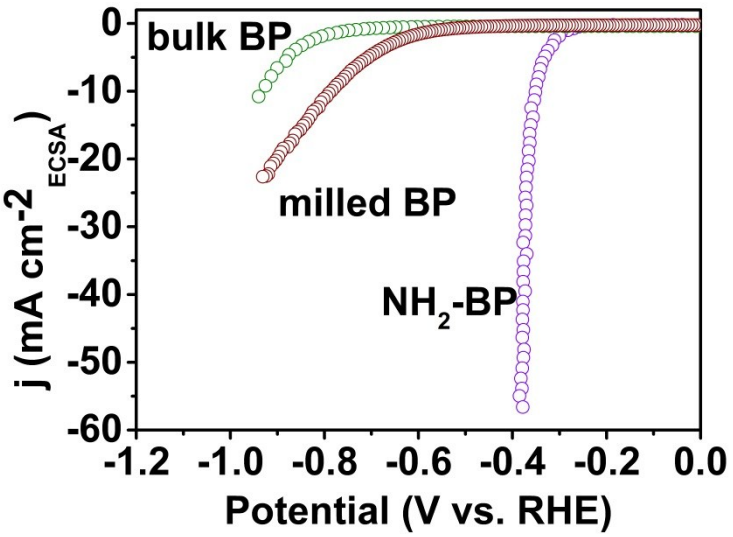

Fig. S12. Voltammograms of bulk BP, milled BP and NH_2-BP in 1 M KOH normalized to the ECSA.

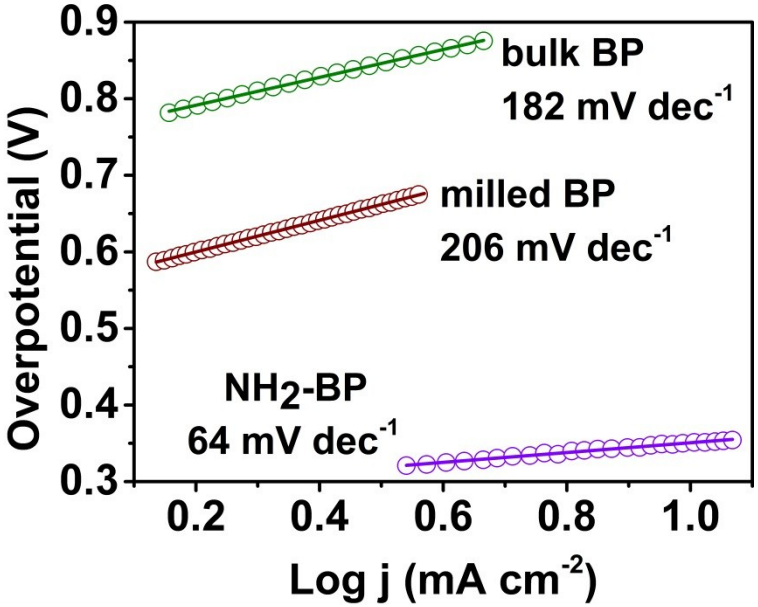

Fig. S13. Tafel plots of bulk BP, milled BP and NH_2-BP nanosheets in 1 M KOH normalized to the ECSA.

Table S1. Electrochemical HER catalysis data of different metal-free catalysts

Catalyst	Overpotential at 10 mA cm^{-2} (V vs. RHE)	Tafel Slope ($mV\ dec^{-1}$)	Electrolyte	References
black phosphorus nanoparticle	0.88	-	0.5 M H_2SO_4	8
black phosphorus	0.35	161	0.5 M H_2SO_4	9
black phosphorus	1.1	212	0.5 M H_2SO_4	10
MPSA-1000 MPSA/GO-1000	0.6 0.45	-	0.1 M KOH	11
GF	0.261	192	1 M KOH	12
N,S-graphitic sheets	0.274	-	1 M KOH	13
N,O,P-graphite carbon@oxidized carbon cloth	0.446	154	1 M KOH	14
N,S-CNT	0.45	133	1 M KOH	15
Co-NRCNTs	0.37	-	1 M KOH	16
NH_2-BP nanosheets	0.29	67	1 M KOH	This work

References

1 S. *J.* Grimme, *Comput. Chem.,* 2006**, 27**, 1787-1799.
2 G. Kresse and J. Hafner, *Phys. Rev. B,* 1993**, 48**, 13115-13118.
3 G. Kresse and J. Furthmüller, *Phys. Rev. B,* 1996**, 54**, 11169-11186.
4 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.,* 1996**, 6**, 15-50.
5 P. E. Blöchl, *Phys. Rev. B,* 1994**, 50**, 17953-17979.
6 G. Kresse and D. Joubert, *Phys. Rev. B,* 1999**, 59**, 1758-1775.
7 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.,* 1996**, 77**, 3865-3868.
8 C. C. Mayorga-Martinez, N. Mohamad Latiff, A. Y. Eng, Z. Sofer and M. Pumera, *Anal. Chem.*, 2016, **88**, 10074-10079.
9 R. He, J. Hua, A. Zhang, C. Wang, J. Peng, W. Chen and J. Zeng, *Nano Lett.*, 2017, **17**, 4311-4316.
10 Y. Lin, Y. Pan and J. Zhang, *Int. J. Hydrogen Energy*, 2017, **42**, 7951-7956.
11 J. Zhang, L. Qu, G. Shi, J. Liu, J. Chen and L. Dai, *Angew. Chem. Int. Ed.*, 2016, **55**, 2230-2234.
12 Y. Shen, L. Li, J. Xi and X. Qiu, *J. Mater. Chem. A*, 2016, **4**, 5817-5822.
13 C. Hu and L. Dai, *Adv. Mater.*, 2017, **29**, 1604942.

14 J. Lai, S. Li, F. Wu, M. Saqib, R. Luque and G. Xu, *Energy Environ. Sci.*, 2016, **9**, 1210-1214.
15 K. Qu, Y. Zheng, Y. Jiao, X. Zhang, S. Dai and S.-Z. Qiao, *Adv. Energy Mater.*, 2017, **7**, 1602068.
16 X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmekova and T. Asefa, *Angew. Chem. Int. Ed.*, 2014, **53**, 4372-4376.