Electronic Supplementary Information

Phosphorene quantum dot interspersed few-layered MoS_2 hybrids as efficient bifunctional electrocatalysts for hydrogen and oxygen evolution

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Experimental Methods

Preparation of 0D/2D heterostructures

Bulk black phosphorus crystal (Smart elements GmbH, Vienna), MoS_2 flakes (Sigma Aldrich) and lithium bis(triflouromethanesulfonyl)imide (LiTFSI) (Sigma Aldrich), were used directly as-received. PQD/MoS_2 heterostructures were synthesized *via* electrochemical exfoliation route in a two-electrode cell. MoS_2 and black phosphorus were taken in a mass ratio of 5:1 and thoroughly mixed using a mortar and pestle to get complete uniformity. The mixture was then made in to circular disc pellets of 8 mm diameter, under an applied pressure of 3.5 tons, which is used as the anode during electrochemical synthesis. In a typical experiment, a conducting substrate (Pt/FTO) is used as the cathode. The anode and cathode were placed in an electrochemical cell kept 1 cm apart. The complete set up was dipped in an electrolyte of *aq*. LiTFSI of concentration 0.1 wt%, as schematically represented in Figure 1A. The reaction was carried out for about 6 h and the obtained green colored solution was centrifuged using vivaspin concentrators at 5000 rpm for 15 min in-order to remove any traces of the bulk material. Phosphorene quantum dots (PQDs) as well as MoS_2 nanosheets were also separately synthesized using the same protocol as mentioned above by appropriately changing the anode.

Electrode preparation and electrochemical characterization

Electrochemical characterizations were conducted using Bio-logic SAS VMP3 workstation. Hydrogen evolution and oxygen evolution studies were performed in 0.1 M KOH using 3-electrode set up with Hg/HgO (in 1 M KCl solution) as the reference electrode and a graphite/Pt rod as the counter electrode. For HER measurements, we used graphite rod as counter electrode, while a Pt wire was used as counter for OER measurements. The as-prepared 1 mL of PQD/MoS2 sample was mixed with 1 mg of carbon black (conducting binder) and sonicated thoroughly for 1 h. 5 μL of the solution was drop coated on to a mirror polished glassy carbon electrode (4 mm) in the RDE setup (ALS instruments - 0.1256 cm2). 1 mL of binder solution was prepared by adding 50 μL of Nafion 117 (sigma Aldrich) to 950 μL of ethanol. 3 μL of the aforementioned solution was drop casted on top of the catalyst dropcasted RDE electrode and was kept for drying. This modified glassy carbon electrode is used as the working electrode for the electrocatalytic studies. The catalyst loading was 0.24 mg cm^{-2}, unless otherwise stated. LSV and RRDE measurements with a scan rate of 10 mV s^{-1} were performed at a rotation rate of 1600 rpm in 0.1 M KOH. EIS measurements were performed in a frequency range 100 kHz – 50 mHz. The electrode potential *versus* Hg/HgO was converted to RHE with the help of Nernst equation:

$$E(vs.\text{RHE})=E(vs.\text{Hg/HgO})+E\text{^}0\ (\text{Hg/HgO})+0.059\times\text{pH}$$

Instrumentation

Materials characterization

Perkin Elmer Lambda950 was used to carry out UV-Vis absorption measurements. HRTEM and EELS characterizations have been done using a transmission electron microscope (FEI, Tecnai F30, 300 keV). XPS measurements were carried out using an ESCA Plus spectrometer (Omicron Nanotechnology Ltd, Germany) using Mg-Kα source. Raman spectroscopy was performed using 532 nm laser using Horiba Xplora Plus Confocal Micro Raman Spectrometer.

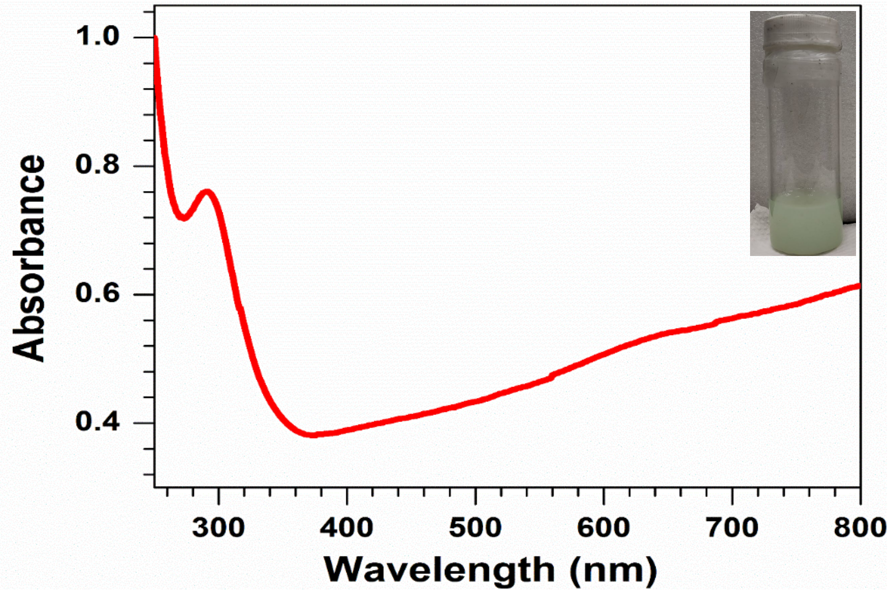

Figure S1. UV-Vis absorption spectrum of PQD/ MoS_2. Photograph of the obtained solution after the electrochemical synthesis is shown as inset.

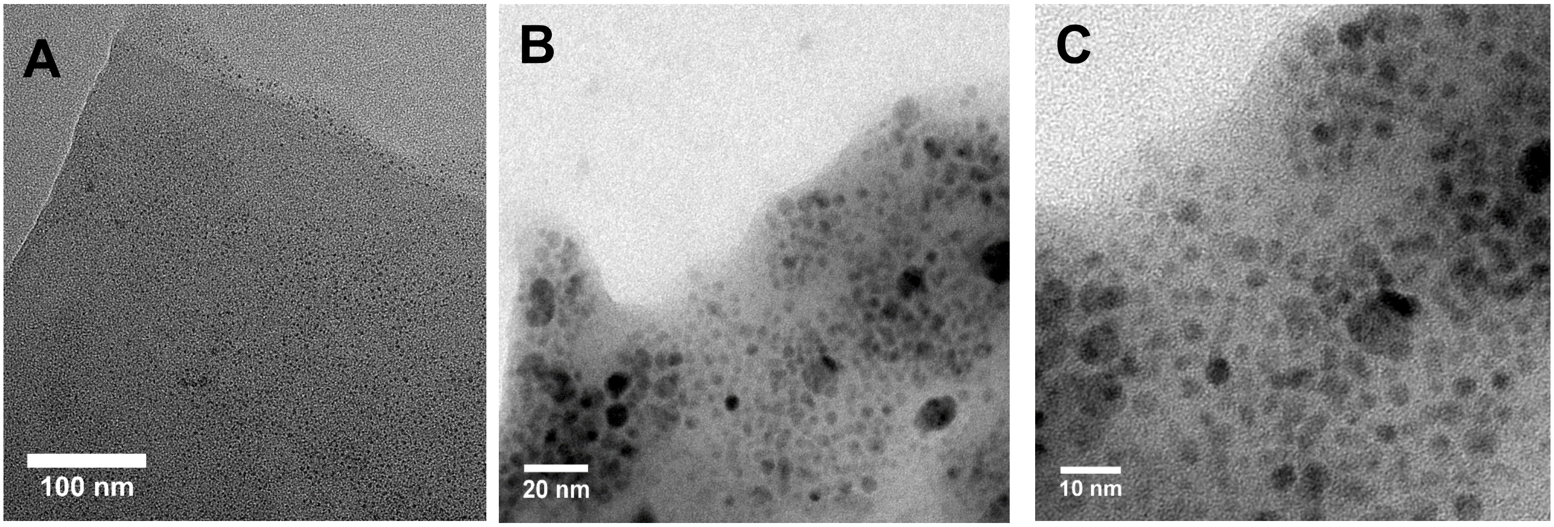

Figure S2. (A) Low and (B, C) high resolution TEM images of PQD/ MoS_2

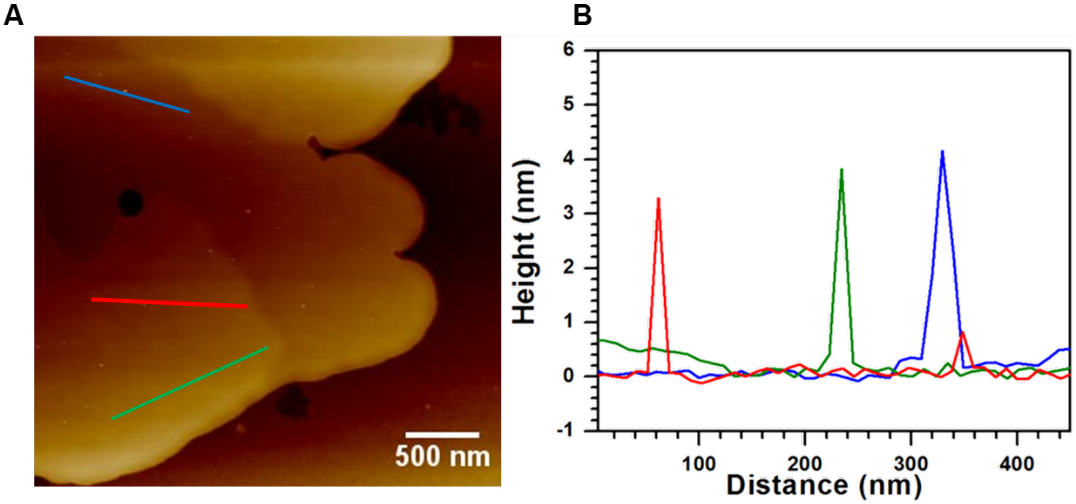

Figure S3. (A) AFM image of PQD/MoS_2 (B) the corresponding height profiles of PQDs interspersed on top of MoS_2 nanosheets from three different spots as marked in (A).

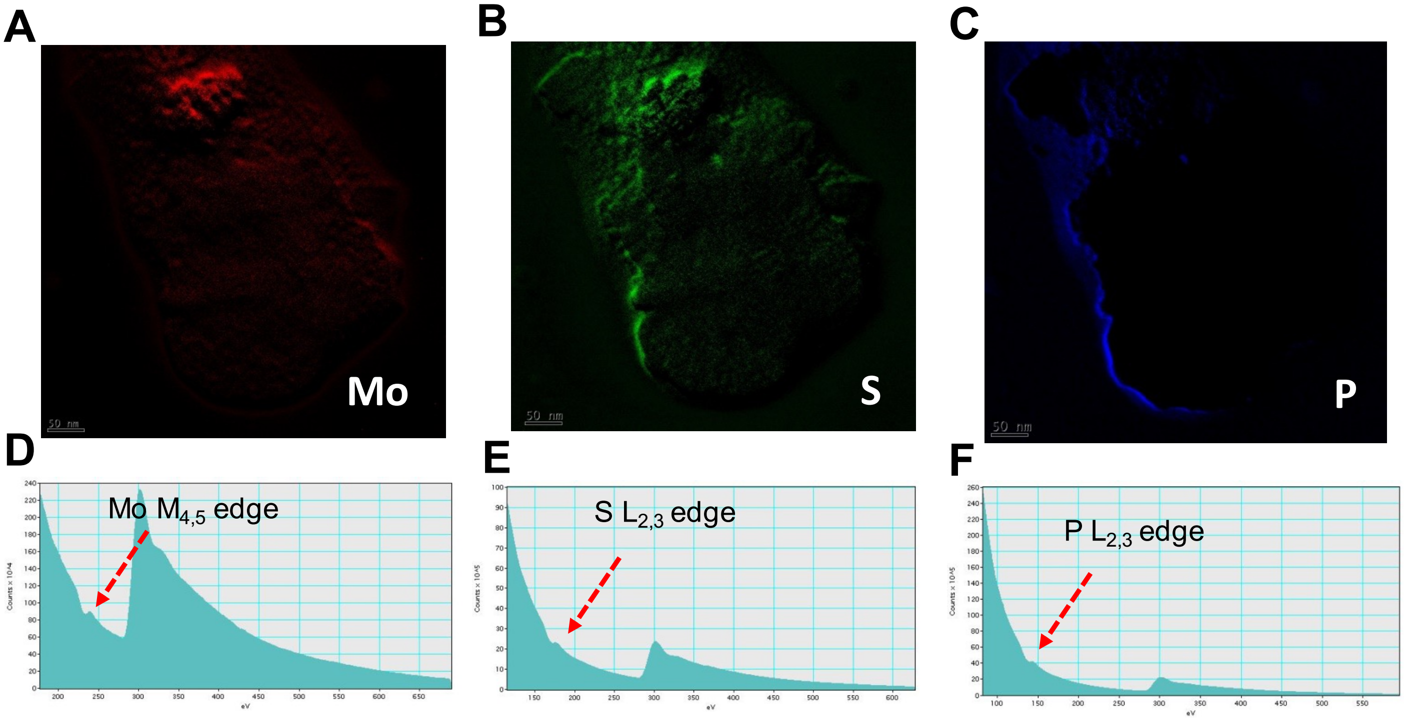

Figure S4. TEM EELS mapping of PQD/ MoS_2 at (A) Mo edge (Binging Energy 230eV), (B) S edge (Binging Energy 1690 eV) (C) P edge (Binging Energy 130eV). EEL spectra from the (D) Mo $M_{4,5}$ edge (E) S $L_{2,3}$ (F) P $L_{2,3}$ edge.

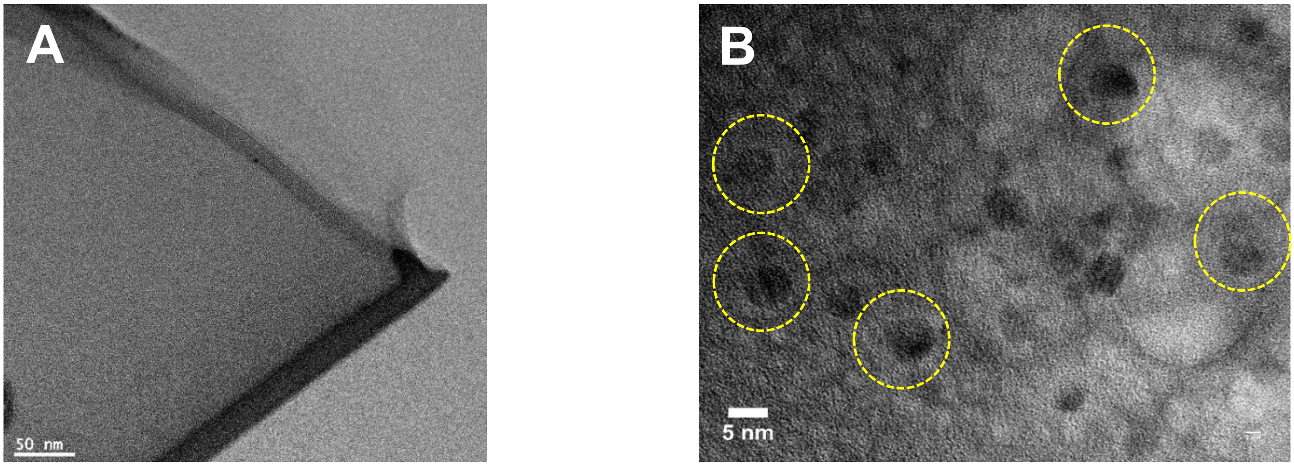

Figure S5. (A) TEM image of MoS_2 nanosheets (B) HRTEM image of PQDs alone prepared using the same technique

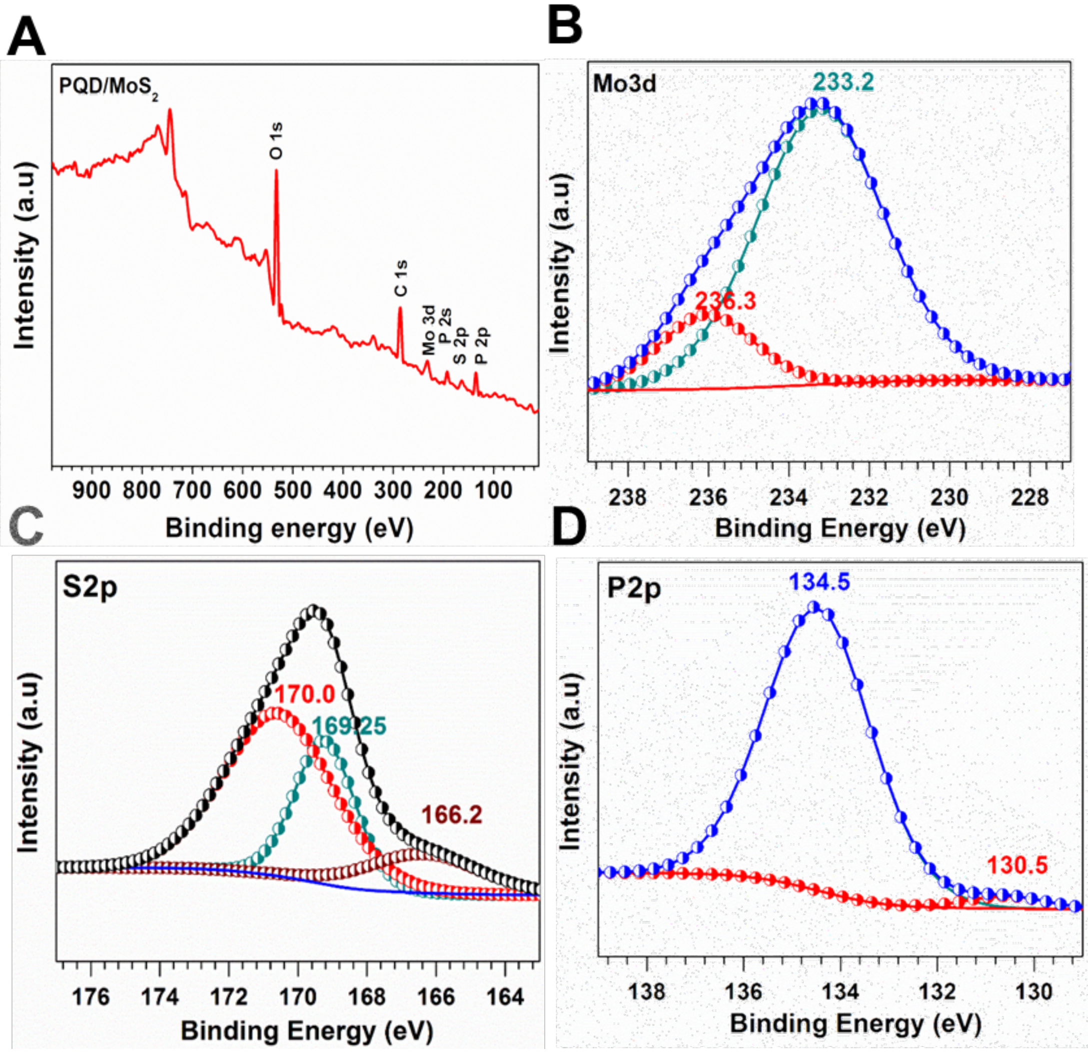

Figure S6. (A) XPS survey spectrum of PQD/MoS$_2$. (B), (C) and (D) are the deconvoluted high resolution Mo 3d, S 2p, and P 2p spectra of PQD/MoS$_2$, respectively.

Electrochemical Surface Area (ECSA) calculation

The electrochemically active surface area (ECSA) of PQD/MoS_2, MoS_2 nanosheets, and PQDs were estimated by determining the double-layer capacitance of the system from CV measurements. The CV measurements were carried out in the double layer region at various scan rates ranging from 20 mV/s to 100 mV/s. The plot of anodic peak current (i_a) or cathodic peak current (i_c) vs. scan rate will yield a straight line with a slope vale of C_{dl}. The ECSA of the catalyst can be calculated by dividing C_{dl} by the specific capacitance (C_s). We have used 0.1M KOH as electrolyte and the C_s value is taken as 0.040 mF cm^{-2}

$$\boldsymbol{ECSA = \frac{C_{dl}}{C_s}}$$

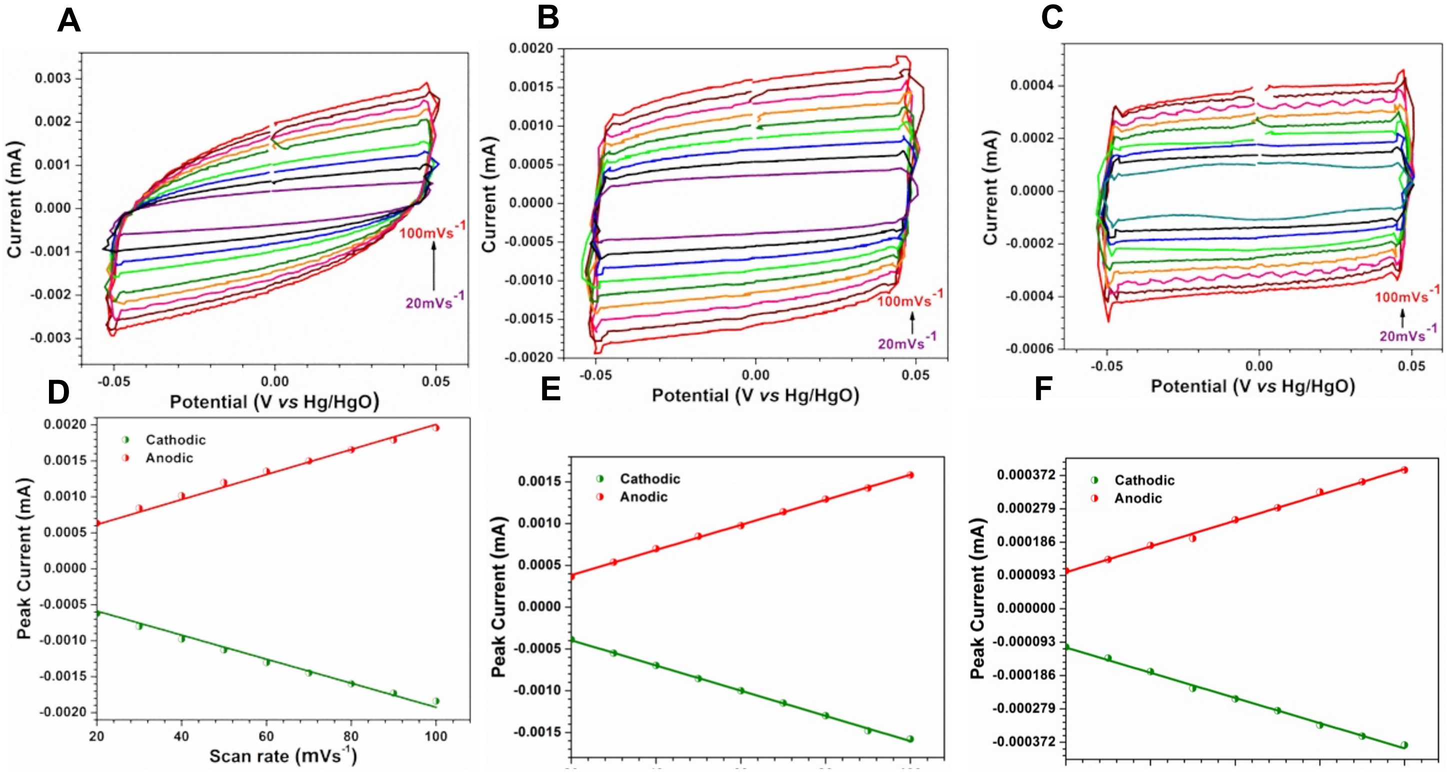

Figure S7. (A) Calculation of ECSA from CV analysis. CV analysis of (A) PQD/MoS_2, (B) MoS_2 nanosheets and (C) PQDs at different scan rates in 0.1 M KOH solution. The peak current *vs*. scan rate plots for (D) PQD/MoS_2, (E) MoS_2 and (F) PQDs where the slope will give the double layer capacitance values of the respective catalysts.

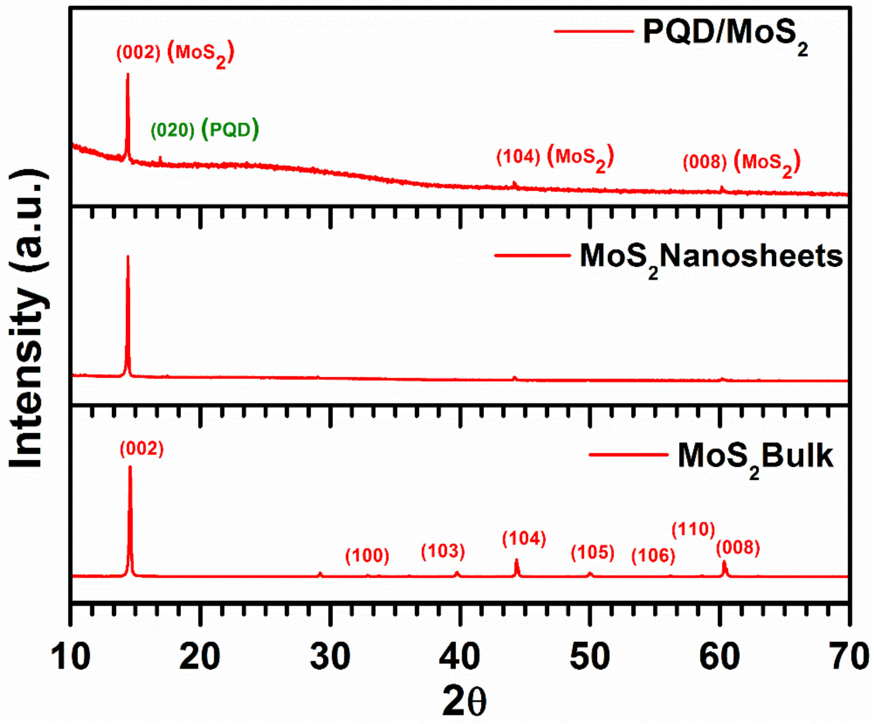

Figure S8. XRD patterns of bulk, exfoliated MoS_2 and PQD/MoS_2.

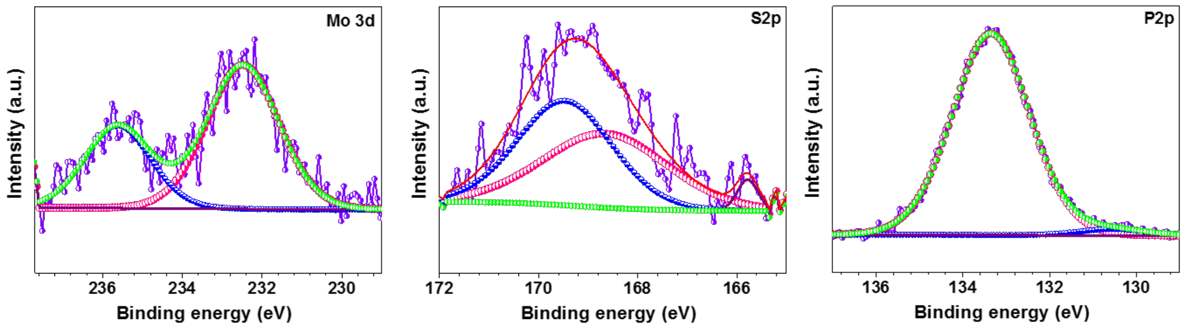

Figure S9. XPS of PQD/MoS_2 after electrochemical characterizations

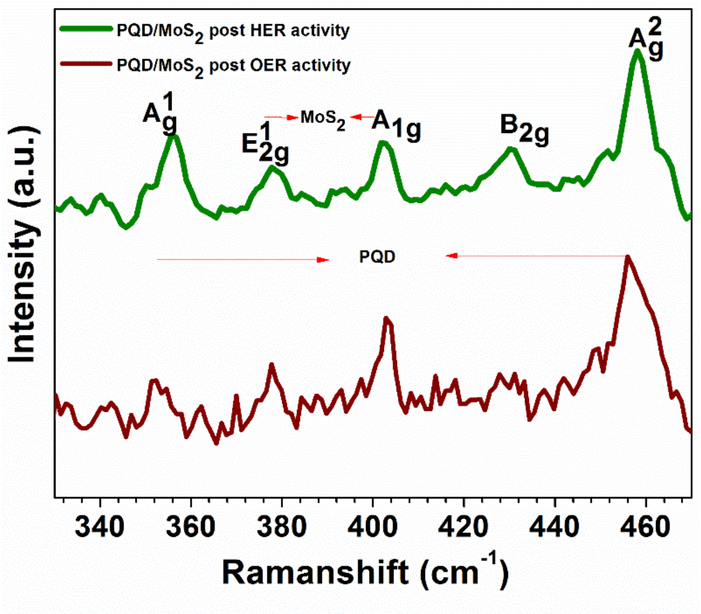

Figure S10. Raman spectrum of PQD/MoS_2 after electrochemical characterizations

Faradaic efficiency calculation:

We determined the Faradaic efficiency, with experiment conducted on a 5 mL of 0.1M KOH solution in a two compartment cell separated by a suitable ion exchange membrane. Electrochemical water splitting has been carried out in a two compartment electrochemical cell with both the electrodes modified with the catalysts. A constant potential of 2.2 V is applied for 4 h. The evolved gas analyzed using Schimadzu Gas Chromatograph GC 2014, with thermal conductivity detector and N_2 carrier gas. The moles of hydrogen detected by GC were calibrated using injected volume of pure H_2. N_2 gas purged continuously at a flow rate of 5mL/min throughout the electrolysis and the outlet of the cathodic compartment fed directly to the sampling loop of GC. A gas chromatograph run was initiated every 30 minutes.

Faradaic efficiency is found to be 100+/- 4%. Faradaic efficiency calculated by the following equation:

Faradaic efficiency (%), $\eta = \frac{I_{H_2}}{I} \times \mathbf{100}$

$$\text{Where, } \boldsymbol{I_{H_2}} = \emptyset_{H_2} \times \boldsymbol{Q} \times \frac{\boldsymbol{2Fp}}{\boldsymbol{RT}}$$

$\boldsymbol{I_{H_2}}$ is the partial current of hydrogen evolved $\emptyset_{H_2}$ is the volume concentration of hydrogen, Q is the volumetric flow rate of an injected gas, F is the faraday constant, p is the atmosphere pressure, T is the temperature of an electrochemical cell, R is the ideal gas constant I is a steady-state total current during hydrogen evolution.

Table S1. Comparison of OER performance of PQD/MoS_2 with other BP-based hybrid electrocatalysts tested in alkaline solution.

Materials	Electrolyte	η_0 (mV)	Tafel slope (mV dec^{-1})	Ref
BP-CNT	1 M KOH	370 (100 mA cm^{-2})	72.88	[1]
MXene-BP QDs	1 M KOH	360	64.3	[2]
Phosphorene/ N-doped graphene	1 M KOH	310	89	[3]
N-BP QDs	1 M NaOH	430	48	[4]
S-doped phosphorene	1 M KOH	310 (onset)	75	[5]
Te-doped phosphorene	1 M KOH	260 (onset)	Not mentioned	[6]
BP/Co_2P	1 M KOH	517 (100 mA cm^{-2})	78	[7]
PQD/MoS_2	0.1 M KOH	370	46	This work

References

(1) Q. Jiang, L. Xu, N. Chen, H. Zhang, L. Dai, S. Wang, *Angew.Chem. Int. Ed.* **2016**, 55, 13849-13853.

(2) X.-D. Zhu, Y. Xie, Y.-T. Liu, , *J. Mater. Chem. A* **2018**, 6, 21255-21260.

(3) Z. Yuan, J. Li, M. Yang, Z. Fang, J. Jian, D. Yu, X. Chen, L. Dai, , *J. Am. Chem. Soc.* **2019**, 141, 4972.

(4) R. Prasannachandran, T. V. Vineesh, A. Anil, B. M. Krishna, M. M. Shaijumon, *ACS Nano* 2018, 12, 11511-11519.

(5) Y. Chang, A. Nie, S. Yuan, B. Wang, C. Mu, J. Xiang, B.Yang, L. Li, F. Wen, Z. Liu,*Nanotechnology* **2018**, 30, 035701.

(6) Z. Zhang, M. Khurram, Z. Sun, Q. Yan, *Inorg. Chem.* **2018**,57, 4098-4103.

(7) J. Wang, D. Liu, H. Huang, N. Yang, B. Yu, M. Wen, X.Wang, P. K. Chu, X. F. Yu , *Angew. Chem. Int. Ed.* **2018**, 57, 2600-2604.

Acknowledgements

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