Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

SUPPORTING INFORMATION

P doped molybdenum dioxide on Mo foil with high electrocatalytic activity of hydrogen evolution reaction

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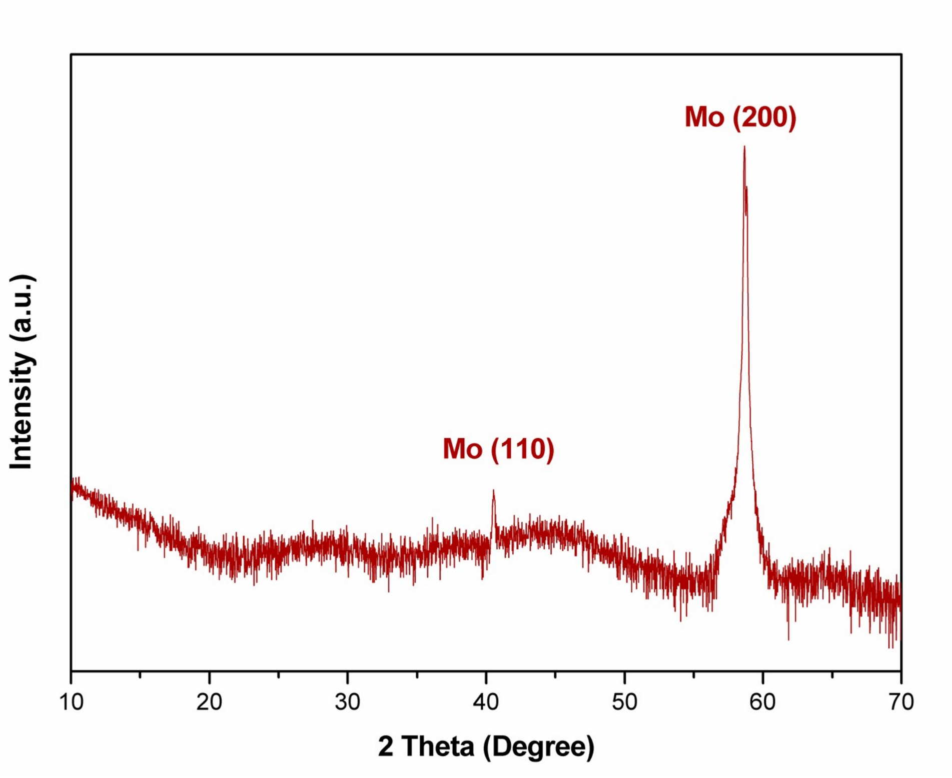

Fig. S1 XRD pattern of Mo foil.

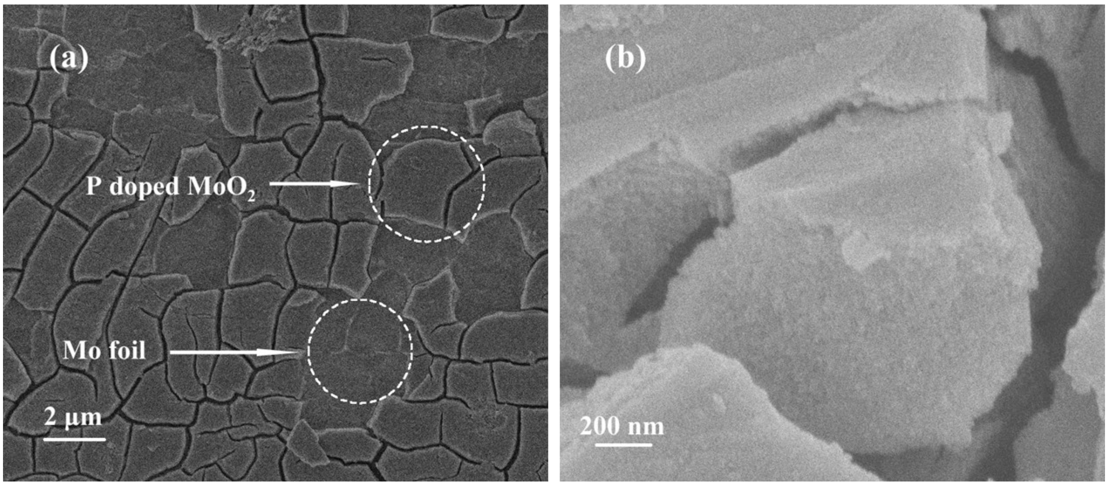

Fig. S2 SEM images of obtained P doped MoO_2 on Mo foil (a) at low magnification and (b) at high magnification.

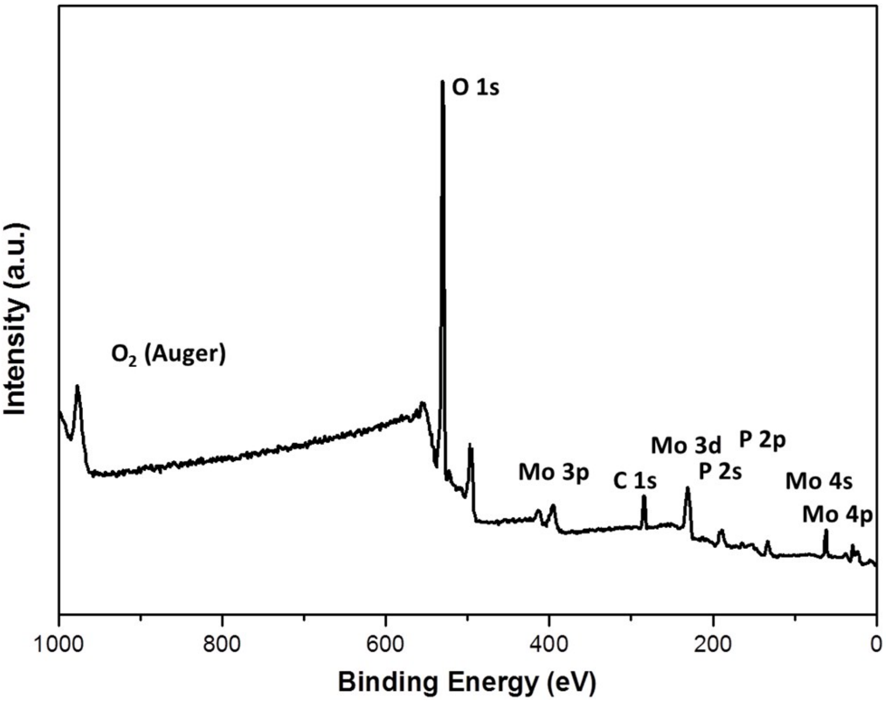

Fig. S3 XPS survey scan of obtained P doped MoO_2 on Mo foil.

Table S1 Ratios of different elements in obtained P doped MoO_2 on Mo foil estimated from XPS analysis.

Element	Mo 3d	P 2p	O 1s	C 1s
Ratio (%)	23.72	2.08	60.78	13.42

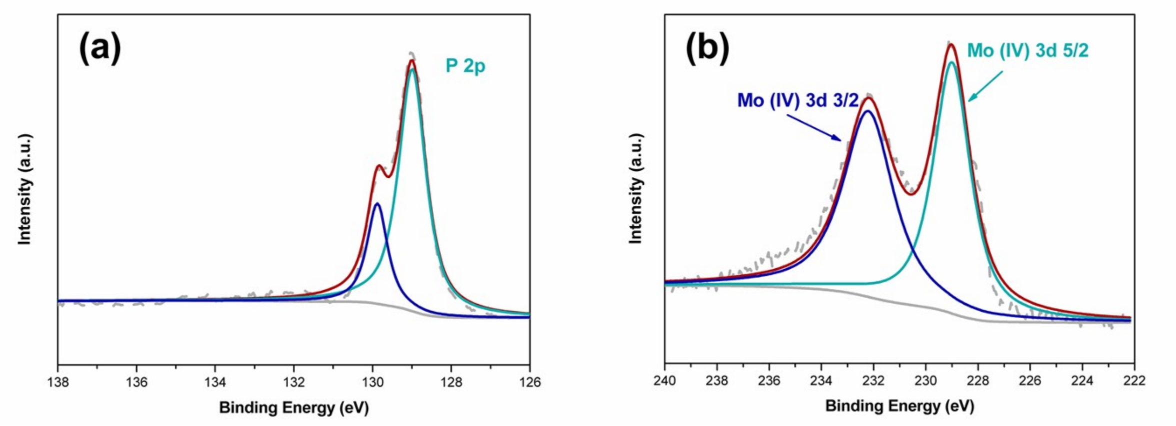

Fig. S4 High-resolution XPS spectra of P doped MoO_2 on Mo foil after HER. (a) P 2p scan, and (b) Mo 3d scan .

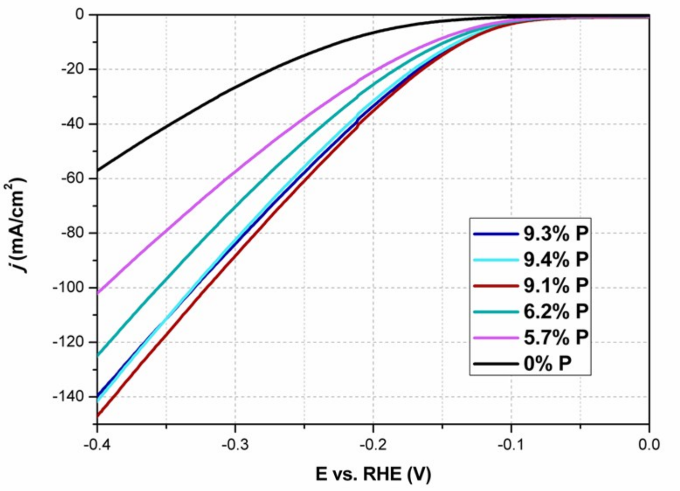

Fig. S5 Polarization curves of P doped MoO_2/Mo foils with different contents of P (MoO_2P_x). The content of P was measured by EDS analysis.

Table S2 HER activities of related MoO_2-based and MoP materials.

Samples	Onset Potentials (mV vs. RHE)	Tafel Slope (mV/dec)
MoO_2/rGO composite[8]	190	49.2
MoP[15a]	50	54
MoP NPs[15b]	40	54
MoP nanosheets[15c]	100	56.4
$MoO_2P_{0.1}$ on Mo foil	80	62

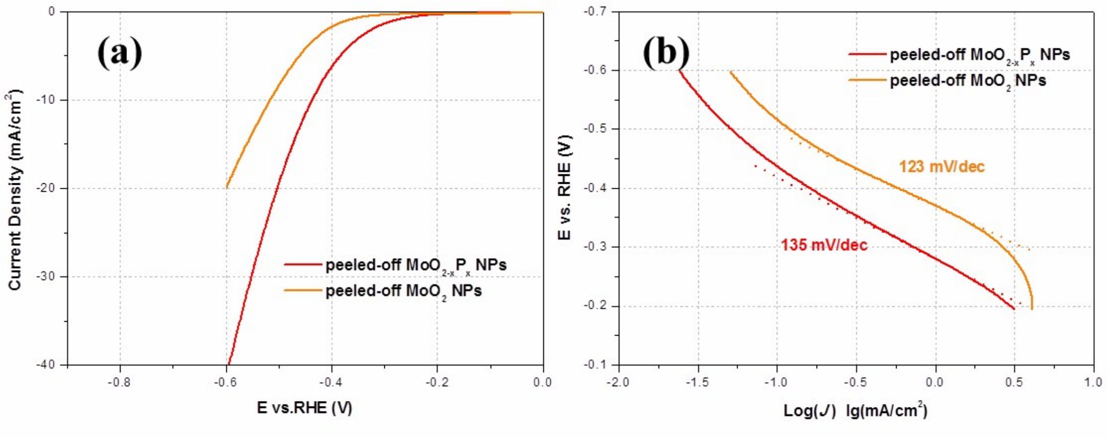

Fig. S6 (a) Polarization curves and (b) Tafel slope of samples peeled off from obtained MoO_2 / Mo foil and P doped MoO_2 / Mo foil.

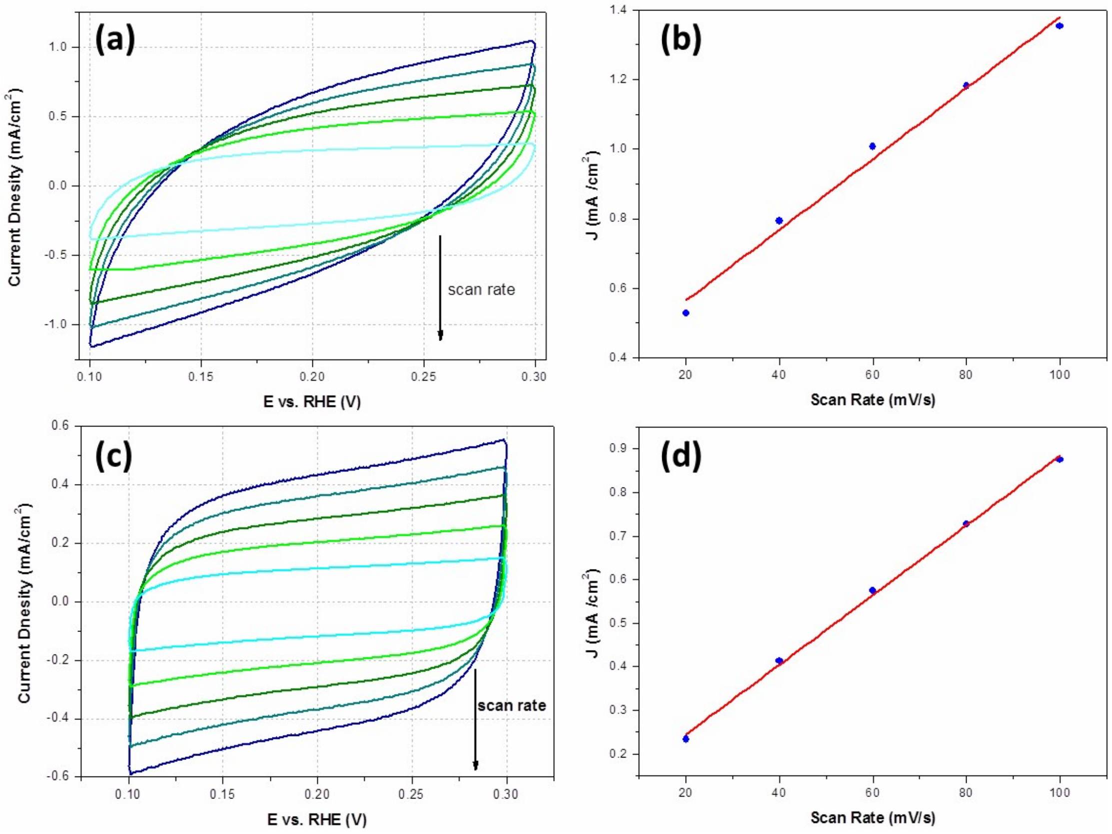

Fig. S7 Cyclic voltammograms of samples peeled off from (a) P doped MoO_2 on Mo foil and (c) MoO_2 on Mo foil measured at different scanning rates (20-100 mV s^{-1}) in 0.5 M H_2SO_4 with the same loading. Corresponding scanning rate dependence of the current density of samples peeled off from (b) P doped MoO_2 on Mo foil and (d) MoO_2 on Mo foil at 0.2 V vs. RHE.

It is generally supposed that the amount of active sites in HER is directly proportional to electrochemically active surface area (ECSA). The electrochemically active surface area was assessed by capacitance measurements as it is presumed to be linearly proportional to the double layer capacitance (C_{dl}).[1, 2] Therefore, the relative value of electrochemically active surface area can be obtained by normalization of C_{dl}. It can be seen from Fig. S7b and S7d that the slope of P doped MoO_2 on Mo foil is bigger than that of MoO_2 on Mo foil, clearly demonstrating that with P doping, the number of active sites of the MoO_2 on Mo foil for HER significantly increased.

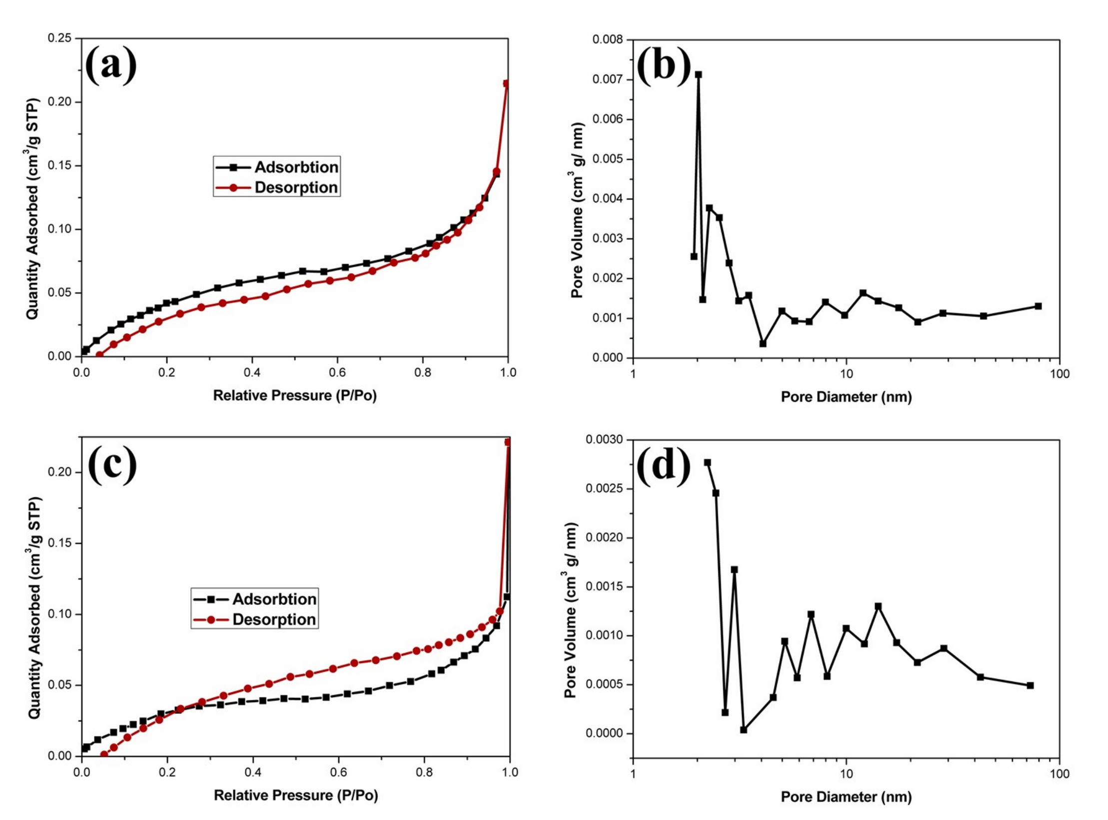

Fig. S8 (a) Nitrogen adsorption/desorption isotherms and (b) pore distribution of P doped MoO$_2$ on Mo foil sample. (c) Nitrogen adsorption/desorption isotherms and (d) pore distribution of MoO$_2$ on Mo foil sample. BET surface areas of P doped MoO$_2$ on Mo foil and MoO$_2$ on Mo foil are 2 m^2/g Mo foil and 2 m^2/g Mo foil, and the average pore size is 7.4 nm and 7.7 nm, respectively.

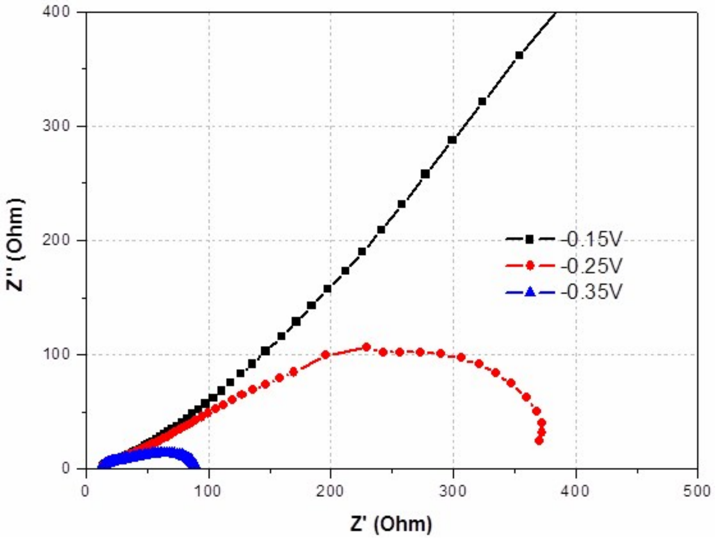

Fig. S9 Electrochemical impedance spectroscopy of samples peeled off from P doped MoO$_2$ on Mo foil at −150 mV, −250 mV and −350 mV vs. RHE. It can seen when overpotential increased, the resistance of sample decreased from about 1000 ohm (at -150 mV) to 85 ohm (at -350 mV).

References:
(1) S. Trasatti and O. A. Petrii, *Pure & Appl. Chem.*, 1991, 63, 711-734.
(2) J. D. Benck, Z. B. Chen, L. Y. Kuritzky, A. J. Forman and T. F. Jaramillo, *ACS Catal.* 2012, **2**, 1916-1923.