

Self-Assembly Precursor-Derived MoP Supported  
on N,P-Codoped Reduced Graphene Oxides as  
Efficient Catalysts for Hydrogen Evolution Reaction

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**Supporting Information**

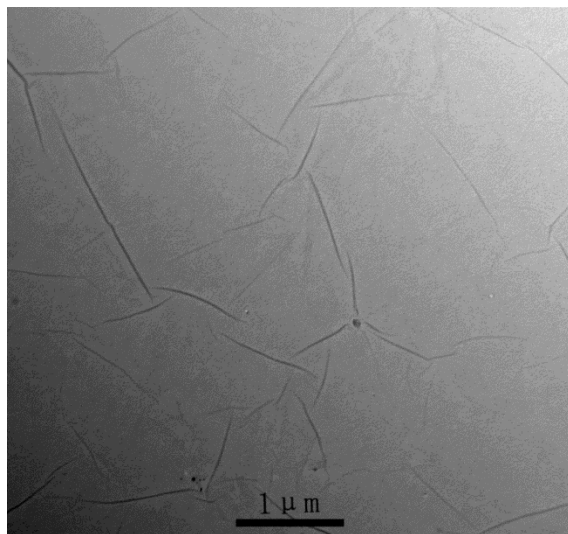
### **Preparation of the control samples.**

*Synthesis of MoP nanoparticles.* The synthesis method for MoP nanoparticles was the same as the MoP/N,P-rGO except removing GO.

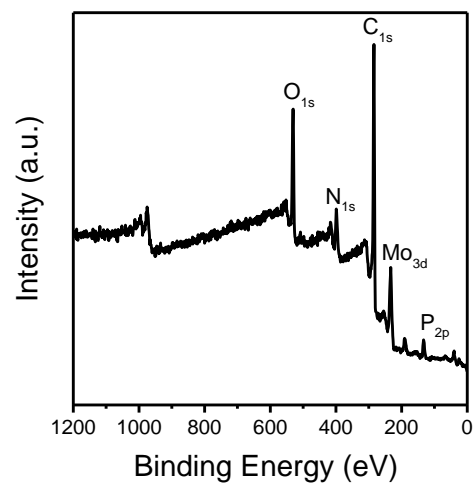
*Synthesis of MoP/rGO.* 20 mg of GO were dissolved in 4 mL of deionized water and sonicated for at least 30 min to form a homogeneous mixture. Then 50 mg of ammonium molybdate was added, and followed by adding 16 mL of ethylene glycol. This mixture was further sonicated for another 30 min, and then transferred into a 40 mL Teflon-lined autoclave. The autoclave placed in oven and hold at 200 °C for 24 h. After the temperature cooled down to room temperature, the precipitate was collected and washed with deionized water and ethanol for several times, and dried at 60 °C for 12 h. The products were placed in a quartz tube with 1 g of  $\text{NaH}_2\text{PO}_2$ , and the quartz tube was vacuumed. Then the quartz tube heated to 800 °C and maintained at this temperature for 2 h. After cooling to room temperature, the products collected and washed with deionized water.

*Synthesis of N-rGO.* The synthesis method for N-rGO was same as the MoP/N,P-rGO except removing phosphomolybdic acid and phytic acid.

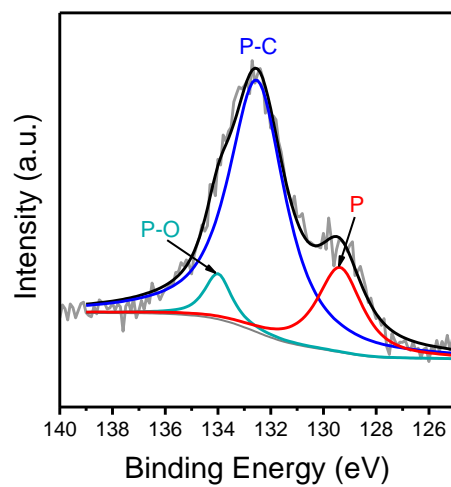
*Synthesis of N,P-rGO.* The synthesis method for N,P-rGO was same as the MoP/N,P-rGO except removing phosphomolybdic acid.



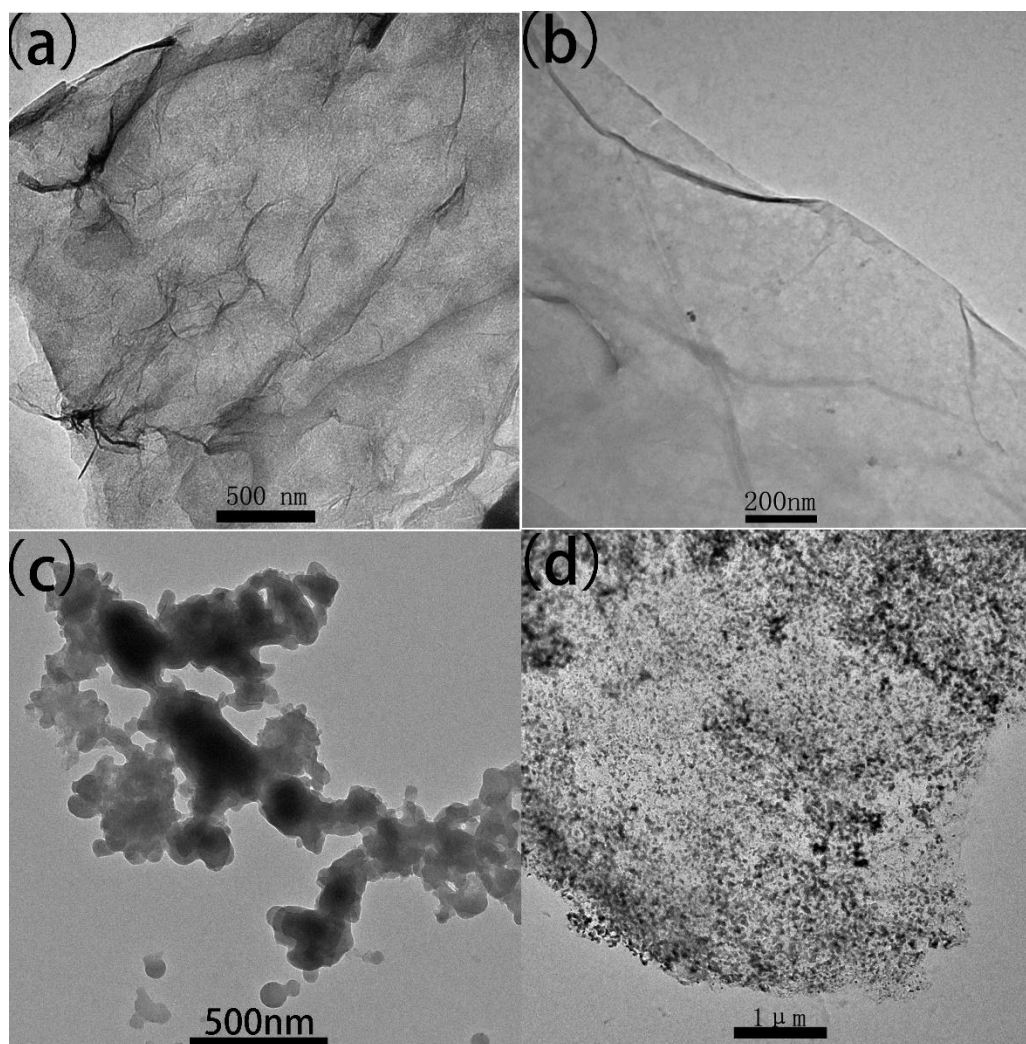
**Figure S1.** TEM image of GO.



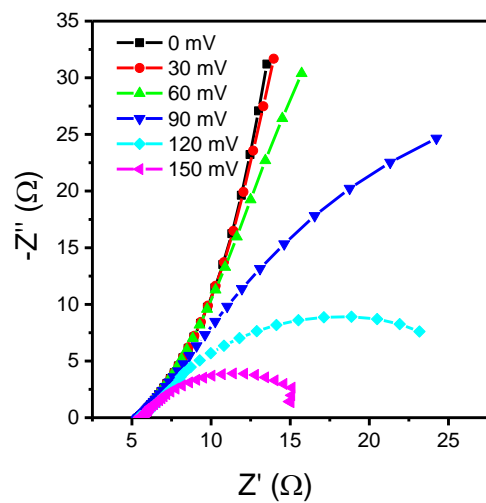
**Figure S2.** XPS survey scan of MoP/N,P-rGO.



**Figure S3.** XPS P 2p core level spectra of N,P-rGO.



**Fig. S4** TEM images of (a-d) NrGO, N,P-rGO, MoP NP and MoP/rGO.



**Fig. S5.** Nyquist plots of MoP/N,P-rGO at an different overpotential.

**Table S1.** Comparison of electrocatalytic performance of MoP-based HER catalysts

Catalysts	Loadings (mg cm <sup>-1</sup> )	Overpotential @ 10 mA cm <sup>-2</sup> (mV)	Tafel slope (mV dec <sup>-1</sup> )	Reference
MoP/N,P-rGO	0.41	115	54	<b>This work</b>
MoP@C@rGO	0.7	168	79	<i>ACS Appl. Mater. Interfaces</i> <b>2018</b> , DOI: 10.1021/acsami.8b07133
MoP@HCC	0.26	129	48	<i>Nanoscale</i> <b>2018</b> , 10, 14594-14599
MoP@NPC-H	0.5	141	59	<i>ACS Sustainable Chem. Eng.</i> <b>2018</b> , 6, 7676-7686
MoP@PC	0.14	258	59	<i>ACS Appl. Mater. Interfaces</i> <b>2018</b> , 20, 17140-17146
MoP@PC-rGO	0.14	234	54	<i>ACS Sustainable Chem. Eng.</i> 2018, DOI:10.1021/acssuschemeng.8b01575
MoP/rGO	1.6	152	88	<i>Cataly Sci Tech</i> , <b>2017</b> , 668-676.
MoP@NPC/rGO	0.4	218	57	<i>Chem. Commun.</i> <b>2017</b> , 53, 12576-12579
MoP/SN	0.5	104 <sup>a</sup>	45	<i>ACS Catal.</i> <b>2017</b> , 7, 3030-3038
MoP/SNG-20	0.5	99 <sup>a</sup>	54	
MoP NPs@NC	2	115	65	<i>Nanoscale</i> <b>2016</b> , 8, 17256-17261
MoS <sub>0.2</sub> P <sub>0.8</sub>	0.28	120 <sup>a</sup>	57	<i>Adv. Mater.</i> <b>2016</b> , 28, 1427-1432
MoP <sub>2</sub> /CC	7.8	58	63	<i>J. Mater. Chem. A</i> <b>2016</b> , 4, 7169-7173
MoP@RGO	0.285	98	58	<i>J. Am. Chem. Soc.</i> <b>2016</b> , 138, 14686-14693
MoP/Ti	1	117	50	<i>Angew. Chem. In .Ed.</i> <b>2014</b> , 53, 14433-14437
MoP S	1	86	50	
MoP S	3	64	50	
MoP	0.36	125	54	<i>Adv. Mater.</i> <b>2014</b> , 26, 5702-5707

a. using Pt wire as the counter electrode. The others used graphite rod as the counter electrode.