Supporting information

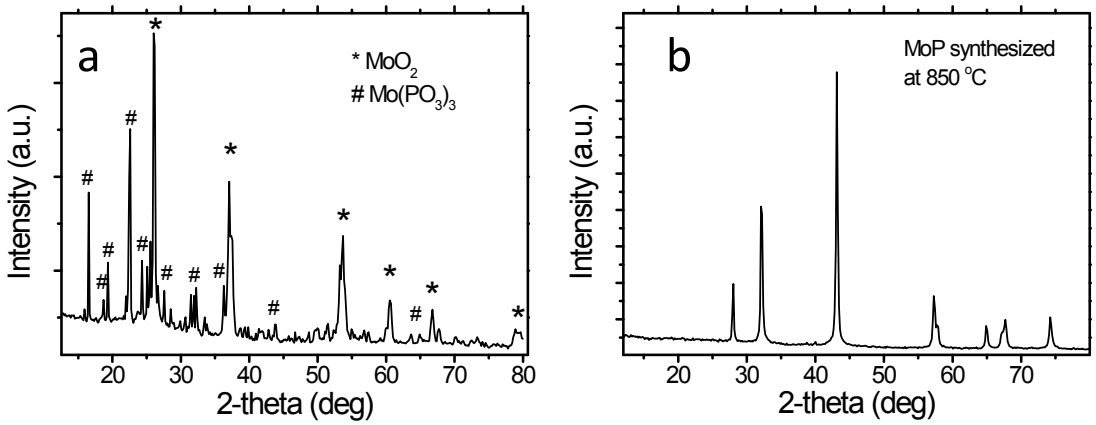

Figure S1. (a) Powder XRD pattern of precursor heated at 600 °C at N_2 atm showing formation of MoO_2 (JCPDS no. 86-0135) and $Mo(PO_3)_3$ (JCPDS no. 82-1031). (b) PXRD pattern of MoP synthesized at 850 °C in H_2 atmosphere.

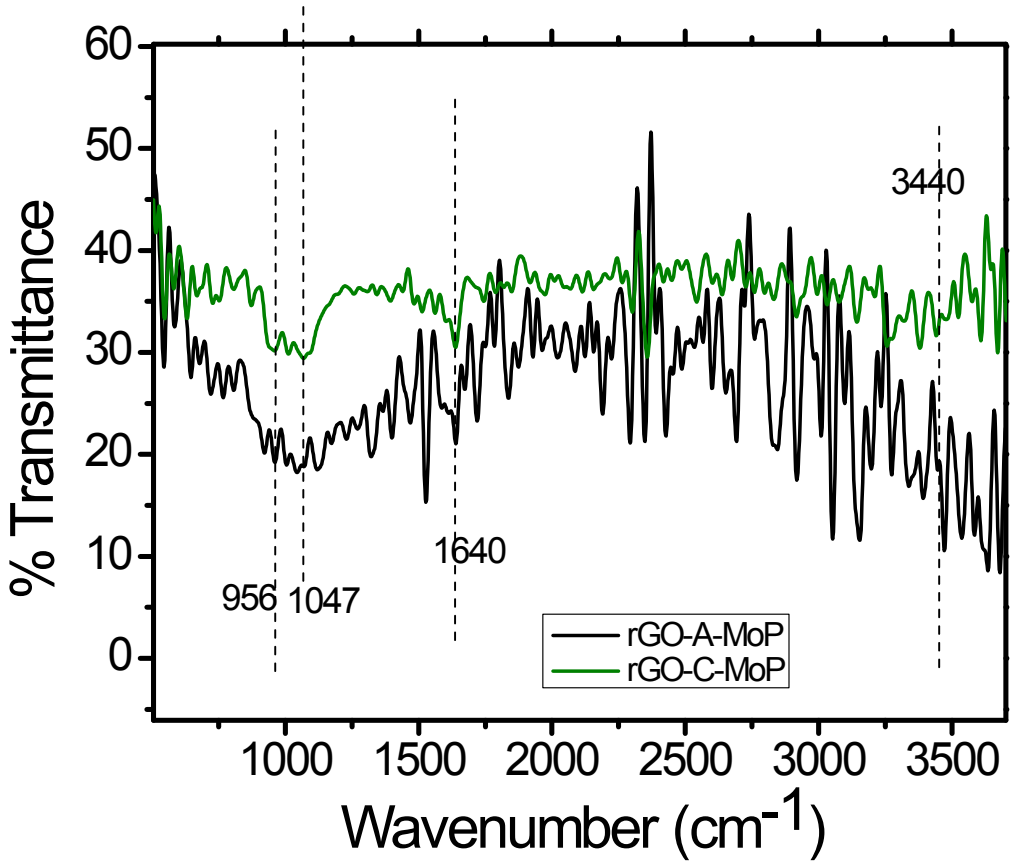

Figure S2. FTIR spectrum of the composites.

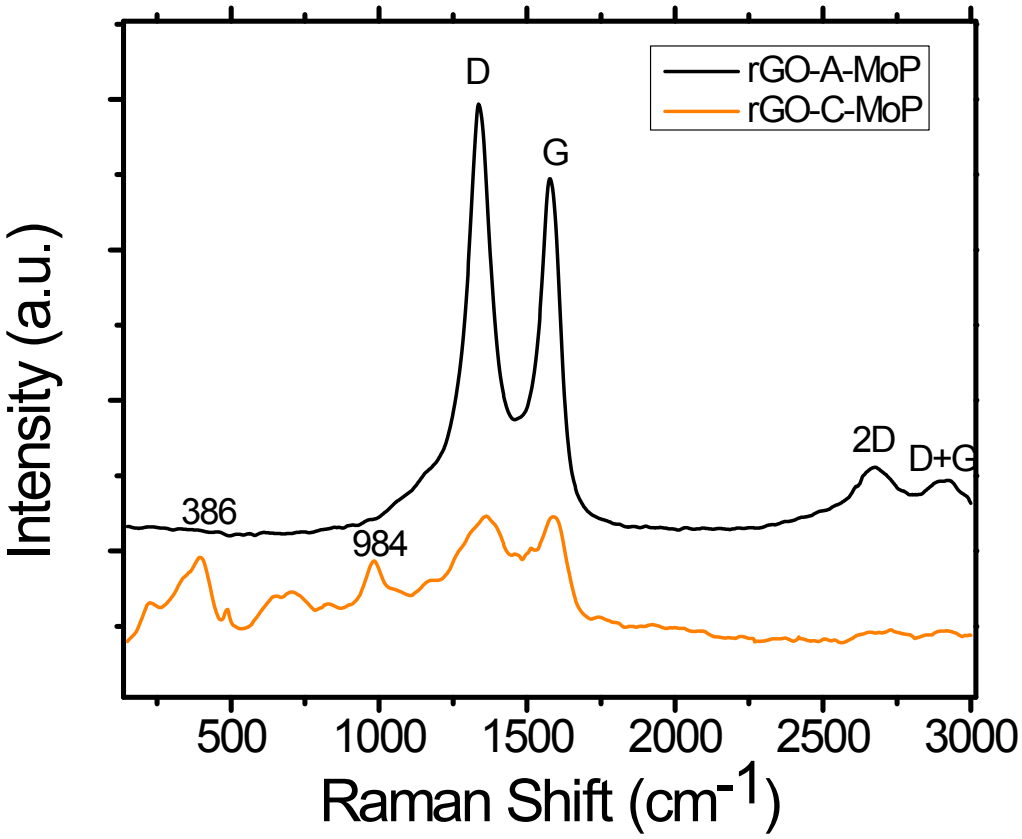

Figure S3. Raman Spectrum of the composites showing graphene signature Raman bands.

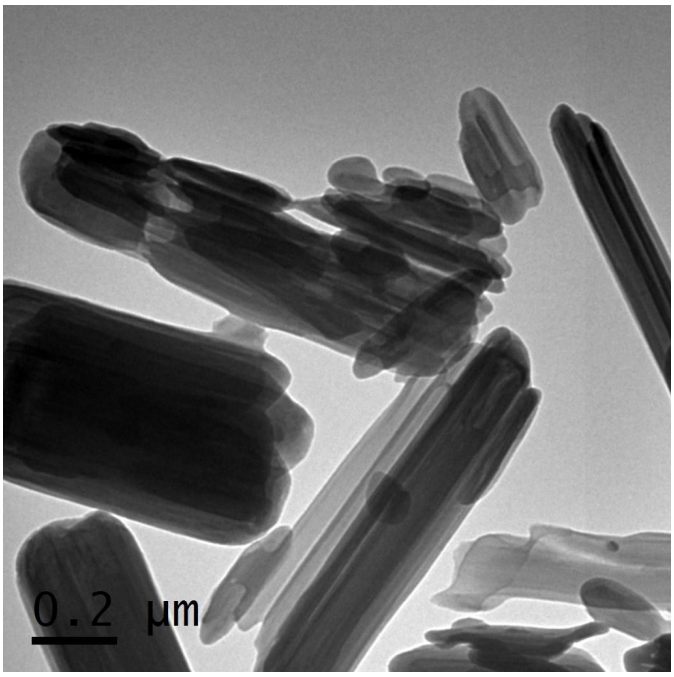

Figure S4: TEM image of anilinium ammonium molybdate complex.

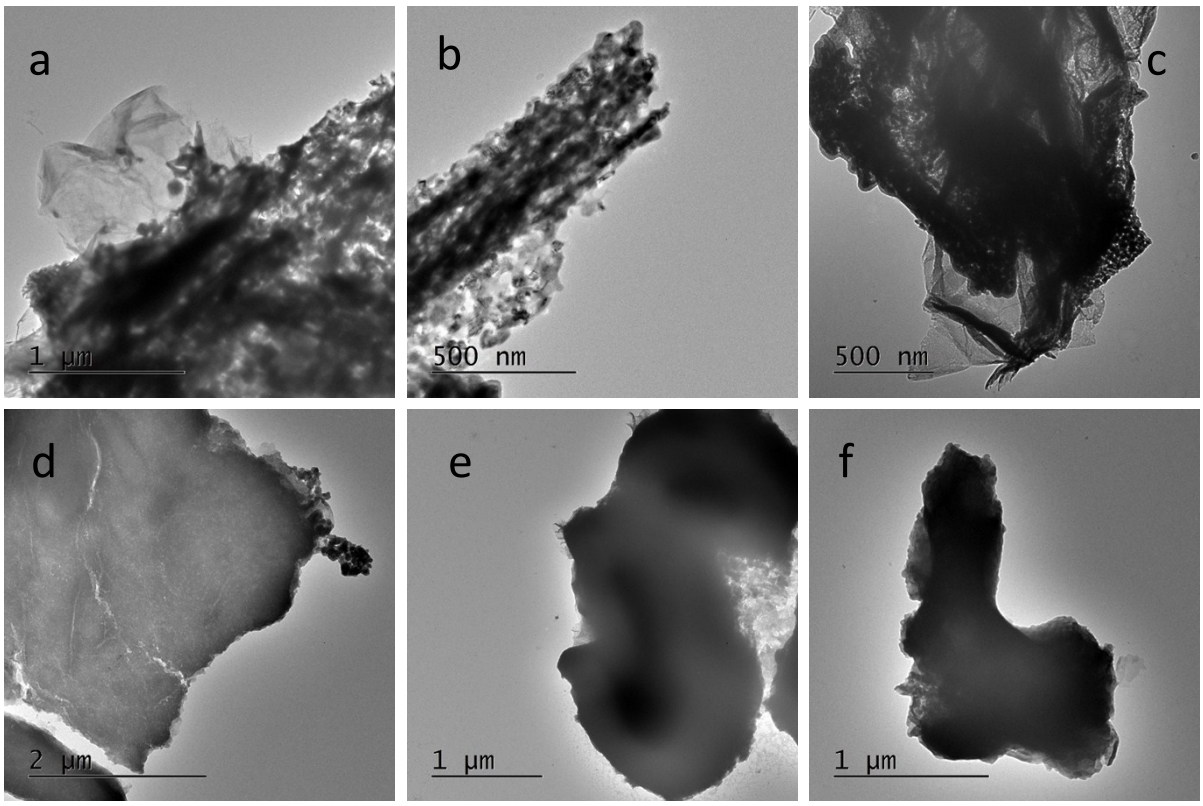

Figure S5. TEM micrographs of (a-c) rGO-A-MoP and (d-f) rGO-C-MoP

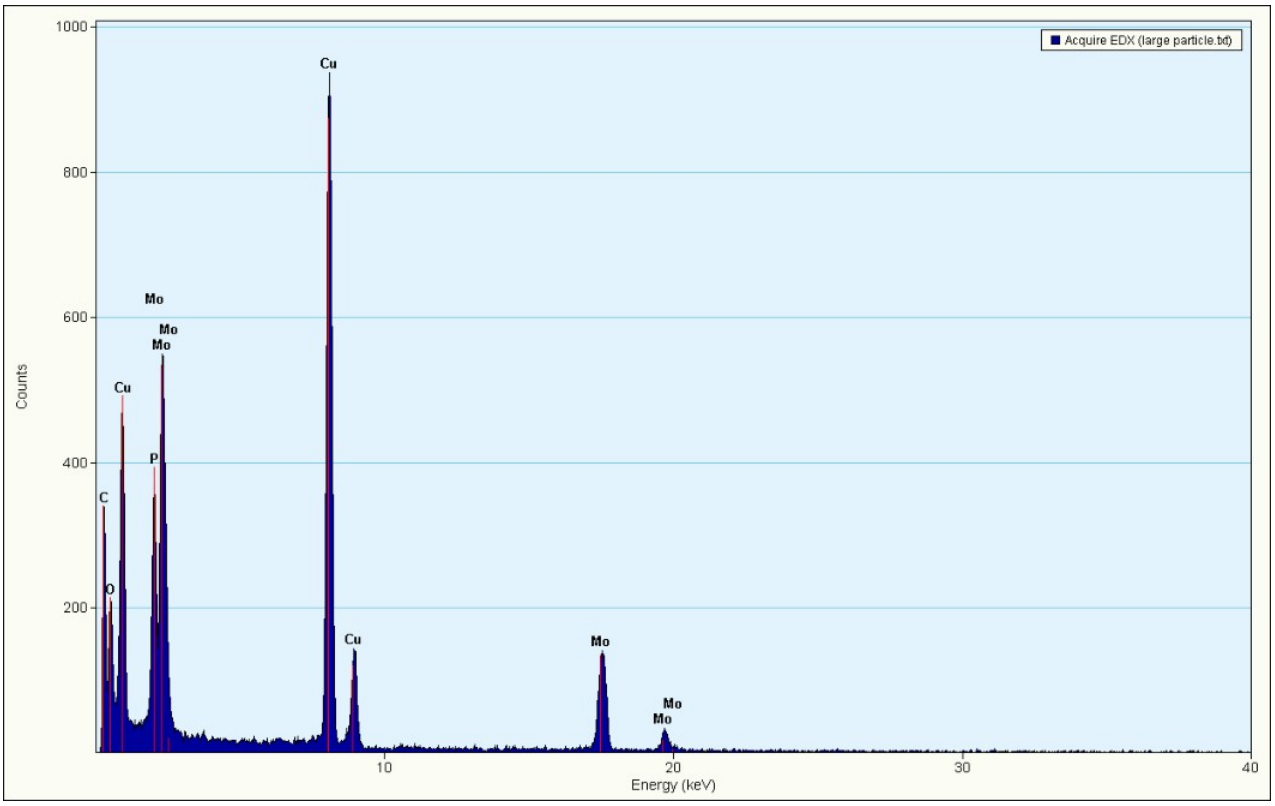

Figure S6. EDAX pattern of rGO-A-MoP composite showing the presence of Mo and P.

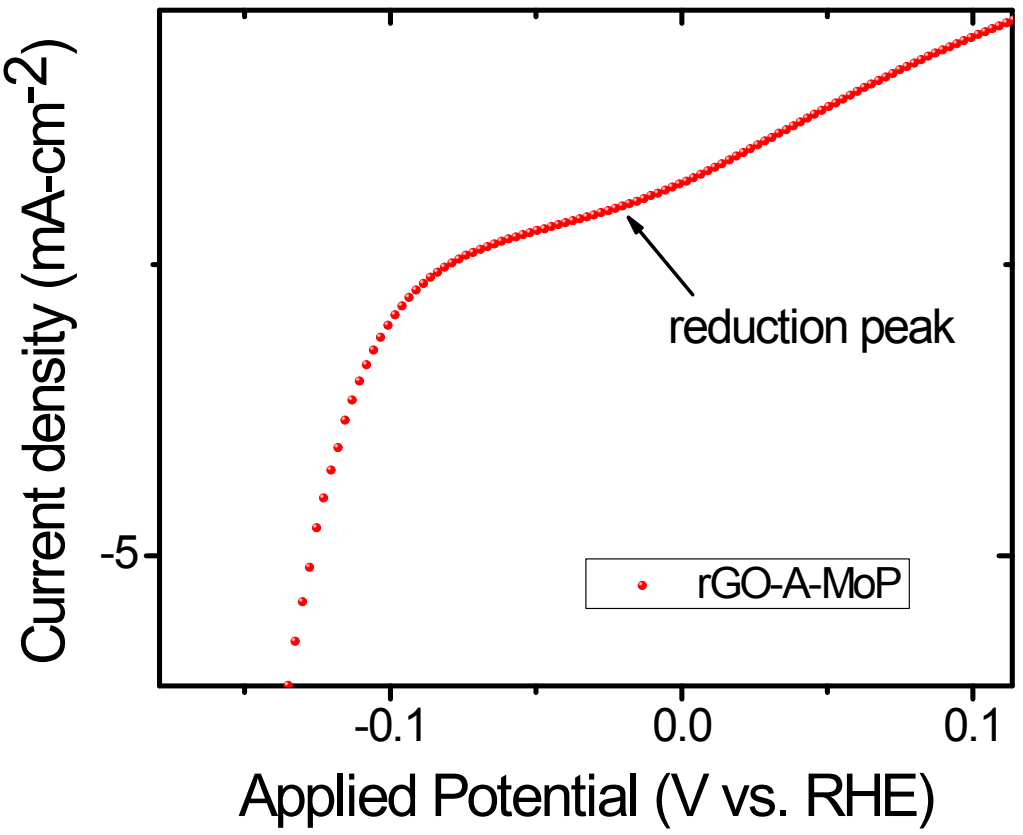

Figure S7. Magnified LSV curve of rGO-A-MoP in 0.5 M H_2SO_4 showing one reduction step before hydrogen evolution.

Electrochemically active surface area (ECSA) analysis:

The electrochemically active surface area (ECSA) for the composites has been calculated from the cyclic voltammogram in the potential range of 0.05 V – 0.45 V vs. RHE where no redox reactions take place.

We have calculated the double layer capacitance (C_{dl}) for the composite at different mass loadings. We used specific capacitance of 40 μF cm^{-2} (a moderate value as reported in a recent report[2]) to calculate ECSA for the electrodes. Therefore the electrochemically active surface area (A_{ECSA}) can be calculated from the below equation.

$$A_{ECSA} = \frac{specific\ capacitance}{40\ \mu F\ cm^{-2}\ per\ cm^{2}_{ECSA}}$$

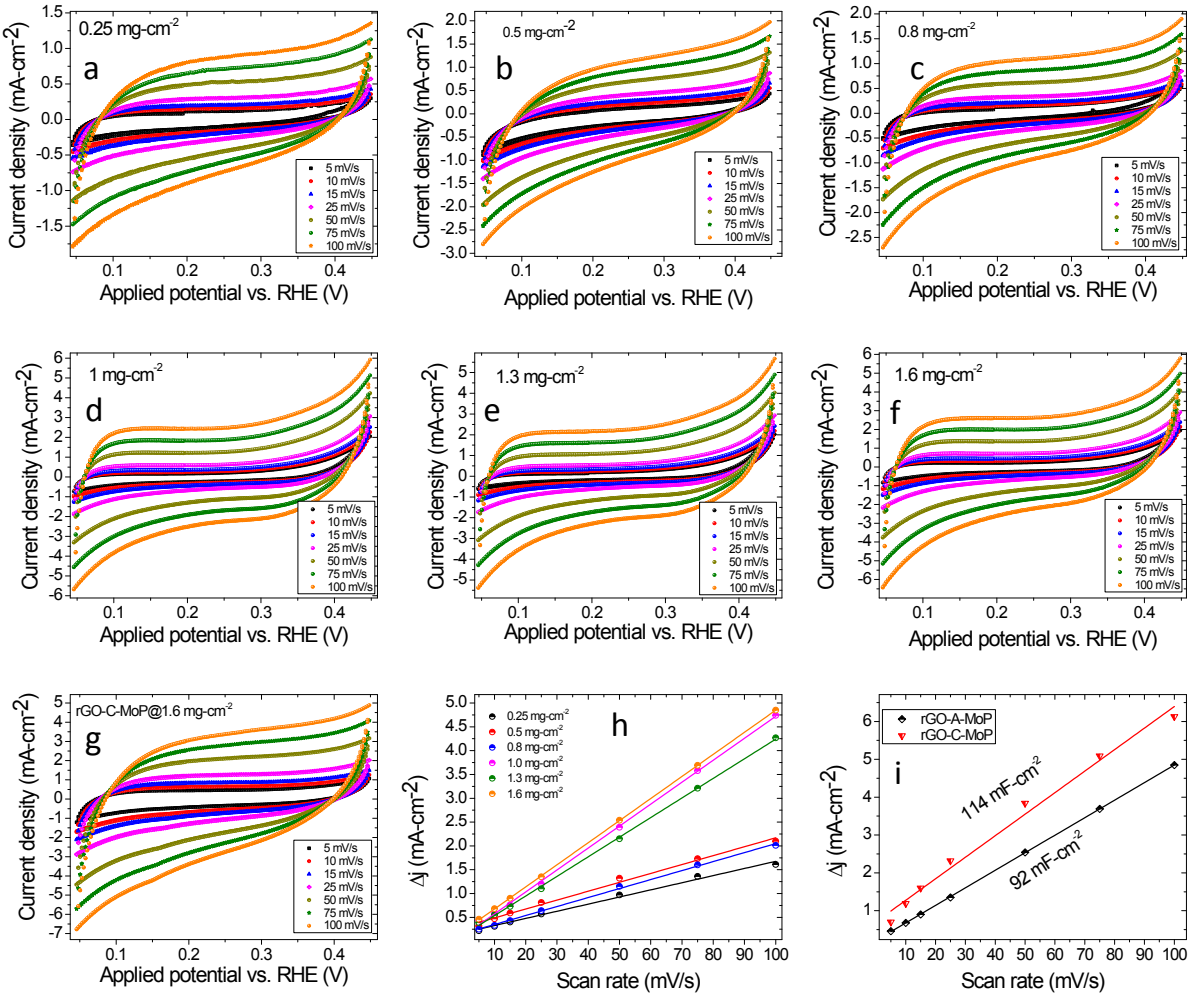

Figure S8. Cyclic voltammogram of the composites in the potential range of 0.05-0.45 V vs. RHE at different scan rates (5, 10, 15, 25, 50, 75 and 100 mV/s) at different mass loading. (a-f) rGO-A-MoP, (g) rGO-C-MoP with mass loading of 1.6 mg/cm^2, (h, i) Current density difference ($\Delta j = ja-jc$) at 0.25 V vs. RHE plotted against scan rate. The slope of the linear fit is equal to the half of the specific capacitance (C_{dl}).

Table S1. Comparison chart of the electrocatalytic activity of our composite and other reports.

System	Reference	Current density $mA\text{-}cm^{-2}$	Tafel slope mV/dec	Mass loading $mg\text{-}cm^{-2}$
rGO-A-MoP	Our work	10@152 mV 20@177 mV	88	1.6
Graphite-MoP	Applied Catal. A: Gen. 2015, 490 (25), 101–107	10@260 mV	63	0.64
MoP	J. Mater. Chem. A,2015, 3,4368–4373	10@150 mV	50	0.1
Amorphous MoP	Chem. Mater. 2014, 26, 4826−4831	10@110 mV 20@140 mV	45	1.0
MoP	Energy Environ. Sci.,2014, 7,2624–2629	10@135 mV	54	0.86
MoP	Chem. Commun., 2014, 50, 11683--11685	10@246 mV	60	0.071
MoP	Adv. Mater. 2014, 26, 5702–5707	10@125 mV 100@271 mV	54	0.36
FeP	Nanoscale, 2015, 7, 4400-4405	10@122 mV	67	0.28
CoP/CNT	Angew. Chem. Int. Ed. 2014, 53, 6710 –6714	10@122 mV	54	0.28
rGO-MoS_2	J. Am. Chem. Soc. 2011,	10@~150 mV	41	0.28

	133, 7296–7299			
Ni5P4-Ni2P Ni5P4-Ni2P Ni5P4-Ni2P	Angew. Chem. Int. Ed. 2015, 54, 8188 –8192	10@120 mV	79	68.2
FeP	*ACS Nano* **2014**, *8*, 11101–11107	10@50 mV	37	1
Ni2P	*J. Am. Chem. Soc.* **2013**, *135*, 9267–9270	20@130 mV 100@180 mV	46, 81	1
FeP	*Angew. Chemie Int. Ed.* **2014**, *53*, 12855–12859	10@55 mV 100@127 mV	38	3.2
CoP	*Angew. Chemie Int. Ed.* **2014**, *53*, 5427–5430	20@85 mV	50	2
MoP	*Adv. Mater.* **2014**, *26*, 5702–5707	10@125 mV 100@200 mV	54	0.36
Ni_5P_4	*J. Mater. Chem. A* **2014**, *3*, 1656–1665	10@118 mV	42	1.99
Cu3P	*Angew. Chemie Int. Ed.* **2014**, *53*, 9577–9581	10@ 143 mV 100@ 276 mV	67	15.2
Mo2C Aniline complex method	Energy Environ. Sci.,2014, 7,387–392	60 at 200 mV (rod) 21 at 200 mV (flaky) 7.3 at 200 mV (Bulky) 1.2 at 200mV	53	0.21

		(commerc)		
Mo2C graphene	Chem. Commun., 2014, 50, 13135--13137	10@130 mV	57, 76	
Mo2C N-doped CNT	*J. Mater. Chem. A* **2015**, *3*, 5783–5788	10@147 mV	71	3
Mo2C	*Angew. Chemie - Int. Ed.* **2014**, *53*, 6407–6410	1@205 mV 3@250 mV	120	0.28
Mo2C/CNT	*Energy Environ. Sci.* **2013**, *6*, 943	1 @ 63 mV 10 @152 mV	55	2
Mo2C nano rods	*Appl. Catal. B Environ.* **2014**, *154-155*, 232–237	32@200 mV	45	0.43
Porous MoC_x	*Nat. Commun.* **2015**, *6*, 1–8	10@142 mV	53	0.8
Mo2C	*J. Power Sources* **2015**, *296*, 18–22	60@200 mV 100@300 mV	55	0.213
nw-W4MoC	*Adv. Funct. Mater.* **2015**, *25*, 1520–1526	80@184 mV	52	1.28
Mo_2C@NC	*Angew. Chemie - Int. Ed.* **2015**, *54*, 10752–10757	1@60 mV 10@124 mV	60	0.28
Mo2C-CNT-graphene	*ACS Nano* **2014**, *8*, 5164–5173	10@130 mV	58	0.65

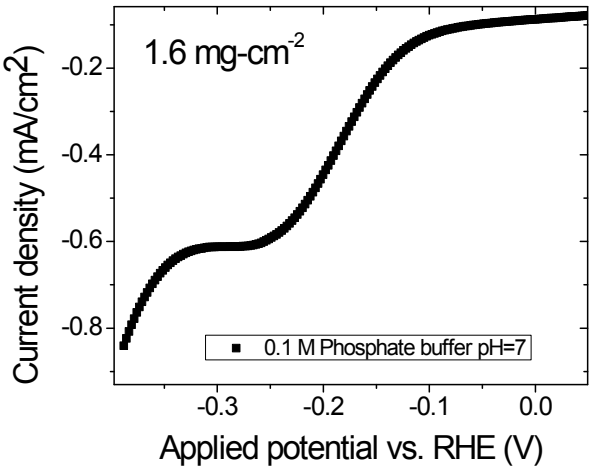

Figure S9. LSV curve of rGO-A-MoP composite in 0.1 phosphate buffer (pH=7.0) and it does not show any HER activity.

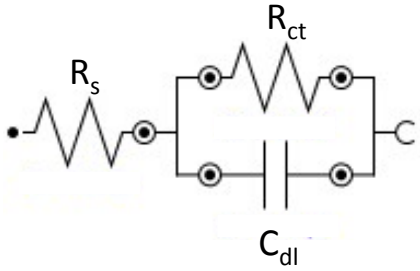

Figure S10. Equivalent circuit used to fit the impedance data.

Table S2. EIS fitting parameters of rGO-A-MoP composite in 0.5 M H_2SO_4 at different applied potentials.

Potential vs. RHE (mV)	R_{ct} (Ohm)	C_{dl} (mF)	R_s (Ohm)
60	7727	0.205	47
80	3124	0.509	38
100	687	2.315	47
120	276	2.533	41
140	121	1.961	36
160	74	1.338	30
200	31	0.536	26

Table S3. EIS semicircle fitting parameters of rGO-A-MoP in 1M KOH at different applied potentials.

Bias (mV vs. RHE)	R_s (Ohm)	R_{ct} (Ohm)	C_{dl} (μF)
0	20	228000	6.9
20	17	121000	13
40	21	55000	28
60	19	26000	60
80	21	10000	155
100	26	3700	188
120	32	1470	166
140	31	614	149
160	29	285	132
180	28	159	116
200	28	98	104
220	29	67	100

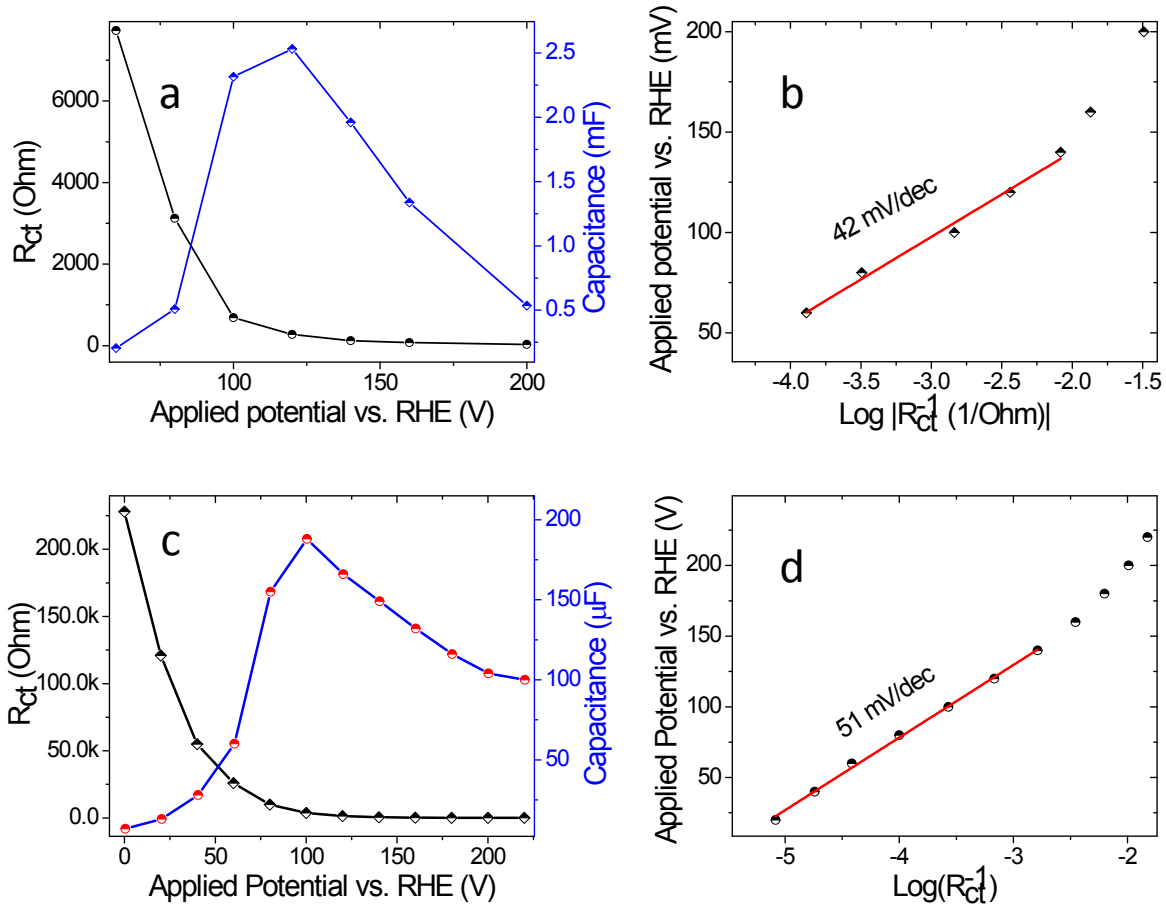

Figure S11. (a) Variation of R_{ct} and capacitance with applied potentials in acidic medium, (b) corresponding Tafel plot calculated from R_{ct}. (c) Variation of R_{ct} and capacitance with applied potentials in alkaline medium and (d) corresponding Tafel plot calculated from R_{ct}.

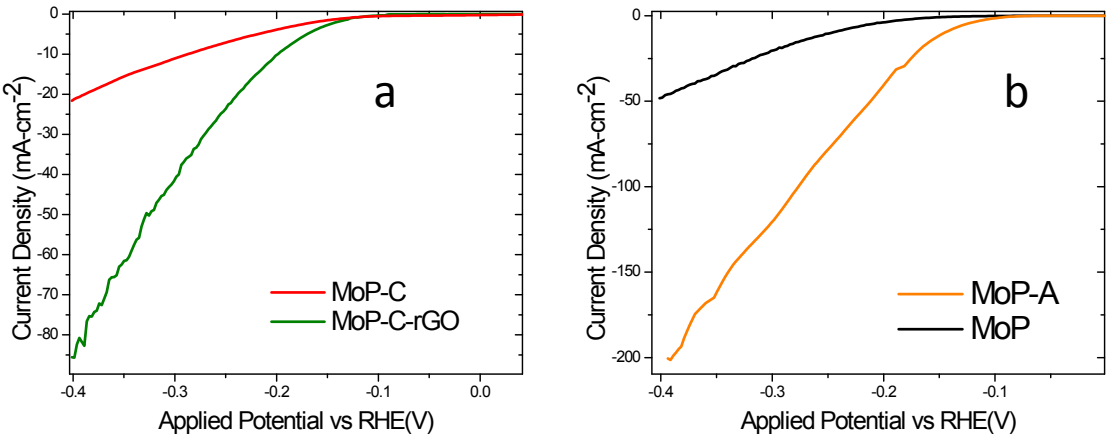

Figure S12. LSV curves of (a) MoP synthesized at 850 °C in presence of citric acid and (b) MoP synthesized at 850 °C in H_2 and MoP-A synthesized at 850 °C in H_2 in presence of aniline.

References:

(1) Jr., W. S. H.; Offeman, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 1939.

(2) Tang, C.; Wang, W.; Sun, A.; Qi, C.; Zhang, D.; Wu, Z.; Wang, D. *ACS Catal.* **2015**, *5*, 6956–6963.