Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information

Defective crystalline molybdenum phosphides as bifunctional catalysts for hydrogen evolution and hydrazine oxidation reactions in water splitting

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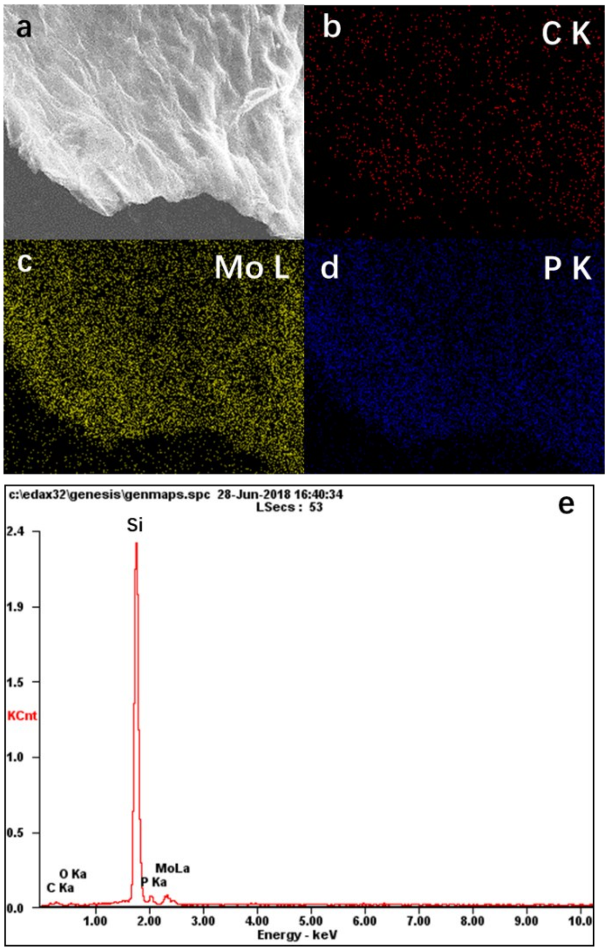

Fig. S1. An SEM image (a) and the corresponding EDS maps (b-d) and an EDS spectrum (e) of D-MoP/rGO. The Si peak in (e) comes from the Si wafer support.

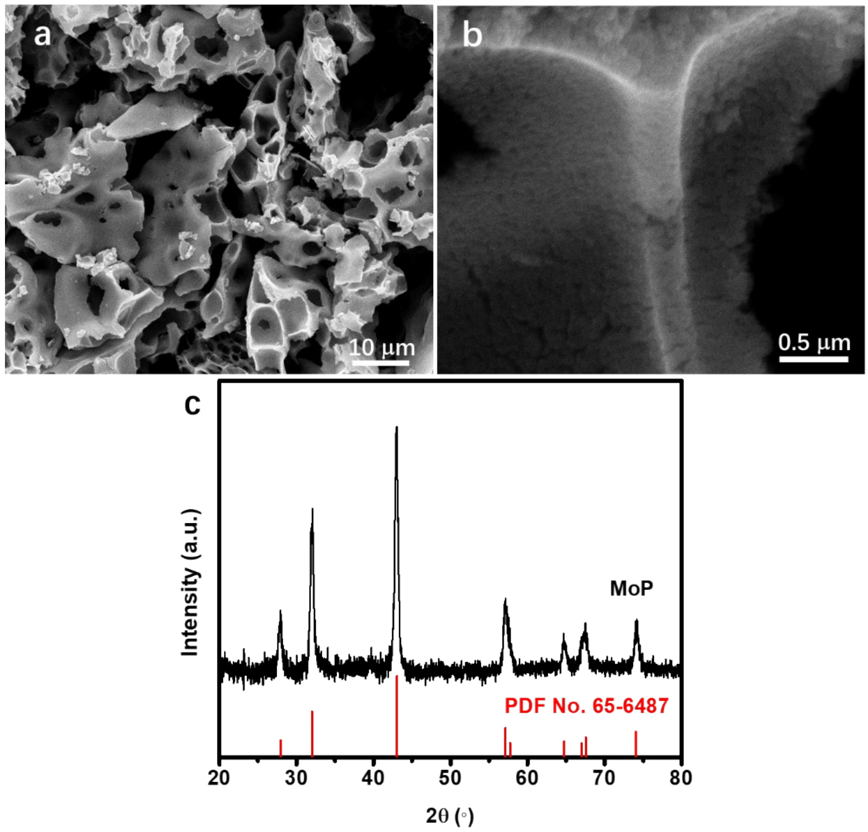

Fig. S2. (a,b) SEM images and (c) an XRD pattern of bulk MoP.

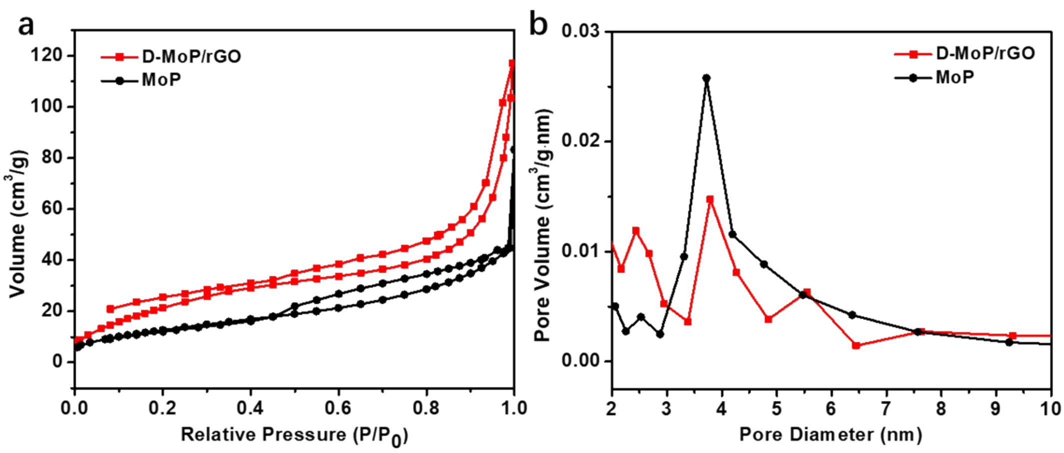

Fig. S3. (a) N_2 adsorption-desorption isotherms and (b) the pore size distribution of D-MoP/rGO in comparison with a bulk MoP sample.

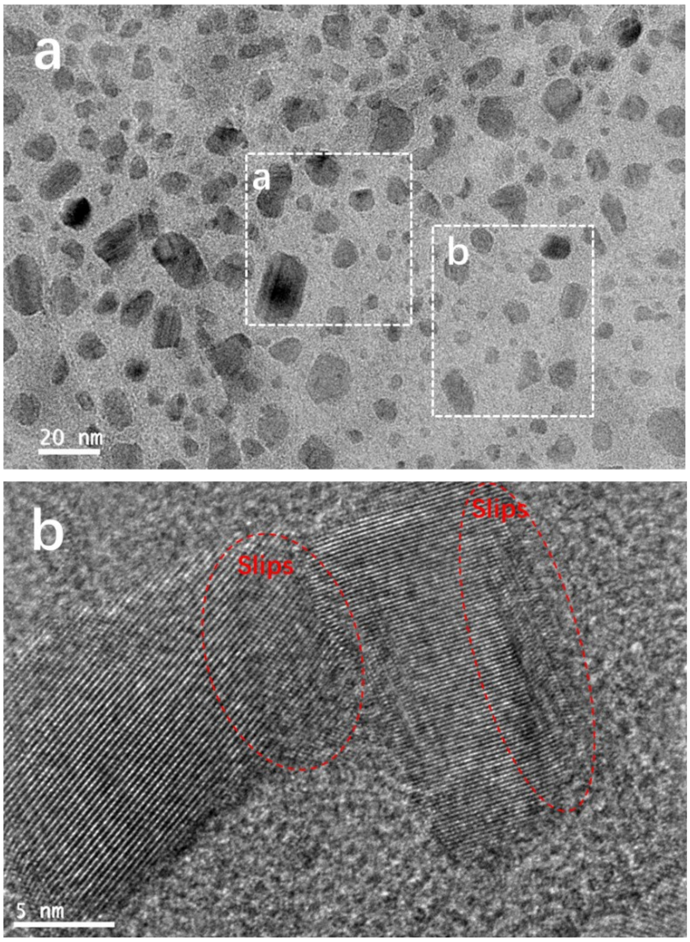

Fig. S4. The TEM images of D-MoP/rGO. (a) Figure 2a and 2b are extracted from the selected area (white squares) in this image. b) The HRTEM image of D-MoP/rGO show slips in the crystal structure of MoP.

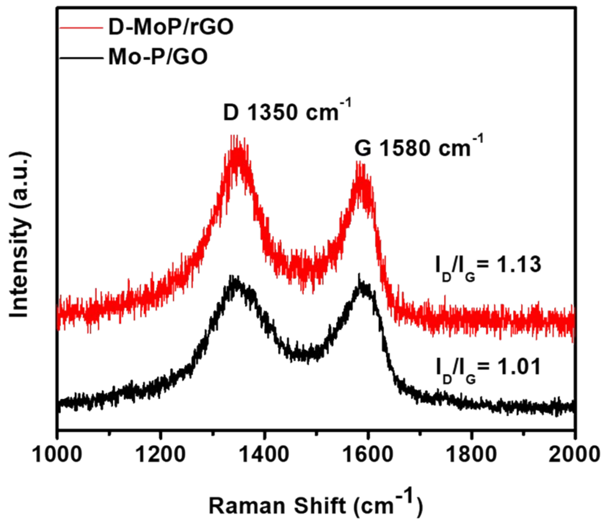

Fig. S5. Raman spectra of D-MoP/rGO and the GO supported precusors (donated as Mo-P/GO).

The Raman spectrum of D-MoP/rGO exhibits typical D and G bands of carbon materials at 1370 and 1594 cm^{-1}, respectively. The I_D/I_G ratio of D-MoP/rGO at 1.13 is much higher than that of Mo-P/GO at 1.01. This demonstrates the present of the defects on the rGO after thermal annealing along with optimized conductively of the hybrid.

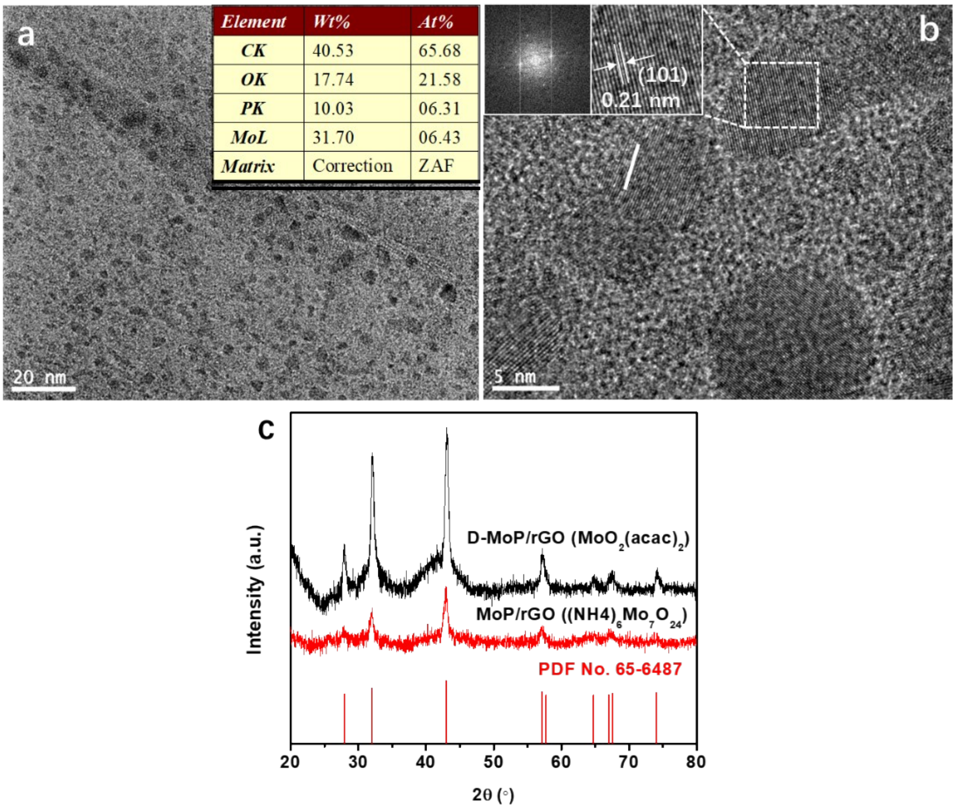

Fig. S7. Characterization of MoP/rGO synthesized by using $(NH_4)_6Mo_7O_{24}$ as the Mo precursor. (a) TEM and (b) HRTEM images of MoP/rGO. The inset of (a) is the EDX elemental distribution. (c) XRD patterns. (d) *i*R-corrected LSV polarization curves of MoP/rGO, D-MoP/rGO, and Pt/C in 1.0 M KOH.

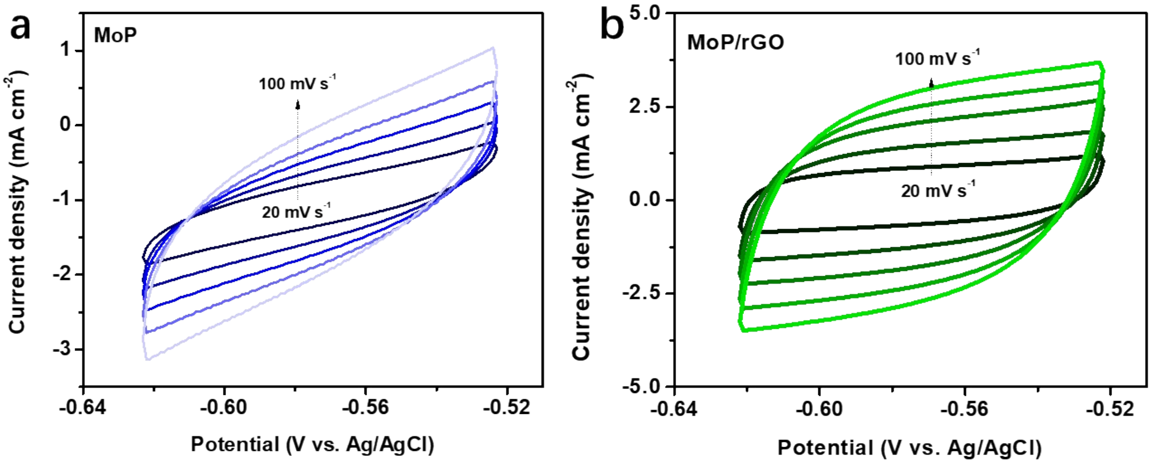

Fig. S7. CVs of bulk MoP and MoP/rGO in a non-faradaic capacitance current range at the scan rates of 20, 40, 60, 80 and 100 mV s^{-1}.

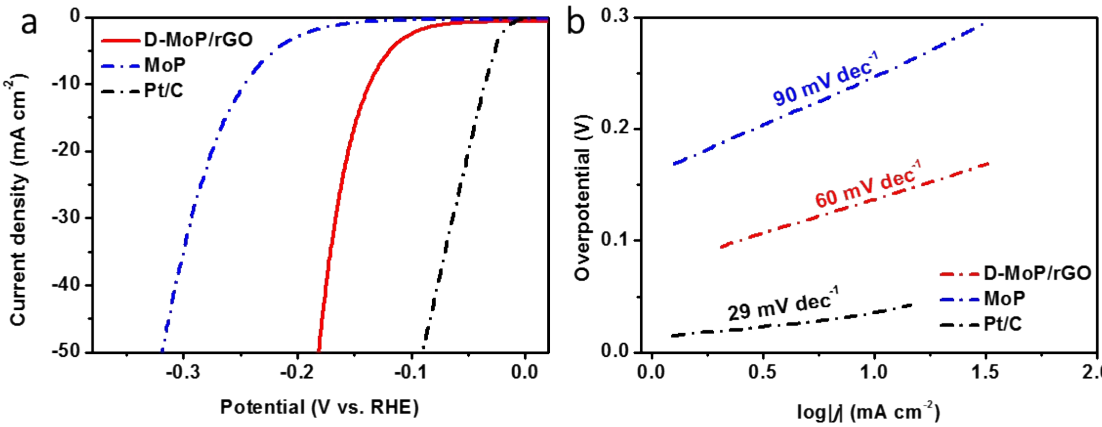

Fig. S8. (a) HER LSV polarization curves of D-MoP/rGO, MoP, and Pt/C in 0.5 M H_2SO_4 and (b) the corresponding Tafel plots.

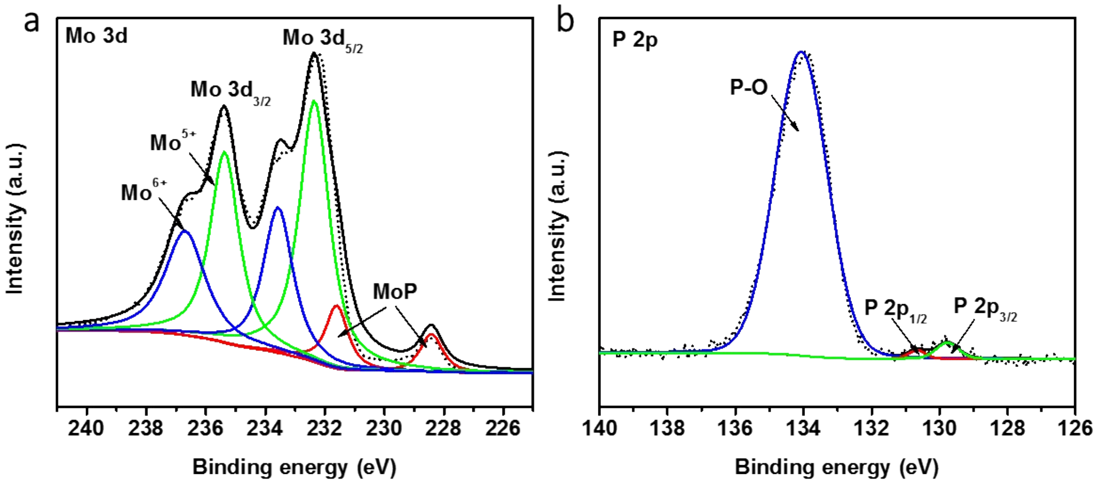

Fig. S9. XPS spectra of D-MoP/rGO after the HER test. (a) Mo 3d and (b) P 2p spectra.

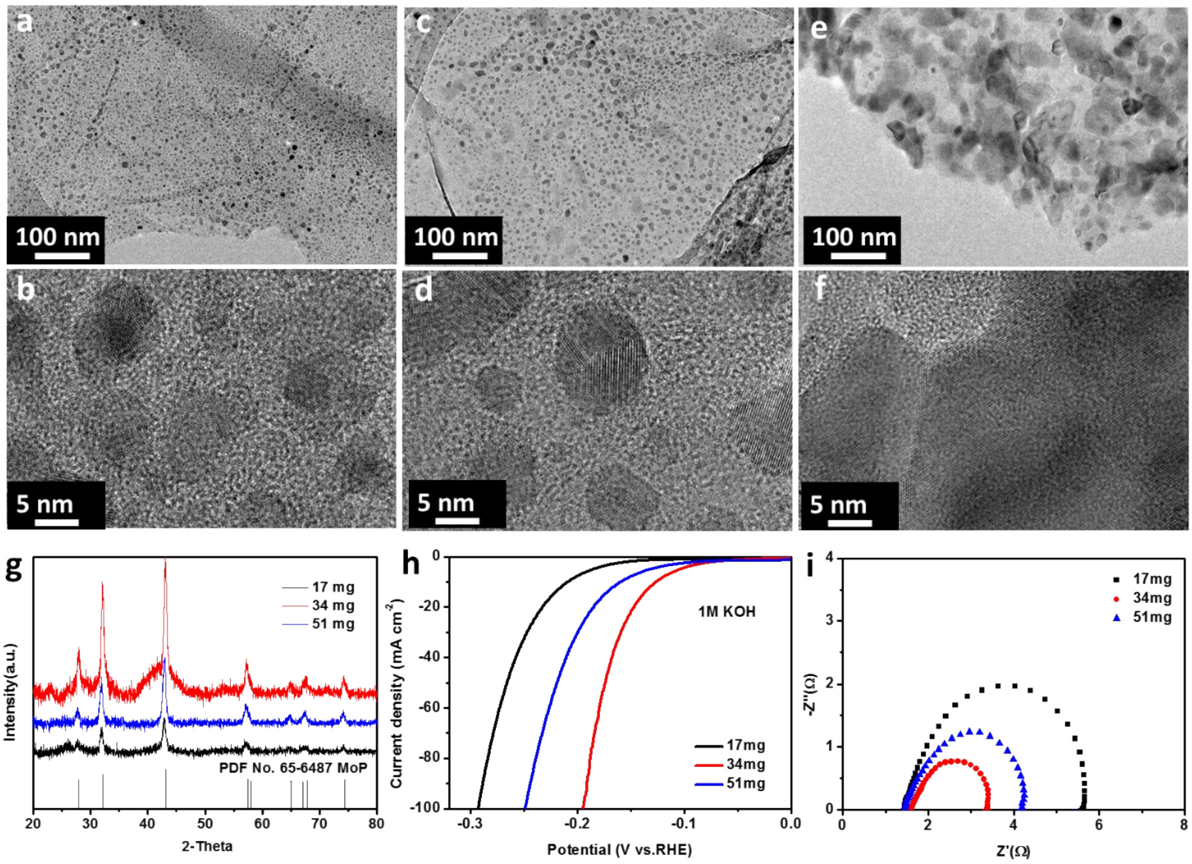

Fig. S10. TEM images of crystalline MoP/rGO synthesized using different amount of $MoO_2(acac)_2$, (a,b) 17 mg, (c,d) 34 mg, (e.f) 51 mg. (g) XRD patterns of these samples. (h) HER LSV polarization curves of these samples in 1.0 M KOH and (i) their corresponding Nyquist plots.

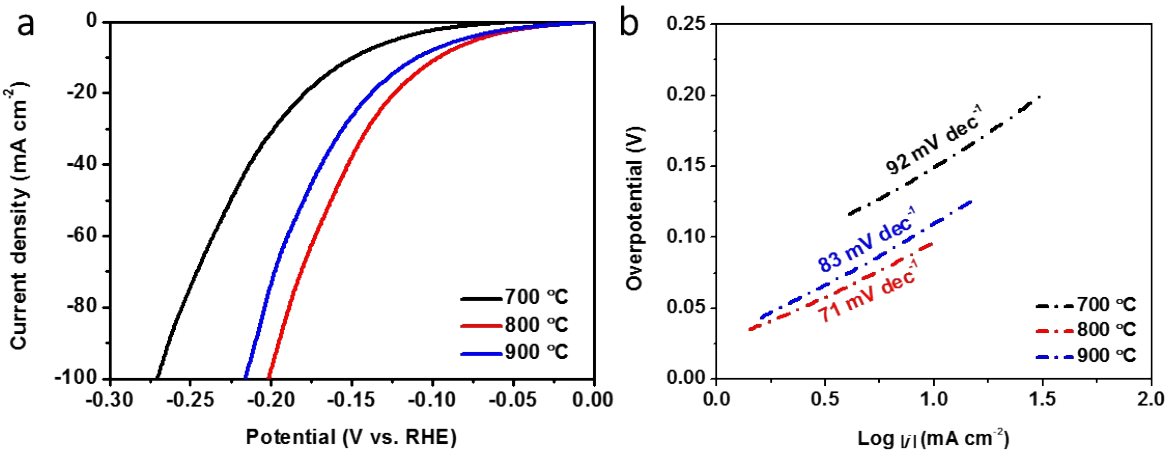

Fig. S11. HER LSV polarization curves of D-MoP/rGO synthesized at different annealing temperatures (electrolyte:1.0 M KOH)

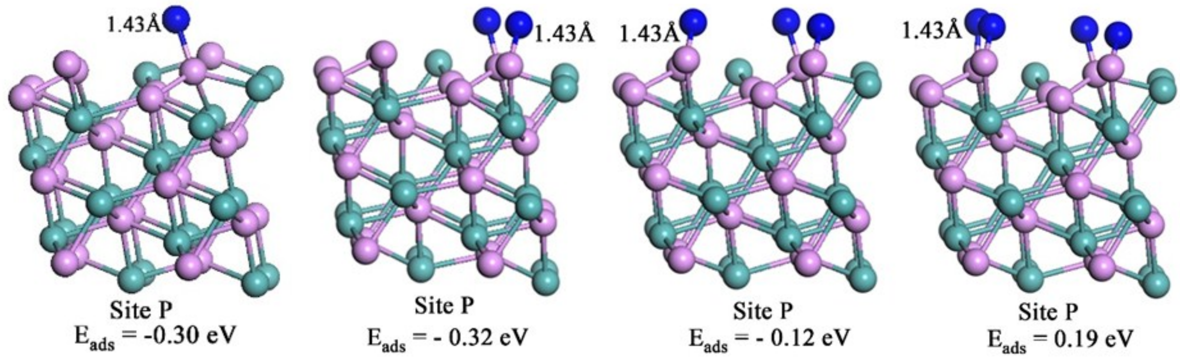

Fig. S12. Adsorption models of 1H, 2H, 3H, 4H atoms on MoP (111)-Mo surfaces.

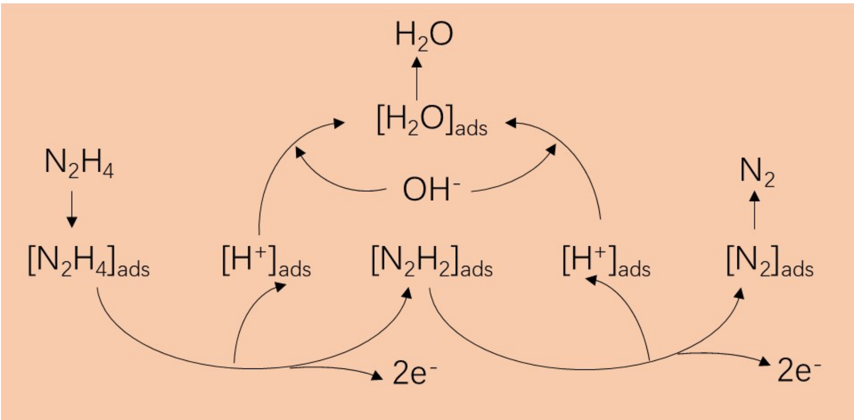

Fig. S13. Schematic illustration of the proposed reaction steps for hydrazine oxidation on D-MoP/rGO.

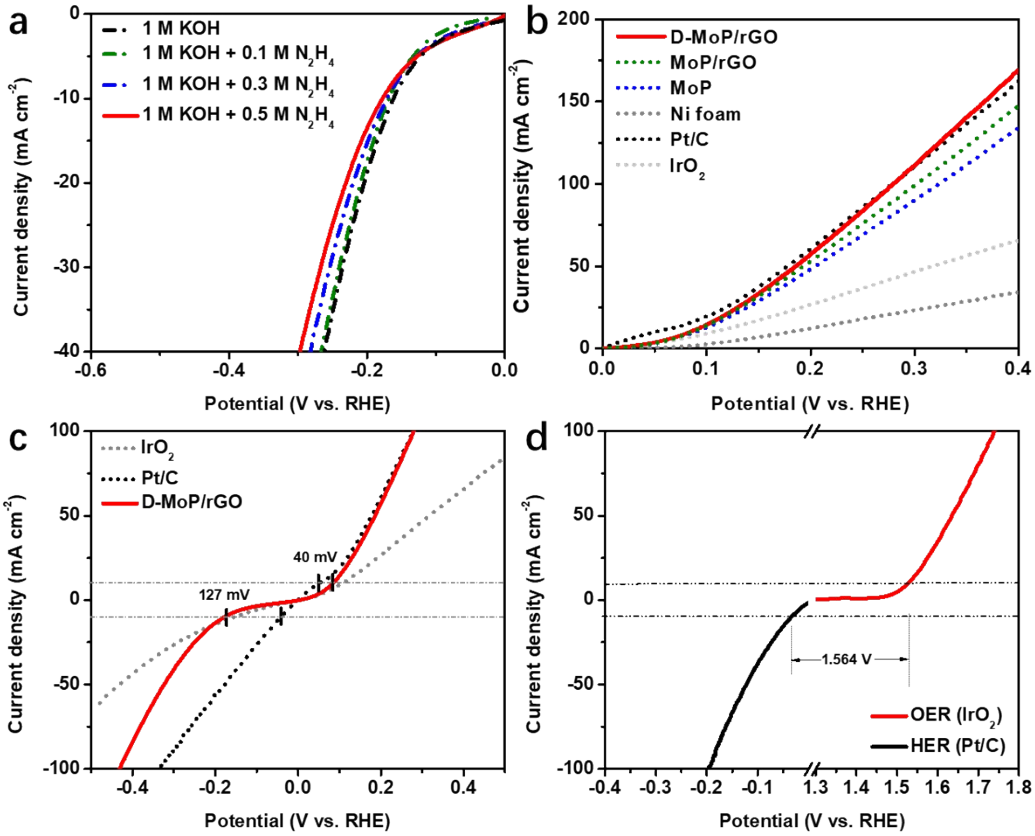

Figure S14. (a) HER LSV polarization curves of D-MoP/rGO in 1.0 M KOH containing different amount of hydrazine. (b) LSV polarization curves of various catalysts for the HER/HzOR couple in 1.0 M KOH containing 0.5 M N_2H_4. (c) LSV polarization curves of D-MoP/rGO, Pt/C and IrO_2 for the HER/HzOR couple in 1.0 M KOH containing 0.5 M N_2H_4. (d) LSV polarization curves of Pt/C (HER) and IrO_2 (OER) in 1.0 M KOH.

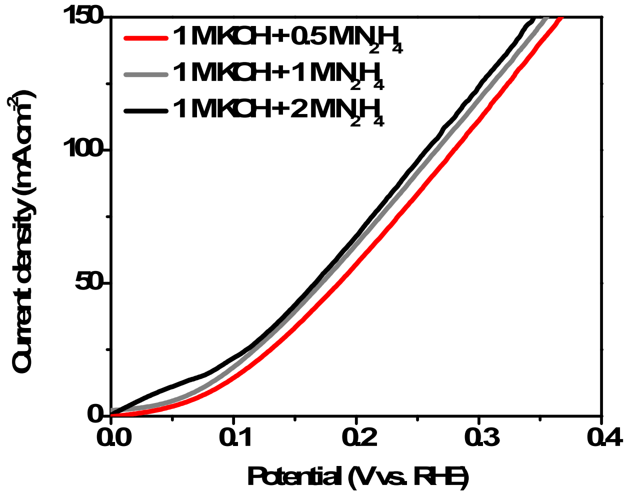

Fig. S15. LSV polarization curves of D-MoP/rGO for hydrazine oxidation in 1.0 M KOH containing hydrazine at different concentrations.

Table S1. HER activities of Mo- and P- based electrocatalysts under alkaline (1.0M KOH) media.

Catalysts	Electrolyte	η_{onset} (mV)	Tafel slope (mV dec^{-1})	j_{geo} (mA cm^{-2})	Loading (mg cm^{-2})	Reference
D-MoP/rGO	**1.0 M KOH**	**38**	**71**	**10 @η= 122 mV 30 @η= 158 mV**	**1.5**	***This work***
MoP/NC	1.0 M KOH	-	50	10 @η= 170 mV	~0.56	*Appl. Catal., B.* **2019,** 245, 656
MoP/CNTs-700	1.0 M KOH	34	73	10 @η= 86 mV	0.5	*Adv. Funct. Mater.* **2018**, 28, 1706523
MoP-RGO	1.0 M KOH	-	62	10 @η= 150 mV	0.42	*Electrochim. Acta,* **2017***,* 232, 254
MoP	1.0 M KOH	50	-	30 @η= 180 mV	0.86	*Energy Environ. Sci.* **2014***, 7,* 2624
MoCx nano-octahedrons	1.0 M KOH	80	59	10 @η= 151 mV	0.8	*Nat. Commun.* **2015**, 6,6512
Ni-MoS_2	1.0 M KOH	45	60	10 @η= 98 mV	0.89	*Energy Environ. Sci.* **2016**, 9, 2789
MoO_2	1.0 M KOH	0	41	10 @η= 10 mV	2.9	*Adv. Mater.*, 2016, 28, 3785-3790
FeP NAs/CC	1.0 M KOH	86	146	10 @η= 218 mV	1.5	*ACS Catal.* **2014***, 4,* 4065
Ni_5P_4(pellet)	1.0 M NaOH	-	98	10 @η= 49 mV	50 mg in 6 mm pellet	*Energy Environ. Sci.* **2015***, 8,* 1027
Ni_2P(pellet)	1.0 M NaOH	-	118	10 @η= 69 mV		
Porous Co phosphide/Co phosphate thin film	1.0 M KOH	-	-	30 @η= 430 mV	0.1	*Adv. Mater.* **2015***, 27,* 3175
Co-P film	1.0 M KOH	-	42	10 @η= 94 mV	Co=2.52 P=0.19	*Angew. Chem. Int. Ed.* **2015***, 54,* 6251
$Ni_{0.33}Co_{0.67}S_2$	1.0 M KOH	50	118	10 @η= 88 mV	0.3	*Adv. Energy Mater.* **2015***, 5,* 1402031

Table S2. The values of ΔE_{H*}, $\Delta E_{ZPE(H*)}$, ΔE_{ZPE} and ΔG_{H*} of H* at the surface of MoP (111) and MoP (111)-Mo.

		ΔE_{H*}/eV	$\Delta E_{ZPE(H*)}$/eV	ΔE_{ZPE}/ eV	ΔG_{H*}/ eV
MoP (111)	1H	-0.300813	0.206958	0.069122	-0.43
	2H	-0.292545	0.413850	0.276014	-0.22
	3H	-0.097355	0.616084	0.478248	0.18
	4H	-0.068716	0.816629	0.678793	0.41
MoP (111)-Mo	1H	-0.299527	0.210584	0.072748	-0.43
	2H	-0.324443	0.420035	0.282199	-0.24
	3H	-0.120011	0.622901	0.485064	0.16
	4H	0.193886	0.792931	0.655095	0.65

Table S3. Cell voltage of different electro-catalysts for overall water splitting.

Catalysts	Electrolyte	Cell voltage (V)	Current density (mA cm^{-2})	Durability (h)	Reference
D-MoP/rGO	**1.0 M KOH +0.5 M N_2H_4**	**0.74**	**100**	**12**	***This work***
Cu_3P/CF	1.0 M KOH +0.5 M N_2H_4	0.4	10	3	*Inorg. Chem. Front.* **2017**, *4*, 420
Ni_2P/NF	1.0 M KOH +0.5 M N_2H_4	0.45	100	10	*Angew. Chem. Int.Ed.* **2017**, *129*, 860- 864
CoP/TiM	1.0 M KOH +0.1 M N_2H_4	0.3	40	5.5	*ChemElectroChem* **2017**, 4, 481
Tubular $CoSe_2$ nanosheet	1.0 M KOH +0.5 M N_2H_4	0.164	10	14	*Angew. Chem. Int. Ed.* **2018**, 57, 7649
Ni_2P NF/CC	1 M KOH +0.5 M urea	1.35	50	-	*J. Mater. Chem. A* **2017**, *5*, 3208
Co-P/rGO	1.0 M NaOH	1.70	10	-	*Chem. Sci.*, **2016**, 7, 1690
FeP NTs	1.0 M KOH	1.69	10	14	*Chem. Eur. J.* **2015**, & 21, 1
Cu@NiFe LDH	1.0 M KOH	1.54	10	48	*Energy Environ. Sci.* **2017**, 10, 1820
NiFeOx/CFP	1.0 M KOH	1.51	10	200	*Nat. Commun.* **2015**, *6*, 7261
Co_1Mn_1CH/NF	1.0 M KOH	1.68	10	-	*J. Am. Chem. Soc.* **2017**, 139, 8320