Electronic Supplementary Information (ESI)

Facile Synthesis, Characterization and DFT Studies of Nanostructured Nickel – Molybdenum - Phosphorous Planar Electrodes as Active Electrocatalyst for Hydrogen Evolution Reaction

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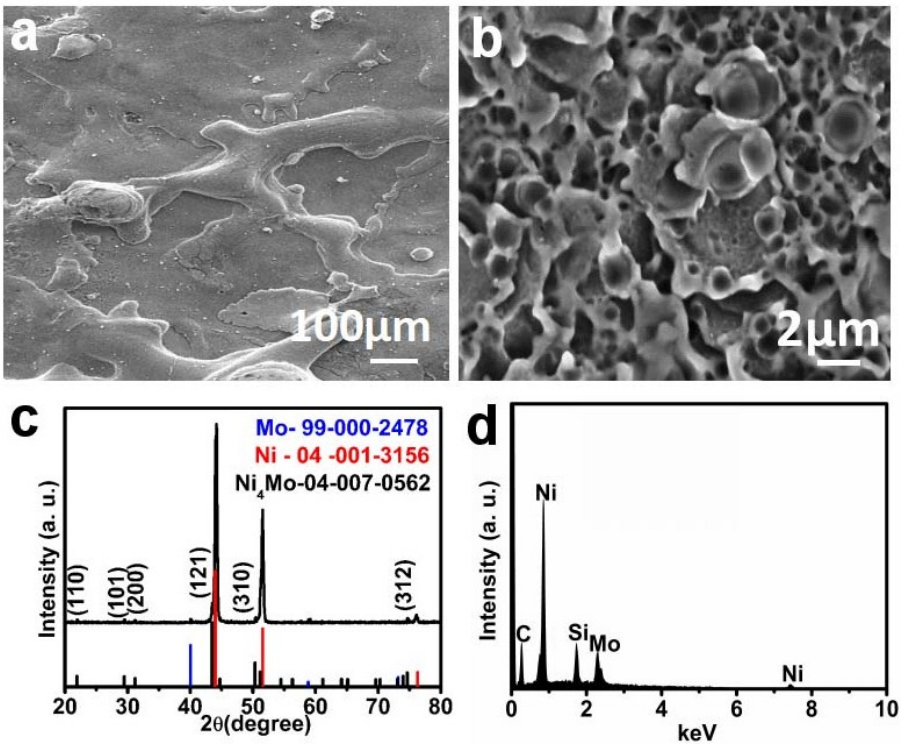

Fig. S1 (a) Low- and (b) high-magnification SEM images of Ni@Ni-Mo.

(c) Surface XRD pattern and (d) EDX spectrum.

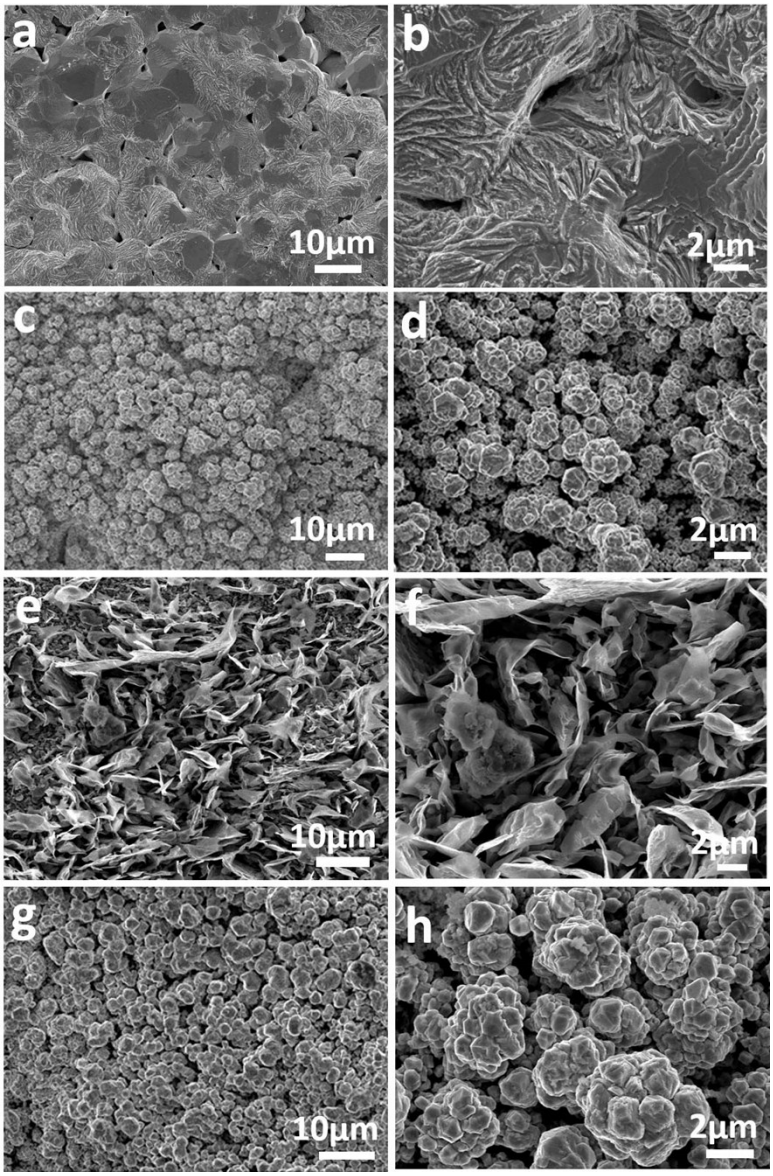

Fig. S2 SEM images of the samples prepared at (a,b) 500°C, (c,d) 600°C, (e,f) 700°C and (g,h) 800°C.

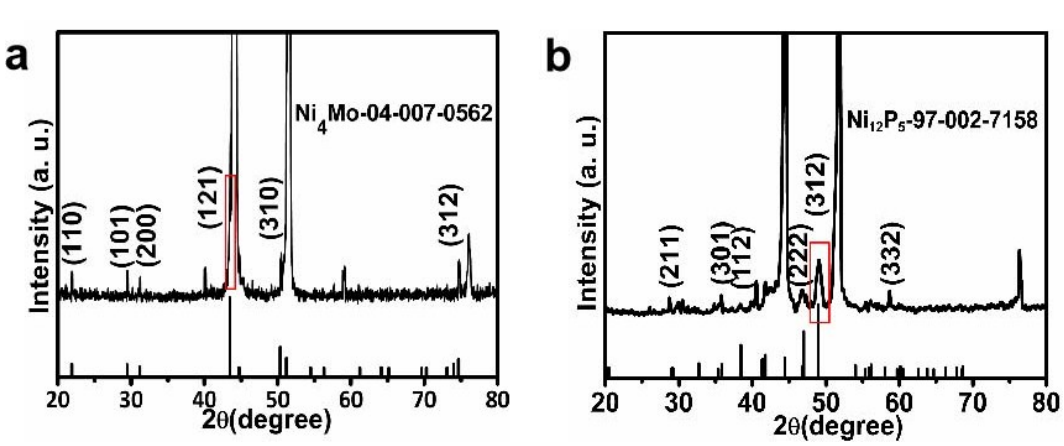

Fig. S3 XRD patterns of (a) Ni_4Mo and (b) $Ni_{12}P_5$.

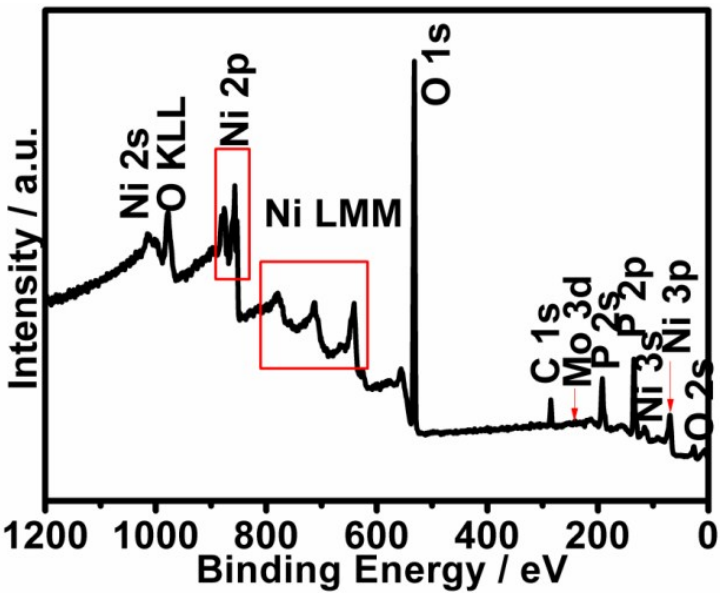

Fig. S4 XPS survey of Ni-Mo-P surface.

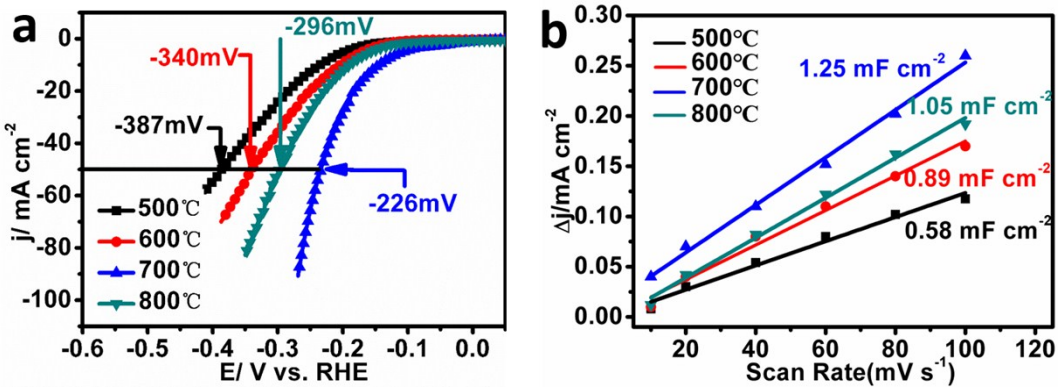

Fig. S5 (a) Polarization curves of the Ni-Mo-P electrodes synthesized at different phosphorization temperature in 1.0 M KOH solution with a scan rate of 10 mV s^{-1}. (b) The capacitive current densities at 0.075 V as a function of scan rate for Ni-Mo-P synthesized at different temperature.

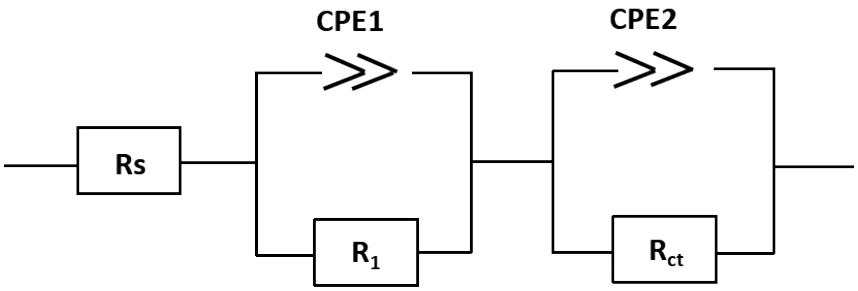

Fig. S6 The equivalent circuit model used to fit the Nyquist plots.

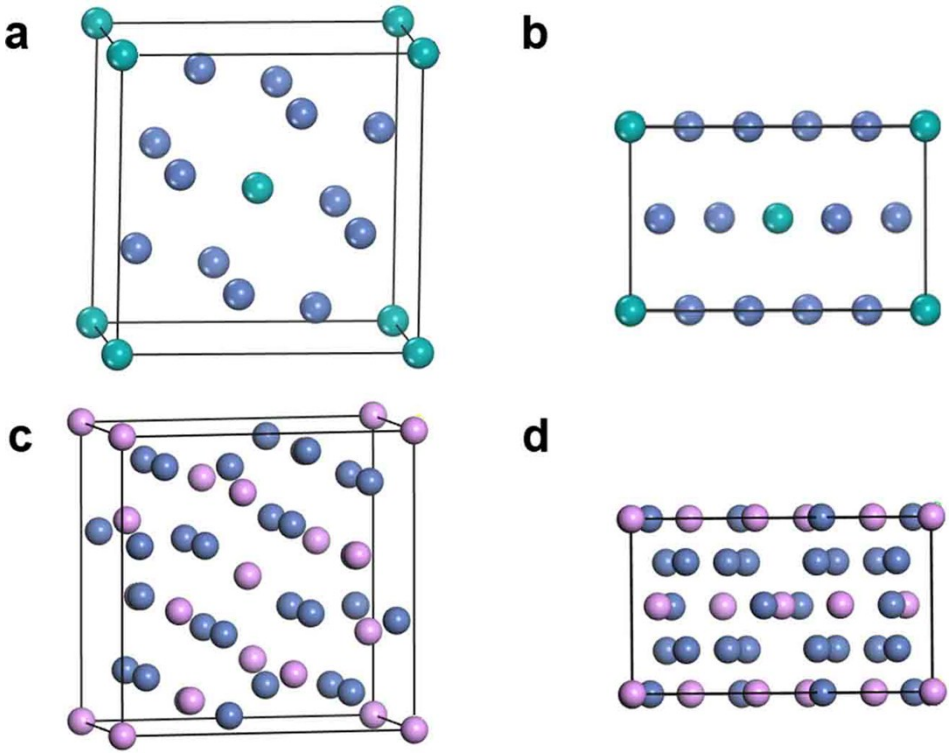

Fig. S7 (a) Side and (b) top views of the optimized structure of Ni_4Mo (a = b=5.725 Å, c = 3.559 Å). (c) Side and (d) top views of the optimized structure of $Ni_{12}P_5$ (a = b = 8.629 Å, c = 5.036 Å). Ni atoms: blue, Mo atoms: tawny brown, P atoms: purple.

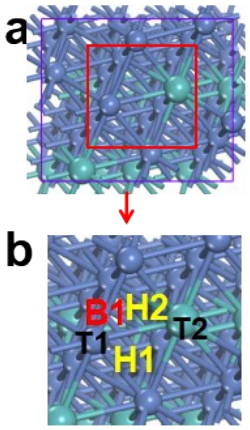

Table S1 Adsorption Energy on $Ni_4Mo(101)$ facet

position	adsorption energy (eV)	d (Ni-H) (Å)	d (Mo- H) (Å)
T1	-0.761		1.695
T2	-0.426	1.605	
B1	-0.753	1.613	1.714
H1	-0.391	1.513 1.764	1.734

Fig. S8 (a) top-down view of the Ni_4Mo (101) and (b) possible adsorption sites of corresponding surface. Table S1. Adsorption energies and structure parameters for the hydrogen adsorption onto 5 Layer of Ni_4Mo (101). The preferable adsorption sites were highlighted with red rectangle. All the following discussions have the similar highlight.

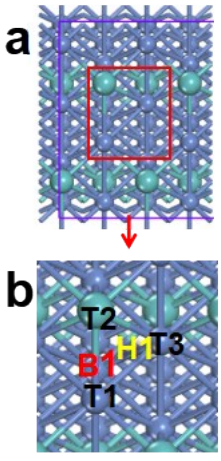

Table S2 Adsorption Energy on $Ni_4Mo(110)$ facet

position	adsorption energy (eV)	d (Ni-H) (Å)	d (Mo- H) (Å)
T1	-0.542	1.641	
T2	-0.239	1.751	
T3	-0.506	1.953	
B1	-0.552	1.607	1.940
H1	-0.459	1.659	1.983

Fig. S9 (a) top-down view of the Ni_4Mo (110) and (b) possible adsorption sites of corresponding surface. Table S2. Adsorption energies and structure parameters for the hydrogen adsorption onto 5 Layer of Ni_4Mo (110).

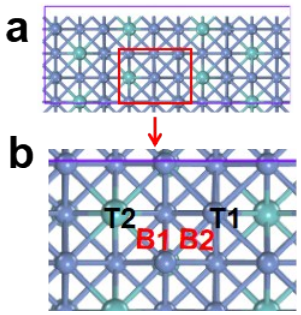

Table S3 Adsorption Energy on Ni_4Mo(310) facet

position	adsorption energy (eV)	d (Ni-H) (Å)	d (Mo- H) (Å)
T1	-0.465	1.698 1.593	
T2	-0.961	1.727	
B1	-0.747	1.563	1.863
B2	-0.478	1.681 1.598	

Fig. S10 (a) top-down view of the Ni_4Mo (310) and (b) possible adsorption sites of corresponding surface. Table S3. Adsorption energies and structure parameters for the hydrogen adsorption onto 5 Layer of Ni_4Mo (310).

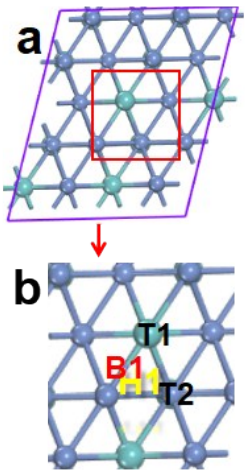

Table S4 Adsorption Energy on Ni_4Mo(312) facet

position	adsorption energy (eV)	d (Ni-H) (Å)	d (Mo- H) (Å)
T1	-0.550	1.690	1.838
T2	-0.714	1.646	1.883
B1	-0.713	1.661	1.873
H1	-0.886	1.668	1.873

Fig. S11 (a) top-down view of the Ni_4Mo (312) and (b) possible adsorption sites of corresponding surface. Table S4. Adsorption energies and structure parameters for the hydrogen adsorption onto 5 Layer of Ni_4Mo (312).

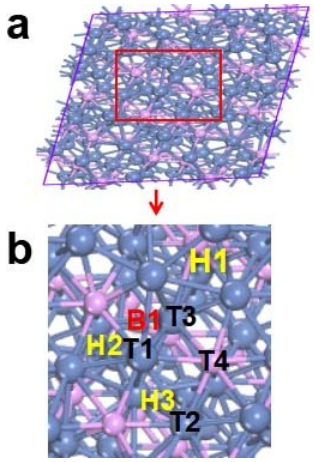

Table S5 Adsorption Energy on $Ni_{12}P_5$(312) facet

position	adsorption energy (eV)	d (Ni-H) (Å)	d (P- H) (Å)
T1	-0.659	1.618 1.665	
T2	-0.423	1.628 1.628	
T3	-0.581	1.620 1.663	
T4	-0.763	1.838	1.621
B1	-0.643	1.610 1.664	
H1	-1.035	1.624 1.443 1.652	
H2	-0.649	1.648 1.613	1.817
H3	-0.595	1.645 1.687	1.698

Fig. S12 (a) top-down view of the $Ni_{12}P_5$ (312) and (b) possible adsorption sites of corresponding surface. Table S5. Adsorption energies and structure parameters for the hydrogen adsorption onto 5 Layer of $Ni_{12}P_5$ (312).

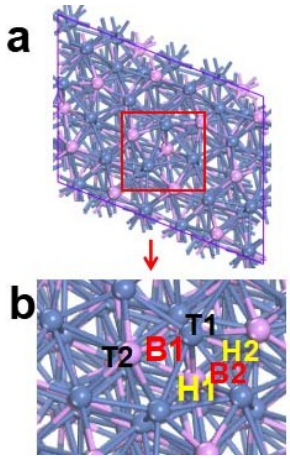

Table S6 Adsorption Energy on $Ni_{12}P_5$(211) facet

position	adsorption energy (eV)	d (Ni-H) (Å)	d (P- H) (Å)
T1	0.555	1.504	
T2	-0.167		1.430
B1	-0.042	1.670	1.564
B2	-0.076	1.704 1.760	
H1	-0.136	1.685 1.691 1.751	
H2	0.049	1.647 1.652	1.811

Fig. S13 (a) top-down view of the $Ni_{12}P_5$ (211) and (b) possible adsorption sites of corresponding surface. Table S6. Adsorption energies and structure parameters for the hydrogen adsorption onto 5 Layer of $Ni_{12}P_5$ (211).

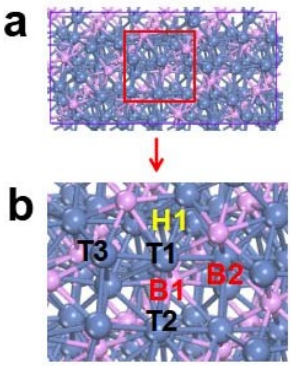

Table S7 Adsorption Energy on $Ni_{12}P_5$(301) facet

position	adsorption energy (eV)	d (Ni-H) (Å)	d (P- H) (Å)
T1	-0.426	1.618 1.649	
T2	-0.714	1.701 1.725 1.741	
T3	-0.537	1.658 1.797	
B1	-0.481	1.756 1.737	
B2	0.159	1.601	1.721
H1	-0.554	1.614 1.653	2.904

Fig. S14 (a) top-down view of the $Ni_{12}P_5$ (301) and (b) possible adsorption sites of corresponding surface. Table S7. Adsorption energies and structure parameters for the hydrogen adsorption onto 5 Layer of $Ni_{12}P_5$ (301).

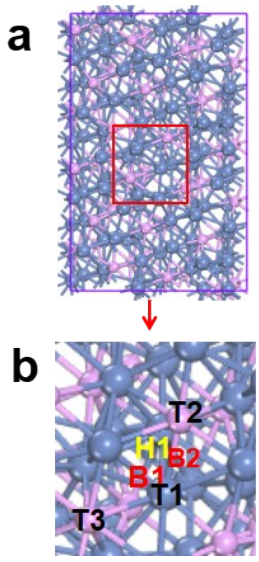

Table S8 Adsorption Energy on $Ni_{12}P_5$(332) facet

position	adsorption energy (eV)	d (Ni-H) (Å)	d (P- H) (Å)
T1	0.567	1.694 1.586	
T2	0.369	1.643	1.635
T3	-0.244		1.581
B1	0.694	1.590 1.735	
B2	0.698	1.578 1.770	
H1	0.355	1.481 3.476	2.710

Fig. S15 (a) top-down view of the $Ni_{12}P_5$ (332) and (b) possible adsorption sites of corresponding surface. Table S8. Adsorption energies and structure parameters for the hydrogen adsorption onto 5 Layer of $Ni_{12}P_5$ (332).

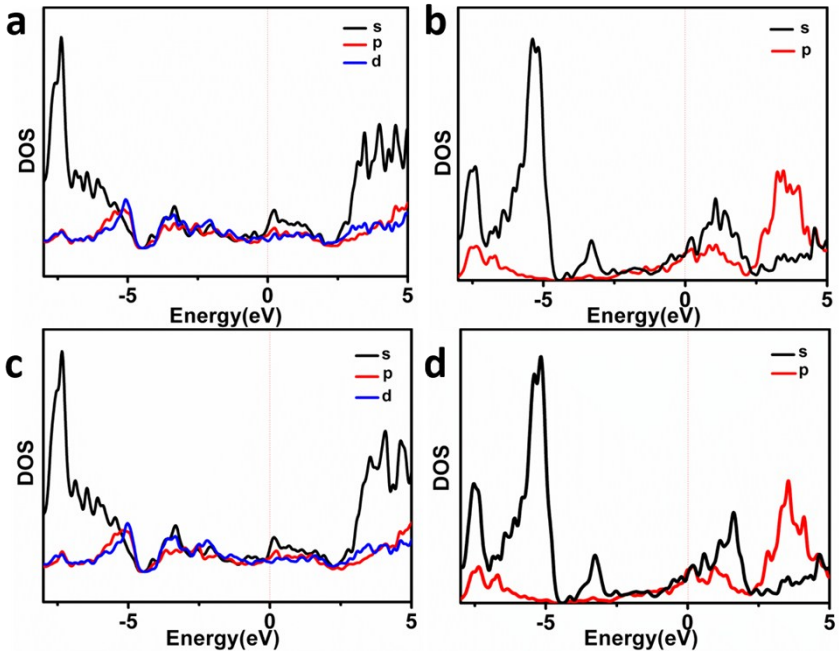

Fig. S16 Projected density of states (PDOS) for (a) Ni and (b) P in $Ni_{12}P_5$, and (c) Ni and (d) P in Mo-doped $Ni_{12}P_5$.

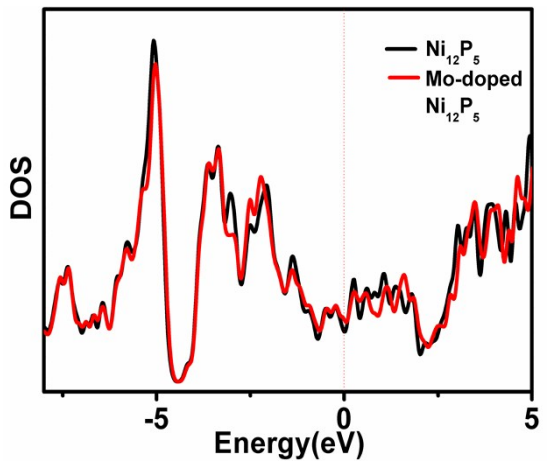

Fig. S17 DOS of d band of $Ni_{12}P_5$ and Mo-doped $Ni_{12}P_5$.