Electronic Supporting Information

Semimetallic MoP_2: An active and stable hydrogen evolution electrocatalyst over the whole pH range

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Experimental Section

Materials: Sulfuric acid (H_2SO_4) and oxalic acid ($H_2C_2O_4$) were purchased from Beijing Chemical Works. Sodium hypophosphite (NaH_2PO_2), potassium phosphate (KH_2PO_4, K_2HPO_4), and potassium hydroxide (KOH) ethanol were purchased from Aladdin Reagent. Sodium fluoride (NaF) and sodium sulfate (Na_2SO_4) were purchased from Xinglong Chemical Corp. Nafion (5 wt%) and Pt/C (20 wt%) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. De-ionized water (Mini-Q) was employed as solvent.

Preparation of MoO_x NPs/Mo and MoP_2 NPs/Mo: To prepare MoO_x nanoparticles on Mo plate (MoO_x NPs/Mo), Mo plate (1 cm×2 cm) was cleaned by ultrasonication with ethanol and water for several times. Electrochemical anodic treatment was carried out in a 100 mL H_2O solution containing 1 mmol Na_2SO_4, 1 mmol NaF and 15 mmol $H_2C_2O_4$. Anodization was conducted at a constant current density of 25 mA cm^{-2} for 20 min. To obtain MoP_2 NPs/Mo, the as-prepared MoO_x NPs/Mo and NaH_2PO_2 were put into a porcelain boat (Mo to P is 1: 20) and calcined at 750 °C under N_2 atmosphere for 2 h. The loading of MoP_2 NPs on Mo was about ~0.18 mg cm^{-2}. MoP_2/Mo was also synthesized by first oxidizing bare Mo plate in air at 300 °C for 2 h, followed by phosphidation under similar experimental conditions and used as a control catalyst.

Characterizations: X-ray diffraction (XRD) patterns were collected on a Rigaku X-ray diffractometer equipped with a Cu K_α radiation source. The morphology and structure were characterized by scanning electron microscopy (SEM, XL30 ESEM FEG) and transmission electron microscopy (TEM, HITACHI H-8100). X-ray photoelectron spectroscopy (XPS) was obtained on an ESCALABMK II X-ray photoelectron spectrometer.

Electrochemical characterization: The electrochemical tests for were performed on a CHI 660E electrochemical workstation using a three-electrode cell configuration. The as-prepared electrodes, was assembled as the working electrode along with graphite rod as auxiliary electrode and Ag/AgCl (3.0 M KCl) as reference electrode. The polarization curves were measured in 0.5 M H_2SO_4 (pH = 0), 1.0 M phosphate buffered solution (PBS, pH = 7) and 1.0 M KOH (pH = 14) at the scan rate of 2 mV s^{-1} at room temperature (~25 ℃), respectively. All measured potentials vs. Ag/AgCl were converted to a reversible hydrogen electrode (RHE) scale. Thus, in 0.5 M H_2SO_4, $E_{RHE} = E_{Ag/AgCl} + 0.197$ V, whereas in 1.0 M PBS, $E_{RHE} = E_{Ag/AgCl} + 0.610$ V, and in 1.0 M M KOH, $E_{RHE} = E_{Ag/AgCl} + 1.023$ V. Electrochemical impedance spectroscopy

(EIS) were carried out over the frequency range from 0.01 kHz to 100 Hz with an amplitude of 5 mV. All measured polarization curves were corrected for background current and iR loss.

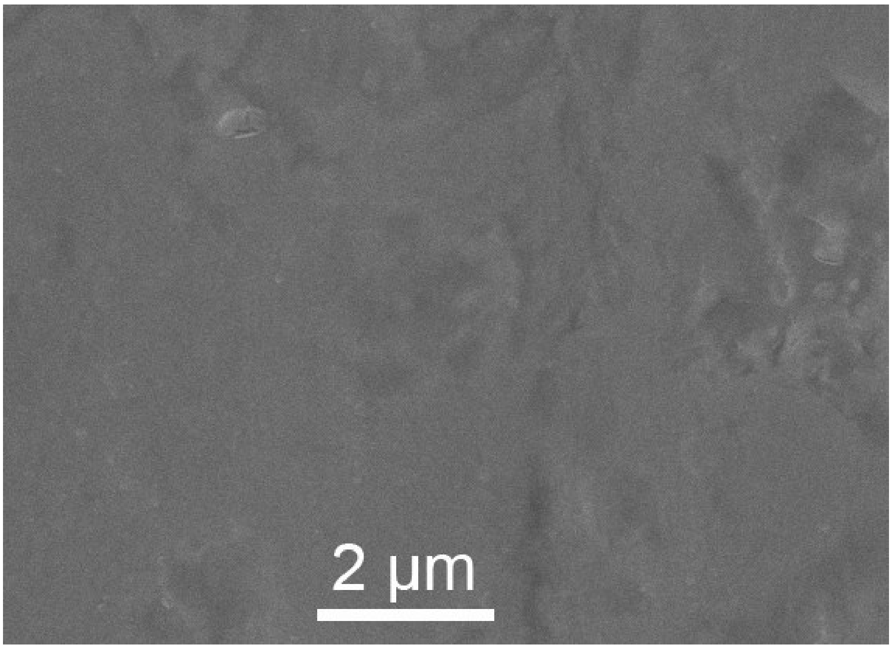

Fig. S1 SEM image of bare Mo plate.

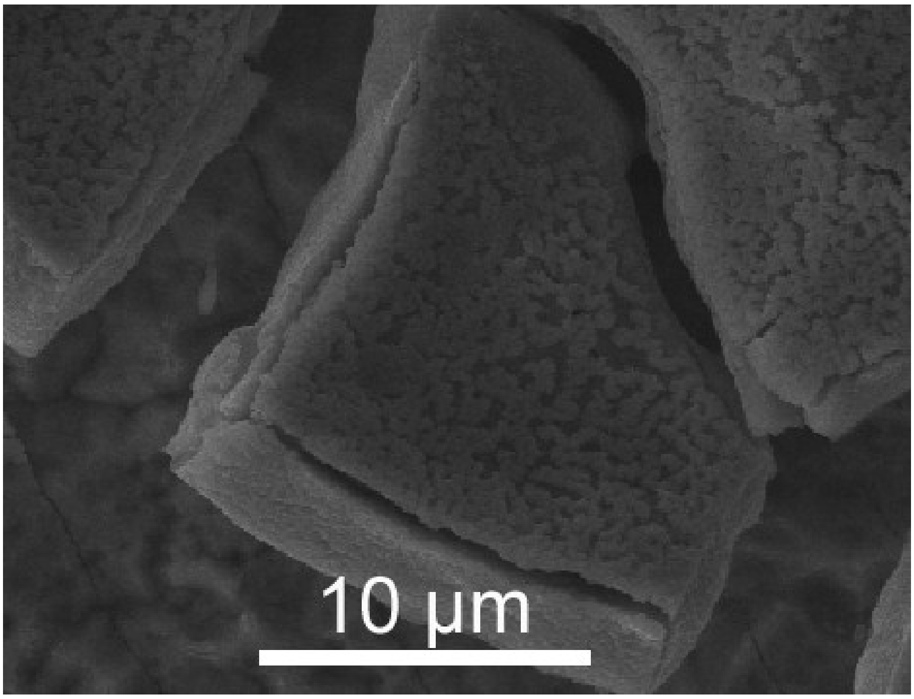

Fig. S2 SEM image of MoP_2 NPs/Mo.

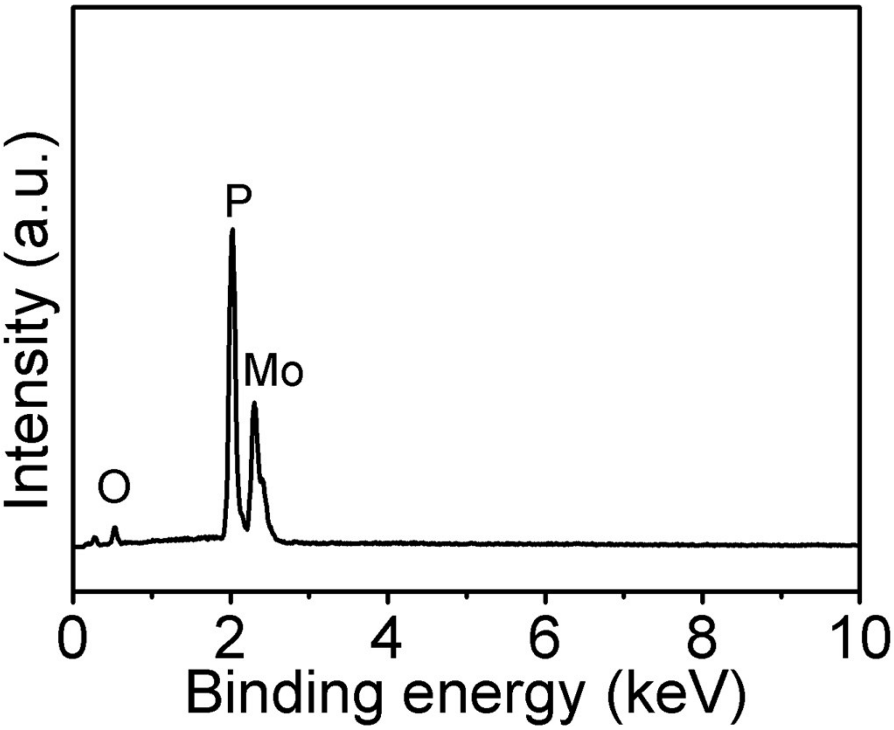

Fig. S3. EDX spectrum of MoP_2 NPs/Mo.

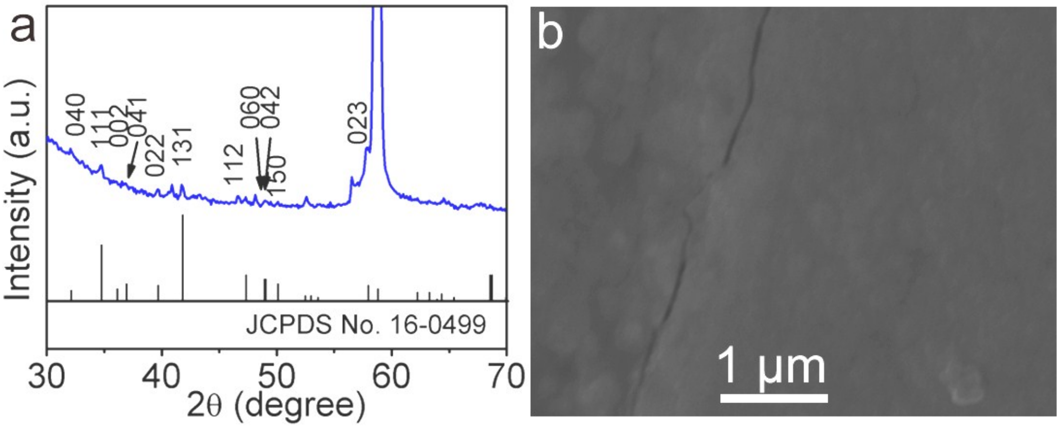

Fig. S4. (a) XRD pattern and (b) SEM image of the MoP_2/Mo.

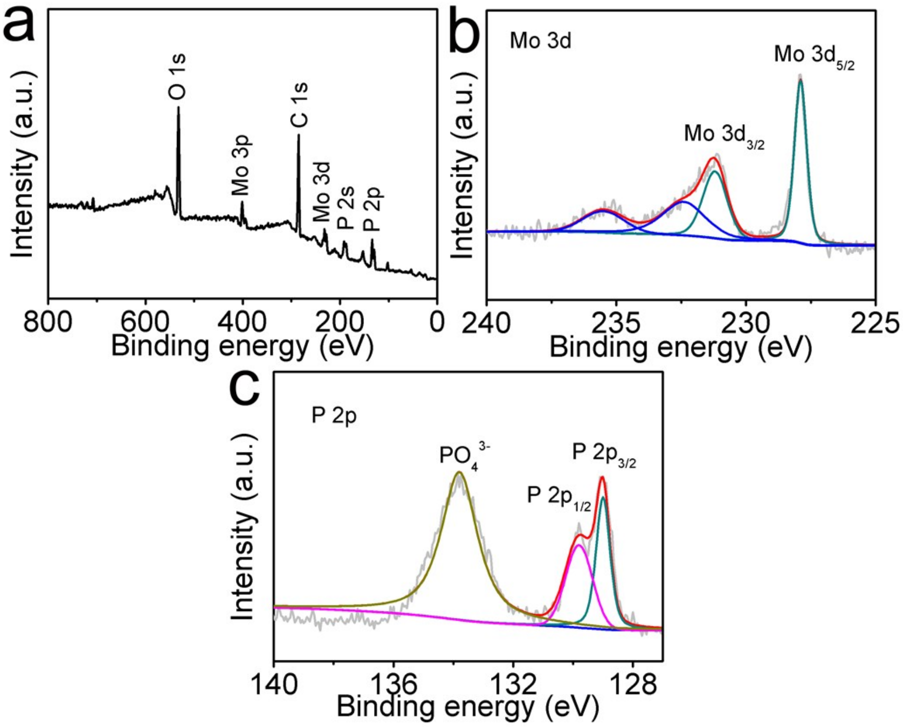

Fig. S5. (a) XPS survey spectrum of MoP_2 NPs/Mo. XPS spectrum of (b) Mo 3d and (c) P 2p regions for MoP_2 NPs/Mo.

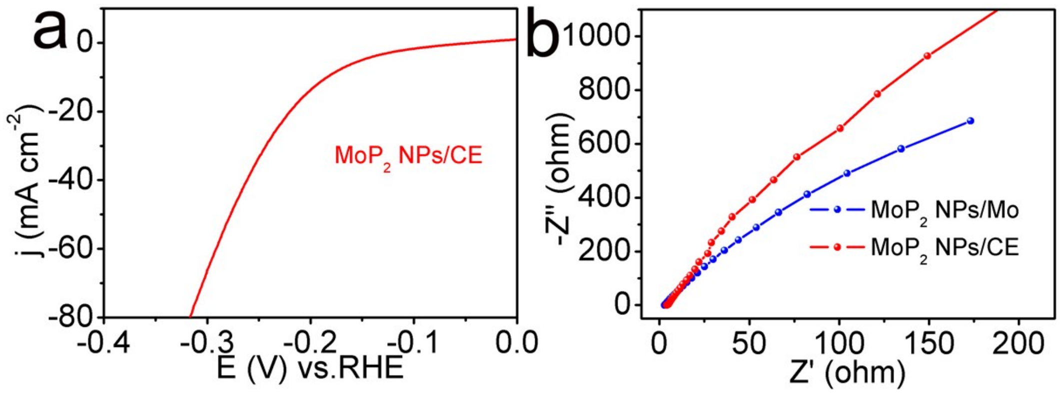

Fig. S6 (a) Polarization curves of MoP_2 NPs modified carbon electrode. (b) Nyquist plots of MoP_2 NPs/Mo and MoP_2 NPs modified carbon electrode recorded at 0.28 V vs. RHE in 0.5 M H_2SO_4.

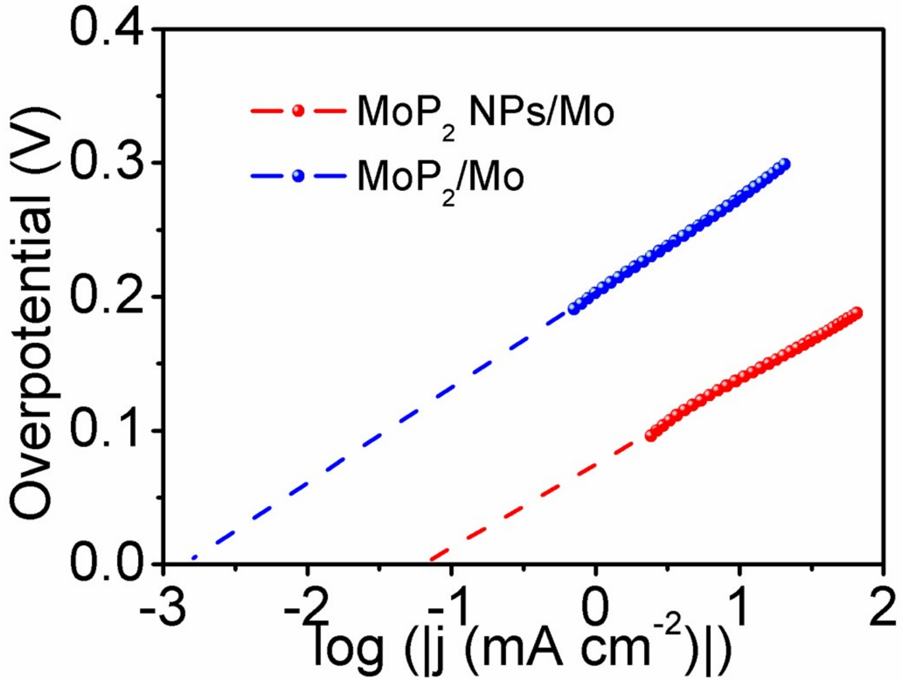

Fig. S7. Calculation of exchange current density of MoP_2 NPs/Mo and MoP_2/Mo by applying extrapolation method to the Tafel plot.

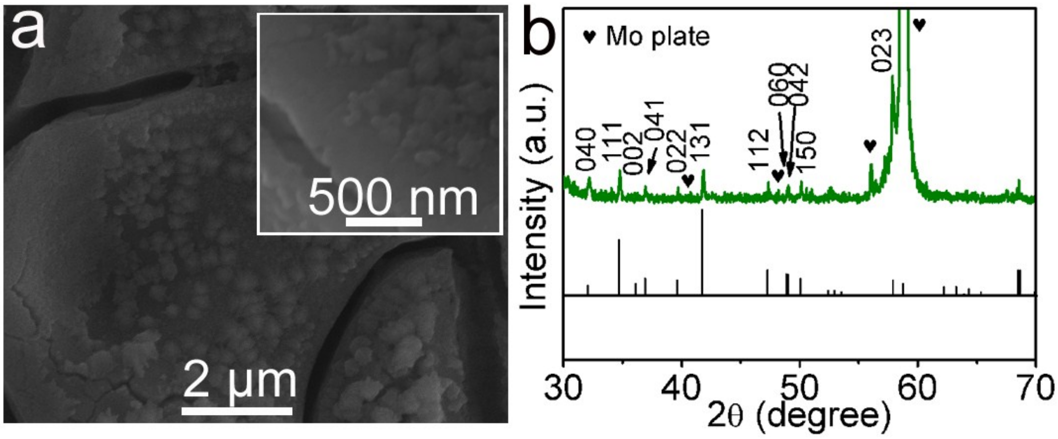

Fig. S8 (a) SEM images and (b) XRD pattern of MoP_2 NPs/Mo after the durability measurements**.**

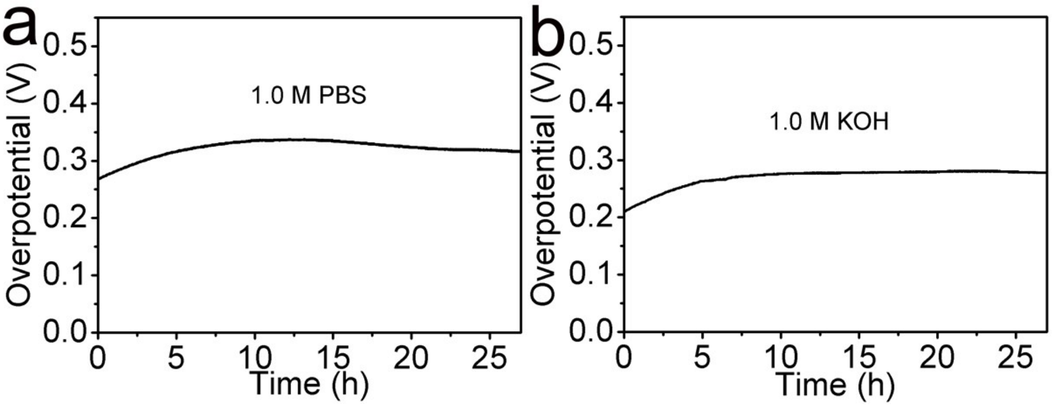

Fig. S9 Chronopotentiometric curves of MoP_2 NPs/Mo at a constant current density of 20 mA cm^{-2} (without iR correction) in (a) 1.0 M PBS and (b) 1.0 M KOH.

The absorption spectrum in the wavelength range of 200–700 nm was measured to study the band structure of MoP_2 NPs (**Fig. S10**). The band-gap value of MoP_2 nanoparticles is 2.8 eV according to the following equation:[1]

$$(\alpha h v)^{1/n} = A(hv - E_g) \qquad (1)$$

Where A is proportionality constant, h is Planck's constant, v is the frequency of vibration and α is an absorption coefficient. The value of n depends on the type of optical transition of the semiconductor ($n = 2$ for an indirect transition).

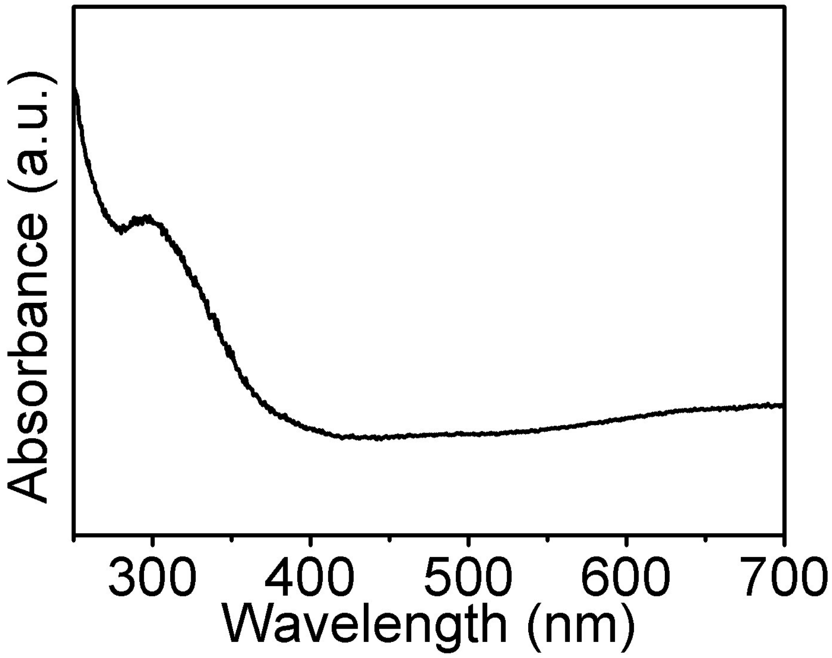

Fig. S10 UV-vis absorption spectrum of the MoP_2 nanoparticles.

Table S1 Comparison of HER performance in acidic media for MoP_2 NPs/Mo with other Mo-based HER electrocatalysts.

Catalyst	**Onset *η* (mV)**	**Current density (*j*, mA cm^{-2})**	***η* at the corresponding *j* (mV)**	**Ref.**
MoP_2 NPs/Mo	50	10	143	This work
		100	199	
MoP	100	10	246	2
MoP/CF	100	10	200	3
MoP nanoparticle	50	30	180	4
MoP interconnected network nanoparticles	40	10	125	5
amorphous MoP	-	10	90	6
3D MoP	-	10	105	7
$MoS_{2(1-x)}P_x$		10	150	8
MoS_2/Mo foil	~150	18.6	300	9
MoS_2/Mo	-	10	168	10
amorphous MoS_x	-	10	200	11
MoS_x/graphene/CC	-	100	~225	12
PPy/MoS_x/GCE	60	50	60	13
MoN	-	70	300	14
Mo_2C@NC	-	10	124	15

Table S2 Comparison of HER performance in neutral media for MoP_2 NPs/Mo with other Pt-free HER electrocatalyst.

Catalyst	**Current density (*j*, mA cm^{-2})**	**Overpotential at the corresponding *j* (mV)**	**Ref.**
MoP_2 NPs/Mo	2	152	This work
	10	211	
MoP/CF	1	~300	3
MoS_2/Mo	2	172	10
WP NAs/CC	2	95	16
CoP/CC	2	65	17
Co-NRCNTs	2	380	18
FeP/Ti	10	102	19
bulk Mo_2C	1	200	20
bulk Mo_2B	1	250	20
H_2-CoCat/FTO	2	385	22
Co-S/FTO	2	83	22
$CuMoS_4$ crystals	2	210	23

Table S3 Comparison of HER performance in basic media for MoP_2 NPs/Mo with other Pt-free HER electrocatalyst.

Catalyst	**Current density (*j*, mA cm^{-2})**	**Overpotential at the corresponding *j* (mV)**	**Ref.**
MoP_2 NPs/Mo	2	119	This work
	10	194	
MoS_2/Mo	2	172	10
WP NAs/CC	10	150	16
CoP/CC	10	209	17
Co-NRCNTs	10	370	18
bulk Mo_2B	1	250	20
Ni	10	400	20
Co-S/FTO	1	480	22
Ni_2P nanoparticles	20	250	24
Ni wire	10	350	25
Ni-Mo alloy/Ti foil	10	80	25

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