Supporting Information

Porous superstructures constructed from ultrafine FeP nanoparticles for highly active and exceptionally stable hydrogen evolution reaction

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Experimental details

Materials

Iron (III) chloride hexahydrate ($FeCl_3$•$6H_2O$, ≥98.0% purified lumps), sodium dodecyl sulfate (SDS, ≥99.0%), Nafion solution (~5 wt%) and Pt/C (20 wt% Pt on Vulcan XC-72R) were purchased from Sigma-Aldrich. Sodium hypophosphite monohydrate (NaH_2PO_2•H_2O), Anhydrous ethanol and sulfuric acid (H_2SO_4, ~98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals are of analytical purity and used without further purification. Water (18.2 MΩ/cm) was purified by a Millipore Direct-Q system. Hydrogen was obtained from gas generator (SPH-300).

Synthesis of urchin-like FeOOH microspheres

Urchin-like FeOOH microspheres were prepared as follows: 2.025 g $FeCl_3$•$6H_2O$ was added to a

200 ml ethanol/water (1/1, v/v) solution containing 0.5 wt% SDS. The mixture was stirred for 1 h at room temperature and then heated to 70 ˚C for 3 h. After that, the yellow product was filtered and washed by using deionized water and anhydrous ethanol for several times and finally vacuum-dried at 60 ˚C.

Synthesis of FeP SS

For the preparation of FeP SS, a desired amount of as-prepared urchin-like FeOOH microspheres powders and 1.0 g $NaH_2PO_2•H_2O$ were placed at two separate positions in one closed porcelain crucible with $NaH_2PO_2•H_2O$ at the upstream side of the furnace. After the tube was purged with Ar carrier gas, the sample was heated at rate of 3 ˚C/min to 300 ˚C for 3 h and then cooled down naturally. The collected product was ultrasonically dispersed into a 1 M HCl solution to remove unreacted FeOOH microspheres. A large amount of black powders were finally obtained by centrifugation.

Synthesis of FeOOH NR and FeOOH NS

For preparation of FeOOH NR, 2.025 g $FeCl_3•6H_2O$ was added to a 200 ml ethanol/water (1/1, v/v). The solution was stirred for 1 h at room temperature and then heated to 70 ˚C for 3 h. After that, the yellow products were filtered and washed by deionized water and anhydrous ethanol for several times and finally vacuum-dried at 60 ˚C. For preparation of FeOOH NS, 2.025 g $FeCl_3•6H_2O$ was added to a 200 ml H_2O. The solution was stirred for 1 h at room temperature and then heated to 70 ˚C for 3 h. After that, the yellow products were filtered and washed by deionized water and anhydrous ethanol for several times and finally vacuum-dried at 60 ˚C.

Synthesis of FeP NR and FeP NS

For the preparation of FeP NR and FeP NS, a desired amount of as-prepared either FeOOH NR or FeOOH NS powders and 1.0 g $NaH_2PO_2•H_2O$ were placed at two separate positions in one closed porcelain crucible with $NaH_2PO_2•H_2O$ at the upstream side of the furnace. After the tube was purged with Ar carrier gas, the sample was heated at rate of 3 ˚C/min to 300 ˚C for 3 h and then cooled down naturally. The collected product was ultrasonically dispersed into a 1 M HCl solution to remove unreacted FeOOH NR or FeOOH NS. A large amount of black powders were finally obtained by centrifugation.

Characterization

Materials morphology and structure were examined by field-emission scanning electron

microscopy (FE-SEM, Hitachi S4800), transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin), and X-ray diffraction (XRD, Bruke D8). Surface area and pore size were analyzed using a micromeritics surface area measurement analyzer (ASAP 2020). Electrochemical measurements were performed on a Autolab PGSTAT302N. X-ray photoelectron spectroscopy (XPS) was conducted on a Kα X-ray photoelectron spectroscope (Thermo Fisher, E. Grinstead, UK) with an Al Kα X-ray radiation (1486.6 eV photons) for excitation.

Electrochemical measurements

All electrochemical measurements were carried out on a three-electrode system at room temperature using GC-RDE with catalyst loaded glass carbon electrode (GCE) as working electrode, a graphite rod and Ag/AgCl (3M KCl solution, Alfa Aesar) as counter electrode and reference electrode, respectively. For a typical preparation of catalyst ink for working electrode, 5 mg catalyst powder and 1 mg carbon black were dispersed in 0.95 ml ethanol and 50 µl 5 wt% Nafion solution to form a homogeneous dispersion after ultrasonication for 30 min. In general, 8 µl catalyst ink (containing 40 µg catalyst) was loaded onto a GC-RDE of 3 mm in diameter (~0.566 mg/cm^2) for polarization and CP test. During all of the electrochemical measurements, high-purity H_2 was purged into the electrolyte to saturate it. Polarization measurements were conducted in 0.5 M H_2SO_4 with a scan rate of 5 mV/s. As a comparison, commercial Pt/C was measured under the same conditions at the rotating rate of 1600 rpm. All the potentials reported in this work were done by *iR* correction, which were given vs. the reversible hydrogen electrode (RHE) according to $E_{vs.RHE} = E_{vs.Ag/AgCl} + E^{\theta}_{Ag/AgCl} + 0.059 \times pH - i \times R$. The stability of FeP SS was examined by a 24 h chronopotentiometry (CP) test at 10 mA/cm^2. Electrochemical impedance spectra (EIS) were performed at -10, -20, -30, -50, -70, -90, -110, -130, -150 mV in the range of 100 KHz to 0.1 Hz, respectively.

Supplementary Figures:

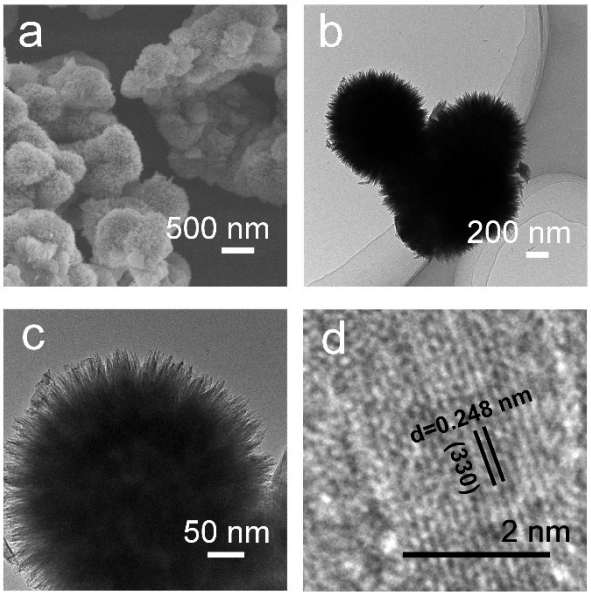

Figure S1. (a) SEM and (b-d) TEM images of urchin-like FeOOH mircospheres.

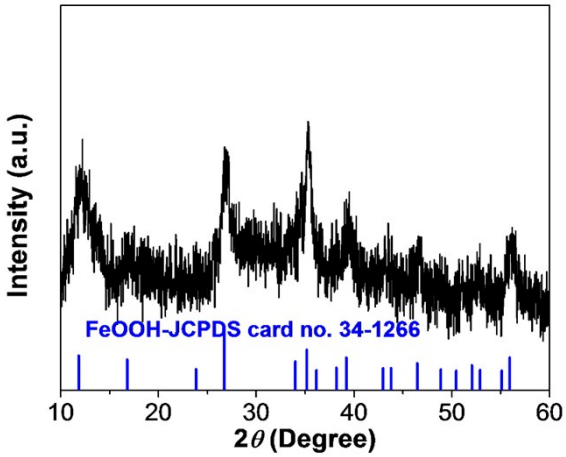

Figure S2. XRD spectrum of urchin-like FeOOH mircospheres.

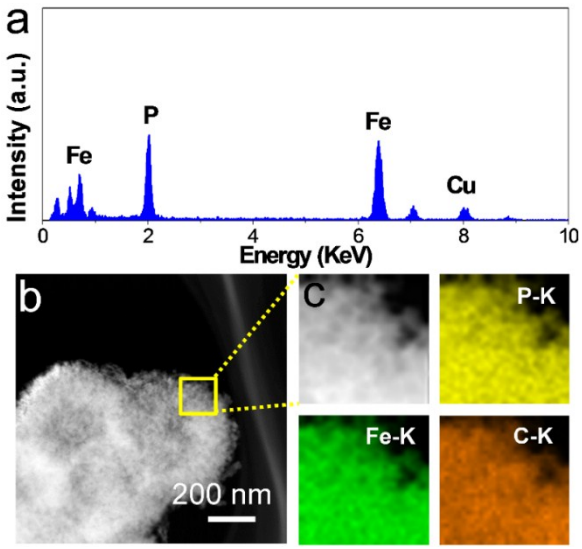

Figure S3. (a) EDX, (b) STEM image, and (c) Element mapping of FeP SS.

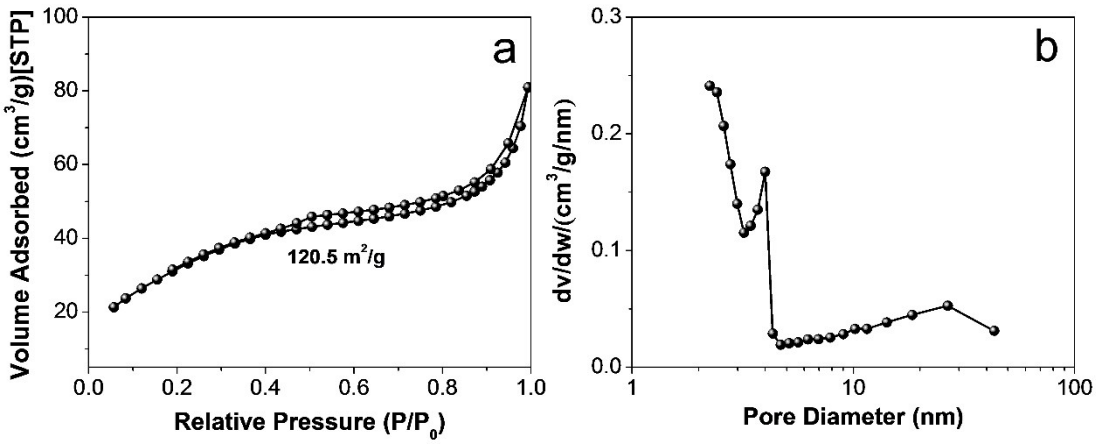

Figure S4. (a) Nitrogen adsorption isotherm and (b) Pore size distribution of urchin-like FeOOH mircospheres.

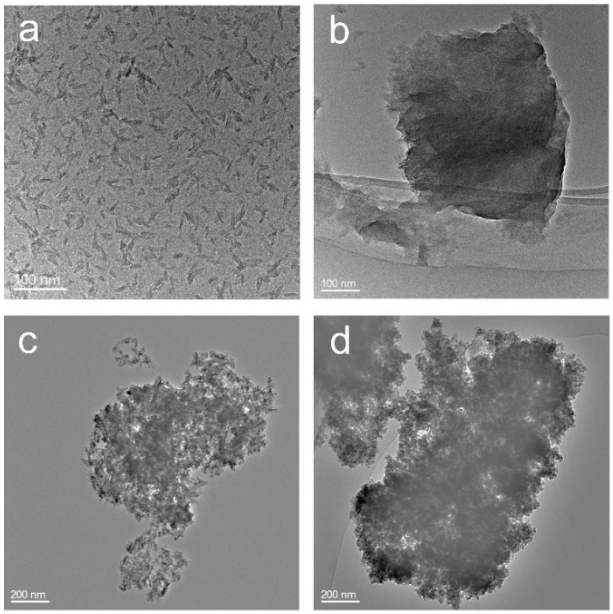

Figure S5. TEM images of (a) FeOOH NR and (b) FeOOH NS precursors and corresponding FeP NR (c) and FeP NS (d), respectively.

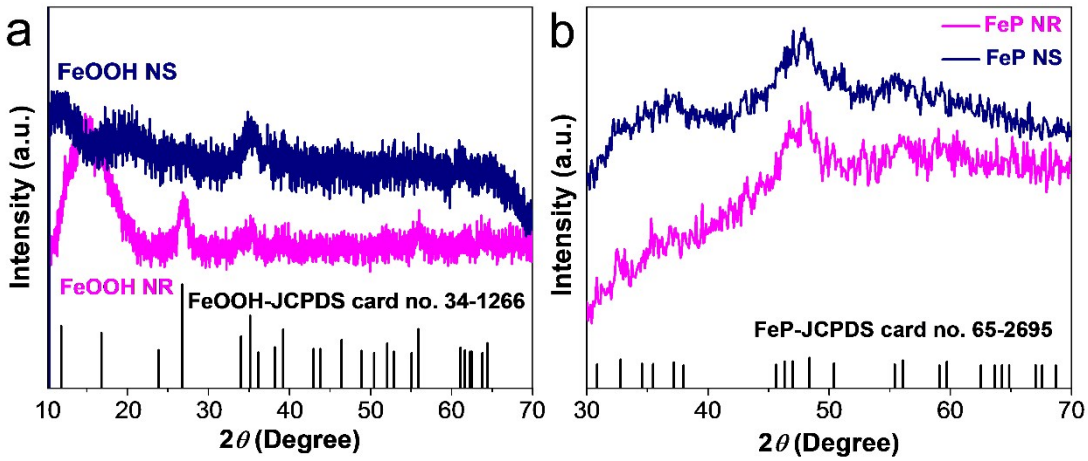

Figure S6. (a) XRD plots of prepared FeOOH NR and FeOOH NS. (b) XRD plots of FeP NR and FeP NS.

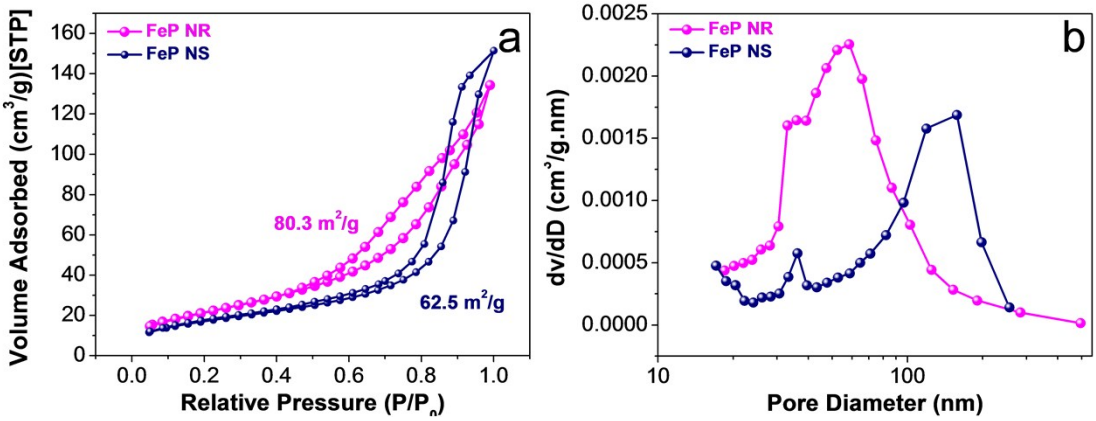

Figure S7. (a) Nitrogen adsorption isotherm and (b) Pore size distribution of FeP NR and FeP NS. The BET surface areas of FeP NR and FeP NS are 80.3 m^2/g and 62.5 m^2/g, respectively. In addition, the main pores in the cases of FeP NR and FeP NS are macropores around 80-100 nm.

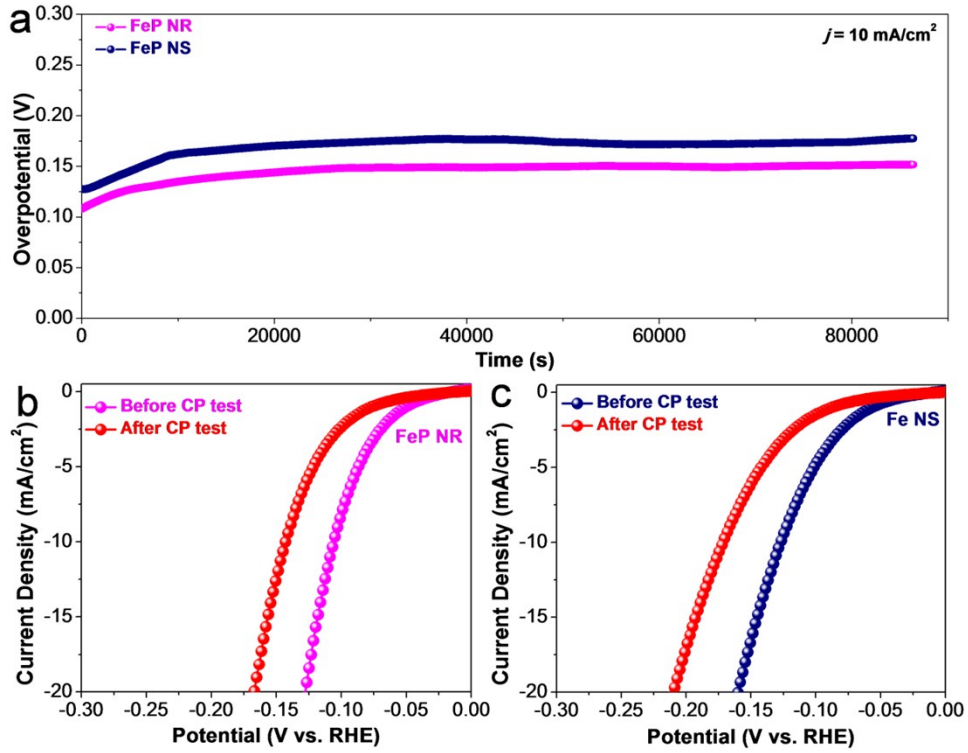

Figure S8. (a) CP of FeP NR and FeP NS. LSV plots of (b) FeP NR and (c) FeP NS before and after CP test for 24 h.

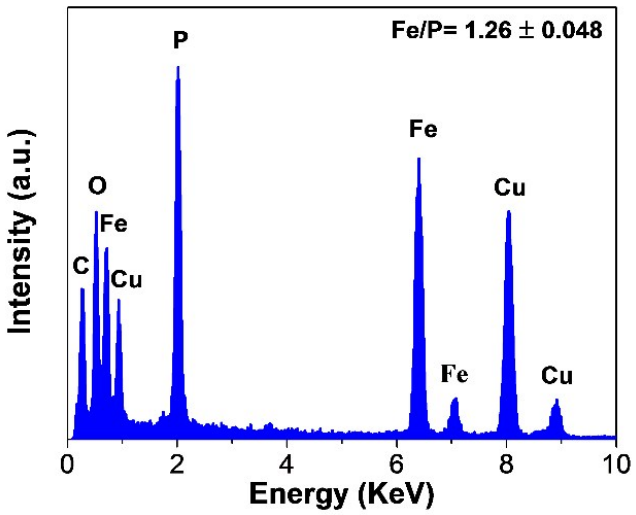

Figure S9. EDX of FeP SS after CP test for 24 h.

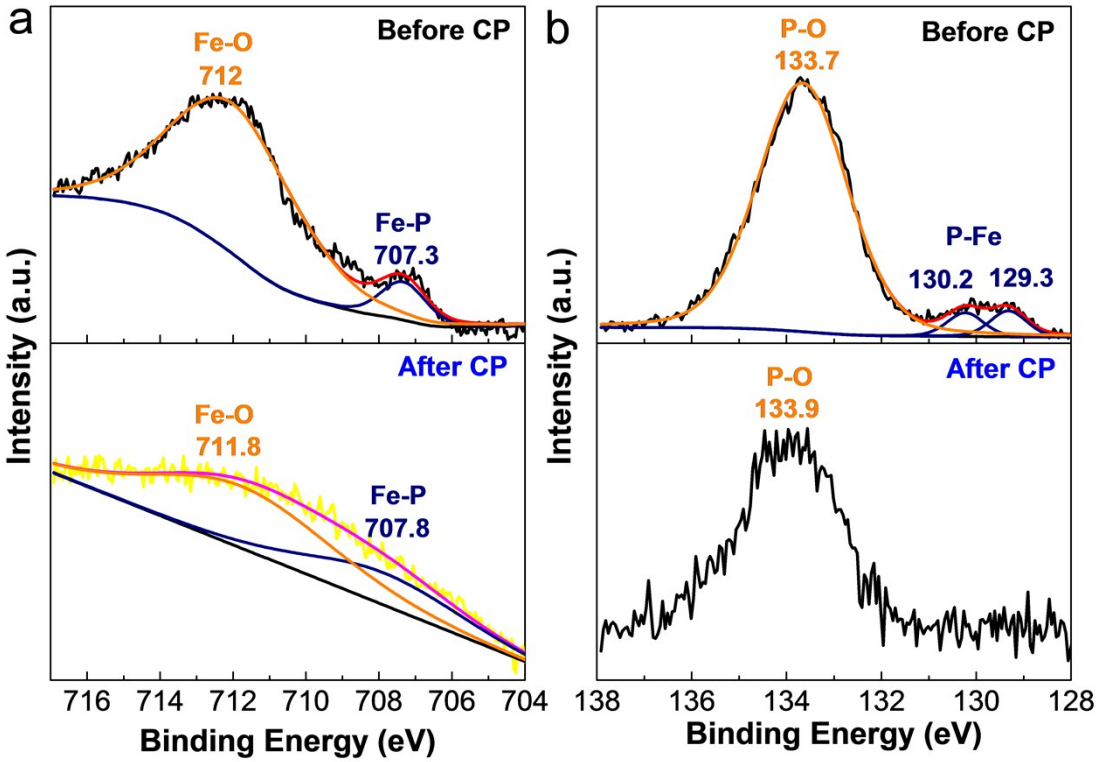

Figure S10. (a) Fe $2p_{3/2}$ and (b) P 2p XPS of FeP NS before and after CP tests, respectively.

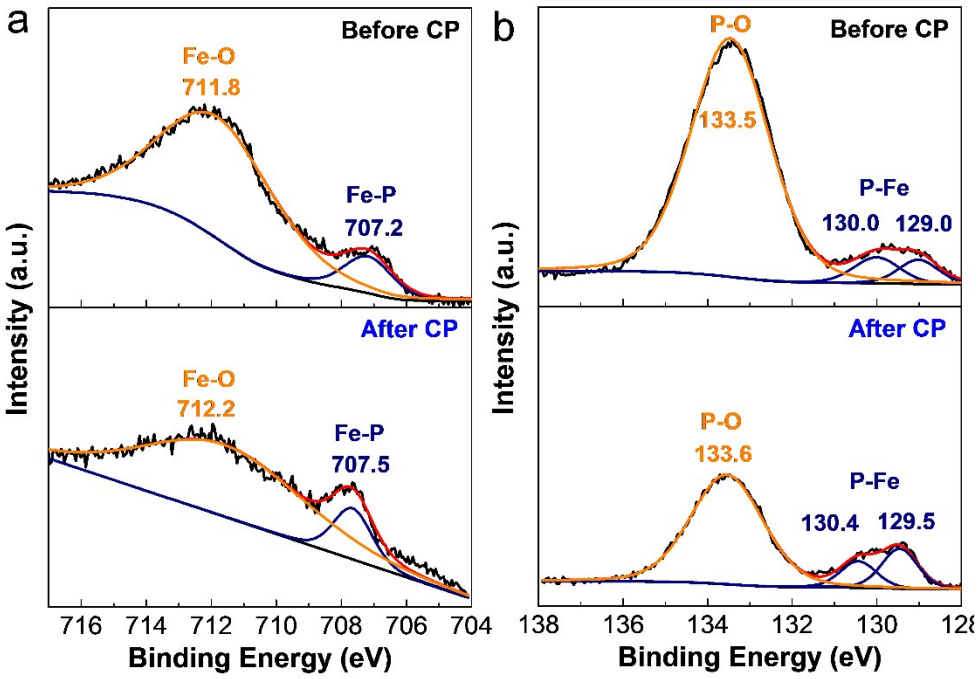

Figure S11. (a) Fe $2p_{3/2}$ and (b) P 2p XPS of FeP NR before and after CP tests, respectively.

Table S1. Summary of HER performance of our FeP SS and previously reported catalysts as listed in Figure 5.

Catalyst	Loading (mg/cm^2)	Electrolyte	η_{10} (mV)	Ref.
FeP SS	**0.142**	0.5 M H_2SO_4	**102**	**This work**
	0.556	0.5 M H_2SO_4	**66**	
FeP nanosheets	0.28	0.5 M H_2SO_4	240	[37]
MoP	0.86	0.5 M H_2SO_4	140	[17]
CoP	0.285	0.5 M H_2SO_4	226	[38]
FeP/grephene	0.28	0.5 M H_2SO_4	123	[39]
MoS_2/RGO	0.285	0.5 M H_2SO_4	150	[40]
Hydrogenated FeP	0.72	0.5 M H_2SO_4	145	[24]
Fe_2P-ND/FG	0.4	0.5 M H_2SO_4	91	[41]
CoP/CNT	0.285	0.5 M H_2SO_4	122	[38]
$CoMoS_3$	0.5	0.5 M H_2SO_4	171	[42]
Porous MoC_x	0.8	0.5 M H_2SO_4	142	[43]
Fe_2P/NGr	1.71	0.5 M H_2SO_4	138	[34]
Ni_2P/Ti[a]	2.0	0.5 M H_2SO_4	120	[44]
NiS	1	0.5 M H_2SO_4	94	[45]
$CoSe_2$	N/A	0.5 M H_2SO_4	193	[46]
WSe_2	2.5	0.5 M H_2SO_4	230	[47]
WP	0.49	0.5 M H_2SO_4	161	[48]
MoS_2	0.19	0.5 M H_2SO_4	160	[49]