Supporting Information for

Rational Assembly of Hierarchically Porous Co_xFe_{1-x}S₂@Carbon Superparticles for Efficient Hydrogen Evolution

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EXPERIMENTAL SECTIONS

1. Materials

Cobalt acetylacetonate (99.9%) and iron acetylacetonate (99.9%) were purchased from Alfa-Aesar. Oleylamine (OAm, 70%), oleic acid (OA, 90%), benzyl ether (98%), dodecyltrimethylammonium bromide (DTAB, 98%), and Nafion were purchased from Sigma-Aldrich. Sulfur powder (S, 99.99%) and carbon disulfide (CS₂) were purchased from Aladdin. Anhydrous ethanol, n-hexane, concentrated sulfuric acid, acetic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification. FeS₂@C SPs, with a BET surface area of 50.8 m^2 g⁻¹ and 8.1 wt.% carbon content, were synthesized according to our previous work.¹

2. Synthesis and self-assembly of CoFe₂O₄ NPs

Monodisperse CoFe₂O₄ NPs, with a diameter of 9 nm, were synthesized according to the reported procedure.² To assemble porous SPs, 50 mg of CoFe₂O₄ NPs in 1 mL of hexane were added into a DTAB aqueous solution (10 wt%). The mixture was mechanically stirred to form an oil-in-water emulsions. The resulting emulsions were heated at 50 °C under stirring to remove hexane. The porous CoFe₂O₄ SPs were collected by a magnet and washed with deionized water. Solid CoFe₂O₄ SPs were prepared when the concentration of the DTAB solution was changed to 2 wt%, as well as the ratio of oil/water was changed from 1/50 to 1/10.

3. Preparation of P-Co_xFe_{1-x}S₂@C SPs

The as-prepared porous and solid $CoFe_2O_4$ SPs were heated at 400 °C in Ar for 2 h to carbonize the OA ligands. 1 M acetic acid solution was used to partially etch

 $CoFe_2O_4$ NPs for 1 h (denoted as P-CoFe_2O_4@C-1 SPs). The P-CoFe_2O_4@C-1 SPs were washed several times with water followed by drying under vacuum.

To synthesize P-Co_xFe_{1-x}S₂@C-1 SPs, the mixture of P-CoFe₂O₄@C-1 SPs and sulfur powder was heated at 400 °C under Ar. After cooling to room temperature, the resulting P-Co_xFe_{1-x}S₂@C-1 SPs were rinsed with carbon disulfide and then washed with water and ethanol several times, before drying at 90 °C under vacuum for 12 h. P-Co_xFe_{1-x}S₂@C-0 SPs and Co_xFe_{1-x}S₂@C SPs were synthesized through a similar procedure without the partial etching step.

4. Material characterization

Powder X-ray diffraction (XRD, X'pert PRO, Cu Kα radiation), scanning electron microscopy (SEM, Zeiss Ultra-55, 5 kV), and transmission electron microscopy (TEM, Tecnai G2 20 TWIN, 200 kV) were used to characterize the structure and morphology of the as-prepared samples. Leica EM TIC 3X argon ion cutter was used to prepare cross-sections of SPs. X-ray photoelectron spectroscopy (XPS, PHI 5000C&PHI5300) and inductively coupled plasma atomic emission spectrometry (ICP-AES, iCAP 7400) were used to analyze the valence states and contents of elements, respectively. Thermogravimetric analysis (TGA, TGA1 Mettler Toledo) was carried out to determine the content of carbon. The porosity and Brunauer-Emment-Teller (BET) surface area were determined by N₂ adsorption/desorption technique (Tristar II 3020).

5. Electrochemical measurements

To prepare P-Co_xFe_{1-x}S₂@C-1 SPs as catalysts on the glassy carbon electrode (GCE), 1 mg of catalysts was mixed with 250 μ L of ethanol, 0.25 mg of Ketjenblack, and 6 μ L of 5 wt% Nafion solution by at least 30 min sonication to from a homogeneous ink. Then, 8 μ L of ink was drop-cast onto the GCE (3 mm in diameter) and then dried under vacuum.

Electrochemical measurement was performed in a standard three-electrode system controlled by an AUTOLAB potentiostat/galvanostat apparatus (N204). The measurement was made in a H₂-saturated 0.5 M H₂SO₄ solution. Catalysts on GCE were used as the working electrode, with graphite rod used as the counter electrode and Ag/AgCl electrode used as the reference electrode. Linear sweep voltammetry (LSV) was carried out at 10 mV s⁻¹ for the polarization curves. Chronopotentiometry was measured under a constant current density of 10 mA cm⁻². All polarization curves were iR-corrected.



Figure S1. Diameter distribution histogram of macropores in P-CoFe₂O₄@C SPs.



Figure S2. TEM image of ~ 9 nm CoFe₂O₄ NPs used for making superparticles.



Figure S3. SEM images of CoFe₂O₄@C SPs at (a) high- and (b) low magnifications.



Figure S4. N₂ adsorption-desorption isotherms of P-CoFe₂O₄@C SPs and CoFe₂O₄@C SPs.



Figure S5. (a, b) SEM images of P-Co_xFe_{1-x}S₂@C-0 SPs; (c) Cross-sectional SEM image of a single P-Co_xFe_{1-x}S₂@C-0 SP; (d) SEM image of Co_xFe_{1-x}S₂@C-0 SPs.



Figure S6. (a) N₂ adsorption-desorption isotherms of P-Co_xFe_{1-x}S₂@C-0 SPs and P-Co_xFe_{1-x}S₂@C-1 SPs; (b) Pore size distribution of P-Co_xFe_{1-x}S₂@C-0 SPs and P-Co_xFe_{1-x}S₂@C-1 SPs according to desorption branch data.



Figure S7. (a) TGA curves of $Co_xFe_{1-x}S_2@C-1$ SPs and $P-Co_xFe_{1-x}S_2@C-0$ SPs at a temperature ramp of 10 °C min⁻¹ in air; (b) XRD patterns of $P-Co_xFe_{1-x}S_2@C-0$ SPs and $P-Co_xFe_{1-x}S_2@C-1$ SPs.



Figure S8. (a) XPS spectrum of P-Co_xFe_{1-x}S₂@C-1 SPs; (b) Co 2p, (c) Fe 2p, (d) S 2p XPS spectra.



Figure S9. Cyclic voltammograms of (a) $Co_xFe_{1-x}S_2@C$ SPs, (b) P- $Co_xFe_{1-x}S_2@C-0$ SPs, (c) P- $Co_xFe_{1-x}S_2@C-1$ SPs; (d) Cathodic and anodic charging currents measured, plotted as a function of the scan rate.



Figure S10. Nyquist plots of $Co_xFe_{1-x}S_2@C$ SPs, P-Co_xFe_{1-x}S₂@C-0 SPs, and P-Co_xFe_{1-x}S₂@C-1 SPs.



Figure S11. Bode plots of phase angle as a function of frequency for various electrocatalysts.



Figure S12. (a, b) SEM images of P-Co_xFe_{1-x}S₂@C-1 SPs after stability test; (c) SEM and corresponding elemental mapping of P-Co_xFe_{1-x}S₂@C-1 SPs after stability test.



Figure S13. (a, b) TEM images of P-Co_xFe_{1-x}S₂@C-1 SPs after stability test.



Figure S14. XPS Spectra of P-Co_xFe_{1-x}S₂@C-1 SPs after HER testing: (a) Fe 2p, (b)

Co 2p, (c) S 2p, and (d) C 1s XPS spectra.

Sample	Electrolyte	Overpotential at 10 mA/cm ² (mV)	Ref.
P-Co _x Fe _{1-x} S ₂ @C-1 SPs	0.5 M H ₂ SO ₄	-137	This work
CoS _{1.097} /MoS ₂	0.5 M H ₂ SO ₄	-228	ACS Appl. Energy Mater. 2019, 2, 7504
Co ₉ S ₈ -MoS _x	0.5 M H ₂ SO ₄	-161	ACS Appl. Nano Mater. 2018, 1, 1083
Cobalt sulfide hollow nanostructures	1.0 M H ₂ SO ₄	~350	J. Mater. Chem. A 2016, 4, 9014
Cobalt sulfide nanoprisms	$0.5 H_2 SO_4$	-275	<i>Chem. Commun.</i> 2015, <i>51</i> , 4252
cobalt–nickel sulfide composites	$0.5 H_2 SO_4$	~-163	J. Mater. Chem. A 2016,4, 9744
Cobalt sulfide nanosheet/graphene/carbon nanotube nanocomposites	0.5 H ₂ SO ₄	-142	Angew. Chem., Int. Ed. 2014, 126, 12802
Zinc cobalt sulfide hollow polyhedra	0.5 H ₂ SO ₄	-176	Nanoscale, 2018, 10, 1774

Table S1. HER performance comparison between our $P-Co_xFe_{1-x}S_2@C-1$ SPs and representative sulfide nanocatalysts reported previously.

REFERENCS

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(2) Sun, S.; Zeng, H.; Robinson, D. B.; Raoux, S.; Rice, P. M.; Wang, S. X.; Li, G., Monodisperse MFe₂O₄ (M = Fe, Co, Mn) Nanoparticles. *J. Am. Chem. Soc.* 2004, *126* (1), 273-279.