Supporting information

Phase controllable fabrication of zinc cobalt sulfide hollow polyhedrons as high-performance electrocatalysts for the hydrogen evolution reaction

Bowei Zhang,‡[a] *Guang Yang,*‡[a,b] *Chaojiang Li,*[a,c] *Junsheng Wu,**[d] *Shiji Hao,* [a,b] *Jianyong Feng,*[a] *Dongdong Peng*[a] *and Yizhong Huang**[a]

[a]School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

[b]Interdisciplinary Graduate School, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

[c]Department of Mechanical Engineering, State Key Laboratory of Tribology, Tsinghua University, Beijing 100084, China

[d]Institute of Advanced Materials and Technology, University of Science and Technology Beijing, Beijing, 100083, China

Corresponding Authors: Yizhong Huang (yzhuang@ntu.edu.sg); Junsheng Wu (wujs76@163.com)

‡ Equal contribution

1 Experimental Procedures

1.1 Synthesis of Zn-Co-ZIFs

All chemicals and solvents were analytical grade and used without purification. In this synthesis process, $Co(NO_3)_2 \cdot 6H_2O$ (614mg) and $Zn(NO_3)_2 \cdot 6H_2O$ (419 mg) were dissolved in 25 mL methanol to form a transparent solution, which was subsequently mixed with 25 mL of methanol containing 2-methylimidazole (1232 mg). The resulting solution was shook till complete mixing and then kept still for 24 h at room temperature. The as-obtained precipitation was centrifuged and washed with ethanol for four times before drying in vacuum oven at 60 ℃.

1.2 Synthesis of Co-ZIFs

$Co(NO_3)_2 \cdot 6H_2O$ (1023 mg) was dissolved in 25 mL methanol to form a transparent solution, which was subsequently mixed with 25 mL of methanol containing 2-methylimidazole (1232 mg). The rest procedures are the same as stated in 1.1.

1.3 Synthesis of Zn-Co-S Hollow Polyhedra

1.3.1. Zn-Co-S-500-1: 30 mg dried powder of ZnCo-ZIFs was transferred into a round-bottomed flask containing 0.1 M thioacetamide and 50 mL isopropanol. The resulting solution was stirred for 72 h at room temperature. The as-prepared product was collected after centrifugation, wash with ethanol and drying in vacuum at 60 ℃ for 24 h followed by the annealing at 500 ℃ for 2 h.

1.3.2. Zn-Co-S-500-2: The procedure is the same as the one for the synthesis of Zn-Co-500-1 except that the concentration of thioacetamide solution is 0.5 M.

1.3.3. Zn-Co-S-300: The procedure is the same as the one for the synthesis of Zn-Co-500-2 except that the annealing is conducted at 300 ℃ 2 h.

1.4 Synthesis of Co-S-300 Hollow Polyhedra

The precursor Co-ZIFs went through the same procedures as depicted in 1.3.3. The annealing condition is 300 ℃ for 2 h.

2 Characterization

X- ray diffraction (XRD) patterns of the as-prepared products were characterized by X-ray powder diffractometer (Bruker D8 Advance, Germany) using Cu Kα radiation (λ=1.5406 Å). The morphology and internal structures were clarified using field emission scanning electron microscope (FESEM, JEOL JSM-7600F, Japan) and high-resolution transmission electron microscope (HRTEM, JEOL JEM-2100F, Japan), respectively. The X-ray photoelectron spectroscopy (XPS, Omicron analyzer EA 125) was used to analyze the surface element electron state. The Brunauer-Emmett-Teller (BET) specific surface areas of the post-annealing hollow polyhedral sulfides were measured using Micromeritics ASAP Tristar II 3020.

3 Electrochemical measurement

The resulted samples ink (Zn-Co-S-500-1, 2 and Zn-Co-S-300) was prepared by ultrasonically mixing 7.4 mg of the catalyst powder with the mixture of 800 μL H_2O, 1160 μL ethanol and 40 μL 5 % Nafion solution for 1 h to form a homogeneous catalyst ink. Then, 15 μL of the catalyst ink was carefully dropped onto the polished glassy carbon rotating disk electrode (RDE, ϕ 5 mm) so that the catalyst loading is 0.283 mg cm^{-2}.

Electrochemical measurements of cyclic voltammetry were performed using an Autolab PGSTAT30 Electrochemical Workstation with a three-electrode cell system. A glass carbon RDE coated with the catalyst ink was used as the working electrode, an Ag/AgCl (sat. KCl) electrode as the reference electrode, and a graphite rod as the counter electrode. The electrochemical experiments were conducted in N_2 saturated 1.0 M KOH electrolyte for the hydrogen evolution reaction at room temperature. The potential range is cyclically scanned at a scan rate of 2 mV s^{-1} and a rotating speed of 2000 rpm. Electric impedance spectroscopy measurements in N_2 saturated 1.0 M KOH electrolyte was carried out at -0.18 V vs. RHE from 10^5 to 0.1 Hz. All potentials reported in HER testing were converted from vs. Ag/AgCl to

vs. RHE by adding 0.197 V. iR (current times internal resistance) compensation was applied in polarization and controlled potential electrolysis experiments to account for the voltage drop between the reference and working electrodes using NOVA 2.0. The durability of the samples in 1 M KOH was assessed via long-term controlled potential electrolysis at -0.18 V vs RHE for 10 h.

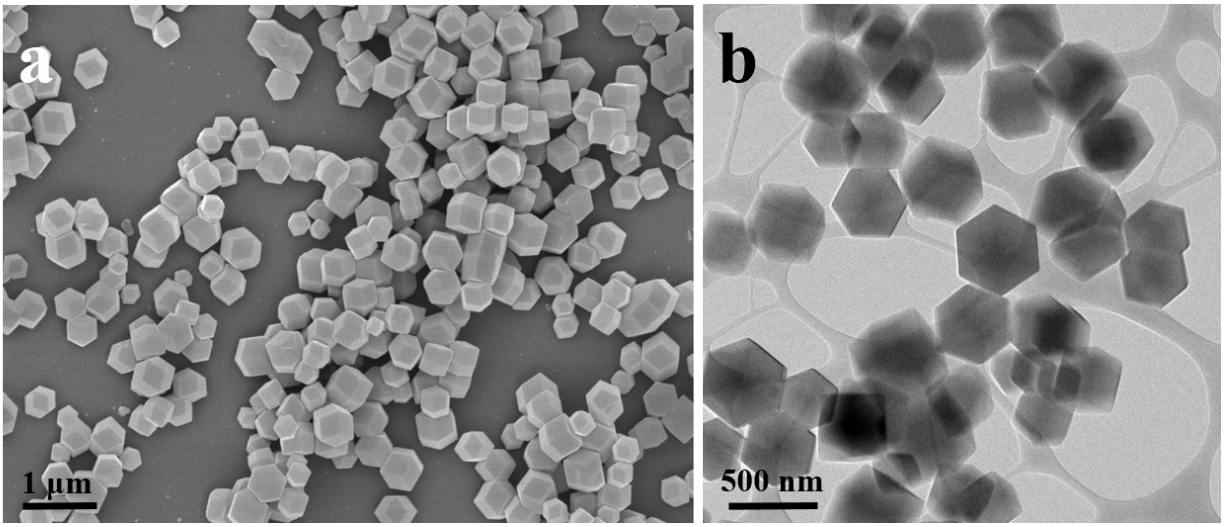


Figure S1. (a) SEM image and (b) low magnification TEM image of Zn-Co ZIFs.

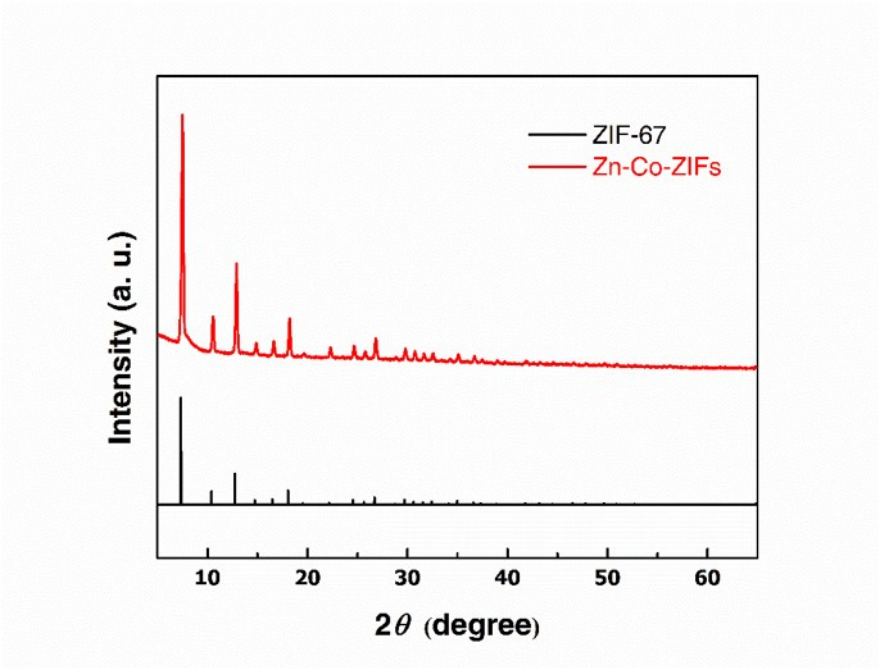
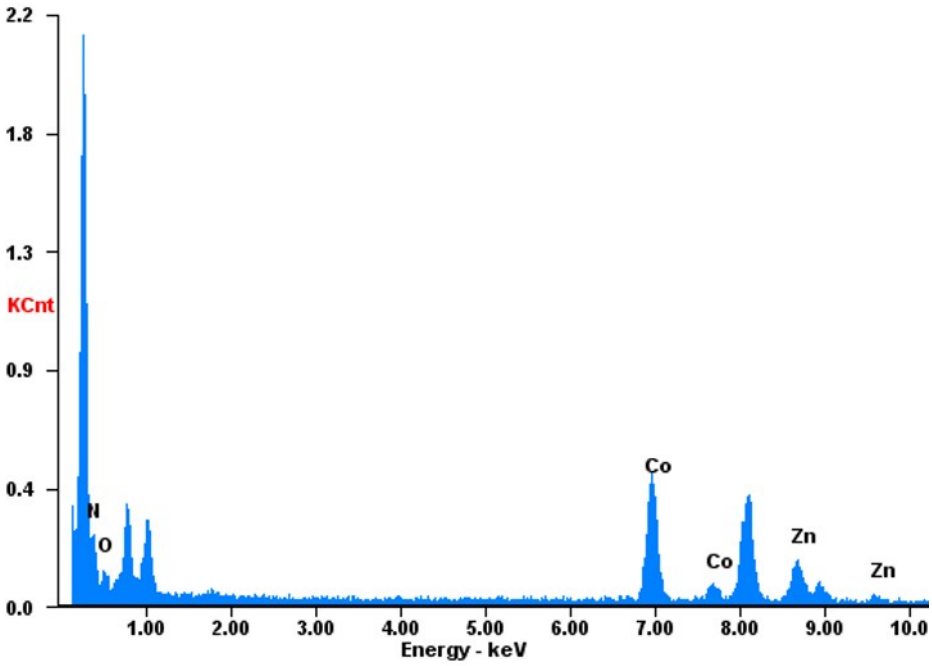


Figure S2. XRD patterns of Zn-Co ZIFs.



Element	Wt%	At%
NK	26.79	58.89
OK	02.84	05.46
CoK	47.65	23.82
ZnK	22.72	11.83
Matrix	Correction	MThin

Figure S3. (a) EDX of Zn-Co ZIFs. (b) Elemental ratio of N, O, Co and Zn.

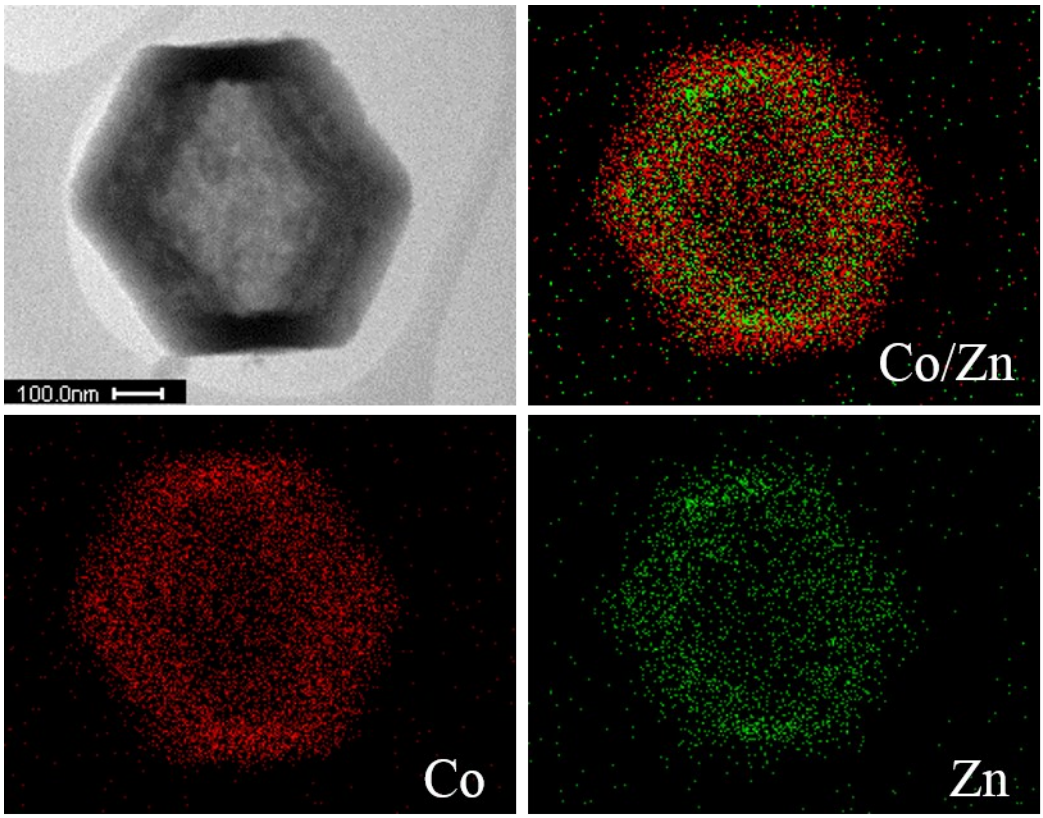


Figure S4. STEM-EDX mapping of a Zn-Co-S polyhedron obtained from a sulfidation process at 80 ℃.

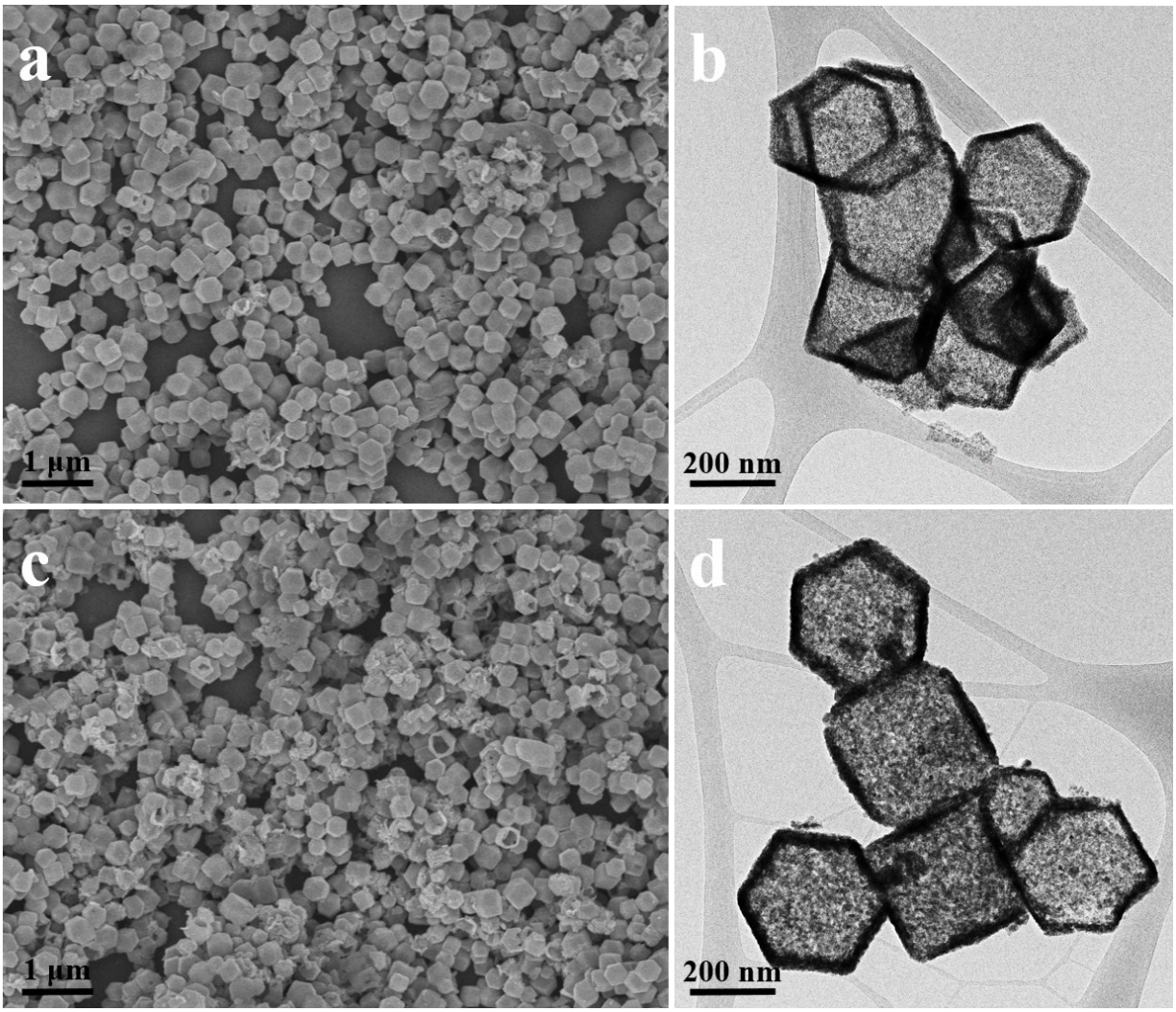


Figure S5. (a) SEM image and (b) low magnification TEM image of Zn-Co-S-500-1. (c) SEM image and (d) low magnification TEM image of Zn-Co-S-500-2.

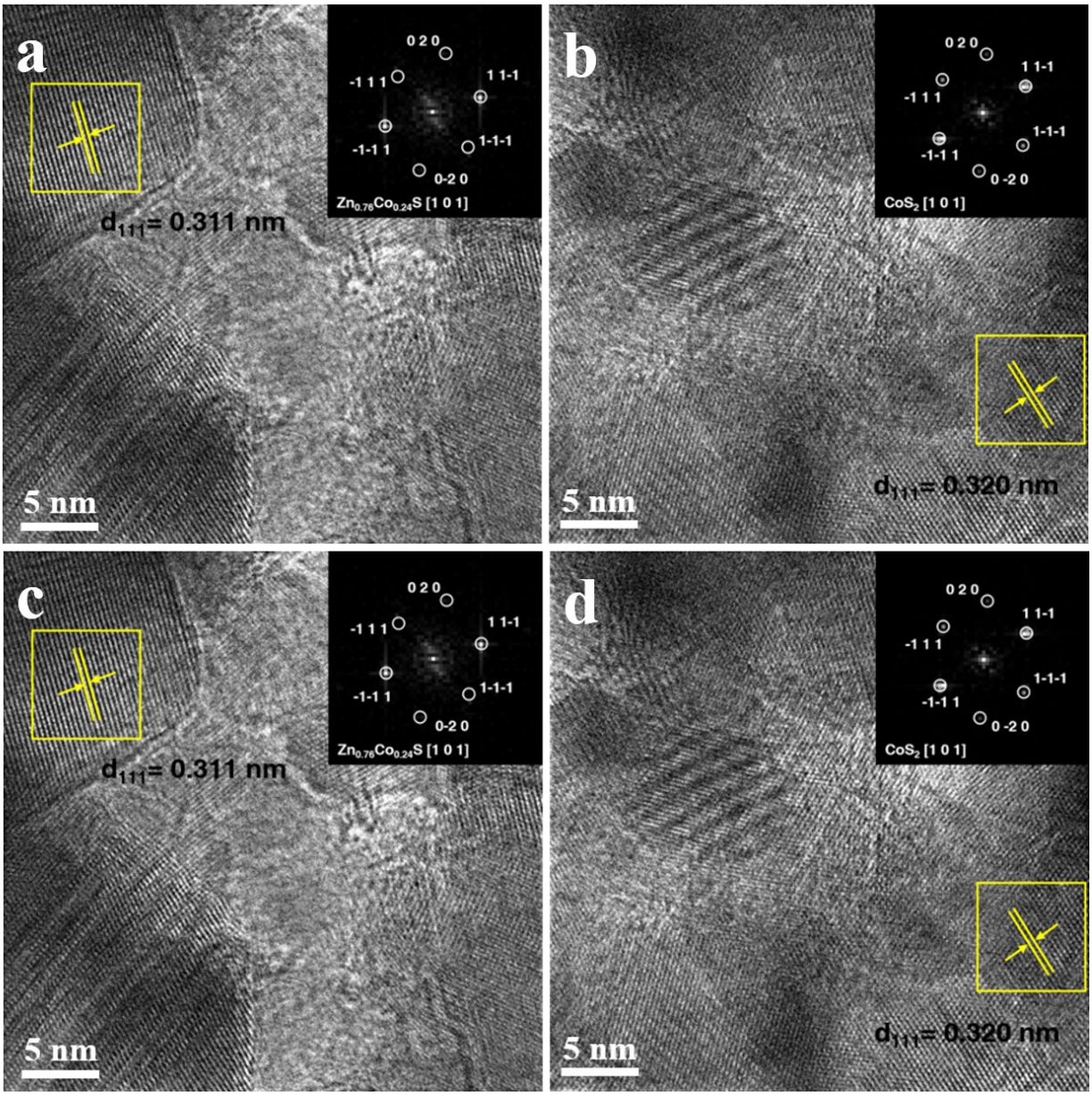


Figure S6. (a- b) HRTEM images of Zn-Co-S-500-1. (c- d) HRTEM image of Zn-Co-S-500-2.

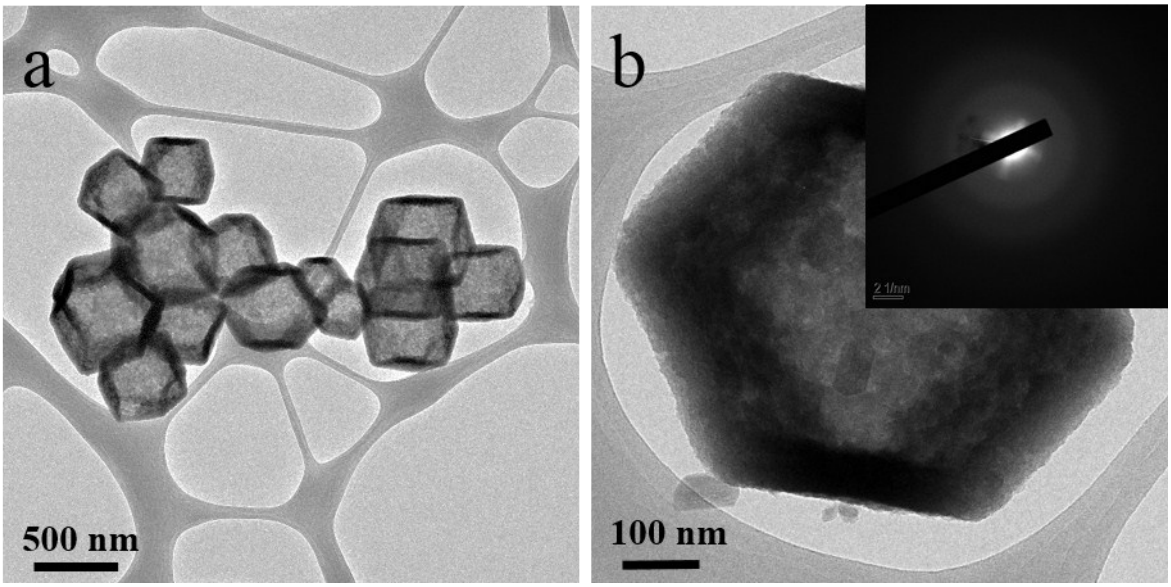


Figure S7. a) Low magnification TEM image of Co-S-300; b) HRTEM image of Co-S-300 with inset SAED pattern.

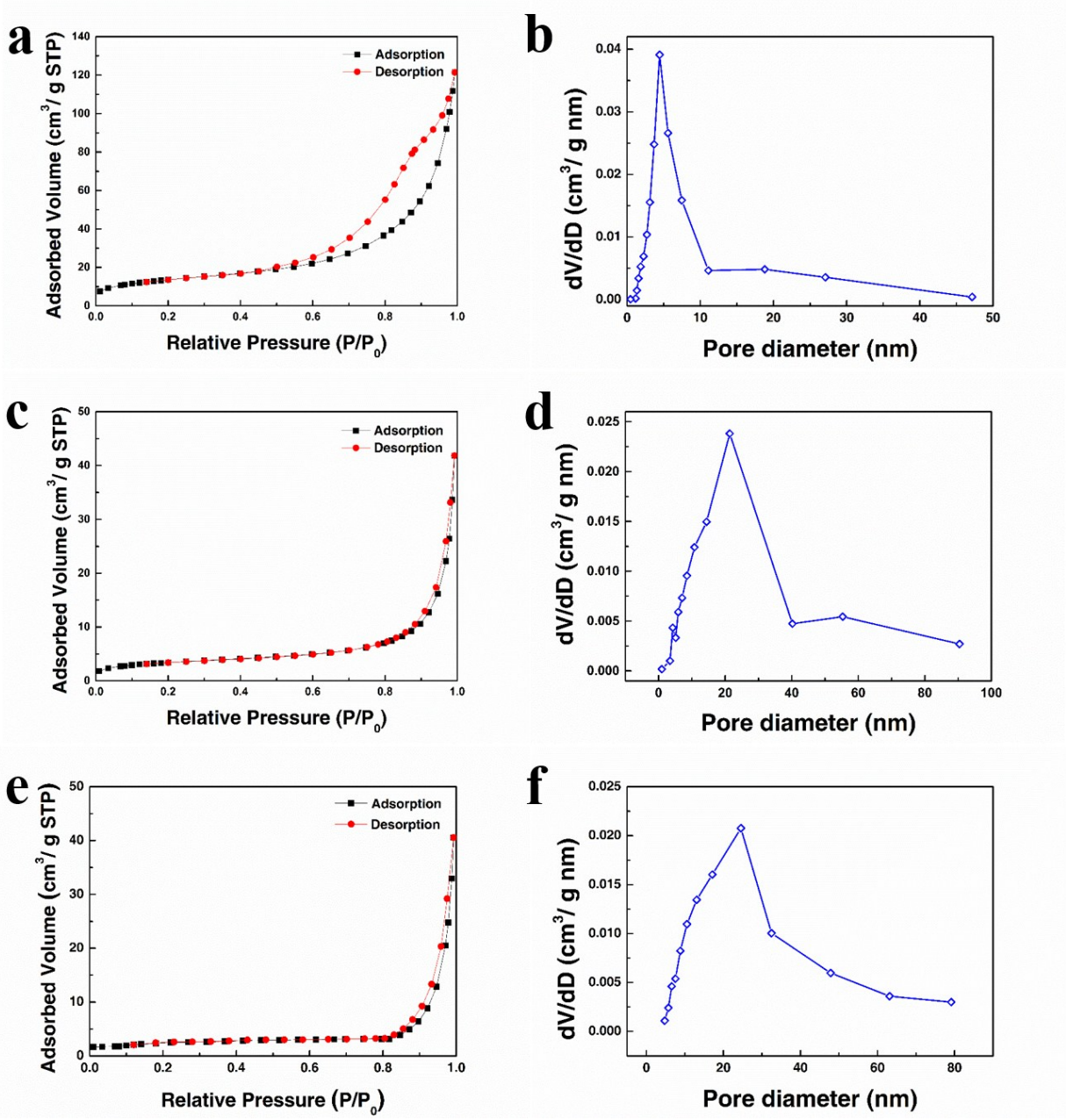


Figure S8. N_2 adsorption–desorption isotherms and determined pore size distribution of Zn-Co-S-300 (a, b), Zn-Co-S-500-1 (c, d) and Zn-Co-S-500-2 (e, f), respectively.

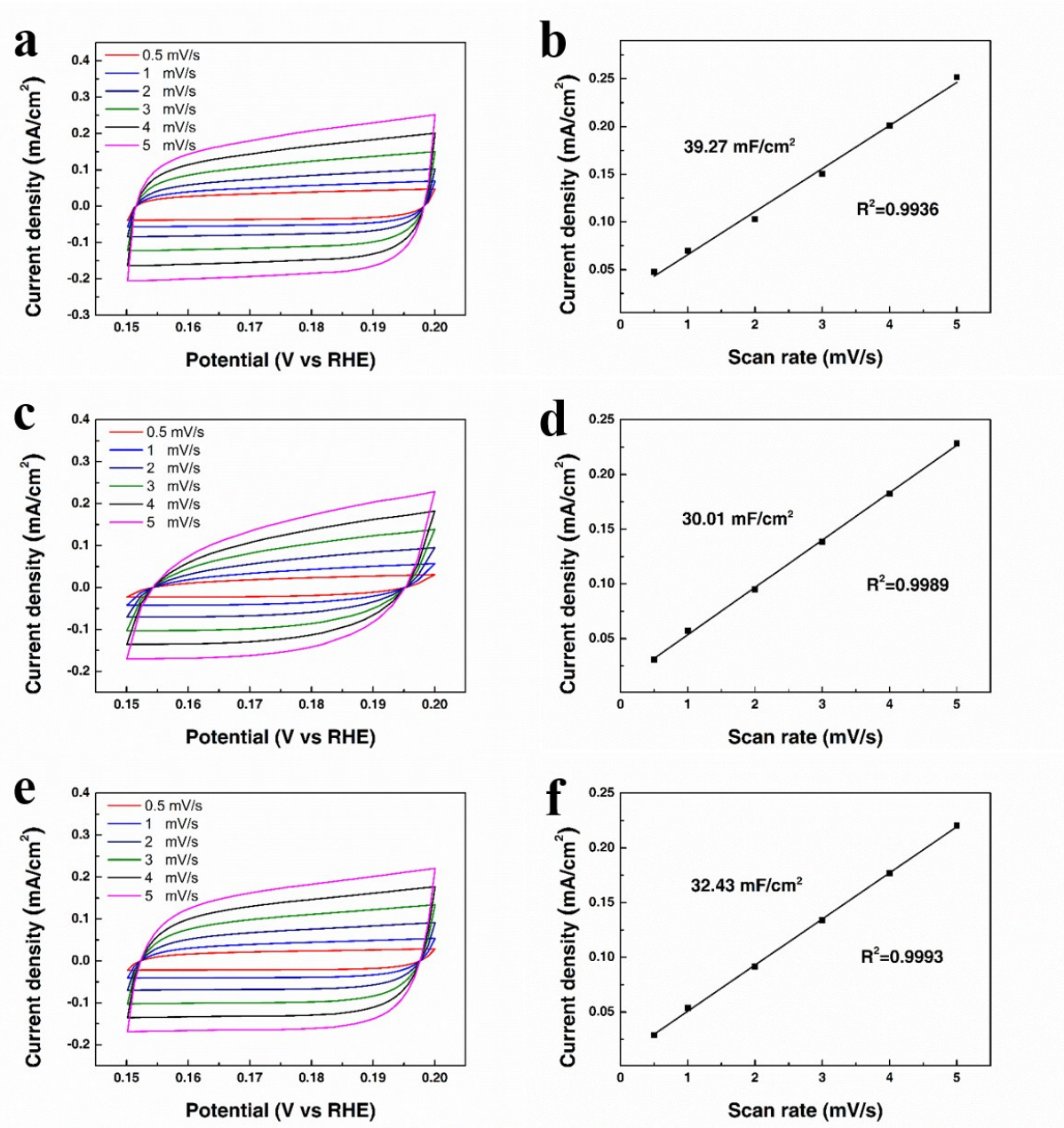


Figure S9. a,c,e) Cyclic voltammograms for the Zn-Co-S-300, Zn-Co-S-500-1 and Zn-Co-S-500-2 electrodes in the approximate region of 0.15–0.20 V vs. RHE at various scan rates and b,d,f) the corresponding linear fitting of the capacitive currents vs scan rates to estimate the C_{dl}.

Table S1. Atomic percentages of the elements in Zn-Co-S-300 calculated from XPS survey spectra.

Element	Zn	Co	S	C
Percentage (%)	12.1	24.1	56.3	7.5

Table S2. Comparison of HER performance in alkaline media for Zn-Co-S-300 with other HER electrocatalysts.

Catalyst	Electrolyte	Tafel slope (mV dec^{-1})	Overpotential at -10 mA cm^{-2} (mV)	Reference
Zn-Co-S-300	1 M KOH	86.3	176	This work
CoS_2 nanopyramids/ 3D CFP	1 M KOH	---	250	[1]
CoS_2	1 M KOH	133	244	[2]
$Zn_{0.76}Co_{0.24}S/CoS_2$	1 M KOH	164	238 (20 mA cm^{-2})	[3]
Zn-Co-S NN	1 M KOH	109	234	[4]
$NiCo_2S_4$ NWs	1 M KOH	141	228 (20 mA cm^{-2})	[5]
$NiCo_2S_4$ NW/NF	1 M KOH	58.9	210	[6]
Co_9S_8-Ni_xS_y/Nif	1 M KOH	88	163	[7]
Hollow CoS	1 M KOH	97	>210	[8]

CoS/CC	1 M KOH	98	192	[9]
Co_9S_8/C	1 M KOH	---	250	[10]

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