Electronic Supplementary Information

NiS₂ nanodotted carnation-like CoS₂ for enhanced electrocatalytic water splitting

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This file includes Experimental Section, Fig. S1-S13, and Table S1-S3.

Experimental Section

Materials

All the chemicals used in this study, including NaOH, Na₂EDTA, Ni(NO₃)₂·6H₂O, and Co(NO₃)₂·6H₂O, were commercially obtained from J&K scientific Co. Ltd. (Beijing, China). Sulfur powder was obtained from Energy Chemical (Shanghai, China), RuO₂ and Nafion were obtained from Alfa Aesar (Tianjin, China). Deionized and decarbonated water with an electrical conductivity of less than 10^{-6} S cm⁻¹ was used. All the chemicals were analytically graded, and used in the experiments without further purification.

Preparation of [NiEDTA]²⁻/Co(OH)₂ precursor

The $[NiEDTA]^{2-}/Co(OH)_2$ precursor was prepared by using a conventional coprecipitation method. In brief, 0.7 g of Na₂EDTA and 0.5 g of Ni(NO₃)₂·6H₂O were dissolved in 60 mL distilled water with 30 min of ultrasonication at room temperature. Simultaneously, a certain amount of NaOH was added to the resultant solution to adjust the pH to 5.0. Then, the slurry was slowly added dropwise into a mixture solution (100 mL) of hexamethylenetetramine (2 g) and Co(NO₃)₂·6H₂O (2 g) with strong stirring in a N₂ atmosphere. After the solution was completely added, the final solution was then transferred into a Teflon-lined stainless autoclave and was maintained at 120 °C for 20 h in an electric oven. After the temperature of the autoclave had lowered naturally to room temperature, the [NiEDTA]²⁻/Co(OH)₂ precursor was collected after being washed several times with distilled water and ethanol until pH \approx 7.0, followed by drying at 60 °C for 12 h.

Preparation of NiS₂/CoS₂/C electrocatalyst

The NiS₂/CoS₂/C electrocatalyst was obtained through the sulfurization of the [NiEDTA]²⁻/Co(OH)₂ precursor. Typically, the collected [NiEDTA]²⁻/Co(OH)₂ and sulfur powders were used at a Co/S molar ratio of 1:3. Each reactant was placed separately on one of the two sides of a porcelain boat with the sulfur powder on the upstream side. The reactants were then calcined at 500 °C for 2 h with a temperature ramping rate of 2 °C min⁻¹ in Ar atmosphere to obtain carnation-like NiS₂/CoS₂/C microstructure.

Characterization

The X-ray diffraction (XRD) patterns of the samples were collected using an X-ray diffractometer (Shimadzu XRD-6000) with filtered radiation (Cu K α , λ = 1.5418 Å). The morphologies and dimensional sizes were observed by scanning electron microscopy (SEM, ZEISS Supra 55) and transmission electron microscopy (TEM, JEM-2100). X-ray photoelectron spectra (XPS) were measured using a sample predried onto a silicon wafer and Al K α radiation (Thermo VG Scientific, 1486.6 eV, 400 W, 15 kV) under high vacuum conditions. Thermogravimetric (TG) analysis was carried out using a commercial instrument (HCT-1, China) at a temperature ramping rate of 10 °C min⁻¹ in air. The specific surface areas and pore size distributions of the samples were quantitatively estimated by measuring N₂ adsorption/desorption isotherms using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The isotherms were acquired at 77 K with a Quantachrome apparatus (Nova 1200). The samples were dried under vacuum at 393 K for 8 h before taking the measurements. Elemental analysis was employed for metal ions using a Shimadzu inductively coupled plasma optical emission spectrometer (ICP-OES). Cs-corrected scanning transmission electron microscopy (STEM) imaging and electron energy-loss spectra (EELS)

diagrams were recorded using a JEOL JEM-ARM200F instrument (200 kV) equipped with a cold field emission gun and a spherical aberration corrector for probe correction.

Electrochemical measurement

All the electrocatalytic tests were performed using a commercial one-compartment equipment at room temperature. The equipment contains three electrodes: (i) the working electrodes that are prepared directly by using the as-prepared catalysts and samples of commercial IrO_2 ; (ii) the counter electrode from a platinized carbon electrode; and (iii) the reference electrode from a saturated calomel electrode (SCE) attached to a commercial CHI 760E electrochemical workstation (Shanghai, China). In detail, to prepare the working electrode, either the as-prepared catalyst or the commercial IrO_2 and Pt/C (5 mg) was dispersed into a solution of EtOH (1 mL) and Nafion (5%, 50 µL) followed by the ultrasonication for 30 min to obtain the ink. A 120 µL loading of the as-prepared ink was optimized onto one piece of carbon paper (1 × 3 cm²) based on recent studies,^[13, 44] thus yielding a catalyst loading of ca. 0.2 mg cm⁻².

All the electrocatalytic tests were conducted in KOH solution (1 M). Linear sweep voltammetry (LSV) was applied to the electrolyte at a certain scan rate (5 mV/s) for HER and OER. Tafel plots were quantitatively calculated from the beginning of the linear regime of the linear sweep voltammetry results. The calculation of all Tafel plots involved more than one decade, and all of the potentials were used versus RHE for HER and OER. In the KOH solution (1 M), the calculation follows the equation: E (RHE) = E (SCE) + 0.059 × pH+ 0.241. Time-dependent current density curves were recorded using the abovementioned three-electrode system. Electrochemical impedance spectroscopy (EIS) was conducted in the potentials of 180 mV and -130 mV for OER and HER, respectively. The overall water splitting performances of the materials were tested in the two-electrode system using symmetric electrodes as the cathode and anode in 1.0 M KOH solution.



Fig. S1 (a) XRD pattern and (b) SEM image of $[NiEDTA]^{2-/\alpha}-Co(OH)_2$ precursor.



Fig. S2 (a) Raman spectrum and (b) low-magnification SEM image of carnation-like $NiS_2/CoS_2/C$.



Fig. S3 Histograms of size distribution of (a) NiS_2 nanodots and (b) CoS_2 nanosheets in $NiS_2/CoS_2/C$.



Fig. S4 (a) Raman spectra of NiS₂/CoS₂/C and CoS₂/C. (b) TGA curve of NiS₂/CoS₂/C.

As shown in Fig. S4b, three stages can be observed in TGA curve. An initial weight loss before 250 °C is attributed to the loss of adsorbed species such as moisture etc..^[1] The second weight loss between 250 °C and 450 °C should be due to the carbon combustion.^[2] The last weight loss after 450 °C comes from the oxidation of metal sulfides.^[3] Based on the stage of carbon combustion, the carbon content in the NiS₂/CoS₂/C composite can be roughly determined to be about 17.5 wt.%.

Reference:

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Fig. S5 XPS spectra of NiS₂/CoS₂/C: (a) full scan survey, (b) Co 2p, (c) Ni 2p, and (d) S 2p, (e) C 1s, and (f) N 1s. Co 2p XPS spectrum of CoS₂ /C was also included in (b) for comparison.

X-ray photoelectron spectra (XPS) was used to examine the species and chemical states of the NiS₂/CoS₂/C composite. Fig. S5a shows the full spectrum, demonstrating the coexistence of the Co, Ni, S, C and N elements. In the Co 2p spectrum (Fig. S5b), two strong peaks are centered at 778.1 eV and 794.1 eV, representing the signals of the Co 2p_{3/2} and Co 2p_{1/2} states involved in the binding of Co(II) with S, respectively. In addition, two satellite peaks at 782.2 and 803.5 eV are observed that are associated with the shake-up excitation from Co³⁺ cations.¹, ² Note that the decoration of NiS₂ leads to the shift of Co 2p to lower 0.6 eV of energy level (Fig. S5b), suggesting that the interaction between NiS₂ nanodots and CoS₂ nanosheets.³ In the Ni 2p spectrum, two strong peaks are clearly visible at 854.1 and 872.4 eV (Fig. S5c), which are well related to the electronic configurations of Ni 2p3/2 and 2p1/2, respectively, thus revealing the existence of Ni²⁺/Ni³⁺ after the sulfurization.⁴⁻⁶ For S 2p, the high-resolution spectrum is deconvoluted into two strong peaks centered at 162.5 eV and 163.6 eV (Fig. S5d) that are assigned to the sulfide structure.⁷ Furthermore, another binding energy is observed at 168.5 eV, which is associated with sulfur oxides (SO_x) .⁸ In the case of C 1s, the spectrum is split into three peaks at 284.8, 285.9, and 288.6 eV (Fig. S5e) that are ascribed to C-C, C-S, and C–O, respectively. In addition, the N 1s spectrum is deconvoluted into three peaks at 398.4, 399.2, and 400.4 eV (Fig. S5f) that are assigned to the graphitic N, pyridine N, and pyrrole N,

respectively. The presence of these peaks strongly suggests that nitrogen is successfully doped into the carbon.⁹

Reference:

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Fig. S6 Nitrogen adsorption/desorption isotherms and pore size distributions: (a) NiS₂/CoS₂/C, (b) CoS₂/C, and (c) Co(OH)₂.



Fig. S7 (a) XRD pattern, (b) SEM image, (c) TEM image, and (d) HRTEM image of CoS₂/C composite. Inset in (c) is the histogram of size distribution.

The SEM/TEM image shows that the carnation-like CoS_2/C microstructure consists of CoS_2 nanosheets (Fig. S7b and S7c), and the HRTEM further reveals that no NiS₂ nanodots with black contrast are seen on the observed CoS_2 nanosheets with gray contrast (Fig.S7c and S7d). In addition, the pristine CoS_2 nanosheets have a mean size distribution of 20.6 ± 2.5 nm, which is indeed identical to that of the NiS₂/CoS₂/C composite. On the other hand, all the above-discussed results support that the NiS₂ nanodots are indeed embedded on the CoS_2 nanosheets that are derived from the confined [EDTA]^{2–} guest and the $Co(OH)_2$ host.

Fig. S8 Nyquist plots for NiS₂/CoS₂/C, CoS₂/C and Co(OH)₂, recorded at 180 mV vs. RHE.

Fig. S9 (a-c) CV curves measured at scan rates varying from 20 to 100 mV/s for NiS₂/CoS₂/C, CoS₂/C and Co(OH)₂. (d) Current density at 0.2 V vs SCE plotted as a function of scan rates.

Fig. S10 (a) XRD pattern and (b) SEM image of NiS₂/CoS₂/C electrode after OER tests.

Fig. S11 (a) Co 2p and (b) Ni 2p XPS spectra of NiS₂/CoS₂/C after OER tests.

Fig. S12 (a) Nyquist plots for NiS₂/CoS₂/C, CoS₂/C and Co(OH)₂ at -130 mV vs. RHE. (b) Time-dependent current density curves for NiS₂/CoS₂/C at the overpotential of 200 mV and 230 mV. The electrolyte is 1.0 M KOH.

Fig. S13 Polarization curves of NiS₂/CoS₂/C before and after 1000-cycle CV scanning between -0.3 and 0.1 V *vs.* RHE. The electrolyte is 1.0 M KOH.

Materials	Loading mass $(max - 2)$	Overpotential $(m W \otimes m A \otimes m^{-2})$	Tafel slope	Reference
	$(mg \ cm^2)$	$(mv(a) mA cm^2)$	(mv dec ⁻)	
NiCo LDH	1.25	367@10	49	Nano Lett., 2015 , <i>15</i> , 421- 1427
CoS ₂ Nanosphere	1.5	290@10	57	Nanoscale, 2018 , 10, 4816-4824
CoS ₂ Nanotube	1.2	276@10	81	<i>Nanoscale Horiz.</i> , 2017 , <i>2</i> , 342-348
CuS/NiS ₂	0.2	290@10	36	<i>Adv. Funct. Mater.</i> , 2017 , 27, 1703779
Ni _x S _y -NSCs	0.25	270@10	68.9	Small, 2018, 14, 1703273.
NiCo ₂ S ₄	0.07	337@10	64	<i>Green Chem.</i> , 2017 , <i>19</i> , 3023
MoS_2 - Ni_3S_2	13	249@10	57	ACS Catal., 2017 , 7, 2357- 2366
NiCoS	0.21	320@10	58.5	<i>Int. J. Hydrogen Energy</i> , 2018 , <i>43</i> , 8815-8823
NiS ₂ /CoS ₂ /C	0.2	310@20	74	This work

Table S1. Comparison of OER performance between the NiS₂/CoS₂/C composite and the cobalt/nickel-based electrocatalysts reported previously. The electrolyte is 1.0 M KOH.

Table S2. Comparison of HER performance at 10 mA cm⁻² between the NiS₂/CoS₂/C composite and the cobalt/nickel-based electrocatalysts reported previously. The electrolyte is 1.0 M KOH.

Materials	Loading mass (mg cm ⁻²)	Overpotential (mV)	Tafel slope (mV dec ⁻¹)	Reference
NiCoFe-LDHs/CFC	0.4	200	57	ACS Energy Lett., 2016 , 1, 445-453
CoS ₂ Nanosphere	1.5	193	100	Nanoscale, 2018 , 10, 4816-4824
CoS ₂ Nanotube	1.2	193	88	<i>Nanoscale Horiz.</i> , 2017 , <i>2</i> , 342-348
NiCo ₂ S ₄ Nanowire	-	210	58.9	<i>Adv. Funct. Mater.</i> , 2016 , <i>26</i> , 4661–4672
NiS ₂ /MoS ₂	0.2	204	65	ACS Catal., 2017 , 7, 6179–6187
Co-S Sheet	0.32	190	131	ACS Nano, 2016 , 10, 2342-2348
CoS _x /Ni ₃ S ₂ @NF	2.83	204	113	ACS Appl. Mater. Interfaces, 2018 , 10, 33, 27712-27722
NiS ₂ /CoS ₂ /C	0.2	165	83	This work

Table S3. Comparison of overall-water-splitting performance at 10 mA cm⁻² between the NiS₂/CoS₂/C composite and the cobalt/nickel-based electrocatalysts reported previously. The electrolyte is 1.0 M KOH.

Materials	Loading mass (mg cm ⁻²)	Overall voltage (V@10 mA cm ⁻²)	Durability (h)	Reference
CoS ₂ Nanosphere	1.5	1.54	10	Nanoscale, 2018 , 10, 4816-4824
CoS ₂ Nanotube	1.2	1.67	20	<i>Nanoscale Horiz.</i> , 2017 , <i>2</i> , 342-348
NiCo ₂ S ₄ Nanowire	-	1.63	50	<i>Adv. Funct. Mater.</i> , 2016 , <i>26</i> , 4661–4672
Ni _{2.3%} -CoS ₂	0.97	1.66	12	<i>Elelctrochem.Commun.</i> , 2016 , <i>63</i> , 60-64
NiCo ₂ S ₄	4.0	1.68	10	<i>Nanoscale</i> , 2015 , 7, 15122
NiS ₂	0.272	1.56	10	ACS Nano, 2017 , 11, 11574-11583
Co-S Sheet	0.32	1.679	2	ACS Nano, 2016 , 10, 2342–2348
CoS _x /Ni ₃ S ₂ @NF	2.83	1.572	30	ACS Appl. Mater. Interfaces, 2018 , 10, 33, 27712-27722
$(Ni_{0.33}Co_{0.67})S_2$	3.0	1.57	30	ACS Appl. Mater. Interfaces, 2018 , 10, 27723–27733
NiS ₂ /CoS ₂ /C	0.2	1.61	24	This work