Electronic Supplementary Information

Bifunctional CdS@Co₈S₉/Ni₃S₂ Catalyst for Efficient Electrocatalytic-

and Photo-Assisted Electrocatalytic- Overall Water Splitting

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Experimental Detail

1. Preparation of the samples

1.1 CdS@CoNiS core-branch nanoarrays on Co/Ni alloy foam

The CdS@CoNiS core-branch nanoarrays were in situ grown on commercial Co/Ni alloy foam by a simple one-step hydrothermal synthesis strategy similar as our previous report.^[1] Firstly, a piece of Co/Ni alloy foam $(1 \times 3 \text{ cm}^2)$ was sequentially cleaned using acetone, water, 0.1 M HCl and alcohol respectively. Then the cleaned foam was submerged into a 50 mL Teflon-lined autoclave containing a certain amounts Cd(NO₃)₂, thiourea and glutathione water solution. After striving for about 5 min, the autoclave was sealed and maintained at varying optimized temperature for 3 hours. After cooled down to room temperature, the obtained samples were washed with water and ethanol and dried at 60 °C.

Four different CdS@CoNiS-x samples with changing the CoNiS shell thicknesses were prepared by varying the hydrothermal synthesis temperature from 190 to 220 °C, and denoted as CdS@CoNiS-190, CdS@CoNiS-200, CdS@CoNiS-210, CdS@CoNiS-220, respectively.

1.2 CoNiS nanosheets on Co/Ni alloy foam

For comigration pure CoNiS nanosheets electrode was fabricated on Co/Ni alloy foam. The synthesis process of CoNiS nanosheets electrode is similar as CdS@CoNiS electrodes, except for without adding of Cd(NO₃)₂ precursors.

2. Materials characterization

The power X-ray di \Box raction (XRD) patterns of the materials were recorded on a Rigaku D/Max 2550 X-ray di \Box ractometer with Cu K a radiation ($\lambda = 1.5418$ ° A). The distribution of various elements in the products was exhibited by X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250Xi spherical analyzer. The transmission electron microscope (TEM) images were taken using a Philips-FEI Tecnai G2S-Twin microscope equipped with a field emission gun operating at 200 kV. The scanning electron microscope (SEM) images were taken using a FEI Nano SEM 430. The photo-luminescence spectra (PL) were measured using a model RF-5301PC (Hitachi, Japan) with an excitation wavelength of 340 nm at room temperature. UV-visible diffuse-reflectance spectra (UV-Vis DRS) were recorded on a Hitachi U-3010 UV-vis spectrophotometer using BaSO₄ as the reference sample.

3. Electrochemical measurements

All the electrochemical (EC) and photo-electrochemical (P-EC) measurements were performed in a H-type photoelectrochemical cell controlled by CHI 650D electrochemical workstation (Inc., Shanghai, China). The H-type photoelectrochemical cell was filled with 1M KOH electrolyte solution, and a piece of Nafion 117 proton exchange membrane were used to confirm the separation of generated H₂ and O₂ gas. For OER measurement, the synthesized photoelectrodes were used as working electrodes and a piece of Pt foil work as a counter electrode, and Ag/AgCl electrode is adopted as reference electrode. For HER measurement, the working electrodes was Pt foil and the synthesized CdS@CoNiS-x was used as counter electrode. Both the OER and HER polarization curves were performed at 1 mV s⁻¹ after the pretreatment of performing LSVs at 20 mV s-1 for 20 cycles until the oxygen evolution currents showed negligible change. The EC and P-EC water splitting activity parameters for CdS@Co₈S₉/Ni₃S₂ electrodes were measured without iR compensated. The electrochemical impedance spectroscopy (EIS) and Mott-Schottky (M-S) test were both performed in the same 1 M KOH electrolytes. The EIS were recorded via a computer controlled IM6e impedance measurement unit (Zahner Elektrik, Germany) over a frequency range of $0.01 - 10^5$ Hz with an ac amplitude of 5 mV, and in the Mott-Schottky measurements, the corresponding increment, amplitude and frequency were 50 mV, 5 mV, 1000 Hz, respectively. The ECSA for each CSNS-x sample was estimated from the electrochemical double-layer capacitance (C_{dl}) obtained from the cyclic voltammetry (CV) scans (-0.05 V - 0.95 V, vs. RHE). The voltage-time curve was created using the data from the chronopotentiometry test with or without light irradiation. For all the P-EC measurements, A 300 W cm⁻² Xe light (CEL-HXF300E) with an visible light filter ($\lambda > 420$ nm) was used as the light source, and the light source was 10 cm away from the working electrodes.

4. Evaluated the H₂ and O₂ production amount

In order to identified the H_2 and O_2 production amount during EC or P-EC process, The H-type photoelectrochemical cell were connected with a homemade sealing device as shown in the following digital photograph (Scheme S1). Using displacement method, the generated H_2 and O_2 amount were artificially calculated by metering the corresponding glass tube, each volume of the glass tube is 50 mL. Notably, in these processes, it can not be avoided that there may some metering errors presences. Thus, the Faradic efficiency fluctuates around 100%.

5. Calculation sections

5.1 Potentials measured were calibrated to the reversible hydrogen electrode (RHE) using the following equation (1):

$$E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.197 \,\, \text{V} + 0.059 \,\, \text{pH}$$
(1)

where the measured pH is 13.4 in this work.

5.2 The OER overpotentials were defined by the following equation (2):

$$\eta_{OER} = E_{(RHE)} - 1.23 V$$
 (2)

5.3 The Tafel plot of PEC or PC process is obtained by replotting the corresponding LSV curve as a plot of log(j) versus applied potentials (η), and it is expressed as following equation (3):^[2]

$$\eta = \alpha + b \log j + j R s \tag{3}$$

where η (V) denotes the applied overpotential, j (A cm⁻²) is related to the current density, b (V dec⁻¹) represents the Tafel slope, and Rs (Ω cm-2) is the total area-specific uncompensated resistance of the system.

5.4 The Faradaic efficiency was obtained based on the previous literatures by using the equation (4): ^[3]

Faradaic efficiency (%) =
$$\frac{m (mol) \times n \times F}{Q (C)} \times 100\%$$
 (4)

where m is the mount of H_2 (mol), n is the electron transfer number (2 for H_2), F is the Faraday constant (96,485 C mol⁻¹) and Q is the total charge (C).

5.5 The electron lifetime (τ_n) can be determined by the electron transfer resistance (R_{ct}) and chemical capacitance (CPE) according to following equation (5):^[4-5]

$$\tau_{n}(s) = R_{ct}(\Omega \text{ cm}^{2}) \times \text{CPE}(\text{F cm}^{-2})$$
(5)

5.6 The optical band-gap structures were estimated by using the Kubelka-Munk method, according to the following equation (6):^[6]

$$\alpha hv = A (hv - Eg)^{1/2}$$
(6)

where α , h, v, A and Eg is the absorption coefficient, Planck constant, light frequency, constant value and the band gap energy, respectively.

5.7 According to the previously reported methods,^[7] the ECSA was estimated by the electrochemical double-layer capacitance (C_{dl}) obtained from the cyclic voltammetry (CV) scans, and it was calculated as the following equation (7):

$$ECSA (cm2) = C_{dl} / C_s$$
(7)

where the C_{dl} is derived from the plot of non-Faradaic capacitive current densities (j_c) against the scan rates (v), j_c = v C_{dl} ; C_s is the specific electrochemical doublelayer capacitance, which is a general specific capacitances of $C_s = 0.04$ mF cm⁻², as the samples are measured in an alkaline solutions.^[8]

6. Figure sections



Scheme S1. (A) The overview digital photograph of our home-made gas collection equipment; (B) the measuring state for calculating the generated gasses.



Fig. S1. (A) SEM image of Co/Ni foam, corresponding elements mapping results of Co (B) and Ni (C), and energy dispersive spectroscopy (EDS) result (D).



Fig. S2. Corresponding elements mapping results of (A) CdS@CoNiS-190, (B) CdS@CoNiS-200, (C) CdS@CoNiS-210 and (D) CdS@CoNiS-220, respectively.

Table S1. The weight and atomic ratio of Co, Ni, Cd, and S in CdS@CoNiS-190 fromthe HRTEM EDS result.

Element	Weight%	Atomic%
S K	24.38	51.38
Co K	5.6	6.42
Ni K	0.16	0.19
Cd K	69.86	42.01
Totals	100.00	100.00



Fig. S3. Fitted electrochemical impedance spectroscopy (EIS) equivalent circuit of Co@CoNiS-x samples

Samples	Rs	Rct 1	CPE 1	τ1 (s)	Rct 2	CPE 2	τ2 (s)
	$(\Omega \text{ cm}^2)$	$(\Omega \text{ cm}^2)$	(F cm ⁻²)		$(\Omega \text{ cm}^2)$	(F cm ⁻²)	
190	0.7493	3.144	0.00689	0.0217	224.6	0.00765	1.718
200	0.7732	3.035	0.00744	0.0226	154.8	0.00697	1.079
210	0.7845	2.968	0.00624	0.0185	136.4	0.00563	0.768
220	0.6629	0.9796	0.0185	0.0181	198.7	0.00456	0.906
CoNiS	0.745	0.9699	0.0315	0.0306	233	0.00863	2.011

 Table S2 Electrochemical impedance spectra fitting results.



Fig. S4. The C_{dl} measurements CV plots in a non-Faradic region with different scan rates from 10 to 50 mV s⁻¹, (A) for pure CoNiS, (B) for CdS@CoNiS-190, (C) for CdS@CoNiS-200, (D) for CdS@CoNiS-210 and (E) for CdS@CoNiS-220. (F) the compared C_{dl} results for all the synthesized samples.



Fig. S5. Comparison of ECSA towards the different CdS@CoNiS-x catalysts.



Fig. S6. Optical properties of CdS@CoNiS-x samples: (A) UV-vis absorption spectroscopy, (B) photo-luminescence (PL) measurement spectra; (C) Tauc plots translated from (B); and Mott–Schottky (MS) plots for CoNiS (D), CdS@CoNiS-190 and CdS@CoNiS-200 (E), and CdS@CoNiS-210 and CdS@CoNiS-220 (F), respectively.



Fig. S7. (A) Band gap structures of typical pure CdS and synthesized CdS@CoNiS-x and CoNiS samples in this work. (B) Tentative energy band diagram between CdS and CoNiS junction in relation to the redox potentials for $2H^+/H_2$ and O_2/OH^- .



Fig. S8. Compared transient photocurrent measurement results for CdS@CoNiS-190, CdS@CoNiS-210 and pure CoNiS electrodes.



Fig. S9. (A) Compared XRD results for fresh and used CdS@CoNiS-210 before and after 8 h long-term P-EC and EC water splitting; SEM of CdS@CoNiS-210 after EC (B) and P-EC (C); Corresponding element energy mapping results of EC (D) and P-EC (E) used CdS@CoNiS-210.



Fig. S10. Compared survey XPS spectra (A) and corresponding high-resolution of Cd 3d (B), S 2p (C), Co 2p (D), Ni 2p (E) and O 1s (F) of fresh and EC/P-EC used CdS@CoNiS-210 samples.



Fig. S11. Comparable instantaneous photocurrent intensity before and after 8 h long time P-EC process of CdS@CoNiS-210.

7. References

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