



## Supplementary Information for

### Interfacial Engineering of Cobalt Sulfide/Graphene Hybrids for Highly Efficient Ammonia Electrosynthesis

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## Methods

**The synthesis of graphene oxide (GO).** All of the chemicals were of analytical grade and used without further purification. GO was synthesized from graphite powder by using the modified Hummers' method<sup>S1</sup>. Typically, 1.5 g of graphite powder was added to a 9:1 mixture of concentrated H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub> (180:20 mL), and then 9.0 g KMnO<sub>4</sub> was slowly added to the above solution under continuous stirring. Then, the mixed system was heated to 60 °C and maintained for 12 h under continuous stirring. The solution was poured into 200 ml of ice water with 10 ml of H<sub>2</sub>O<sub>2</sub> (30%) after cooling to room temperature. The remaining solid product was collected by centrifugation and washed in succession with 200 mL of water, 200 mL of 30% HCl, and 200 mL of ethanol (twice). The as-prepared GO was added to deionized water and continuously ultrasonicated to form a homogenous aqueous dispersion (2 mg ml<sup>-1</sup>).

**The synthesis of MS<sub>2</sub>/NS-G, MS/NS-G and NS-G hybrid catalysts.** In a typical process, 0.2 mmol metal chloride salt (CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, FeCl<sub>3</sub> or SnCl<sub>4</sub>·5H<sub>2</sub>O) was added to 10 ml of deionized water under continuous stirring until complete dissolution. Then, 50 ml of GO (2 mg ml<sup>-1</sup>) aqueous dispersion was added to the above solution and stirred for 12 h. The MCl<sub>x</sub>/GO precursor was obtained through a freeze-drying process from the above solution. Next, 25 mg of the resulting MCl<sub>x</sub>/GO precursor was placed at the centre of a tube furnace, and 2.0 g of thiourea was placed at the upstream side near the precursor. Then, the furnace was heated to 500 °C at a

ramping rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  under a flowing Ar atmosphere and maintained for 2 h. Finally, the  $\text{MS}_2/\text{NS-G}$  (M=Co, Ni, Fe and Sn) hybrid material was collected after the system was cooled to room temperature. Moreover, the synthetic procedure for  $\text{MS}/\text{NS-G}$  is similar to that for  $\text{MS}_2/\text{NS-G}$  except for the use of 200 mg of thiourea during the annealing treatment. NS-G was prepared by using the same strategy as  $\text{MS}_2/\text{NS-G}$  without adding the metal salt.

**Structural Characterization.** X-ray powder diffraction (XRD) was performed using a Philips X'Pert Pro Super diffractometer with Cu-K $\alpha$  radiation ( $\lambda=1.54178\text{ \AA}$ ). Transmission electron microscopy (TEM) was performed on a JEM-2100F field-emission electron microscope operated at an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) images were recorded on a JEOL JSM-6700F SEM. High-resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and corresponding energy-dispersive X-ray spectroscopy (EDS) mapping analyses were executed on a JEOL JEM-ARF200F TEM/STEM with a spherical aberration corrector. X-ray photoelectron spectra (XPS) were obtained on an ESCALAB MK II X-ray photoelectron spectrometer with Mg K $\alpha$  as the excitation source. The binding energies obtained in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.5 eV. The absorbance data of the spectrophotometer were measured on an ultraviolet-visible (UV-Vis) spectrophotometer (SOLID3700). Co L-edge, S L-edge, C K-edge and N K-edge XANES spectra were measured at the U19 beam line of the National Synchrotron

Radiation Laboratory (NSRL, Hefei) in total electron yield (TEY) mode by collecting the sample drain current under a vacuum greater than  $10^{-7}$  Pa.

**Electrochemical Measurements.** The electrochemical tests were carried out in a three-electrode system on an electrochemical workstation (CHI660B) at room temperature. Electrochemical reduction of  $N_2$  to ammonia was performed in a two-compartment cell at room temperature, and the cells were separated by a Nafion 117 membrane. A Ag/AgCl (saturated KCl solution) electrode was used as the reference electrode, and a graphite rod was used as the counter electrode. The cathode was prepared as follows: 4 mg of catalyst powder, 1 ml of alcohol and 40  $\mu$ l Nafion solution (Sigma Aldrich, 5 wt %) were mixed and sonicated for at least 1 h to form a homogeneous ink. Then, a certain volume of catalyst ink was drop-casted onto carbon paper with a loading of 0.2 mg  $cm^{-2}$ . The area of carbon paper electrode is  $1 \times 2$   $cm^2$  and the practically immersing area in the electrolyte was  $1 \times 1$   $cm^2$ . The electrolyte volume in the two parts of H-cell is 30 ml. For electrocatalytic  $N_2$  reduction, potentiostatic tests were conducted in  $N_2$ -saturated 0.05 M  $H_2SO_4$  for 2 h, which was purged with  $N_2$  for 30 min before the measurement. Pure  $N_2$  was continuously fed into the cathodic compartment with a properly positioned sparger during the experiments.

The yield rate of  $NH_3$  formation was calculated as Equation S1, where  $c$  was the total mass concentration of  $NH_3$ ,  $V$  was the volume of the electrolyte,  $t$  was the reduction reaction time, and  $m$  was the loading mass of catalysts.

$$r_{NH_3} = (C_{NH_3} \times V) / t \times m_{cat}. \quad (S1)$$

The Faradaic efficiency (FE) of NRR was calculated as Equation S2, where  $F$  was the Faraday constant,  $Q$  was the charge, and  $n$  was the total molar weight of  $NH_3$  product.

$$FE = 3F \times n_{NH_3} / Q \quad (S2)$$

**Product quantification.** The ammonia concentration was spectrophotometrically determined by the indophenol blue method with modification<sup>11,25</sup>. Typically, 2 mL of solution was removed from the cathode electrochemical reaction vessel. Then, 2 mL of a 1 M NaOH solution containing 5 wt% salicylic acid and 5 wt% sodium citrate was added to the electrolyte, followed by the addition of 1 mL of 0.05 M NaClO and 0.2 mL of 1 wt %  $C_5FeN_6Na_2O$  (sodium nitroferricyanide) solution. After 2 h at room temperature, the absorption spectrum was measured using a UV-vis spectrophotometer. The formation of indophenol blue was determined using the absorbance at a wavelength of 655 nm. The concentration-absorbance curves were calibrated using standard ammonia chloride solutions containing the same concentrations of  $H_2SO_4$  as those used in the electrolysis experiments (SI Appendix, Fig. S8).

The hydrazine concentration of the electrolyte was estimated by the Watt and Chrisp method<sup>11,12,25</sup>. A mixture of para-(dimethylamino)benzaldehyde (5.99 g), HCl (concentrated, 30 mL) and ethanol (300 mL) was used as a colour reagent. First, 2 mL of solution was removed from the cathode electrochemical reaction vessel. Then, 2 mL of colour reagent was added to the electrolyte, and the absorption spectrum was

measured using a UV-vis spectrophotometer after 30 min at room temperature. The formation of hydrazine was determined using the absorbance at a wavelength of 455 nm. The concentration-absorbance curves were calibrated using standard hydrazine solutions containing the same concentrations of H<sub>2</sub>SO<sub>4</sub> as those used in the electrolysis experiments (SI Appendix, Fig. S9).

**<sup>15</sup>N<sub>2</sub> isotope labelling experiment.** The <sup>15</sup>N<sub>2</sub> gas was purchased from Cambridge Isotope Laboratories, Inc. Before the electrochemical reduction experiment, the electrolyte was purged with high-purity Ar to remove the <sup>14</sup>N<sub>2</sub> from solution and then was pre-saturated with <sup>15</sup>N<sub>2</sub> for 30 min with a flow rate of 5 sccm. After <sup>15</sup>N<sub>2</sub> electrochemical reduction for 20 h at a potential of -0.2 V, the electrolyte was concentrated and the obtained <sup>15</sup>NH<sub>4</sub><sup>+</sup> product was identified using <sup>1</sup>H NMR spectroscopy with water suppression (Bruker AVANCE AV III 400).

## S1. Synthesis process of various MS<sub>2</sub>/NS-G and MS/NS-G materials

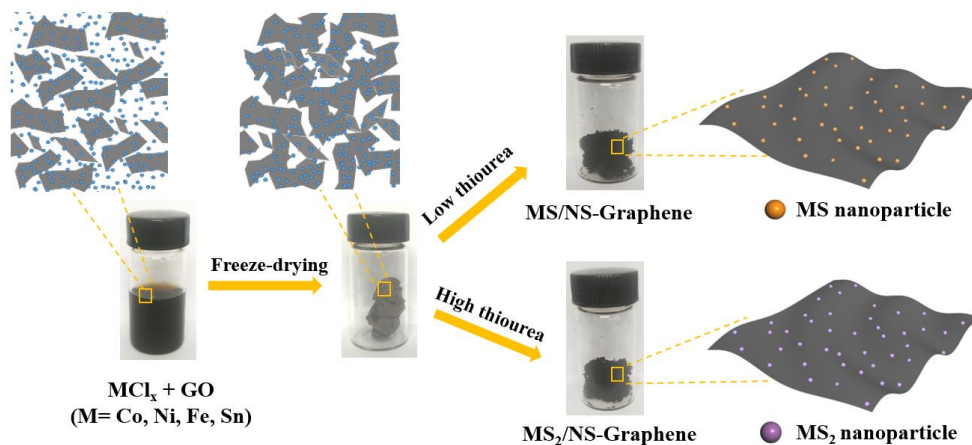


Figure S1 Schematic illustration for the synthesis process of various MS<sub>2</sub>/NS-G and MS/NS-G hybrid materials (M= Co, Fe, Ni and Sn).

## S2. The XRD pattern and TEM image of NS-G sample

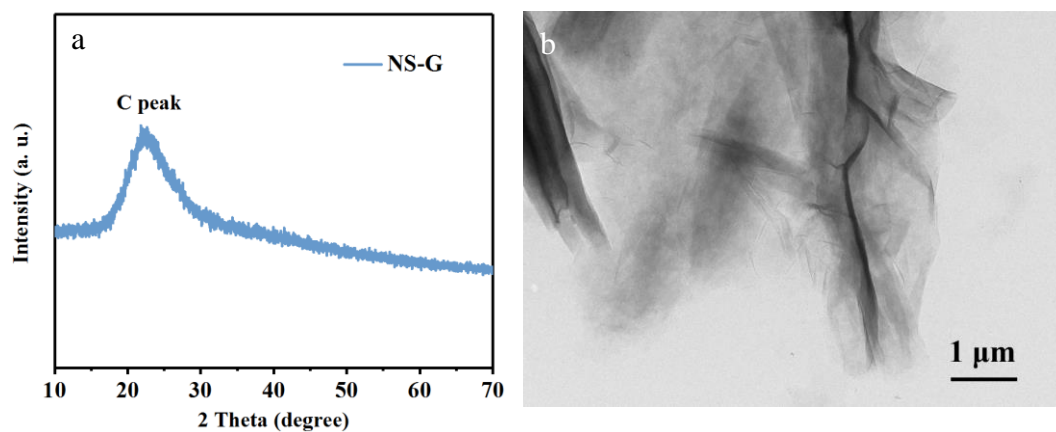


Figure S2 The a) XRD pattern and b) TEM image of as-obtained NS-G product.

### S3. XRD patterns of CoS<sub>x</sub>/NS-G sample

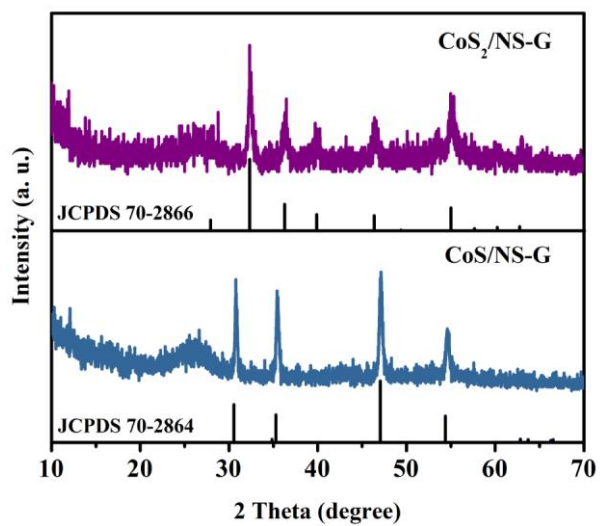


Figure S3 XRD patterns of as-prepared CoS<sub>2</sub>/NS-G and CoS/NS-G hybrid materials

### S4. TEM characterizations of as-prepared CoS/NS-G sample

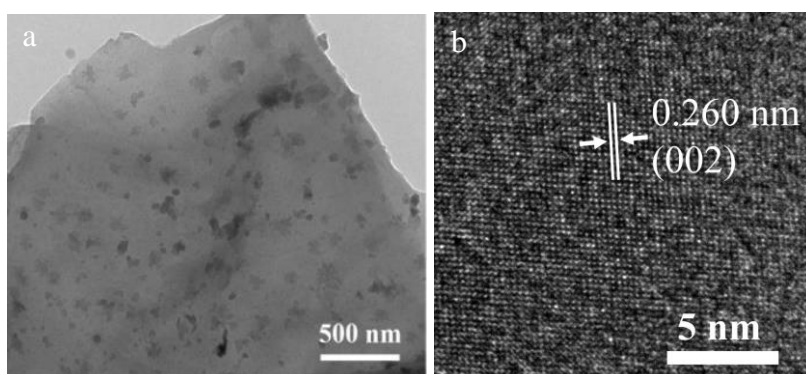


Figure S4 a) TEM image and b) corresponding HRTEM image of CoS/NS-G hybrid product.



### S5. The EDS spectrum of as-prepared CoS<sub>2</sub>/NS-G product

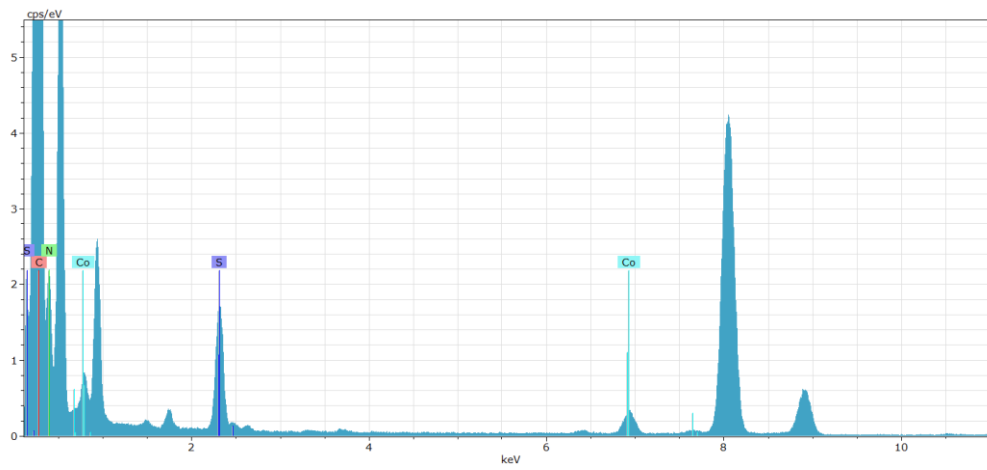


Figure S5 The EDS spectrum of as-prepared CoS<sub>2</sub>/NS-G hybrid.

## S6. The EDS spectrum and elemental mapping images of CoS/NS-G product

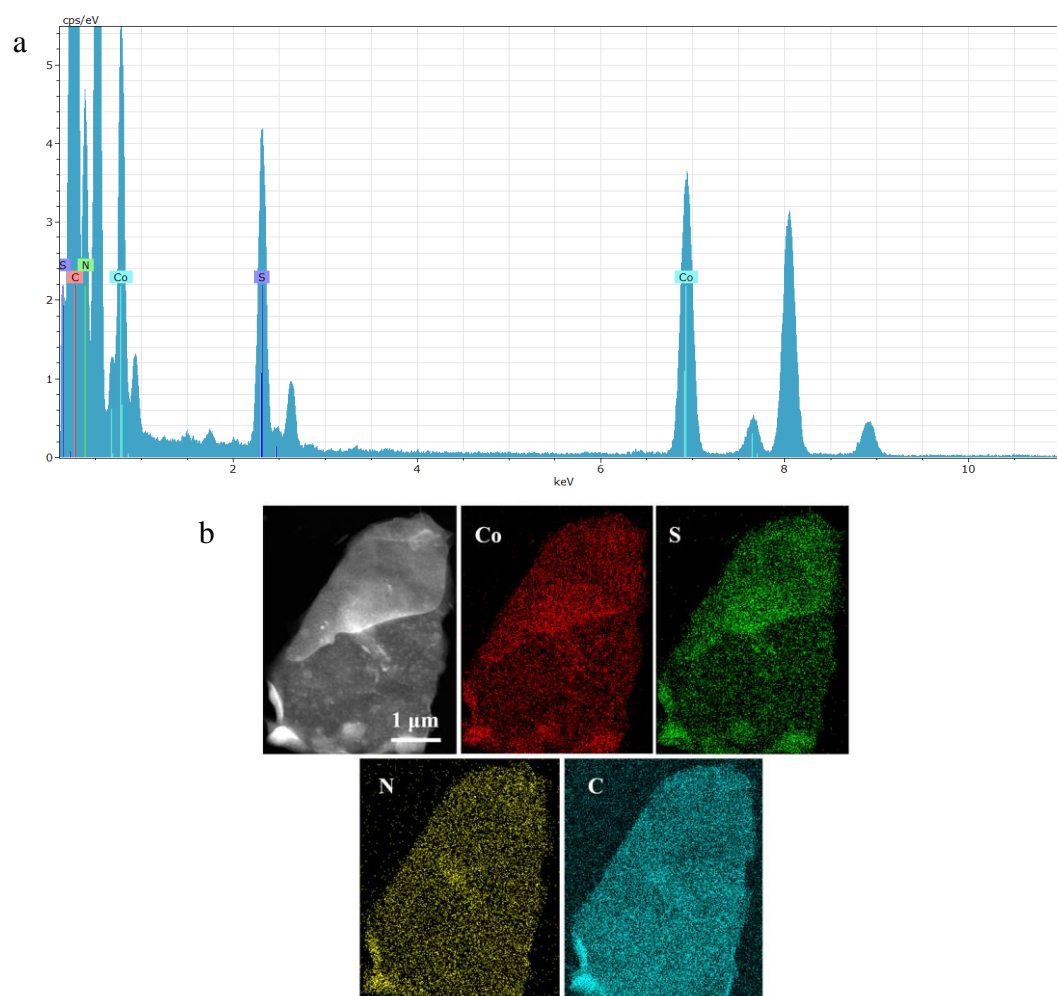


Figure S6 a) The EDS spectrum, b) HAADF-STEM image and corresponding elemental mapping for CoS/NS-G hybrid.

### S7. The N 1s spectra of CoS<sub>2</sub>/NS-G and CoS/NS-G products

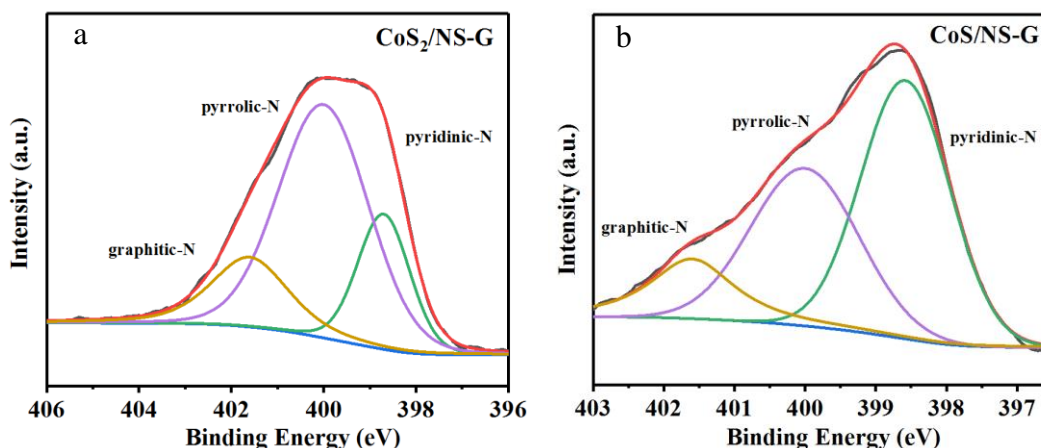


Figure S7 The N 1s spectra for a) CoS<sub>2</sub>/NS-G and b) CoS/NS-G hybrids.

### S8. Absolute calibration of the indophenol blue method using ammonium chloride solutions of known concentration as standards

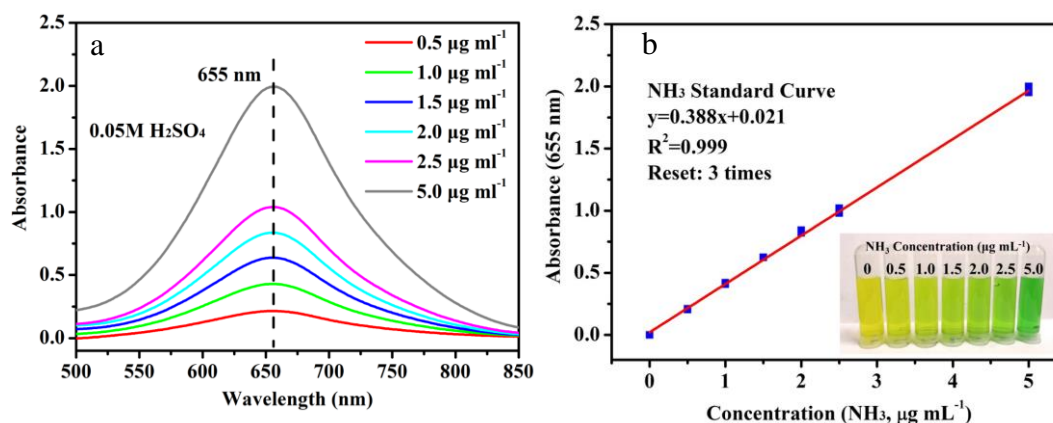
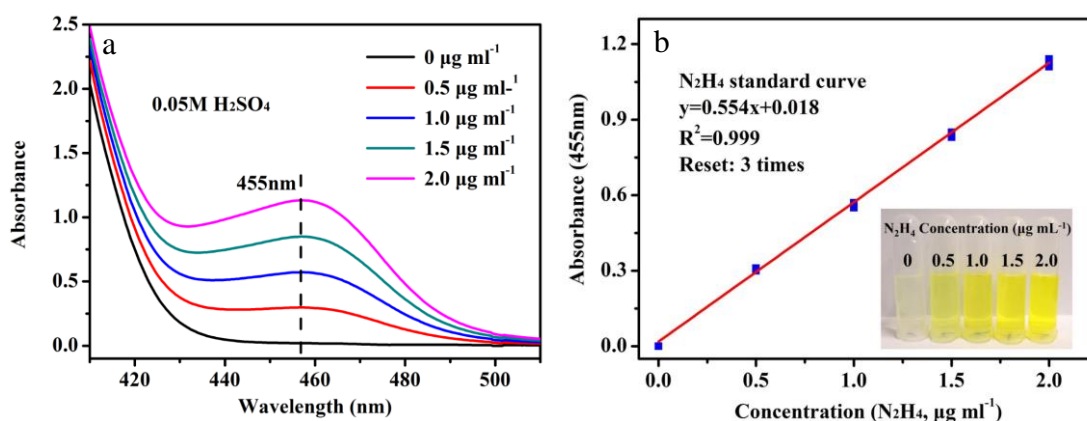


Figure S8 a) UV-vis curves of indophenol assays with NH<sub>4</sub><sup>+</sup> ions after incubated for 2 hours and b) calibration curve used for estimation of NH<sub>3</sub> by NH<sub>4</sub><sup>+</sup> ion of different concentrations. The absorbance at 655 nm was measured by UV-vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with NH<sub>4</sub><sup>+</sup> ion concentration ( $y = 0.388x + 0.021$ ,  $R^2=0.999$ ) of three times independent calibration curves. The inset of b) shows the chromogenic reaction of indophenol indicator with NH<sub>4</sub><sup>+</sup> ions.

### S9. Absolute calibration of the Watt and Chrisp method using hydrazine hydrate solutions of known concentration as standards



### S10. Yield Rate of $NH_3$ and Faradaic efficiency of CoS/NS-G at each given potential

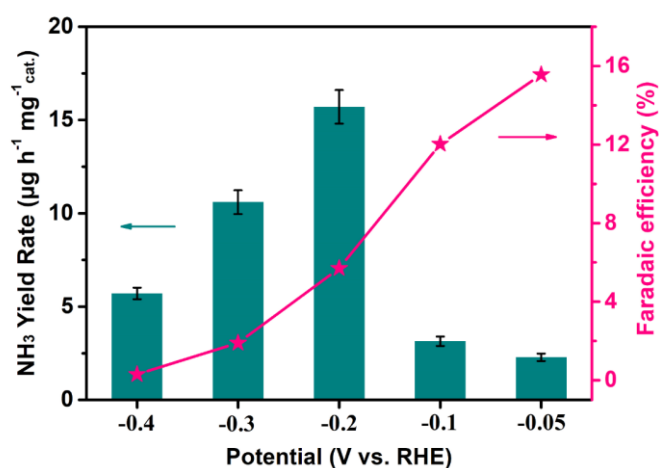


Figure S10  $NH_3$  yield and Faradaic efficiency of as-prepared CoS/NS-G catalyst at each given potential.

### S11. Yield rate of $\text{NH}_3$ for different catalysts at $-0.2\text{ V}$

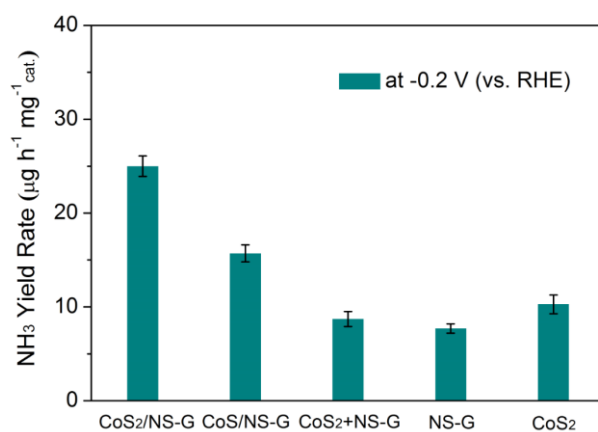


Figure S11 Yield rate of  $\text{NH}_3$  for different catalysts at  $-0.2\text{ V}$  (vs. RHE) at room temperature and ambient pressure.

## S12. XRD patterns and TEM images of other MS<sub>2</sub>/NS-G and MS/NS-G samples

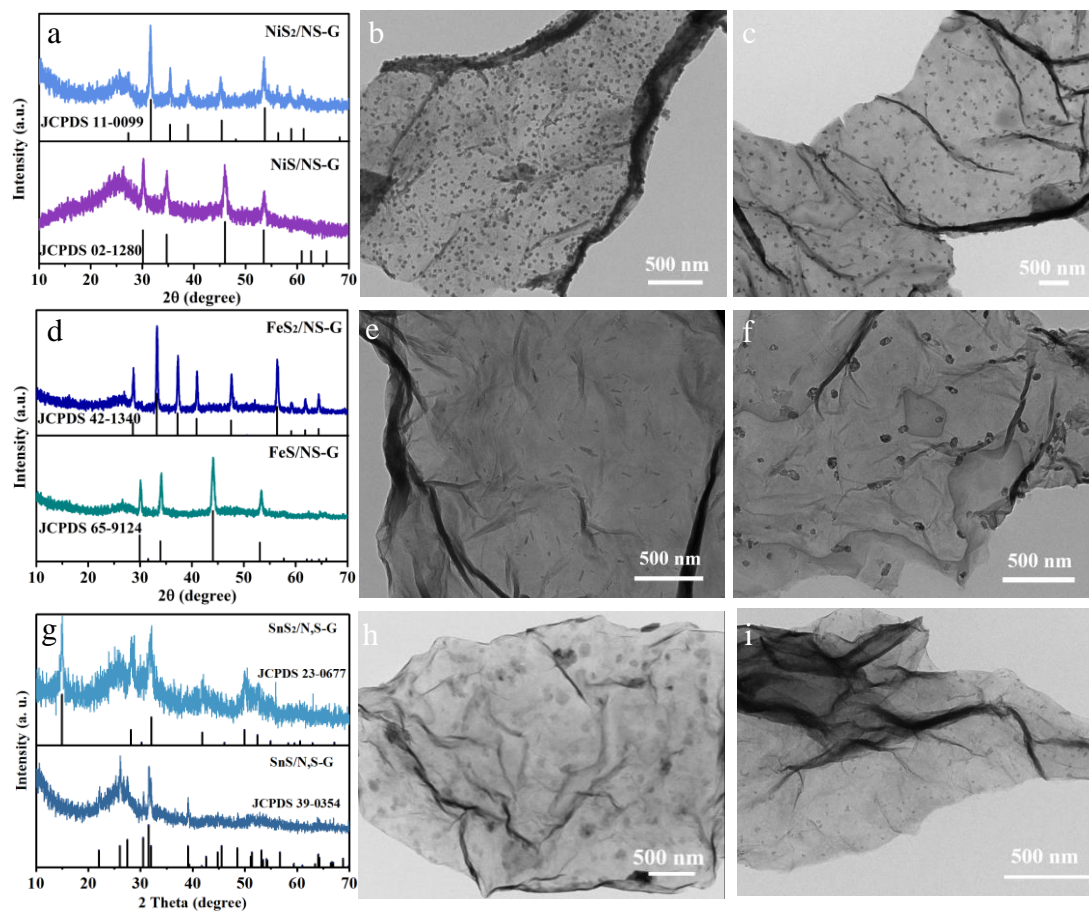


Figure S12 a-c) XRD patterns and TEM images of NiS<sub>2</sub>/NS-G and NiS/NS-G hybrids; d-f) XRD patterns and TEM images of FeS<sub>2</sub>/NS-G and FeS/NS-G hybrids; g-i) XRD patterns and TEM images of SnS<sub>2</sub>/NS-G and SnS/NS-G hybrids.

### S13. The XPS spectra of as-prepared NiS<sub>2</sub>/NS-G and NiS/NS-G products

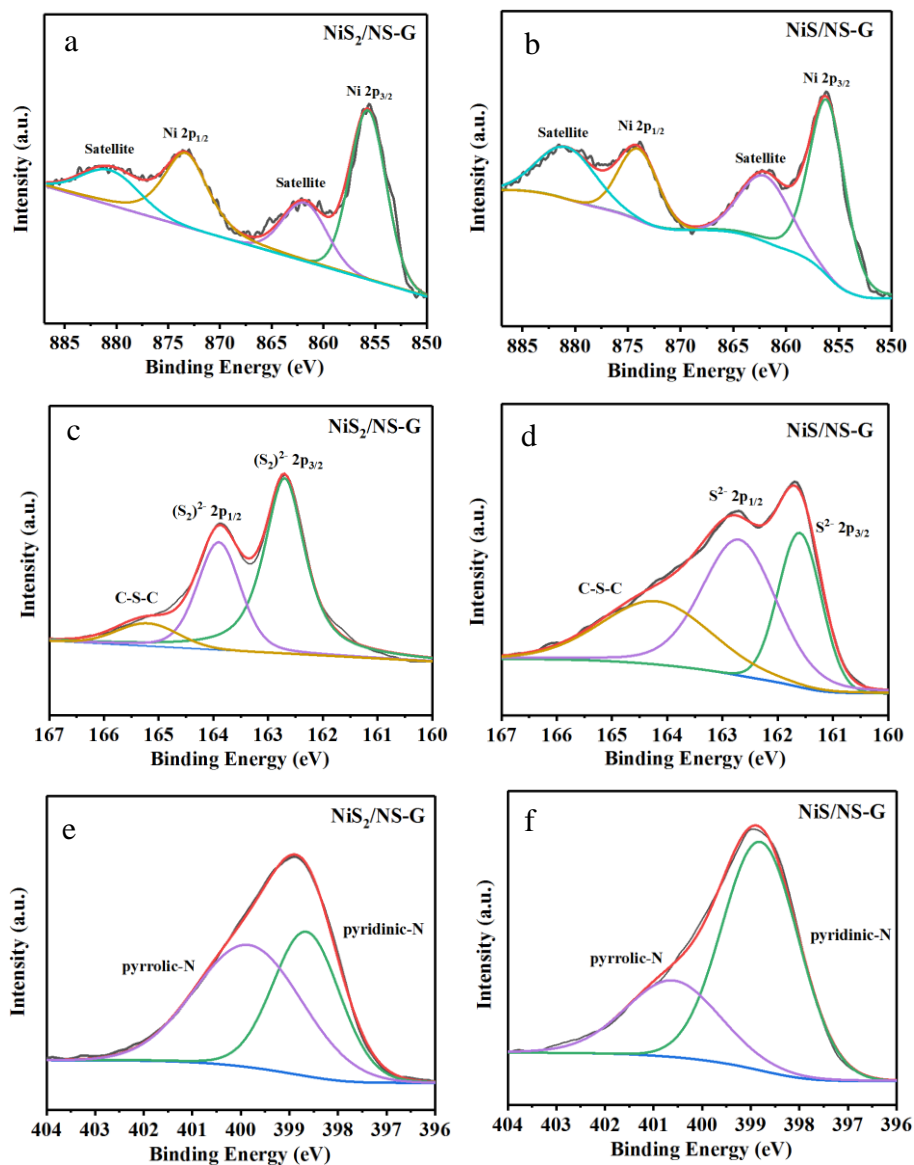


Figure S13 The a-b) Ni 2p, c-d) S 2p as well as e-f) N 1s spectra of as-obtained NiS<sub>2</sub>/NS-G and NiS/NS-G hybrid.

### S14. The XPS spectra of as-prepared FeS<sub>2</sub>/NS-G and FeS/NS-G products

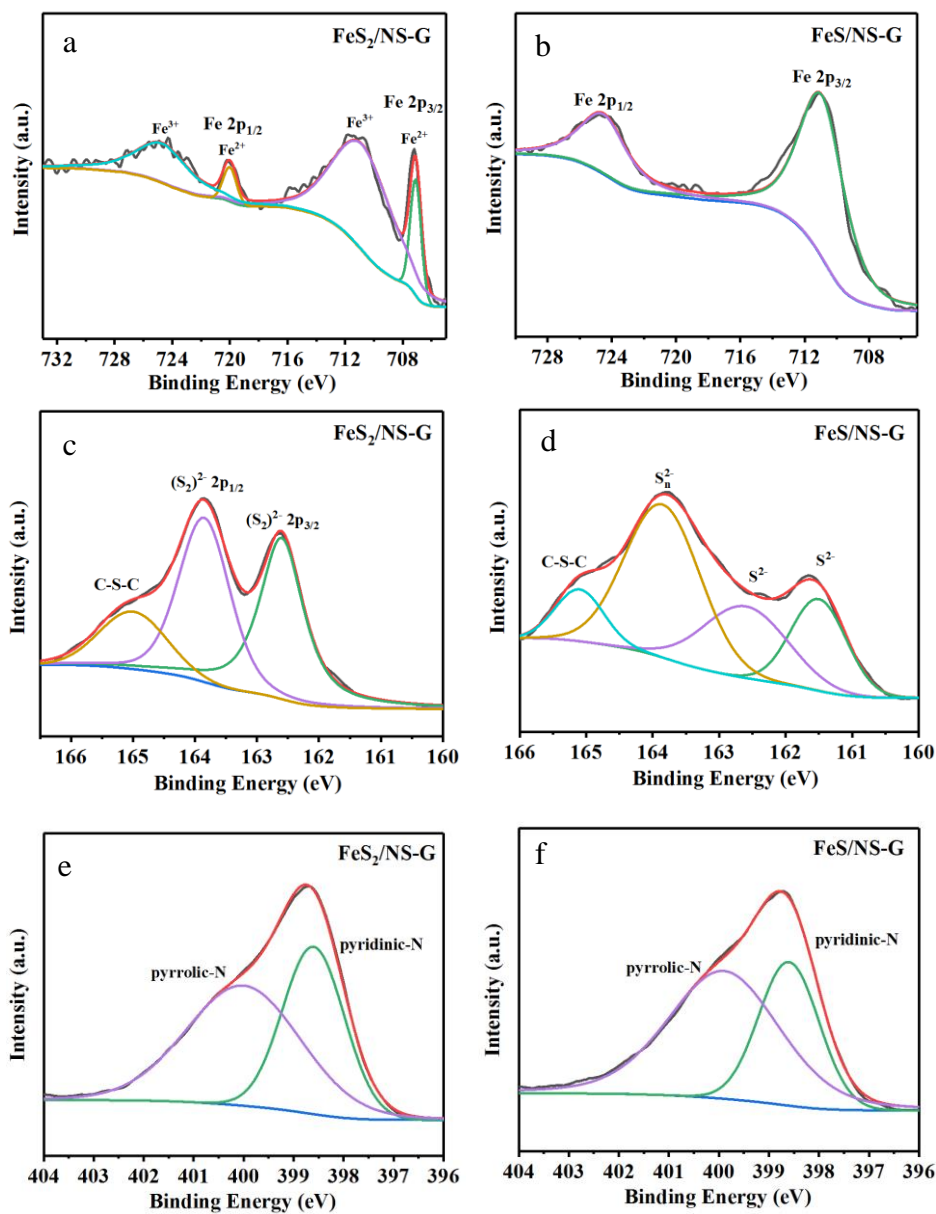


Figure S14 The a-b) Fe 2p, c-d) S 2p as well as e-f) N 1s spectra of as-obtained FeS<sub>2</sub>/NS-G and FeS/NS-G hybrid.



### S15. The XPS spectra of as-prepared SnS<sub>2</sub>/NS-G and SnS/NS-G products

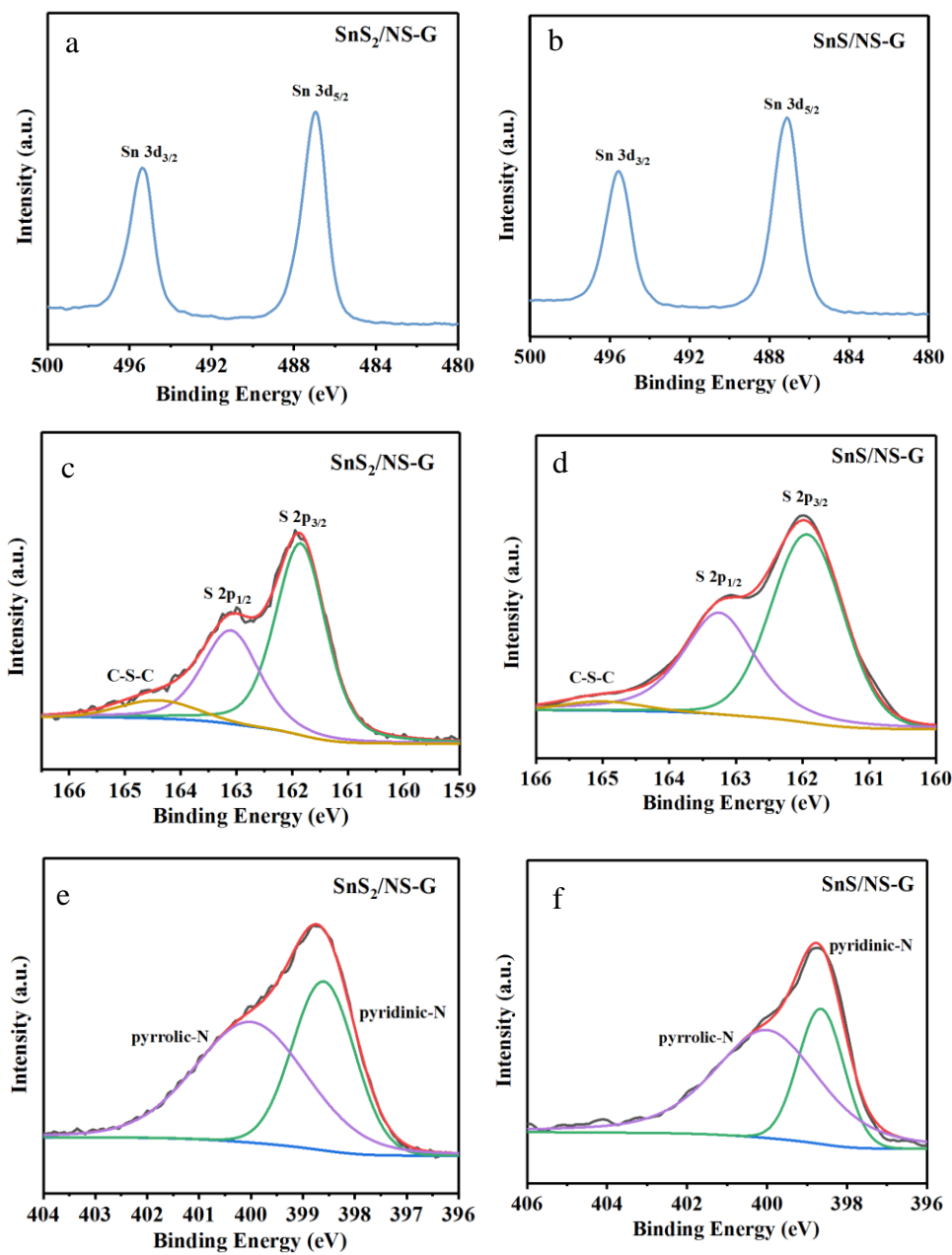


Figure S15 The a-b) Sn 3d, c-d) S 2p as well as e-f) N 1s spectra of as-obtained SnS<sub>2</sub>/NS-G and SnS/NS-G hybrid.

### S16. Comparison of NH<sub>3</sub> yield rate for other strong coupled hybrids.

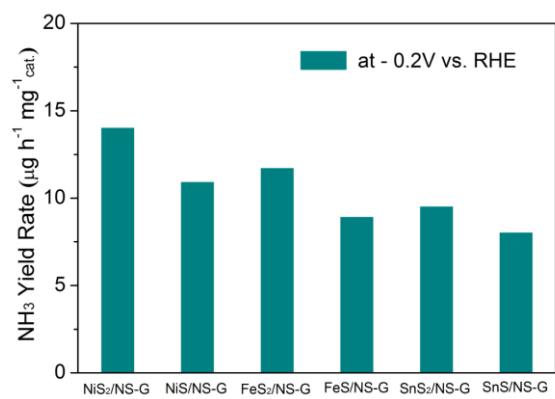


Figure S16 Comparison of NH<sub>3</sub> yield rate for other strong coupled hybrids.

**S17. TEM images and particle size distribution of CoS<sub>2</sub>/NS-G hybrids synthesized by different amount of cobalt salt.**

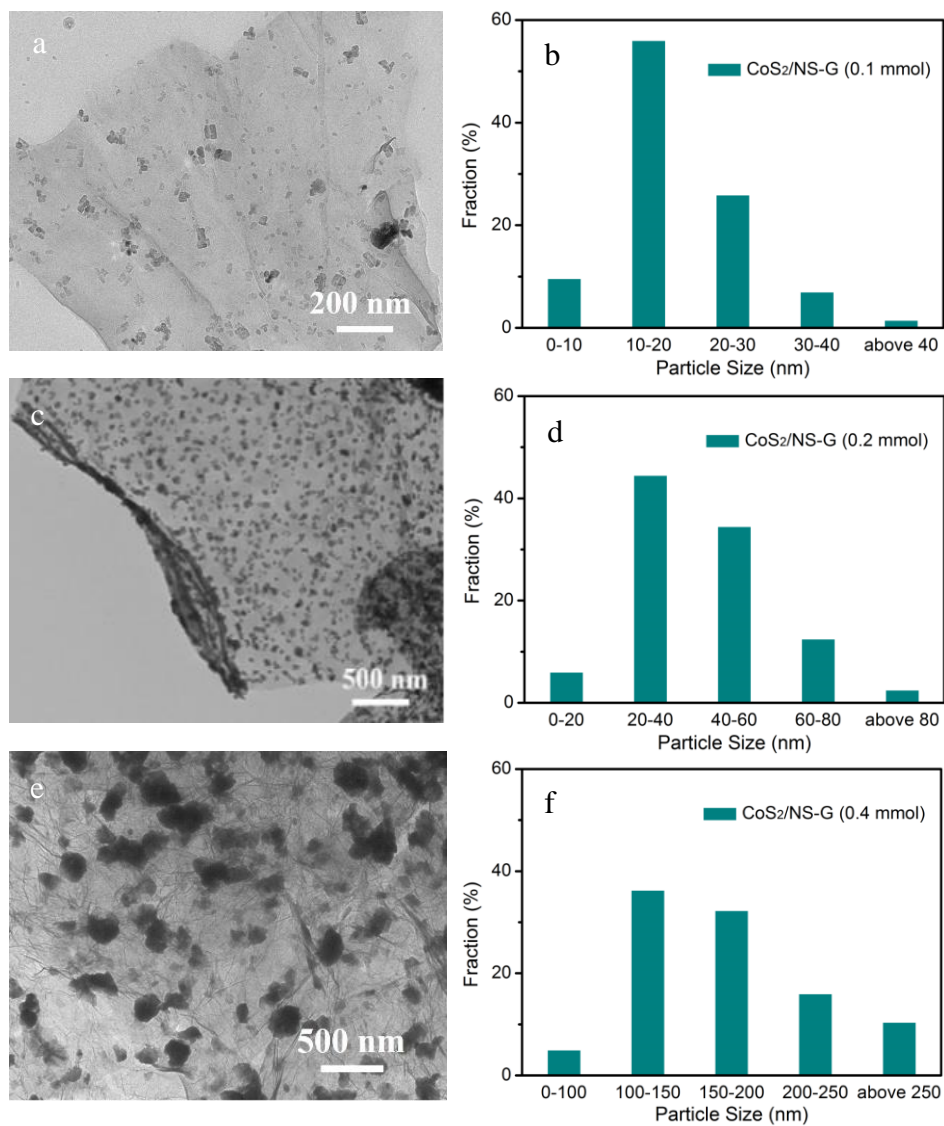


Figure S17 TEM images and particle size distribution of CoS<sub>2</sub>/NS-G hybrids synthesized by different amount of cobalt salt: a-b) 0.1 mmol CoCl<sub>2</sub>; c-d) 0.2 mmol CoCl<sub>2</sub>; e-f) 0.4 mmol CoCl<sub>2</sub>.

**S18. Chronoamperometric response of as-prepared CoS<sub>2</sub>/NS-G hybrid.**

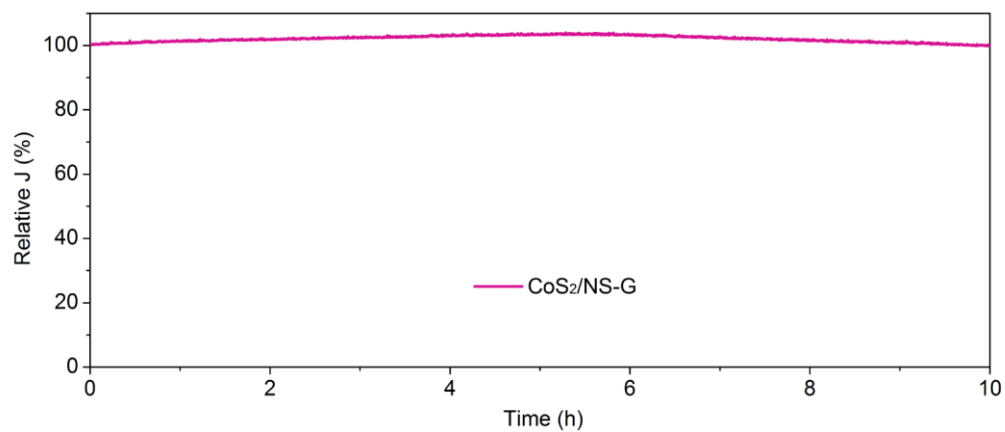


Figure S18 Chronoamperometric response of as-prepared CoS<sub>2</sub>/NS-G catalyst in N<sub>2</sub>-saturated 0.05M H<sub>2</sub>SO<sub>4</sub> solution.

**S19. TEM image of CoS<sub>2</sub>/NS-G catalyst after NRR test.**

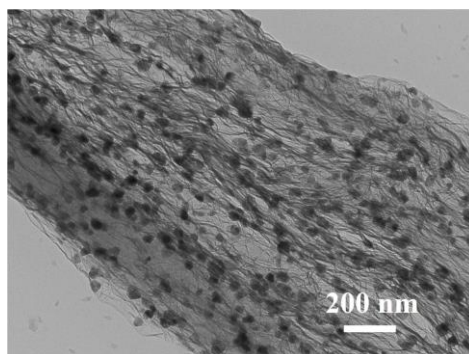


Figure S19 TEM image of CoS<sub>2</sub>/NS-G hybrid after NRR test.

**S20. The XPS spectra and XRD patterns of as-prepared CoS<sub>2</sub>/NS-G before and after NRR test.**

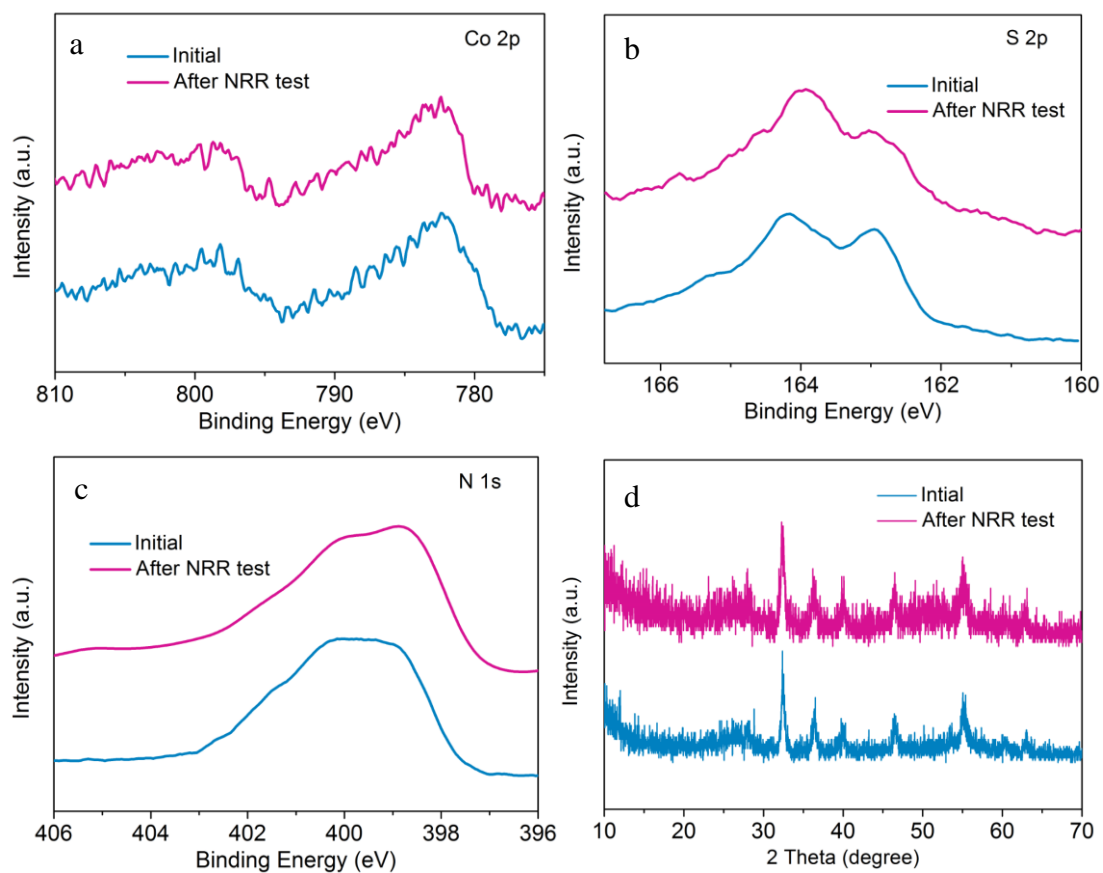


Figure S20 High-resolution XPS spectra of a) Co 2p, b) S 2p and c) N 1s and d) XRD patterns for the CoS<sub>2</sub>/NS-G hybrid before and after NRR test.

## S21. Schematic illustration for NH<sub>3</sub> electrosynthesis by catalysts of CoS<sub>x</sub>/NS-G under ambient conditions.

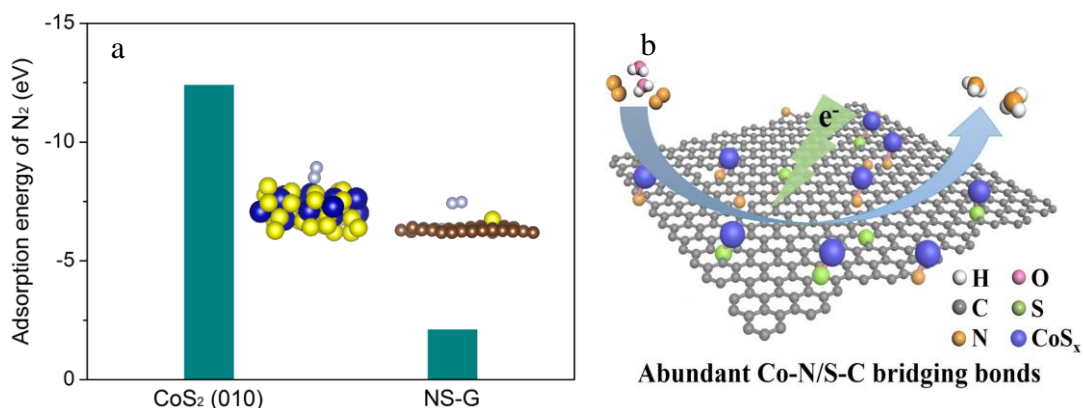


Figure S21 a) Optimized structures of the systems formed by adsorbing a nitrogen and comparison of nitrogen adsorption energy for CoS<sub>2</sub> and NS-G (Co: blue; S: yellow; C: brown; N: gray). b) Schematic illustration for NH<sub>3</sub> electrosynthesis by catalysts of CoS<sub>x</sub>/NS-G under ambient conditions.

First-principle calculations were performed by the density functional theory (DFT) using the Vienna Ab-initio Simulation Package (VASP) package<sup>S2</sup>. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was used to describe the electronic exchange and correlation effects<sup>S3</sup>. The K points meshing for Brillouin zone was set up as a  $3 \times 3 \times 1$  grid Monkhorst Pack Scheme. The spin-polarized simulation was run with a cutoff energy of 400 eV throughout the computations. Due to the periodic conditions, the vacuum layer was set to be 15 Å along z-axis to avoid interactions between neighboring images. The calculations convergence of energies was  $10^{-6}$  eV and force was 0.01 eV/Å. In consideration of Vander Waals force between adsorptions and adsorbents, Grimme's D2 (DFT-D2) was adopted in adsorption process. As shown in Figure S21a, N<sub>2</sub> molecule is more likely to be captured by the Co-site in the (010) surface for CoS<sub>2</sub> while NS-G exhibit little absorption for nitrogen. Cobalt sulfide exhibits N<sub>2</sub> adsorption energy of -12.39 eV, which is lower than

NS-G (-2.09 eV). This result demonstrates that nitrogen is easier to adsorb onto the cobalt sulfide nanoparticles for CoS<sub>2</sub>/NS-G hybrid during NRR process.

**S22. The reaction kinetics and electron transport rates have been further determined using the Butler-Volmer approach.**

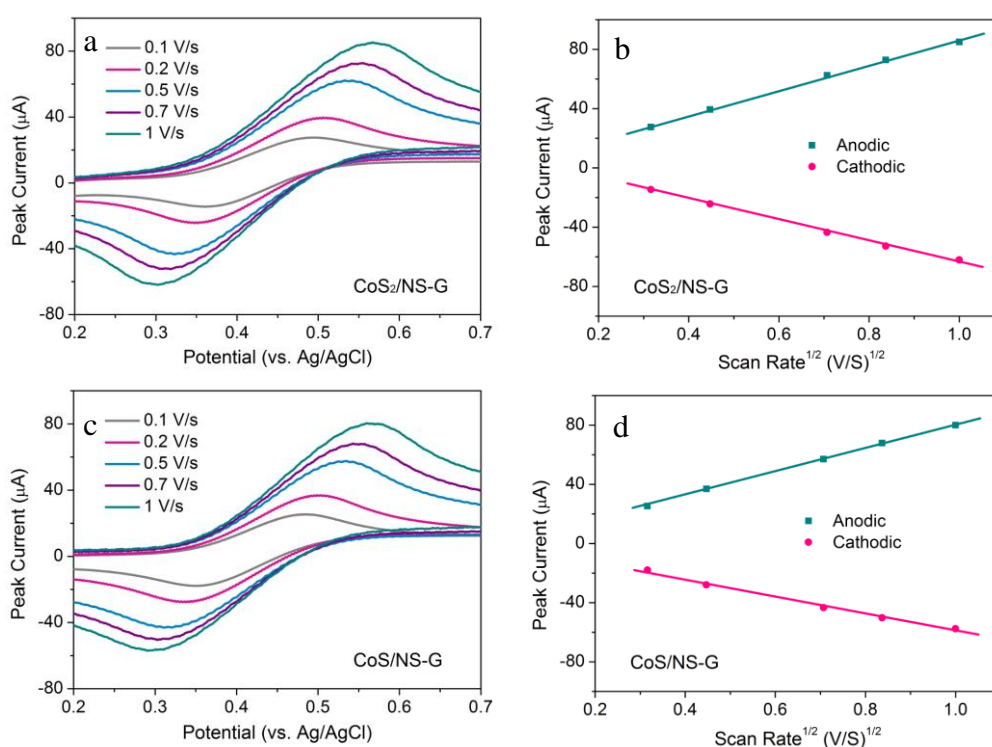


Figure S22 Variable scan rate cyclic voltammetry curves and corresponding current density vs scan rate<sup>1/2</sup> plot of CoS<sub>2</sub>/NS-G (a, b) and CoS/NS-G (c, d) by using ferrocene as model analyte.

The reaction kinetics and electron transport rates have been further determined using the Butler-Volmer approach<sup>S4,S5</sup>. As shown in Figure S22a and S22c, the anodic and cathodic peaks separated with the increasing scan rate by using ferrocene as model analyte. The apparent rate constant of these hybrids can be calculated according to the

Laviron formalism using the following set of equation<sup>S4</sup>:

$$E_{p,c} = E^{o'} - \frac{2.3RT}{\alpha nF} \log\left[\frac{\alpha nFv}{RTk_{app}}\right]$$
$$E_{p,a} = E^{o'} - \frac{2.3RT}{(1-\alpha)nF} \log\left[\frac{(1-\alpha)nFv}{RTk_{app}}\right]$$

where  $E_{p,a}$  is the potential of the anodic peak,  $E_{p,c}$  is the potential of the cathodic peak,  $E^{o'}$  is the formal potential calculated by averaging the anodic and cathodic potentials at slow scan rates,  $v$  is the scan rate,  $\alpha$  is the electron-transfer coefficient,  $k_{app}$  is the apparent rate constant,  $R$  is the ideal gas constant,  $T$  is the absolute temperature,  $F$  is the Faraday constant, and  $n$  is the number of electrons transferred. The electron transfer rates of  $19.5 \text{ s}^{-1}$  and  $7.8 \text{ s}^{-1}$  were measured for  $\text{CoS}_2/\text{NS-G}$  and  $\text{CoS}/\text{NS-G}$ , respectively. Thus it can be concluded that  $\text{CoS}_2/\text{NS-G}$  exhibits superior charge transfer ability than that of  $\text{CoS}/\text{NS-G}$  which is consist with the XANES result.



### S23. Product of hydrazine detected by the Watt and Chrisp method.

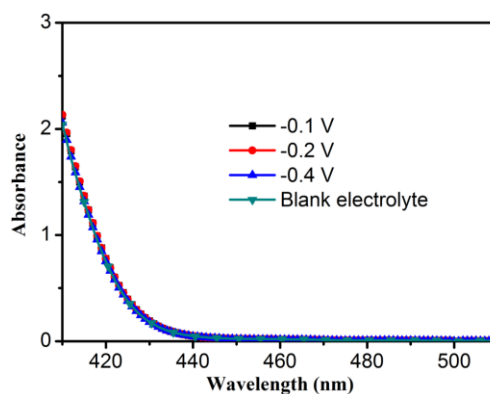


Figure S23 UV-vis absorption spectra of the electrolytes stained by the Watt and Chrisp method after potentiostatic tests under different conditions.

Chronoamperometric experiments under  $N_2$  gas flow were implemented for  $CoS_2/NS-G$  hybrid under different potentials. The hydrazine was spectrophotometrically detected by the Watt and Chrisp method. And the absorbance at 455 nm was measured by UV-vis spectrophotometer which implies the formation of hydrazine during NRR process. The corresponding UV-Vis absorption spectra are shown in **Figure S23**, the intensity of absorption peak at 455 nm for the electrolyte tested at different potentials is the same as blank electrolyte, which suggests there was no product of hydrazine has been produced in NRR process. Therefore, cobalt sulfide hybrid cannot catalyze nitrogen being reduced to hydrazine in the electrochemical test.

## S24. Charge transfer resistances of different catalysts.

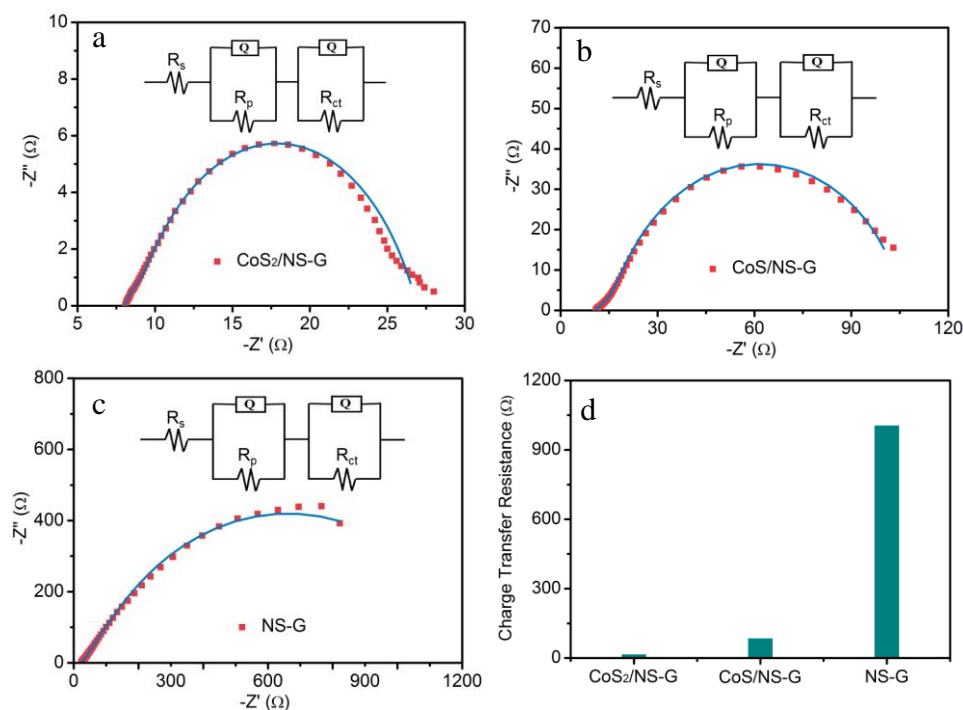


Figure S24 Nyquist plots of a) CoS<sub>2</sub>/NS-G, b) CoS/NS-G and c) NS-G. Inset: the equivalent circuit used for fitting the Nyquist plots. d) Comparison of the charge transfer resistance ( $R_{ct}$ ) of CoS<sub>2</sub>/NS-G, CoS/NS-G and NS-G catalysts.

The as-obtained EIS data were fitted by using a simplified circuit model (Figure S24a-c insert). As shown in Figure S24a-c, two clear semicircles were observed, one in the high-frequency region related to the surface porosity and the other in the low-frequency region related to the charge transfer process. In Figure S24d, the charge transfer resistance ( $R_{ct}$ ) of CoS<sub>2</sub>/NS-G, CoS/NS-G and NS-G during NRR process are 17.9  $\Omega$ , 87.3  $\Omega$  and 1007.0  $\Omega$ , respectively. CoS<sub>2</sub>/NS-G catalyst exhibits smallest charge transfer resistance than that of CoS/NS-G and NS-G, indicating that strong Co-N/S-C bonds lead to faster reaction kinetics by accelerating electron transfer.

### S25. $^{15}\text{N}$ isotope labeling experiment.

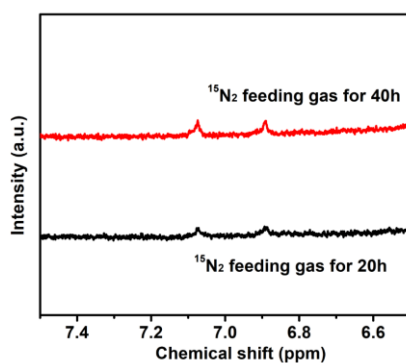


Figure S25 NMR spectra for the electrolyte after NRR test for different durations at -0.2 V in  $^{15}\text{N}_2$ .

### S26. UV-vis absorption spectra of different electrolytes.

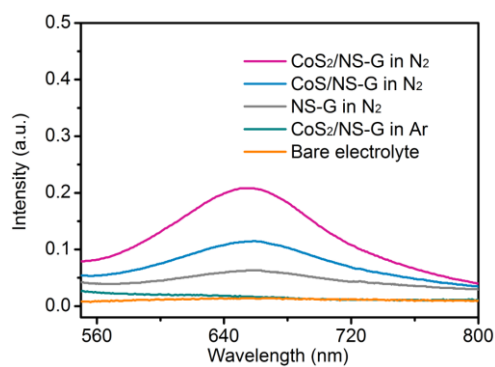


Figure S26 UV-vis absorption spectra of the electrolytes stained with indophenol indicator after potentiostatic tests under different conditions.

## S27. The relationship of NH<sub>3</sub> yield rate and interfacial interactions.

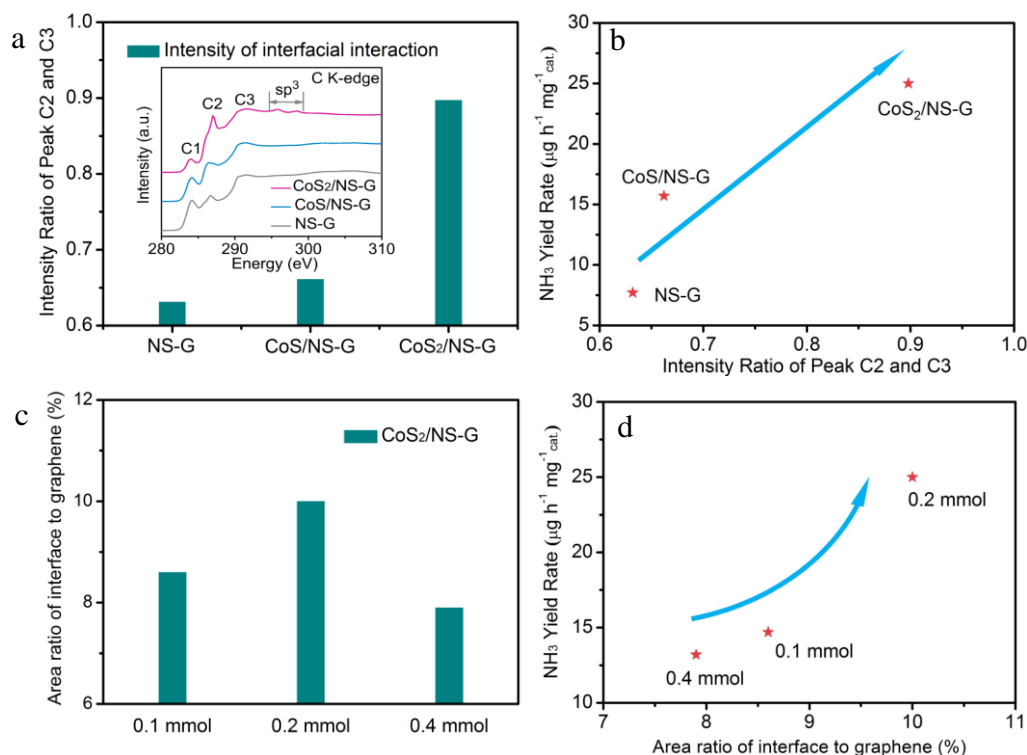


Figure S27 a) Comparison of the interfacial intensity of CoS<sub>2</sub>/NS-G, CoS/NS-G and NS-G. Inset: C K-edge XANES spectra of CoS<sub>2</sub>/NS-G, CoS/NS-G and NS-G. b) The relationship of interfacial intensity and NH<sub>3</sub> yield rate. c) Comparison of interface area of CoS<sub>2</sub>/NS-G synthesized by different amount of cobalt salt. d) The relationship of interface area and NH<sub>3</sub> yield rate.

To characterize the extent of the interfacial interactions, the normalized intensity ratio of peak C2 relative to C3 are shown in Figure S27a. Compared with CoS/NS-G, CoS<sub>2</sub>/NS-G exhibits an increased intensity ratio of C2/C3, which demonstrates that a stronger interfacial interaction was constructed in CoS<sub>2</sub>/NS-G and would enable superior charge transfer ability for NRR. The relationship of NH<sub>3</sub> yield rate and interfacial interactions is summarized in Figure S27b. With the increase of interfacial interaction intensity (intensity ratio of peak C2/peak C3), the hybrids exhibits an improved NRR efficiency with NH<sub>3</sub> yield rate as indicator.

The interface conducting area was represented by calculating the nanoparticle area

in TEM images. Figure S27c shows the area ratio of interface to graphene support. The CoS<sub>2</sub>/NS-G (0.2 mmol) exhibit largest interfacial area than that of 0.1 mmol and 0.4 mmol. The relationship of NRR efficiency and interface area is summarized in Figure S27d. With the increase of interface area ratio, the strong-coupled CoS<sub>2</sub>/NS-G exhibits an improved NH<sub>3</sub> yield rate, which further confirms the important role of interfacial engineering.

### S28. Stability test of CoS<sub>2</sub>/NS-G for NRR.

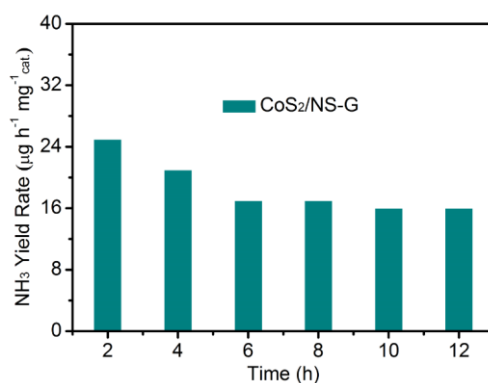


Figure S28 NH<sub>3</sub> yield rate at -0.2V of CoS<sub>2</sub>/NS-G hybrid material under different reaction

Chronoamperometric experiments under N<sub>2</sub> gas flow were implemented to verify the NRR stability for CoS<sub>2</sub>/NS-G hybrid. The ammonia was spectrophotometrically determined by the indophenol blue method. Figure S28 shows the NH<sub>3</sub> yield rate at 0.2V of CoS<sub>2</sub>/NS-G hybrid material under different reaction time. CoS<sub>2</sub>/NS-G exhibit good stability with NH<sub>3</sub> yield rate of 16.1 µg h<sup>-1</sup> mg<sup>-1</sup> cat. after 12 hours constant voltage test.

**Table S1. The intensity ratio of peak C1 and C2 relative to C3 in C K-edge XANES spectra of as-prepared hybrid catalysts.**

Catalysts	C1/C3	C2/C3
NS-G	0.547	0.632
CoS/NS-G	0.406	0.662
CoS <sub>2</sub> /NS-G	0.209	0.898

**Table S2. Comparison of NRR catalytic performance for well-developed electrocatalysts recorded at room temperature and atmospheric pressure**

	System/Catalyst	Conditions	Yield and Faradaic efficiency	Reference
<b>Non-Noble-Metal based Electrocatalysts</b>	Carbon rod   0.05 M H <sub>2</sub> SO <sub>4</sub>   CoS <sub>2</sub> /NS-G	Room temperature and atmospheric pressure	25.0 $\mu\text{g h}^{-1} \text{mg}^{-1}$ (-0.2 V) and 25.9% Faradaic efficiency (-0.05 V)	This work
	Carbon rod   0.05 M H <sub>2</sub> SO <sub>4</sub>   CoS/NS-G	Room temperature and atmospheric pressure	15.7 $\mu\text{g h}^{-1} \text{mg}^{-1}$ (-0.2 V) and 15.6% Faradaic efficiency (-0.05 V)	This work
	Pt foil   0.1 M HCl  Polymeric Carbon Nitride	20 °C and atmospheric pressure	8.09 $\mu\text{g h}^{-1} \text{mg}^{-1}$ (-0.2 V) and 11.59% Faradaic efficiency (-0.05 V)	24
	Carbon rod   0.1M KOH  MOF derived N-doped	Room temperature and atmospheric pressure	$3.4 \times 10^{-6} \text{ mol cm}^{-2} \text{ h}^{-1}$ (-0.3 V) and 10.2% Faradaic efficiency (-0.3 V)	22
	Pt plate  0.1 M HCl  Bi <sub>4</sub> V <sub>2</sub> O <sub>11</sub> - CeO <sub>2</sub> hybrid nanofibers	Room temperature and atmospheric pressure	23.21 $\mu\text{g h}^{-1} \text{mg}^{-1}$ (-0.2 V) and 10.16% Faradaic efficiency (-0.2 V)	25
	Pt plate  0.5 M Li <sub>2</sub> SO <sub>4</sub>   PEBCD	Room temperature and atmospheric pressure	$\sim 2.01 \mu\text{g h}^{-1} \text{cm}^{-2}$ (-0.7 V) and 2.91% Faradaic efficiency (-0.4 V)	S6
	Pt plate   0.1 M HCl  Nitrogen-Doped Porous Carbon	Room temperature and atmospheric pressure	15.7 $\mu\text{g h}^{-1} \text{mg}^{-1}$ (-0.2 V) and 1.45% Faradaic efficiency (-	23

			0.2 V)	
	Pt foil   0.05 M H <sub>2</sub> SO <sub>4</sub>   N-Doped Porous Carbon	Room temperature and atmospheric pressure	1.40 mmol g <sup>-1</sup> h <sup>-1</sup> (-0.9 V) and 1.42% Faradaic efficiency (-0.9 V)	S7
	Pt wire   3.0 M KCl   Fe <sub>2</sub> O <sub>3</sub> -CNT	20 °C and atmospheric pressure	2.2*10 <sup>-3</sup> g m <sup>-2</sup> h <sup>-1</sup>	17
<b>Noble-Metal based Electrocatalysts</b>	Pt mesh   0.5 M Li <sub>2</sub> ClO <sub>4</sub>   Au nanocages	20 °C and atmospheric pressure	3.9 µg cm <sup>-2</sup> h <sup>-1</sup> (-0.5 V) and 30.2% Faradaic efficiency (-0.2 V)	S8
	Carbon rod   0.05 M H <sub>2</sub> SO <sub>4</sub>   Ru SAs/N-C	Room temperature and atmospheric	120.9 µg h <sup>-1</sup> mg <sup>-1</sup> (-0.2 V) and 29.6% Faradaic efficiency (-0.2 V)	S9
	Pt plate   0.1 M HCl   amorphous-Au/CeO <sub>x</sub> -RGO	Room temperature and atmospheric pressure	8.3 µg h <sup>-1</sup> mg <sub>pd</sub> <sup>-1</sup> (-0.2 V) and 10.10% Faradaic efficiency (-0.2 V)	S10
	Pt gauze   0.1 M PBS   Pd/C	Room temperature and atmospheric pressure	4.9 µg h <sup>-1</sup> mg <sup>-1</sup> (-0.05 V) and 8.2% Faradaic efficiency (0.1 V)	13
	Pt plate   0.1 M HCl   Au-TiO <sub>2</sub> sub-nanocluster	Room temperature and atmospheric pressure	21.4 µg h <sup>-1</sup> mg <sup>-1</sup> (-0.2 V) and 8.11% Faradaic efficiency (-0.2 V)	11
	Pt plate   0.1 M KOH   Au nanorods	Room temperature and atmospheric pressure	1.648 µg h <sup>-1</sup> cm <sup>-2</sup> (-0.2 V) and ~4% Faradaic efficiency (-0.2 V)	12
	Pt plate   0.1 M KOH   PdCu/rGO	Room temperature and atmospheric pressure	2.8 µg h <sup>-1</sup> cm <sup>-2</sup> (-0.2V) and ~4.5% Faradaic efficiency (0 V)	14
	Carbon rod   0.1 M KOH   Rh nanosheet	Room temperature and atmospheric pressure	23.88 mg h <sup>-1</sup> mg <sup>-1</sup> (-0.2 V) and ~0.65% Faradaic efficiency (0 V)	S11

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