Supporting Information for

Chemical Coupled NiCoS/C Nanocages as Efficient Electrocatalyst for Nitrogen Reduction Reaction

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#Equal Contribution

Experimental Section

Preparation of ZIF-67 nanocubes. 150 mg of $Co(NO_3)_2•6H_2O$ and 10 mg of hexadecyl trimethyl ammonium bromide (CTAB) were dissolved in 3 mL and 2 mL of deionized water, respectively, and stirred for 5 minutes to form a mixed solution. 2.25 g of 2-methylimidazole was weighed, dissolved in 35 mL of deionized water, and quickly added to the above mixed solution under stirring. After stirring for 10 min, it was allowed to stand at room temperature for 5 h. It was washed three times with ethanol and dried at 60 °C to obtain ZIF-67 nanocubes.

Preparation of NiCo-LDH@ZIF-67 nanoboxes. 20 mg of ZIF-67 was dissolved in 10 mL of ethanol to obtain a solution A. 100 mg of $Ni(NO_3)_2•6H_2O$ was dissolved in 10 mL of ethanol to obtain a solution B. The solution A and the solution B were uniformly mixed, ultrasonicated until the purple color was removed, centrifuged, washed once with ethanol, and dried at 60 °C to obtain NiCo-LDH@ZIF-67 nano-boxes.

Preparation of NiCoS/C nanocages. 20 mg NiCo-LDH@ZIF-67 sample and 100 mg of sulfur powder were placed at both ends of the magnetic boat and calcined in a tube furnace. The final product NiCoS/C nano-box catalyst was obtained by first passing N_2 gas for 30 min at room temperature and heating to 350 °C at 1.5 °C min^{-1} for 2 h.

Preparation of NiCoS nanocages. ZIF-67 in the NiCo-LDH@ZIF-67 nanoboxes was removed. First, 20 mg of the NiCo-LDH@**ZIF-67** nanoboxes was dispersed in 20 mL of deionized water. The mixed solution was heated to 85 °C until the purple color disappeared. Then the product was washed by ethanol for several times and dried at 60 °C overnight. The dried sample was further annealed with sulfur powder at 350 °C for 2 h with a ramp rate of 1.5 °C min^{-1} under a flow of nitrogen gas.

Characterization. X-ray diffraction analysis (XRD) was performed in the range of 2-80° in order to examine the composition of the sample on the X'Pert PRO MPD. Scanning electron microscopy (SEM) was performed on a Hitachi, S-4800 instrument to study the morphology and sample structure of the sample. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were tested on a JEM-2100UHR instrument, and operational analysis was performed at 200 KV, which was also used to study the structure and morphology of the sample. The sample can be analyzed by X-ray photoelectron spectroscopy (XPS) on a VG ESCALABMK II spectrometer with an AlKa (1486.6 eV) photon source. 1H NMR spectra were recorded on a Bruker 500 with Probe TXI using a 3 mm tube at a temperature of 25 °C. Temperature-programmed desorption (N_2-TPD) of N_2 experiments were conducted on a Quantachrome ChemBET Pulsar TPR/TPD. These two samples were first pretreated at 150 °C for 1 hour in a 50 mL/min He stream and then cooled to 50 °C under a He atmosphere. These samples were adsorbed to N_2 for 3 hours, and the remaining N_2 was purged by He for half an hour. Finally, the desorption of N_2 was carried out by heating from 50 °C to 350 °C at a rate of 10 °C min^{-1}.

Electrochemical measurements. All electrochemical performance tests were performed at room temperature using an electrochemical workstation (Shanghai Chenhua Instrument Corporation, China) and two electrolytic cell, which was connected by salt bridge. All tests were conducted by using a three-electrode system. NiCoS/C was dropped on carbon paper to dry naturally as a working electrode, Ag/AgCl (saturated KCl electrolyte) was used as a reference electrode, and graphene rod was used as a counter electrode. The purity of all gases (N_2, Ar) used in the experiments was 99.999%. The potentials in all tests were calibrated by the following equation, E (V *vs.* RHE) = E (V *vs.* Ag/AgCl)+0.197+0.059×pH. In the NRR chronoamperometry experiment, 60 mL of the electrolyte solution was first saturated with N_2 for at least 30 minutes, and then tested in N_2 saturated 0.1 M Li_2SO_4 electrolyte while the entire test process was stirred at 500 rpm (Notably, the Li_2SO_4 used was pretreated at 800 ℃ about 4h in Ar.). In every cycling test, the operating condition (such as the flow rate of N_2 (~50 sccm) and the stirring speed (~500 rpm)) and environmental condition remain unchanged. Before each cycle, the electrolytic cell must be washed thoroughly to reduce the external influence, and saturate the electrolyte with N_2 for at least 30 minutes. To prepare the working electrode, 5 mg of the obtained catalyst was first weighed, 1.0 mL of absolute ethanol and 50 μL of Nafion solution (5.0 wt%) were added, and dispersed uniformly under ultrasonic treatment to form a homogeneous catalyst ink. 20 μL of the prepared catalyst ink was uniformly spread on 1.0×1.0 cm^2 of commercial carbon paper, and air-dried at room temperature.

Determination of Ammonia: The concentration of NH_3 produced in the nitrogen reduction reaction was measured by the indophenol blue method. First, 1.0 mL of the electrolyte was taken out from the cathode chambend 1.0 mL (containing sodium citrate (5.0 wt%) and salicylic acid (5.0 wt%)) NaOH solution was added to the above 1.0 mL electrolyte solution. Then, 0.5 mL of a NaClO solution and 100 μL of a sodium nitroferric cyanide solution (1.0 % by weight) were separately added to the above mixture. After standing at room temperature for two hours, the UV-vis absorption spectrum was measured at a wavelength of 500-800 nm. The standard curve method was used to estimate the NH_4 concentration in the solution.[1] The fitting curve of NH_4^+ concentration of 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 μg mL^{-1} of 0.1 M Li_2SO_4 solution ($y = 0.509x+0.04065$, $R^2=0.999$) shows a good linear relationship between NH_4^+ concentration and absorbance.

Determination of Hydrazine: The concentration of N_2H_4 produced in the nitrogen reduction reaction was analyzed by the Watt and Chrisp methods. First, the preparation of the color developing reagent was carried out by mixing $C_9H_{11}NO$ (5.99 g), HCl (30 mL) and C_2H_5OH (300 mL). Then, 1.0 mL of the electrolyte solution was mixed with 1.0 mL of the color developing reagent, and rapidly stirred at room temperature for 15 minutes. Finally, the absorbance was measured at a wavelength of 455 nm using a UV-vis 2700 spectrophotometer. The standard curve method was also used to estimate the concentration of N_2H_4 produced in the electrolyte.[2] A fitted curve of 0.1 M Li_2SO_4 solution ($y = 1.184x+0.02371$, $R^2=0.999$) with N_2H_4 concentrations of 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 μg mL^{-1} showed a good linear relationship between N_2H_4 concentration and absorbance.

Calculation of NH_3 Yield Rate (R_{NH_3}) and FE: The Faraday efficiency of nitrogen reduction is to describe the ratio of the amount of charge used to synthesize NH_3 to the total charge passing through the electrode during electrolysis. The total amount of NH_3 produced is usually measured by using a colorimetric method. Assuming three electrons are needed to generate an ammonia molecule, the FE can be calculated as follows:

Faradaic efficiency (FE,%)=$(3F\times C_{NH_4^+}\times V)/Q\times100\%$

Calculate average NH_3 yeild using the following equation:

Average NH_3 yeild = $(C_{NH_4^+} \times V)/(t \times m)$

where F is the faraday constant, $C_{NH_4^+}$ is the measured concentration of NH_4^+, V is the electrolyte volume, Q is the sum of electric charge recorded by electrochemical workstation, t is the reaction time, and m is the mass loading of catalyst on commercial carbon paper.

DFT calculations

DFT calculations were performed in the Vienna ab initio simulation package (VASP). A spin-polarized GGA PBE functional, all-electron plane-wave basis sets with an energy cutoff of 520 eV, and a projector augmented wave (PAW) method were adopted. A (3×3×1) Monkhorst-Pack mesh was used for the Brillouin-zone integrations to be sampled. The conjugate gradient algorithm was used in the optimization. The convergence threshold was set 1×10^{-4} eV in total energy and 0.05 eV/Å in force on each atom.

The adsorption energy change (ΔE_{abs}) was determined as follows:

$$\Delta E_{abs} = E_{total} - E_{sur} - E_{mol}$$

where E_{total} is the total energy for the adsorption state, E_{sur} is the energy of pure surface, E_{mol} is the energy of molecule.

The free energy change (ΔG) for adsorptions were determined as follows:

$$\Delta G = E_{total} - E_{sur} + \Delta E_{ZPE} - T\Delta S$$

where E_{total} is the total energy for the adsorption state, E_{sur} is the energy of pure surface, ΔE_{ZPE} is the zero-point energy change and ΔS is the entropy change.

Figures

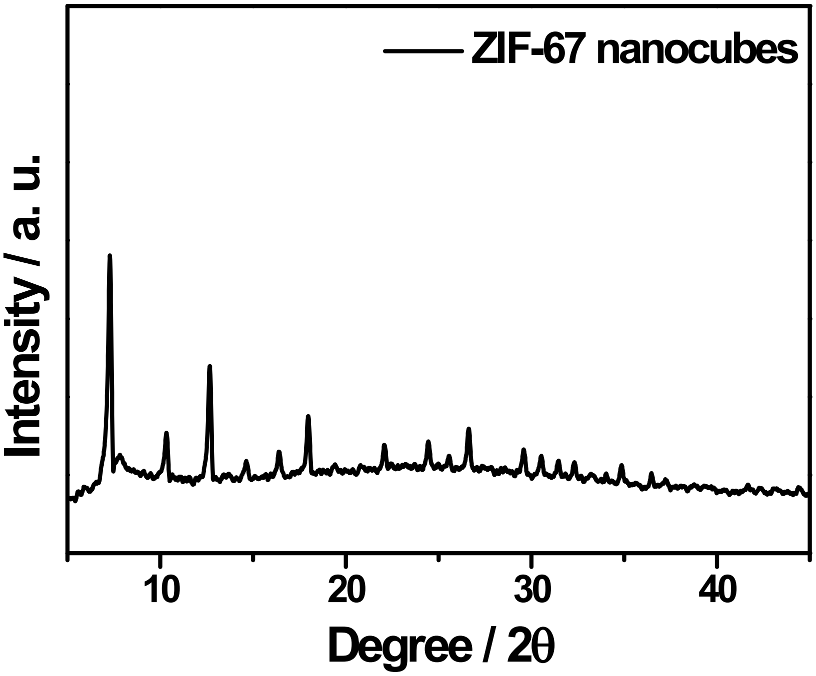

Fig. S1 XRD pattern of ZIF-67 nanocubes.

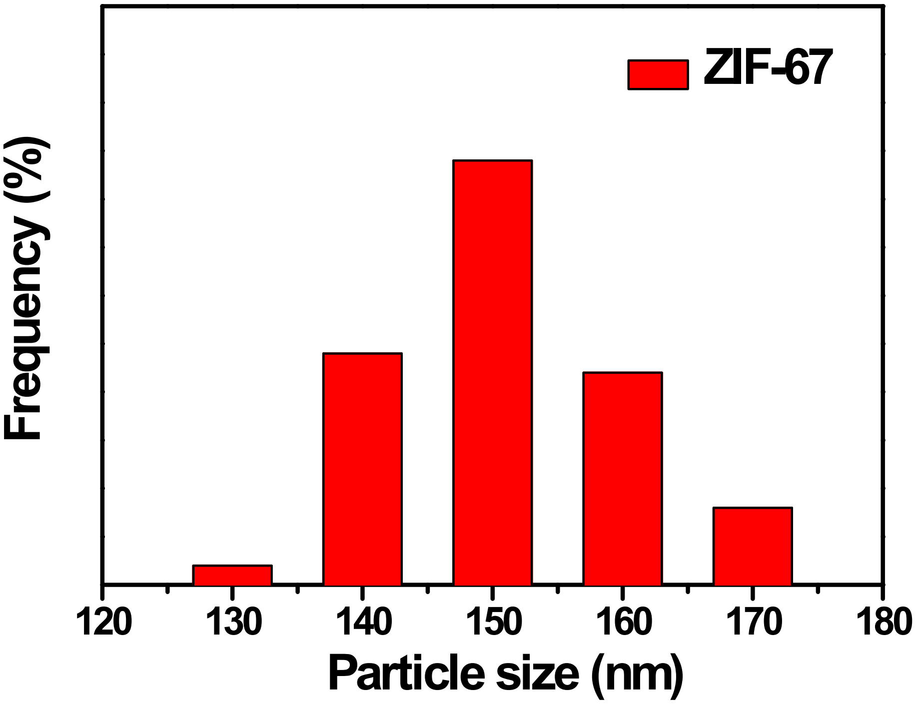

Fig. S2 Particle size distribution of ZIF-67.

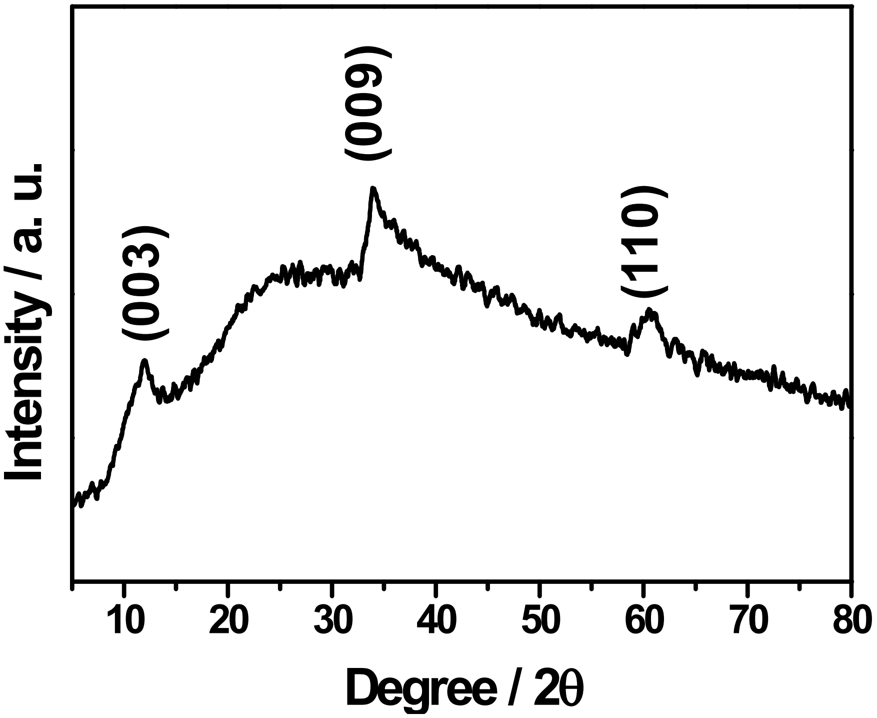

Fig. S3 XRD pattern of as-prepared NiCo-LDH@ZIF-67 nanoboxes.

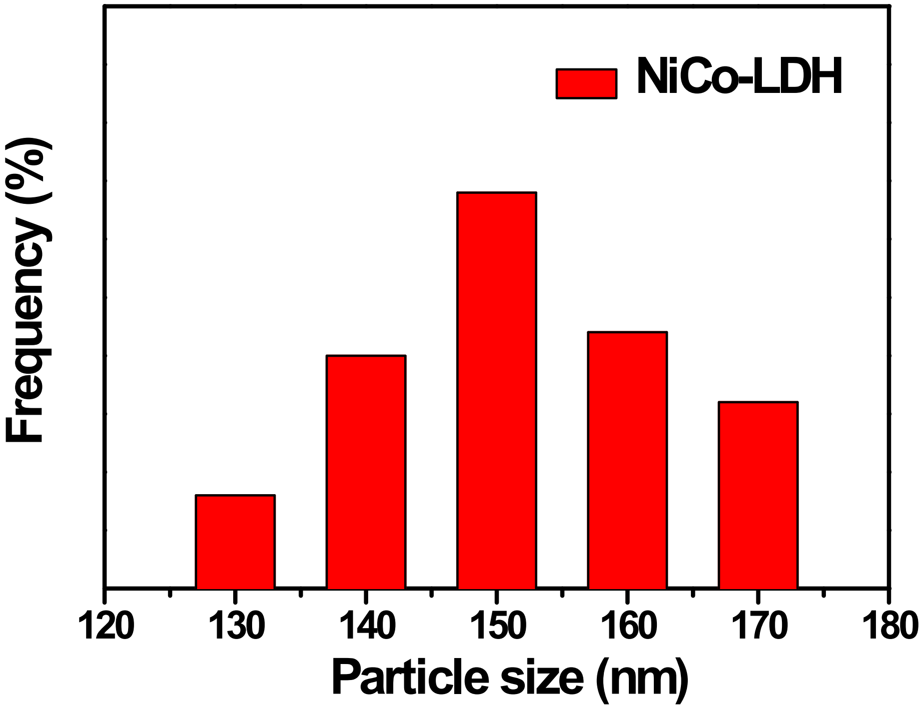

Fig. S4 Particle size distribution of NiCo-LDH@ZIF-67 nanoboxes.

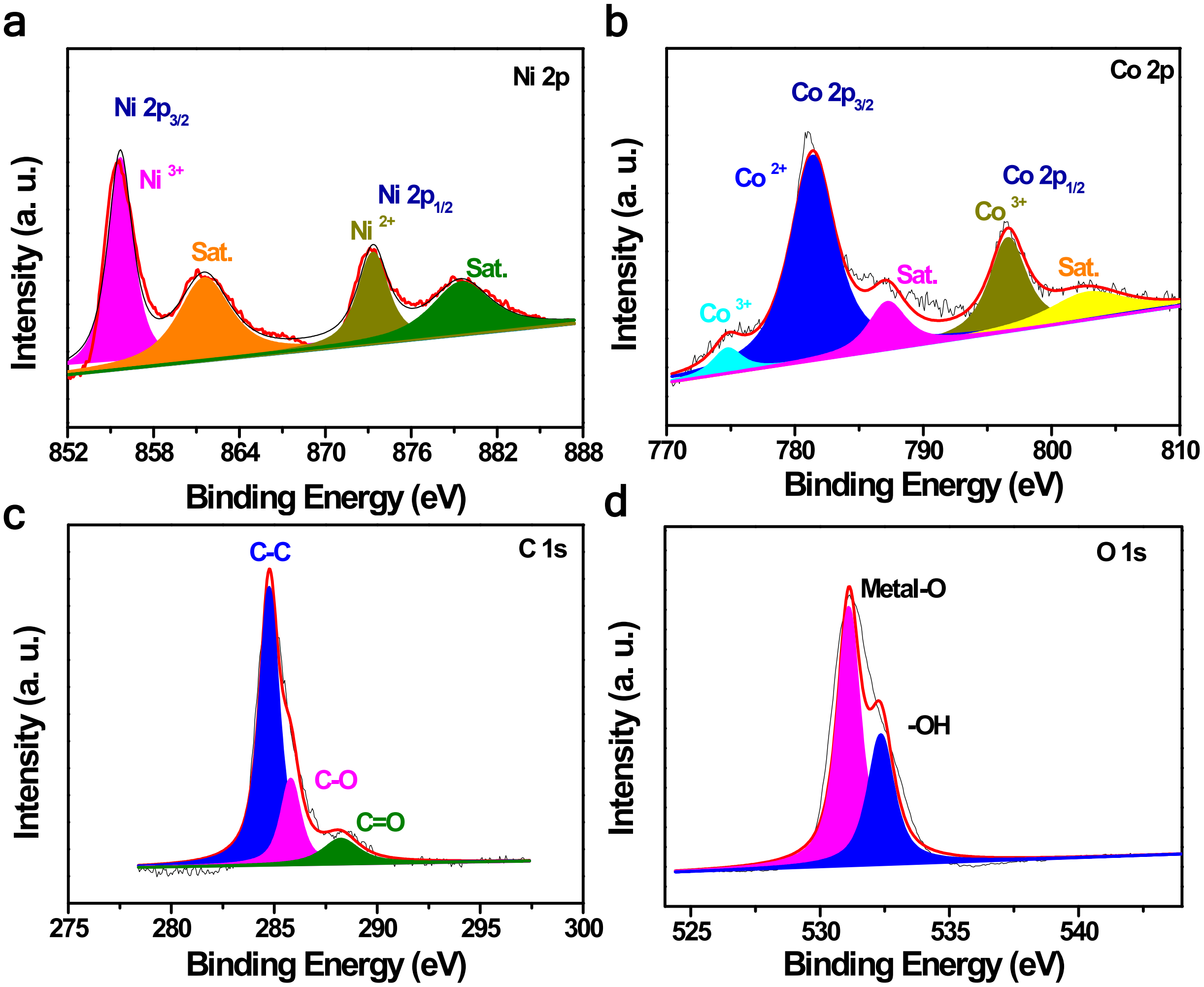

Fig. S5. a) XPS spectra of Ni 3d, b) Co 2p c) C 1s and d) O 1s of the NiCo-LDH@ZIF-67.

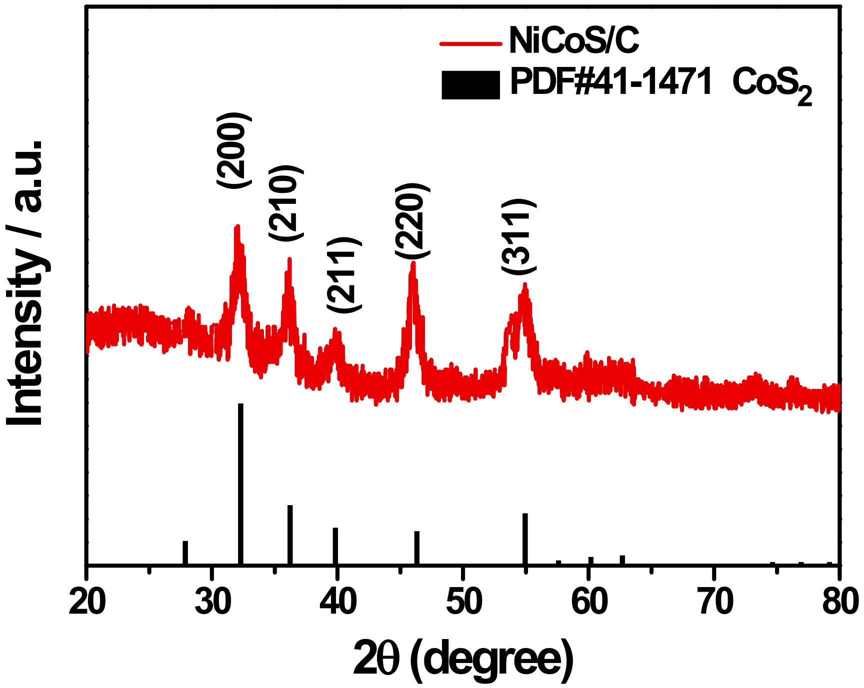

Fig. S6 XRD pattern of as-prepared NiCoS/C nanocages.

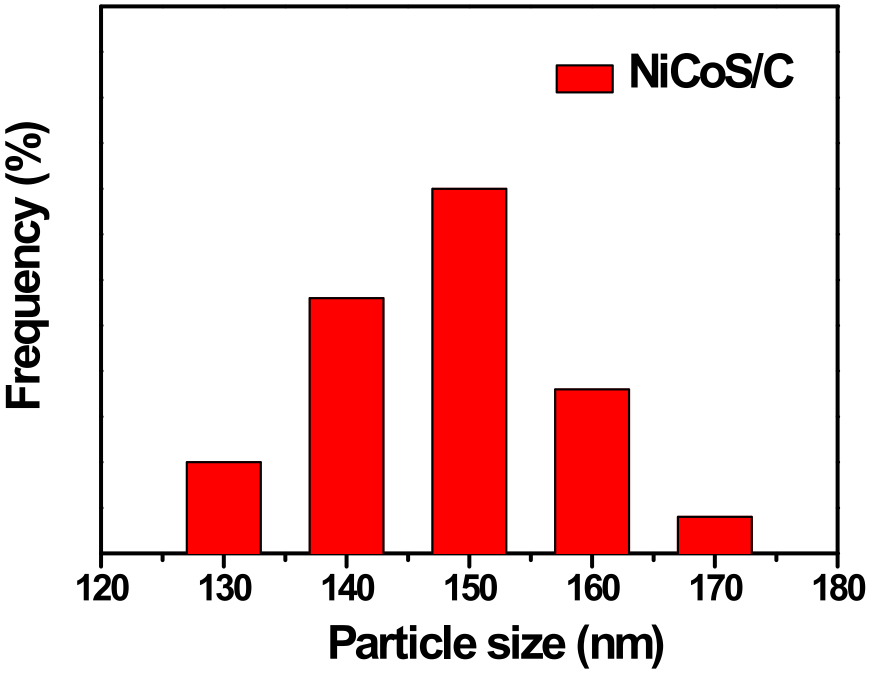

Fig. S7 Particle size distribution of NiCoS/C nanocages.

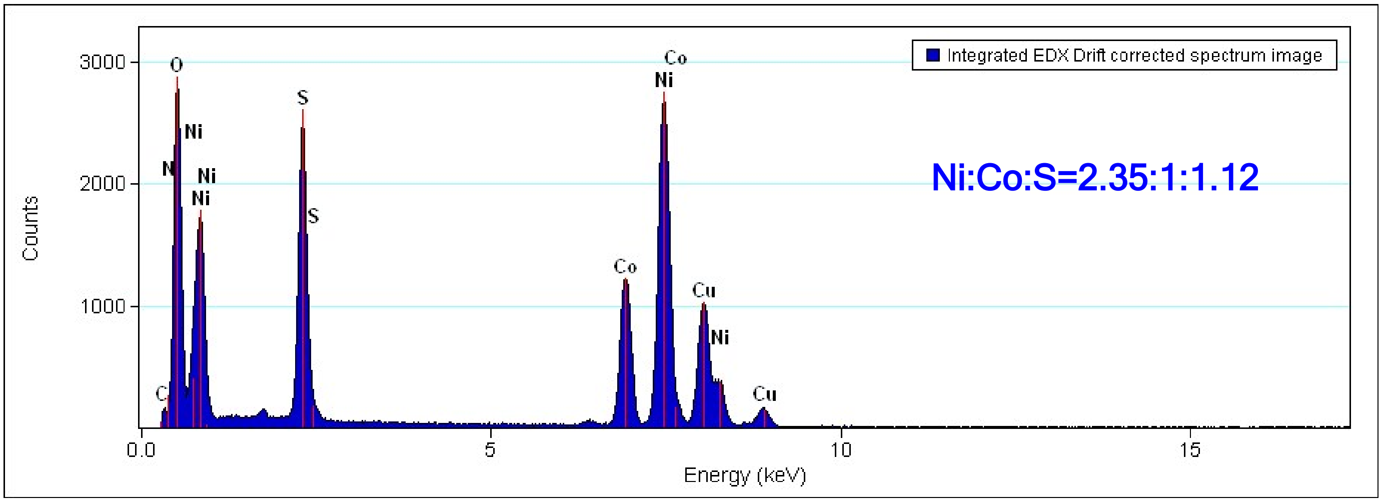

Fig. S8 EDX spectrum of NiCoS/C nanocages.

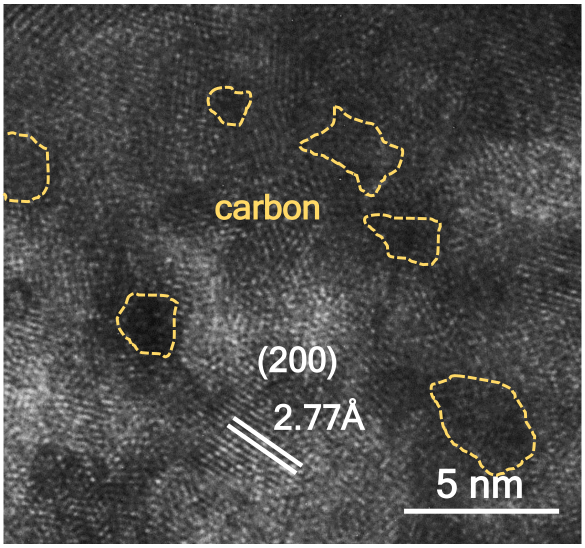

Fig. S9 HRTEM images of NiCoS/C nanocages.

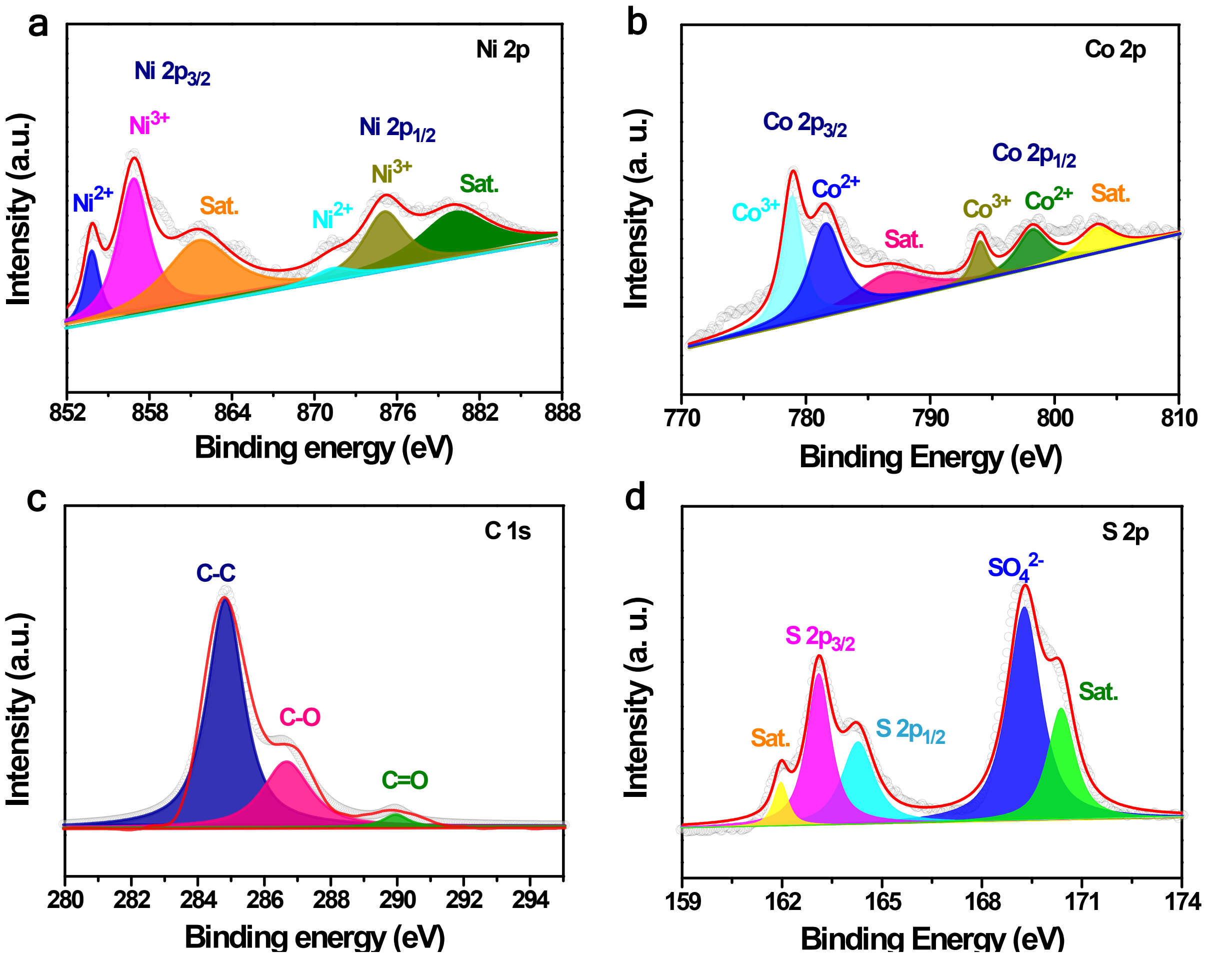

Fig. S10 (a) The XPS spectrum of the NiCoS/C: (a) Ni 2p region; (b) Co 2p region; (c) C 1s region; (d) S 2p region.

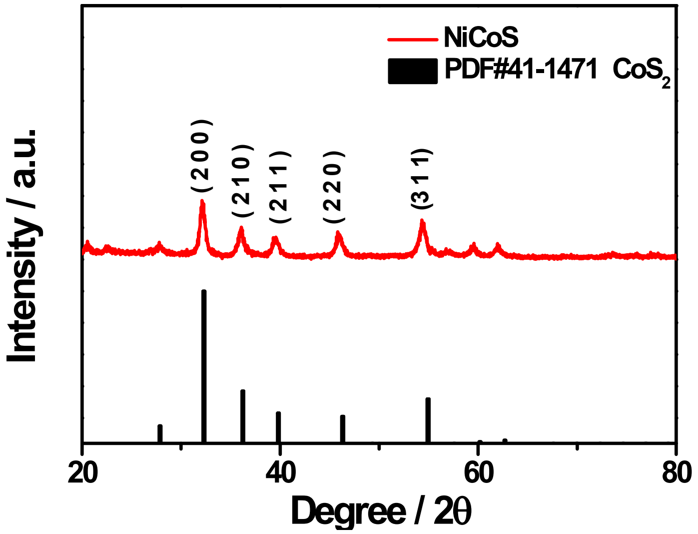

Fig. S11 XRD pattern of as-prepared NiCoS nanocages.

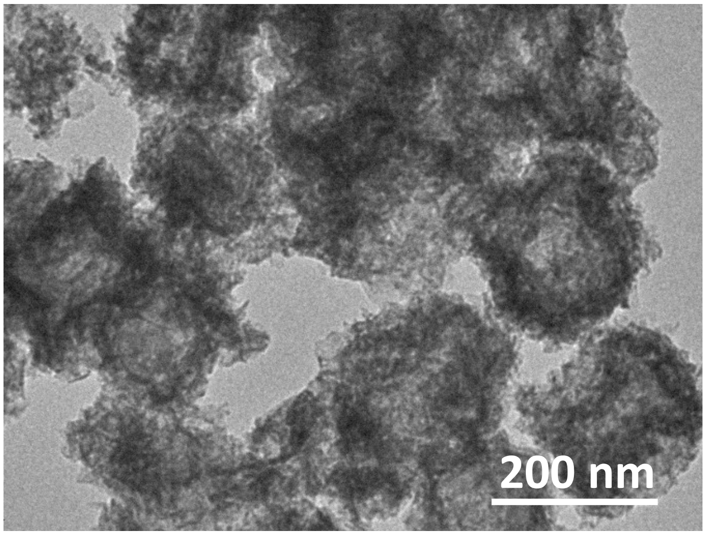

Fig. S12 TEM images of NiCoS nanocages.

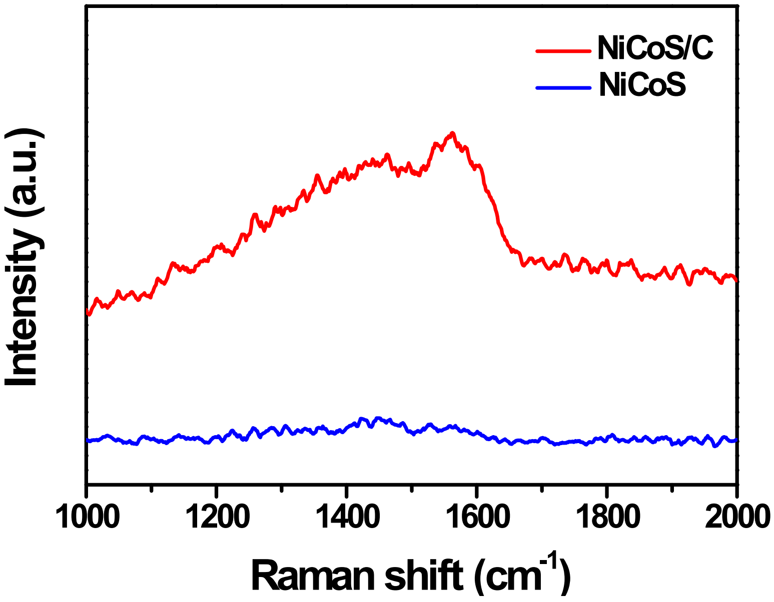

Fig. S13 Raman spectra of NiCoS and NiCoS/C nanocages.

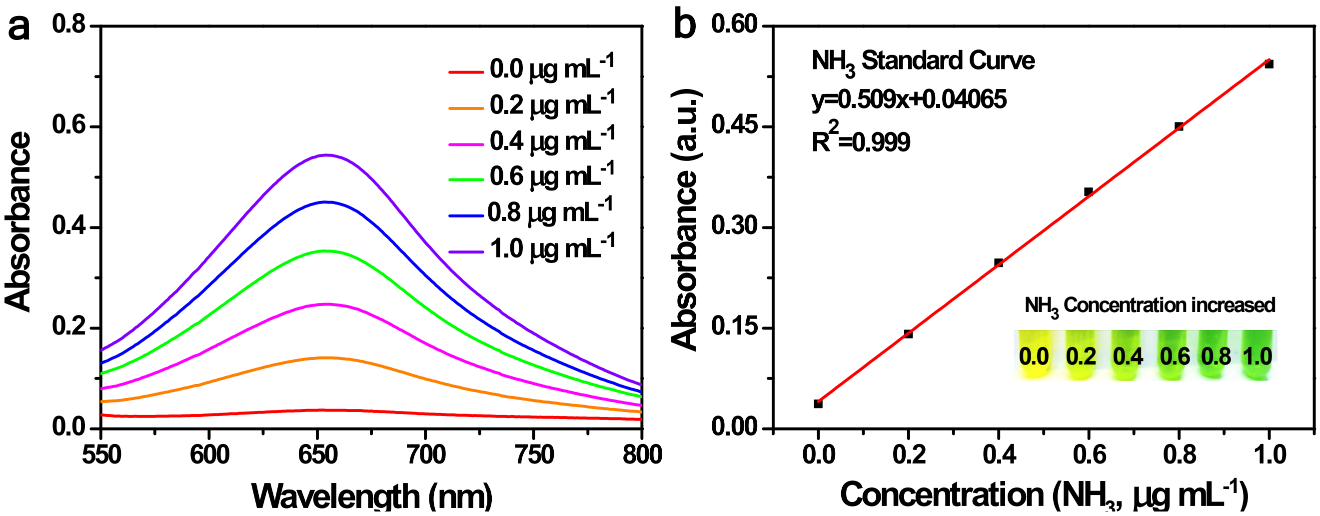

Fig. S14 UV-Vis absorption spectra of indophenol assays with NH_4^+ ions after incubated for 2 h at room temperature. (b) Calibration curve used for estimation of NH_4^+.

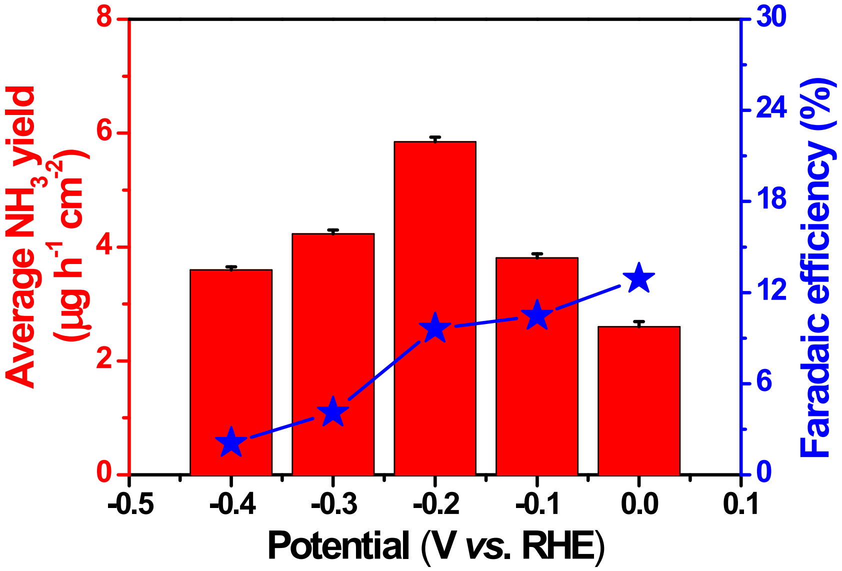

Fig. S15 The ammonia yield about area and Faraday efficiency of NiCoS/C nanocages at different voltages**.**

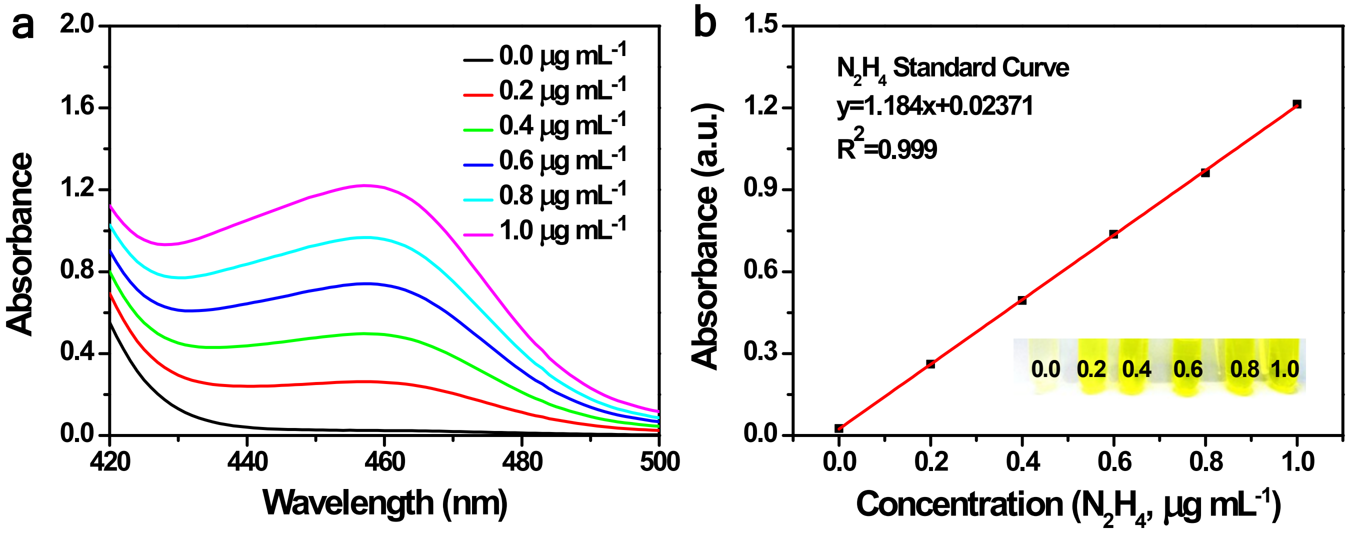

Fig. S16 UV-Vis absorption spectra of various N_2H_4 concentrations at room temperature. (b) The calibration curve used for estimation of N_2H_4.

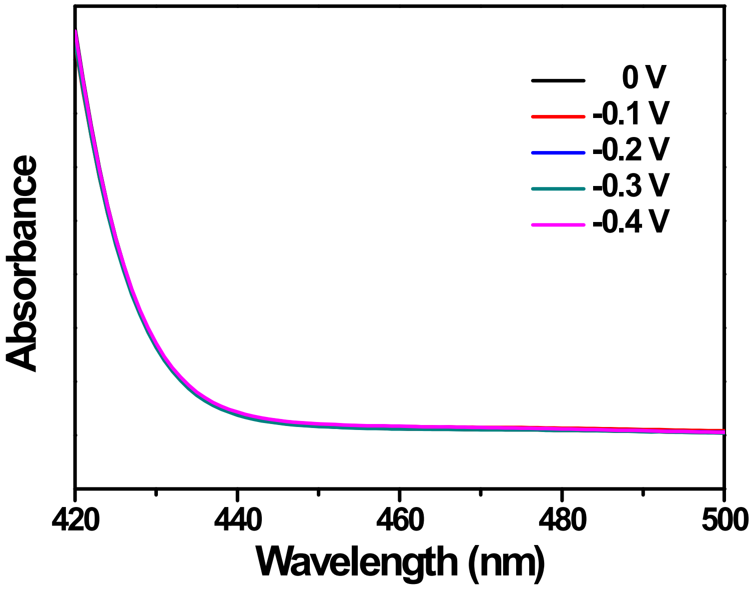

Fig. S17 UV-visible absorption curves at different voltage.

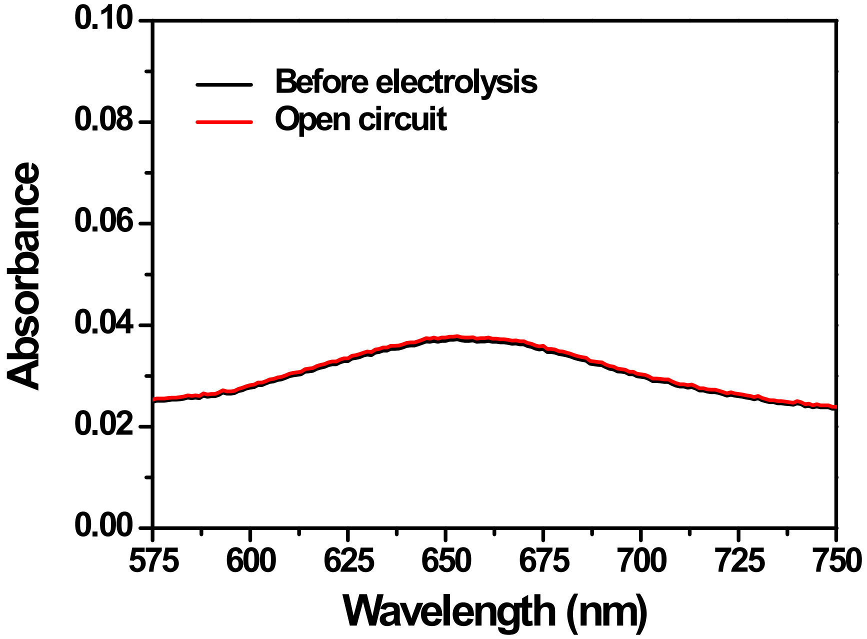

Fig. S18 UV-Vis absorption spectra of the electrolyte stained with indophenol indicator before and after electrolysis at - 0.2 (V *vs.* RHE).

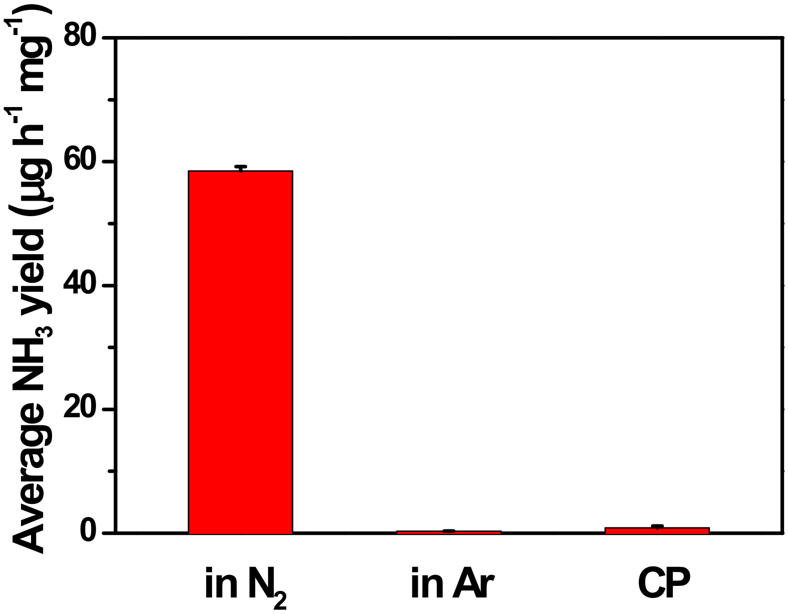

Fig. S19. Blank control test in 0.1 M Li_2SO_4 solution at - 0.2 (V *vs.* RHE).

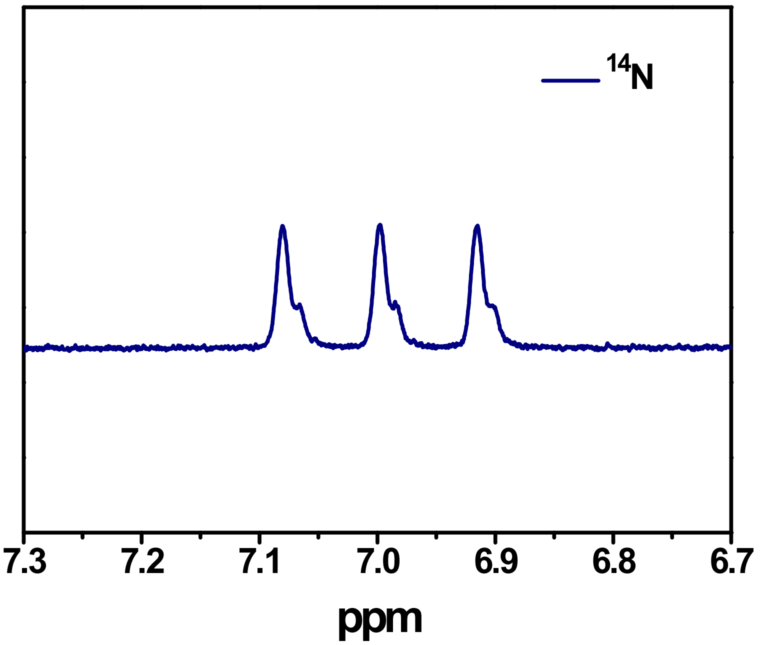

Fig. S20 ^{1}H NMR spectra of electrolyte after electrolysis at the potential of -0.2 (V *vs.* RHE) under $^{14}N_2$ atmosphere.

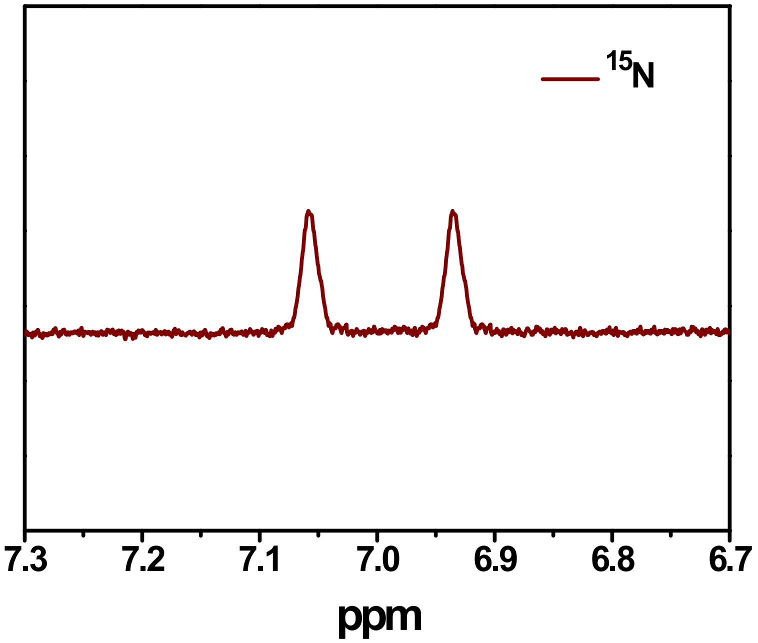

Fig. S21 ^{1}H NMR spectra of electrolyte after electrolysis at the potential of -0.2 (V *vs.* RHE) under $^{15}N_2$ atmosphere.

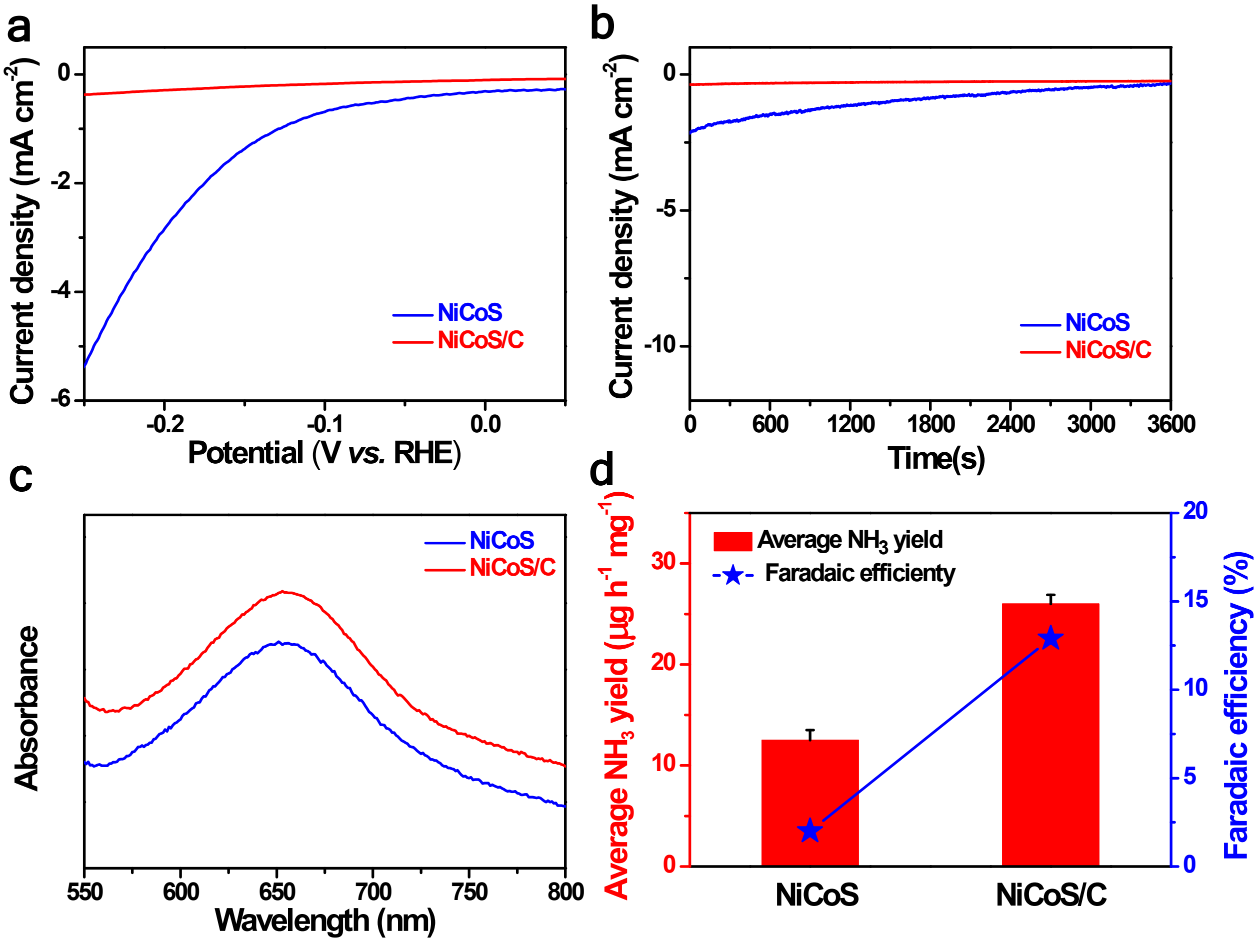

Fig. S22 (a) LSV polarization curves of NiCoS and NiCoS/C nanocages in N_2 saturated 0.1 M Li_2SO_4 solution; (b) time current curves of 1h; (c) UV-visible absorbance spectra of ammonia produced in the electrolyte; (d) ammonia yield and FE of NiCoS and NiCoS/C nanocages at 0 V (*vs*. RHE).

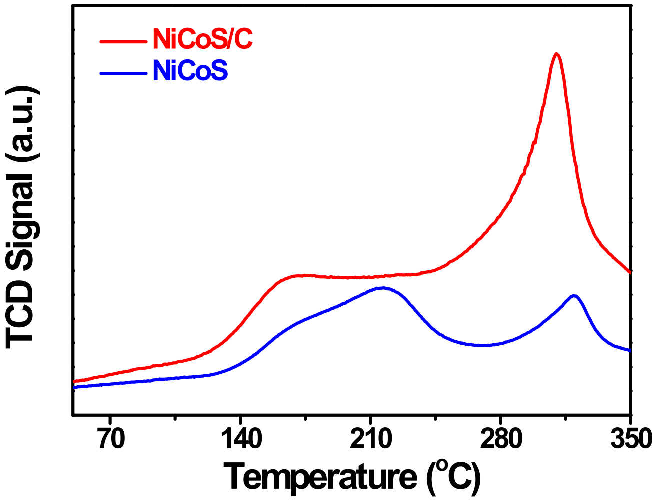

Fig. S23 a) N_2-TPD profiles of NiCoS and NiCoS/C nanocages.

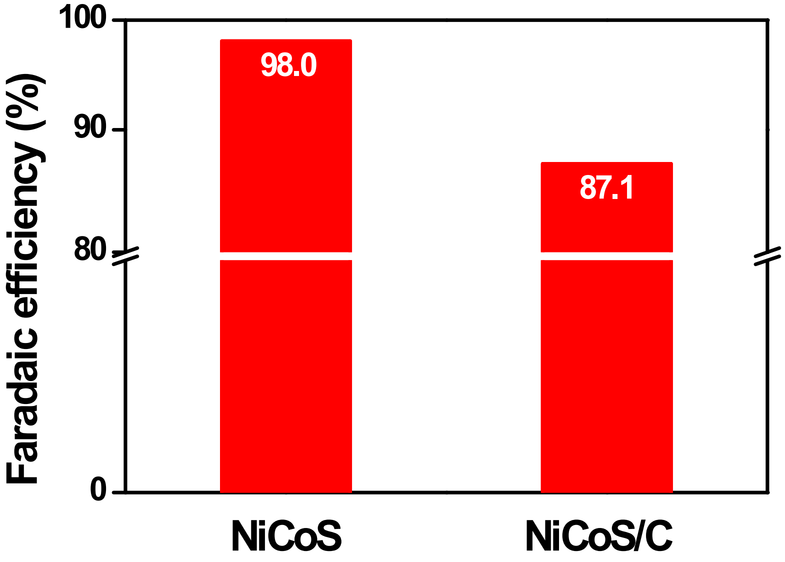

Fig. S24 FE of H_2 at 0 V (*vs.* RHE).

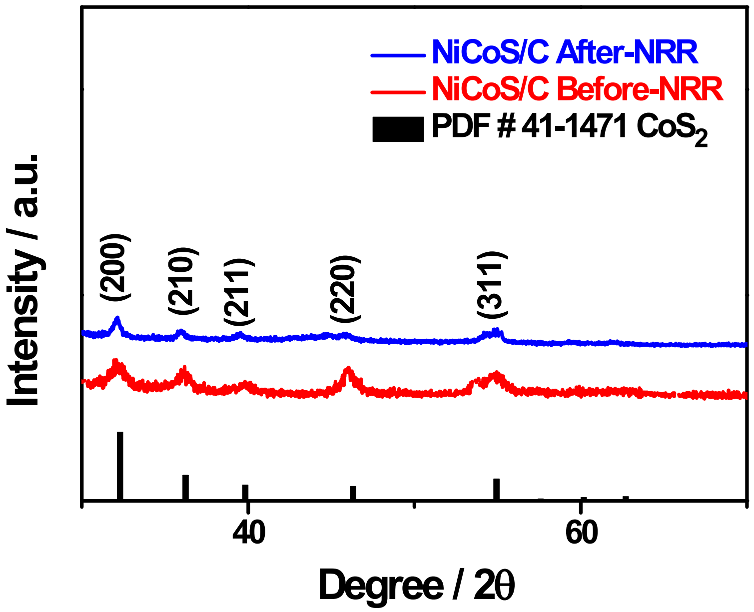

Fig. S25 XRD patterns of the NiCoS/C before and after NRR measurement in N_2-saturated 0.1 M Li_2SO_4 solution at -0.2 V (*vs.* RHE) for 12 h.

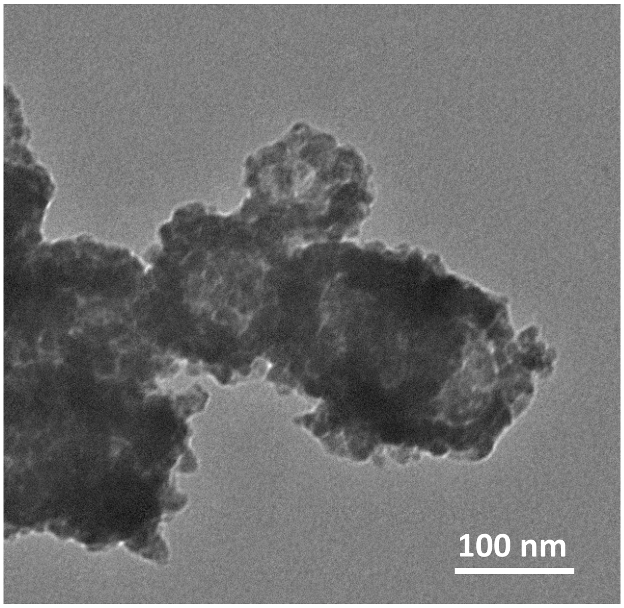

Fig. S26 TEM image of the NiCoS/C after NRR measurement in N_2-saturated 0.1 M Li_2SO_4 solution at -0.2 V (*vs.* RHE) for 12 h.

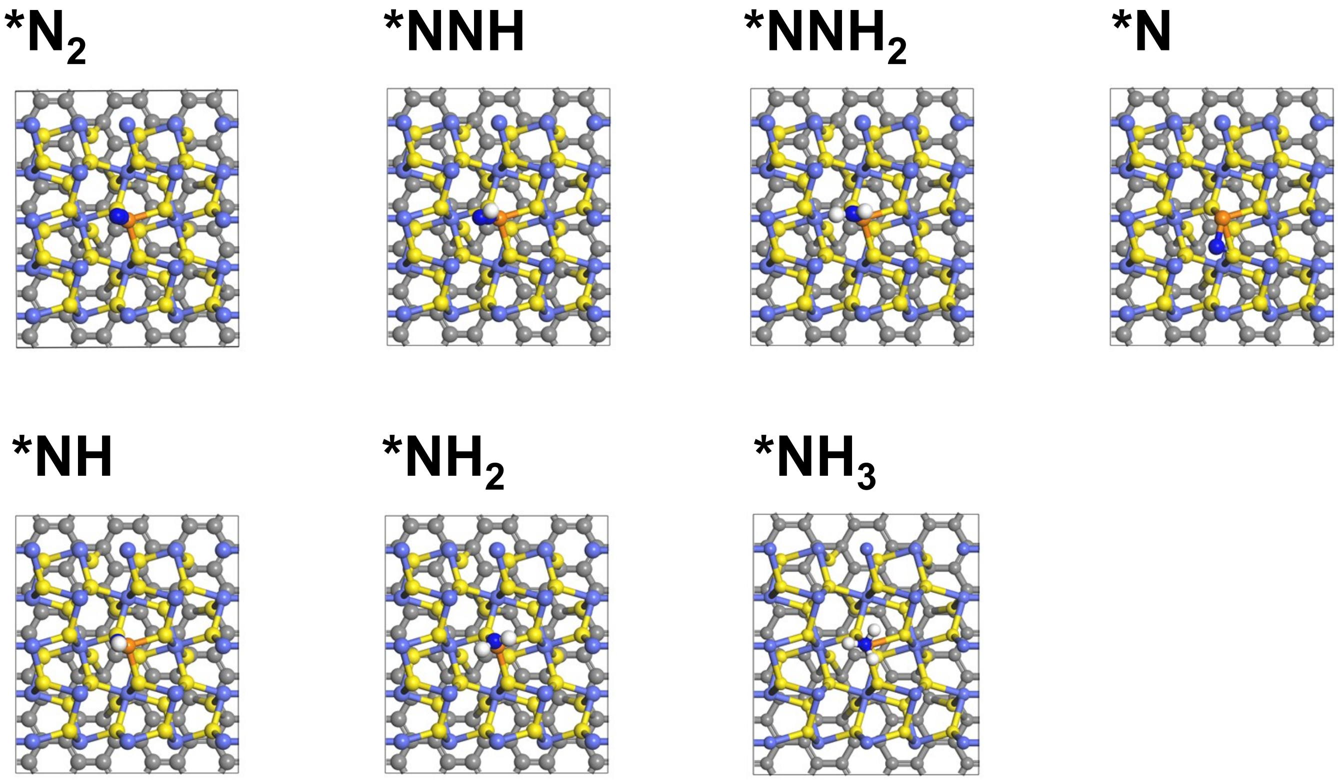

Fig. S27 The reaction path carried out around the optimized geometry of the NiCoS/C intermediate. Color code: orange, Ni; light blue, Co; yellow, S; gray, C; dark blue, N; white, H.

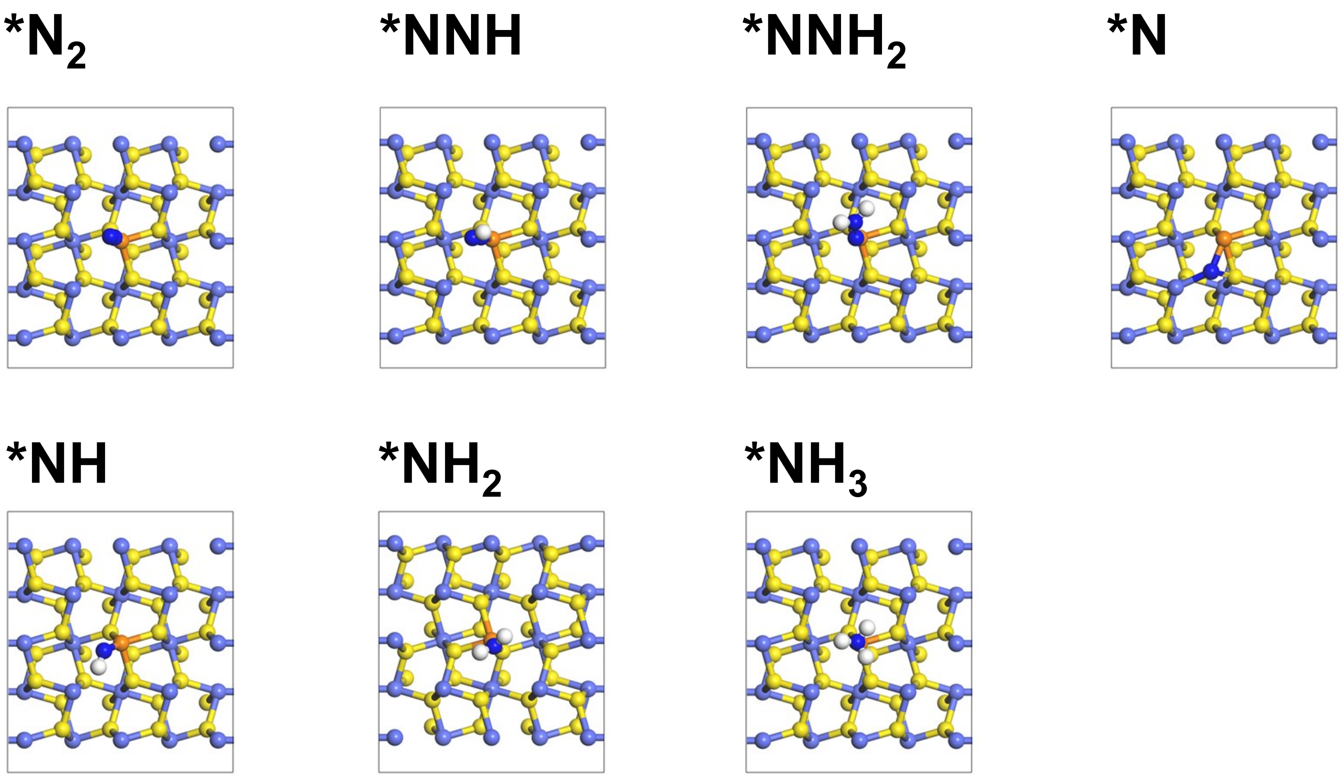

Fig. S28 The reaction path carried out around the optimized geometry of the NiCoS intermediate. Color code: orange, Ni; light blue, Co; yellow, S; dark blue, N; white, H.

Table S1. The comparable results of our work and other recently reported NRR electrocatalysts at 0 V (vs. RHE).

Catalyst	Electrolyte	Potential (V vs.RHE)	Yield rate ($\mu g\ h^{-1} mg^{-1}$)	Faradaic efficiency (%)	Ref.
NiCoS/C	0.1M Li_2SO_4	0	26.0	12.9	This work
Fe_{SA}-N-C	0.1 M KOH	0	7.48	56.55	[3]
CoP	1.0 M KOH	0	2.485	7.36	[4]
Au/TiO_2	0.1 M HCl	0	3.1	0.82	[5]
$Pd_{0.2}Cu_{0.8}$/rGO	0.1 M HCl	0	1.66	4.5	[6]
Pd/C	0.1M PBS	0	4.5	7.5	[7]

Table S2. Free energy barriers (eV) for the different states along NRR mechanism at standard conditions (298.15 K).

	N_2*	NNH*	NNH_2*	N*	NH*	NH_2*	NH_3*	$NH_3(g)$	*H
NiCoS/C	0.02	2.93	2.25	1.82	1.13	-0.31	-0.61	-0.97	0.22
NiCoS	0.06	3.05	2.71	1.89	0.91	-0.66	-1.43	-0.97	0.75

Table S3. S, ZPE values for each NiCoS/C intermediate.

	ZPE(eV)		TΔS(eV)	
	NiCoS	C-NiCoS	NiCoS	C-NiCoS
N_2*	0.176	0.177	0.0021	0.0017
NNH*	0.368	0.365	0.0009	0.0008
NNH_2*	0.495	0.503	0.0015	0.0011
N*	0.066	0.074	0.0021	0.0015
NH*	0.279	0.284	0.0018	0.0013
NH_2*	0.372	0.461	0.0009	0.0006
NH_3*	0.420	0.519	0.0008	0.0006

References

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