Specific Synthesis of CoS$_2$ Nanoparticles Embedded in Porous Al$_2$O$_3$ Nanosheets for Efficient Hydrogen Evolution and Enhanced Lithium Storage

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Experimental section

Synthesis of Co$_6$Al$_2$CO$_3$(OH)$_{16}$·4H$_2$O nanosheets

All chemicals or materials were utilized directly without any further purification prior to use. Briefly, concentrated ammonium hydroxide (12.5 mL), ethylene glycol (12.5 mL), Co(NO$_3$)$_2$ aqueous solution (5 mL, 1 M), Al(NO$_3$)$_3$ aqueous solution (2 mL, 1 M), and Na$_2$CO$_3$ aqueous solution (5 mL, 1 M) were added step by step under strong stirring with intervals of 2 min. After that, the precursor solution was stirred for another 20 min, and then the mixture changed into purple solution. Afterwards, the precursor solution was transferred into a Teflon-lined stainless-steel autoclave with a volume of 50 mL. And thermal treatment was performed on the Teflon liner in an electric oven at 180 °C for 15 h. After the autoclave was cooled down naturally to room temperature in air, samples deposited at the bottom of Teflon were collected and washed by centrifugation for at least three cycles using deionized water and one cycle using pure ethanol. The as-synthesized samples were then dried in a normal oven at 60 °C overnight to remove the absorbed water and ethanol for the subsequent fabrication and characterizations.

Synthesis of CoS$_2$ NP/Al$_2$O$_3$ NS

The second step was carried out in a tube furnace to convert the Co$_6$Al$_2$CO$_3$(OH)$_{16}$·4H$_2$O nanosheets into CoS$_2$ NP/Al$_2$O$_3$ NS. Briefly, the graphite boat containing precursor power (Co$_6$Al$_2$CO$_3$(OH)$_{16}$·4H$_2$O nanosheets) were placed in the center of a fused silica tube on a reactor equipped with both pressure and gas flow controllers. An alumina boat containing 1 g of S powder (Sigma-Aldrich, 99.5−100.5%) was placed in the tube at the farthest upstream position within the tube furnace. The tube was purged of air and maintained at 780 Torr under a steady flow of Ar carrier gas (99.999%) at 25 sccm. The furnace temperature was ramped to 400 °C at a rate of ~10℃ min^{-1} and held at this temperature for 1 h. After cooling under Ar flow, the samples were rinsed with CS$_2$ (Sigma-Aldrich, 99.9%) and dried with nitrogen.

For comparison, bare CoS_2 NP was prepared with the same procedure except for adding ethylene glycol and $Al(NO_3)_3$ in the hydrothermal process.

Preparation of pure Al_2O_3 nanosheets

First, we weighed 300 mg CoS_2 NP/Al_2O_3 NS in 50 mL hot concentrated hydrochloric acid and stirred for 1 day. After that, the sample was collected by centrifugation and washed with pure ethanol and D.I. water, and then dried in an oven. The content of Al_2O_3 in CoS_2 NP/Al_2O_3 NS was calculated from the formula:

$Al_2O_3\% = W(Al_2O_3)/W(CoS_2$ NP/Al_2O_3 NS$)*100\%$

where $W(Al_2O_3)$ and $W(CoS_2$ NP/Al_2O_3 NS$)$ are the weight of Al_2O_3 and CoS_2 NP/Al_2O_3 NS, respectively.

Materials Characterization

A field-emission scanning electron microscope (SEM, JEOL JSM-7800F) coupled with an EDS analyzer (JEOL, JSM-7800F), TEM coupled with an EDS analyzer (Philips, Tecnai, F30, 300 kV), X-ray photoelectron spectrometery with a ESCALAB250 analyzer (XPS), powder X-ray diffraction with Cu K_α radiation (XRD, Bruker D8 Advance), Brunauer-Emmett-Teller surface area measurement (BET, Quantachrome Autosorb-6B surface area and Pore size analyzer) were used to characterize the obtained samples.

Electrochemical Measurements

For HER studies, electrochemical measurement was fulfilled on a CHI660E electrochemistry work-station, which was conducted in a three-electrode device including a working electrode of clean glassy carbon electrode (GCE) (0.07 cm^2), a reference electrode of saturated calomel electrode (SCE), and a counter electrode of Pt foil. The catalyst suspension was prepared as follows: 4 mg of the obtained CoS_2 NP/Al_2O_3 NS composite was dispersed ultrasonically in 100 μL of a diluted Nafion solution (0.5wt %) and 300 μL of ethanol. Then, 4 μL of the suspension was dropped on the GCE (mass loading 0.57 mg cm^{-2}) and air-dried as working electrode. Linear sweep voltammetry (LSV) was carried out between -0.2 to -0.6 V at a scanning rate of 5 mV s^{-1} in 0.5 M H_2SO_4 solution. The durability analysis was taken by cyclic voltammetry (CV) scanning from -0.2 to -0.6 V at 50 mV s^{-1} for 1000 cycles. The stability estimation was taken by galvanostatic measurement for 10 h at an electrostatic current density of -10 mA cm^{-2}. According to the equation E(RHE) = E(SCE) + 0.281 V, all the potentials were involved in reversible hydrogen electrode (RHE) in 0.5 M H_2SO_4 solution. The onset potential is defined as the potential at the current density of -1.0 mA cm^{-2} for HER.

For LIBs test, a homogeneous mixture composed of CoS_2 NP/Al_2O_3 NS, carbon black, and polyvinyl difluoride (PVDF) using 1-methyl-2-pyrrolidinone (NMP) as solvent in a weight ratio of

70:20:10 was prepared under strong magnetic stirring for at least 1 d. Then some of the mixture was extracted and spread onto Cu foils. Before and after the samples were spread, the Cu foils were weighed using a high-precision analytical balance. The read difference was the exact mass for the coated samples on Cu foils. Normally, the sample loadings range from 1.6 to 1.8 mg·cm^{-2}. The obtained pieces of Cu covered with samples were then used as working electrodes with 1M LiPF$_6$ in ethylene carbonate and diethyl carbonate (EC/DMC=1:1 v/v) as electrolyte. Celgard 2400 was applied as the separator film to isolate the two electrodes. Pure Li foil (99.9%, Aldrich) used as the counter electrode and reference electrode. The cell was assembled in an argon filled glove box in which moisture and oxygen concentrations were strictly limited to below 0.1 ppm. The galvanostatic cycling was performed using a Neware battery testing system. The Electrochemical impedance spectroscopy (EIS) was measured by the CHI604E Electrochemical Analyzer with the frequency range from 0.01 to 100000 Hz with a sine wave with amplitude of 5.0 mV.
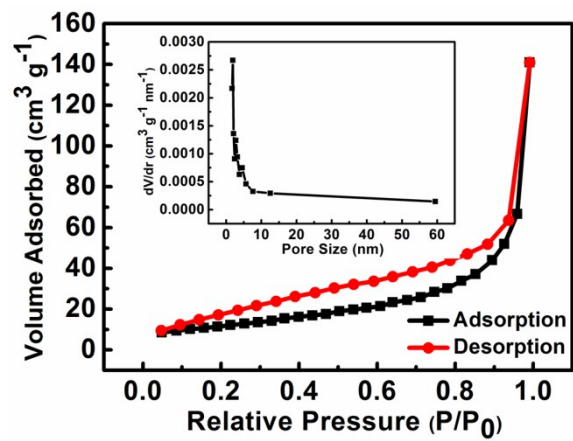
Fig. S1 The nitrogen absorption/desorption curve of the CoS_2 NP/Al_2O_3 NS and the inset profile shows the corresponding pore size distribution.
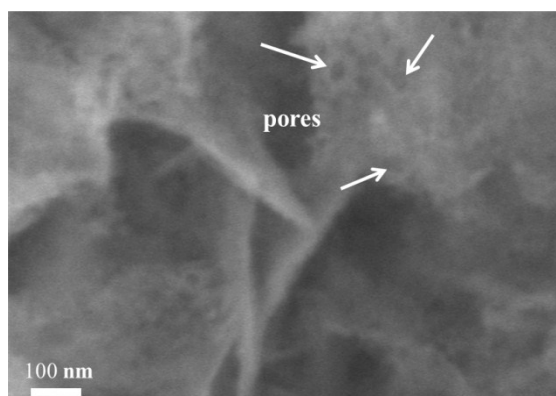
Fig. S2 SEM image of the CoS$_2$ NP/Al$_2$O$_3$ NS after the dissolution of CoS$_2$ nanoparticles in the hot concentrated hydrochloric acid.
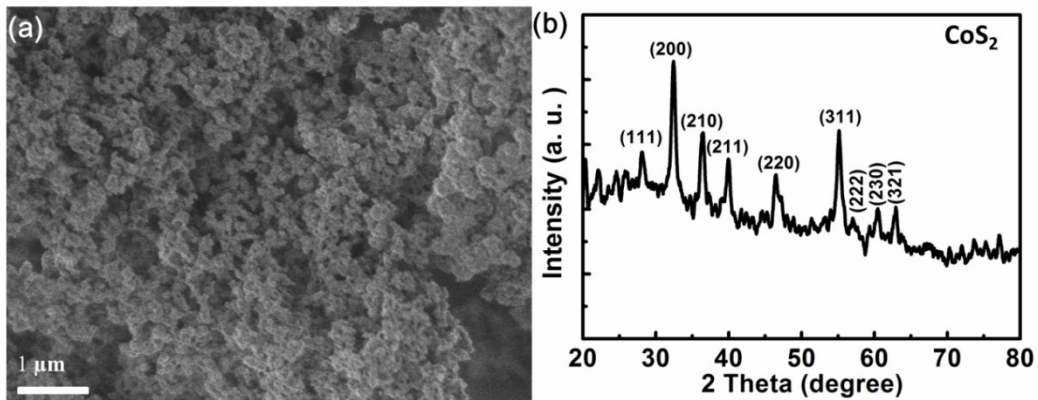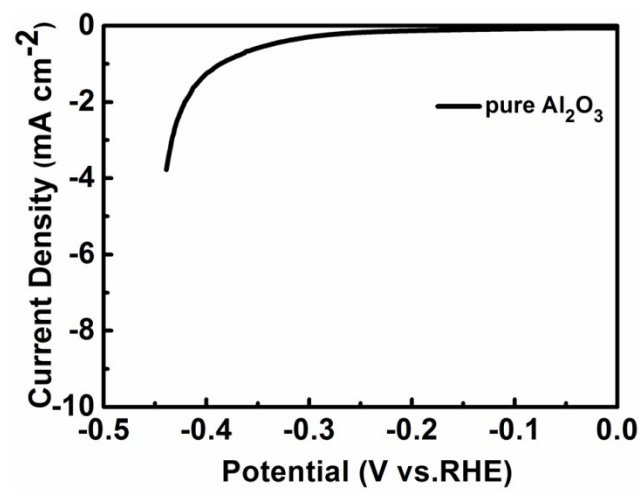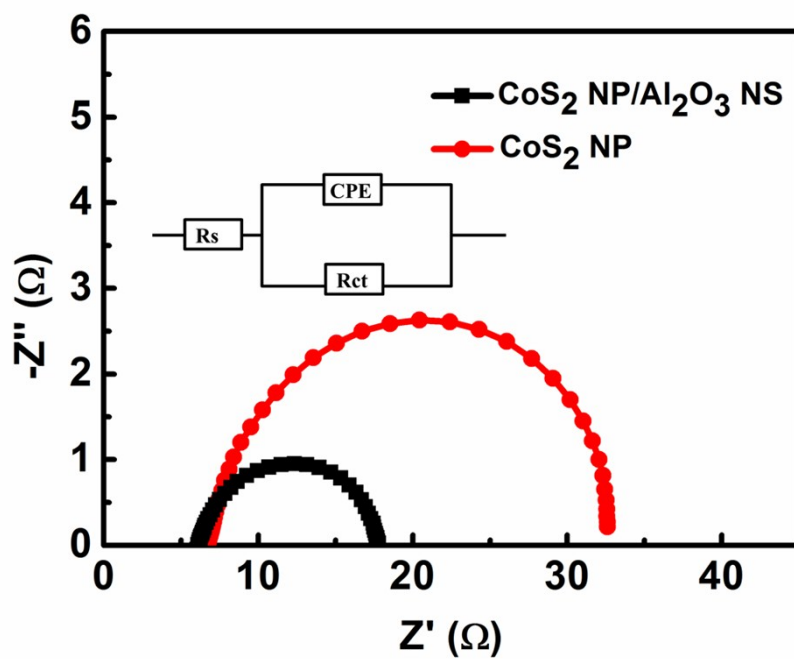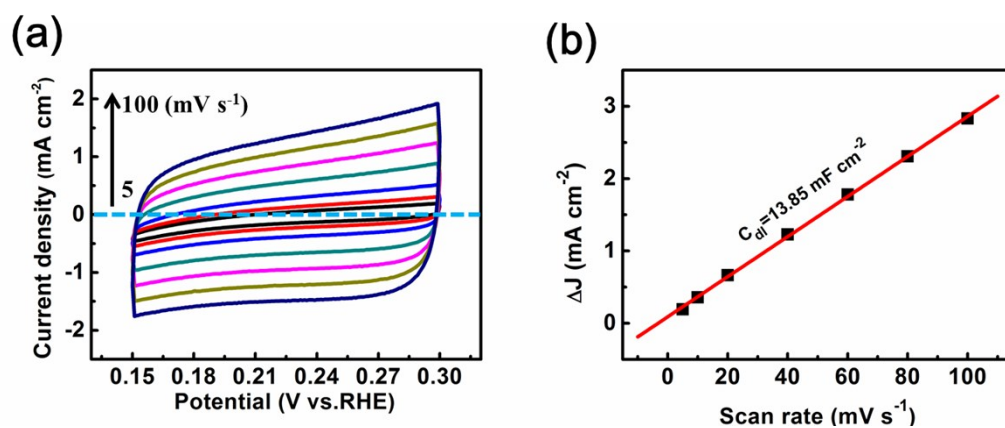
Fig. S3 (a) SEM image and (b) XRD pattern of bare CoS$_2$ NP.

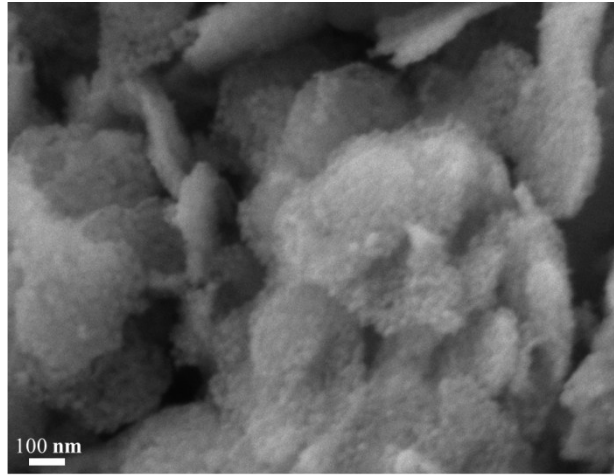**Fig. S4** The polarization curve of the bare Al_2O_3.

Fig. S5 Nyquist plots of the CoS_2 NP/Al_2O_3 NS and CoS_2 NP tested at a given overpotential of 90 mV and the inset shows the equivalent circuit.
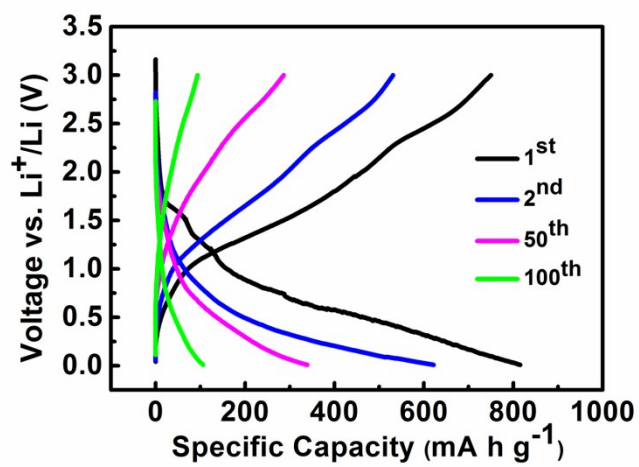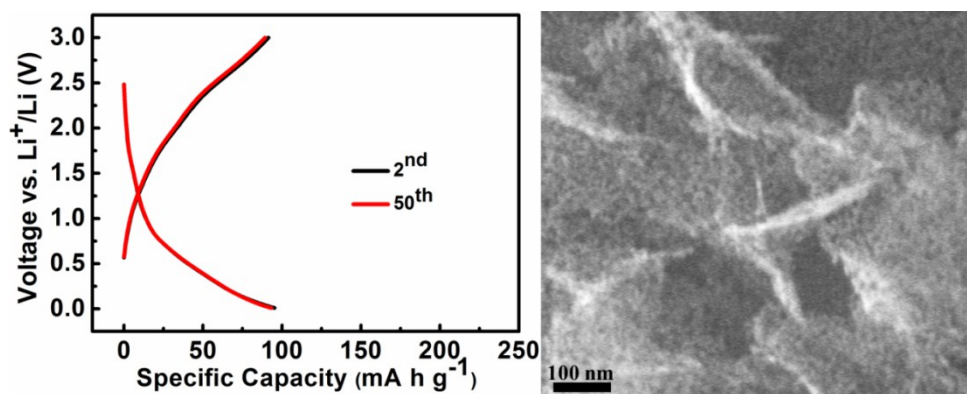
Fig. S6 (a) CV curves of the CoS_2 NP tested at various scan rates from 5 to 100 mV s^{-1}. (b) The capacitive currents at 0.225 V vs. RHE as a function of scan rate for CoS_2 NP.
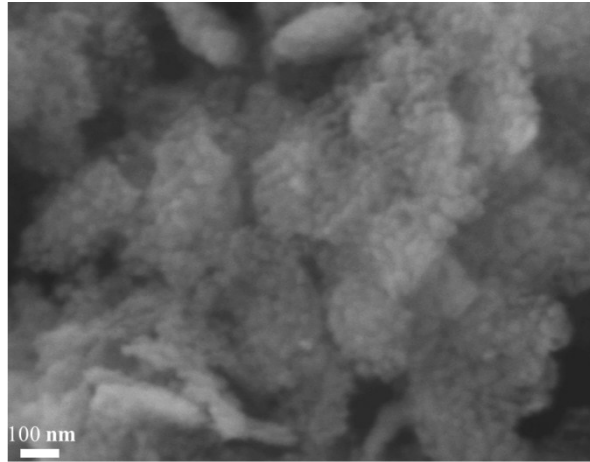
Fig. S7 The SEM image of the CoS$_2$ NP/Al$_2$O$_3$ NS after the galvanostatic measurement for 10 h.

Fig. S8 Galvanostatic charge/discharge curves of the bare CoS$_2$ NP at 100 mAh g^{-1}.

Fig. S9 (a) Galvanostatic charge/discharge curves of the bare Al_2O_3 nanosheets and (b) the SEM image of the Al_2O_3 nanosheets after running for 50 cycles.

Fig. S10 SEM image of the CoS$_2$ NP/Al$_2$O$_3$ NS composite after 150 charge/discharge cycles at 100 mA g^{-1}.

Table S1. HER performance of CoS_2 NP/Al_2O_3 NS composite compared with other transition metal-based catalysts reported in the previous literature.

Catalysts	Electrolyte	Onset overpotential (mV)	Tafel slope (mV dec^{-1})	η_{10}* (mV)
MoS_2@CoS_2 nanocomposite[1]	0.5 M H_2SO_4	-	73.4	87
MoS_2 nanosheet array/Ti foil[2]		150	51	225
CoS_2 nanopyramid array/Ti[3]		81	72	193
CoS_2 nanosheet/Graphene/Carbon Nanotube[4]		-	51	142
CoS_2-MoS_2/CNTs[5]		70	67	-
CoS_2 nano-octahedra on carbon fibre network		63	73	136
This work		53	50.9	115

* η_{10}: overpotential requirement for current density of 10 mA cm^{-2}.

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