Supporting Information

Highly Boosted Gas Diffusion for Enhanced Electrocatalytic Reduction of N_2 to NH_3 on 3D Hollow Co-MoS$_2$ Nanostructures

Libin Zeng[†,‡], Xinyong Li[†,‡], Shuai Chen[†], Jiali Wen[†], Farnood Rahmati[†], Joshua van der Zalm[†], Aicheng Chen[*†]

[†] Electrochemical Technology Center, Department of Chemistry, University of Guelph, 50 Stone Road East, Guelph, ON N1G 2W1, Canada

[‡] State Key Laboratory of Fine Chemicals, Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China

Experimental Section

Chemicals

Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), cetyltrimethylammonium bromide (CTAB), 2-methylimidazole ($CH_3C_3H_2N_2H$), sodium citrate (CH_3COONa), potassium hexacyanoferrate (III) ($K_4Fe(CN)_6$), sodium sulfate (Na_2SO_4), sodium hydroxide (NaOH), sodium salicylate ($C_7H_5O_3Na$), sodium hypochlorite (NaClO), sodium nitroferricyanide (III) ($C_5FeN_6Na_2O$), and ammonium chloride (NH_4Cl) were purchased from Sigma-Aldrich Chemical Reagent Co. Ltd. Nafion (1 wt.%) solution, hydrogen peroxide (H_2O_2), and ethanol were purchased from Aladdin Ltd. Ammonium tetrathiomolybdate (($NH_4)_2MoS_4$) was purchased from New Jersey, USA. All reagents were of analytical grade and used without further purification. Further, a cation exchange membrane (CEM) was purchased from the DuPont Company. Deionized water (18.2 MΩ cm) was used in all experiments.

Characterization of nanomaterials

A field-emission scanning electron microscopy (FE-SEM) (Hitachi, USA) and high-resolution transmission electron microscopy (HRTEM) (FEI Tecnai F30 electron microscope, using a 200 kV accelerating voltage) were used to characterize the morphology and crystallinity of the as-prepared Co-MoS$_2$ catalysts. X-ray diffraction (XRD) with a diffractometer with Cu $K\alpha$ radiation (PW1050-3710, Japan, source light at the wavelength (λ) of 0.1541 nm) was employed to investigate the crystalline structure of the as-prepared catalysts. The chemical compositions and oxidation states of

the as-prepared Co@MoS$_2$ catalysts were investigated via X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-α XPS spectrometer, USA). The specific surface area and pore size distribution were elucidated by nitrogen adsorption/desorption isotherms on a Quantachrome instrument (NOVA 4200e, USA). Raman spectra were recorded at 532 nm using a Raman spectrophotometer (Renishaw Canada Ltd.).

**Table S1.** Comparison of MoS$_2$-based catalysts for the electrochemical synthesis of ammonia.

| Catalysts	Conditions	Faradaic Efficiency (%)/ Bias (V *vs.* RHE)	Ammonia Yield (μg h^{-1} mg$^{-1}_{cat.}$)/Bias	Ref.
MoS$_2$ nanosheets	25°C, 0.1 M Na$_2$SO$_4$	1.17/-0.5	13.09/-0.5	1
Defect-rich MoS$_2$ nanoflowers	25°C, 0.1 M Na$_2$SO$_4$	8.34/-0.4	29.28/-0.4	2
S@MoS$_2$ nanosheets	25°C, 0.1 M Li$_2$SO$_4$	9.81/-0.2	43.4/-0.2	3
N@MoS$_2$ nanoflowers	25°C, 0.1 M Na$_2$SO$_4$	9.14/-0.3	69.82/-0.3	4
Au@MoS$_2$ nanosheets	20°C, 0.1 M KOH	9.7/-0.3	25.00/-0.3	5
Ru@MoS$_2$	50°C, 0.1 M Na$_2$SO$_4$	17.6/-0.15	6.98/-0.15	6
MoS$_2$@rGO	20°C, 0.1 M LiClO$_4$	4.56/-0.45	24.82/-0.45	7
Co-MoS$_2$ (20:1)	20°C, 0.1 M Na$_2$SO$_4$	11.21/-0.4	129.93/-0.4	This work
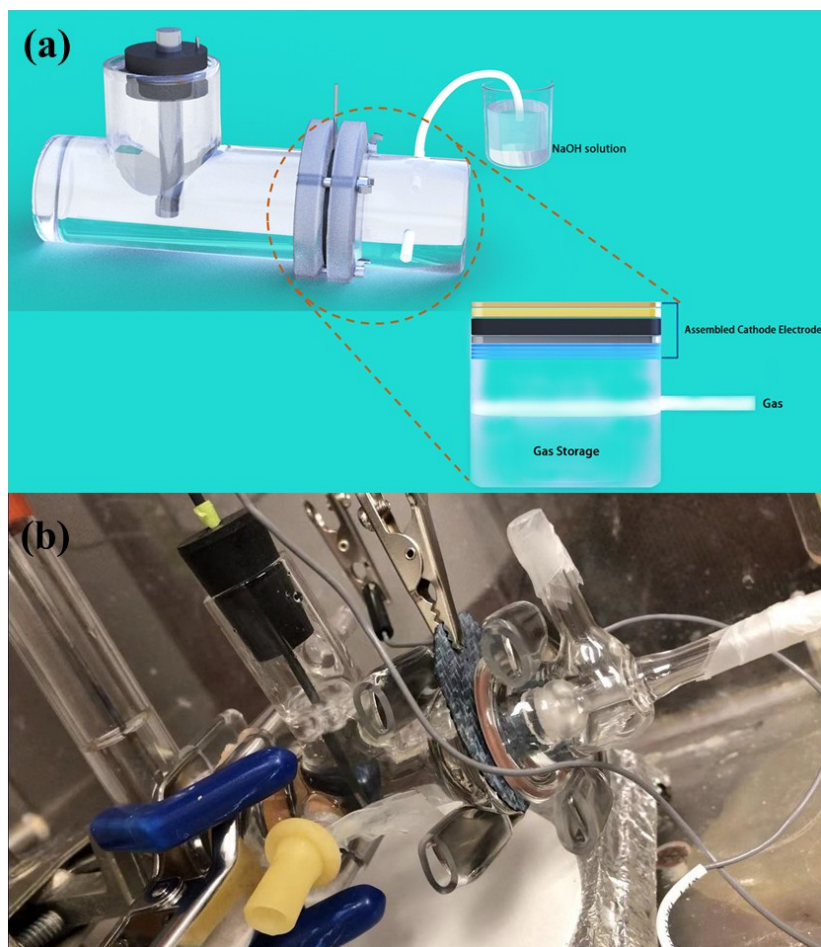
Scheme S1. (a) Schematic diagram of the constructed two-chamber cell used for the NRR; (b) the

original image of the electrochemical cell system.
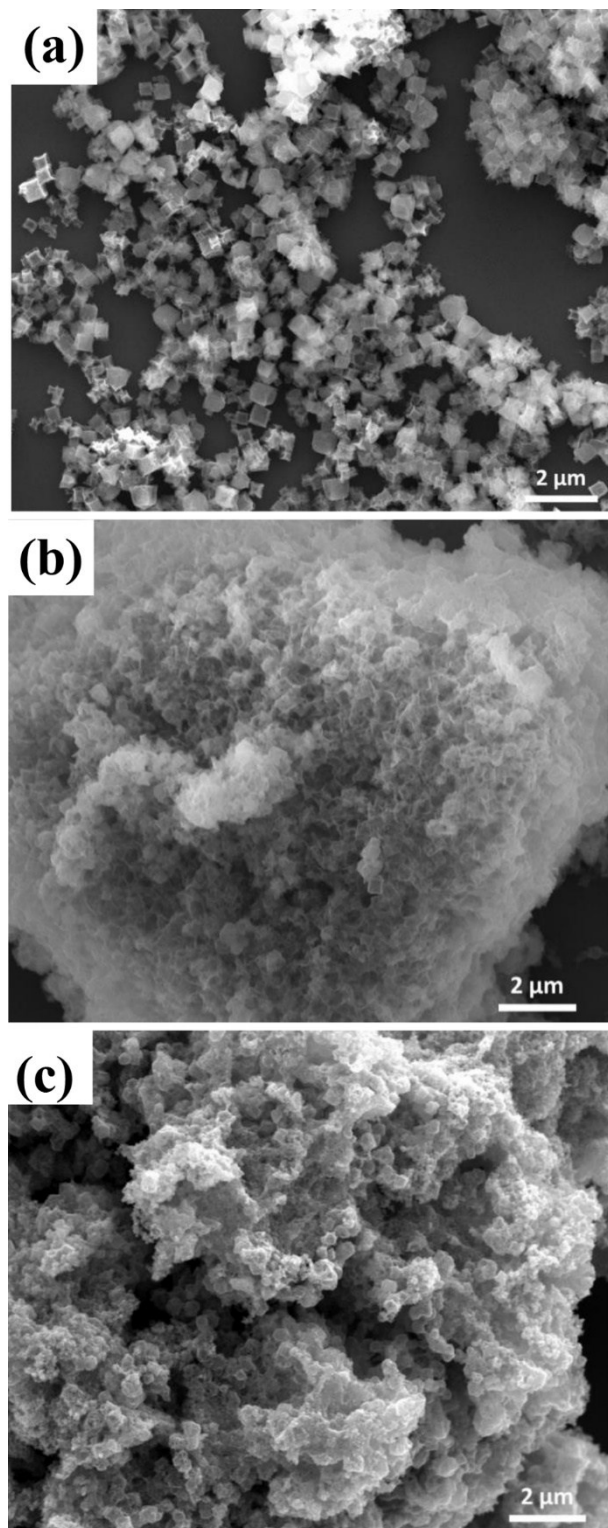
Figure S1. SEM images of Co-MoS$_2$ catalysts: (a) Co-MoS$_2$ (20:1), (b) Co-MoS$_2$ (10:1), and (c) Co-MoS$_2$ (1:1) samples.
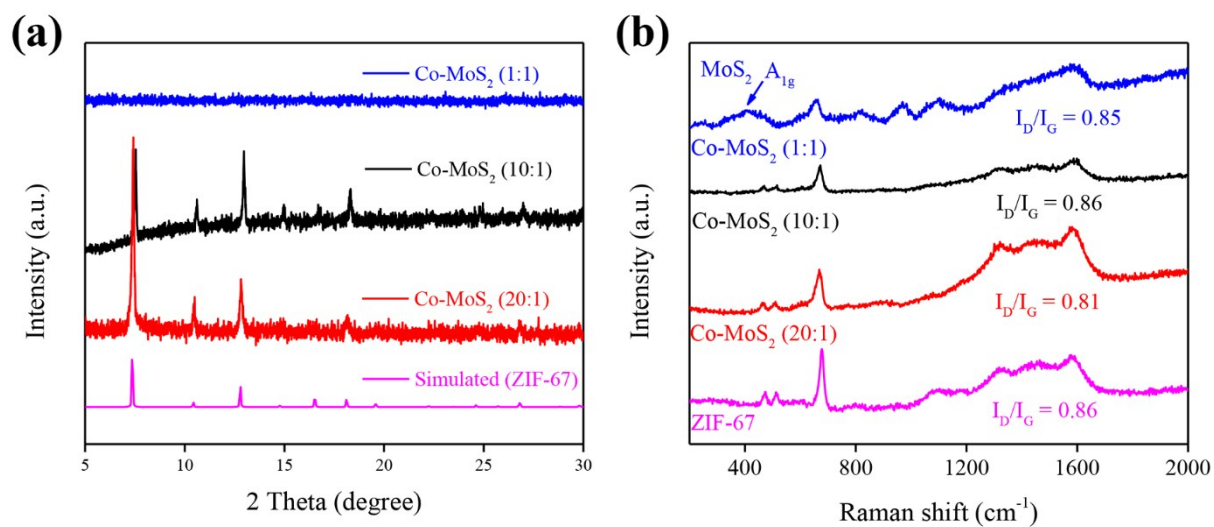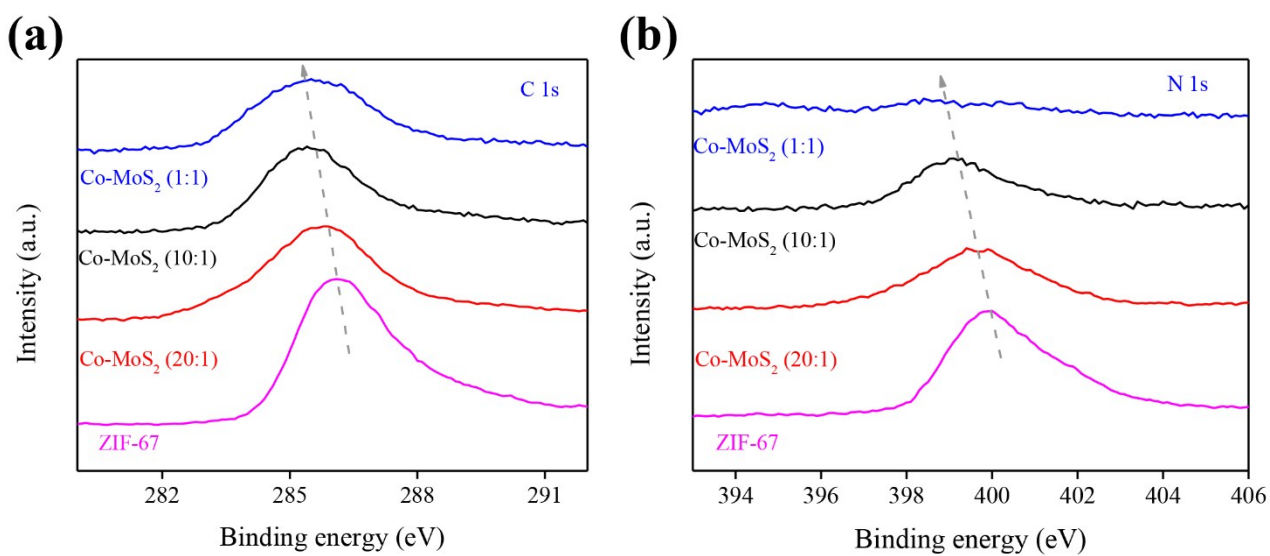
Figure S2. (a) XRD spectra of Co-MoS$_2$ (20:1), Co-MoS$_2$ (10:1), Co-MoS$_2$ (1:1) and simulated pattern of ZIF-67 structure samples; (b) the corresponding Raman spectra with the excitation at 532 nm.
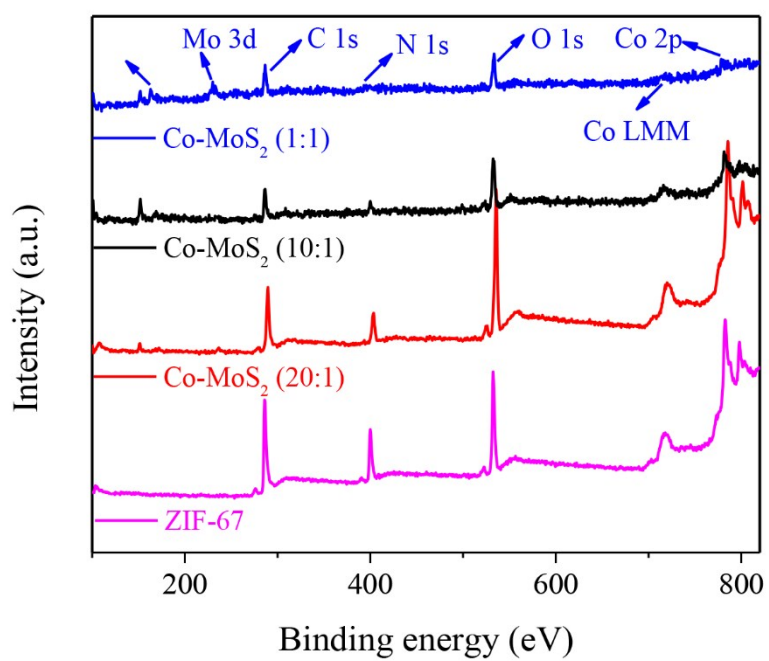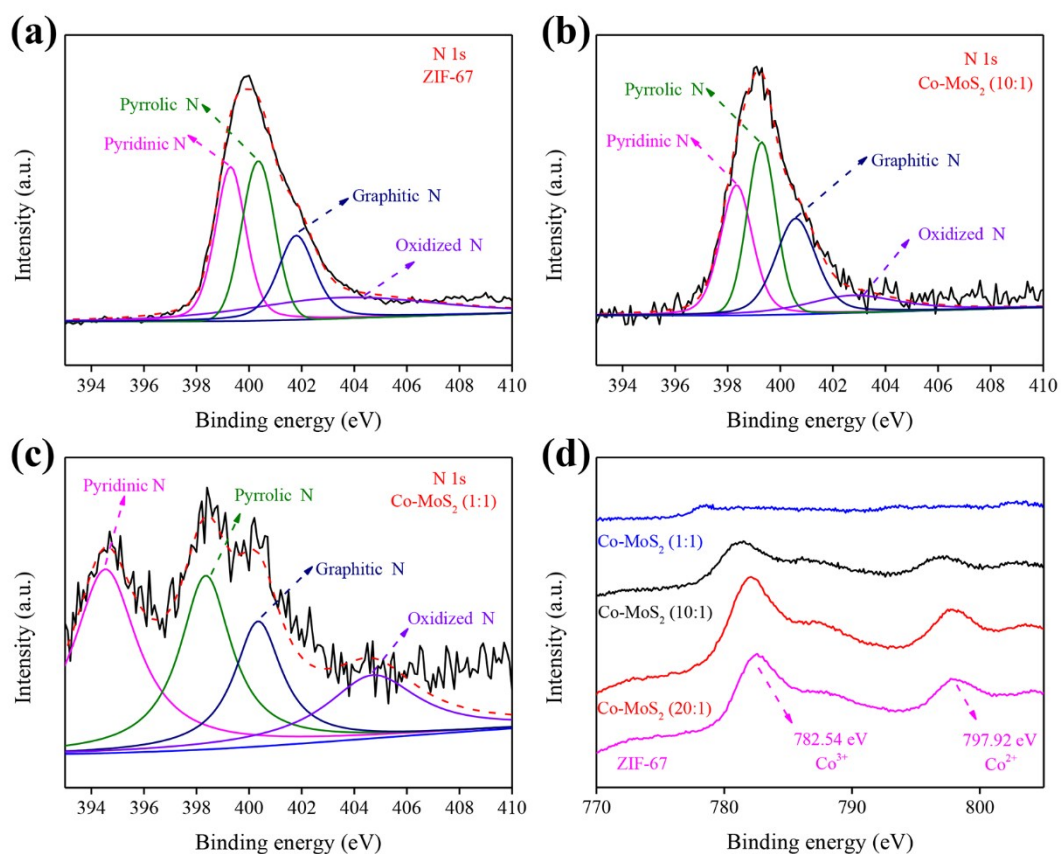
Figure S3. XPS surveys of the as-prepared ZIF-67 and the Co-MoS$_2$ catalysts.
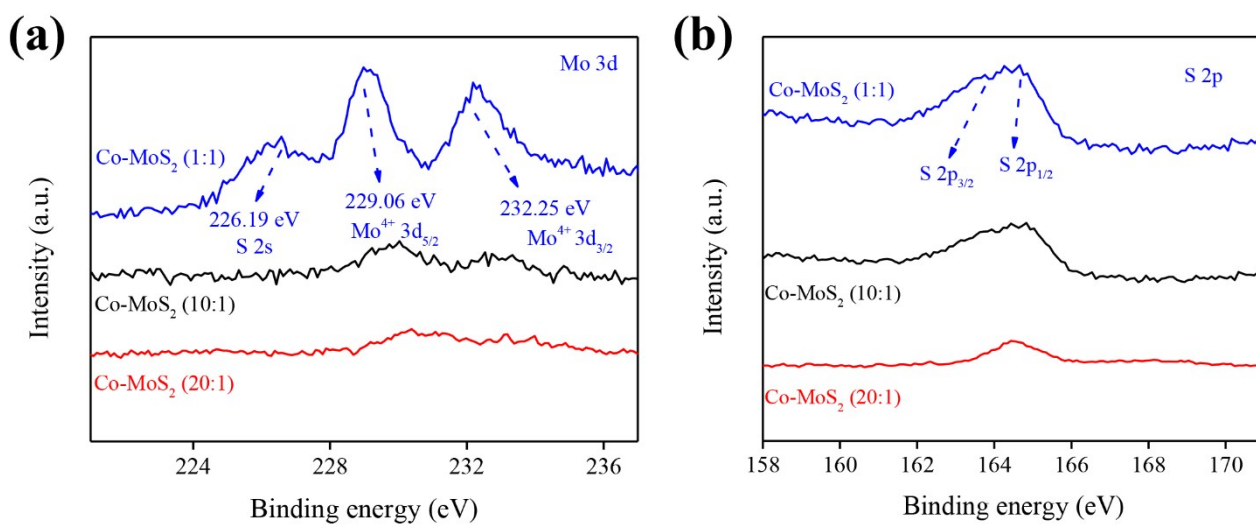
Figure S4. High-resolution XPS spectra of C 1s (a) and N 1s (b) of ZIF-67 and the different Co-doped MoS$_2$ samples, respectively.
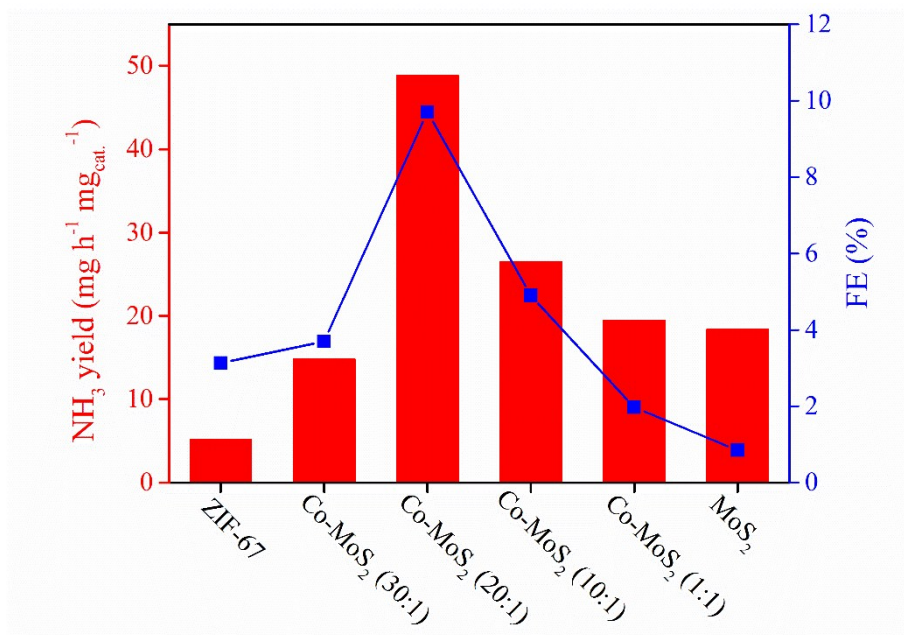
Figure S5. High-resolution XPS spectra and the fitted N 1s spectra of (a) ZIF-67, (b) Co-MoS$_2$ (10:1) and (c) Co-MoS$_2$ (1:1) catalysts; (d) high-resolution XPS spectra of Co 2p of ZIF-67 and the Co-doped MoS$_2$ samples.
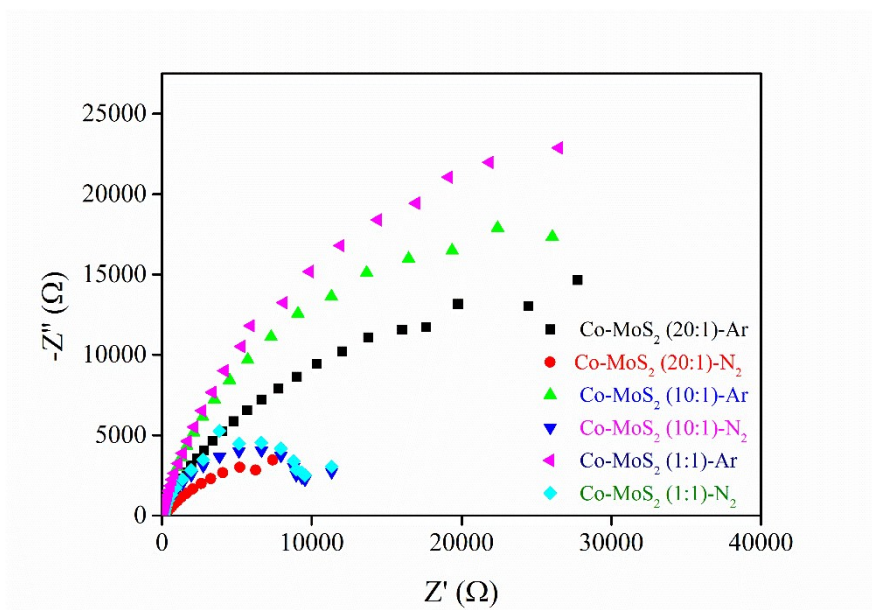
Figure S6. High-resolution XPS spectra of Mo 3d (a) and S 2p (b) of the Co-doped MoS_2 samples.
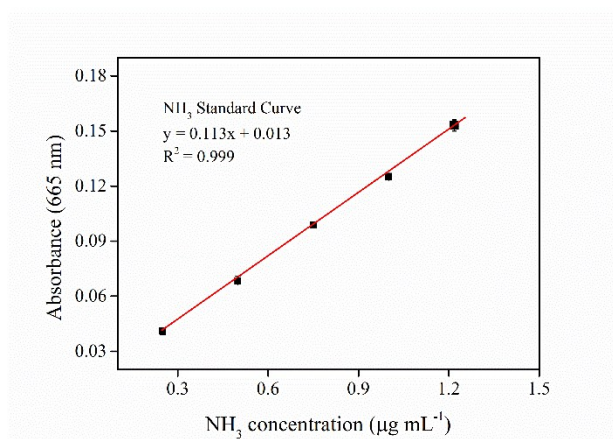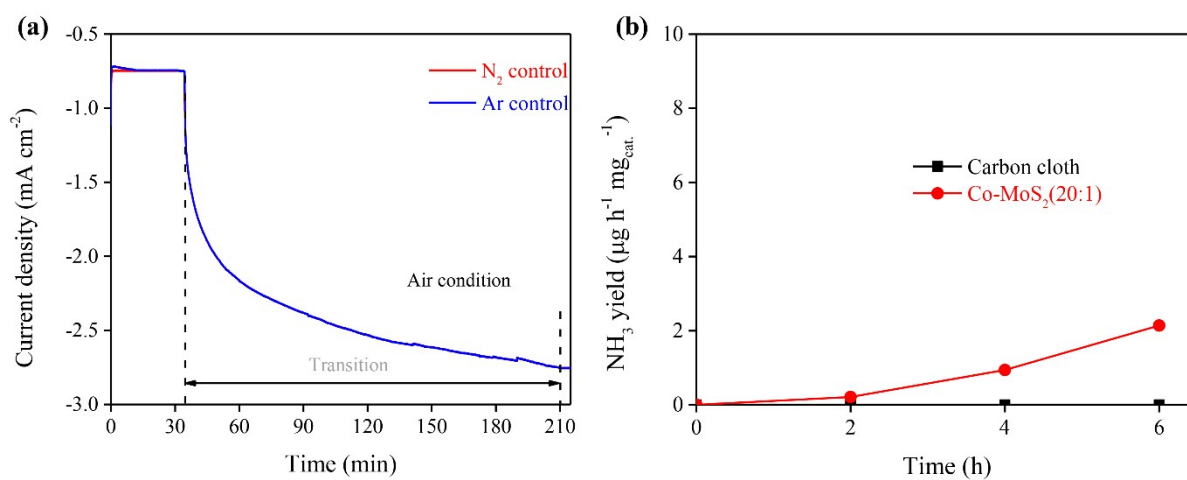
Figure S7. Calibration curve used for the estimation of NH_3 via NH_4^+ ion concentration.
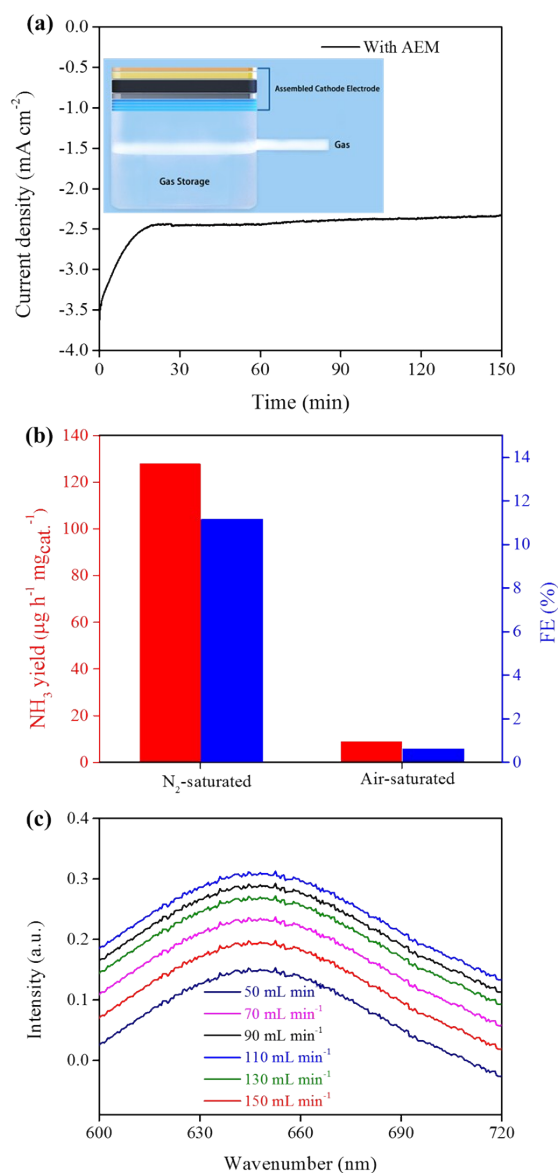
Figure S8. NH$_3$ yields and corresponding FEs of the different catalysts at -0.4 V *vs*. RHE.

Figure S9. Electrochemical impedance spectra of the different Co-MoS$_2$ catalysts recorded under the Ar-/N$_2$-saturated conditions.

Figure S10. (a) Chronoamperometry curves of the carbon black under N_2 and Ar (30 min), and the corresponding air transition stage (-0.4 V vs RHE); (b) NH_3 yield over carbon black and Co-MoS_2(20:1) catalyst at the potential of -0.4 V vs RHE, respectively, where Ar gas was purged through the solution for 30 min and then was stopped.

Figure S11. (a) Chronoamperometric curves of the Co-MoS$_2$ catalyst during the gas transition with CEM at the applied electrode potential of -0.4 V vs. RHE; (b) corresponding NH$_3$ yields and FEs at selected positions; (c) UV-vis spectra of the NRR under different N$_2$ flow rate.
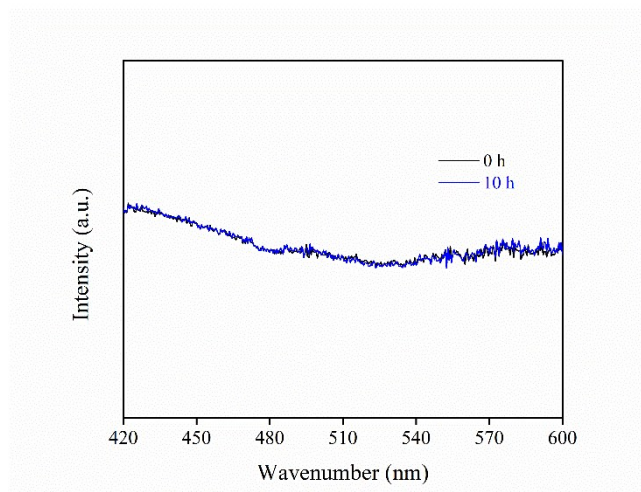
Figure S12. UV-Vis spectra of the NRR prior to and following the 10-hour electrolysis at -0.4 V *vs*. RHE with the GDE.

References

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