Supporting Information

Re-dispersion of Mo-based Catalysts and the Rational Design of Super Small-sized Metallic Mo Species

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EXPERIMENTAL

Materials

Potassium hydroxide (KOH) and concentrated hydrochloric acid (HCl) were obtained from Sinopharm Chemical Reagent Co., Ltd. Sodium hydroxide (NaOH), sodium salicylate ($C_7H_5NaO_3$, AR, ≥99.5%), sodium nitroferricyanide dehydrate, sodium hypochlorite solution (5.0%) and dopamine hydrochloride were purchased from Aladdin. All chemicals without any further treatment were analytical. Commercial CC (carbon cloths, HCCP330) was purchased from Shanghai Hesen Electric Co. Ltd., China.

Electrochemical Measurements

Determination of ammonia

Spectrophotometry measurement with salicylic method[1]: 6.404 g sodium salicylate and 1.28 g sodium hydroxide dissolved in 1000 mL deionized water which was used as coloring solution; A mixture of 8 mL sodium hypochlorite (5 wt %), 3 g sodium hydroxide and 100 mL deionized water was used as a oxidation reagent; 0.1g $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ diluted to 10 ml with deionized water was used as catalyst reagent. Standard ammonium solution in the alkaline solution as follow: 4 mL of sample was taken. Then 50 μL of oxidizing solution, 4 mL H_2O, 500 μL of colouring solution and 50 μL of catalyst solution were added respectively to the sample solution. Standard ammonium solution in the acid solution as follow: 4 mL of sample was taken. Then 4 mL H_2O, 1 mL KOH (1 M), 50 μL of oxidizing solution, 500 μL of colouring solution, 50 μL of catalyst solution were added respectively to the sample solution. Absorbance

measurements were performed after 1 hour at λ =670 nm. The calibration curve below was used to calculate the ammonia concentration.

Spectrophotometry measurement with Nessler reagent in the alkaline solution[2]: NH_4Cl solutions with various concentrations were placed in the test tubes. Then KOH solution (0.1 M) were added to each test tube until the volume reached 10 mL. 1 mL sodium potassium tartrate (0.2 M) and 1 mL of Nessler reagent were added to each test tube one after another. Absorbance measurements were performed after 20 min at λ= 425 nm. The calibration curve below was used to calculate the ammonia concentration (Figure S13).

Determination of hydrazine

The hydrazine present in the electrolyte was estimated by the method of Di Bao and Qi Zhang.[3] A mixture of 5.99 g para-(dimethylamino) benzaldehyde, 300 mL ethanol and 30 mL HCI (concentrated) was used as a color reagent. Calibration curve in the alkaline solution was plotted as follow: First, preparing a series of reference solutions and 3 mL of sample was taken; Second, adding 2 mL H_2O and 5 mL above prepared color reagent were added respectively to the sample solution, and then stirring 10 min at room temperature. Last, the absorbance of the resulting solution was measured at 456 nm. Calibration curve in the acid solution was plotted as follow: 2 mL of sample was taken. Then 2 mL H_2O, 1 mL KOH (1 M) and 5 mL color reagent were added respectively to the sample solution, and then stirring 10 min at room temperature. Last, the absorbance of the resulting solution was measured at 456 nm.

Faradaic efficiency

The Faradaic efficiency for NRR was defined as the quantity of electric charge used for synthesizing ammonia divided by the total charge passed through the electrodes during the electrolysis. The total amount of NH_3 produced was measured using colorimetric methods. Assuming three electrons were needed to produce one NH_3 molecule. The Faradaic efficiency could be calculated as follows: $FE= 3F \times [NH_3] / (17 \times Q)$, where F is the Faraday constant, $[NH_3]$ is the concentration and Q is total charge passed through the electrodes during the reaction duration according to the total current density. The rate of ammonia formation was calculated using the following equation: $R_{NH3}= [NH_3] / t \times m$, where t is the reduction reaction time (h) and m is the loading mass of catalysts (mg cm^{-1}).

Computational Methods

All the theoretical calculations were performed using a plane-wave technique implemented in Vienna ab initio simulation package (VASP)[4, 5] and the revised PBEsol functional.[6] PBEsol functional was used as exchange-correlation functional approximation. The electron-ion interactions were expounded by the projector augmented wave (PAW) approach presented by Blöchl[7] and carried out by Kresse[8] and a plane-wave cutoff energy of 400 eV was used. A Monkhorst−Pack k-point mesh of 4×4×1 and 2×2×1 were used for the Brillouin zone sampling during electronic structure calculation and the structure optimization, respectively. The vacuum space along the z direction was set to be 15 Å and the periodic condition was employed along the x and

y directions. All atoms in the supercell are allowed to relax during the structure optimization except the bottom layer atoms of graphene. The relaxation was stopped when the force residue on the atom was smaller than 0.02 eV/Å. The adsorption energy for metal nanoparticles is defined as

$$E_{ads} = E_{tot} - E_{slab} - E_{metal}$$

where E_{tot} is the total energy of support and metal nanoparticle, E_{slab} is the energy of the clean support alone, and E_{metal} is the energy of metal nanoparticle.

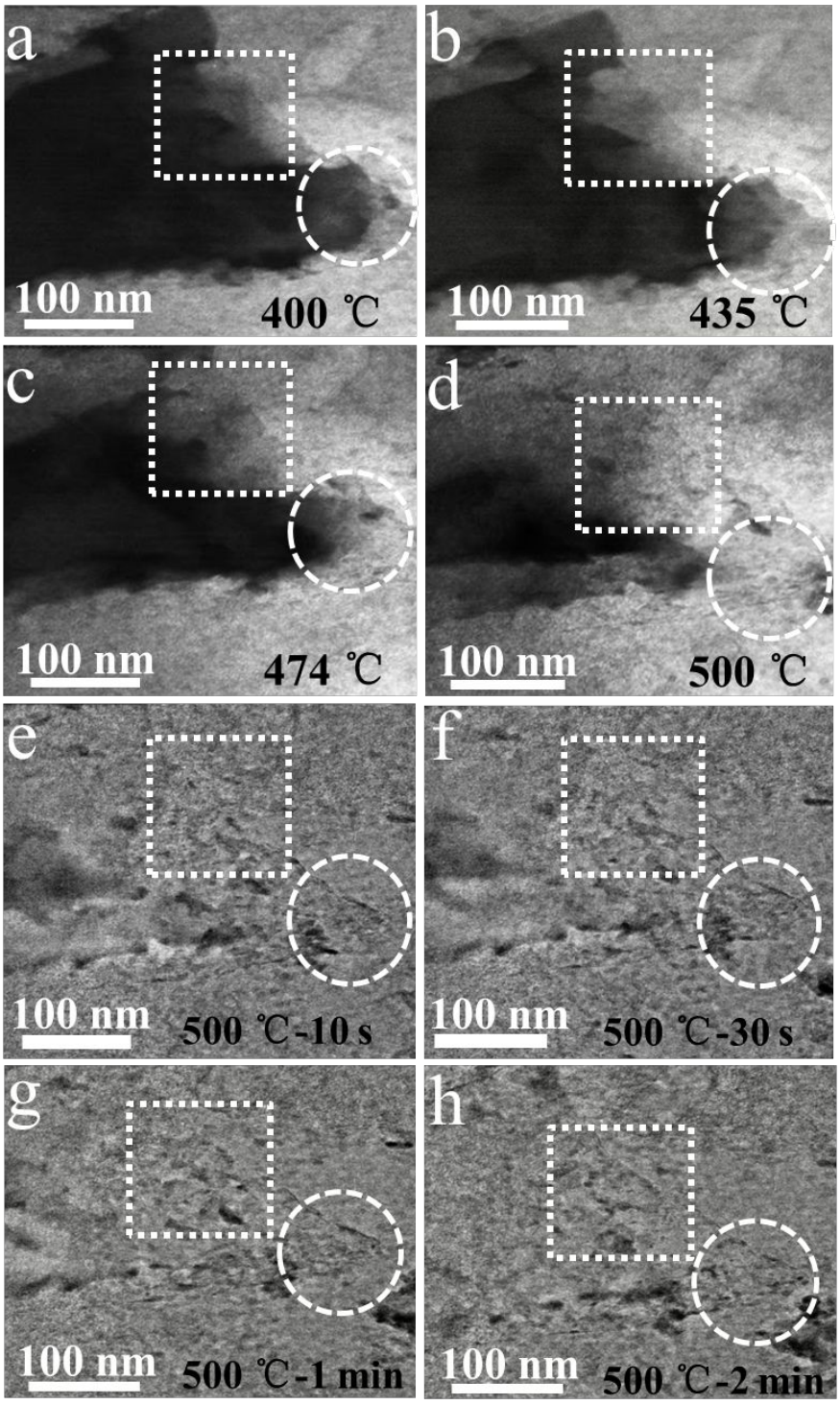

Figure S1 In-situ HRTEM images of the reduction of MoO_2/CC@CN in hydrogen staring 400 °C to 500 °C and then occurring at 500 °C for 5 min. (a) 400 °C, (b) 435 °C, (c) 474 °C, (d) 500 °C, (e) 500 °C for 10 s, (f) 500 °C for 30 s, (g) 500 °C for 1 min, (h) 500 °C for 2 min

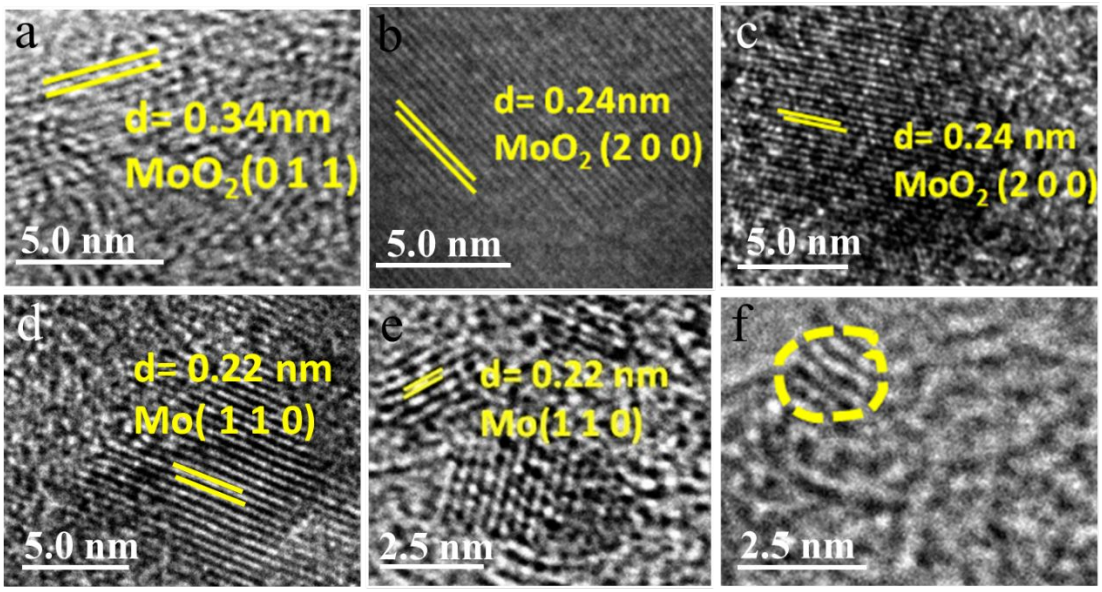

Figure S2 HRTEM images of (a) MoO_2/CC@CN, (b) MoO_2-400 °C-1h/CC@CN, (c) MoO_2-450 °C-1h/CC@CN, (d) Mo-500 °C-5min/CC@CN, (e) Mo-500 °C-1h/CC@CN and (f) Mo-500 °C -8h/CC@CN.

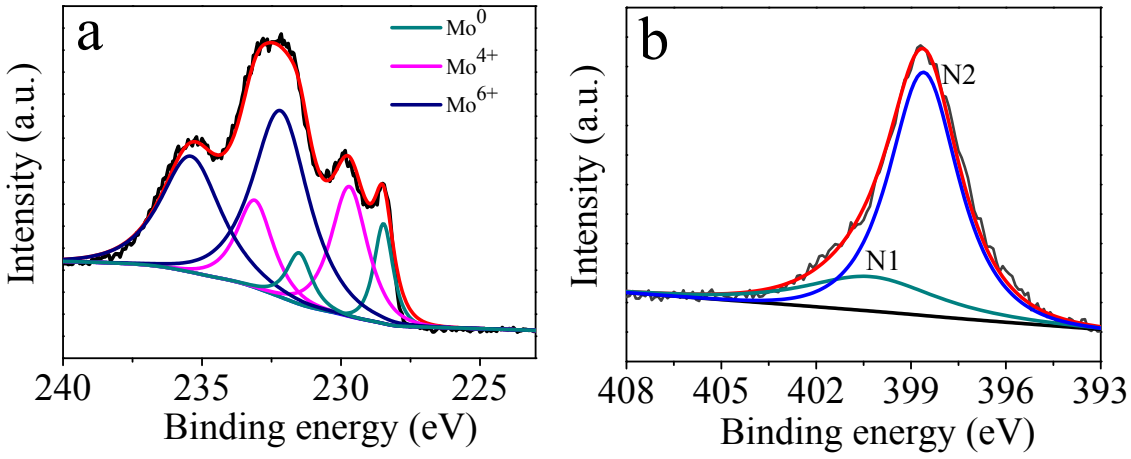

Figure S3 (a) and (b) The Mo 3d and N 1s XPS fine scan spectrum of Mo-500 °C-8h/CC@CN (N1: pyrrolic N, N2: pyridinic N), respectively.

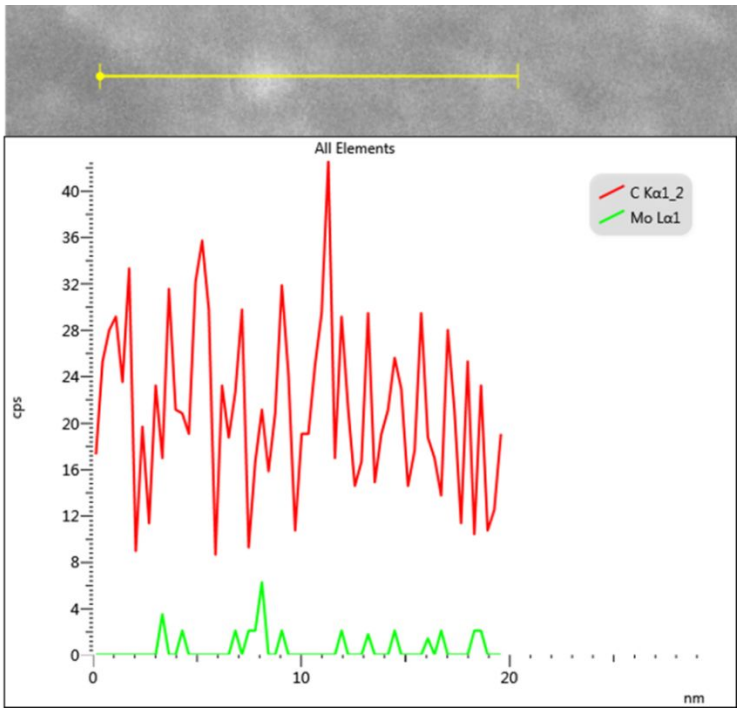

Figure S4 STEM-EELS line scan crossing a Mo-500 °C-10h/ACC-600.

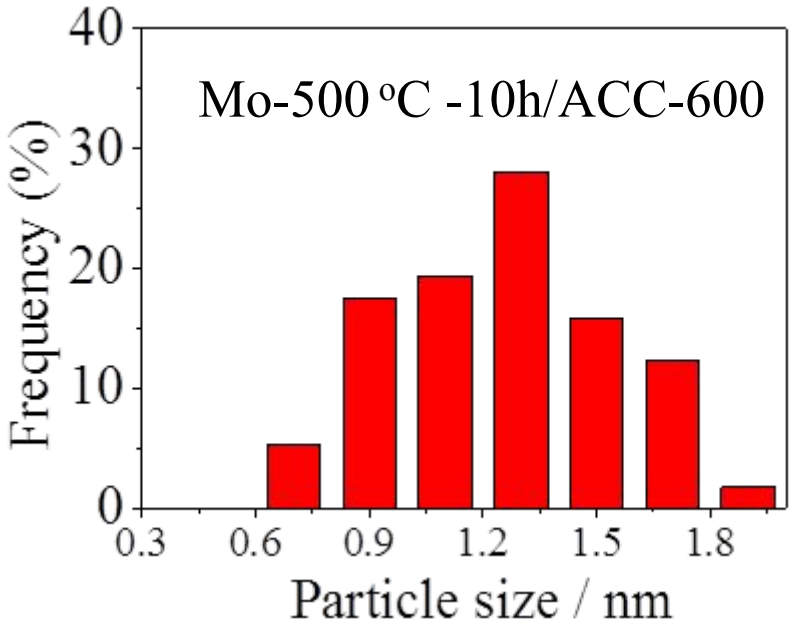

Figure S5 Mo nanoparticle size distribution of Mo-500 °C-10h/ACC-600.

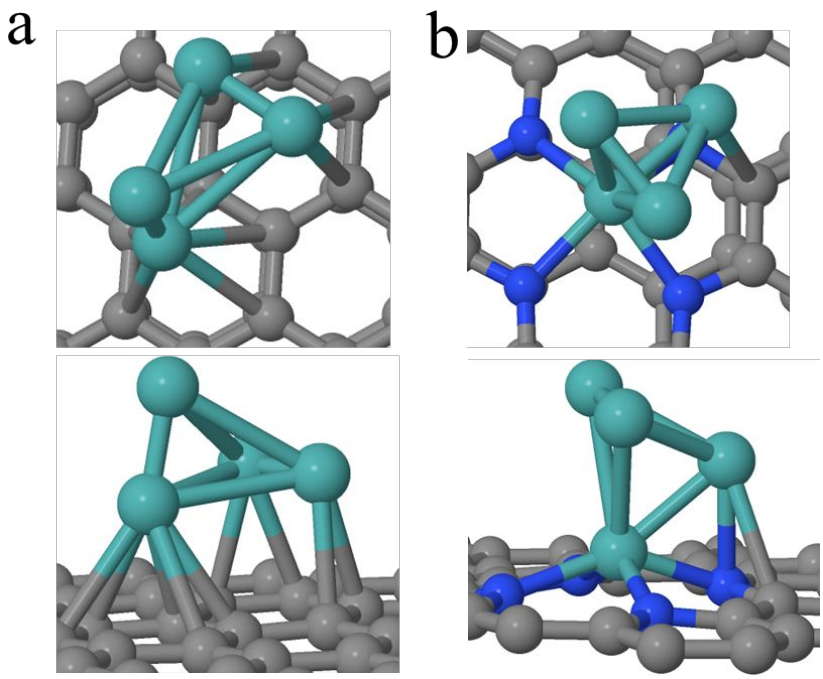

Figure S6 The top and side images of Mo-cluster on (a) graphene and (b) doped-N graphene (Mo: green; C: gray; N: blue)

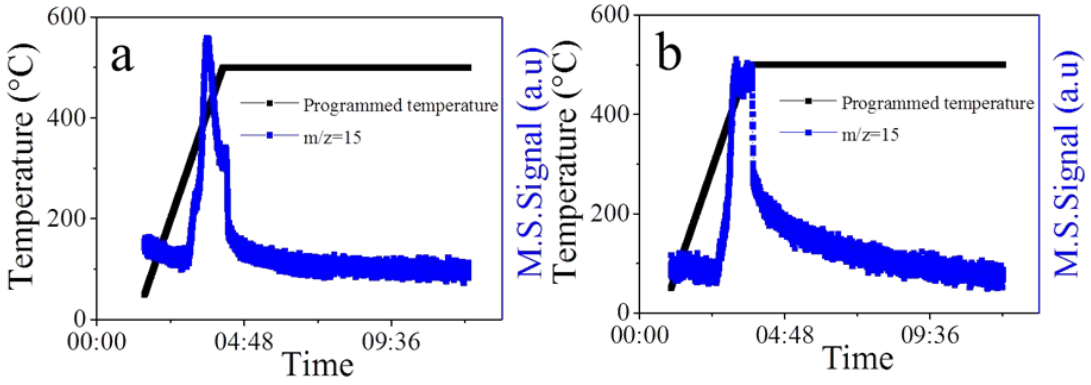

Figure S7 (a) and (b) H_2-TPR-MS patterns of MoO_2/CC@CN and MoO_2/ACC-600, respectively: mass spectra for CH_4.

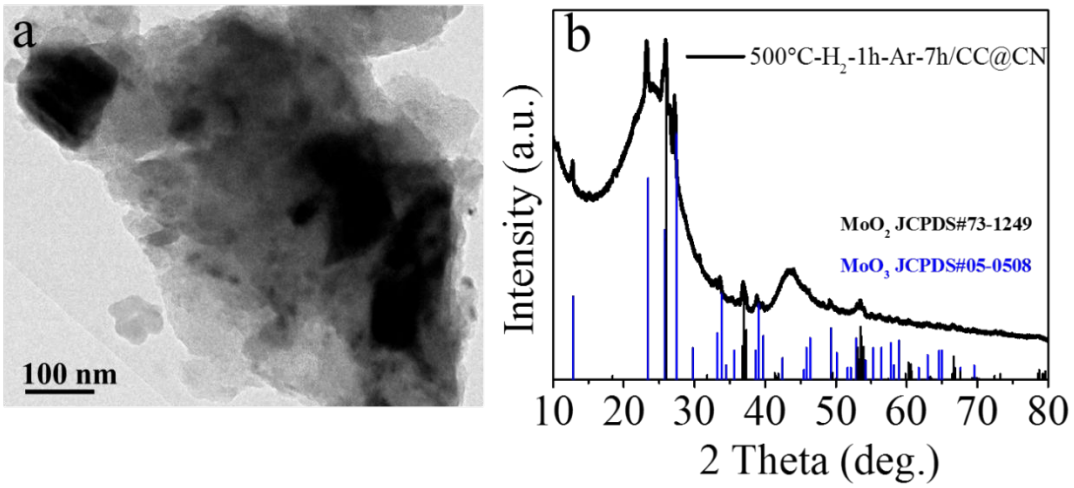

Figure S8 (a) HRTEM images of 500 °C-H_2-1h-Ar-7h/CC@CN. (b) XRD patterns of 500 °C-H_2-1h-Ar-7h/CC@CN.

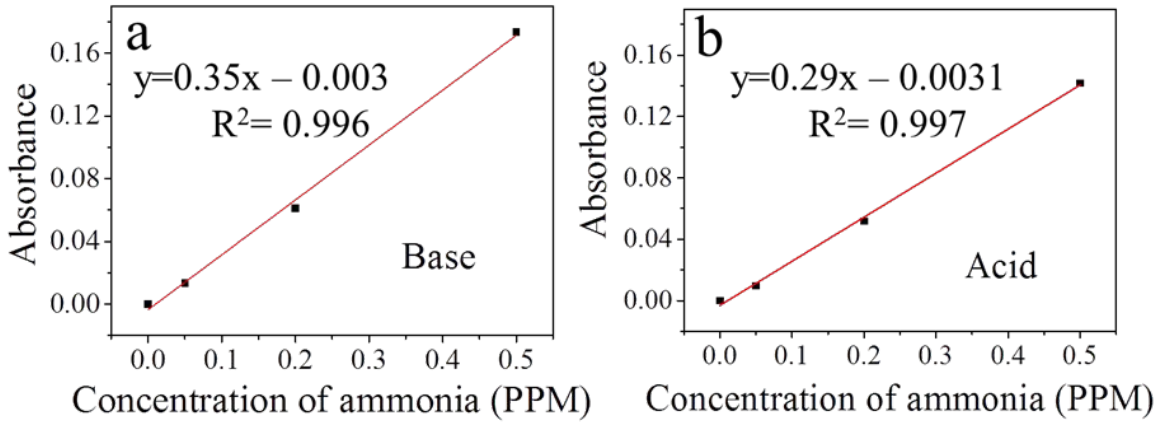

Figure S9 (a) and (b) Calibration curve used for estimation of NH_3 in base and acid, respectively.

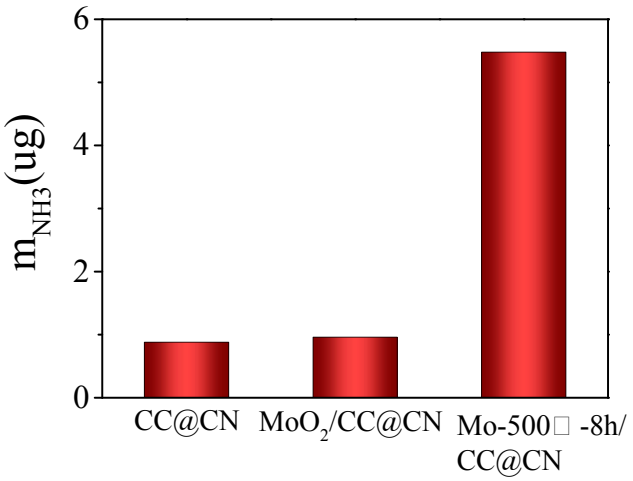

Figure S10 The amount of NH_3 with CC@CN, MoO_2/CC@CN and Mo-500 °C-8h/CC@CN electrode after 3h electrolysis at 0 V under ambient conditions, respectively.

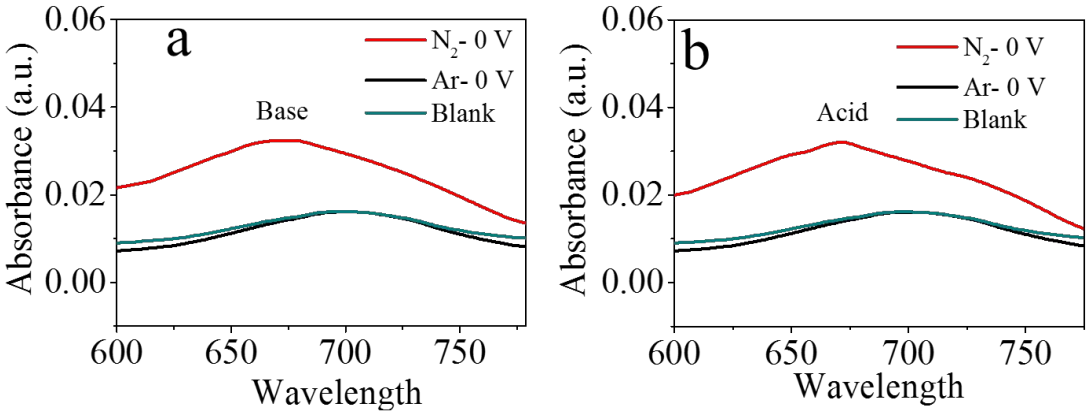

Figure S11 (a) and (b) UV-vis absorption spectra after potentiostatic tests in N_2 and Ar at 0 V versus RHE in base and acid, respectively.

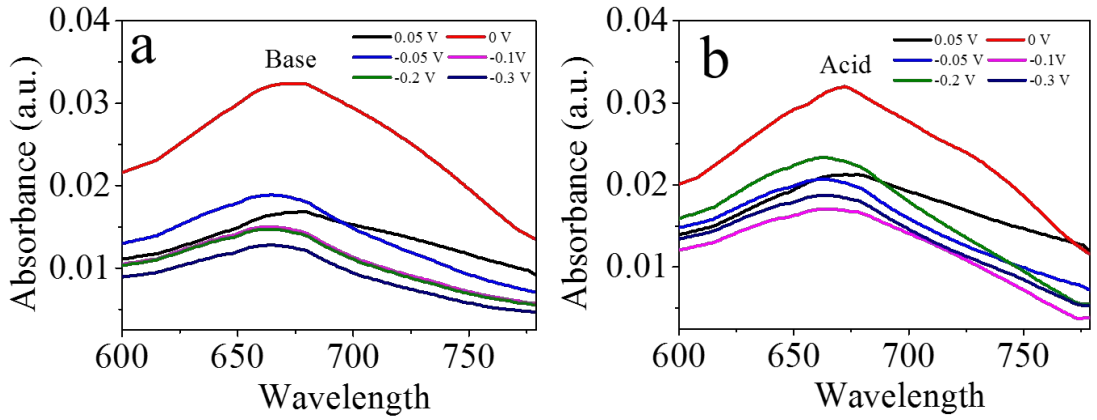

Figure S12 (a) and (b) Comparison of absorbance spectra at different potential in N_2 in base and acid, respectively.

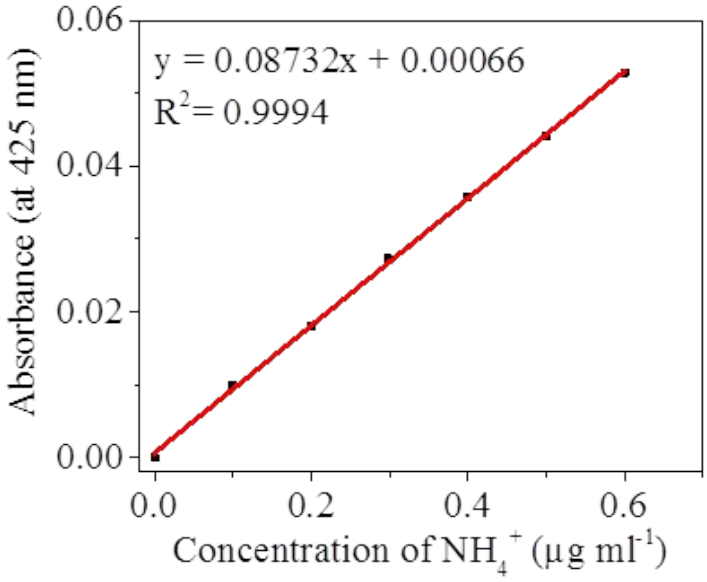

Figure S13 Calibration curve used for estimation of NH_3 in base using Nessler reagent.

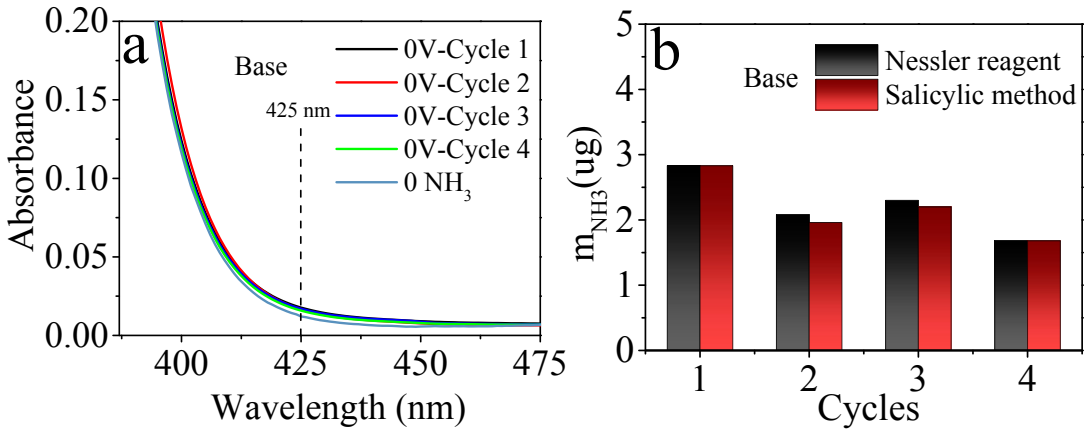

Figure S14 (a) Absorbance spectra of cycling test of Mo-500 °C-8h/CC@CN in base using Nessler reagent. (b) The amount of NH_3 with Mo-500 °C-8h/ CC@CN electrode after 3h electrolysis at 0 V under ambient conditions in base by Nessler reagent and Salicylic method, respectively.

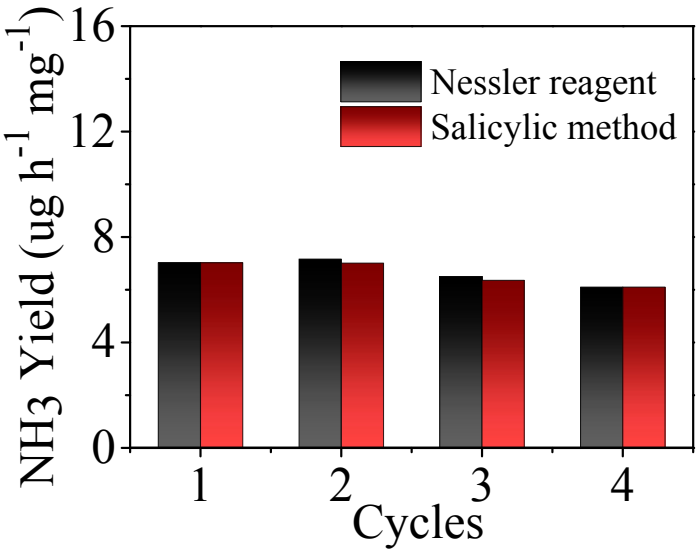

Figure S15 Yield of NH_3 with cycling test of Mo-500 °C-8h/CC@CN used by Nessler reagent and Salicylic method, respectively .

Table S1. The contents of Mo and N for Mo-500 °C-8h/CC@CN

Mo-500 °C-8h/CC@CN	**Mo %**	**N %**
Before calcination	1.35	0.27
After reduction	1.34	0.19

Table S2 Summary of the representative reports on N_2 fixation.

Process	System/Catalyst	Conditions	Yield	Testing Method	Reference
Harsh condition	Ru (7.8 wt%)-loaded Y_5Si_3	400 °C	1.9 mmol $g^{-1}h^{-1}$	Ion chromatography	Ref. 9
	Fe_2O_3/AC (Molten hydroxide)	250 °C, atmospheric pressure	8.27×10^{-9} mol s^{-1} cm^{-2}	Salicylic method	Ref. 10
	Fe/Ru-based catalysts	350~550 °C,200~300 atm	~20% (N_2 conversion rate)	----	Ref. 11
Electrocatalysis	Pt plate/0.1 M KOH/ N_2, Mo-500 °C -8h/CC@CN	room temperature and atmospheric pressure	7.03 ug h^{-1} mg^{-1} and 22.3% FE	Salicylic method	**This work**
	Pt plate/0.1 M HCl/ N_2, Au-TiO_2 sub-nanocluster	room temperature and atmospheric pressure	8.11% (current efficiency)	Indophenol blue method	Ref. 12
	graphite plate/0.1 M KOH/ N_2, Au	room temperature and atmospheric pressure	1.648 ug h^{-1} cm^{-2} (NH_3) 0.102 ug h^{-1} cm^{-2}	Nessler's reagent and Ammonia colorimetric assaykit	Ref. 3

			(N_2H_4 H_2O)		
	Fe_2O_3	250 °C, 25 bar, 1.0 V	35% (N_2 conversion rate)	Salicylic method	Ref. 13
	Pt plate/ionic liquids, THF, ethanol/ N_2, Ni plate	room temperature	1.7% (current efficiency)	Berthelot method	Ref. 14
	Pt plate/0.1 M HCl/ N_2, amorphous-Au/CeO_x-RGO	room temperature and atmospheric pressure	8.3 ug h^{-1} mg^{-1} and 10.10% Faradaic efficiency (FE)	Indophenol blue method	Ref. 15
Photocatalysis	BiOBr, H2O (sacrificial agent)	λ > 420 nm	1.08 ppm (1 h)	Nessler's reagent	Ref. 16
	Diamond, KI (sacrificial agent)	λ > 190 nm	0.8 ppm (24 h)	Indophenol blue method	Ref. 17

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