Supporting Information

Enhanced Electrocatalytic Nitrate Reduction to Ammonia with Silver Nanocubes

Swathi M. Gowdru,[a] Priyadarshini HN,[a] Yi-Chia Chen,[a] Kuan-Chang Wu,[a,b] Chia-Che Chang,[c] Di-Yan Wang[a]

[a] Department of Chemistry, National Taiwan Normal University, Taipei, 11677, Taiwan

[b] Department of Chemistry, Tunghai University, Taichung 40704, Taiwan.

[c] National Synchrotron Radiation Research Center (NSRRC), Hsinchu 30076, Taiwan

E-mail: diyanwang@ntnu.edu.tw

Experimental Section

Materials

1,5-Pentanediol (97%) and silver nitrate (99.99%) were purchased from Alfa Aesar. Copper (II) chloride dehydrate was purchased from Fisher Scientific. Polyvinylpyrrolidone (average M_w ~55,000) and ethanol were purchased from Sigma-Aldrich. Copper (Cu; 99%) foil was acquired from UBIQ technology CO., LTD. Sulfuric acid (H_2SO_4; 99.999%), phenol (C_6H_5OH;100%), ammonium-15N chloride ($^{15}NH_4Cl$; ≥ 99%), sodium nitrate-15N ($Na^{15}NO_3$; ≥ 99%), dimethyl sulfoxide-d6 (D6-DMSO; 99.9%) and sodium sulfate (Na_2SO_4) were procured from Sigma-Aldrich. Sulfonamide ($C_6H_8N_2O_2S$; 98%), phosphoric acid (H_3PO_4; 85%), hydrochloric acid (HCl; 37%) and *N*-(1-naphthyl) ethylenediamine dihydrochloride ($C_{12}H_{14}N_2$; 98%) were procured from Across organics. Sodium hydroxide (NaOH; ACS 97+%) and sodium hypochlorite (NaClO; 6-14% active Cl basis) were procured from Shimakyu's pure chemicals and Honeywell-Fluka, respectively. All chemicals were used without further purification

Synthesis of AgNCs

Silver nanocubes (AgNCs) were prepared by polyol reaction according to our previous studies.[1]

Fabrication of the catalysts on Cu foil

After synthesis of AgNCs it was dropped coated on Cu foil, before using catalysts for NO_3^-RR it was treated with sodium sulfate (0.1M Na_2SO_4) solution by simple cyclic voltammetry method to remove the surfactant of polyvinylpyrrolidone (PVP).

Material characterization

The morphologies of the prepared samples were examined by thermal scanning electron microscopy (SEM). Phase analysis was performed using X-ray diffraction (XRD) instrument (Rigaku Mini flex 600). The chemical states of the prepared samples were analyzed using X-ray photoemission spectroscopy (XPS) at the ULVAC-PHI (Quantes) of the NTU.

Electrochemical setup and measurements

A conventional three electrode system with H-cell (CHI-660 electrochemical analyzer) was used to study the electrocatalytic nitrate reduction reaction. Herein, the as-prepared samples on Cu foil (1 x 1 cm^2 dimension) were used as working electrode along with standard calomel electrode (SCE) as the reference electrode which was placed together on one side of the H-cell and platinum (Pt) wire as the counter electrode on the other side which was separated by Nafion 211 membrane. All the potentials in this work were converted to reversible hydrogen electrode (RHE) according to the Nernst equation

[$E_{RHE} = E_{SCE} + 0.245\ V + 0.059 * pH$].

In this work, 0.05 M Na_2SO_4 +100 ppm $NaNO_3$ was used as an electrolyte.

Ammonia (NH_3) detection

Primary NH3 detection and quantification were carried out using Indophenol method with UV-vis spectroscopy. Briefly, 100 µL of NaClO (pCl=6-14) in 1 M NaOH was added to 1 mL of electrolyte in the first step. In the following steps, 100 µL of 0.5 M phenol and 50 µL 0.002 M sodium nitroprusside were added to the above solution. After mixing gently, it was stored in dark conditions for 30 min and recorded absorbance at λ = 640 nm.[2]

Nitrite (NO_2^-) detection

Griess test was adopted to detect and quantify the NO_2^- in the solution. 0.1 g of *N*- (1-naphthyl) ethyl diamine dihydrochloride, 1.0 g of sulfonamide and 2.94 mL of phosphoric acid were

dissolved in 50 mL water to develop Griess reagent. 0.5 mL of as prepared Griess reagent was mixed with 0.5 mL of the test solution and 1 mL of H_2O and absorbance was recorded at $\lambda = 540$ nm after letting it react for 15 min.[3]

NMR measurements

The detection of NH_3 was carried out by ^{1}H-NMR. The solution for NMR detection prepared as follows: 1 mL of the test solution was mixed with 0.2 mL of d6-DMSO and 0.05 mL 0.01 M freshly prepared HCl.

^{15}N Isotope labeling studies

^{15}N isotopic labelling experiments were carried out using the electrolyte prepared by mixing 0.05 M Na_2SO_4 with 100 ppm $Na^{15}NO_3$. AgNCs-SST as working electrode to perform electrocatalytic reduction which was carried out at -0.36 V over different periods. After completion of the reaction, it was mixed with d6-DMSO and HCl as discussed above and tested for ^{1}H NMR.

NH_3 yield rate (Y_{NH3}) calculation

$$\text{Yield rate}_{mass}\ (NH_3) = (c(NH_3) \times V) / (t \times A) \qquad \text{Eq. 1}$$

Where $c(NH_3)$ is the measured concentration of NH_3, V is the volume of electrolyte, t is the duration time of the reduction reaction, and A is the geometric area of the cathode (1×1 cm^2).

Calculation of Faradic efficiency (FE) towards NH3

Assuming 8 electrons are required to produce one molecule of NH_3 in 0.05 M Na_2SO_4 with 100 ppm $Na^{15}NO_3$ electrolyte, FE was calculated as follows:

$$FE = (8F \times C_{NH3} \times V) / (17 \times Q) \qquad \text{Eq. 2}$$

Where F stands for Faradaic constant (96485 C/mol) and Q stands for total quantity of supplied coulomb.

NO_2^- yield rate (Y_{NO2^-}) calculation

$$\text{Yield rate}_{mass}\ (NO_2^-) = (c(NO_2^-) \times V) / (t \times A) \qquad \text{Eq. 3}$$

Where $c(NO_2^-)$ is the measured the concentration of NO_2^-, V is the volume of electrolyte, t is the duration time of the reduction reaction, and A is the geometric area of the cathode (1×1 cm^2).

Calculation of Faradic efficiency (FE) towards NO_2^-

Assuming 2 electrons are required to produce one molecule of NO_2^- in 0.05 M Na_2SO_4 with 100 ppm $Na^{15}NO_3$ electrolyte, FE was calculated as following:

$$FE = (2F \times C_{NO2^-} \times V) / (46 \times Q) \quad \text{Eq. 4}$$

Where F stands for Faradaic constant (96485 C/mol) and Q stands for total quantity.

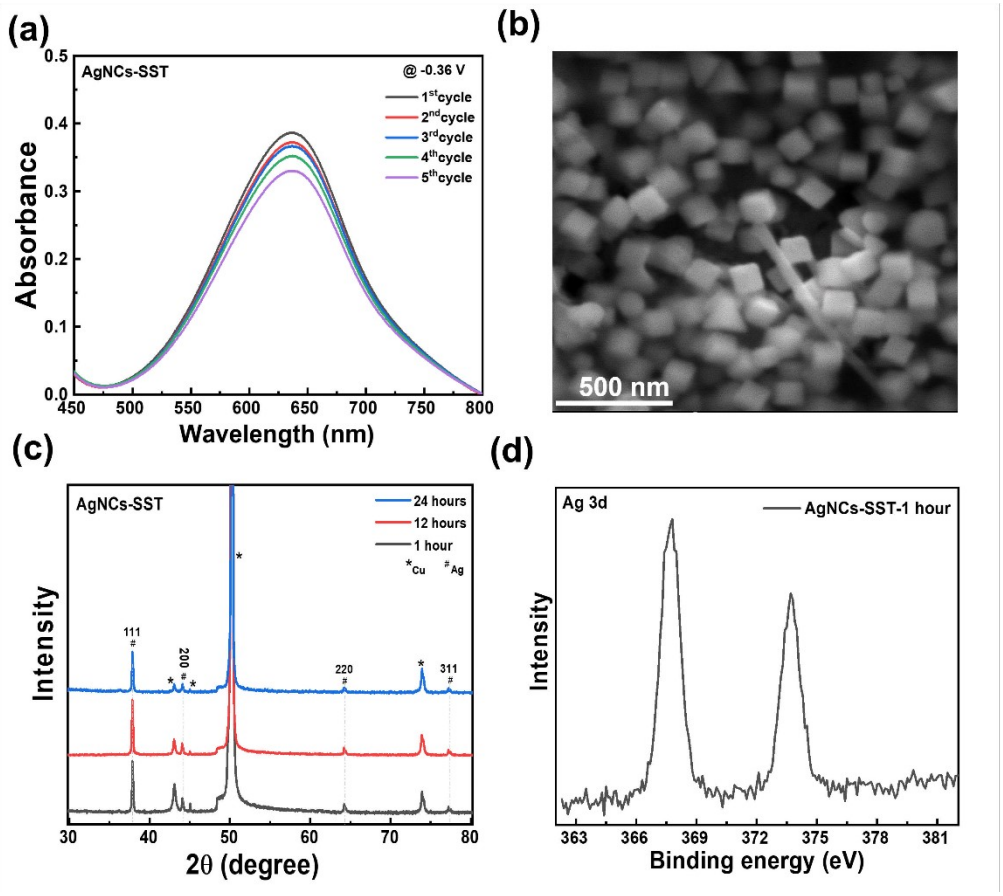

Fig. S1. (a) UV-vis absorption spectra of the electrolytes colored with indophenol indicator after the reaction for 5 consecutive cycles at -0.36 V potential. (b) SEM image of AgNCs-SST samples on Cu foil after NO_3^-RR reaction for 1 hour at -0.36 V potential. (c) XRD patterns of AgNCs –SST samples coated on Cu foil after NO_3^-RR reaction at different hours (1, 12 & 24 and at -0.36 V potential). (d) XPS spectrum of Ag 3d for AgNCs-SST after 1 hour i-t curve (at -0.36 V potential)

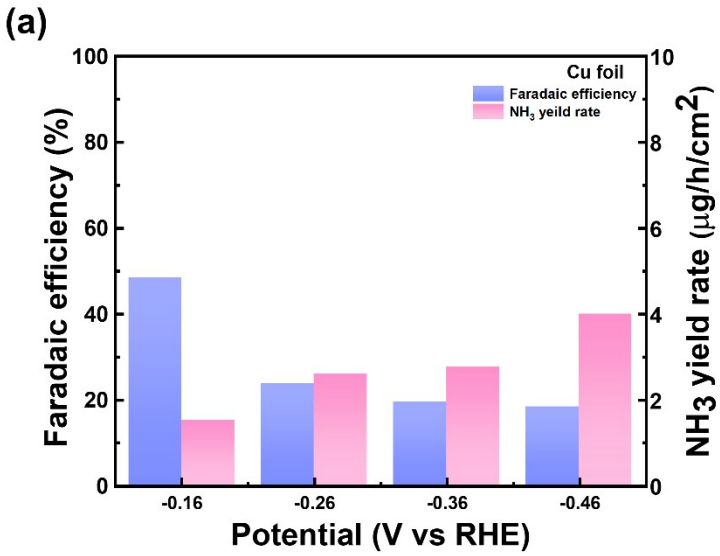

Fig. S2. (a) Faradaic efficiency and NH_3 yield rate of Cu foil at different potentials.

Refrences

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