

Supporting Information

Electrochemical reduction of nitrate on silver surface and the *in situ* Raman spectroscopy study

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Experimental details

Chemicals

Nafion (5 wt%), NaHS·2H₂O and K¹⁵NO₃ (99 atom%; ≥99.0%) were purchased from Sigma-Aldrich. Silver nitrate (AgNO₃), polyvinyl pyrrolidone, potassium hydroxide (KOH), potassium nitrate (KNO₃), sodium hydroxide (NaOH), zinc acetate ((CH₃COO)₂Zn·2H₂O), salicylic acid, sodium nitroprusside dihydrate, sodium hypochlorite aqueous solution, phosphoric acid, sodium citrate were purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were of analytical grade and used as received without further purification, unless otherwise specified.

Characterization

X-ray diffraction (XRD) was performed on a Philips X'Pert Pro Super diffractometer with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). The scanning electron microscopy (SEM) images were taken on a JEOL JSM-6700F SEM. The transmission electron microscopy (TEM) was carried out on a JEM-2100F field emission electron microscope at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) analyses were performed on a VGESCALAB MKII X-ray photoelectron spectrometer with an excitation source of Mg K $\alpha = 1253.6 \text{ eV}$, and the resolution level was lower than 1 atom%. The ultraviolet-visible (UV-Vis) absorbance spectra were measured on UV-Vis Spectrophotometer (Shimadzu UV-2600). The isotope labeling experiments were measured by ¹H-NMR measurement (Bruker 600 MHz system).

Determination of ion concentration

The UV-Vis spectrophotometer was used to detect the ion concentration in the solution after the test and the electrolytes are diluting to low concentration to fit the range of the calibration curve. The specific detection methods are as follows:

Determination of ammonia-N:

The method of indophenol blue was used to detect the produced ammonia. First, after the catalysis was completed, a certain amount of electrolyte was taken out from the electrolytic cell and diluted to the detection range to ensure that the ammonia

concentrations in the test solution were within the linear range of the indole blue method. The color reagent was made up of 50 g/L salicylic acid solution, 10 g/L sodium nitroprusside dihydrate solution and 0.05 mol/L sodium hypochlorite solution. Then, 0.5 mL of salicylic acid solution, 0.1 mL of sodium nitroprusside dihydrate solution and 0.1 mL of sodium hypochlorite solution were added to 1 mL of the diluted electrolyte in sequence. The solution was mixed completely and sitted for 1 h. The sample was calculated using its absorbance at 658 nm. The concentration-absorbance curve was calibrated using a series of standard ammonium chloride solutions. The specific solution preparation method are as follows:

Salicylic acid solution (50 g/L): 5 g salicylic acid, 5 g sodium citrate and 27.5 mL sodium hydroxide solution [$c(\text{NaOH})=2 \text{ mol/L}$] were added into 25 mL water, then the solution was diluted with ultrapure water to 100 mL. It was stable for one month at room temperature.

Sodium nitroprusside dihydrate solution (10 g/L): 1 g of sodium nitroprusside dihydrate was dissolved in 100 mL of ultrapure water.

sodium hypochlorite solution (0.05 mol/L): 1mL sodium hypochlorite, diluted it with sodium hypochlorite [$c(\text{NaOH})=2 \text{ mol/L}$] to 0.05 mol/L. It was stable for two months in the refrigerator.

Determination of nitrite-N:

First, p-aminobenzene sulfonamide (20 g) was added into the mixture of 250 mL ultrapure and 50 mL phosphoric acid ($\rho=1.70 \text{ g/mL}$). Then, ethylenediamine dihydrochloride (1 g) was dissolved in the above solution. Finally, the solution was diluted to 500 mL with ultrapure water for using as a color reagent. A certain amount of electrolyte was taken out from the electrolytic cell and diluted to the detection range. Next, 1 mL of the above diluted solution was mixed with 0.1 mL of color reagent uniformly, and the absorption intensity at the wavelength of 540 nm was recorded after sitting for 20 minutes. The concentration-absorbance curve was calibrated using a series of standard sodium nitrite solutions.

Calculation of ammonia yield, and Faradaic efficiency

The calculation of ammonia yield uses the following equation:

$$Yield(NH_3) = (C \times V)/(m \times t)$$

where C is the concentration of NH_3 (aq), V is the volume of the electrolyte, m is the mass of loaded catalyst and t is the reaction time.

The calculation of Faraday efficiency uses the following equation:

$$Faradaic\ efficiency = [(C \times V \times F \times n)/Q] \times 100\%$$

where C is the concentration of NH_3 (aq) in the electrolyte, V is the volume of the electrolyte, n is the number of electrons transferred (For NH_3 , n=8; for NO_2^- , n=2), F is the Faraday constant (96500 C mol^{-1}), and Q is the total charge passing the electrode.

^{15}N isotope labeling experiment

$K^{15}NO_3$ (99 atom%; $\geq 99.0\%$) was used as the N-source, the isotopic labeling nitrate reduction experiments were carried out using the above electrochemical nitrate reduction methods. After 3 h of performing potentiostatic electrolysis, the pH value was adjusted to be acidified to 2~3 with the HCl solution. Then, DMSO (dimethyl sulfoxide) was mixed with the acidified electrolyte. $^{15}NH_4^+$ was detected by 1H NMR measurement. (1H NMR, Bruker 600 MHz). Also, $^{14}NH_4^+$ was detected by 1H NMR by the same method except for the N-source was $K^{14}NO_3$.

FDTD simulations

In FDTD simulations, the quasi-cavity model is composed by infinitely-long ZnO nanosheet array with thickness of 30 nm and height of 400 nm. The ZnO nanosheets were vertically and periodically placed on an infinite ZnO plane, and the period between adjacent nanosheets was set as 415 nm. Ag nanocubes were placed along surface of the ZnO nanosheet or plane with intervals of 5 nm, and the permittivity of ZnO and Ag were respectively obtained from Ref. 1-2.^{1,2} Wavelength of the incident light and the monitored one were both set as 532 nm, which corresponds well with experimental values. In the X-Y and Z directions, periodic and perfectly matched layer absorbing boundary condition are respectively adopted.

Supplementary Figures

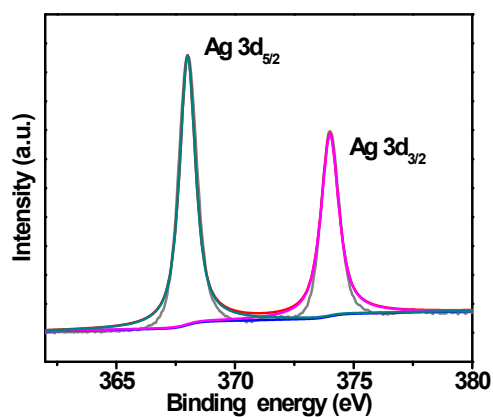


Fig. S1. XPS of synthesized Ag nanocrystals.

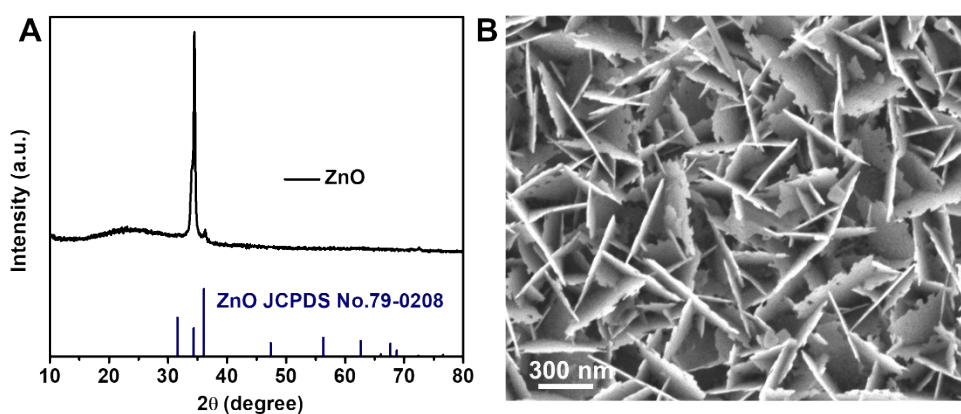


Fig. S2. (A) XRD and (B) SEM image of synthesized ZnO nanowalls.

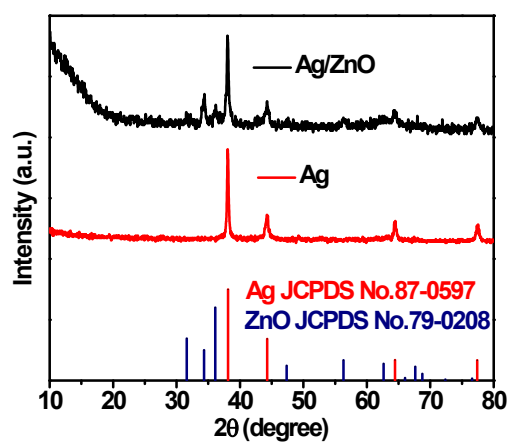


Fig. S3. Comparison of XRD patterns of Ag/ZnO and Ag nanocrystals.

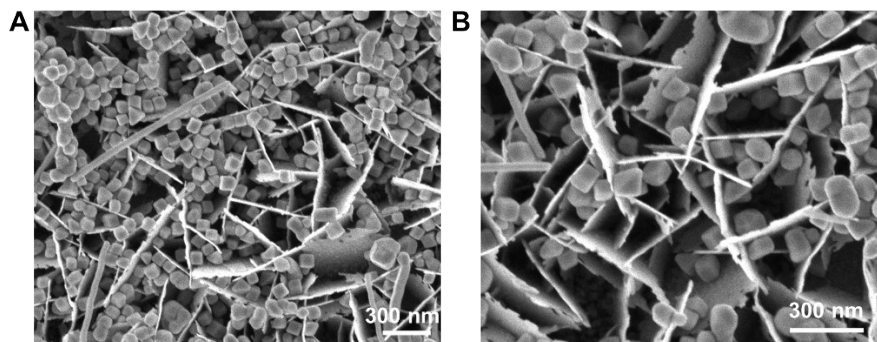


Fig. S4. SEM images of Ag/ZnO with different magnification. Together with the SEM image of Fig. 2B, it can be clearly observed that Ag nanocrystals were loaded on ZnO nanowalls or on the bottom of the cavity.

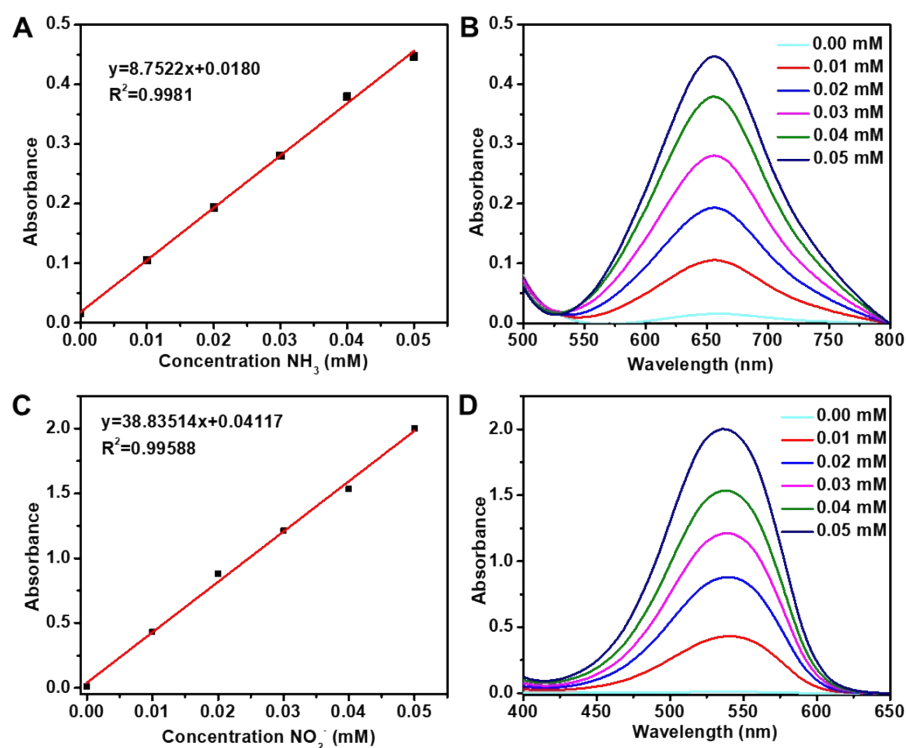


Fig. S5. Plotting of standard curves of (A, B) ammonia, (C, D) nitrite in 1 M KOH solution.

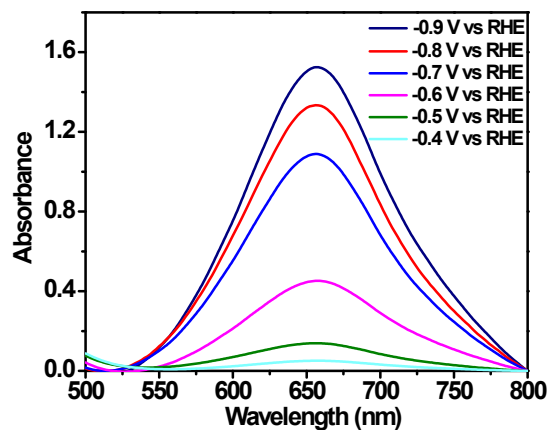


Fig. S6. UV-Vis absorption spectra of ammonia in nitrate reduction performances of Ag nanocrystals at different applied potentials.

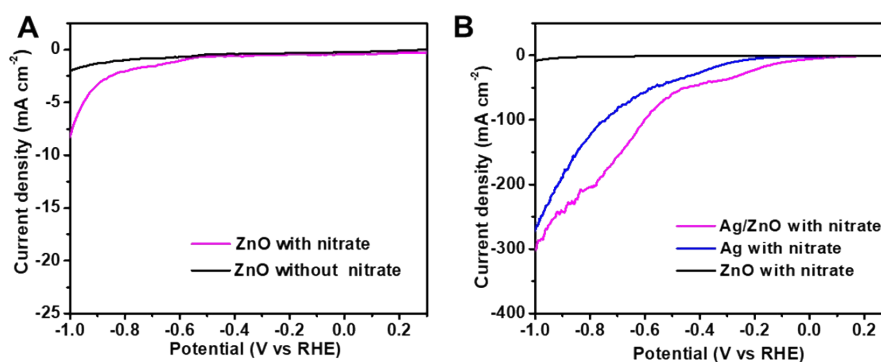


Fig. S7. (A) LSV curves of ZnO in 1 M KOH electrolyte with and without nitrate; (B) LSV curves of Ag nanocrystals, Ag/ZnO and ZnO electrodes with nitrate.

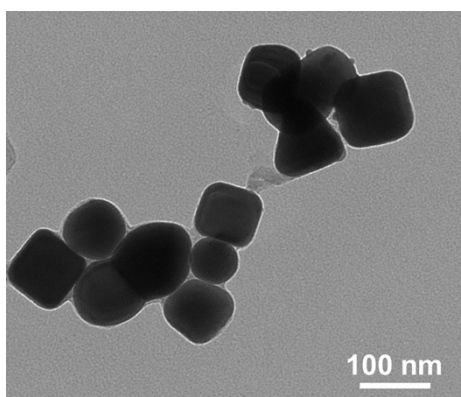


Fig. S8. TEM images of Ag nanocrystals after long-time catalytic performance.

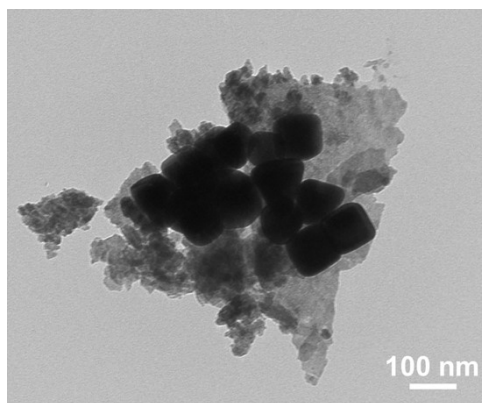


Fig. S9. TEM image of Ag/ZnO after long-term catalytic performance.

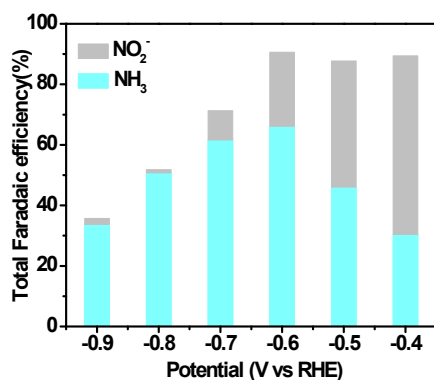


Fig. S10. Nitrate reduction performance of Ag: Faradaic efficiency of ammonia and nitrite at different potentials in 1 M KOH with 0.1 M KNO₃.

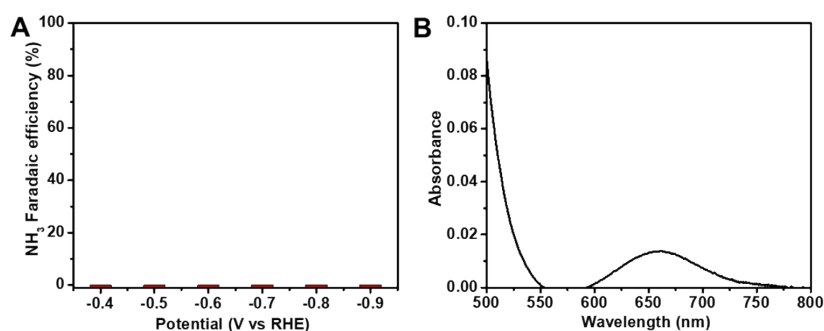


Fig. S11. (A) ammonia Faradaic efficiency in pure 1 M KOH at different applied potentials, (B) UV-Vis absorption spectra of possible ammonia in KNO₃ before electrocatalytic performance.

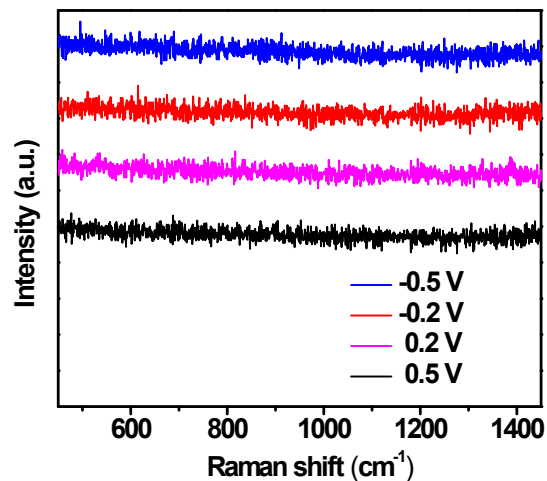


Fig. S12. SERS spectra of nitrate reduction on Ag nanocrystals in 1 M KOH with KNO_3 existed, all the potentials are relative to the reversible hydrogen electrode (RHE). No obvious Raman signal can be observed.

1. P. B. Johnson and R. W. Christy, Optical Constants of the Noble Metals, *Physical Review B*, 1972, **6**, 4370-4379.
2. C. Stelling, C. R. Singh, M. Karg, T. A. F. König, M. Thelakkat and M. Retsch, Plasmonic Nanomeshes: Their Ambivalent Role as Transparent Electrodes in Organic Solar Cells, *Sci Rep-Uk*, 2017, **7**, 1-13.