

Electronic Supplementary Information (ESI)

From inert to active: a cocktail-like mediation of Ag/Ni mixture for electrocatalytic ammonia oxidation reaction

Yongzhen Jin,^{a,b,c} Xin Chen^{b,c} and Jianhui Wang*^{a,b,c}

^a *School of Materials Science and Engineering, Zhejiang University, 38 Zheda Road, Hangzhou 310027, China.*

^b *Key Laboratory of 3D Micro/Nano Fabrication and Characterization of Zhejiang Province, School of Engineering, Westlake University, 18 Shilongshan Road, Hangzhou 310024, China.*

^c *Institute of Advanced Technology, Westlake Institute for Advanced Study, 18 shilongshan Road, Hangzhou 310024, China.*

1. Experimental Section

1.1 Materials

Ag powder (MACKLIN, 99.5 %); Ni powder (MACKLIN, 99.9 %); NaOH (MACKLIN, ≥ 99.8 %), NH_4Cl (MACKLIN, $\geq 99.5\%$); Nafion (Canrd, $> 99.9\%$), Isopropanol (MACKLIN, ≥ 99.5 %), Carbon black (Canrd).

1.2 Sample preparation

The Ag/Ni samples with different molar ratio (4:1, 1:1, 1:2, 1:3, 1:13) were prepared by hand-milling the pristine Ag and Ni powders (~8 mg) in a mortar for 15 minutes. The samples with the Ag:Ni molar ratio from 1:3 to 1:1 show a very similar electrocatalytic performance, all of which are much superior to those sample (4:1 and 1:13). Therefore, we selected the Ag/Ni sample (1:2) for a systematic study.

The Ag/Ni ink was prepared by dispersing 8 mg Ag/Ni sample and 4 mg carbon powders in 1.0 mL solution of water (680 μL), isopropanol (300 μL), and nafion (20 μL) followed by ultrasonication for 5 minutes. The Ag and Ni inks were prepared in the same way.

The catalyst inks were coated on a glassy carbon electrode (sample loading, 0.5 mg cm^{-2}) or Ni foam (sample loading, 1.0 mg cm^{-2}) or Au deposited PTFE membrane electrode (sample loading, 1.0 mg cm^{-2}). The glassy carbon electrode was used for cyclic voltammograms (CV) test. The Ni foam electrode was used to test the long-time stability and faradic efficiencies of reaction products. And the Au deposited PTFE membrane electrode was used for in-situ DEMS measurement.

1.3 Material characterizations

X-ray powder diffraction (XRD) patterns were obtained on a Bruker D8 Advance powder diffractometer, using Cu $K\alpha$ ($\lambda = 1.5418 \text{ \AA}$) as the radiation source. The scanning electron microscopy (SEM) images were taken on a Hitachi Regulus 8230. The images of transmission electron microscopy (TEM) and high resolution

transmission electron microscopy (HRTEM) as well as the elemental mapping were obtained by using a Talos F200X G2 electron microscope (Thermo Fisher Scientific) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher ESCALAB Xi+. The binding energies were calibrated using C 1s peak at 284.8 eV as standard. Ion chromatography (Thermo Fisher ICS 6000) was applied to identify the liquid products in the electrolyte.

1.4 Electrochemical measurements

Electrochemical measurements were measured in a three-electrode cell on a workstation (CHI660E, Shanghai, China) using a carbon rod as the counter electrode, a saturated Hg/HgO as the reference electrode and the glassy carbon loaded with catalysts as the working electrode. Before the measurement, the electrolyte (1.5 M NaOH or 1.5 M NaOH + 0.5 M NH₄Cl) was bubbled with an Argon gas flow for 20 min to remove air. CV tests were performed at a scan rate of 25 mV s⁻¹. The electrochemically active surface areas (ECSA) of the electrocatalysts were evaluated by the equation of $ECSA = R_f / m_{\text{loading}}$. The rough factor R_f values were determined by dividing the double layer capacitance (C_{dl}) with the value of 0.060 mF cm⁻². The C_{dl} was half of the liner slope, which was obtained by plotting the $\Delta j = j_a - j_c$ at -0.15 V vs. Hg/HgO against the scan rate (10, 30, 50, 70, 90 mV s⁻¹, respectively)

1.5 In-situ DEMS analysis

Differential electrochemical mass spectrometry (DEMS, Linglu Shanghai) measurements were carried out for in-situ analysis of gas products during EAOR, such as N₂ (28 m/z), O₂ (32 m/z), NO (30 m/z), NO₂ (46 m/z) and N₂O (44 m/z). The working electrode was the Ag/Ni on Au deposited PTFE membrane (50 μm thickness, 20 nm pore) that only allows the penetration of volatile and hydrophobic species.

1.6 Collection of gas products by drainage method

A sealed H-shaped electrolytic cell was used for collection of gas products during a two hours' chronoamperometry (CA) test at 0.7 V vs. Hg/HgO, where the Ag/Ni on Ni foam, Hg/HgO electrode, and the carbon rod were used as the working electrode,

the reference electrode, and the counter electrode, respectively.

1.7 Calculation of the faradic efficiency

The faradic efficiency of H₂ was calculated according to the equation (1):

$$\text{H}_2 \text{ faradic efficiency} = \frac{2 \times V_{\text{H}_2} \times F}{V_m \times Q} \times 100\% \quad (1)$$

Where V_{H_2} is the volume of H₂ collected by the drainage method; V_m is the molar volume of the gas (22.4 L mol⁻¹); F is the faraday constant (96485 C mol⁻¹), Q is the total charge consumed in the measurement.

The faradic efficiency of N₂ was calculated according to the equation (2):

$$\text{N}_2 \text{ faradic efficiency} = \frac{6 \times V_{\text{N}_2} \times F}{V_m \times Q} \times 100\% \quad (2)$$

Where V_{N_2} is the volume of N₂ collected by the drainage method; V_m is the molar volume of the gas (22.4 L mol⁻¹); F is the faraday constant (96485 C mol⁻¹), Q is the total charge consumed in the measurement.

The faradic efficiencies of NO₂⁻ and NO₃⁻ were calculated according to the equation (3) and (4), respectively:

$$\text{NO}_2^- \text{ faradic efficiency} = \frac{6 \times c_{\text{NO}_2^-} \times V \times F}{M \times Q} \times 100\% \quad (3)$$

$$\text{NO}_3^- \text{ faradic efficiency} = \frac{8 \times c_{\text{NO}_3^-} \times V \times F}{M \times Q} \times 100\% \quad (4)$$

Where $c_{\text{NO}_2^-}$ and $c_{\text{NO}_3^-}$ are the concentration of NO₂⁻ and NO₃⁻ ion produced in the electrolyte determined by ion chromatography, respectively; V is the volume of electrolyte (30 mL); M is the molar mass of NO₂⁻ and NO₃⁻; F is the faradic constant (96485 C mol⁻¹), Q is the total charge consumed in the measurement.

2. Supplementary Figures

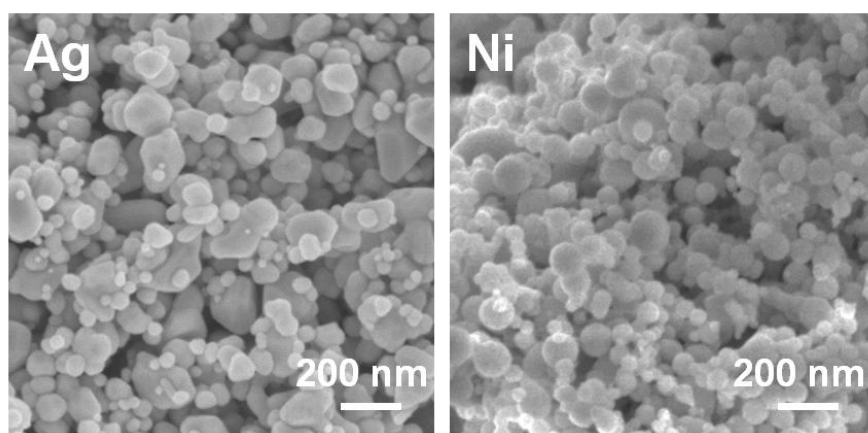


Fig. S1 SEM images of pristine Ag and Ni powders.

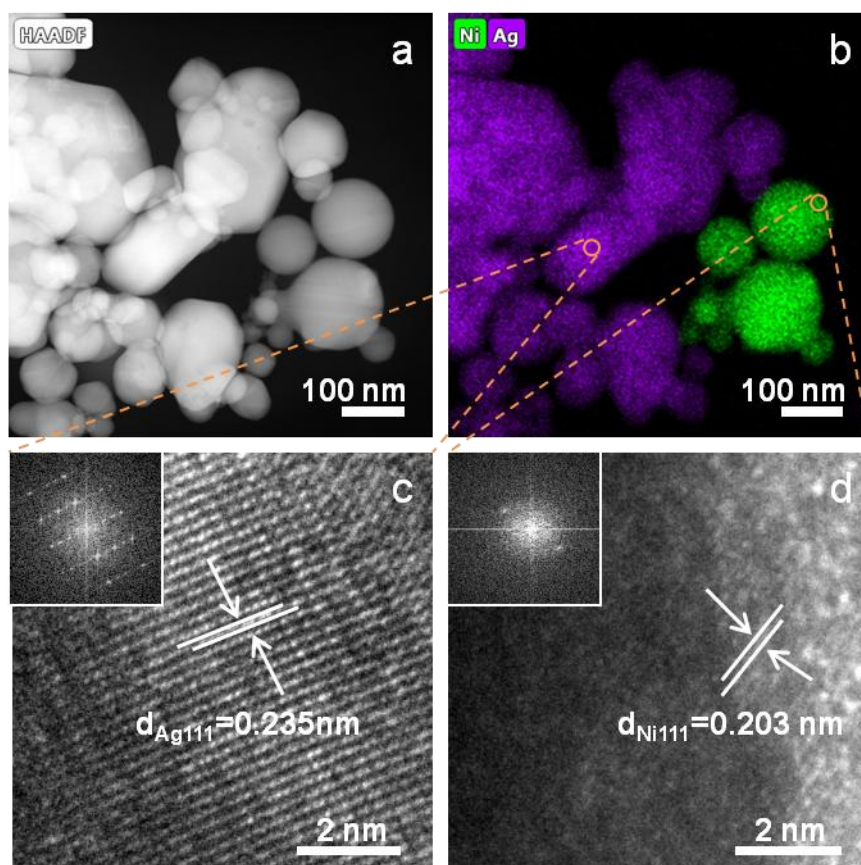


Fig. S2 a) The high-angle angular dark-field (HAADF) image and b) element mapping image of the Ag/Ni sample. HRTEM images of Ag c) and Ni d) particle in the Ag/Ni sample. The insets display the derived FFT patterns. The lattice spacing of 0.235 nm and 0.203 nm correspond to the character of Ag (111) and Ni (111), respectively.

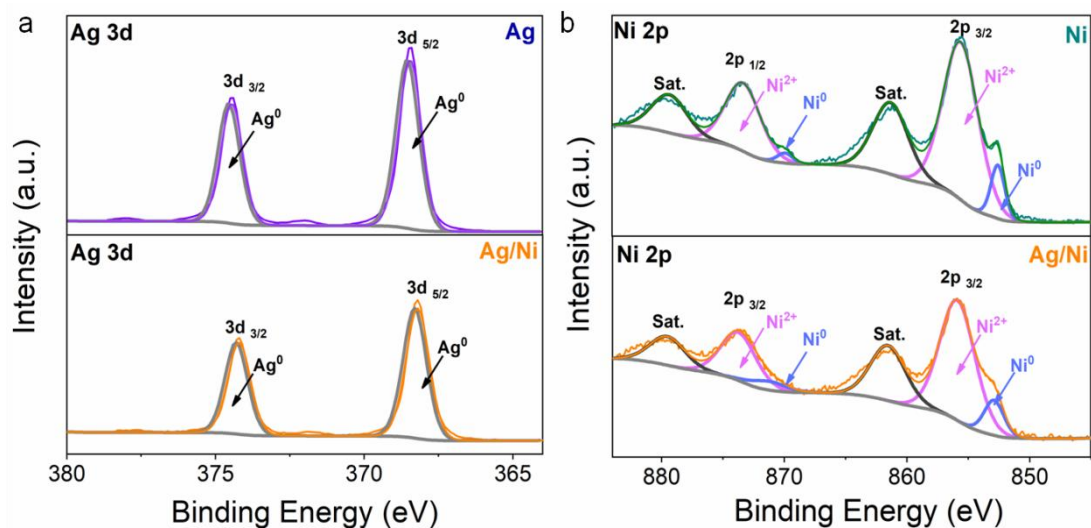


Fig. S3 XPS spectra. a) Ag 3d of pristine Ag and Ag/Ni mixture. b) Ni 2p of pristine Ni and Ag/Ni mixture.

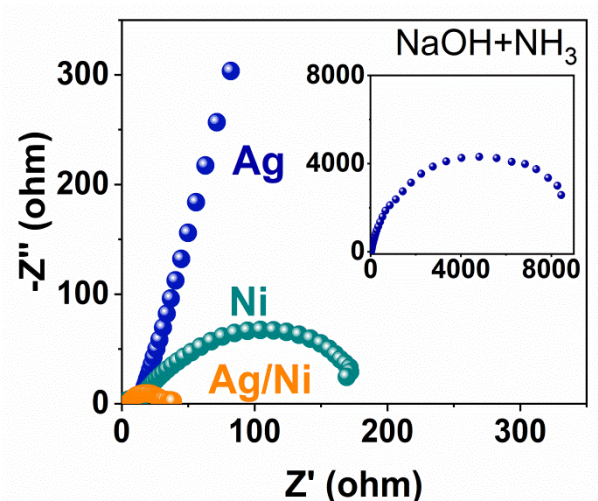


Fig. S4 Electrochemical impedance spectra (EIS) of Ag/Ni, Ag and Ni samples coated on a glassy carbon electrode tested at 0.6 V (vs. Hg/HgO).

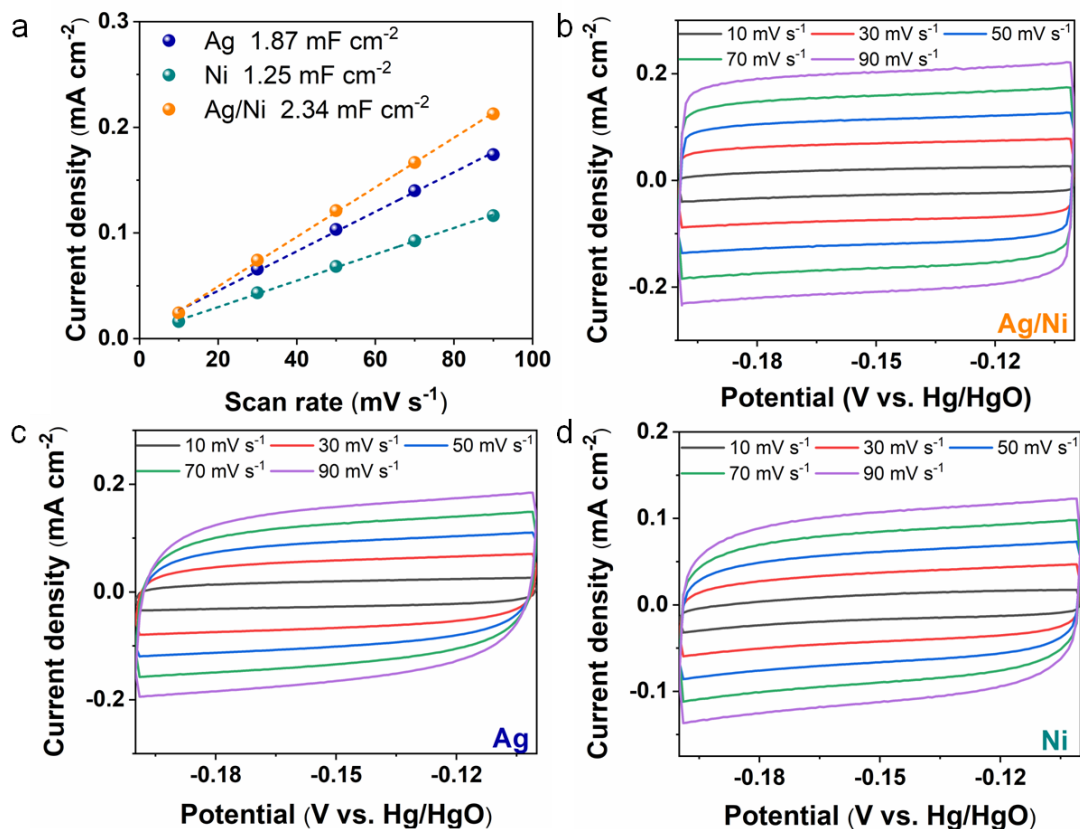


Fig. S5 a) Plots of the current density versus the scan rate to determine the double layer capacitance (C_{dl}) of the Ag/Ni, Ag and Ni catalysts. b-d) CV curves of the Ag/Ni (b), Ag (c), Ni (d) in the electrolytes of 1.5 M NaOH + 0.5 M NH₃ at different scan rates.

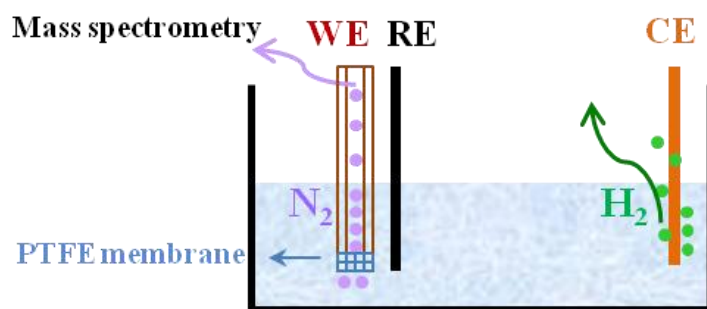


Fig. S6 Schematic diagram of the DEMS measurement. The anodic gas products are exclusively detected by DEMS.

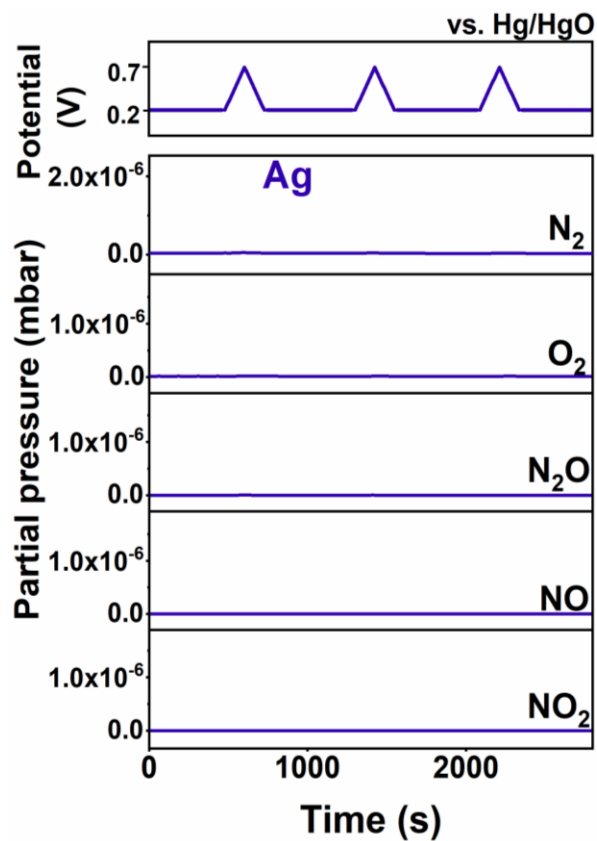


Fig. S7 DEMS signals during the CV scans of pristine Ag in the electrolyte of 1.5 M NaOH + 0.5 M NH₃.

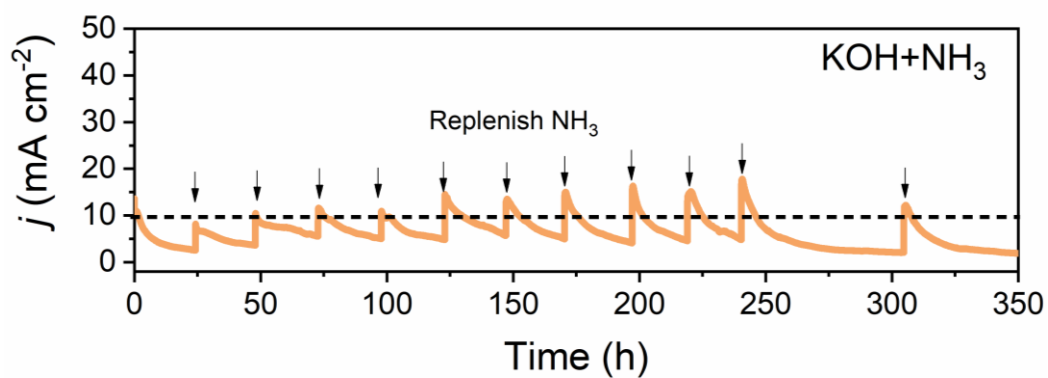


Fig. S8 Chronoamperometric responses of the Ag/Ni catalyst on a Ni foam electrode at 0.55 V (vs. Hg/HgO).

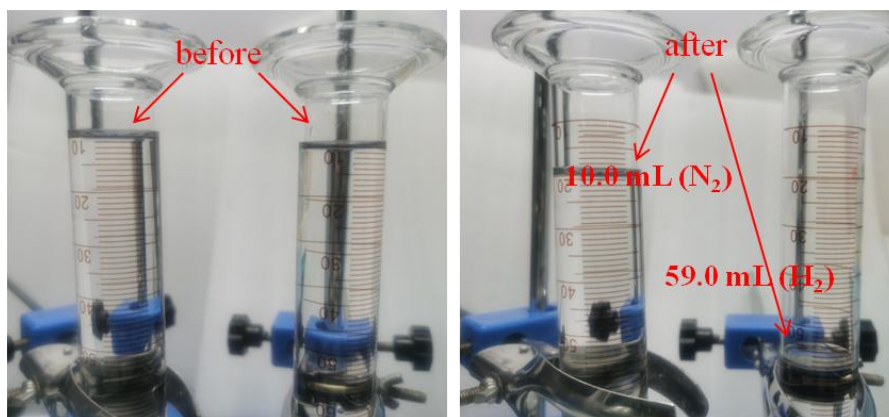


Fig. S9 Collection of the cathodic (H_2) and anodic (N_2) gas products of the Ag/Ni catalyzed EAOR by the drainage method. The gas products were generated during a 2 hours' CA test at 0.7 V (vs. Hg/HgO).

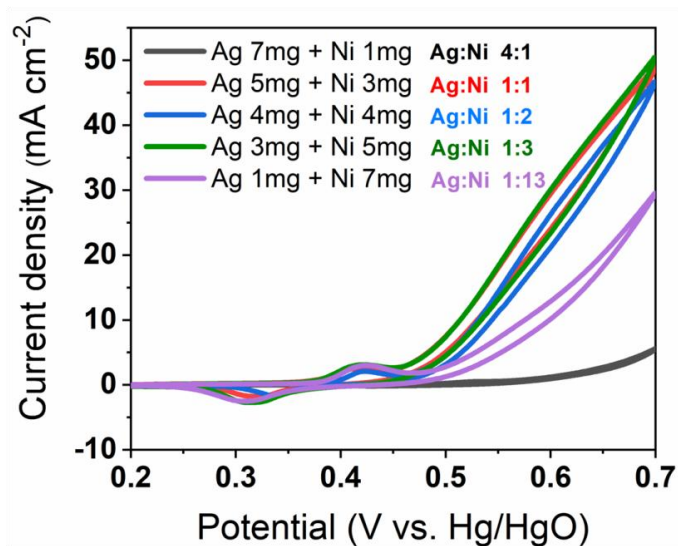


Fig. S10 CV curves of Ag, Ni and Ag/Ni on the glassy carbon electrode normalized by the geometric area.

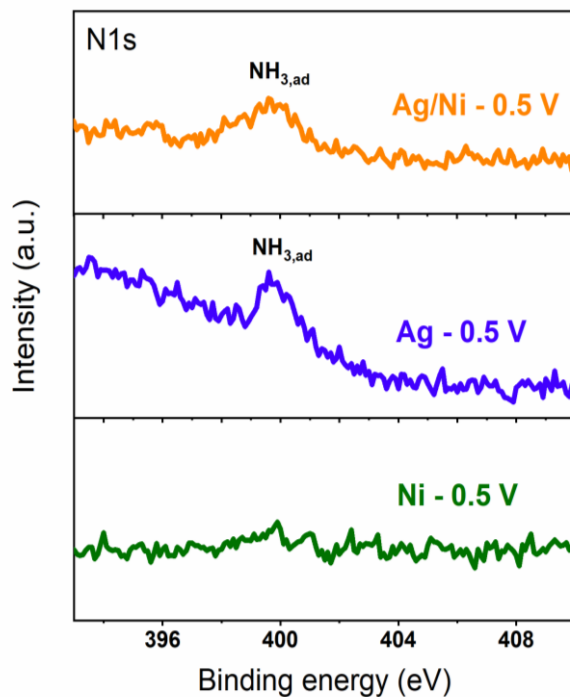


Fig. S11 N1s XPS spectra of Ag/Ni, Ag and Ni samples after a CA test. The samples were tested in the electrolyte of 1.5 M NaOH + 0.5 M NH₃ at 0.5 V (vs. Hg/HgO) followed by 20 times' rinses with deionized water and a dry at 60 °C for 5 hours. Clearly, significant N1s signal at 400 eV can be found on the Ag and Ag/Ni samples while no N1s signal on the Ni sample, which supports the absorption of NH₃-species on the Ag.

3. Supplementary Tables

Table S1. Electrochemical active surface area of various samples.

Sample	Ag/Ni	Ag	Ni
C_{dl} (mF cm ⁻²)	2.34	1.87	1.25
R_f	39.00	31.17	20.83
ECSA (cm ² mg ⁻¹)	78.00	62.34	41.66

Table S2. Faradic efficiencies of N₂ and H₂ in the Ag/Ni catalyzed EAOR.

Sample	Total charge (C)	V (N ₂) (mL)	V (H ₂) (mL)	Faradic efficiency (N ₂) (%)	Faradic efficiency (H ₂) (%)
Ag/Ni	432.1	10	49	59.8	97.7

The gas products of H₂ and N₂ were collected in a sealed H-shaped electrolytic cell at 0.7 V vs. Hg/HgO for two hours.

Table S3. Faradic efficiencies of NO₂⁻ and NO₃⁻ in the Ag/Ni catalyzed EAOR.

Sample	Total charge (C)	c (NO ₂ ⁻) (mg L ⁻¹)	c (NO ₃ ⁻) (mg L ⁻¹)	Faradic efficiency (NO ₂ ⁻) (%)	Faradic efficiency (NO ₃ ⁻) (%)
Ag/Ni	430.1	19.56	372.98	1.7	32.3

The liquid products of NO₂⁻ and NO₃⁻ were collected at 0.7 V vs. Hg/HgO for two hours.