Supporting Information

Accelerated ammonia electrosynthesis of cobalt hydroxide through electronic modulation with ultralow noble metal

doping

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Experimental details

Chemicals

Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, > 99%), hydrochloric acid (HCl) were purchased from Aladdin Chemical reagent Co., Ltd. (Shanghai, China). Ruthenium trichloride hydrate (RuCl₃·xH₂O) was purchased from Adamas. Ammonium fluoride (NH₄F) was purchased from Macklin and sodium silicate solution. K¹⁵NO₃ (99 atom%; \geq 99.0%) was purchased from Sigma-Aldrich. Urea, potassium hydroxide (KOH), potassium nitrate (KNO₃), sodium hydroxide (NaOH), and other reagents related to determination of ion concentration (salicylic acid, sodium nitroprusside dihydrate, sodium hypochlorite aqueous solution, Trisodium citrate (C₆H₅Na₃O₇·2H₂O), hydrogen tetrachloroaurate(III) (HAuCl₄·4H₂O, 99.99%), phosphoric acid, sodium citrate and p-aminobenzene sulfonamide were purchased from Sinopharm Chemical Reagent Co., Ltd. (3-aminopropyl) trimethoxysilane 97% were purchased from Alfa Aesar. All the chemicals were used directly without further purification.

Materials and methods

Synthesis of electrode material

Firstly, a piece of NF ($1 \times 4 \text{ cm}^2$) was placed in ethanol, hydrochloric acid, deionized water to rinse and ultrasonic clean several times. The Ru-Cu(OH)₂/NF electrode was prepared by a simple one-step hydrothermal treatment at 120°C for 12 h. This reaction system consisted of 0.289 g Co(NO₃)₂·6H₂O, 20 mg RuCl₃·xH₂O, 0.45 g CH₄N₂O, 0.148 g NH₄F and a piece of processed Ni foam (NF: 4.0 cm × 1.0 cm × 1.7 mm). After hydrothermal reaction, Ru-Co(OH)₂/NF electrode could be achieved by rinsing with ethanol and water, then drying at 60°C for a short time. The Co(OH)₂/NF electrodes were prepared by using the same method without Ruthenium elements.

Synthesis of gold nanoparticles (Au NPs)

Au NPs were synthesized using the seed growth method.¹ The specific steps are as follows: First, 2.2 mM sodium citrate was dissolved in 100 mL of ultra-pure water and heated to boiling under vigorous stirring conditions, then 1 mL of HAuCl₄ solution (25

mM) was quickly added to the boiling solution. A color change from light yellow to blue-gray and finally to deep purple-red can be observed. The solution was cooled down to 90°C under continuous stirring. Then, 1 mL of HAuCl₄ solution (25 mM) was quickly injected into the aforementioned solution, and kept for 30 min, and the above process was repeated twice to obtain the seed solution. To obtain the Au NPs, 55 mL of seed solution was added to a mixed solution of 53 mL of ultra-pure water and 2 mL of sodium citrate (60 mM), then the solution was heated to boiling for 10 min, followed by quickly injection of 1 mL of HAuCl₄ solution (25 mM) under boiling conditions and kept for 30 min, and then another 1 mL of HAuCl₄ solution was injected in the above solution for another 30 min. The above steps were repeated three times to obtain the final product.

Synthesis of Au@SiO₂

The Au@SiO₂ was prepared according to the reported literature.² In a typical process, 0.4 mL of 1 mM (3-aminopropyl) triethoxysilane (ATPMS) was added to 30 mL of the as-prepared Au NPs solution, with vigorously stirring at room temperature for 15 min. Then, 3.2 mL of NaSiO₃ aqueous solution (0.54%) was added to the above mixture under stirring at room temperature for 3 min, followed by transferring to an oil bath pot at 98°C for stirring 20 min. After that, the solution was cooled downing rapidly in an ice water bath, and then the Au@SiO₂ with a thin shell thickness was obtained.

Material characterization

X-ray diffraction (XRD) was performed on a Philips X'Pert Pro Super diffractometer with Cu K α radiation ($\lambda = 1.54178$ Å). 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 $\alpha = 1253.6$ eV, and the resolution level was lower than 1 atom%. Raman spectra were performed on a LabRAM HR Evolution Raman spectrometer, and the exposure time was 2 s. 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 400 MHz system).

Electrocatalytic measurement of nitrate reduction

The electrochemical measurement was tested on electrochemical workstation (CHI 660E, Shanghai Chenhua) in a standard three-electrode system. The Ru-Co(OH)₂/NF (0.5 cm \times 0.5 cm) and Co(OH)₂/NF were used as the working electrodes. The platinum gauze and the Hg/HgO electrode were used as counter electrode and reference electrode, respectively. All the potentials were recorded to reversible hydrogen electrode (RHE) by the Nernst equation. For nitrate reduction, the linear sweep voltammetry (LSV) was carried out in Ar saturated 1 M KOH solution with 0.1 M KNO₃ contained. Then the potentiostatic tests were tested to quantify the nitrate performance at every 0.1 V from 0 V to -0.4 V. The electrochemical impedance spectroscopy (EIS) measurements were operated at 0 V from 0.1-10⁵ Hz. Cyclic voltammetry (CV) was performed at various scan rates (10, 20, 30, 40, 50, 60, 80, 90, 100 mV s⁻¹) in region of 0.2~0.3 V. The electrochemical double-layer capacitance (C_{dl}) of various samples can be determined from the cyclic voltammograms. The C_{dl} was estimated by plotting the Δj (j_{anod}-j_{cathod}) at 0.25 V vs RHE against the scan rate, where the slope is twice C_{dl}.

Determination of ion concentration

The products in the electrolytes before and after electrochemical process were detected by the UV-Vis spectrophotometer. The detailed methods are as follows:

Determination of nitrite-N:

P-aminobenzene sulfonamide (4 g), N-(1-naphthyl) ethylenediamine dihydrochloride (0.2 g), phosphoric acid (10 mL, ρ =1.70 g mL⁻¹) were mixed and diluted to 100 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 uniformity, 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.

Determination of ammonia-N:

Produced ammonia was quantified by the indophenol blue method. 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 composed of 50 g L⁻¹ salicylic acid solution, 10 g L⁻¹ sodium nitroprusside dihydrate solution and 0.05 mol L⁻¹ sodium hypochlorite solution. 1 mL of the diluted electrolyte was mixed with 0.5 mL of salicylic acid solution, 0.1 mL of sodium nitroprusside dihydrate solution and 0.1 mL of sodium hypochlorite solution. The absorption intensity at the wavelength of 660 nm was recorded after sitting for 1 h. 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⁻¹): 10 g salicylic acid, 10 g sodium citrate and 55 mL sodium hydroxide solution $[c(NaOH)= 2 \text{ mol } L^{-1}]$ were added into 50 mL water, then the solution was diluted with ultrapure water to 200 mL. It was stable for one month at room temperature.

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

¹⁵N isotope labeling experiment

The isotopic labeling nitrate reduction experiments were carried out using the above electrochemical nitrate reduction methods, except the N-source was replaced by $K^{15}NO_3$ (99 atom%; \geq 99.0%). After performing potentiostatic electrolysis for 2 h, the pH of the electrolyte was 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 400 MHz). $^{14}NH_4^+$ was also detected by ¹H

NMR by the same method except for the N-source was K¹⁴NO₃.

In situ Raman spectroscopy measurements

Raman spectra were collected via the Horiba HR Evolution Raman microscope system. We conducted the electrochemical experiments on a homemade Raman spectroelectrochemical cell with 1 M KOH and 0.1 M KNO₃ contained. The tested optical images are shown in Fig. S9, the working electrode is placed directly below the transparent window, allowing the optical instrument to view the working electrode through the quartz window above. During the measurement, the long-focus objective of $50 \times$ was adopted, and the laser power was set as 4.8 mW with wavelength of 633 nm. The diffraction grid was 600 gr/mm, and integration time was set as 2 s. In each experiment, the Raman frequency was calibrated with silicon wafers.

Differential Electrochemical Mass Spectrometry (DEMS)

measurements

DEMS was performed on a Hiden Analytical Mass Spectrometer (HPR 40) for in situ analysis of intermediates and products. The electrolyte containing 1.0 M KOH and 0.1 M KNO₃ was purged with Ar for 30 min to remove dissolved oxygen before measurement. The mass signals were collected at -0.4 V vs RHE and four cycles were performed.

Calculation of ammonia yield and Faradaic efficiency

The calculation of ammonia yield uses the following equation:

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

where C is the concentration of NH_3 (aq), V is the volume of the electrolyte, and s is the electrode geometric area and t is the reaction time.

The calculation of Faradaic 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) or NO_2^- (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 Faradaic constant (96485 C mol⁻¹), and Q is the total charge passing the electrode.



Fig. S1. TEM images of (A) Au NP_S and (B) Au@SiO₂.



Fig. S2. SEM image of Ru-Co(OH)₂/NF.



Fig. S3. Plotting of standard curves of (A, B) ammonia, (C, D) nitrite in 1 M KOH solution.



Fig. S4. (A) UV-Vis absorption spectra of ammonia in nitrate reduction performances of Ru-Co(OH)₂/NF at different applied potentials; (B) Faradaic efficiency of ammonia and nitrite at different potentials in 1 M KOH with 0.1 M KNO₃ of Ru-Co(OH)₂/NF; (C) UV-Vis absorption spectra of ammonia in nitrate reduction performances of Co(OH)₂/NF at different applied potentials; (D) Faradaic efficiency of ammonia and nitrite at different potentials in 1 M KOH with 0.1 M KNO₃ of Co(OH)₂/NF. Very small amount of nitrite is detected on both Ru-Co(OH)₂/NF and pure Co(OH)₂/NF catalysts, and the corresponding largest FE is as low as 2.1% at the applied potentials, indicating the *NO₂ (* represents the surface of catalyst) can be quickly transformed into NH₃ rather than desorbed into the electrolytes to form nitrite.



Fig. S5. Characterizations of Ru-Co(OH)₂/NF after the catalytic process: (A) XRD patterns, (B) TEM image, (C) SEM image.



Fig. S6. (A) Ammonia Faradaic efficiency in pure 1 M KOH, (B) UV-Vis absorption spectra of possible ammonia in KNO₃ before electrocatalytic performance and negligible ammonia can be detected.



Fig. S7. Cyclic voltammetry curves of (A) Ru-Co(OH)₂/NF, (B) Co(OH)₂/NF in the region of $0.2 \sim 0.3$ V vs RHE.



Fig. S8. Electrochemical performance of $Ru-Co(OH)_2/NF$ and $Au@SiO_2/Ru-Co(OH)_2/NF$. The coating ultrathin silica shell is exactly used to prevent Au core from direct contact with the reactive species, thus, no obvious variation of performance would be brought in by the SERS-active $Au@SiO_2$.



Fig. S9. (A) the optical image of the in-situ electrochemical SERS cell; (B) the optical image of the objective approaching to the quartz window.



Fig. S10. Online DEMS results of nitrate reduction on Ru-Co(OH)₂/NF.



Fig. S11. In situ electrochemical Raman spectra of nitrate reduction on Ru- $Co(OH)_2/NF$ without Au@SiO₂ deposited. (All the potentials are relative to RHE). For further to verify the importance of SERS technique, we conducted in-situ Raman test without the deposition of Au@SiO₂. No reliable Raman signal of reaction intermediates can be observed, demonstrating the negligible enhancement of Raman signals with the absence of SERS-active substrate.

Catalysts	Electroreduction	NH ₃ Yield rate	Referenc	Potential under
	condition	/Faradaic	e	optimal
		efficiency		ammonia
				efficiency
CoFe LDH	1 M KOH + 1400	$0.93 mmol h^{-1}$	3	-0.45 V vs PHE
	ppm NO ₃ ⁻	$cm^{-2}/97.68\%$		0.45 V VS KILL
BiFeO ₃	0.1 M KOH+ 0.1	90.45 mg h^{-1}	4	-0.6 V vs PHE
	M KNO ₃	$mg_{cat}^{-1}/96.85$ %		0.0 V VS KITE
Cu-N ₄	$0.5 M Na_2SO_4 +$	2742.6 $\mu g h^{-1}$	5	-0.89 V vs RHE
	0.2 M NaNO ₃	$mg_{cat}^{-1}/82.1$ %		
CuAg-DAT	0.5 M KOH +	$0.64 \text{ mmol } h^{-1}$	6	–0.6 V vs RHE
	0.05 M KNO ₃	cm ⁻² /96 %		
Ni-MOF/NF	$0.1 \text{ M } \text{Na}_2 \text{SO}_4 +$	110.13 $\mu g h^{-1}$	7	-1.4 V vs RHE
	$1.5 \text{ g } \text{L}^{-1} \text{ NaNO}_3$	cm ⁻² /96.4 %		
CuSA NPC	0.01 M PBS +	$2602 \mu g cm^{-2}$	8	–1.1 V vs RHE
	$500 \text{ mg } L^{-1} \text{ NO}_3^{-1}$	$h^{-1}/87.2\%$		
FeOOH/CP	0.1 M PBS + 0.1	2419 $\mu g h^{-1}$	9	–0.5 V vs RHE
	M NaNO ₃	cm ⁻² /92%		
O-Cu-	0.1 M PBS + 500	$436\pm85 \mu g h^{-1}$	10	–0.4 V vs RHE
PTCDA	ppm NO ₃ ⁻	cm ⁻² /85.9%		
CuPd/CN	$0.5~M~K_2SO_4~+$	$0.0904 \ mol \ mg^{-1}$	11	–0.4 V vs RHE
	200 ppm NO_3^-	$h^{-1}/96.16\%$		
Ru-	1 M KOH + 0.1	$0.14 \text{ mmol } \text{cm}^{-2}$	This	-0.1 V vs RHE
Co(OH) ₂ /NF	M KNO ₃	$h^{-1}/96.6\%$	work	

Table S1 Comparison of ammonia synthesis activity by Ru-Co(OH)₂/NF and other catalysts.

Table S2 The charge transfer resistance (R_{ct}) value of each sample.

Catalyst	$R_{ct}\left(\Omega ight)$	
Ru-Co(OH) ₂	108.8	
Co(OH) ₂	395.2	

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