Electronic Supplementary Information

Boosting Electrocatalytic Nitrogen Fixation Via Energy-Efficient Anodic Oxidation of Sodium Gluconate

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1. Experimental details

1.1. Materials and characterization

All reagents were of analytical purity and used as received without further purification. Distilled water was used throughout all experiments. The carbon cloth were purchased from Changde Liyuan New Material Co., Ltd., China.

The morphologies of the samples were observed on a field-emission scanning electron microscope (FE-SEM, FEI QUANTAFEG250, FEI Company, USA). Powder X-ray diffraction data (PXRD) for crystal structure characterization were recorded on a Bruker SMART APEX CCD-based diffractometer (Cu K α radiation, λ =1.5418 Å).

1.2 Material Preparation

1.2.1 Activation of CCs

CCs (4 × 0.5 cm) were carefully cleaned with ethanol and distilled water, respectively, by sonication to take out the surface impurities. Then the **CC**s were sonicated for 5 min in an ultrasound bath in 3 mol L⁻¹ dilute hydrochloric acid, subsequently rinsed several times with distilled water to remove hydrochloric acid.

1.2.2 Synthesis of H₄BDPO (H₄L) ligand

The preparation of ligands was based on the original published literature.¹ 5aminoisophthalic acid (3.62 g, 0.02 mol), NaOH (1.2 g, 0.03 mol) and NaHCO₃ (2.1 g, 5 mol) was dissolved in water (60 mL) before continuous stirring at room temperature for 30 min, and the mixture was called solution a. Then, cyanuric chloride (1.84 g, 0.01 mol) dissolved was mixed with 1, 4-dioxane (10 mL). The mixture was added drop by drop to solution a with stirring about 1h. Finally, raising the temperature to 110 °C and continue stirring for another 12 hours. The resulting solution was adjusted to pH = 2 with HCl (1 M) solution. The solid was collected by filtration, rinsed several times with distilled water, and dried to obtain ligand H₄BDPO.

1.2.3 Synthesis of JUC-1000/CC

JUC-1000/CC was prepared by three-electrode system electrodeposition method as follows. 0.4g (1.66 mmol) Cu(NO₃)₂·3H₂O and 0.2g H₄BDPO (0.44 mmol) was dissolved into mixed solution with 5 mL DMF and 0.2mL distilled water under continuous stirring at room temperature. Then the JUC-1000/CC was got by constant potential electrolysis in a mixture solvent at -1.5 V for 15 min at room temperature before activation 3 h. During the electrodeposition process, CC, Hg/HgO electrode and Pt wire were used as working electrode, reference electrode and counter electrode, respectively.

1.2.4 Synthesis of RuO₂/CC

 RuO_2 was prepared according to the literature.² Briefly, 1.3 g of $RuCl_3 \cdot 3H_2O$ and 0.5 mL KOH (1.0 M) were added into 50 mL distilled water and stirred for 45 min at 100 °C. Then the above solution was centrifuged and washed with water for several times, followed by drying at 70 °C. Finally, the product was annealed at 300 °C for 3 h

in a tube under in air. 20 mg of RuO₂ was dispersed into 250 μ L of water/ethanol (v/v = 1:1) and 10 μ L of 5 wt% Nafion under sonication for 10 min. Then 45 μ L of the RuO₂ ink was loaded onto a bare CC of 1.0 cm², then dried in air overnight.

1.3 Electrochemical Measurements

Electrochemical measurements were performed with a RST5200F electrochemical analyzer (Zhengzhou Shiruisi Instrument Co., Zhengzhou, China). To evaluate the feasibility of electro-oxidation of sodium gluconate (ECSG) replacement of water oxidation, the cyclic voltammetry (CV) tests were performed in a standard threeelectrode system using JUC-1000/CC as the working electrode, a Pt sheet (0.5×1.0) cm²) and an Hg/HgO electrode as the counter electrode and reference electrode, respectively. These were conducted in 1.0 M Na₂SO₄ electrolyte with and without 1.0 M sodium gluconate (SG) at room temperature. The as-prepared materials (0.5×1.0 cm²) were used as the working electrode, respectively. A Pt wire and a Hg/HgO electrode were used as the counter electrode and reference electrode, respectively. The temperature of solution was kept at 25 °C for all the measurements. The potentials reported in this work were calibrated to reversible hydrogen electrode (RHE), other than especially explained, using the following equation: $E_{RHE} = E_{Hg/HgO} +$ (0.098 + 0.059 pH) V, where $E_{Hg/HgO}$ is the experimentally measured potential against Hg/HgO reference, pH is 7.

The Tafel plots are employed to evaluate the OER catalytic kinetics and fitted with the following equation: $\eta = blogj + a$, where j is the current density and b is the Tafel

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slope.

Electrochemical impedance spectroscopy (EIS) measurements were performed from 10^5 to 1 Hz with amplitude of 5 mV. Electrochemical active surface area (ECSA) for as-prepared catalysts was estimated by double layer capacitance (C_{dl}) at the solid/liquid interface.³ The C_{dl} was measured by cyclic voltammograms (CVs) collected in region of 1.16–1.26 V vs Hg/HgO in no apparent Faradaic processes. C_{dl} was determined by the the equation $j = v \times C_{dl}$, where C_{dl} is equal to the slope of a straight line yielded by current density (j) versus scan rate (v).

The Faraday efficiency (FE %) was estimated from the experimental number of moles of the gas and the theoretical number of moles of the gas calculated by the charge passed through the electrode.

$$n(\text{theoretical}) = \frac{Q}{zF}$$
(1)

Where n_g is the number of moles of the gas produced, Q is the charge passed through the electrodes, z means z mole electrons per mole H₂ (z = 2), F is Faraday constant (96485 C mol⁻¹). Thus, Faradaic efficiency can be determined by the following equation:

$$FE\% = \frac{n_g \text{ (experimental)}}{n_g \text{ (theoretical)}}$$
(2)

The NRR test for JUC-1000/CC as catalyst. The NRR test was performed utilizing a Htype two-compartment electrolytic-cell, which was separated by Nafion 115 membrane. The operating voltage was range from -1.2 V to -0.2 V and converted to the reversible hydrogen electrode (vs.RHE) scale of -0.7 V to 0.3 V. No positive voltage was applied during the NRR test. The as-prepared JUC-1000/CC as the working electrode together with a reference electrode (Pt sheet, $0.5 \times 1.0 \text{ cm}^2$) were placed in the cathodic compartment using N₂-saturated 1.0 M Na₂SO₄ as electrolyte. The counter electrode (Hg/HgO) was placed on the anodic compartment using 1.0 M Na₂SO₄ as electrolyte, in which the as-prepared catalyst is not used. Before the tests, the membrane was protonated by first boiling in ultrapure water for 1 h and treating in H₂O₂ (5%) aqueous solution at 80 °C for another 1 h, respectively. And then, the membrane was treated in 0.5 M H₂SO₄ for 3 h at 80 °C and finally in water for 6 h.

Determination of NH₃. Concentration of produced NH₃ was spectrophotometrically determined by the indophenol blue method. Typically, 2 mL Na₂SO₄ electrolyte was taken from the cathodic chamber, and then 2 mL of 1.0 M NaOH solution containing 5% salicylic acid and 5% sodium citrate was added into this solution. Subsequently, 1 mL of 0.05 M NaClO and 0.2 mL of 1% C₅FeN₆Na₂O·2H₂O were add into the above solution. After standing at room temperature for 2 h, the UV-Vis absorption absorption spectrum was measured at a wavelength of 655 nm. The concentration-absorbance curves were calibrated using standard NH₄Cl solution with a serious of concentrations. The concentration–absorbance curve used for estimation of NH₃ was calibrated using standard NH₄Cl solution with NH₄⁺ concentrations of 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 µg mL⁻¹ in 0.1 M Na₂SO₄. The fitting curve (y =0.51x + 0.09794, R² = 0.997) shows good linear relation of absorbance value with NH₄⁺ concentration

by five times independent calibrations.

Determination of N₂H₄. The N₂H₄ in the electrolyte was estimated by the method of Watt and Chrisp. A mixture of p-C₉H₁₁NO (5.99 g), HCI (concentrated, 30 mL) and C₂H₅OH (300 mL) was used as a color reagent. In detail, 5 mL electrolyte was removed from the electrochemical reaction vessel, and added into 5 mL above prepared color reagent and stirring 10 min at room temperature. The absorbance of the resulting solution was measured at 455 nm.

Determination of FE. The FE for N₂ reduction was defined as the amount of electric charge used for synthesizing NH₃ divided the total charge passed through the electrodes during the electrolysis. The total amount of NH₃ produced was measured using colorimetric methods. Assuming three electrons were needed to produce one NH₃ molecule, the FE could be calculated as follows:

$$FE = \frac{3F \times [NH_3] \times V}{17 \times Q}$$
(3)

The rate of NH₃ formation was calculated using the following equation:

$$U_{NH_3} = \frac{[NH_3] \times V}{t \times m_{cat}}$$
(4)

Where F is the Faraday constant, $[NH_3]$ is the measured NH_3 concentration, V is the volume of the PBS electrolyte for NH_3 collection, t is the reduction time and m_{cat} . is the catalyst mass.

1.4 Product analysis

1.4.1 Esterification of sample

After being concentrated, the sample solution is adjusted to pH 3-4 with 60% nitric acid, and then crystallize under -4 °C, washed with ice water for 3 times, and dried to obtain the sample. Under strict nitrogen protection, 0.5 g sample and 6.0 mL of 10% acetyl chloride solution in 5.0 mL of toluene react at 80 °C for 2 h. The sample solution was transferred to a 50 mL centrifuge tube, and washed three times with 3.0 mL of sodium carbonate solution (10%). The sodium carbonate solution was combined in a 50 mL centrifuge tube, and centrifuged at 5000 rpm for 5 minutes. The supernatant was taken as a test solution and measured by a gas chromatograph. The standard assay solution for glucose monoester and glucose diester is the same as the above procedure.

1.4.2 Gas chromatogram measurements

Analyses were performed with a Agilent 6890N gas chromatograph. The injector and detector temperatures were kept at 240 and 280 °C. N₂ was used as the carrier gas at a constant flow rate of 1.0 mL/min. The GC oven program was the following: after 5 min at 140 °C, the oven was heated at 4 °C/min to 240 °C (hold time of 10 min).

1.5 The conductivity of the Cu^{II}-MOF

The electric-conductivity of the **Cu^{II}-MOF** was tested using Van der Pauw (VDP) method,⁴ which was performed with an ECOPIA HMS-5000 Hall measurement system in ambient surroundings. A constant current and magnetic field of 20 mA and

0.55 T were used, respectively. In the VDP method, the contacts are located at the edges of the conducting surface. Two adjacent electrodes are used to carry current and the two other electrodes are used to measure voltage. The slope of voltage–current scan is used to calculate resistance for each combination of electrode connections. When four contacts on the sample are symmetrically located with respect to the surface and the composition on the sample is homogenous, both R_{vertical} and R_{horizontal} should be very close. R_s is calculated from Van der Pauw equation and is multiplied by the thickness of the sample to obtain the resistivity. Conductivity is the inverse of resistivity.

 $exp(-R_{vertical}/R_s) + exp(-R_{horizontal}/R_s) = 1$, R_s is the sheet resistance, $R_{vertical}$ and $R_{horizontal}$ are calculated from series of measurements by using four contacts on the anode surface.

The conductivity of JUC-1000 is 3.1×10^{-4} S cm⁻¹ at 25 °C.



2. Additional Results



Fig. S1 The structure of Cu^{II}-MOF. (a) Structure of L ligand. (b, c) Illustration of the topology of JUC-1000: simplification of the organic L ligand (5-connected node, green) and the inorganic clusters (5-connected node, blue). (d, e) View of the structure of JUC-1000 showing multiple pores in different directions.



Fig. S2 The X-ray photoelectron spectroscopy (XPS) survey spectrum for JUC-1000 sample.



Fig.S3 The FE-SEM image of as-prepared JUC-1000/CC (insets: the individual nanorod with the cross-section).



Fig. S4 The comparison of catalytic NRRa ctivity for JUC-1000/CC and bare CC . NH₃ yield rates and Faradic efficiencies were measured in N₂-saturated 1.0 M Na₂SO₄ electrolyte at -0.3 V vs. RHE.



Fig. S5 (a) UV-Vis absorption spectra of indophenol assays with NH_4^+ ions after incubated for 2 h at room temperature. (b) Calibration curve used for estimation of NH_4^+ .



Fig. S6 UV-Vis absorption spectra of the electrolytes estimated by the method of Watt-Chrisp after 2 h electrolysis in N_2 atmosphere at -0.3 V at room temperature.



Fig. S7 The comparison of XPS spectra in the Cu 2p region for the JUC-1000 samples before and after 20 recycling tests.



Fig. S8 The FE-SEM image of the JUC-1000/CC after 20 recycling tests.



Fig. S9 The comparison of XRD patterns for the JUC-1000 samples after 20 recycling tests and simulated JUC-1000.



Fig. S10 CVs of (a) JUC-1000/CC and (b) bare CC under different scan rates increasing from 70 to 110 mV s⁻¹ in 1 M Na₂SO₄ electrolyte with 1.0 M SG. The linear relationship of the oxidation peak currents versus scan rates for (c) JUC-1000/CC and (d) bare CC.



Fig. S11 Nyquist plots of JUC-1000/CC and bare CC.



Fig. S12 Corresponding NH_3 yield rates and FEs on the JUC-1000/CC and RuO2/CC catalyst with the bifunctional electrocatalyst device in 1.0 M Na_2SO_4 solution with SG.



Fig. S13 Polarization curves for JUC-1000/CC||JUC-1000/CC in 1.0 M Na_2SO_4 anodic electrolyte with and without 1.0 M GA.

Reference

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