Supporting Information

d-Band Center Modulation in CuNi Alloy/Graphene Oxide Catalysts for Enhanced Electrocatalytic Ammonia Synthesis from Nitrate

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1. Experimental Section

1.1 Chemicals and materials

All chemicals employed in this investigation were procured from commercial suppliers and directly utilized in their as-received condition： Single-layer graphene oxide (≥96%) was bought from suzhou tanfeng graphene technology Co., Ltd. Copper chloride ($CuCl_2$•$2H_2O$, ≥99%), Nickle sulfate ($NiSO_4$•$6H_2O$, ≥98.5%), Ethylene glycol ($HOCH_2CH_2OH$, ≥99%), Trisodium citrate dihydrate ($C_6H_5Na_3O_7$•$2H_2O$, ≥99%), Isopropyl alcohol ($(CH_3)_2CHOH$, ≥99.7%), Potassium nitrate(KNO_3 99%) was bought from Tianjin Damao Chemical Regent Factory. Argon (Ar, ≥99.999%), was bought from Panjin Tongyu Gas Co., Ltd. Nafion perfluorinated resin solution (5 wt. %), potassium nitrate−15N ($K^{15}NO_3$, 99atom%, ≥98.5%) was bought from Shanghai Macklin Biochemical Technology Co., Ltd. Potassium sodium tartrate tetrahydrate ($C_4H_4O_4KNa$•$4H_2O$, 99%) , sodium salicylate ($C_7H_5NaO_3$, ≥99.5%), sodium

nitroferricyanide dihydrate ($C_5FeN_6Na_2O•2H_2O$), sodium hypochlorite solution (NaClO, 6−14 % active chlorine basis), ammonium chloride (NH_4Cl, 99.5%) was bought from Shanghai Aladdin Biochemical Technology Co., Ltd. Deionized H_2O with the resistivity of 18 MΩ was used in all experiments.

1.2 Materials synthesis.

Preparation of CuNi@GO composites by liquid-phase reduction. GO (200 mg) was added to 20 mL ethylene glycol (EG) and sonicated to obtain a well-dispersed EG dispersion of GO. Then $NiSO_4$ (13.14 mg) and sodium citrate (200 mg) was dissolved in 50 mL EG and dissolved at room temperature with stirring, then the two solutions were mixed and stirred for 15 minutes. KOH (5 g) was added to 100 g EG and dissolved by ultrasonication to obtain KOH/EG solution, which was used to adjust the pH of the above reaction solution to 10. Keep stirring at room temperature for half an hour and then adjust the pH to 10, transferred to oil bath heated at 180°C for 6 hours, nitrogen is vented throughout the heating process. $CuCl_2•2H_2O$ (8.52 mg) was dissolved in 50mL EG and added it to the reaction solution to continue the reaction for 6 h. The product was centrifuged at the end of the reaction, washed with water for several times, dried under vacuum at 60 °C for 12 hours and ground into powder to obtain Cu_1Ni_1@GO. In this method, Cu_1Ni_1@GO was named according to the $CuCl_2•2H_2O$:$NiSO_4$ of 1:1, Cu_1Ni_2@GO, Cu_2Ni_1@GO was also named in this way.

1.3 Materials characterizations

The morphological characteristics and microstructural features of the composites were systematically characterized using a suite of advanced analytical techniques. Scanning electron microscopy (SEM) analysis was conducted on an FEI Nova Nano SEM 450 system operating at 18 kV acceleration voltage. For nanoscale resolution imaging, transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) coupled with energy-dispersive X-ray spectroscopy (EDS) elemental mapping were

performed using FEI Corporation's Tecnai G2 F30 STWIN instrument at 200 kV. Crystallographic analysis was carried out with a Shimadzu XRD-7000S diffractometer employing Cu Kα radiation (λ = 1.5406 Å), with scanning parameters set at 40 kV/40 mA over a 2θ angular range of 2-80°. Surface chemical composition was determined by X-ray photoelectron spectroscopy (XPS) measurements on an ESCALAB™ 250Xi spectrometer using monochromatic Al Kα excitation, with all binding energies referenced to the adventitious carbon C 1s peak at 284.8 eV. UV−visible absorption spectroscopy was performed via a spectrophotometer (Lambda 365, PERKINELMER).

1.4 Electrochemical nitrate reduction measurements

All electrochemical tests were conducted using an electrochemical workstation (CHI 760E Chenhua, Shanghai) in a three-electrode system. An Ag/AgCl electrode served as the reference electrode, and a platinum wire was used as the counter electrode. For preparing the working electrode, 10 mg of catalyst was dispersed in a mixed solution containing 970 μL isopropanol and 30 μL Nafion. The mixture was sonicated for 1 hour to form a homogeneous catalyst ink. Subsequently, 20 μL of the ink was uniformly coated onto the polished surface of a rotating disk electrode (RDE) (AFMSRCE, PINE) tip to serve as the working electrode. The electrochemical measurements employed a 250 mL electrolyte solution containing 0.1 M KOH and 0.1 M KNO_3. Prior to testing, the electrolyte was purged with high-purity nitrogen gas for 30 minutes to eliminate dissolved oxygen, with continuous nitrogen blanketing maintained throughout the experimental procedure. Linear sweep voltammetry (LSV) was performed at a scan rate of 5 mV s^{-1} across a potential window of -0.8 to -2.0 V (vs. Ag/AgCl). All measurements were conducted under controlled hydrodynamic conditions using a RDE system operating at 1600 rpm to ensure mass transport uniformity.

1.5 Determination of produced ammonia

The quantification of NH_4^+ concentration in post-electrosynthesis solutions was conducted via the indophenol blue method using custom-formulated reagents: (1) Chromogenic Agent A, prepared by ultrasonically dissolving 5.0 g sodium salicylate and 5.0 g sodium potassium tartrate tetrahydrate in 100 mL of 1 M potassium hydroxide solution; (2) Oxidizing Solution B, containing 4.5 mL sodium hypochlorite (6-14% available chlorine) homogenized with 100 mL deionized water; (3) Catalytic Reagent C, synthesized through ultrasonic dispersion of 0.2 g sodium nitroprusside in 20 mL deionized water. Following electrochemical testing, 2 mL of electrolyte was mixed sequentially with 2 mL Agent A, 1 mL Solution B, and 0.2 mL Reagent C. The mixture underwent vortex-assisted homogenization and 1-hour ambient incubation to facilitate chromogenic complex formation. UV-Vis absorption spectra were acquired using a spectrophotometer, with ammonium concentrations determined through a pre-established calibration curve. Final ammonia yield and FE were calculated via electrochemical mass-balance equations, ensuring rigorous correlation between charge transfer and reduction products.

The concentration of N_2H_4 in solution was determined using the Watt and Chrisp method. The chromogenic reagent was prepared by mixing 20 mL of concentrated hydrochloric acid with 200 mL of ethanol, followed by dissolution of 4.0 g of 4-dimethylaminobenzaldehyde. 2 mL of electrolyte was mixed with 2 mL of the reagent, vortexed, and incubated for 10 min. Absorption spectra were recorded on a UV-Vis spectrophotometer, with N_2H_4 exhibiting a maximum absorption peak at 460 nm.

The relevant calculations about the yield rate and the FE are conducted according to the following equations,

$$NH_3\ yield\ (\mu g\ h^{-1} cm^{-2}) = \frac{c_{NH3} \times V}{t \times A}$$

$$FE = \frac{8F \times c_{NH3} \times V}{17 \times Q}$$

Where C_{NH3} is detected ammonia concentration of electrolyte, V is the volume of the

electrolyte (250 mL), t is the electrolysis time (2 h), A represents the effective area of the glassy carbon working electrode (A = 0.196 cm²), F is Faraday constant (96485 C mol^{-1}), Q is the charge passing through of the electrode.

1.6 Calculation details

The electronic exchange-correlation interactions were modeled using the generalized gradient approximation with the Perdew–Burke–Ernzerhof (GGA-PBE) functional. Geometry optimization was governed by rigorously defined convergence criteria: energy tolerance (2.0×10^{-5} Ha), maximum force tolerance (4.0×10^{-3} eV/Å), and atomic displacement tolerance (5.0×10^{-3} Å). For self-consistent field (SCF) calculations, a density matrix convergence threshold of 1.0×10^{-5} and a charge mixing parameter of 0.2 were implemented to ensure numerical stability during iterative cycles.

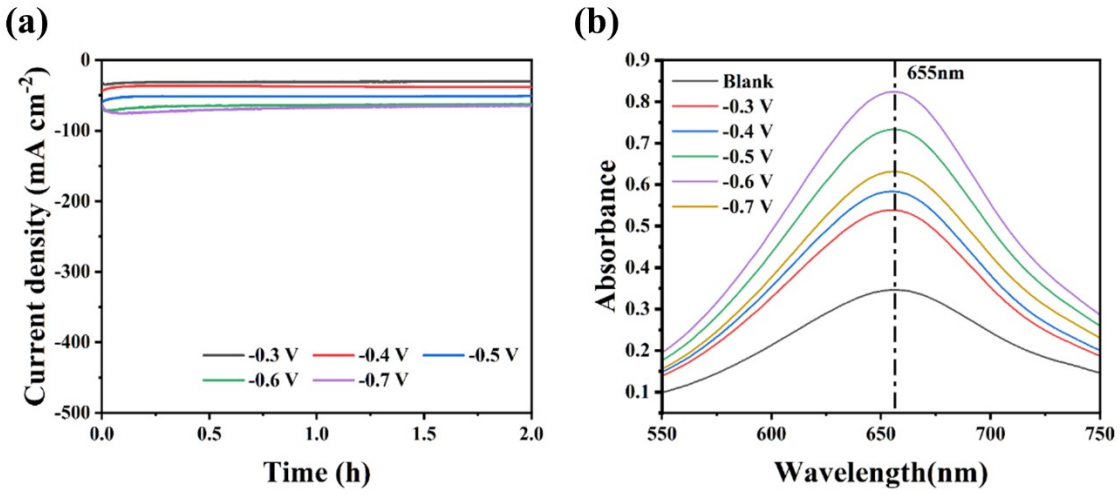

Figure S1. (a) Chronoamperometry curves for Cu_1Ni_1@GO at given potentials in 0.1 M KOH and 0.1 M KNO_3. (b) Corresponding UV-Vis absorption spectra of the electrolyte.

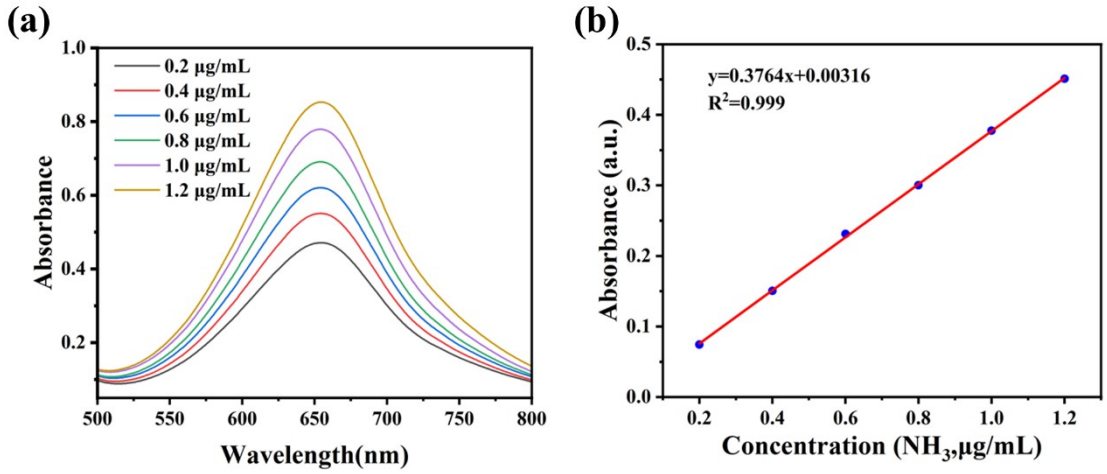

Figure S2. (a) UV-Vis spectra of NH_4^+ standard solutions at varying concentrations using the indophenol blue method. (b) Calibration curve used for the calculation of NH_3 concentrations.

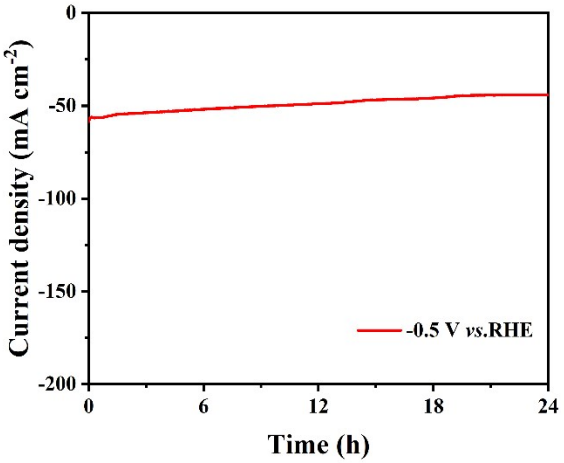

Figure S3. 24 h chronoamperometric test at −0.5 V *vs.* RHE in 0.1 M KOH and 0.1 M KNO_3.

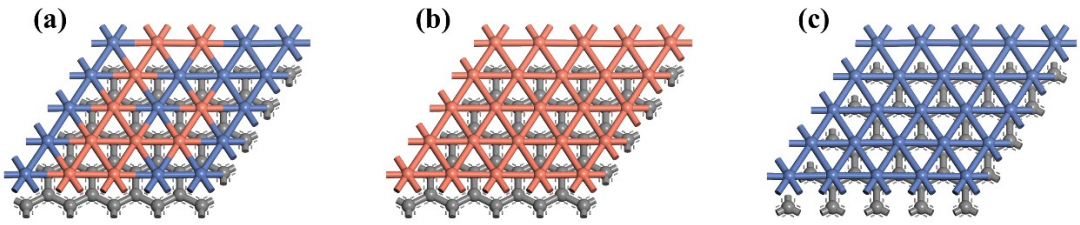

Figure S4. Structure model of (a) Cu_1Ni_1@GO; (b) Cu@GO; (c) Ni@GO.

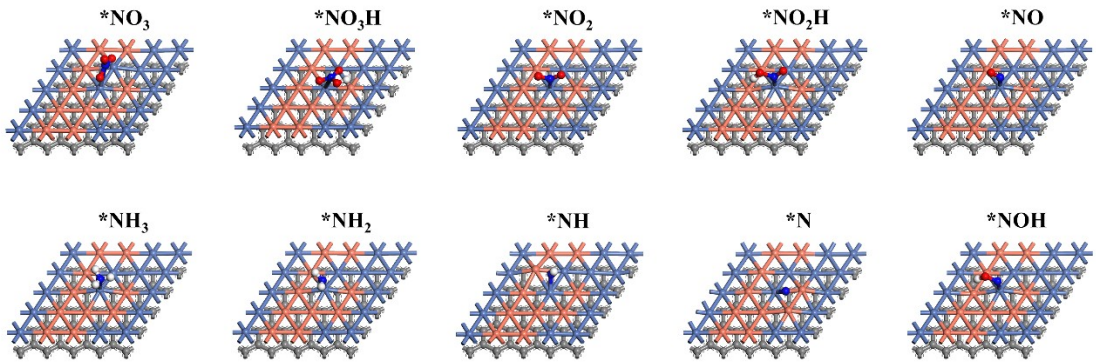

Figure S5. The crystal structure model of NO_3RR intermediate on Cu_1Ni_1@GO.

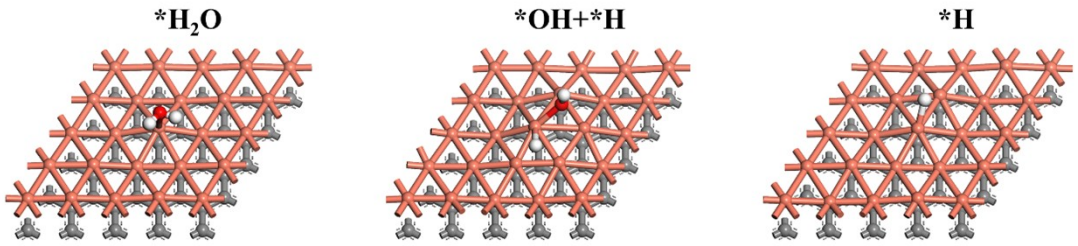

Figure S6. The crystal structure model of HER intermediate on Cu@GO.

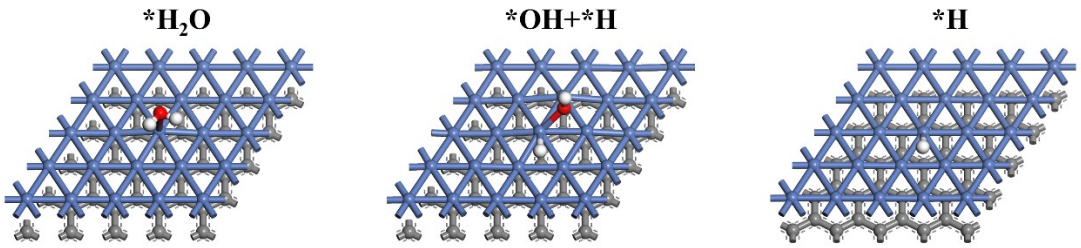

Figure S7. The crystal structure model of HER intermediate on Ni@GO.

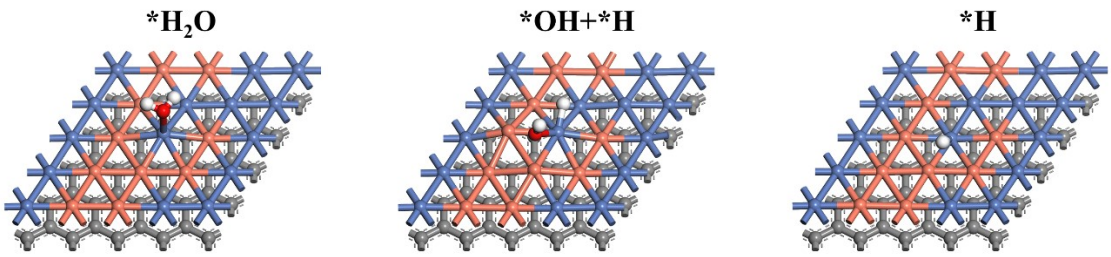

Figure S8. The crystal structure model of HER intermediate on Cu_1Ni_1@GO.