



Supplementary Material

# Assembly of Hydrophobic ZIF-8 on CeO<sub>2</sub> Nanorods as High-Efficiency Catalyst for Electrocatalytic Nitrogen Reduction Reaction

Yiwen Liu †, Xianbin Meng †, Zhiqiang Zhao, Kai Li \* and Yuqing Lin \*

Department of Chemistry, Capital Normal University, Beijing 100048, China

\* Correspondence: likai@cnu.edu.cn (K.L.); linyuqing@cnu.edu.cn (Y.L.)

† These authors contributed equally to this paper.

## 1. Experimental Procedures

**Reagents and Materials:** 1,3,5-Benzenetricarboxylic acid (99%) and 2-methylimidazole (98%) were purchased from Johnson & Johnson Chemical Co., LTD. Cerium (III) nitrate hexahydrate (99.5%) and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99.95%) were purchased from Aladdin Re-agent (Shanghai) Co., LTD. Carbon paper (30 cm 30 cm 0.1 cm) was purchased from Toray Corporation of Japan. Methanol, Nafion, ethanol and HNO<sub>3</sub> were purchased from Sinopharm Chemical Reagent Co. LTD, Shanghai, China. The deionized water was purified by the RO-DI system. The purity of the chemicals used in this study were of analytical grade and could be used without further purification.

**Characterization:** The as-synthesized samples were examined by Bruker D8 advanced powder X-ray diffraction (XRD) system using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The transmission electron microscope (TEM), high-resolution TEM (HRTEM) images and the energy dispersive X-ray spectroscopy (EDS) of the product were characterized using HRTEM (Philips-FEI Tecnai G2S-Twin microscope, Thermo Fisher Scientific, Shanghai, China). Field emission scanning electron microscopy (FE-SEM) images were performed by Hitachi SU8010 SEM. X-ray photoelectron spectra (XPS) were measured by ESCALAB 250 XPS spectrometer, Thermo Fisher Scientific, Shanghai, China equipped with a monochromic 15 Al K $\alpha$  X-ray source, Thermo Fisher Scientific, Shanghai, China.

**Electrochemical performance evaluation:** All the electrochemical tests were evaluated in a H-type electrolytic cell divided by Nafion 211 proton exchange membrane with CHI 600E electrochemistry workstation (Shanghai Chenhua Instrument Co. Ltd., Shanghai, China). An Ag/AgCl (saturated KCl) as the reference and graphite rod as counter electrode. The potentials recorded in this study were transformed into reversible hydrogen electrode (RHE) scale according to formula of  $E (\text{vs. RHE}) = E (\text{vs. Ag/AgCl}) + 0.059 \text{ pH} + 0.197 \text{ V}$ . The Nafion 211 membrane can be used only after the following pretreatment. Firstly, it was held in 5% hydrogen peroxide solution at 80 degrees Celsius for 1 h, and then bathed at 80 °C for another 1 h in deionized water. The NRR competence of an electrode was assessed using controlled potential electrolysis in a 0.5 M K<sub>2</sub>SO<sub>4</sub> electrolyte for 2 h at ambient conditions. The electrolytic cell was purged with N<sub>2</sub> by continuously bubbled with nitrogen for 30 minutes before the reaction. The electrolyte was frequently bubbled with N<sub>2</sub> and continue to stir at a stirring rate about ~500 rpm during the electrolysis process.

**Determination of NH<sub>3</sub> in 0.5 M K<sub>2</sub>SO<sub>4</sub> solution:** The concentration of NH<sub>3</sub> produced in 0.5 M K<sub>2</sub>SO<sub>4</sub> solutions was confirmed by the indophenol blue method. Firstly, 2 mL of cathodic electrolyte, 2 mL of 1 M NaOH solution including 5% sodium citrate, 5% salicylic acid, 1 mL of 0.05 M NaClO and 0.2 mL of 1% C<sub>5</sub>FeN<sub>6</sub>Na<sub>2</sub>O·2H<sub>2</sub>O were mixed together. Then, UV-Vis absorption spectrum was evaluated at 655 nm before incubating at 25 °C for

1 h. The concentration-absorbance curves were calibrated by standard  $\text{NH}_3$  solution with a series of concentrations.

**Determination of hydrazine ( $\text{N}_2\text{H}_4$ ):** The concentration of  $\text{N}_2\text{H}_4$  in electrolyte was confirmed by the technology of Watt and Chrisp. A mixture of 5.99 g  $\text{C}_9\text{H}_{11}\text{NO}$ , 30 mL hydrogen chloride and 300 mL ethanol serve as a color reagent. The standard curve was obtained as follows: Firstly, configuring a battery of different concentrations of hydrazine hydrate solution as reference solution by using 0.5 M  $\text{K}_2\text{SO}_4$ ; Secondly, 5 mL color reagent was added to 5 mL reference solution and stirring 10 min at 25 °C. Thirdly, the absorption spectra of the mixed solution was presented at 460 nm.

**Faradic efficiency and  $\text{NH}_3$  yield rate:** The Faradic efficiency for NRR was calculated as the amount of electric charge used for compounding ammonia and hydrazine hydrate was divided by the total charge across the electrodes in the electrochemical test. Faradic efficiency =  $(3F \times c_{\text{NH}_3} \times V)/(17 \times Q)$ , where  $F$  is the Faraday constant,  $c_{\text{NH}_3}$  is the concentration of the produced  $\text{NH}_3$ ,  $V$  is the number of the electrolyte and  $Q$  is the total electric charge for one electron. Meanwhile, the  $\text{NH}_3$  yield ( $y_{\text{NH}_3}$ ) is calculated by  $y_{\text{NH}_3} = c_{\text{NH}_3} \times V$ . The values of the  $\text{NH}_3$  yield rate ( $R_{\text{NH}_3}$ ) can be derived from the slopes of the curves made by plotting the  $\text{NH}_3$  yields vs reaction times.

## 2. Supplementary Figures

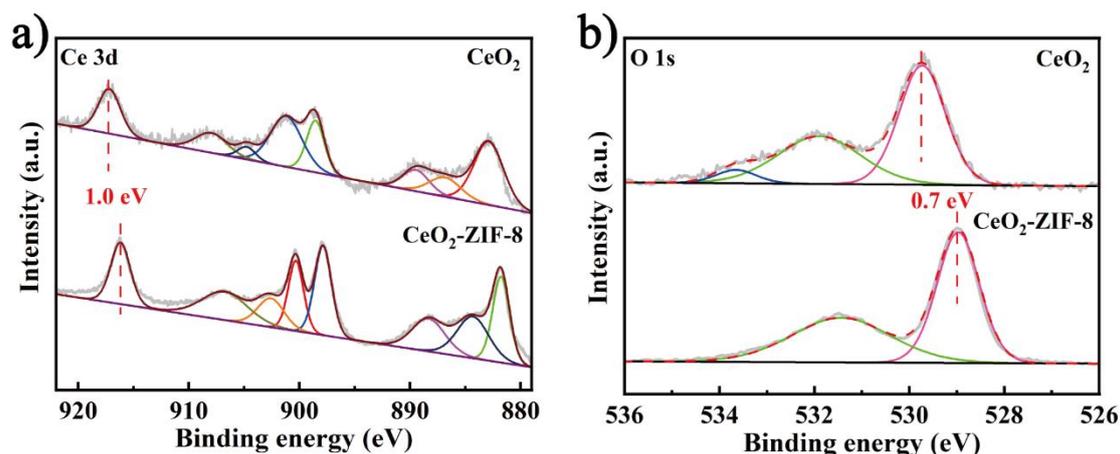


Figure S1. Constitutional element XPS spectra of a) Ce 3d and b) O 1s of  $\text{CeO}_2$  and  $\text{CeO}_2\text{-ZIF-8}$ .

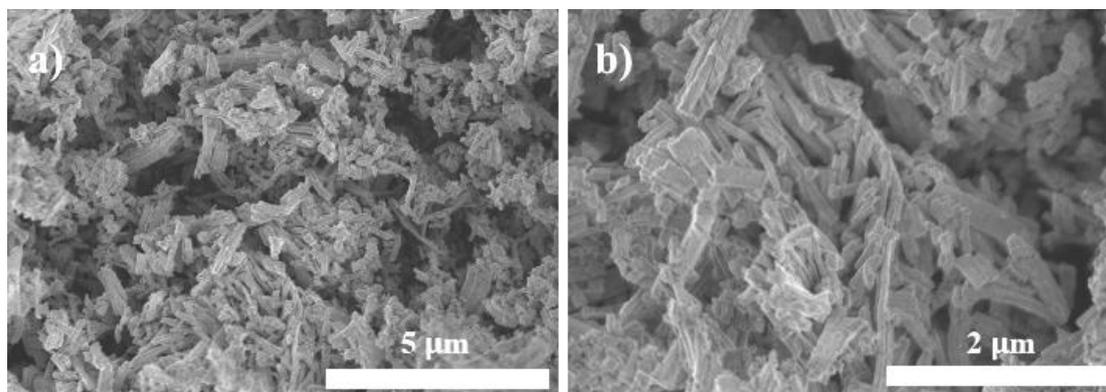


Figure S2. (a,b) SEM images of  $\text{CeO}_2$  with different magnification.

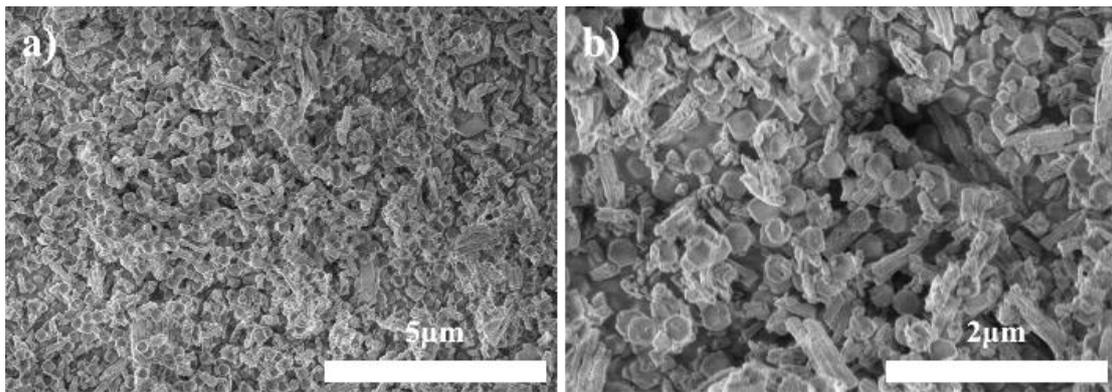


Figure S3. (a,b)SEM images of CeO<sub>2</sub>-ZIF-8 with different magnification.

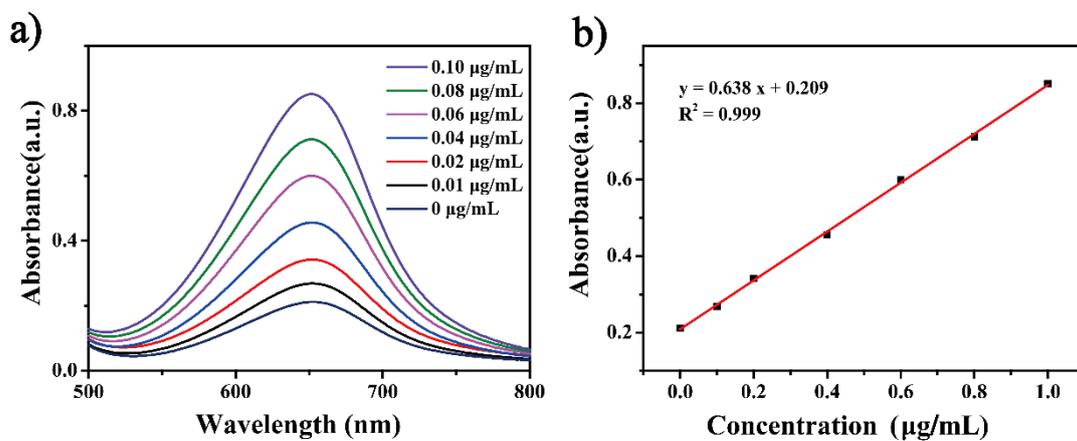


Figure S4. Absolute calibration of the indophenol blue method using ammonium chloride solutions of known concentration as standards. a) UV-Vis curves of indophenol assays with NH<sub>4</sub><sup>+</sup> ions after incubated for 2 h and b) calibration curve used for estimation of NH<sub>3</sub> by NH<sub>4</sub><sup>+</sup> ion concentration. The absorbance at 655 nm was measured by UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with NH<sub>4</sub><sup>+</sup> ion concentration ( $y = 0.638x + 0.209$ ,  $R^2 = 0.999$ ) of three times independent calibration curves.

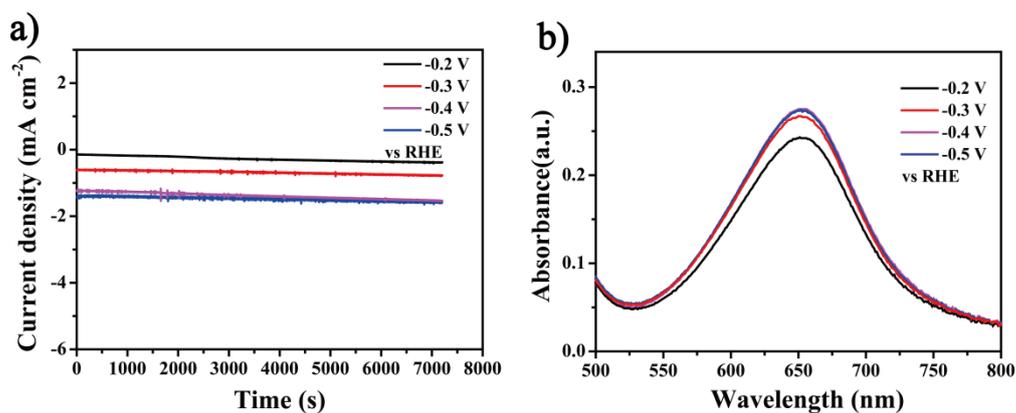
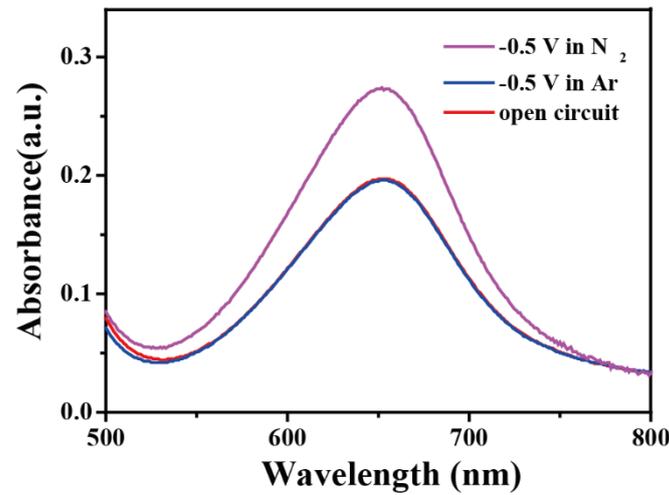
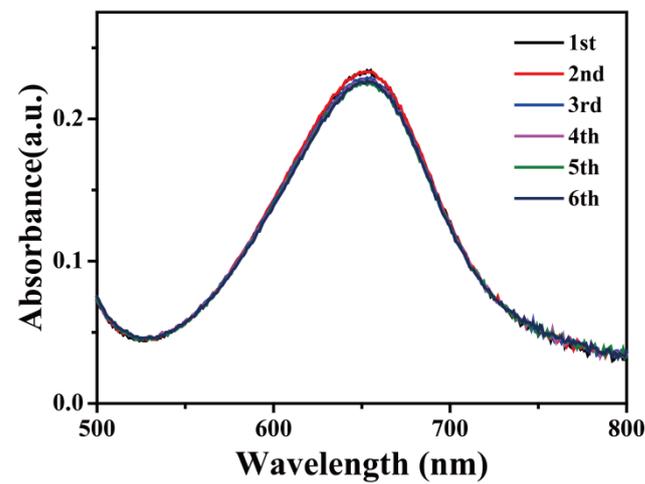


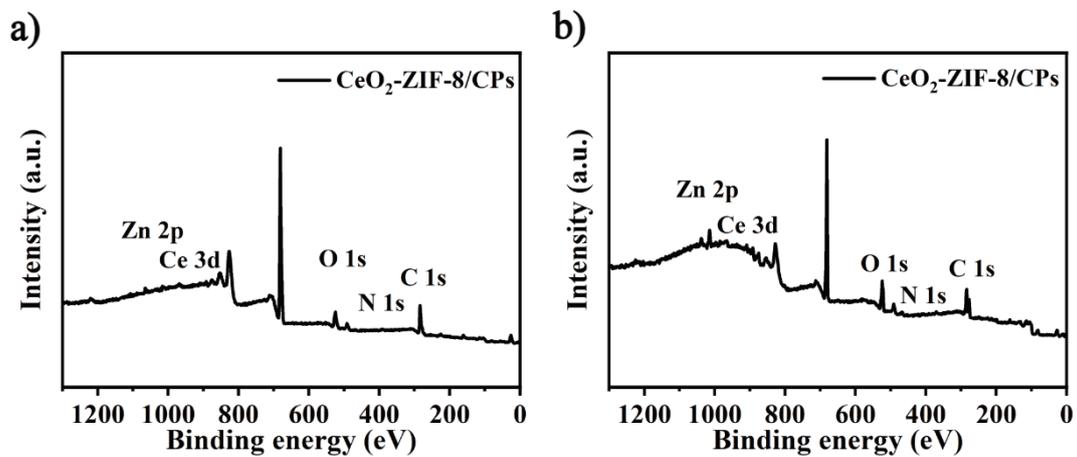
Figure S5. a) Chronoamperometry results at the corresponding potentials of CeO<sub>2</sub>-ZIF-8/CPs, and b) UV-Vis absorption spectra of the K<sub>2</sub>SO<sub>4</sub> electrolyte stained with indophenol indicator after charging at each restricted potential vs RHE under N<sub>2</sub> controls for 2 hours.



**Figure S6.** UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after 2 h NRR electrolysis under different conditions: open circuit in  $N_2$  (red curve), -0.5 V in  $N_2$  (purple curve) and -0.5 V in Ar (blue curve).



**Figure S7.** Cycling test of the  $CeO_2$ -ZIF-8/CPs after consecutive recycling electrolysis in  $N_2$ -saturated 0.5 M  $K_2SO_4$  solution (pH 3.5) at -0.5 V vs RHE for 2 h of each NRR experiment.



**Figure S8.** Full XPS spectrum of  $CeO_2$ -ZIF-8/CPs before a) and after b) NRR.

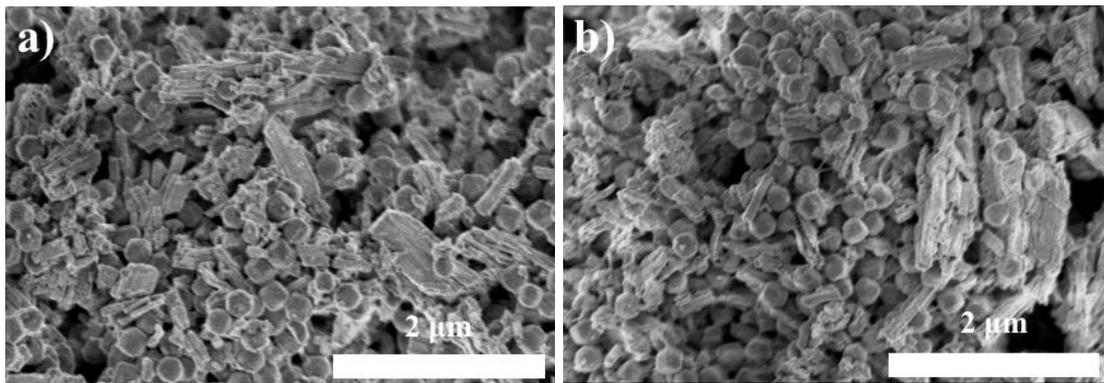


Figure S9. SEM images of CeO<sub>2</sub>-ZIF-8/CPs before a) and after b) NRR.

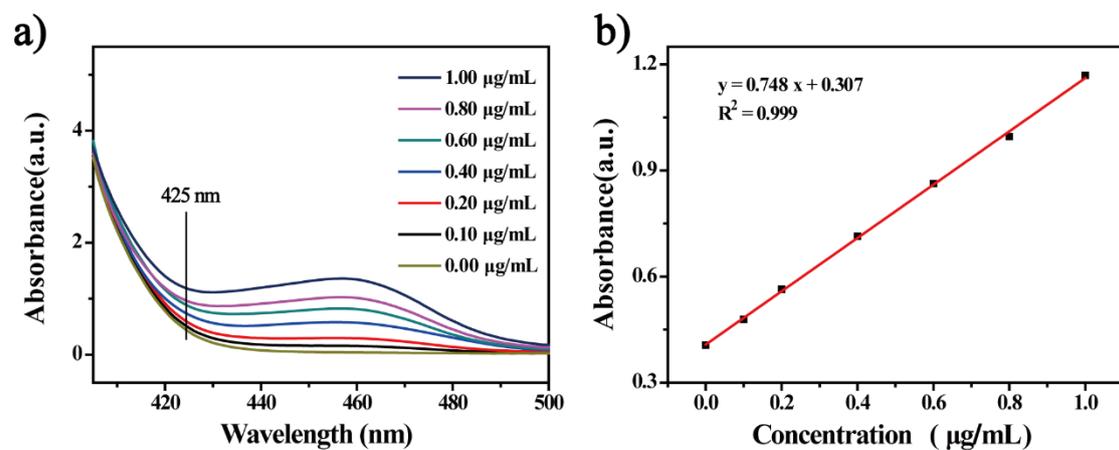


Figure S10. a) UV-Vis absorption spectra of various N<sub>2</sub>H<sub>4</sub> concentrations after incubated for 10 min at room temperature. Calibration curve used for estimation of N<sub>2</sub>H<sub>4</sub> concentrations. b) The absorbance at 425 nm was measured by UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O concentration ( $y = 0.748x + 0.307$ ,  $R^2 = 0.999$ ) of three times independent calibration curves.

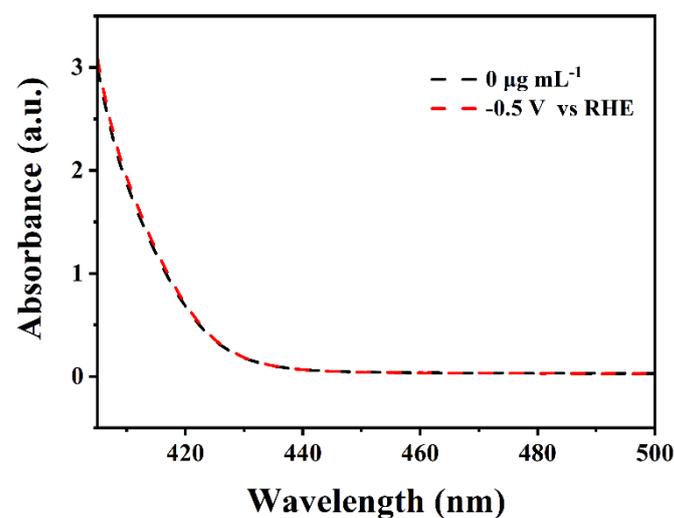


Figure S11. UV-Vis absorption spectrum of the by-produced N<sub>2</sub>H<sub>4</sub> for CeO<sub>2</sub>-ZIF-8/CPs tested in 0.5 M K<sub>2</sub>SO<sub>4</sub> with bubbled N<sub>2</sub> under -0.5 V vs RHE for 2 h.