

Supporting information

Improving oxygen reduction reaction and oxygen evolution reaction activities by Ru-NiCo nanoparticles decorated on porous nitrogen-doped carbon for rechargeable Zn-air batteries and OER electrocatalysts

Lili Sui², Lihua Miao^{1,*}, Ye Kuang³, Xiaoyan Shen¹, Dan Yang¹, He Huang¹,

¹School of Medical Information Engineering, Shenyang Medical College, Shenyang

110043, Liaoning, China

²School of pharmacy, Shenyang Medical College, Shenyang, 110043, Liaoning,

China

³Shenyang Ligong university, School of Renewable Energy, Shenyang 110136, P. R.

China

2. Experimental details

2.1. Materials

The melamine, Cobaltous nitrate, and Nickel nitrate were acquired from Tianjin Damao Chemical Reagent Co., Ltd. The Benchmark 20 wt % Pt/C catalyst was obtained from Aladdin. All reagents were utilized as received without undergoing additional purification.

2.2. Synthesis of NiCo-MOF nanostructures

Initially, all the reagents were used as received without requiring any further purification. In a standard procedure, 3 mM $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 3 mM $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 20 mL of methanol and stirred for 10 minutes to create solution A. Solution B was prepared by dissolving 0.8 g 2-methylimidazole in 20 mL of methanol and stirring for 10 minutes. The two solutions were combined by rapidly pouring solution B into the cobalt nitrate solution, and the stirring continued for 10 minutes. The resulting mixture was allowed to stand at room temperature for 4 hours, followed by three washes with alcohol and deionized water, and then dried overnight at 60 °C. The same approach was used to fabricate Ni-MOF and Co-MOF.

2.3. Synthesis of Ru-NiCo-MOF nanostructures

The samples that were prepared earlier were immersed in a solution of 50 mL deionized water and 0.1 mg RuCl_3 , and the resulting mixture was left to stand at room temperature for 20 minutes.

2.4. Synthesis of Ru-NiCo/NC nanostructures

The synthesis of Ru-NiCo/NC nanostructures was performed using an annealing method. Initially, 3 g of melamine was placed in a porcelain boat upstream, while the samples obtained previously were placed downstream. The mixture was then heated at 900 °C for 2 hours under a nitrogen atmosphere. Subsequently, six different samples were obtained, including Ru-NiCo/NC, Ru-Co/NC, NiCo/NC, Co/NC, and Ni/NC.

2.5. Materials characterizations

Crystal structure and element composition of prepared samples were analyzed by X-ray diffraction analyzer (XRD, Rigaku D/max 2500, Cu K α , $\lambda = 1.5406 \text{ \AA}$) and X-ray photoelectron spectra (XPS, ESCALAB250, Al K α source). The structure and morphology were characterized by scanning electron microscope (SEM, Hitachi SU8020) and transmission electron microscope (TEM, FEI Talos F200X). Brunauer-Emmett-Teller (BET) specific surface areas of the obtained samples were investigated through nitrogen adsorption-desorption analyses using an ASAP 2020.

2.6. Electrochemical measurements

Electrochemistry is measured with CHI760E Electrochemical workstation (Shanghai Chenhua) in a standard three-electrode system. The rotating ring plate electrode (RRDE, glass carbon as disc, with $A = 0.19625 \text{ cm}^2$, Pt as a ring, $A = 0.2198 \text{ cm}^2$) was used as the working electrode substrate. 5 mg of catalyst was added into 1000 μL of deionized water, 485 μL isopropanol ($\text{C}_3\text{H}_8\text{O}$) and 30 μL Nafion (5 wt.%), and then a homogenous solution was obtained by ultrasonic treatment for 60 min. 10.4 μL of suspension was dropped on a glass carbon surface and dried at 25°C. Hg/HgO as reference electrode and Pt foil as counter one. and the Ring was

constantly polarized at 0.6 V. The potentials were estimated according to Equations.

$$E_{\text{RHE}} = E_0 + E_{\text{Hg/HgO}} + 0.059 \text{ pH} - I_d R_s \quad (1)$$

Where E_0 is the measured potential and $E_{\text{Hg/HgO}}$ is 0.098 V, I_d denotes the disk electrode current and R_s is the resistance of the electrolyte.

The electron transfer number (n) was calculated by the diffusion limiting Current density (j_L) at various rotational speeds (ω) according to the Koutecky-Levich equations:

$$1/j = 1/j_L + 1/j_k = 1/B\omega^{1/2} + 1/j_k = 1/(0.2nFC_0D_0^{2/3}\nu^{-1/6}) \omega^{1/2} + 1/j_k \quad (2)$$

where F and ν show the Faraday constant (96485 C mol⁻¹) and the kinematic viscosity of the electrolyte (0.01 cm² s⁻¹); C_0 and D_0 are the bulk concentration (1.2 × 10⁻⁶ mol/cm³) and diffusion coefficient (1.9 × 10⁻⁵ cm²/s) of O₂ in 0.1 M KOH, respectively.

The value of n was also determined by H₂O₂ calculation yield derived from ring current measurements in rotary ring plate electrode (RRED). The H₂O₂ yield and n were calculated by with the following equations:

$$\text{H}_2\text{O}_2(\%) = 200 (I_r/N)/(I_d + I_r/N) = 200 I_r/(NI_d + I_r) \quad (3)$$

$$n = 4I_d/(I_d + I_r/N) = 4 NI_d/(NI_d + I_r) \quad (4)$$

Where I_r and N are the ring electrode current the collection Pt ring efficiency (0.424).

First principle periodic DFT simulations were carried out with the help of the Vienna Ab Initio Simulation Package (VASP). The projector-augmented wave (PAW) [2] approach was used to describe the electron-ion interactions with the generalized

gradient approximation functional proposed by Perdew et al. (GGA-PBE) [3]. The planewave kinetic energy cutoff was fixed at 400 eV, and the Brillouin zone was sampled using a single (Gamma) k-point. Due to the large computational cells and low geometry, the electronic energies for convergence were set to be 10^{-4} eV.

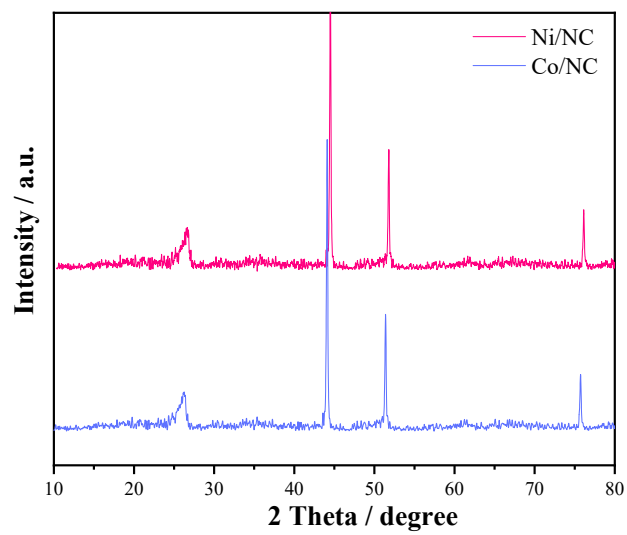


Figure S1 XRD patterns of the samples

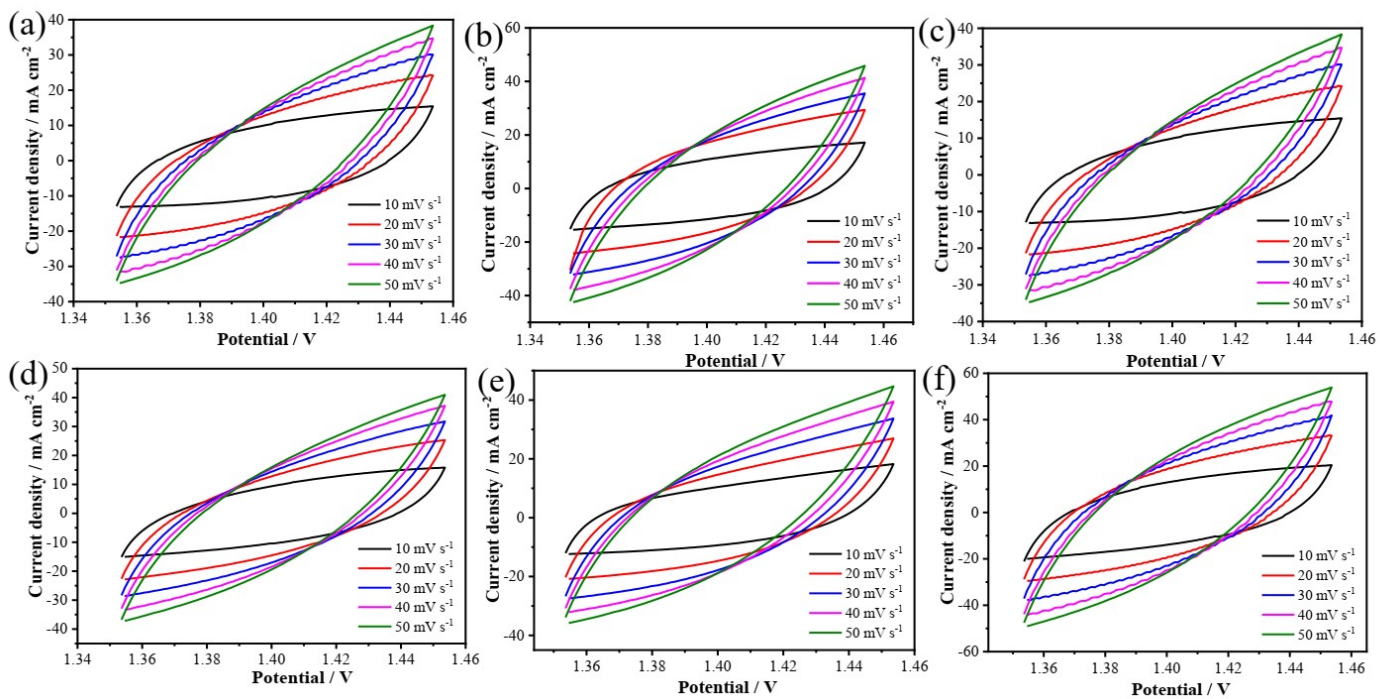


Figure S2 (a) CV curves of the Ru-NiCo/NC samples (b) Ru-Co/NC products (c) Ru-Ni/NC products (d) NiCo/NC products (e) Co/NC samples (f) Ni/NC samples

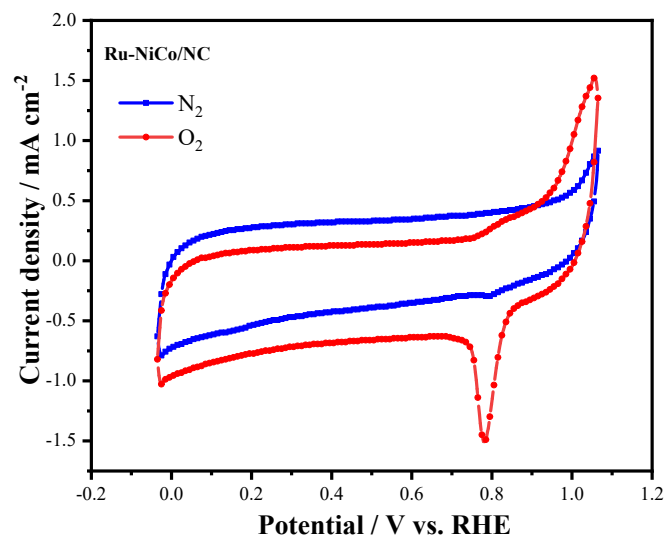


Figure S3 CV curves of the Ru-NiCo/NC samples

Table S1 Summary of the electrochemical performance of the catalysts.

Samples	$E_{1/2}$ (V vs. RHE)	ORR Tafel slope (mV dec ⁻¹)	η_{10} at 10 mA cm ⁻² (mV)	OER Tafel slope (mV dec ⁻¹)	ZAB Power Density (mW cm ⁻²)	Reference
Ru-NiCo/NC	0.84	38.18	342	65.75	132.3	This work
CoNi@NC	0.83	58	400	126	172	S1
CoNi@NCN Ts	0.82	80	320	64	138	S2
CoNi-CoN ₄ - HPC-900	0.78	67.0	470	153.0	116	S3
NiCo@N-C	0.86	79	280	51	108	S4
Ni ₂ Co ₂ -CNR	0.80	83	310	135	122.1	S5

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