

Supporting Information

RuCo Alloy Trifunctional Electrocatalysts with Ratio-Dependent Activity for Zn-Air Batteries and Self-Powered Water Splitting

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Experimental section

Materials

Cobaltous nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%), Ruoodium (III) Chloride Hydr (RuCl_3), Sodium hydroxide (NaOH), Potassium hydroxide (KOH , $\geq 95\%$), and other chemicals used in the experiments were all purchased commercially (Aladdin, China). Nafion D-520 dispersion (5 wt%) was purchased from Alfa Aesar China. The Milli-Q water was obtained from the Milli-Q System. All the materials were used as received without further purification.

Synthesis of RuCo/NPC, Ru/NPC and Co/NPC catalysts

The RuCo/NPC were synthesized by the simple template method. In the typical synthesis, the ground potato mash (10 g) was dissolved in 40 ml of deionized water with SiO_2 (5 g) as a template and stirred for 30 min. Then the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, RuCl_3 were added into the system as Co and Ru source. The amount of Co and Ru is 0.225 g. The mixture was stirred at 80 °C until evenly mixed. After this, the mixture was calcined at 800 °C under Ar atmosphere for 2 h. Then, after being fully carbonized, soak the material in 2 M NaOH at 80 °C for removing the SiO_2 template to obtain the RuCo/NPC catalyst. By simply adjusting the initial mass ratio of RuCo, catalytic materials with different properties can be obtained. The mass ratio of Ru and Co source are respectively 3:7, 5:5, 7:3. The corresponding sample is marked as RuCo/NPC (3:7), RuCo/NPC (5:5) and RuCo/NPC (7:3). The Ru/NPC and Co/NPC were fabricated by a similar method without Ru source or Co source.

Preparation of Pt/C and RuO_2 electrodes

The Pt/C and RuO₂ electrodes were prepared by a typical method. Briefly, commercial Pt/C (5 mg) or RuO₂ (5 mg) was dispersed in a solution of 0.5 mL deionized water, 0.5 mL ethanol, and 20 μ L 5% Nafion solution. That mixture was then ultrasonicated for 20 min to form a homogeneous catalyst ink. And then 20 μ L of the ink was loaded onto the glassy carbon electrode. After that, the electrode was placed in an oven and dried for further testing.

Characterizations

The scanning electron microscopy (SEM) and elemental mapping images were obtained using Magellan400, FEI. The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE with Cu K α radiation (40 kV, 30 mA, $\lambda = 1.54 \text{ \AA}$). The X-ray photoelectron spectroscopy (XPS) spectra were obtained using an IncaX-max50, Oxford. The JEOL JEM 2100F was employed to acquire the transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) images. Nitrogen adsorption-desorption isotherms were measured at -196 $^{\circ}$ C with an ASAP 2010 Surface Area and Pore Size Analyzer System (Micromeritics, Norcross, GA). The specific surface areas were obtained using the multipoint Brunauer-Emmett-Teller (BET) method.

Electrochemical measurements.

All electrochemical measurements were carried out in a typical three-electrode system with a CHI-760E electrochemical workstation (CHI Instruments, Shanghai, China) at room temperature. Graphite rod was used as the counter electrode, and mercury/mercuric oxide (Hg/HgO) electrode as the reference electrode, the glassy

carbon electrode with catalysts as working electrode. All potentials in this study were converted into a reversible hydrogen electrode (RHE) scale according to: $E(\text{RHE}) = E(\text{Hg}/\text{HgO}) + 0.098 + 0.059 \times \text{pH}$. The polarization curves were recorded in 1M KOH with a scan rate of 2 mV s^{-1} and corrected for the iR contribution within the cell. iR drop was compensated at 85% for OER and at 90% for HER. Electrochemical impedance spectroscopy (EIS) was performed at -50 mV overpotential with frequency from 10 MHz to 100 KHz. The electrochemically active surface area (ECSA) was estimated by measuring the capacitive current associated with double-layer charging (C_{dl}) from scan-rate dependence of cyclic voltammetry (CV).

Rotating ring disk electrode (RRDE) measurement was conducted to determine the electron transfer number (n) and peroxide yield for ORR. Linear sweep voltammetry (LSV) from 0.3 V to 1.0 V (vs. RHE) was applied on disk electrode at a scan rate of 5 mV s^{-1} with a rotation speed of 1600 rpm. Corresponding n and H_2O_2 yield were calculated by the following equations:

$$n = \frac{4I_D}{I_D + (I_R/N)} \quad (1)$$

$$\% \text{H}_2\text{O}_2 = 100 \frac{2I_R/N}{I_D + (I_R/N)} \quad (2)$$

where I_D is the Faradaic current at the disk, I_R the Faradaic current at the ring and N is the H_2O_2 collection coefficient at the ring ($n=0.37$).

For construction of Zn-O₂ battery, the prepared RuCo/NPC catalyst (RuCo/NPC (5:5) : RuCo/NPC (7:3)=1:1) was uniformly coated on carbon paper as the cathode ($\sim 1 \text{ mg cm}^{-2}$). A polished Zn plate (0.3 mm) was used as the anode and 6 mol L^{-1} KOH

solution with $0.2 \text{ mol L}^{-1} \text{ Zn(OAc)}_2$ was used as electrolyte. For comparison, a mixture of Pt/C and RuO_2 (mass ratio of 1:1) with the same loading was coated onto carbon paper as cathode. The electrochemical performances of ZABs, such as charge/discharge performance were tested using a PINE electrochemical workstation (Pine Research Instrumentation, USA). And cycling ability tests and specific capacities tests were recorded by a Land CT2001A system, and each discharge and charge period were set to be 30 min. To evaluate the overall water-splitting activity, the electrolyzer device was assembled by two identical electrodes (RuCo/NPC (5:5) as cathode and RuCo/NPC (7:3) as anode) coated on carbon paper with a mass loading of 1 mg cm^{-2} , followed by measuring in 1 M KOH. The LSV curves were collected at a scan rate of 2 mV s^{-1} with iR compensation.

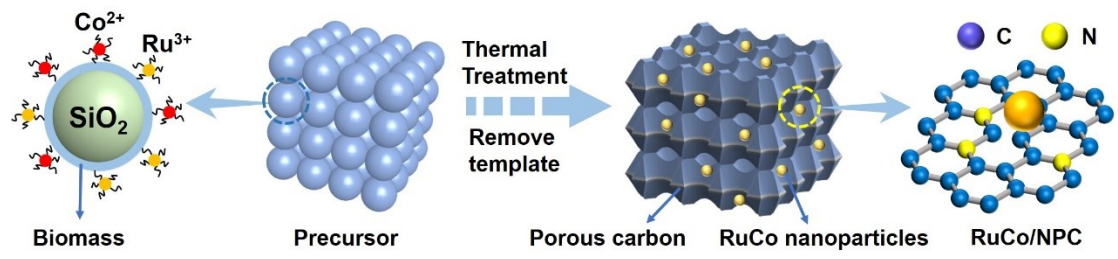


Figure S1. Schematic illustration on synthesis of trifunctional RuCo/NPC electrocatalyst.

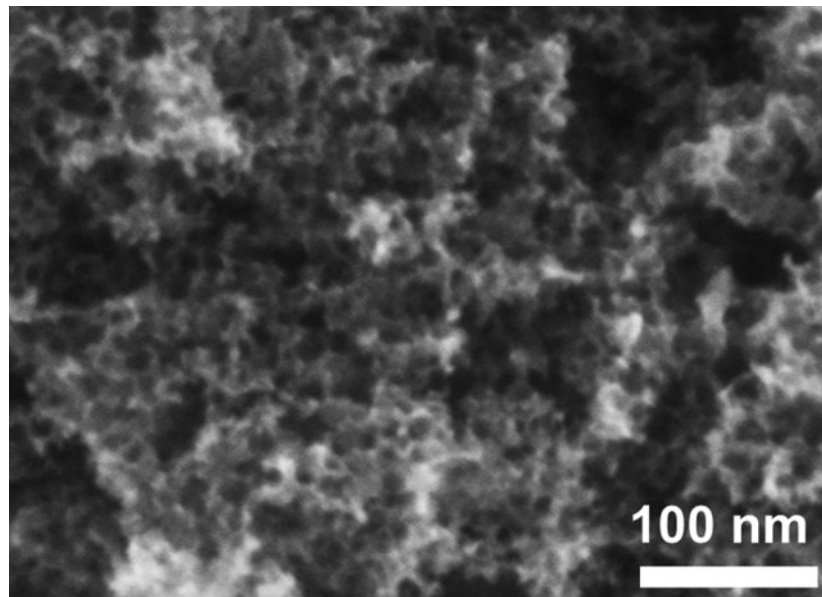


Figure S2. The SEM image of RuCo/NPC catalyst.

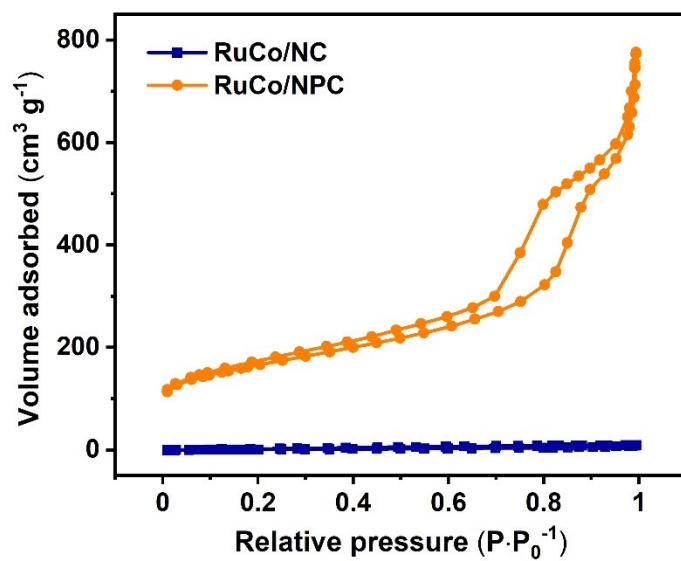


Figure S3. N₂ sorption isotherms of RuCo/NPC and RuCo/NC at -196°C

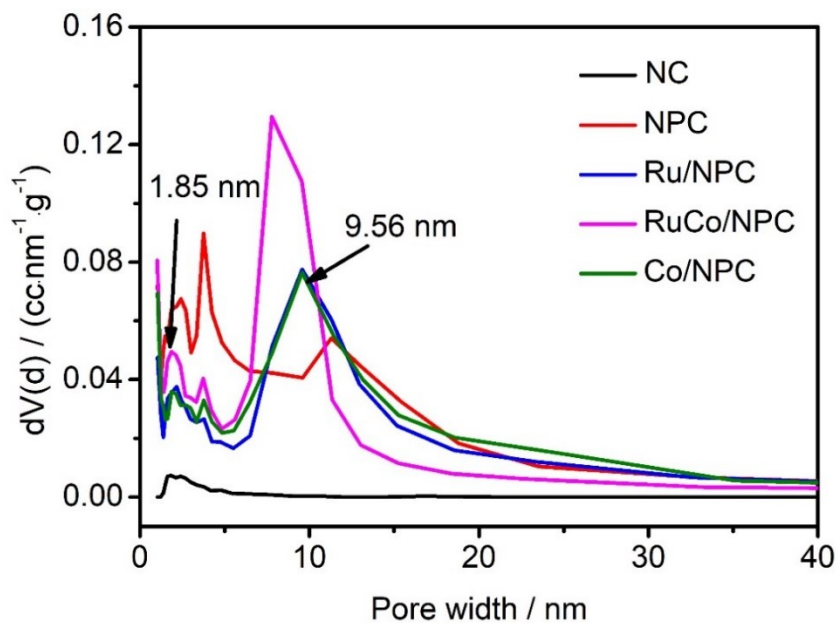


Figure S4. The pore size distribution of RuCo/NPC.

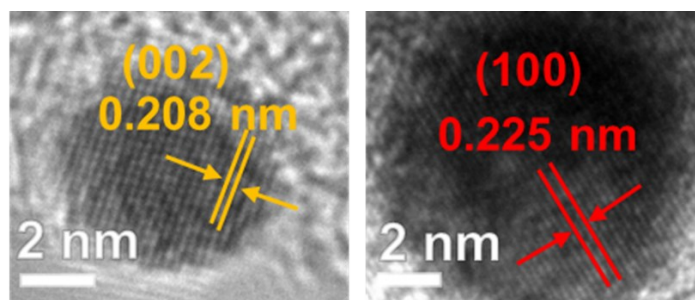


Figure S5. HRTEM images of RuCo alloy nanoparticle.

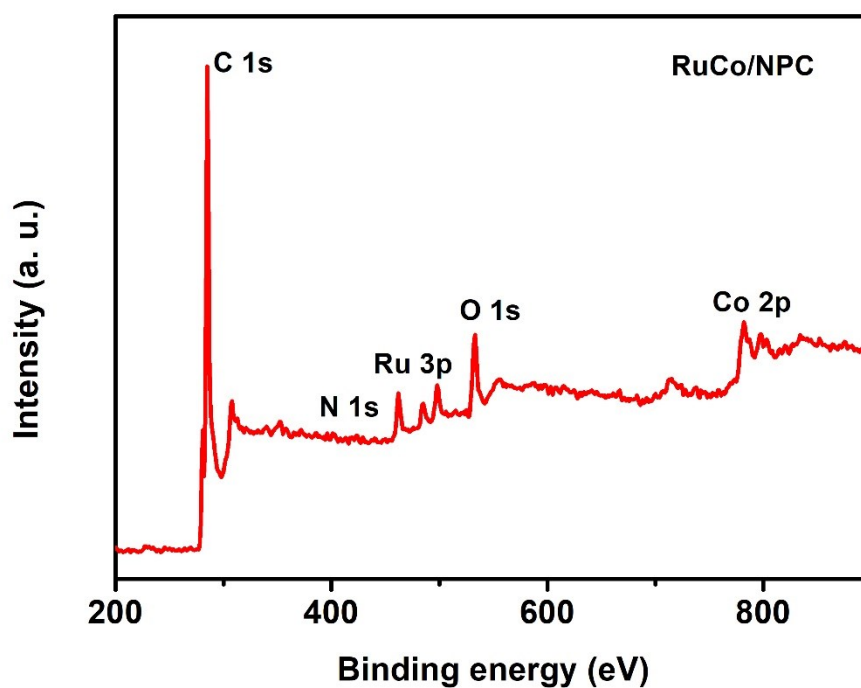


Figure S6. The XPS spectrum of RuCo/NPC.

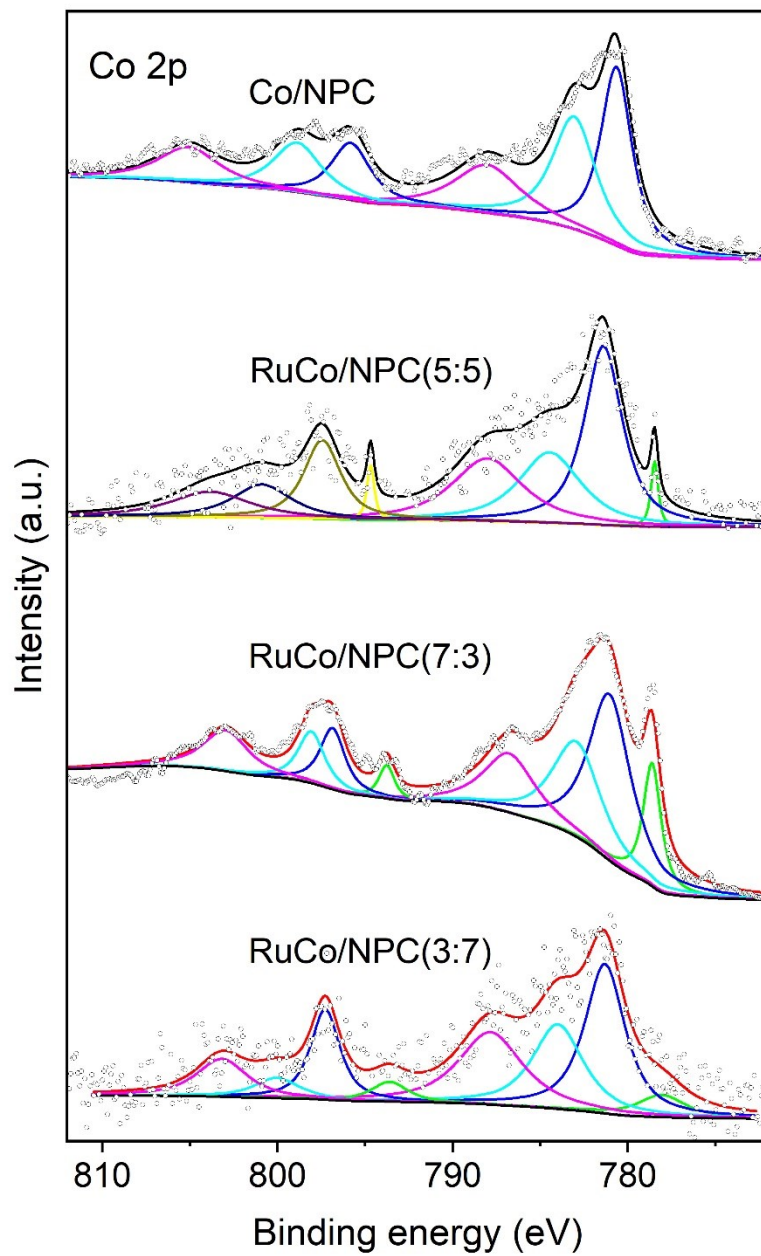


Figure S7. XPS spectra of Co 2p of different RuCo/NPC samples and Co/NPC.

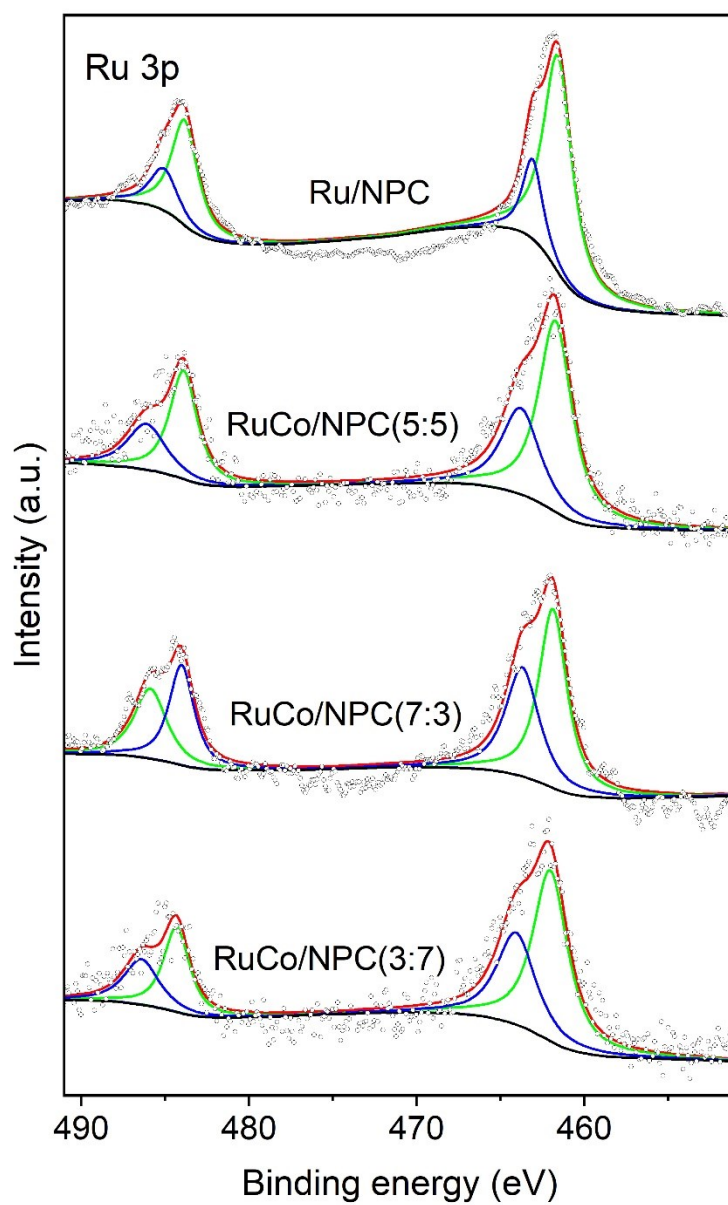


Figure S8. XPS spectra of Ru 3p of different RuCo/NPC samples and Co/NPC.

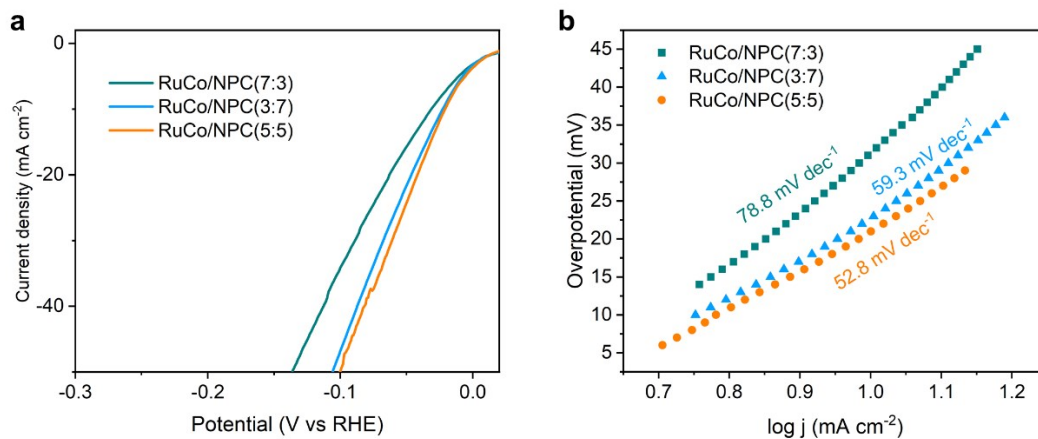


Figure S9. a) HER polarization curves of RuCo/NPC(3:7), RuCo/NPC(7:3) and RuCo/NPC(5:5). b) Corresponding Tafel plots for HER.

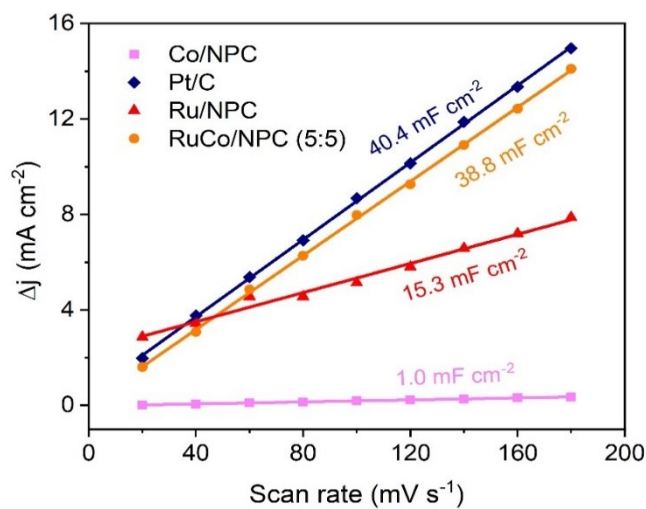


Figure S10. Double layer capacity of Ru/NPC, Co/NPC, Pt/C and RuCo/NPC calculated from CV with different scan rate.

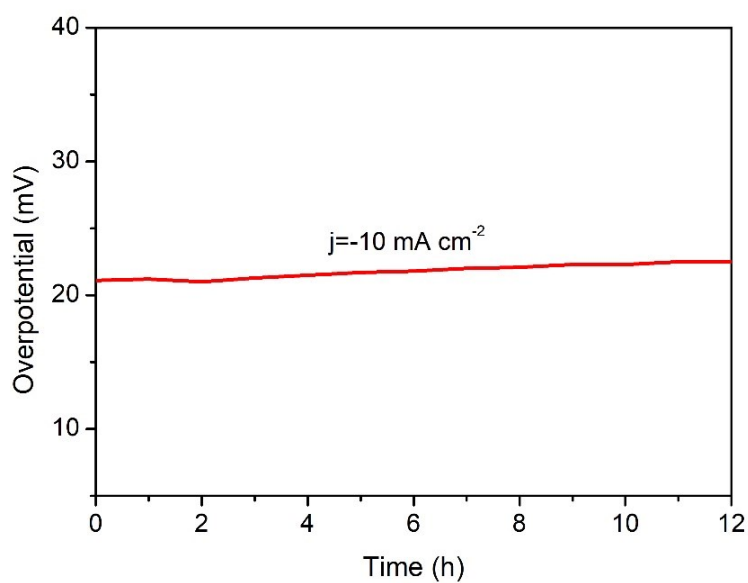


Figure S11. The HER stability of RuCo/NPC (5:5) at 10 mA cm^{-2} for 12 h.

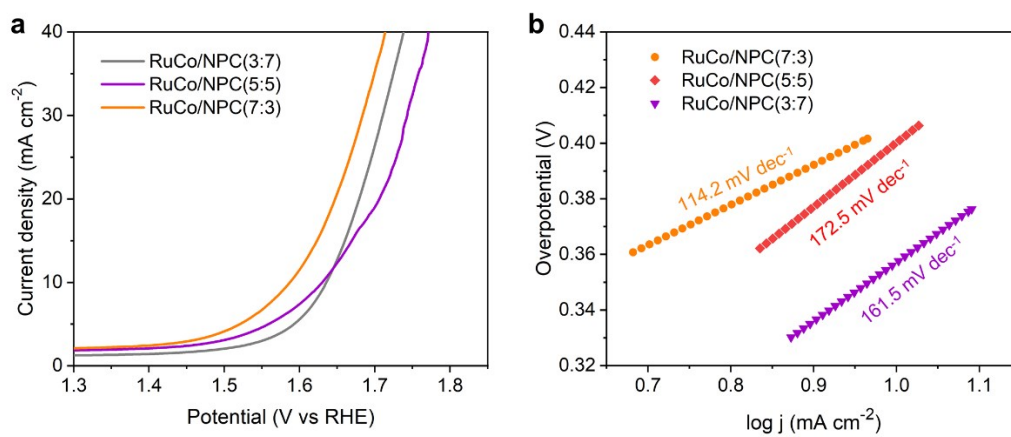


Figure S12. a) OER polarization curves of RuCo/NPC(3:7), RuCo/NPC(7:3) and RuCo/NPC(5:5). b) Corresponding Tafel plots for OER.

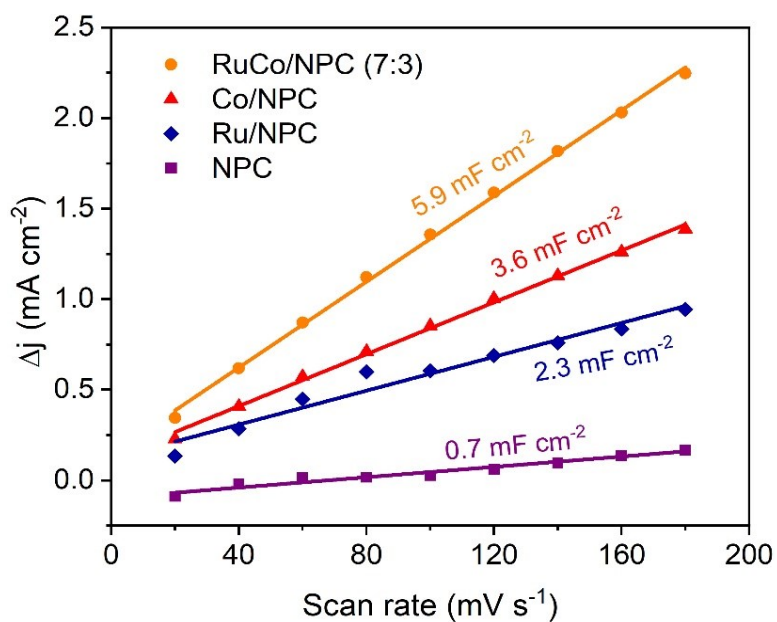


Figure S13. Double layer capacity of Co/NPC, Ru/NPC, NPC and RuCo/NPC (7:3) calculated from CV with different scan rate.

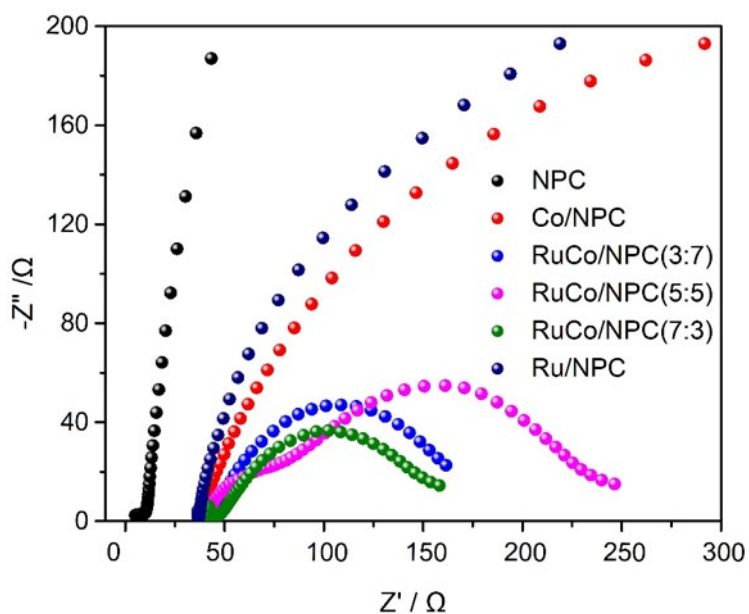


Figure S14. Nyquist plots of RuCo/NPC samples, Ru/NPC, Co/NPC and RuCo/NPC.

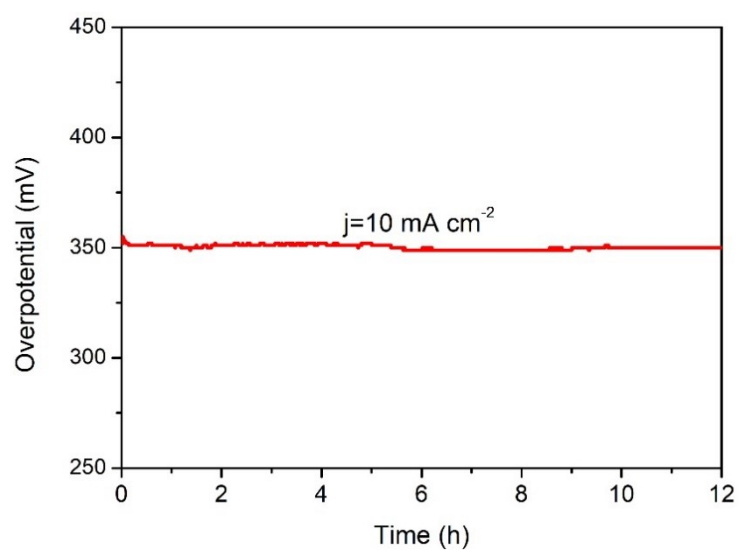


Figure S15. The OER stability of RuCo/NPC (7:3) at 10 mA cm^{-2} for 12 h.

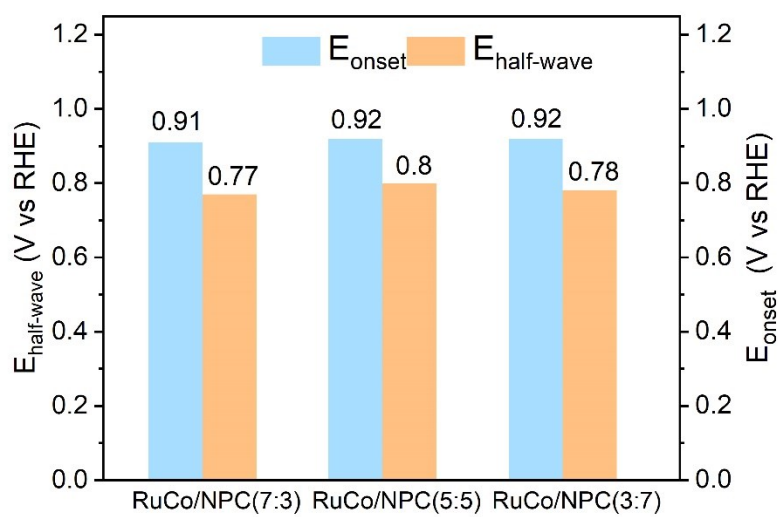


Figure S16. Onset potential and half-wave potential of RuCo/NPC (7:3) RuCo/NPC (3:7) and RuCo/NPC (5:5).

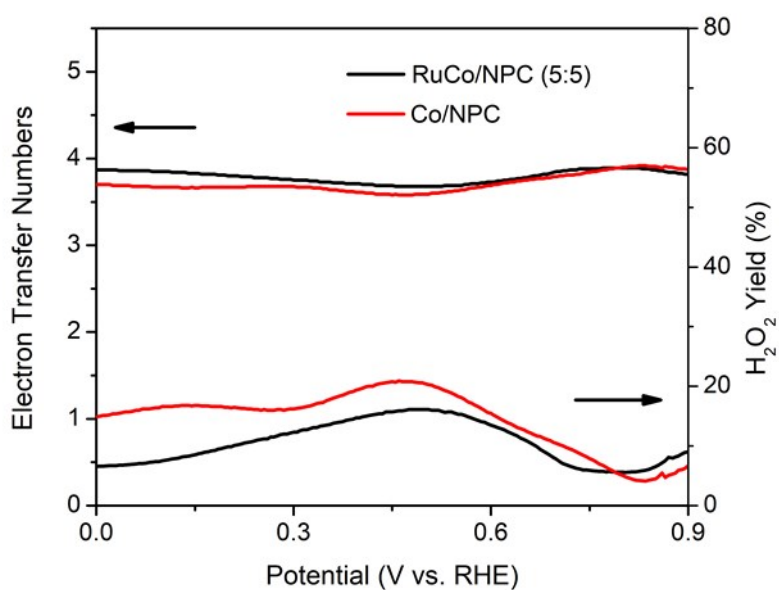


Figure S17. Number of electrons transferred and peroxide yields of Co/NPC and RuCo/NPC (5:5).

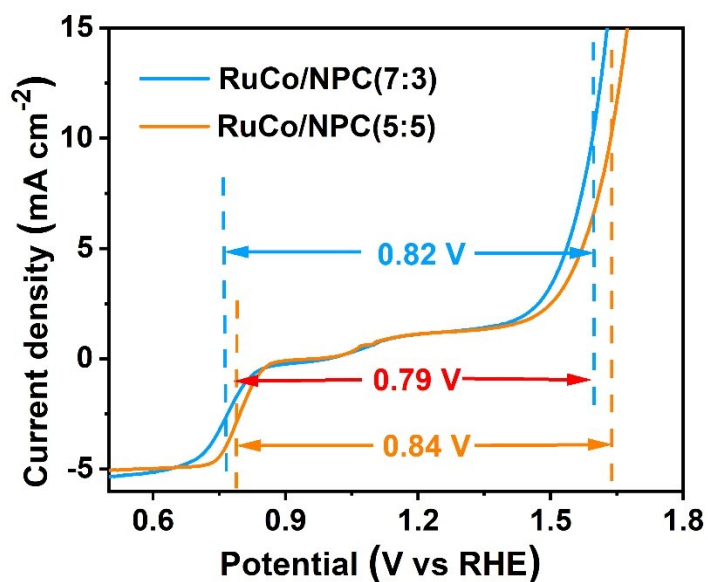


Figure S18. LSV curves of the RuCo/NPC (5:5) and RuCo/NPC (7:3) catalysts for the ORR and OER.

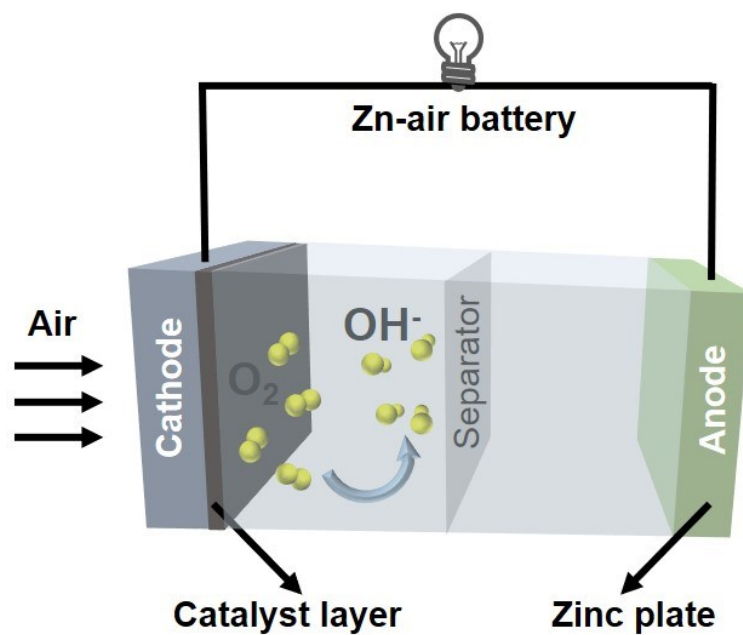


Figure S19. Schematic illustration of self-assembled zinc-air battery (ZAB).

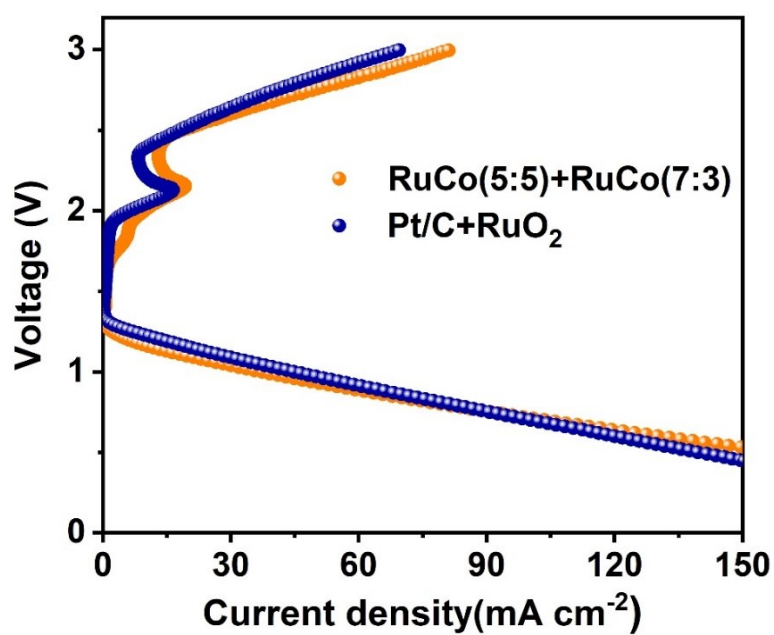


Figure S20. Charge and discharge polarization curves and corresponding power density of ZABs based on RuCo/NPC and Pt/C+RuO₂

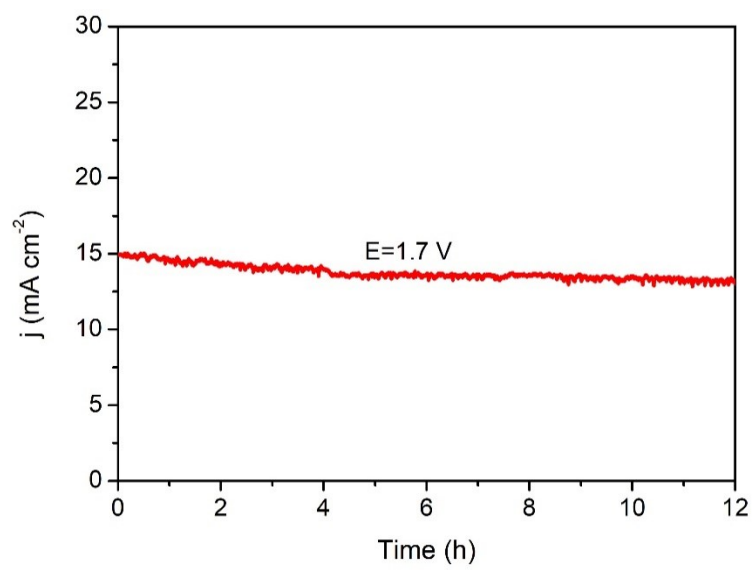


Figure S21. The water splitting durability of RuCo/NPC catalysts at 1.7 V for 12 h.