

Electronic Supplementary Information for
**Hierarchical Co₃O₄ Nanorods Anchored on Nitrogen Doped Reduced
Graphene Oxide: A Highly Efficient Bifunctional Electrocatalyst for
Rechargeable Zn-Air Batteries**

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Electrochemical Measurements

Electrochemical measurements were conducted on a Bio-Logic (VMP3) multichannel station. Before starting experiments, the electrolyte (0.1 M KOH) was saturated with pure oxygen or argon (control experiments) by bubbling the gas into the electrolyte for at least 30 min. In order to ensure electrolyte saturation, purging was continued above the solution during the measurements. CVs were recorded at a scan rate of 20 mV·s⁻¹ after 5 cycles over a potential range of 0.2 to -0.8 V vs. SCE. Potentials recorded were converted into the reversible hydrogen electrode (RHE) scale according to the following equation which stands in 0.1 M KOH:

$$E_{RHE} = E_{SCE} + 0.99 \text{ V in } 0.1 \text{ M KOH} \quad (1)$$

PtRuC 20% (FuelCellStore, USA) was employed as commercial bifunctional electrocatalysts for comparison.

Rotating Ring-Disk Electrode (RRDE) Measurements

Rotating Ring-Disk Electrode was prepared according to the already mentioned recipe, the catalyst ink (4 μ l) was drop-cast on the surface of a glassy carbon disk (Pt ring/GC disk electrode, ALS Co., Ltd) yielding a deposit of 4 mm in diameter. After drying in an oven at 70 °C for ~ 30 min, the disk electrode was scanned cathodically at a scan rate of 20 mV·s⁻¹ while a constant potential of 1.49 V vs. RHE was applied to the ring electrode. The number of electrons transferred and percentage of peroxide formation were calculated according to:

$$n = 4 \times \frac{I_D}{I_D + \frac{I_R}{N}} \quad (5)$$

$$\%HO_2^- = 200 \times \frac{\frac{I_R}{N}}{I_D + \frac{I_R}{N}} \quad (6)$$

where I_D is disk current, I_R is ring current, and N is the current collection efficiency ($N = -I_R/I_D$) of the Pt ring electrode. N was measured by scanning GC disk electrode from 1.44 to 0.99 V vs. RHE at 20 mV·s⁻¹ and applying a constant potential of 1.44 V to the ring electrode in an aqueous solution of 5 mM K₃Fe[CN]₆ and 0.1 M KCl.

Table S1. Structural-compositional comparison between Co₃O₄ NRs samples synthesized

Sample	Specific BET Surface Area (m ² ·g ⁻¹)	Ratio Co ³⁺ /Co ²⁺
Co ₃ O ₄ NRs 400°C	19.1	1.83
Co ₃ O ₄ NRs 500°C	16.2	3.81
Co ₃ O ₄ NRs 600°C	12.2	3.02

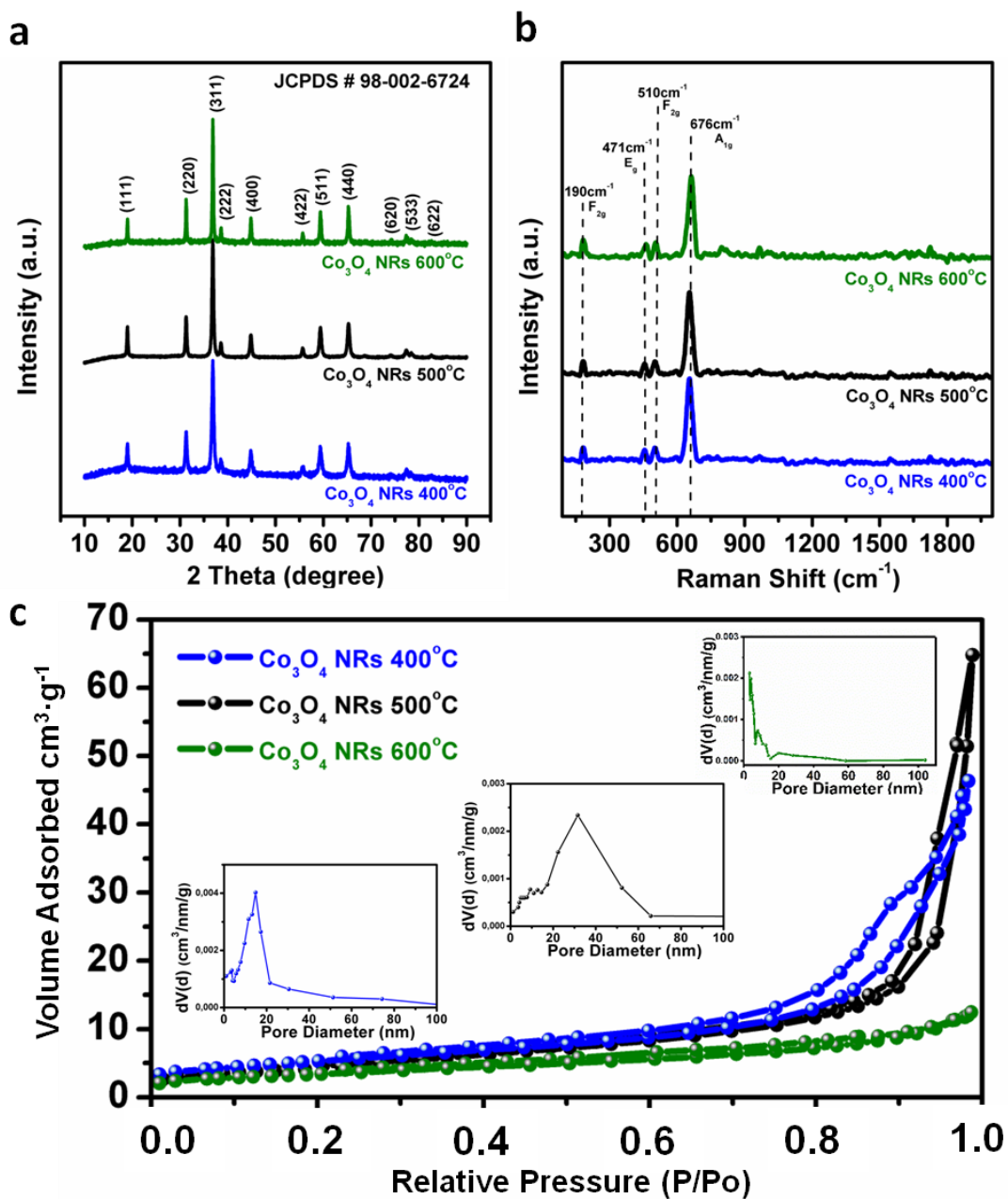


Figure S1. (a) X-ray diffraction patterns (b) Raman spectra, and (c) N_2 adsorption-desorption isotherms and BJH Pore size distribution of Co_3O_4 NRs heat treated at different temperatures.

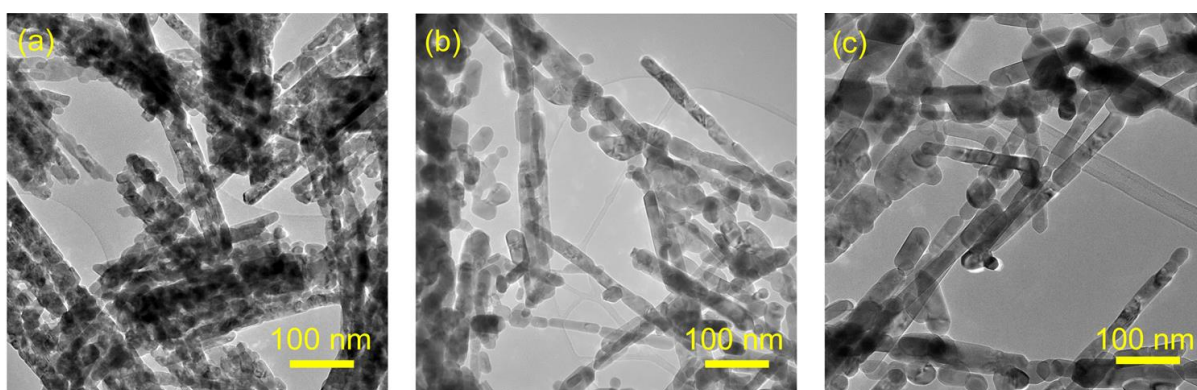


Figure S2. TEM images of Co_3O_4 NRs heat-treated at (a) 400 °C, (b) 500 °C and (c) 600 °C.

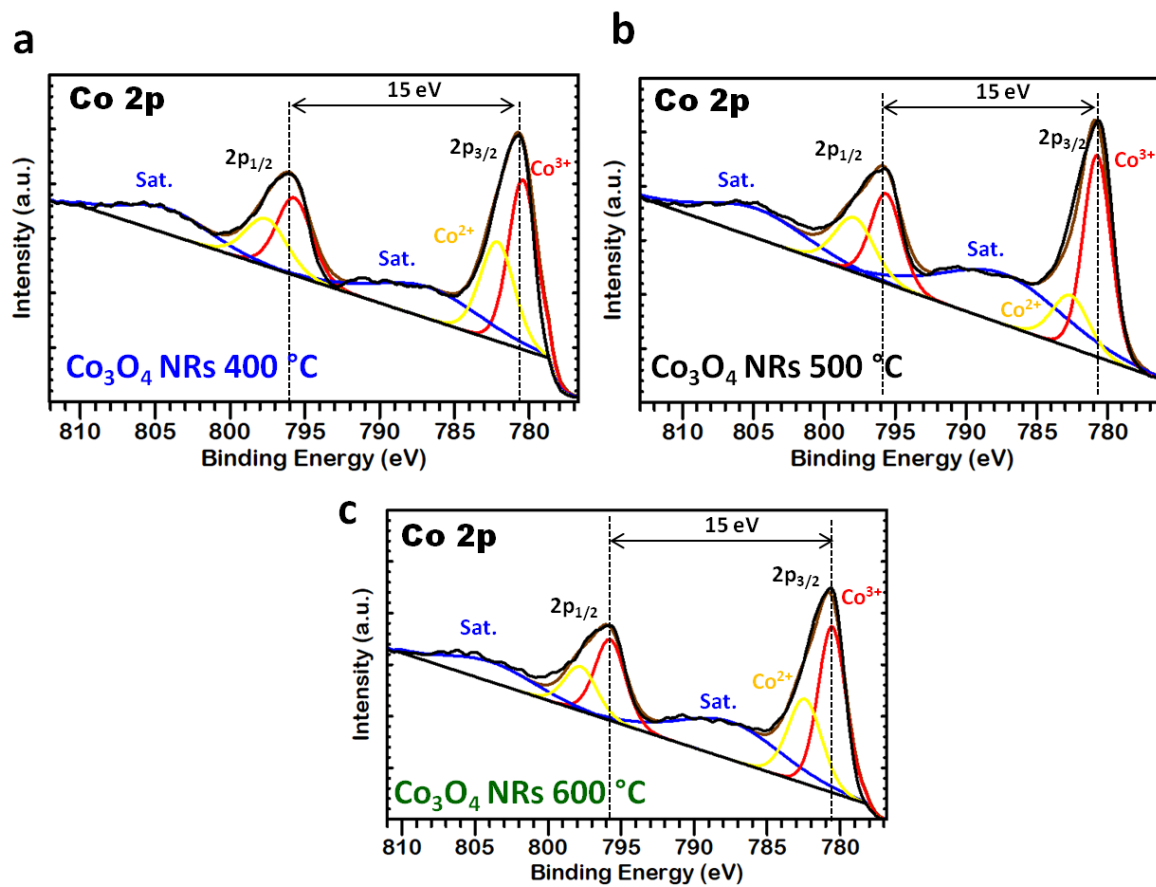


Figure S3. XPS profiles of Co_3O_4 NRs samples heat-treated at (a) 400 °C, (b) 500 °C and (c) 600 °C.

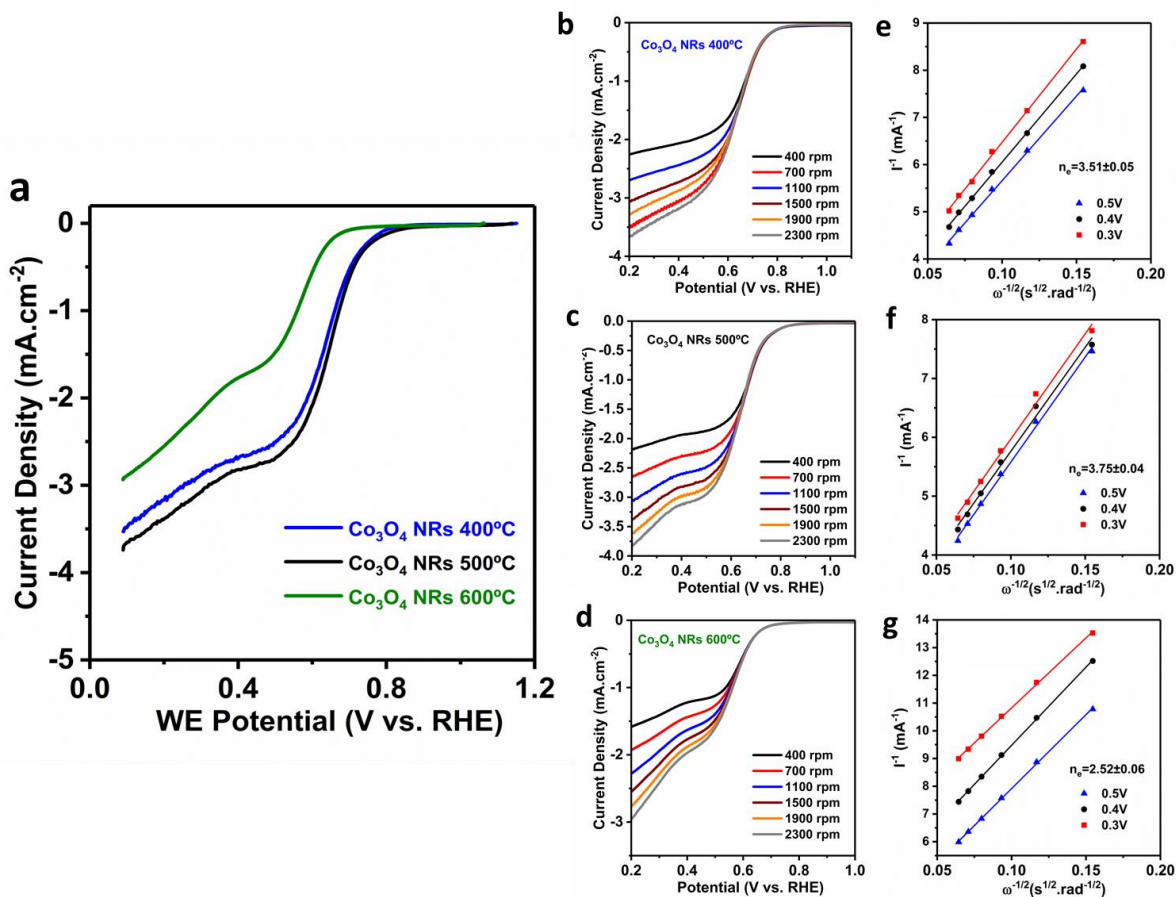


Figure S4. (a) Evaluation of ORR catalytic activity of Co_3O_4 NRs 400 °C, Co_3O_4 NRs 500 °C and Co_3O_4 NRs 600 °C mixed with Vulcan Carbon through LSV curves in O_2 -saturated 0.1 M KOH solution at a scan rate of $20 \text{ mV}\cdot\text{s}^{-1}$. (b-g) rotating disk LSV profiles of different catalysts in O_2 -saturated 0.1 M KOH solution at various rotation rates ranging from 400 to 2300 *r.p.m.* with a scan rate of $20 \text{ mV}\cdot\text{s}^{-1}$, and corresponding *Koutecky-Levich* plot at various potentials: (b,c) Co_3O_4 NRs 400 °C (d,e) Co_3O_4 NRs 500 °C and (f,g) Co_3O_4 NRs 600 °C.

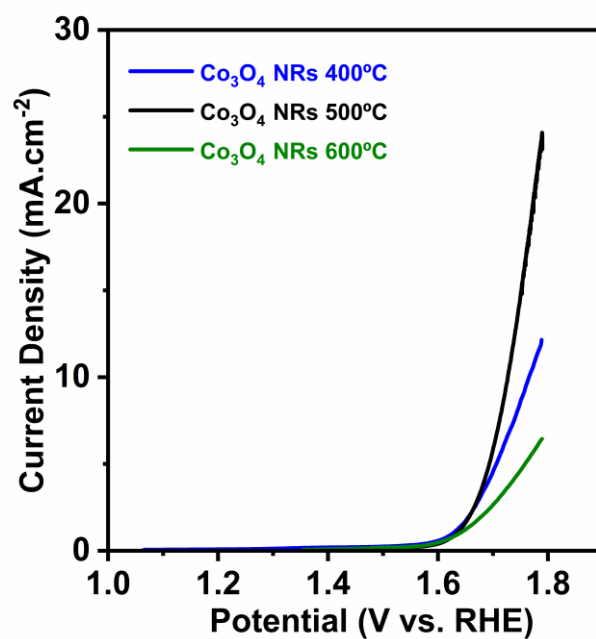


Figure S5. Evaluation of OER catalytic activity of Co₃O₄ NRs 400 °C, Co₃O₄ NRs 500 °C and Co₃O₄ NRs 600 °C mixed with Vulcan Carbon through LSV curves in Ar-saturated 0.1 M KOH solution at a scan rate of 20 mV·s⁻¹.

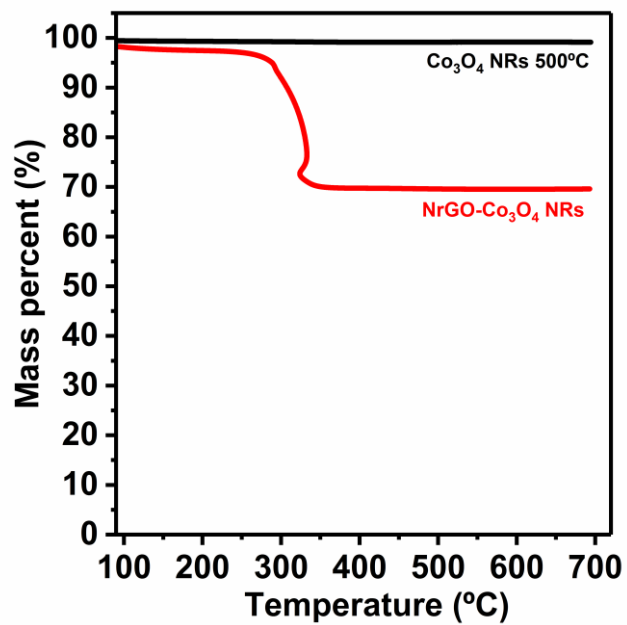


Figure S6. TGA profile of the pure Co_3O_4 NRs 500 °C and its hybrid with N-rGO from room temperature to 700 °C with a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ under air flow.

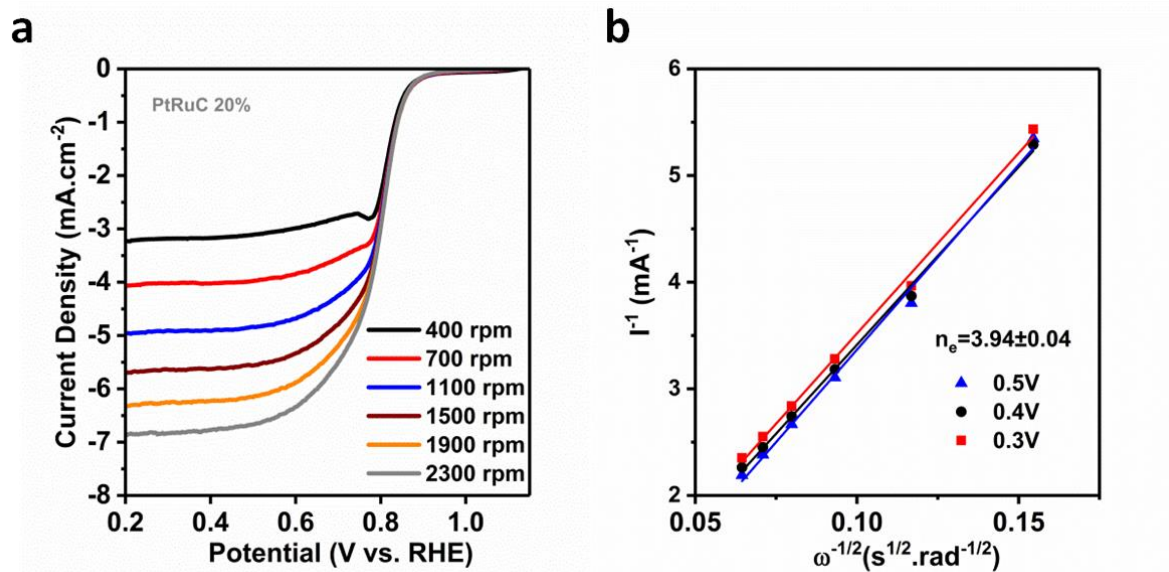


Figure S7. (a) LSV curves of PtRuC 20% at various rotation rates in O₂-saturated 0.1M KOH solution with a scan rate of 20 mV·s⁻¹ and (b) its corresponding Koutechy Levich plot at different potentials

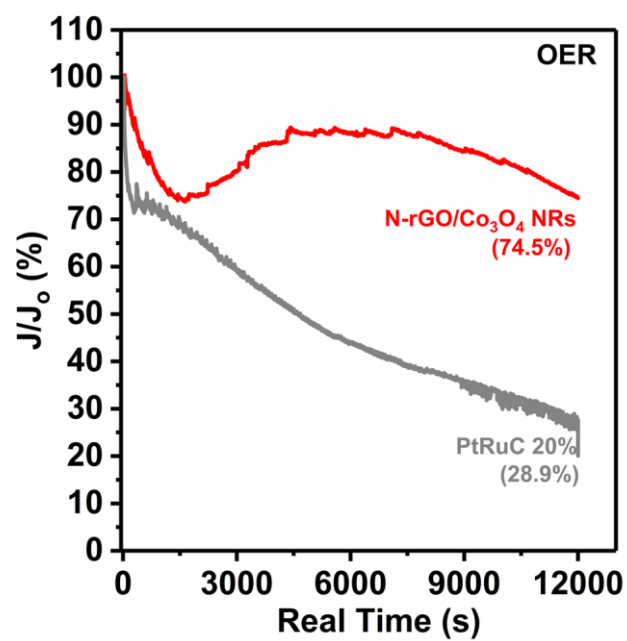


Figure S8. Durability of OER catalytic activity of N-rGO/Co₃O₄ NRs and PtRuC 20%.