

Electronic Supplementary Information

Citrus Sap Stabilised: Regulated Cobalt Ferricyanide Efficiently Enhanced Electrocatalytic Activity and Durability for Oxygen Evolution

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S-I: Experimental Section

Physical characterization of a electrocatalyst

The crystal phase of the as-prepared was determined by POWER-XRD EQUINOX-1000. The elemental composition of RCoFe was analyzed by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer), XPS (X-ray photoelectron spectroscopy) with a K-Alpha-KAN9954133 spectrometer (micro-focused monochromator with variable spot size). The morphology of RCoFe was determined by using a JEOL-JSM-IT 200 scanning electron microscope (SEM) operated at 20 kV. HR-TEM JOEL, JAPAN was used to record transmission electron microscope (TEM) images of the nanomaterials and selected area electron diffraction (SAED) pattern.

Electrode fabrication and electrochemical performance tests

Before modification, the glassy carbon electrode (GCE) was polished by 500 nm and 50 nm aluminum oxide (Al_2O_3) powders to reach a mirror-like luster and then successively washed by doubly distilled water and ethanol three times, respectively. The Nickel Foam electrode was washed with 1 M HCl, rinsed with water and acetone, then dried in order to remove the oxide layer from the nickel surface. To prepare the working electrodes, 5.0 mg of the as-prepared RCoFe electrocatalyst (0.21 mg cm^{-2}) was evenly dispersed in 0.5 mL of propanol, and then the as-obtained solution was treated with ultrasound for 20 min. For comparison, a 0.005 mg/ml commercial IrO_2 suspension was made using a comparable methodology. Before measuring, the slurry was deposited on a pre-cleaned working electrode and allowed to dry at room temperature. Lastly, the as-acquired ink (5 μL) was dropped on the polished GCE owning a diameter of 3 mm. The loading amount of the electrocatalyst was about 0.5 mg cm^{-2} . All the potentials in this work have been calibrated to the reversible hydrogen electrode (RHE), $E_{(\text{RHE})} = E_{(\text{Hg}/\text{HgO})} + 0.923 \text{ V}$.

Electrochemical tests of the as-prepared RCoFe based working electrodes Electrochemical tests of LSV (linear sweep voltammetry), CV (cyclic voltammogram) and EIS (electrochemical impedance spectroscopy) were conducted out with a typical three-electrode system using platinum wire electrode as counter electrode, the as-prepared electrocatalysts based as working electrode referred to Ag/AgCl (3 M KCl) electrode by electrochemical workstation (Biologic SP- 200) in 1.0 M KOH electrolyte. Tafel slopes were calculated according to the Tafel equation of $\eta = a + b \log J$, where η is the overpotential (V, vs. RHE), b the Tafel slope, and j the corresponding current density (mA/cm^2) as well as the Tafel constant. The resistances of RCoFe electrocatalysts were acquired from EIS tests at the overpotential of different mV (vs. RHE) in the frequency scope of 100 kHz to 10 mHz. The durability of RCoFe was tested by cyclic voltammetry (CV) and current-time (i-t) curve tests.

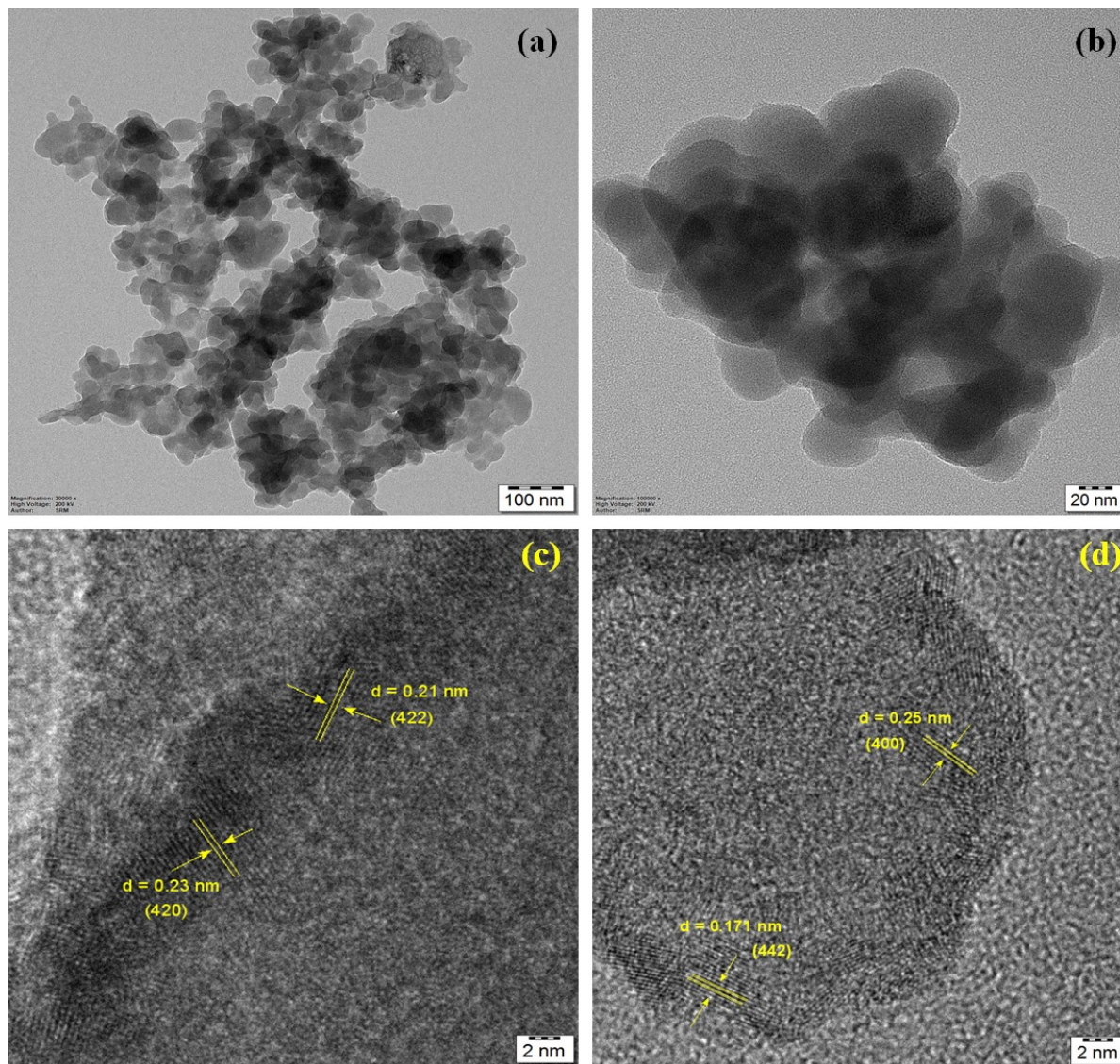
S-II: Figures**Figure S1. (a, b) HR-TEM images in different magnification; (c,d) lattice fringes**

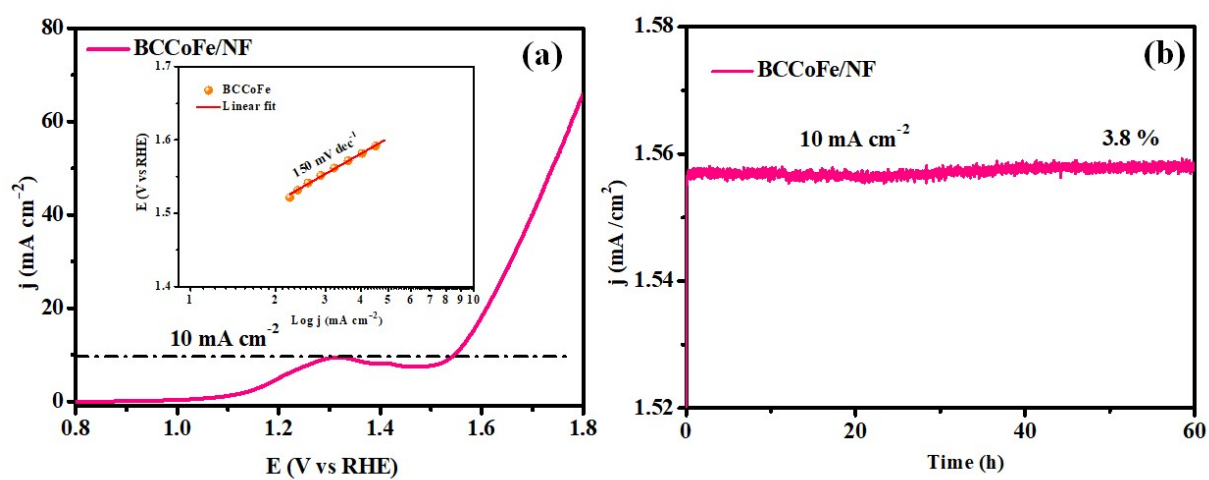
Figure S2.: (a) LSV of BCoFe, inset: Tafel ; (b) Stability of BCoFe

Figure S3. FE-SEM image of post-RCoFe

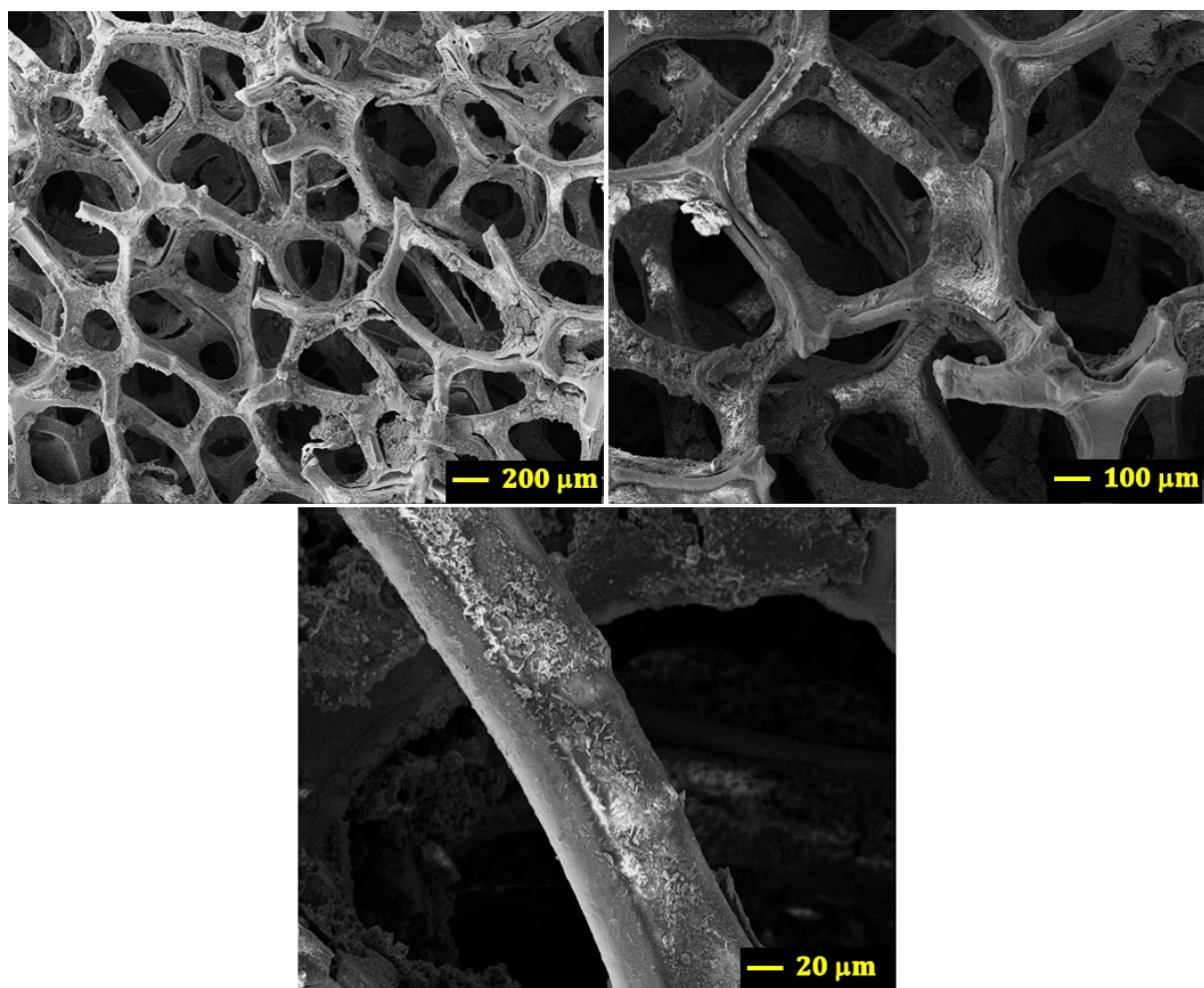


Figure S4. Multiple chemical states of Cobalt in RCoFe

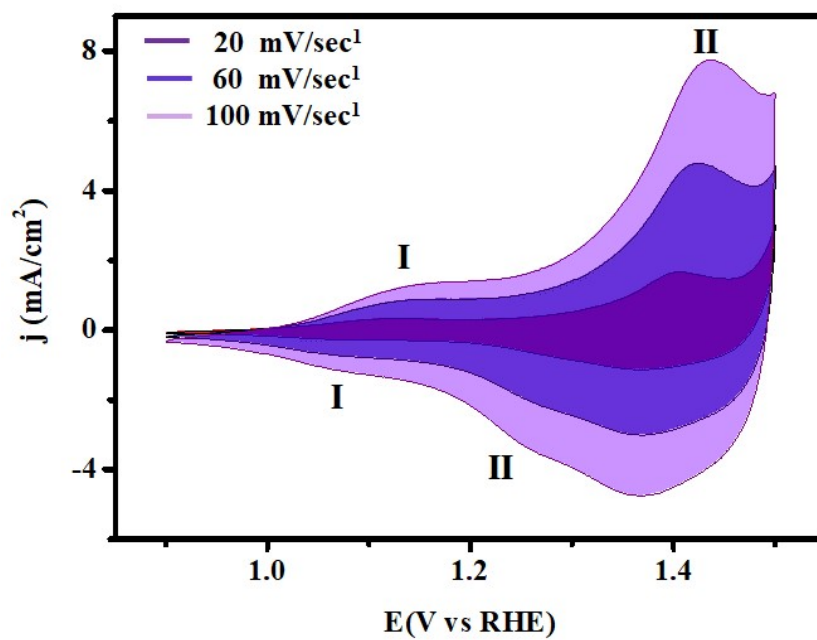
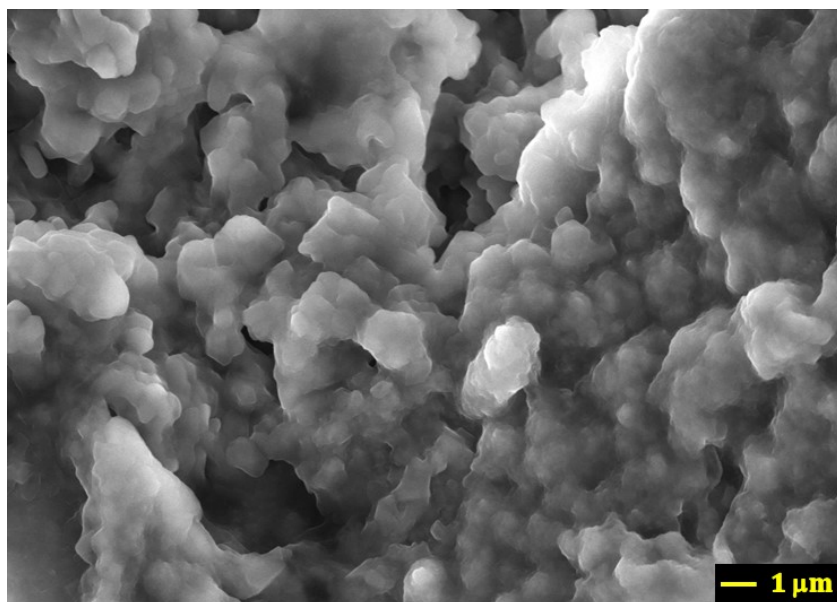


Figure S5. FESEM: After stability of RCoFe



SI-III: Calculations and Tables

SI:C1. Scherrer equation

$$D_{hkl} = 0.9 \lambda / (\beta_{hkl} \cos \theta)$$

where D_{hkl} - crystallite size, λ - X-ray wavelength (Cu, $K\alpha_1$), θ - diffraction angle, and β_{hkl} - full width at half maximum of the diffraction peak.

SI:C2. Tafel equation

$$\eta = a + b \log J,$$

where η is the overpotential (V, vs. RHE), b the Tafel slope, and j the corresponding current density (mA /cm²) as well as the Tafel constant

SI:C3. Turn Over Frequency

$$\text{TOF} = \frac{JxA}{4xnxn},$$

where, J - Current density, A - Area, F - Faraday Constant (96485.3 C mol⁻¹) and n - The number of moles in catalyst.

Using the equation, the turnover frequency is calculated the rate of evolved O₂ molecule per surface active site per second. The TOF can be calculated with an overpotential of 1.6 V vs. RHE.

SI:C4. Calculation of hydrogen generation

Based on the displaced amount of water due to the hydrogen bubbles the amount of hydrogen generated was calculated using the below relationships.

$$\text{Amount of hydrogen generated in 1 h} = \text{amount of water displaced in litres} \quad (1)$$

$$\text{Amount of hydrogen generated in moles for 1 h} = \frac{\text{Amount of water displaced (litres)}}{22.4 \text{ litres}} \quad (2)$$

We also calculated the hydrogen generation rate from the electrical charge passed through the electrode using the equation given below.

$$\left(\text{Current obtained during} \right) \times \left(\text{Time duration for} \right) = \text{Coulomb} \quad (3)$$

water electrolysis each potential

$$\frac{\text{Coulomb} \times F}{96485 \text{ C}} = \text{No. of moles of } e^- \text{ for H}_2 \text{ generation} \quad (4)$$

$$\frac{\text{No. of moles of electron for H}_2 \text{ generation} \times 1 \text{ mole of H}_2 \text{ gas}}{2 \text{ moles of electron}} = \text{Moles of Hydrogen generated} \quad (5)$$

Table S1. Comparison of OER activities over some Co–Fe-based OER catalysts previous reported in the selected studies.

S. No	Electrocatalyst	Substrate	η @ 10 mA/cm ² (mV)	References
1	RCoFe	GC/NF	270/252	This study
2	Co _{0.54} Fe _{0.46} (OOH)	Au/Ti	-	[1]
3	Co-PBA	NF	334	[2]
4	CoFe ₂ O ₄ NPsc	Carbon paper	378	[3]
5	CoFe ₂ O ₄	NF	314	[4]
6	CoFe ₂ O ₄ @NF	NF	308	[5]
7	FeCo Oxide	NF	310	[6]
8	CoFe ₂ O ₄ /PANICNTs	GC	314	[7]
9	CoFe ₃₅ LDH	GC	351	[8]
10	CoFe ₂ O ₄	GC	570	[9]
11	Co-Fe-O/rGO	GC	340	[10]

SI-IV: Reference

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