Electronic Supplementary Information

Efficient oxygen reduction by synergistic effect of nano-sized delafossite ($CuFeO_2$) and multi-walled CNT

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Table S1 The raw materials, combination and sign of products.

m(CNT)/g	m($CuFeO_2$)/g	CNT% / wt%	sample
		0	$CuFeO_2$
0.168	1.514	10	$CuFeO_2$/CNT-10
0.505	1.514	25	$CuFeO_2$/CNT-25
1.514	1.514	50	$CuFeO_2$/CNT-50
4.542	1.514	75	$CuFeO_2$/CNT-75
13.626	1.514	90	$CuFeO_2$/CNT-90
		100	CNT

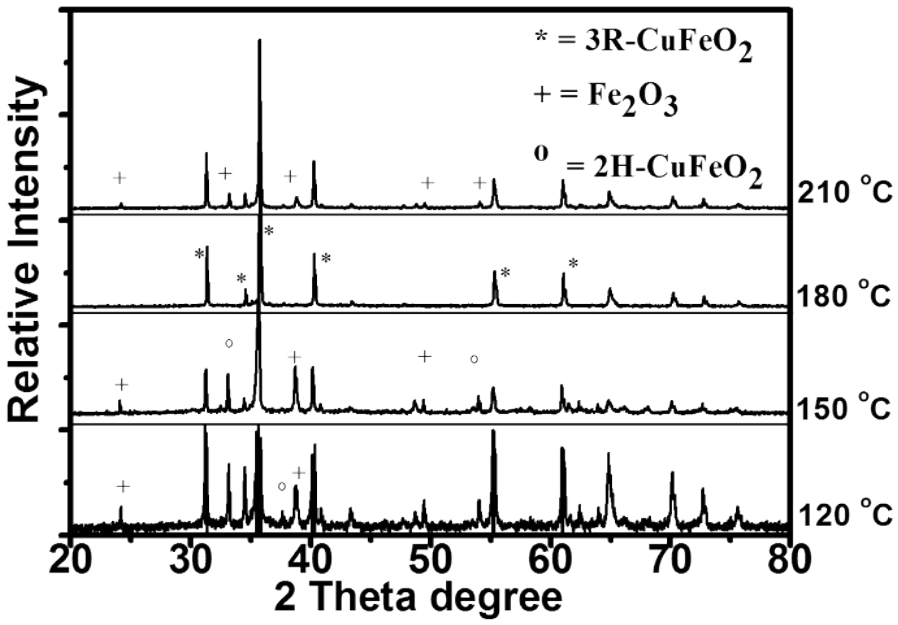


Figure S1 XRD patterns for Cu/Fe-containing samples obtained by heating mixture with $Fe(NO_3)_3 \cdot 9H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ 48 hours at 120 °C, 150 °C, 180 °C and 210 °C, respectively.

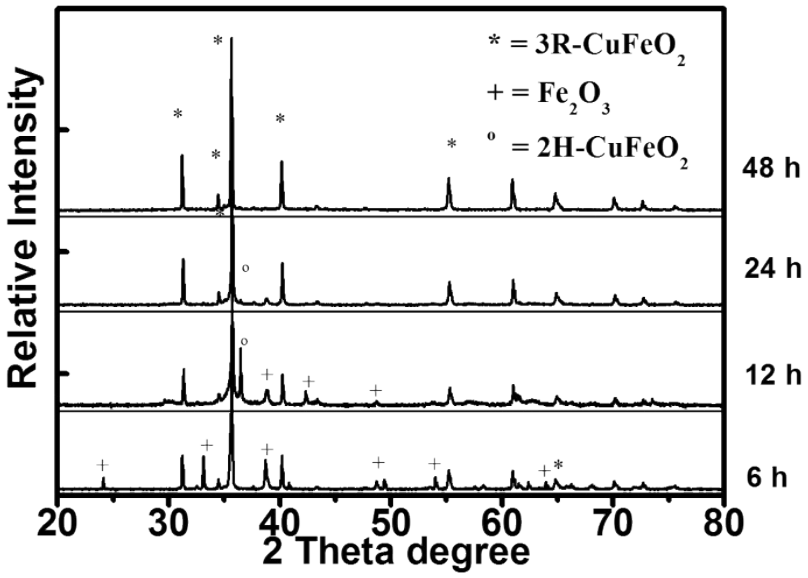


Figure S2 XRD patterns for Cu/Fe-containing samples obtained by heating mixture with $Fe(NO_3)_3 \cdot 9H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ at 180 ^oC during different time (6 hours, 12 hours, 24 hours and 48 hours).

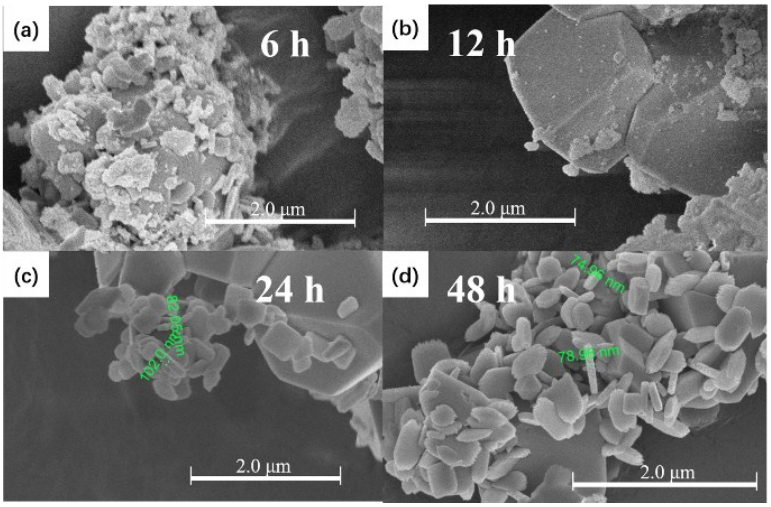


Figure S3 SEM images of $CuFeO_2$ at 180 ^oC during different time (a) 6 hours, (b) 12 hours, (c) 24 hours and (d) 48 hours.

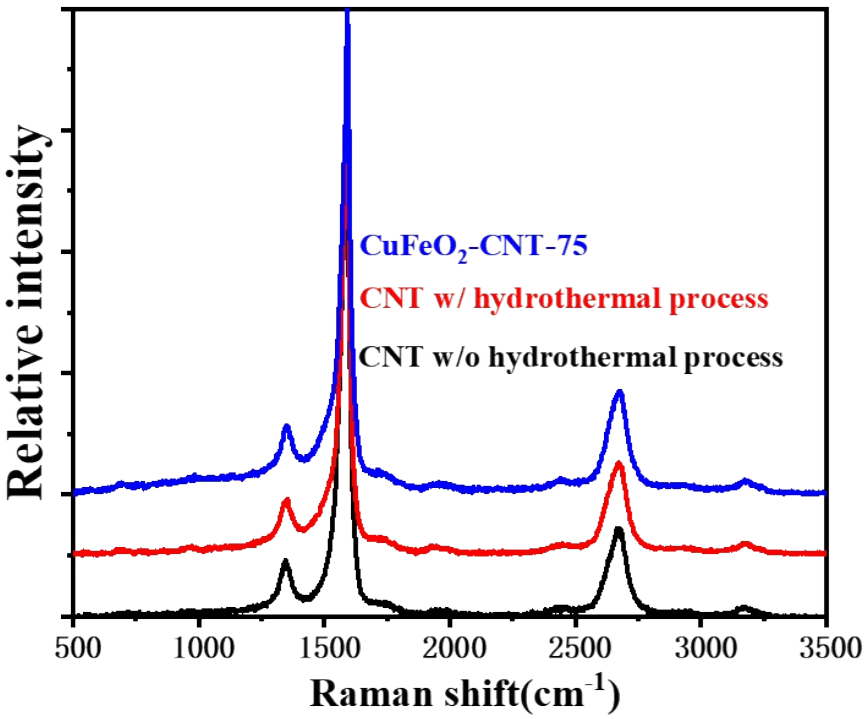


Figure S4 Raman spectroscopic at 532-nm excitation of $CuFeO_2$-CNT-75, solo CNTs with and without hydrothermal process (180 ^oC, 48 hours).

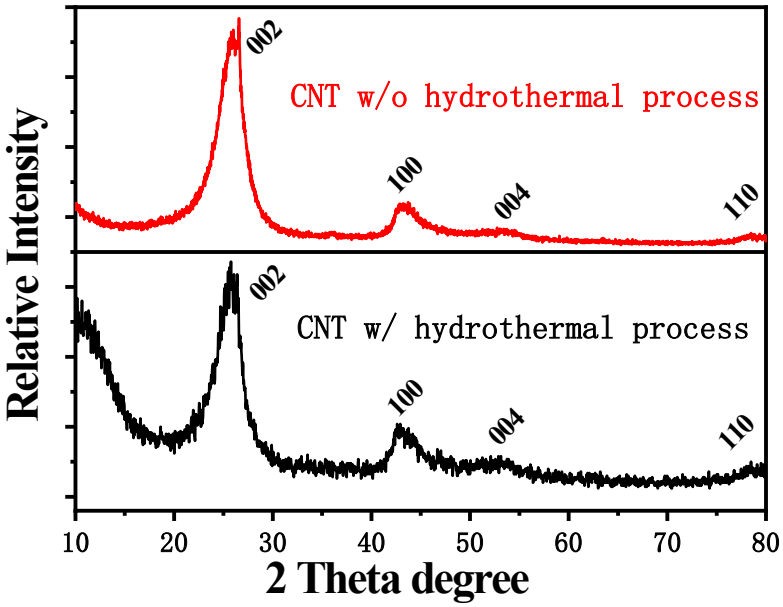


Figure S5 XRD patterns of solo CNTs with and without hydrothermal process (180 °C, 48 hours).

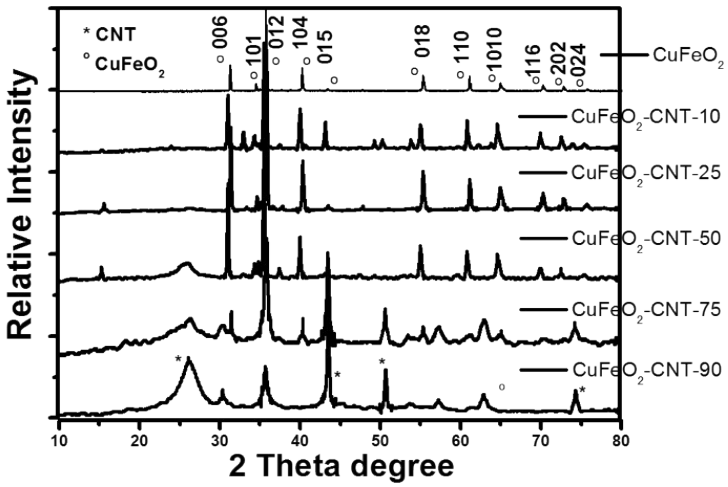


Figure S6 XRD patterns of $CuFeO_2$, $CuFeO_2$-CNT-25, $CuFeO_2$-CNT-50, $CuFeO_2$-CNT-75, $CuFeO_2$-CNT-90 and alone CNT, respectively.

Table S2 Weight ratios of elements C, O, Cu, Fe in the samples. (Among them, elements C, O are measured by EAS, elements Cu, Fe are measured by ICP.)

Elements / Samples	C	O	Cu	Fe
$CuFeO_2$-CNT-75	62.92 wt%	7.01 wt%	8.850 wt%	9.702 wt%
$CuFeO_2$-CNT-75-Physical Mixture	69.43 wt%	7.27 wt%	9.123 wt%	8.639 wt%

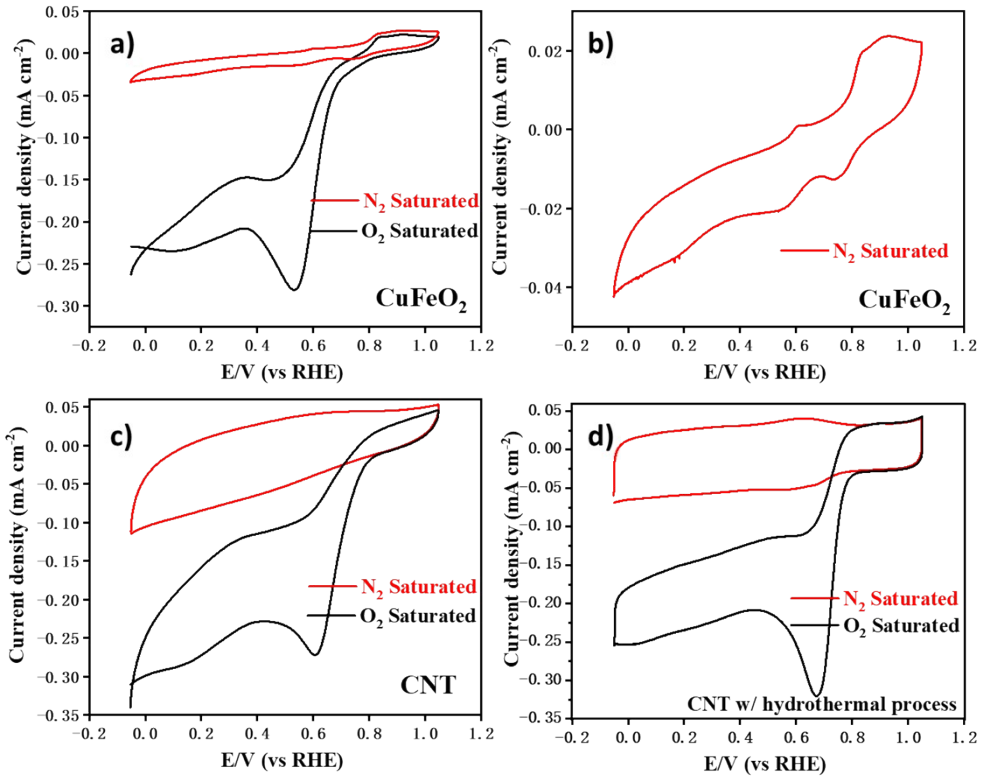


Figure S7 CVs with N_2 or O_2 saturated 0.1 M KOH solution on (a,b) $CuFeO_2$, (c) CNT and (d) CNT with hydrothermal process.

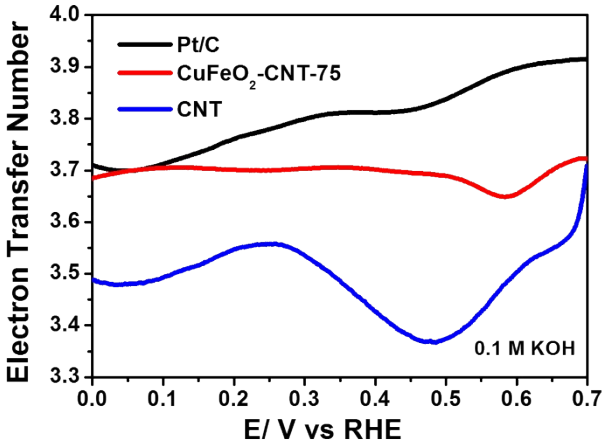
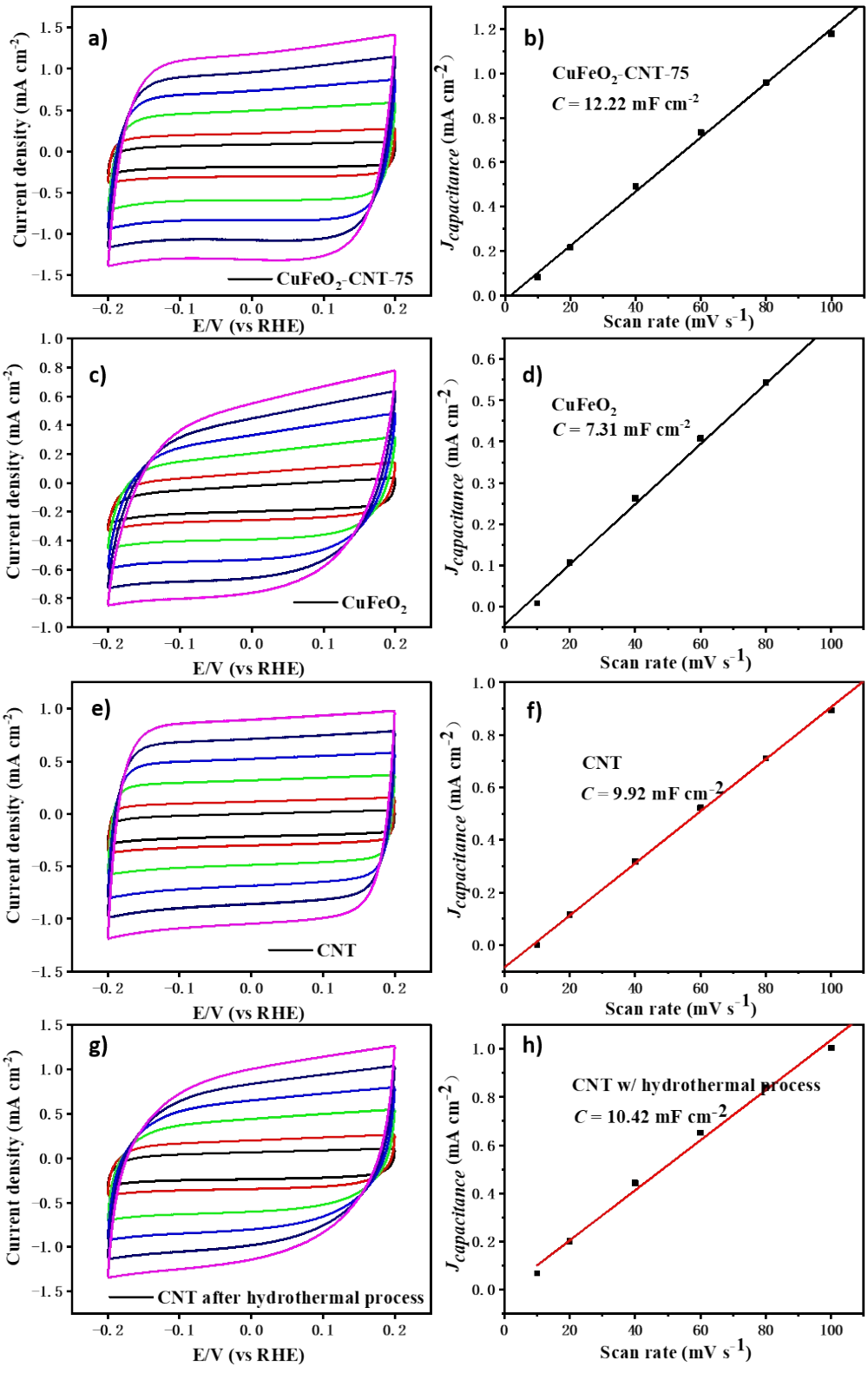


Figure S8 The electron transfer number (n) measured by rotating ring-disk electrode (RRDE) test of $CuFeO_2$-CNT-75, Pt/C and bare CNT. All measurements were conducted on glassy carbon electrodes at 1600 rpm in O_2-saturated electrolytes with a sweep rate of 10 mV s^{-1}. The electron transfer number (n) was determined by the followed equation:

$$n = 4 \times \frac{I_d}{I_d + I_r/N}$$

where I_d is disk current, I_r is ring current and N is current collection efficiency (N) of the Pt ring.[S1] N was determined to be 0.53 from the reduction of $K_3Fe[CN]_6$.


a)
Current density (mA cm-2)
E/V (vs RHE)
CuFeO2-CNT-75
b)
CuFeO2-CNT-75
C = 12.22 mF cm-2
Jcapacitance (mA cm-2)
Scan rate (mV s-1)
c)
Current density (mA cm-2)
E/V (vs RHE)
CuFeO2
d)
CuFeO2
C = 7.31 mF cm-2
Jcapacitance (mA cm-2)
Scan rate (mV s-1)
e)
Current density (mA cm-2)
E/V (vs RHE)
CNT
f)
CNT
C = 9.92 mF cm-2
Jcapacitance (mA cm-2)
Scan rate (mV s-1)
g)
Current density (mA cm-2)
E/V (vs RHE)
CNT after hydrothermal process
h)
CNT w/ hydrothermal process
C = 10.42 mF cm-2
Jcapacitance (mA cm-2)
Scan rate (mV s-1)

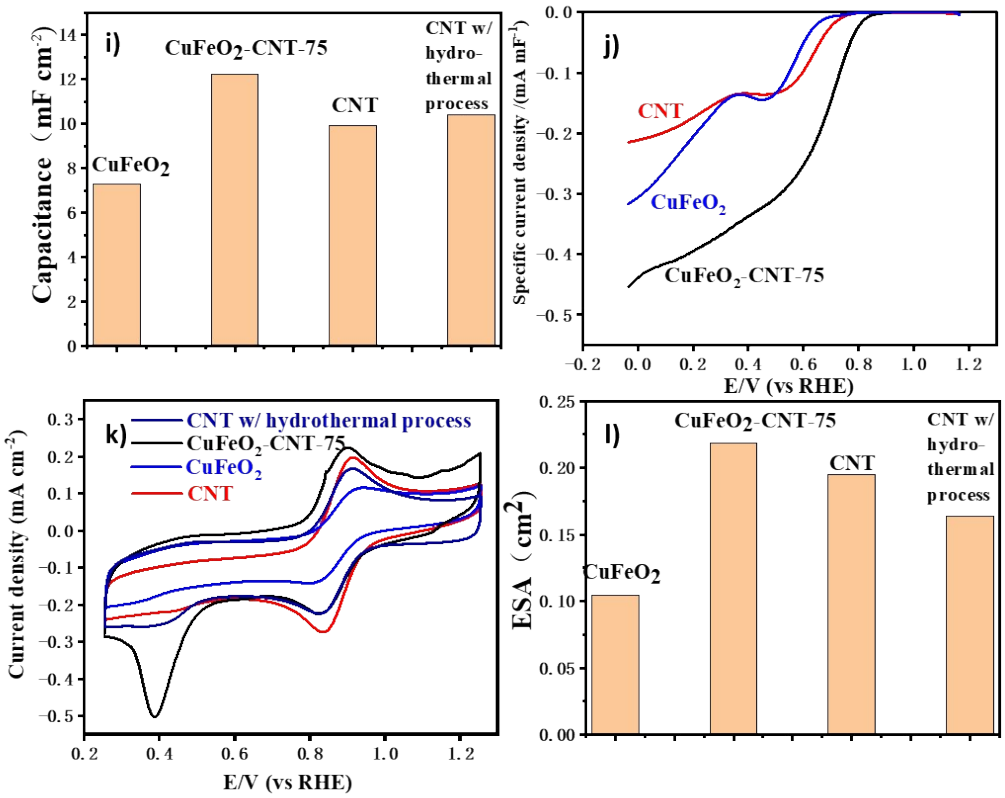


Figure S9 CVs taken over a range of scan rates (10, 20, 40, 60, 80 and 100 $mV \cdot s^{-1}$) with N_2 saturated 0.1 M KOH solution for determination of double-layer capacitance for a (a) $CuFeO_2$-CNT-75, (c) $CuFeO_2$, (e) CNT, (g) CNT with hydrothermal process electrode; (b, d, f, h) Current due to double-layer charging plotted against cyclic voltammetry scan rate; (i) ESA of $CuFeO_2$-CNT-75, $CuFeO_2$, CNT, CNT with hydrothermal process by a double layer capacitance measurement ; (j) RDE polarization curves of $CuFeO_2$-CNT-75, $CuFeO_2$ and CNT with normalized current density; (k) CVs of various electrodes in 5 mM $K_3Fe(CN)_6$/0.1 M KCl solution. [S2] Scan rate: 5 $mV \cdot s^{-1}$; (l) ESA of various electrodes tested by $K_3Fe(CN)_6$ method.

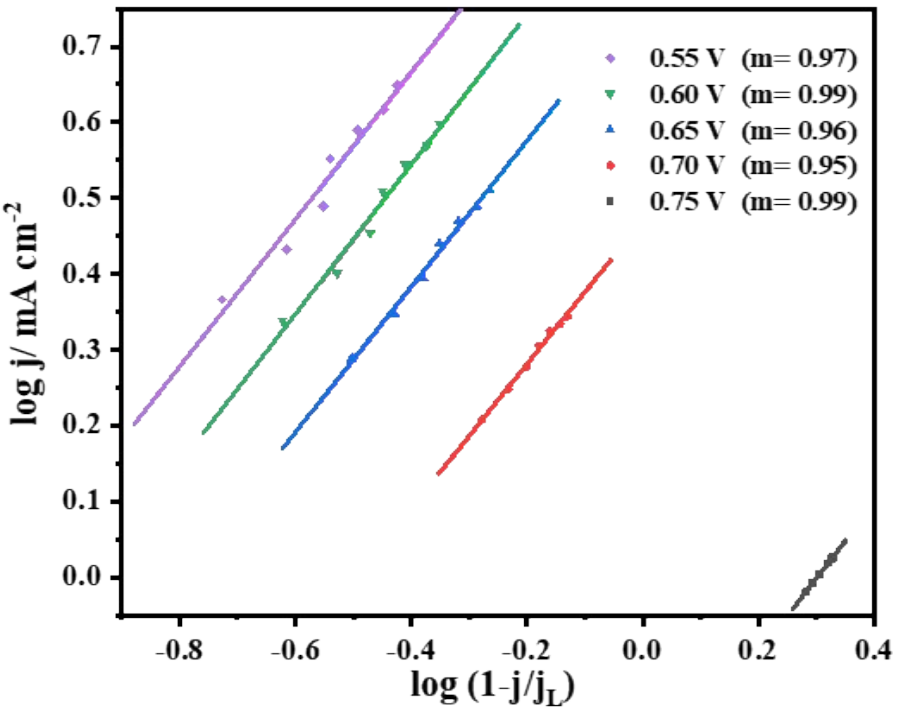


Figure S10 Reaction order plots for ORR on $CuFeO_2$-CNT-75 catalyst at various electrode potentials deduced from the RDE data (Fig. 5a in article).

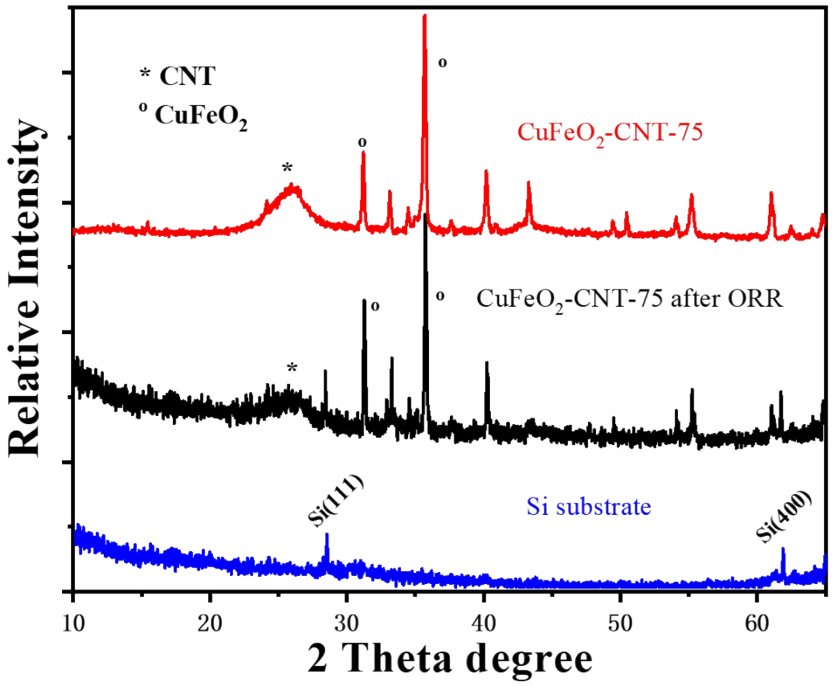


Figure S11 XRD patterns of (a) $CuFeO_2$-CNT-75 (powder) before ORR, (b) $CuFeO_2$-CNT-75 after ORR and (c) bare Si substrate. For XRD test, the $CuFeO_2$-CNT-75 electrode after ORR was washed with distilled water and alcohol solution for three times, transferred on Si substrate and subsequently dried in air. (the peak at 62°: Si (400) under Cu Kβ radiation)

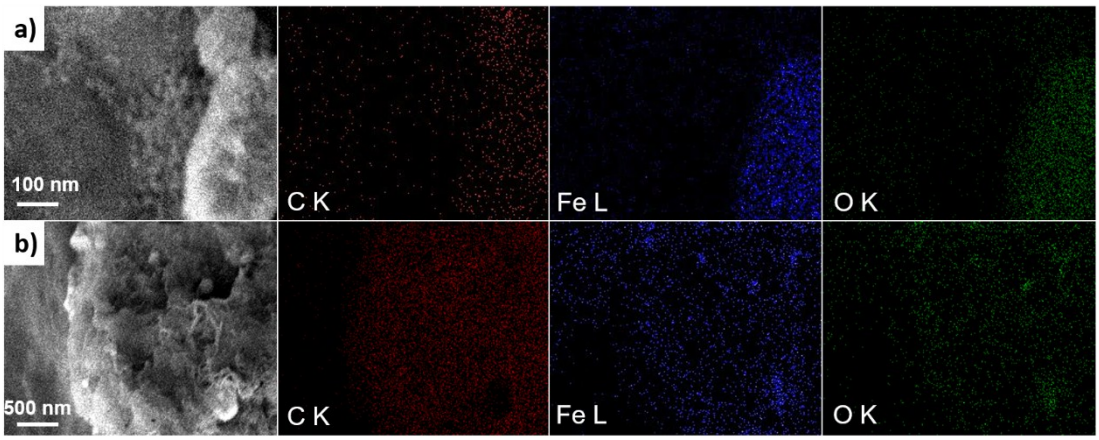


Figure S12 Elemental mappings of $CuFeO_2$-CNT-75 (a) before and (b) after ORR by SEM/EDS.

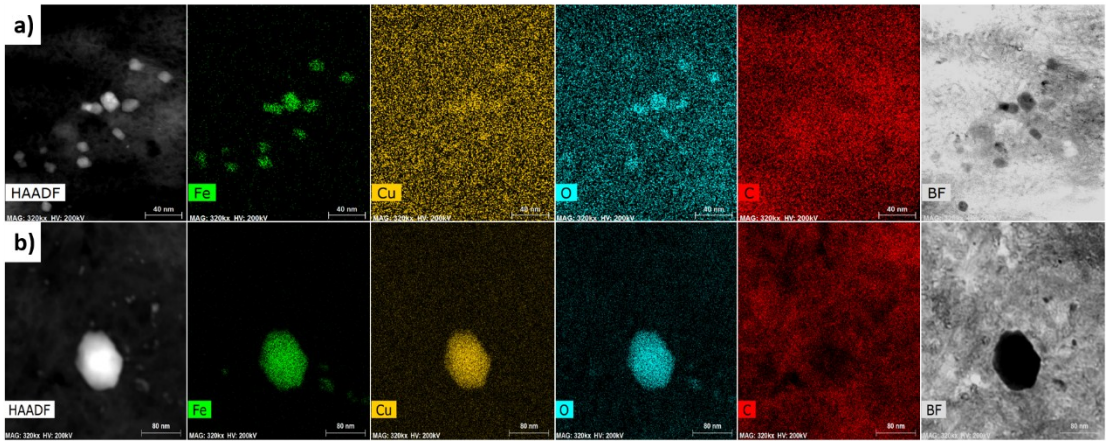


Figure S13 Elemental mappings of $CuFeO_2$-CNT-75 (a) before and (b) after ORR by TEM/EDS.

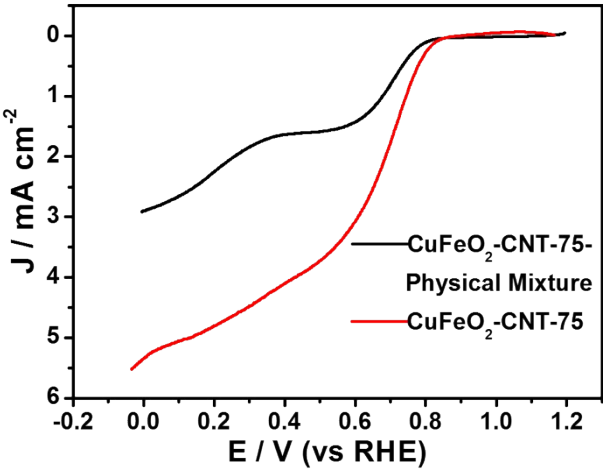


Figure S14 RDE polarization curves of $CuFeO_2$-CNT-75 and physical mixture containing CNT (75 wt%) and $CuFeO_2$ (25 wt%).

Reference

S1 R. Zhou, Y. Zheng, M. Jaroniec and S.-Z. Qiao, *ACS Catalysis*, 2016, **6**, 4720-4728.

S2 B. Zhang, H.-H. Wang, H. Su, L.-B. Lv, T.-J. Zhao, J.-M. Ge, X. Wei, K.-X. Wang, X.-H. Li and J.-S. Chen, *Nano Research,* 2016, **9(9)**, 2606-2615.