

Supplementary Materials: One Simple Strategy towards Nitrogen and Oxygen Codoped Carbon Nanotube for Efficient Electrocatalytic Oxygen Reduction and Evolution

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Materials Characterization

The morphology was characterized by a transmission electron microscope (TEM, Talos F200X G2, Waltham, MA, USA) with high-angle annular dark-field (HAADF) detector. The componential analyses were performed with Fourier transform infrared (FTIR, Thermo Nicolet 6700, Waltham, MA, USA), TEM energy-dispersive X-ray spectroscopy (EDS) mapping and X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra spectrometer, Kratos, UK). The structure was reflected by the Raman spectra (HORIBA iHR550, Kyoto, Japan) with an excitation wavelength of 532 nm. The specific surface areas were acquired by nitrogen adsorption-desorption isotherm (Micrometrics Tristar II, Norcross, GE, USA) and were calculated by the Brunauer-Emmett-Teller (BET) model at a pressure range of $P/P_0 = 0.05-0.3$. The Barrett-Joyner-Halenda (BJH) model was used to analyze pore size distribution of the samples through the adsorption branch on isotherm.

Electrochemical Characterization

The Koutecky-Levich plots for ORR were obtained by linear fitting of the reciprocal rotating speed versus reciprocal current density collected at different potentials from -0.4 V to -0.8 V with the following equation:

$$1/j_D = 1/j_k + 1/B\omega^{1/2} \quad (1)$$

where j_k is the kinetic current in amperes at a constant potential, ω is the electrode rotating speed in rpm, and B is the reciprocal of the slope determined from Koutecky-Levich plots based on Levich Equation:

$$B = 0.2 nFA\nu^{-1/6}C_{O_2}D_{O_2}^{2/3} \quad (2)$$

where n is the number of electrons transferred per oxygen molecule, F is the Faraday constant (96485 C mol^{-1}), D_{O_2} is the diffusion coefficient of O_2 in 0.1 M KOH ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν is the kinetic viscosity, and C_{O_2} is the concentration of O_2 ($1.2 \times 10^{-3} \text{ mol L}^{-1}$). The constant 0.2 is adopted when the rotating speed is in rpm.

The RRDE system (Pine Research Instrumentation, USA) with a $320 \mu\text{m}$ gap Pt ring electrode was employed for measuring the RRDE voltammogram of ORR. The LSVs were collected in O_2 saturated 0.1 M KOH at 1600 rpm . The disk was set to scan from 0 to -1.0 V at a scan rate of 5 mV s^{-1} and the ring was kept at 0.5 V. The collection efficiency of the ring electrodes, N , is 0.37 . The peroxide yield (HO_2^- %) and the electron transfer number (n) were calculated according to the following equations.

$$HO_2^- \% = 200 \times I_r/N/(I_d + I_r/N) \quad (3)$$

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

where I_d stands for the disk current and I_r is the ring current.

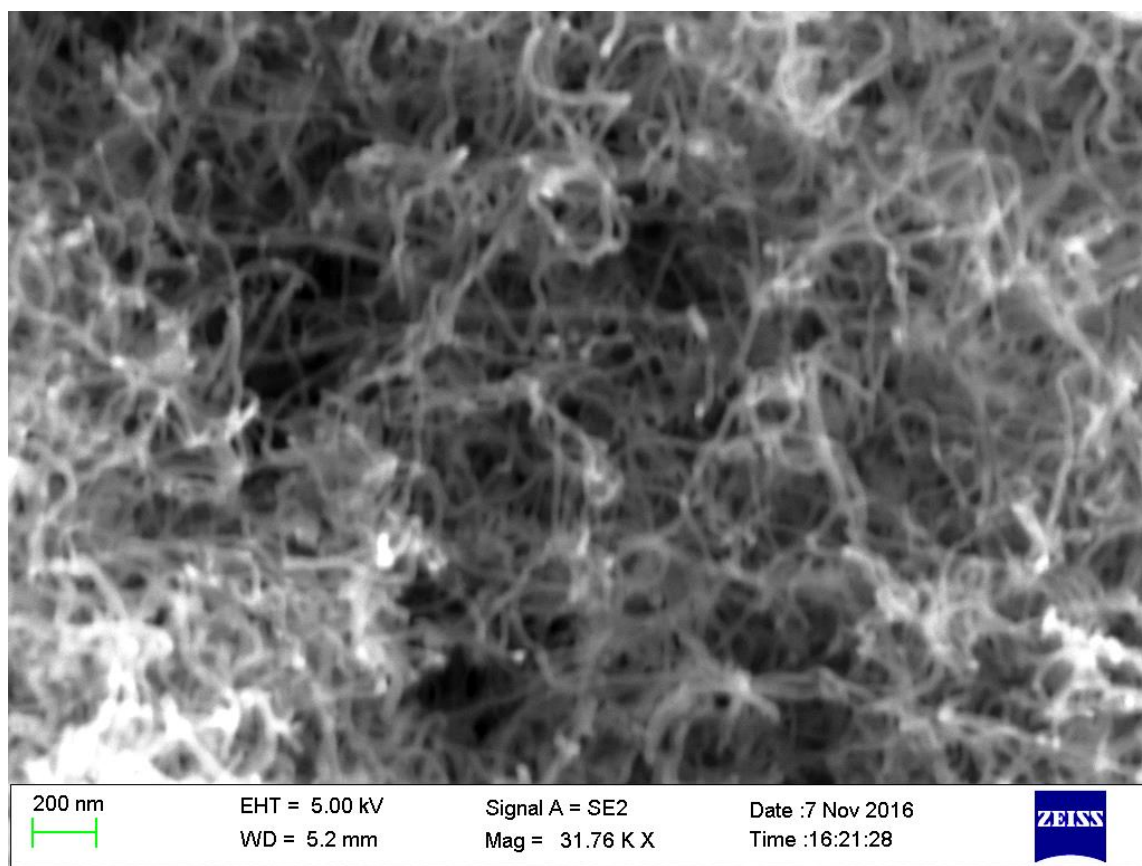


Figure S1. SEM image of N, O-CNT.

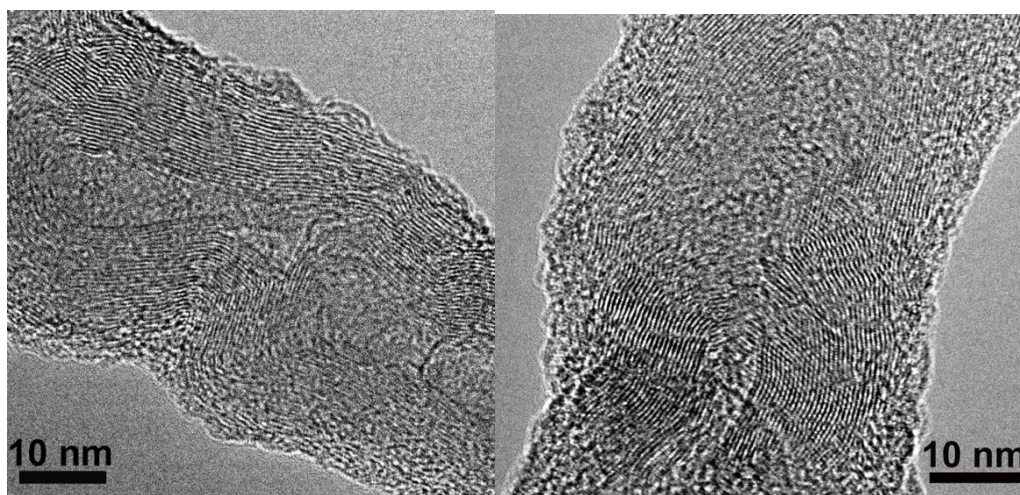


Figure S2. The magnified TEM images of the N, O-CNT.

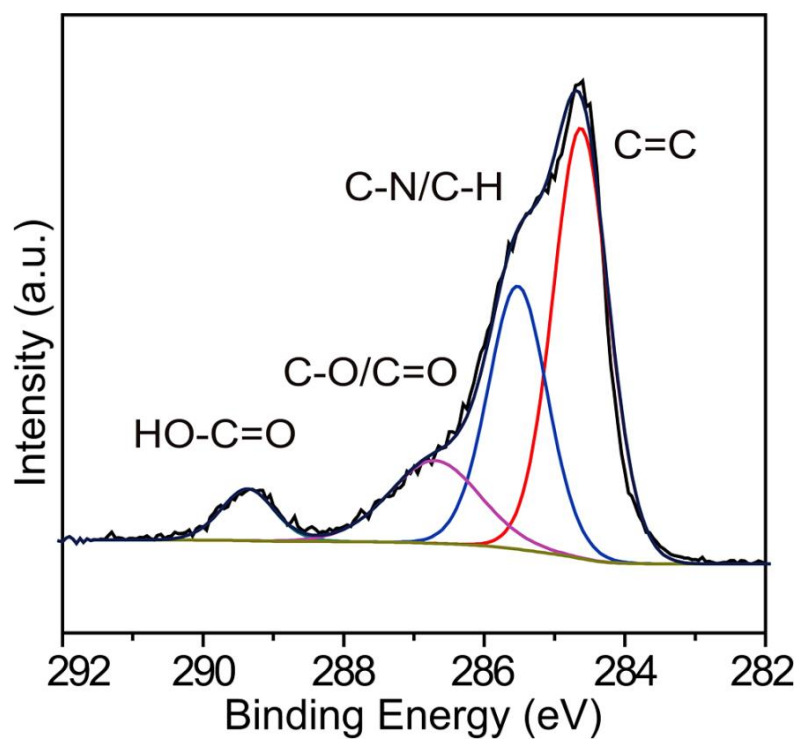


Figure S3. XPS high-resolution spectra of C1s of N, O-CNT.

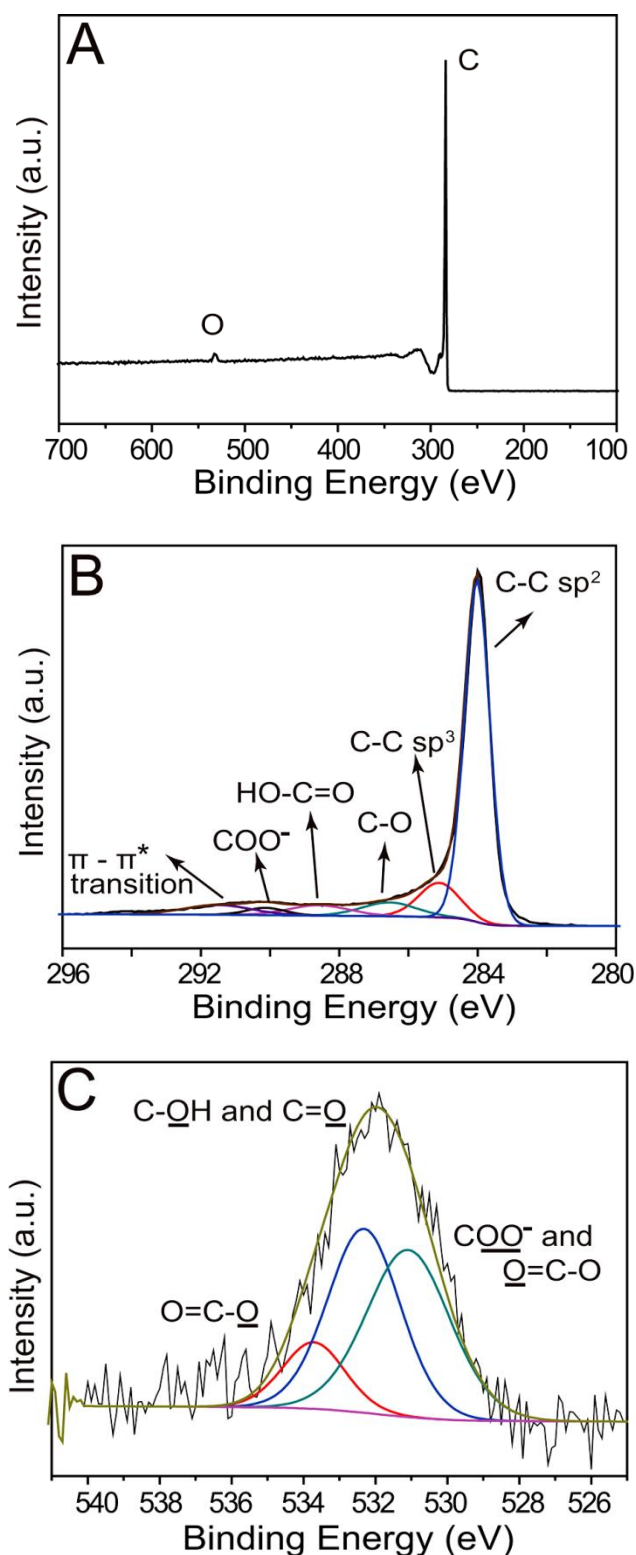


Figure S4. (A) XPS survey scan and the deconvoluted high-resolution spectra of (B) C 1s and (C) O 1s in p-CNT.

The as-received p-CNT contains 97.7 at.% C and only 2.3 at.% O, indicating the intact structure. The C1s can be deconvoluted into six peaks: a main peak at 284.1 eV attributed to the sp^2 graphitic structure, and the peak at 285.2 eV that belongs to sp^3 C bonds caused by defects of the nanotube, whereas the peaks at 286.6, 288.6, and 290.1 eV correspond to the carbon atoms attached to different oxygen moieties. Finally, the peak at 291.5 eV is due to the $\pi-\pi^*$ transition. The O 1s can be

deconvoluted into three peaks at 531.2, 532.3, and 533.8 eV, similar to the oxygen moieties of N, O-CNT.

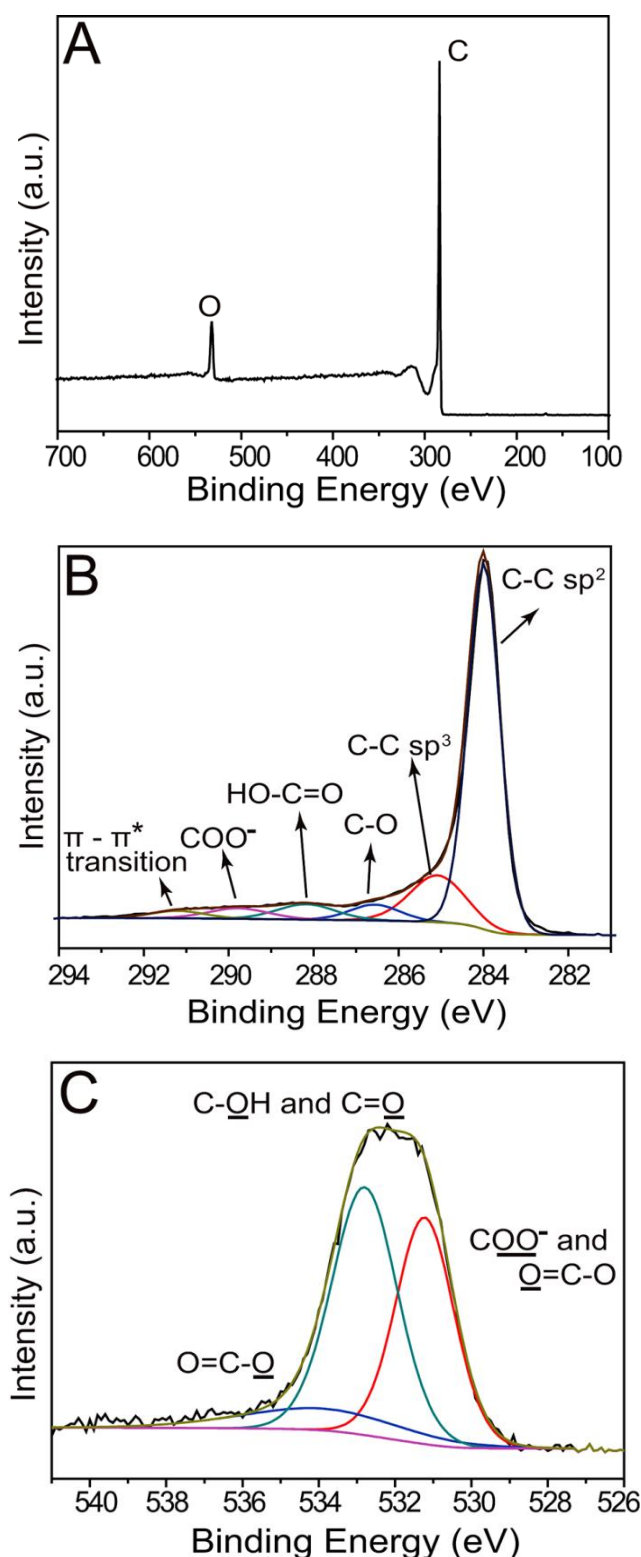


Figure S5. (A) XPS survey scan and the deconvoluted high-resolution spectra of (B) C 1s and (C) O 1s in ox-CNT.

The ox-CNT contains 90.5 at.% C and 9.5 % at.O, due to the introduction of abundant oxygen groups by the oxidation of strong acids. Deconvolution of the C1s and O1s peaks was similar with that of p-CNT.

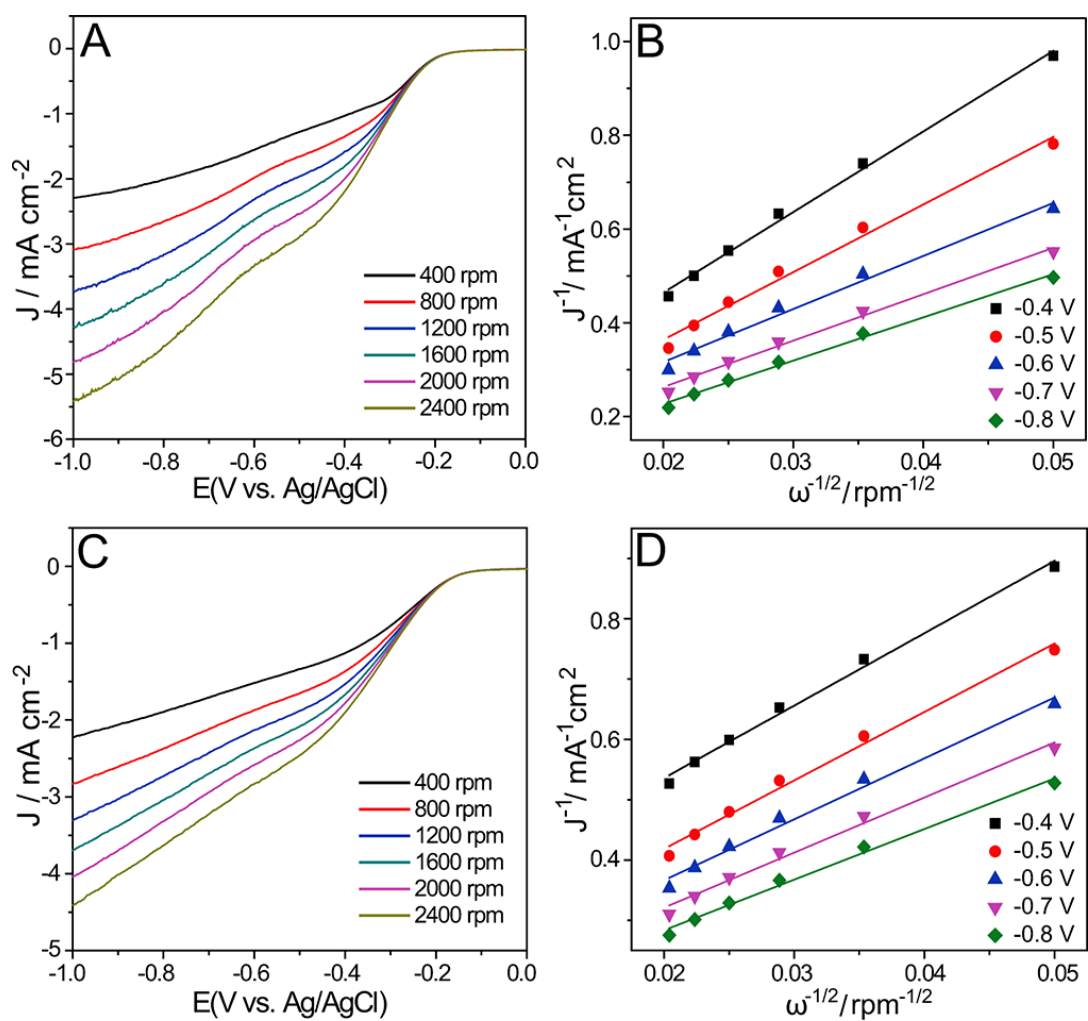


Figure S6. (A, C) LSVs at different rotating speeds from 0 to 2400 rpm, (B, D) K-L plots obtained at different potentials: -0.4, -0.5, -0.6, -0.7 and -0.8 V. (A, B): p-CNT and (C, D): ox-CNT.

Table S1. Comparison of the different OER and ORR metrics of the obtained catalysts.

Catalysts	ORR			OER		ΔE (V)
	Onset potential	$E_{j=-3}$	Tafel slope	$E_{j=10}$	Tafel slope	$E_{j=10} - E_{j=-3}$
	(V vs. Ag/AgCl)	(V vs. Ag/AgCl)	(mV dec ⁻¹)	(V vs. Ag/AgCl)	(mV dec ⁻¹)	
p-CNT	-0.25	-0.673	98	0.73	93	1.4
ox-CNT	-0.23	-0.785	124	0.82	147	1.61
N, O-CNT	-0.16	-0.27	80	0.65	74	0.92