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Supporting Information

Platanus hispanica-inspired Design of Co-Carbon Nanotube Frameworks through Chemical Vapor Deposition: Highly Integrated Hierarchical Electrocatalyst for Oxygen Reduction Reaction

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Experimental section

Materials: Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), glycerol and isopropanol were purchased from Aladdin Industrial Co., (Shanghai, China). Nafion solution (5 wt %), ethanol, and potassium hydroxide (KOH) were obtained from Sinopharm Chemical Reagent Co. The other chemicals were purchased from Sigma-Aldrich. Deionized water (18.2 MX) was used throughout the experiments. All chemicals used were of analytical grade and used as received without further purification.

Synthesis of Co-glycerate precursor: Cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, 0.22g) and glycerol (4.0 mL) were dissolved together in isopropanol (40 mL) under stirring for 2 h to form a transparent solution. And then the solution was transferred to a 100 mL Teflon-lined stainless steel autoclave and kept at 180 ℃ for 6 h. The resulting light pink product (Co-glycerate) was harvested by several rinse-precipitation cycles with ethanol. Finally, the pink powder of Co-glycerate was dried in vacuum at 60 ℃.

Synthesis of Co-CNTFs-750, Co-CNTFs and Co-CNTFs-550: The above obtained Co-glycerate particles were dispersed in a ceramic boat, heated to different temperature of 750, 650 and 550 ^{o}C in a CVD furnace in Ar atmosphere, respectively. Then hydrogen gas (Ar : hydrogen=5:1) was inflated into the furnace for 10 min to reduce the metalic cobalt and form porous carbon spheres. Subsequently, 350 sccm C_2H_4 was introduced for 5 min to in situ grow CNTs through porous Co-carbon spheres. Finally, the sample was rapidly cooled down to room temperature under the flow of argon. The product was noted as Co-CNTFs-750, Co-CNTFs and Co-CNTFs-550, respectively.

Apparatus and Characterization: Powder X-ray diffraction (XRD) patterns were obtained with a XRD-7000 (XRD, Shimadzu XRD-7000) with Cu Kα source radiation at a scanning rate of 2° min^{-1} from 10 to 80°. The morphologies and microstructures were investigated by field-emission scanning electron microscopy (FESEM, JEOL-7800F), transmission electron microscope (TEM, JEM-2100), and

Energy-dispersive X-ray spectroscopy (EDX, INCA X-Max 250). The surface properties of the samples were studied by X-ray photoelectron spectroscopy (XPS, Escalab 250xi, Thermo Scientific). The Brunauer–Emmett–Teller (BET) surface area was measured by using Quadrasorb evo 2QDS-MP-30 (Quantachrome Instruments, USA). Thermogravimetric analysis was performed on Thermo Gravimetric Analyzer (TGA, Q50, USA) at a rate of 5 ℃ min1 under air from 30 to 700 ℃.

Electrochemical measurements: The Co-CNTFs catalyst slurry was prepared by ultrasonically dispersing catalyst (2.0 mg) in a solution containing 1 mL of ethanol-DI water (1:1 vol) and 20 μL of 5 wt % Nafion solution. Then, 25 μL of the slurry was loaded onto a glassy carbon electrode. All electrochemical measurements were carried out on Autolab bi-potential station (CHI Instruments Inc.) by using the as-prepared electrode as working electrode, a platinum foil as counter electrode, and a Hg/HgO (1.0 M NaOH) as reference electrode. The electrolyte was 0.1 M KOH. For fuel crossover effect tests, the current response at -0.15 V Hg/HgO with an RDE rotation rate of 1600 rpm, with 5% (v/v) methanol being added into the O_2-saturated electrolyte around 100 s. Accelerated durability test (ADT) was performed between 0.2 and -0.8 V at 50 mV s^{-1} in 0.1 M KOH solution exposed to atmosphere.

The kinetic-limiting current density (JK) for the ORR was derived from the experimental data using the Koutecky-Levich equation (Eq. 1):

$$\frac{1}{|J|}=\frac{1}{|JL|}+\frac{1}{|JK|}=\frac{1}{B\sqrt{\omega}}+\frac{1}{|JK|}$$

$$B=0.2nFC_0(D_0)^{2/3}\upsilon^{-1/6}$$

where J and JL are the measured current and diffusion limiting current, respectively; ω is the rotation speed in rpm, F is the Faraday constant (96,485 C mol^{-1}), C_0 is the bulk concentration of oxygen (1.2×10^{-6} mol cm^{-1}), D_0 is the diffusion coefficient of oxygen in 0.1 M KOH (1.9×10^{-5} cm^2 s^{-1}), and υ is the kinetic viscosity (0.01 cm^2 s^{-1}). The n can be calculated from the slope of the K-L plot.

The electron transfer number (n) calcuated from the RRDE measurement was based on the disk current (J_{Disk}) and ring current (J_{Ring}) via the following equation:

$$n = 4I_{Disk}/(I_{Disk}+I_{Ring}/N)$$

where $N = 0.37$ is the current collection efficiency of Pt ring.

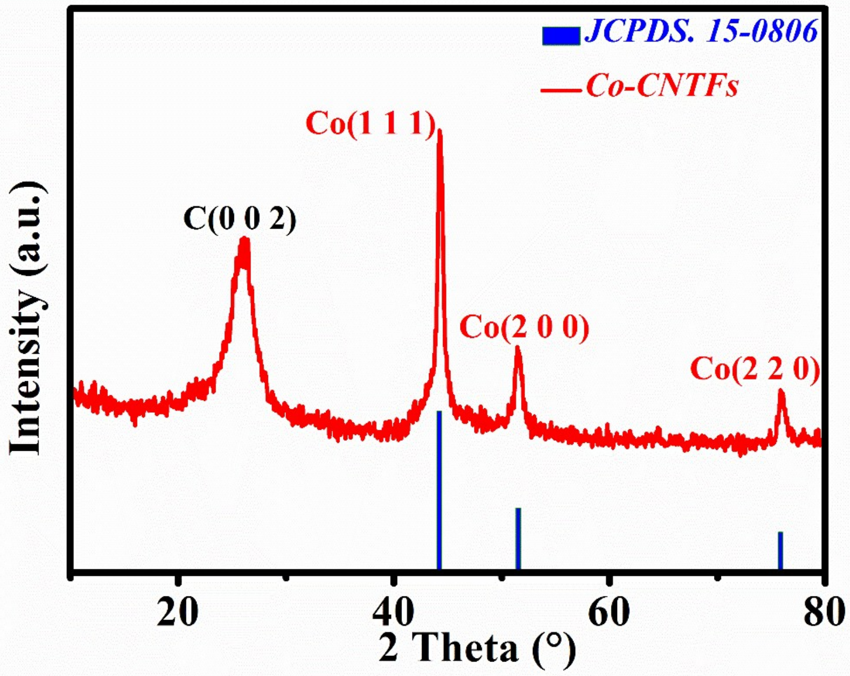

Fig. S1. XRD pattern of the as-prepared Co-CNTFs

Table. S1 The BET surface area, pore volume and average pores radius of all samples.

Samples	BET Surface Area (m^2/g)	Pore Volume (cc/g)	Average Pores Radius (nm)
Commercial CNTs	112.72	0.256	1.7035
Co-PC	194.6	0.372	1.7065
Co-CNTFs	316.7	0.486	3.1476

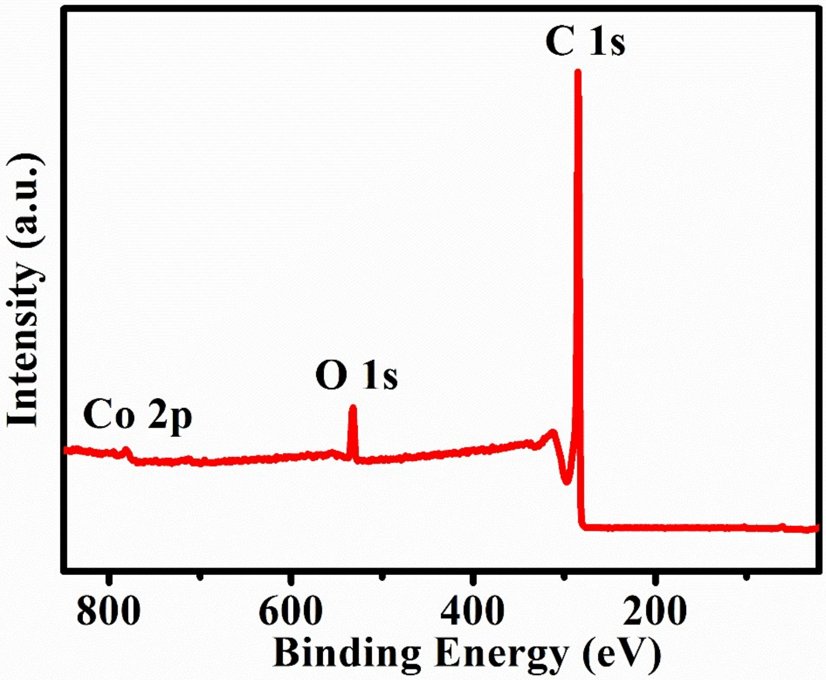

Fig. S2. XPS spectra of Co-CNTFs.

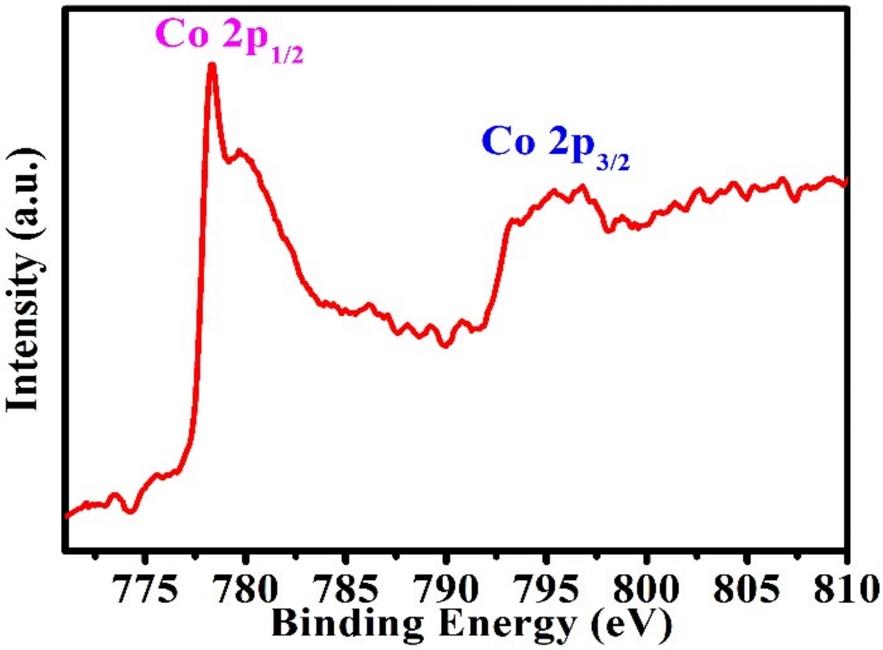

Fig. S3. High-resolution XPS spectra of Co 2p

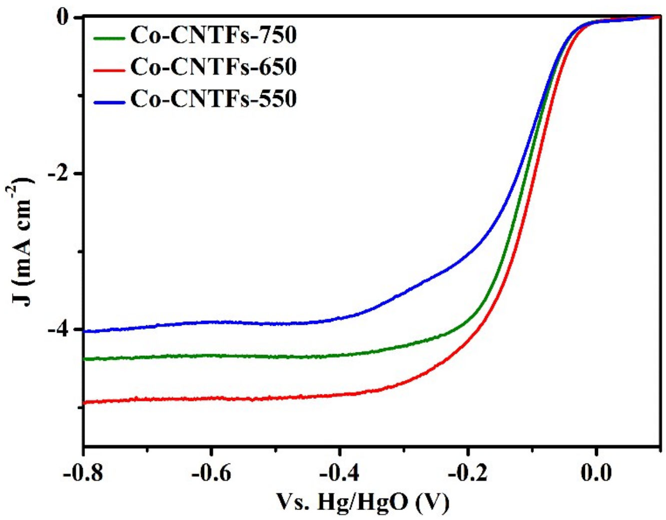

Fig. S4 LSV curves of Co-CNTFs-750, Co-CNTFs and Co-CNTFs-550 at an RDE rotation speed of 1600 rpm with a scan rate of 10 mV s^{-1} in O_2-saturated 0.1 M KOH solution.

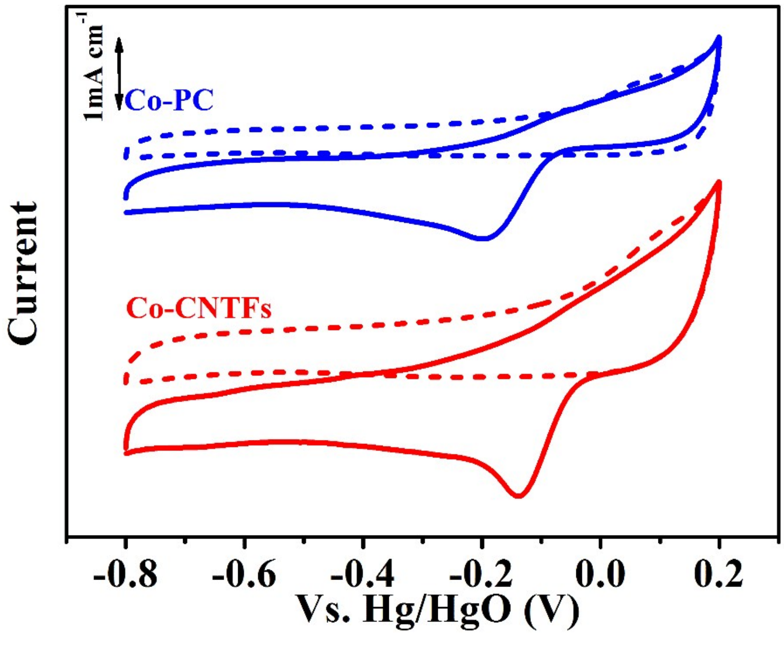

Fig. S5. Cyclic voltammetry (CV) curves of Co-PC and Co-CNTFs on glassy carbon electrodes in O_2-saturated (solid line) or N_2-saturated (dash line) 0.1M KOH.

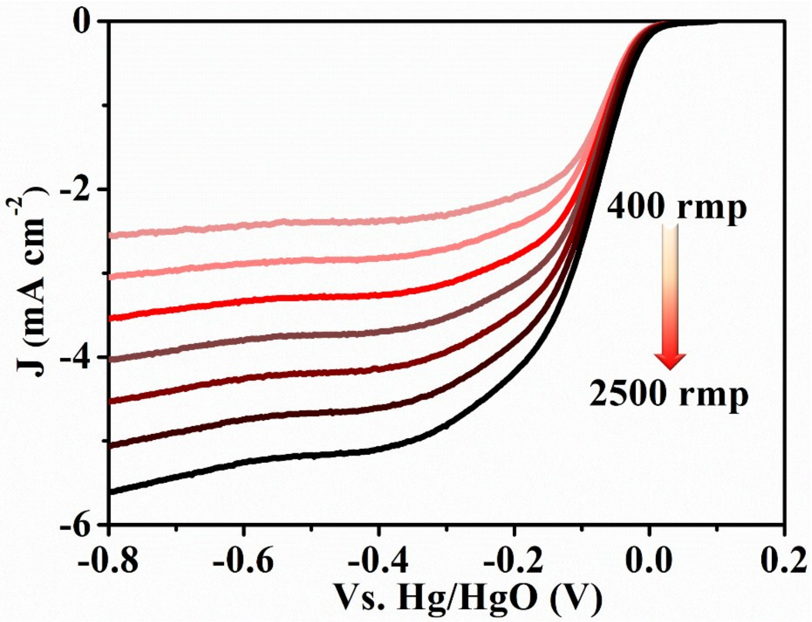

Fig. S6. LSV curves of Co-PC at different rotating speeds with a scan rate of 10 mV s^{-1}.

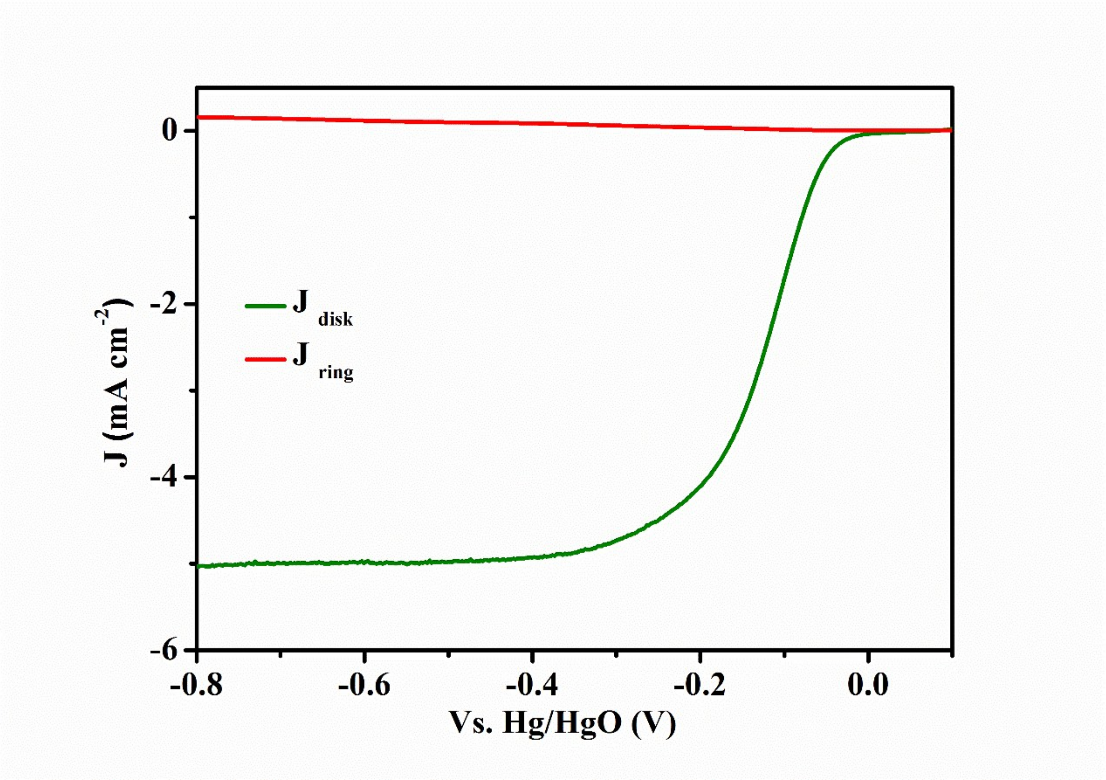

Fig. S7 Rotating ring-disk electrode (RRDE) measurements of Co,N-CNF. The electron transfer number was calculated to be 3.8.

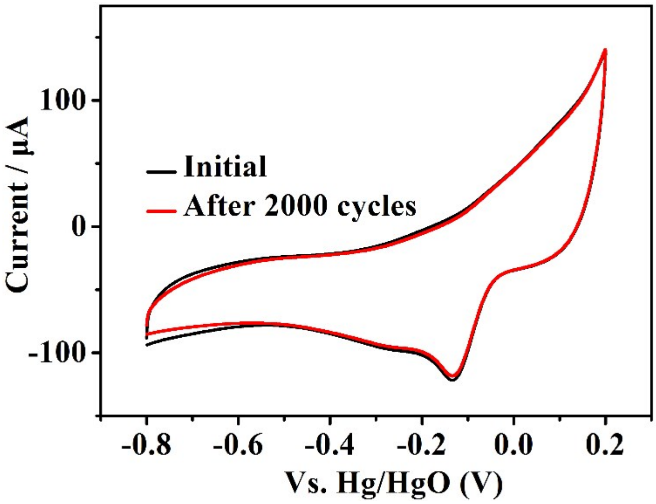

Fig. S8 CV curves of Co-CNTFs in O_2-saturated 0.1 M KOH solution before and after ADT (2000 CV cycles between 0.2 and -0.8 V@50 mV s^{-1} in KOH solution exposed to atmosphere).