Electronic Supplemental Information for

Pyrrolic N doped carbon materials for the electrosynthesis of H_2O_2 through oxygen reduction reaction

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Experimental Section

Materials and Reagents: Carbazole ($C_{12}H_9N$) was purchased from Aladdin Reagent (Shanghai) Co., LTD and carboxylated carbon nanotubes (O-CNT) was bought from Chengdu Organic Chemistry Co., Ltd, Chinese Academy of Sciences. Nafion-117 membrane and carbon paper (Toray, TGP-H-060) were obtained from Tianjin Incole Union Technology Co., Ltd. and Suzhou Shengernuo Technology Co., Ltd., respectively. The ultra-pure water (≥ 18.2 M Ω cm,25 ℃) was used throughout the whole experiment.

Synthesis of P-CZ/O-CNT-500: Typically, 100 mg of carbazole ($C_{12}H_9N$) and 100 mg of carboxylated carbon nanotubes (O-CNT) were grinded evenly in a mortar. Then the mixture of carbazole and O-CNT was transferred to a porcelain boat and put into a tube furnace. The temperature in the tube furnace rose from room temperature to 250 ºC and kept for one hour, then continued to rise to 500 ºC and kept for another hour. The heating rate was 5 ℃ / min and the Ar gas was full of the tube furnace during the whole pyrolysis process. The corresponding product was named P-CZ/O-CNT-500. When the temperature in the second step became 800 ºC, the product was called P-CZ/O-CNT-800.

For comparison, pure carboxylated carbon nanotubes (O-CNT) without carbazole underwent the same pyrolysis process and the corresponding product was recorded as P-O-CNT-500.

Material characterization: Field emission scanning electron microscope (SEM, Hitachi8100) and transmission electron microscope (TEM, Hitachi7700) were applied to characterize the morphology and microstructure of the materials. X-ray photoelectron spectroscopy (XPS, ThermoScientific, US, AlK α radiation) was used to analyze the element composition of the materials. In addition, the materials were also characterized by UV-vis spectrophotometer (UV2450), infrared (IR, Invenio) and Raman (inVia) spectroscopy.

Electrochemical test: All the electrochemical tests were carried out on the electrochemical workstation (CHI730E, Shanghai Chenhua) with a typical three-electrode system. The reference electrode, counter electrode and the working electrode were Ag/AgCl, carbon rod electrode and rotating ring-disk electrode (RRDE, d = 5 mm), respectively. Without special instructions, the rotation speed of the RRDE is 1600

rpm. For all the samples tested, the catalyst ink with a concentration of 5 mg/mL was prepared by dispersing 5 mg of sample in the mixed solution of 800 μL of ultra-pure water, 200 μL of isopropanol and 5 μL of Nafion (5 wt%). Before the electrochemical test, the working electrode was polished with alumina powder (0.05 μm), cleaned with ethanol and dried naturally. Then, 10 μL of catalyst ink was dripped onto the working electrode and dried at 37 ℃ in a drying oven for 30 minutes.

The oxygen reduction reaction (ORR) activity of the catalysts was evaluated by linear sweep voltammetry (LSV) in oxygen-saturated 0.1M phosphate buffered saline (PBS, pH = 7) with a scan rate of 10 mV/s. Before the LSV test, the working electrode was activated by cyclic voltammetry (CV) with a scan rate of 100 mV/s until the CV curves were stable. All the measured potentials are converted to the reversible hydrogen electrode potential (RHE) according to the following formula: $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.0591pH$.

For the RRDE test, the potential on the platinum ring was 1.20 V (vs. RHE). The selectivity of hydrogen peroxide (H_2O_2, %) and electron transfer number of hydrogen peroxide (n) can be calculated using the following formula:

$$H_2O_2\ (\%) = 200 \times \frac{\frac{I_R}{N}}{\frac{I_R}{N} + I_D} \qquad (1\text{-}1)$$

$$n = 4 \times \frac{\frac{I_R}{N}}{\frac{I_R}{N} + I_D} \qquad (1\text{-}2)$$

Where I_D and I_R are disk current and ring disk current respectively, and N is the current collection efficiency of Pt ring (N = 0.37).

The electrochemical active surface area (ECSA) of catalysts was reflected by a double layer capacitance (C_{dl}) which was calculated based on a series of CV curves in the non-faradaic region at the scan rates of 10, 20, 30, 40 and 50 mV s^{-1}.

Hydrogen peroxide (H_2O_2) was electrochemically synthesized via potentiostatic method in an H-type electrolytic cell using Nafion-117 membrane separating the cathode from the anode. The counter electrode was carbon paper (1x1 cm^{-2}), which was cleaned with 0.1 M HCl, acetone and ethanol solution in sequence by ultrasonic wave for 15 minutes and then dried at 60 ℃ for 3 h. The working electrode was the carbon paper pretreated above and coated with P-CZ/O-CNT-500 or the control sample with a mass loading of 0.25 mg cm^{-2} (unless explicitly stated). The reference electrode was Ag/AgCl electrode. The electrolyte in the cathode was 46 mL of 0.1 M PBS with a pH of 7 and saturated with O_2.

The concentration of H_2O_2 was analyzed by cerium sulfate method based on the equation below: $2Ce^{4+} + H_2O_2 = 2Ce^{3+} + O_2 + 2H^+$. After reacting with H_2O_2, the absorbance at 319 nm of Ce^{4+} containing solution will decrease. According to the absorbance-H_2O_2 concentration standard curve, the concentration of H_2O_2 in the H-type cell was detected.

The Faradaic efficiency (FE) for the electrosynthesis of H_2O_2 was calculated via the following formula:

$$\mathrm{FE}(\%) = \frac{Q_{H_2O_2}}{Q_{tot}} = \frac{2 \times F \times V_{tot} \times [H_2O_2]}{Q_{tot} \times 10^6} \qquad (1\text{-}3)$$

Where F is the Faraday constant (in C/mol e^-), the V_{tot} is the volume of the cathodic electrolyte (in mL), $[H_2O_2]$ means the concentration of H_2O_2 in cathodic cell (in mM), and Q_{tot} refers to the amount of charge calculated according to the i-t curve (in C).

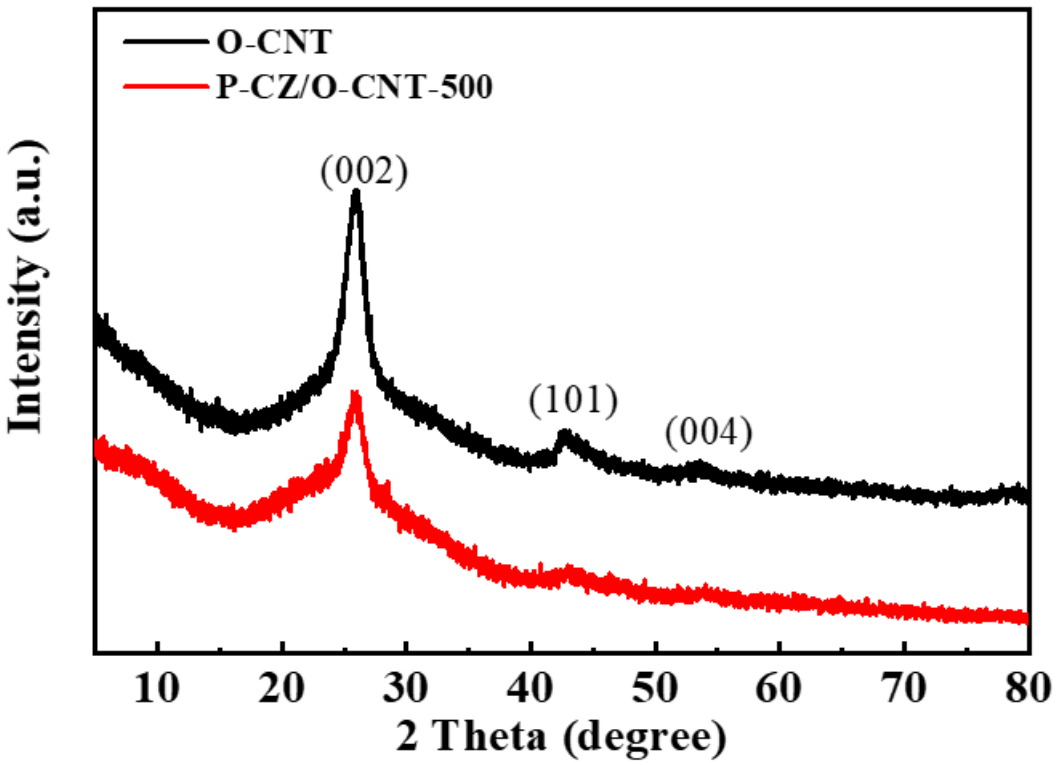

Fig. S1 XRD patterns of P-CZ/O-CNT-500 and O-CNT.

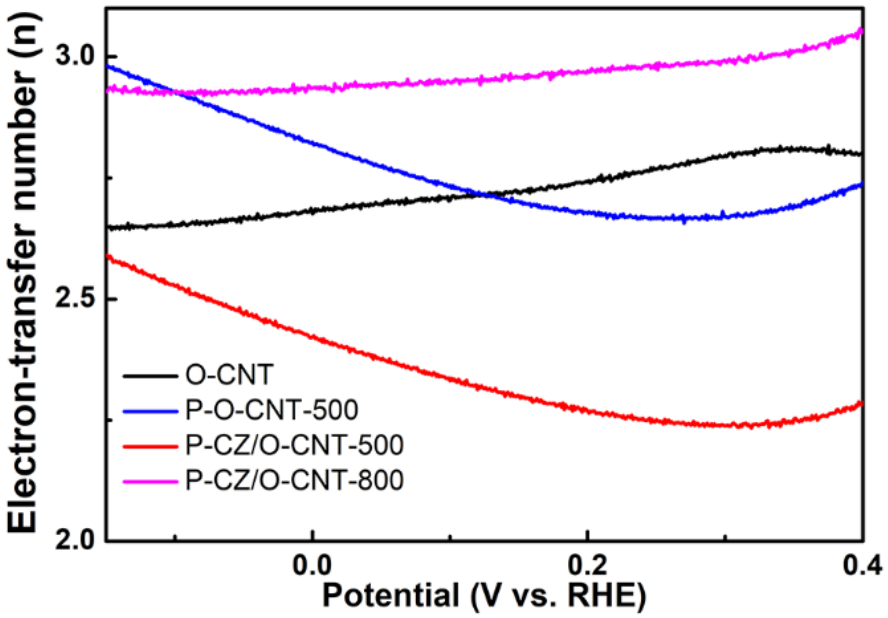

Fig. S2 Calculated electron transfer number of P-CZ/O-CNT-500 and the control catalysts.

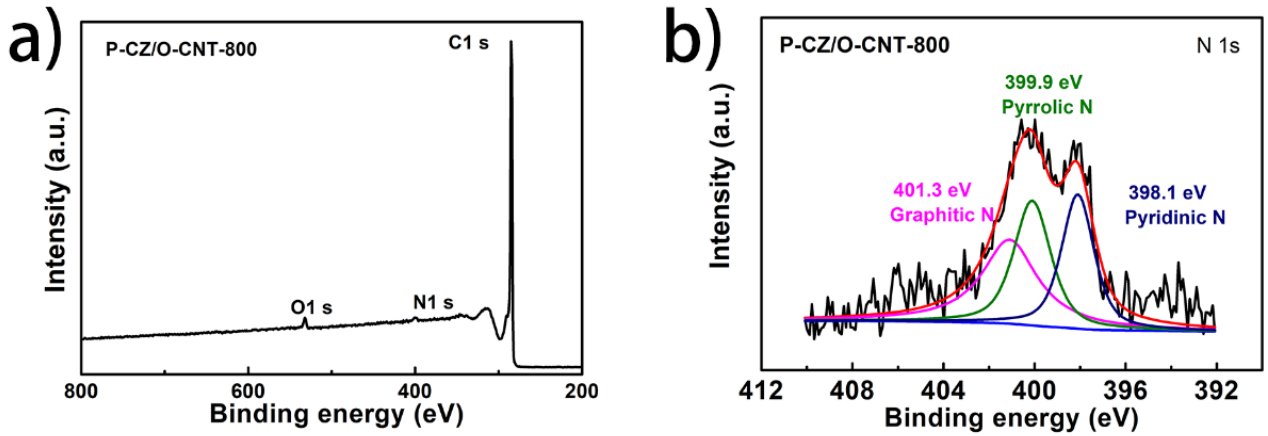

Fig. S3 (a) XPS survey spectrum, **(b)** high-resolution N 1s XPS spectrum of P-CZ/O-CNT-800.

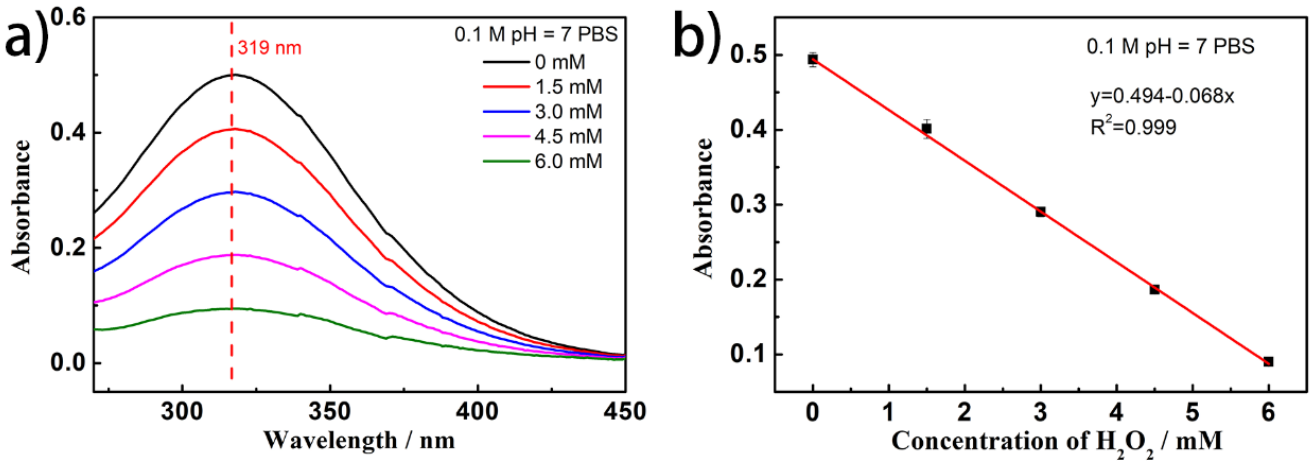

Fig. S4 (a) Ultraviolet-visible spectra of Ce^{4+} solution with different H_2O_2 concentrations and (b) the corresponding standard curve.

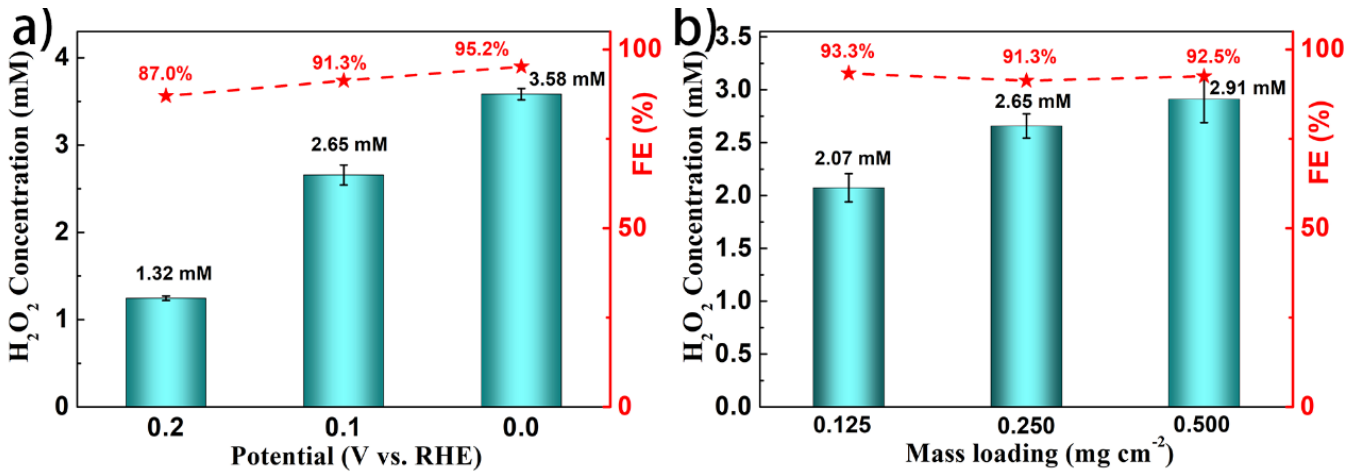

Fig. S5 Effect of potential (a) and mass loading (b) on the H_2O_2 concentration and Faradaic efficiency (FE).

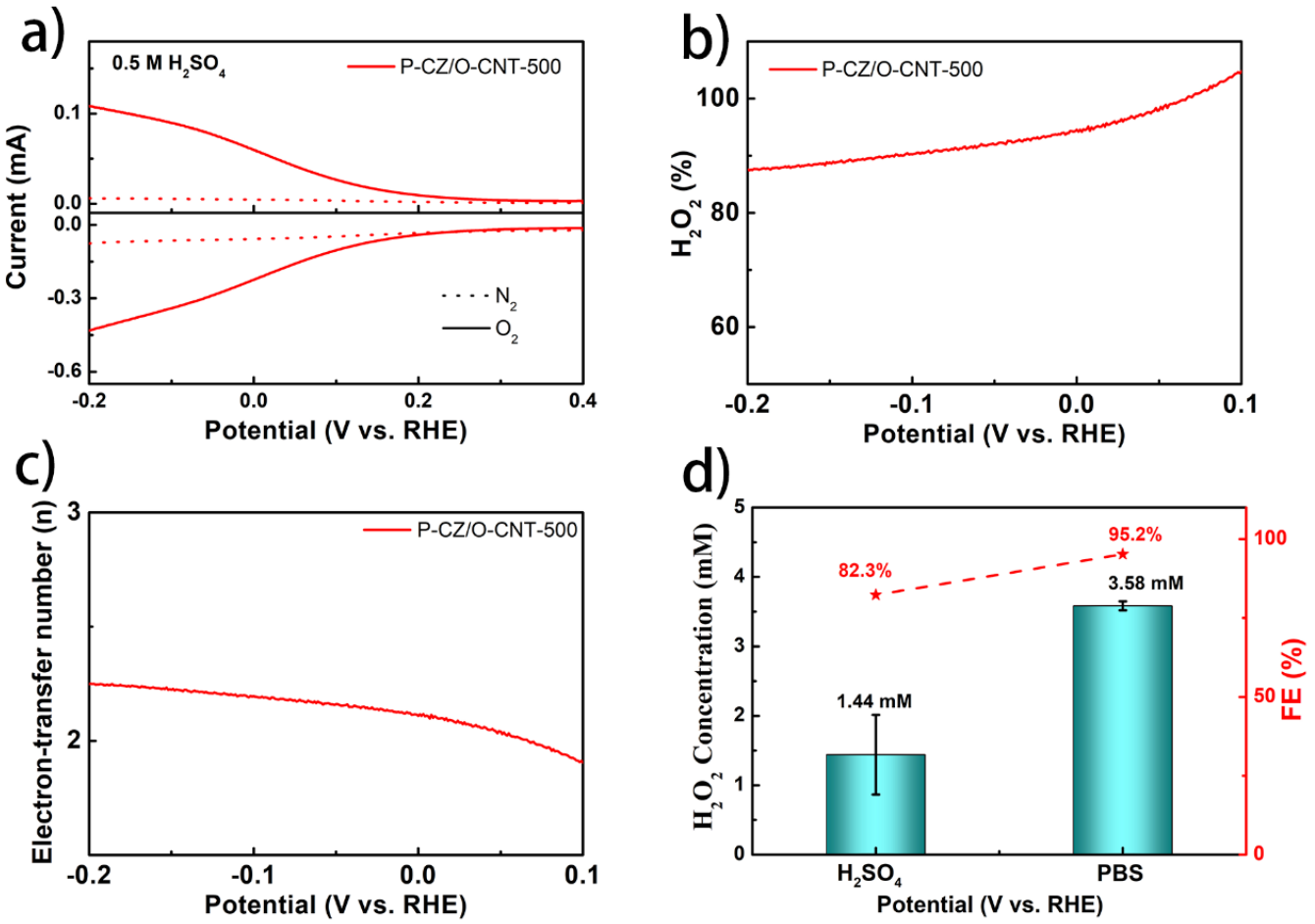

Fig. S6 (a) LSV curves of P-CZ/O-CNT-500 at the rotation speed of 1600 rpm in N_2 and O_2 saturated 0.5 M H_2SO_4, (b) the corresponding H_2O_2 selectivity and (c) calculated electron transfer number. (d) H_2O_2 concentration and Faradaic efficiency (FE) tested in H-type cell.