Supporting Information for

Embedding Pt Nanocrystals in N-doped Porous Carbon/Carbon Nanotubes towards Highly Stable Electrocatalysts for Oxygen Reduction Reaction

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This file includes experimental details and Figure S1-S6.

Experimental Details

Characterization: The Pt loading of Pt@CN_x/CNT was measured via an inductively coupled plasma emission spectrometer (ICP-AES, Shimadzu). Powder X-ray diffraction (XRD) pattern was characterized by a Regaku D/Max-2500 diffractometer equipped with a Cu Ka1 radiation (λ ＝1.54056˚A). The morphologies and structures of catalysts were characterized with tunneling electron microscopy (TEM) JEM-2100F (JEOL, Japan) working at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) data were collected on a Thermo Scientific ESCALab 250Xi using 200 W monochromated Al Kα radiation. The binding energies for all spectra were calibrated with respect to C1s line at 284.8 eV.

Electrochemical measurements:

All electrochemical measurements were carried out via a standard three-electrode-cell system on an electrochemical workstation (CHI 660E, ChenHua, Shanghai, China). The cell consisted of a glassy carbon rotating disk electrode (GC RDE, 4 mm in diameter), an Ag/AgCl reference electrode, and a platinum foil counter electrode. The electrocatalyst was dispersed in isopropyl alcohol and ultrasonicated for 15 minutes to form a uniform catalyst ink. For the preparation of working electrode, the well-dispersed catalyst ink was dropped onto a pre-polished GC disk to obtain the working electrodes with 22 μg_{Pt} cm^{-2}. After drying at room temperature, a drop of 0.1 wt% Nafion solution was spread onto the surface of catalyst layer and dried at room temperature. All of the work electrodes were pre-treated in N_2-purged 0.1 M $HClO_4$ by the potential cycling between 0.05 and 1.1 V at a sweep rate of 50 mV s^{-1} prior to the testing, The CV accelerating durability tests (ADT) were performed by the potential cycling between 0 and 1.2 V (vs. RHE) with a scan rate of 50 mV s^{-1} in N_2-purged 0.1 M $HClO_4$ at room temperature. The electrochemical surface area (ECSA) of Pt in the catalysts was calculated using the following

equation:

$$ECSA = \frac{Q_H}{0.21mC\ cm^{-2} \times [Pt]}$$

Where Q_H (mC) is the charge for the hydrogen adsorption of the CVs, 0.21 mC cm^{-2} is the electrical charge for monolayer adsorption of hydrogen on Pt nanocrystal surface, and [Pt] is the Pt loading on the working electrode.

The ORR polarization curves were obtained in O_2-saturated 0.1 M HClO$_4$ solution at a scan rate of 10 mV s^{-1} and a rotation speed of 1,600 rpm. For ORR test, the Koutecky-Levich equation can be used as follows:[1]

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}$$

Where j_k is the kinetic current density, j is the measured current density, j_d is the diffusion-limited current density, respectively. ω is the electrode rotating rate, and B could be determined from the slope of the K-L plots based on the Levich equation as follows:

$$B = 0.62nF(Do)^{2/3}\vartheta^{-1/6}Co$$

Where n represents the electron transfer number, F is the Faraday constant, Do is the diffusion coefficient of O_2 in 0.1 M HClO$_4$, ϑ is the kinetic viscosity and Co is the bulk concentration of O_2.

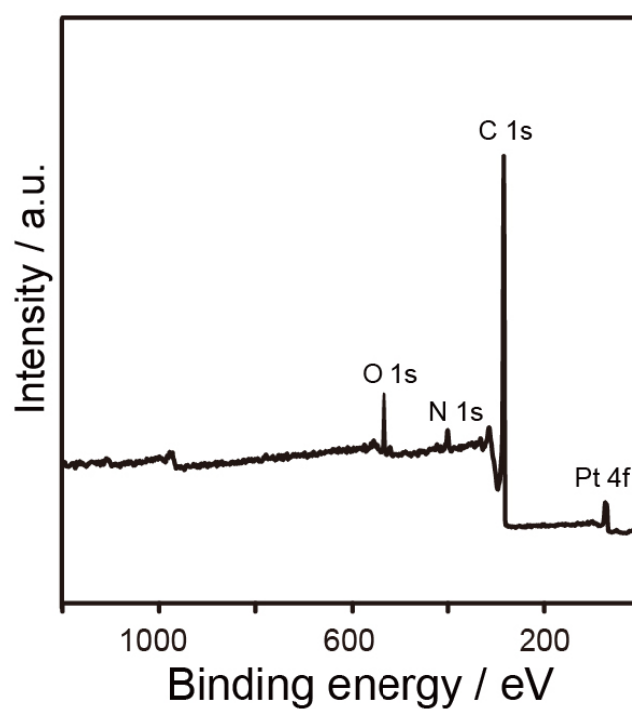The kinetic current densities (j_k) can be calculated by the following relation:

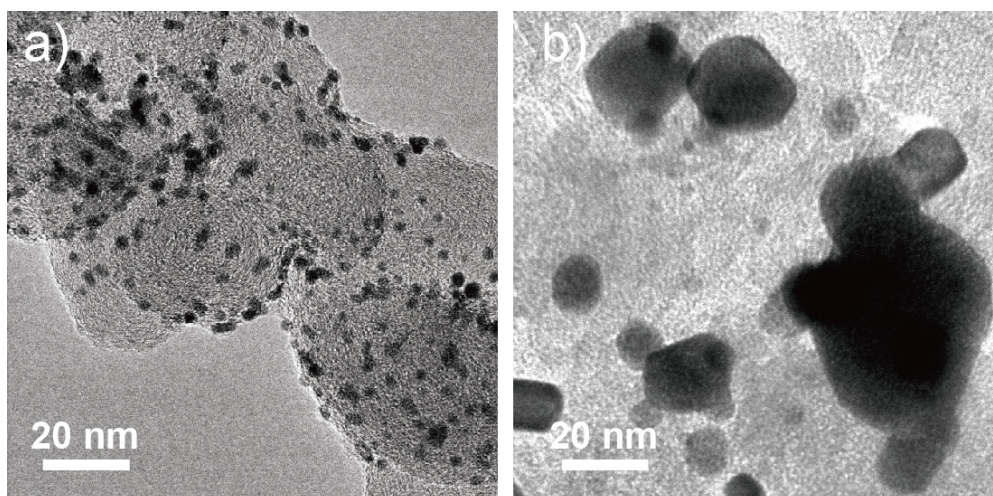$$j_k = \frac{j_d \times j}{j_d - j}$$

References

(1) Zhou W. P.; Yang X.; Vukmirovic M. B.; Koel B. E.; Jiao J.; Peng G., Mavrikakis M.; Adzic R. R. *J. Am. Chem. Soc.* **2009**, *131*, 12755–12762.
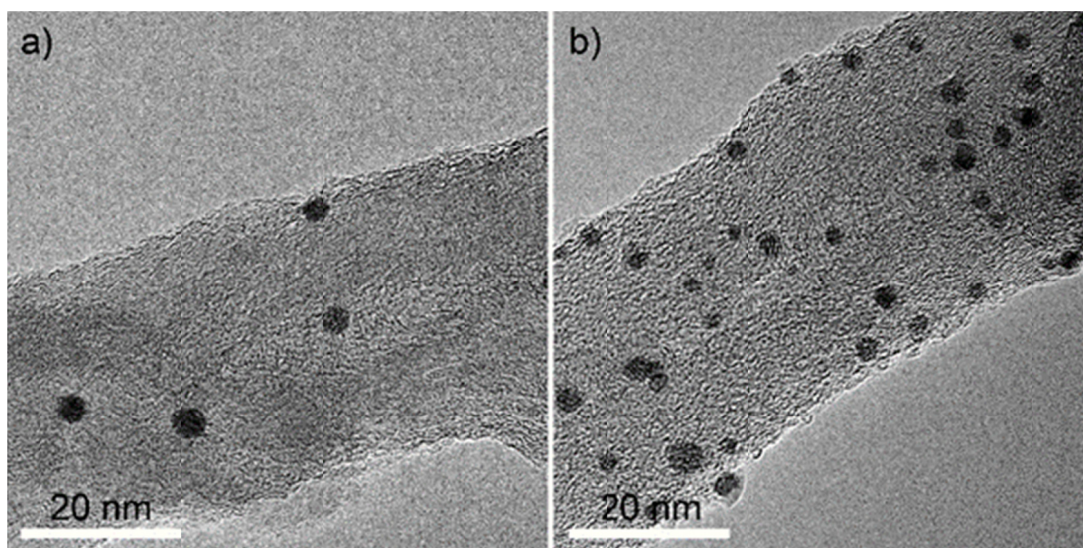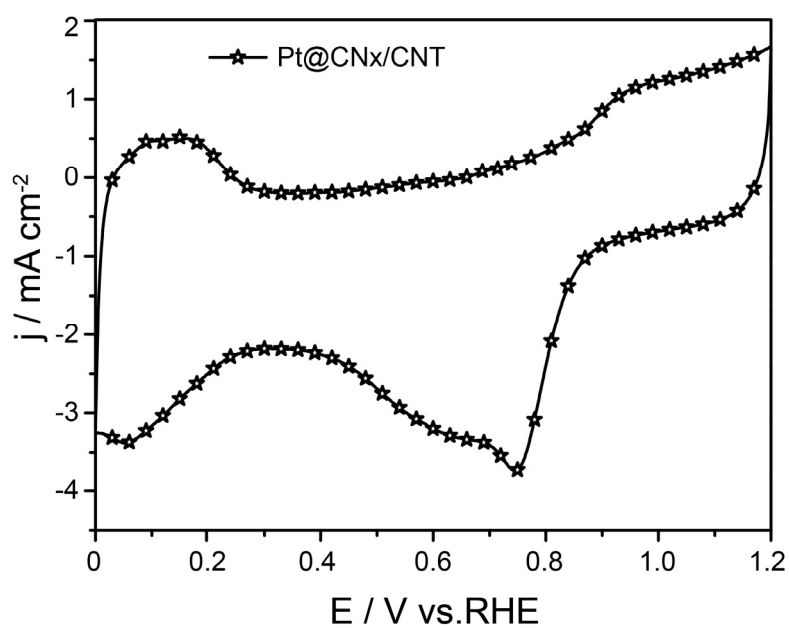
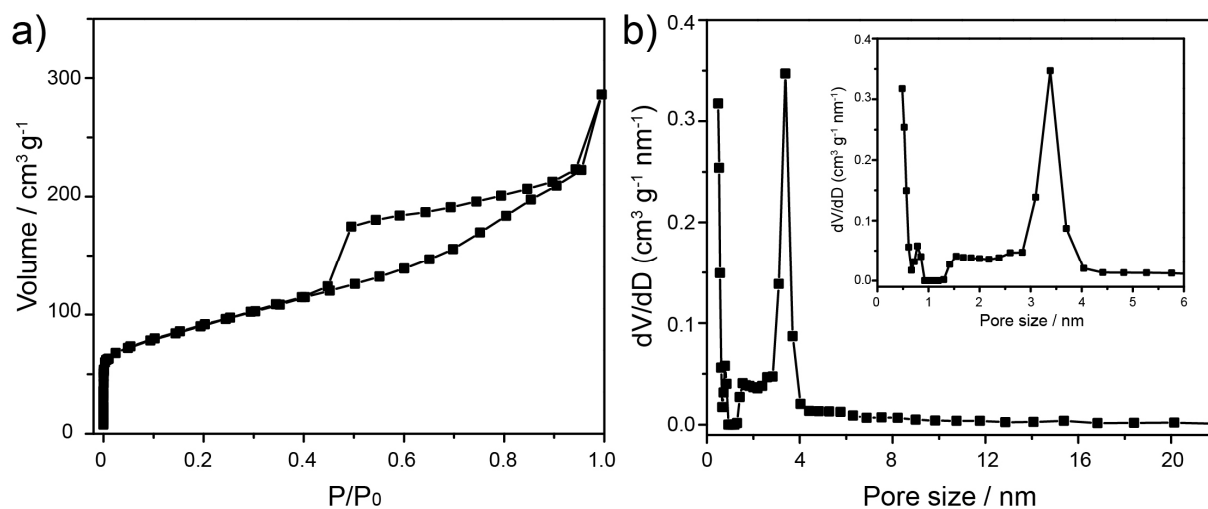**Figure S1.** The TEM images of Pt@CNx/CNT with different Pt loading, (a) 1.3 wt.% and (b) 5.2 wt.%, repesctively.

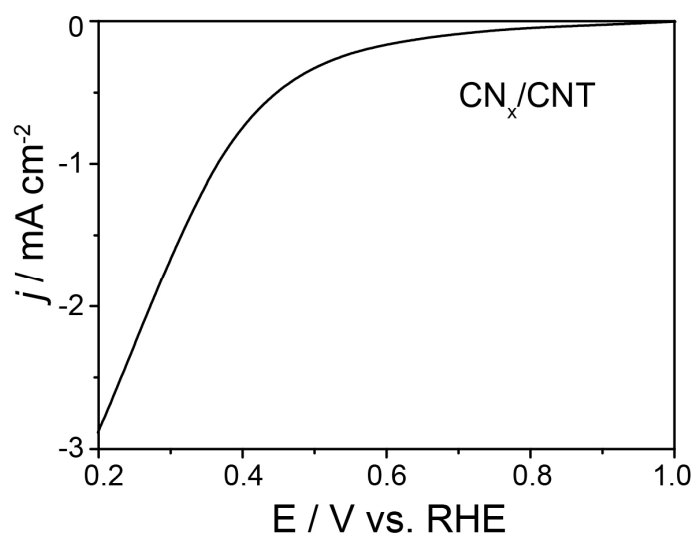**Figure S2**. Wide-scan survey XPS spectrum of Pt@CN$_x$/CNT.

Figure S3. TEM images of JM Pt/C before (a) and after (b) heat treatment at 900 ^{o}C.

Figure S4. CV curves of the Pt@CNx/CNT in O_2-saturated 0.1 M $HClO_4$.

Figure S5. (a) N_2 adsorption-desorption isotherm and (b) pore size distribution of Pt@CNx/CNT. The inset in Figure S5b is the enlarged pore size distribution.

Figure S6. LSV curve of CN_x/CNT recorded in O_2-saturated 0.1 M $HClO_4$ solution at room temperature (1600 rpm, sweep rate 10 mV s^{-1})