

Supplementary Information for

Rational Preparation of Faceted Platinum Nanocrystals Supported on Carbon Nanotubes with Remarkably Enhanced Catalytic Performance

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1. Synthesis and characterization of highly faceted platinum nanocrystals (HFNCs)

Multi-walled carbon nanotubes (CNTs) were purchased from Shenzhen Nanotech Port Co. Ltd, China. A sonochemical oxidation process was performed to introduce more carboxylic groups into CNTs. Typically 0.5 g as-received CNTs was dispersed in a concentrated H₂SO₄-HNO₃ mixture (80ml and 94 ml respectively together with 8ml deionized water) and then sonicated in an ultrasonic bath (100W) at 60°C for 1 hour. After being washed with deionized water, functionalized CNTs can be used in following steps.

A polyol method was used to prepare the highly faceted Pt nanocrystals (HFNCs), in which ethylene glycol was the only solvent. In a typical synthesis, 3mg CNTs was dispersed in 4.5 mL solution containing 60 mM NaNO₂, and 30mM PVP (M_w = 30k). The solution was kept at 140°C for 2h. Then 0.5 mL 100 mM H₂PtCl₆ solution was added into the solution. The reaction mixture was kept at 140°C for 1 hour and then cooled to room temperature. The dispersing of HFNCs strongly depends on the solvent. When acetone was added into the

solution, Pt nanoparticles were separated from the reaction solution through 10 min of centrifugation at 6000 rpm. After dried in air, the HFNCs were dispersed in ethanol at desired concentration. CNTs could be added to this dispersion to obtain CNT-HFNC composites with different loading of Pt.

The morphology and crystalline structure of the products were characterized by a JEOL-200 CX transmission electron microscope (TEM) and a Tecnai F30 high resolution transmission electron microscope (HRTEM). The side lengths of each nanocrystal in the TEM image were measured and the average length was used to represent the size of the corresponding nanoparticle. The X-ray diffraction (XRD) data were recorded using a Rigaku Dmax-2000 X-ray diffractometer by Cu α radiation ($\lambda=1.5406 \text{ \AA}$) with an accelerating voltage of 40 kV.

Figure S1 gives the TEM images of HFNC/CNT composites prepared with the NO_2^-/Pt molar ratios of 5 and 7. It shows that the particle size increased with the increase of NO_2^- concentration. The XRD pattern of HFNC prepared at the NO_2^-/Pt molar ratio of 6 is shown in Figure S2.

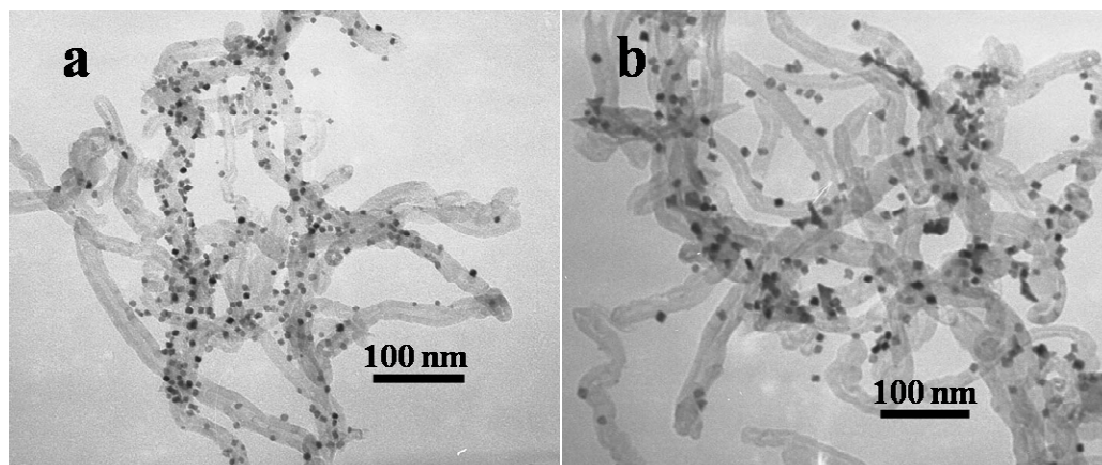


Figure S1. TEM images of HFNC/CNT composites formed when the molar ratio of NO_2^-/Pt is 5 (a) and 7 (b). The HFNCs' average diameters are $7.1\text{nm} \pm 1.4\text{nm}$ (a) and $9.0\text{nm} \pm 1.2\text{nm}$ (b), respectively.

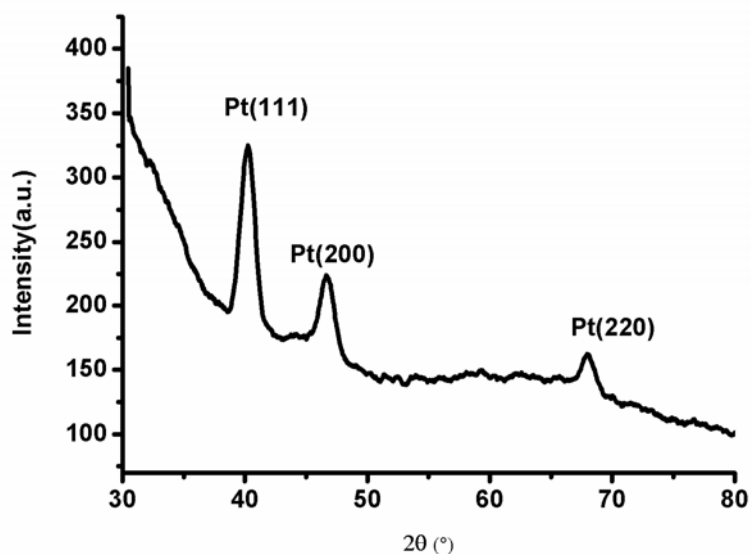


Figure S2. XRD Pattern of HFNCs

2. Discussion about the roles of NaNO_2 and CNTs in the synthesis

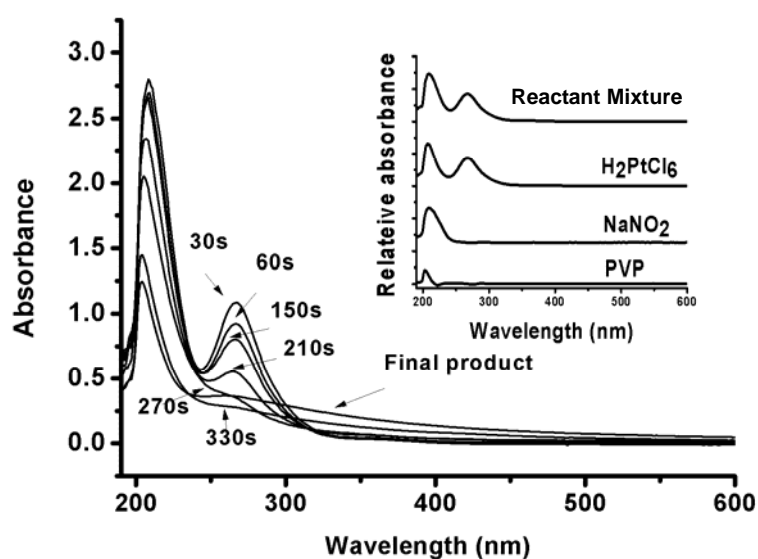


Figure S3. UV-vis spectra of samples taken from reaction solutions at different stage of reaction. The inset is the spectrum of each starting materials and the mixture of them.

The ethylene glycol served as both the solvent and reductant. The reducing rate depended strongly on the shape-controlling reagents, so did the morphology of the products. At 140°C , the reduction was very fast without the addition of NO_2^- , resulting in the formation of small Pt

nanospheres (Figure S4d). With the addition of NO_2^- , the reduction rate became smaller, leading to the formation of HFNCs. In order to track the reaction mechanism, we conducted the UV-Vis measurements of samples at different evolution time (Figure S3). The peak around 210 nm was a combination of the absorption of H_2PtCl_6 , NO_2^- , and PVP, while the peak around 280 nm was attributed to the absorption of H_2PtCl_6 . In a typical synthesis, after the H_2PtCl_6 solution was injected into the solution, the absorbance continuously decreased till the reaction time of 210 s and the reaction solution changed from orange to light yellow. This was ascribed to the consuming of H_2PtCl_6 and the formation of Pt(II) species.¹ During the period of ~ 250 s - 330 s, the color of the solution was becoming darker, indicating the formation of HFNCs.

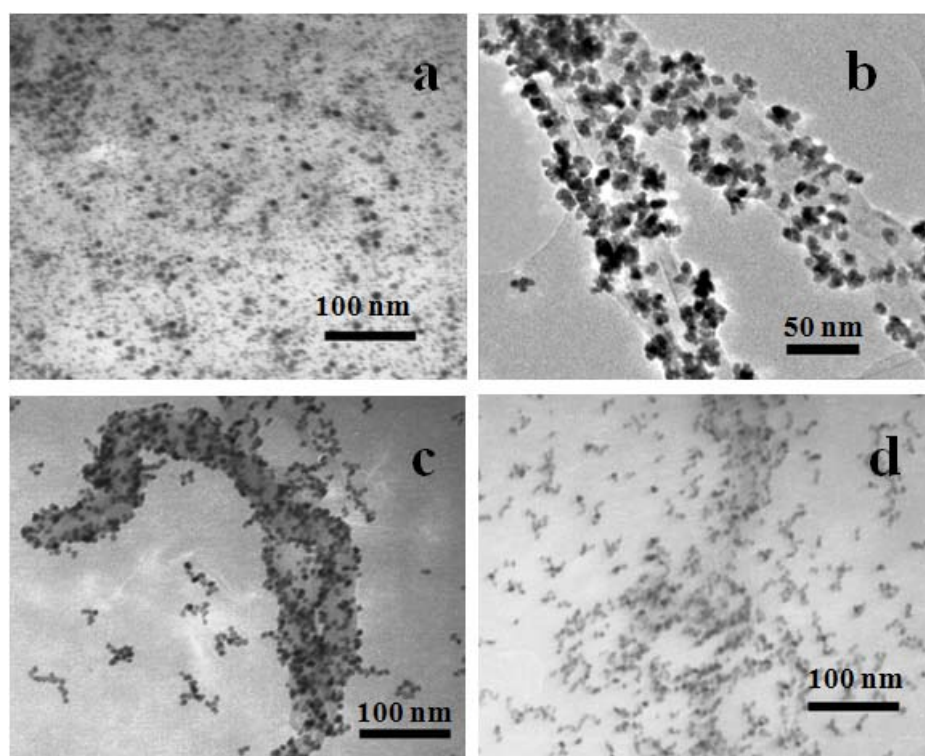
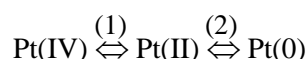


Figure S4. TEM images of Pt nanocrystals from controlled experiments: a) N_2 was bubbled into the solution to exclude O_2 ; b) Instead of NaNO_2 , NaCl was introduced into the solution with a Cl^-/Pt molar ratio of 6; c) Instead of NaNO_2 , NaClO_4 was introduced into the solution with a ClO_4^-/Pt molar ratio of 6; d) No any salt was introduced into the solution.

The reduction of Pt(IV) and the formation of Pt(0) can be divided into two steps:



When the reduction rate is low, Pt(0) atoms continuously and slowly accumulate until reaching a critical concentration. The nucleation occurs then, decreasing the concentration of Pt atoms and halting further nucleation. However, if the formation of Pt(0) is still faster than the consumption after the initial nucleation, the nucleation will last for a period, leading to the formation of Pt nanoparticles with a very broad size distribution. The formation rate of Pt(0) is determined by both step (1) and step (2). We performed several control experiments to verify the mechanism of this system. Firstly, when N₂ was bubbled into the reaction solution to exclude the dissolved O₂, it showed a relatively quicker color change and the formation of polydispersed nanocrystals even with the presence of NO₂⁻ (Figure S4a). It is known that the dissolved oxygen can oxidize Pt atoms to Pt (II) or Pt(II) to Pt(IV) with the aid of anions which can form complex with Pt(II) and Pt(IV) therefore reduce the formation of Pt(0). This indicates that oxygen etching is a key factor in slowing the reaction and the formation of monodispersed nanoparticles with certain morphology. Secondly, when no NaNO₂ was added into the solution, once again polydispersed nanocrystals were obtained (Figure S4d). This indicates that the presence of NO₂⁻ is another important factor. Then, what is the role of NO₂⁻ in the formation of HFNCs? It is predictable that Pt(IV) and Pt(II) may form complexes with NO₂⁻ and lower the formation rate of Pt(0). Also, the oxidation property of NO₂⁻ may further reduce the formation of Pt(0). It was reported that Pt(NO₂)₆²⁻ exhibited a lower reduction rate than PtCl₆²⁻.² We replaced NO₂⁻ with non-oxidative Cl⁻, which can also coordinate with Pt(IV) and Pt(II) just as NO₂⁻. As shown in Figure S4b, multi-armed Pt nanoparticles other than HFNCs were prepared, indicating a change in reacting mechanism. Then we replaced NO₂⁻ with ClO₄⁻, which is a bad ligand, the shape of nanocrystals formed is just similar to that with no salt added.

From the above discussion we can conclude that the oxygen etching, the oxidation and coordination effect of NO₂⁻ work together to slow down the formation of Pt(0), leading to a sudden nucleation and the formation of monodispersed nanocrystals. These particles mainly exposed Pt (111), due to its stability in the reaction environment as a low index facet. In

addition, PVP, besides serving as a protecting agent preventing nanocrystals from aggregation, has been proved to be a stabilizing agent for Pt (111), which retards the growth of nanocrystals along Pt (111) facet.³ Thus the nanocrystals preferentially grow on Pt (110) and Pt (100) and are finally enclosed by Pt (111). What's more important, the formation of atom steps on the nanocrystals' surface is also due to the oxidation etching of Pt by NO_2^- and dissolved oxygen.

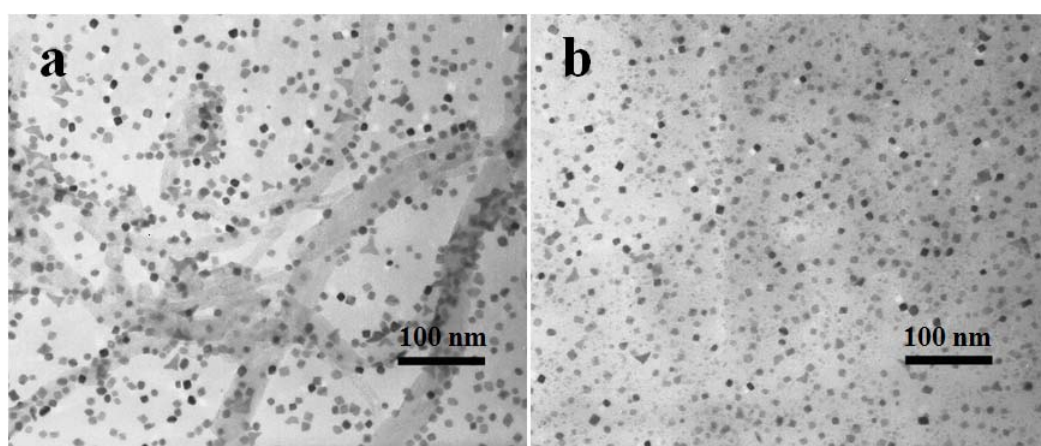


Figure S5. TEM image of HFNCs formed a) with CNTs added, and b) without CNTs added. The ration of NO_2^-/Pt is 6.

The addition of CNTs into the reaction is important to improve the monodispersity of the produced HFNCs and the reproducibility of the reaction (Figure S5). The reason is that the addition of CNTs can introduce heterogeneous nucleation sites, and then lead to a sudden and uniform nucleation of Pt(0), which is beneficial to the formation of monodispersed nanoparticles. When carbon black was used instead of CNTs in the preparation of Pt nanoparticles, similar results were obtained. This indicates that our discussion about the role of CNTs in the preparation of HFNCs is reasonable.

3. Preparation of Pt nanospheres/CNTs used as a comparison sample in electrocatalytic study

3mg CNTs was dispersed in 4.8 mL EG solution containing 3mM PVP ($M_w = 30k$). No

NaNO₂ was added. The solution was placed into an oil bath at 140°C for 2h. 0.05mL of 100mM H₂PtCl₆ solution was then added. The reaction was held in the oil bath for 1 hour. The Pt nanosphere/CNT composites were separated by centrifugation, and then washed with ethanol for 3 times. The TEM image of the sample was shown in Figure S6.

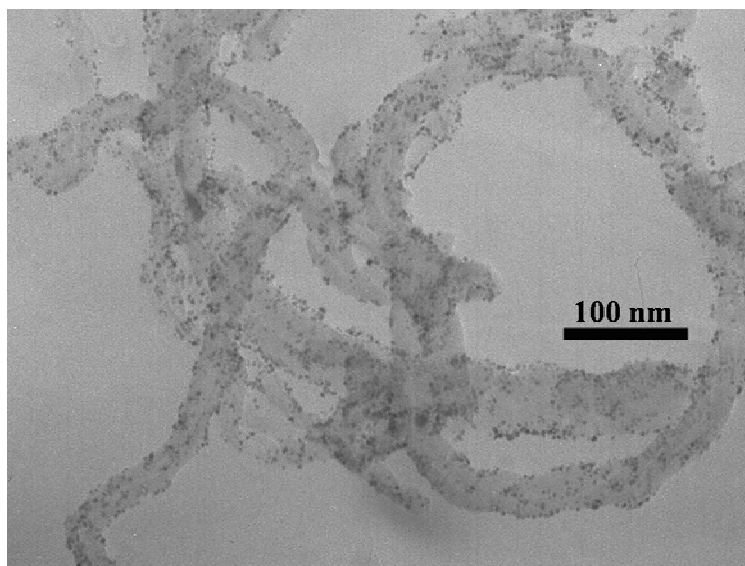


Figure S6. TEM image of Pt nanosphere/CNT sample

4. Electrochemical studies of the HFNC/CNT composites

The electrochemical measurements were conducted in a thermostated standard three-compartment electrochemical cell, using a disc electrode setup with a potentiostat and rotation control (Pine). An AgCl/Ag electrode (SCE) was used in all experiments. A Pt wire was used as the counter electrode. The electrolyte of 0.1 M HClO₄ was prepared using distilled water and concentrated HClO₄ (Aldrich).

Figure S7 shows the current-potential curves of the HFNC/CNT sample and the comparison Pt nanosphere/CNT sample for oxygen reduction reaction (ORR) recorded at room temperature with a scanning rate of 5 mV/s in O₂-saturated HClO₄ solution (0.1 M) with the rotation speed of 1600rpm. Figure S8 is the cyclic voltammograms of the two samples with a scanning rate of 100 mV/s in N₂-saturated HClO₄ solution (0.1 M).

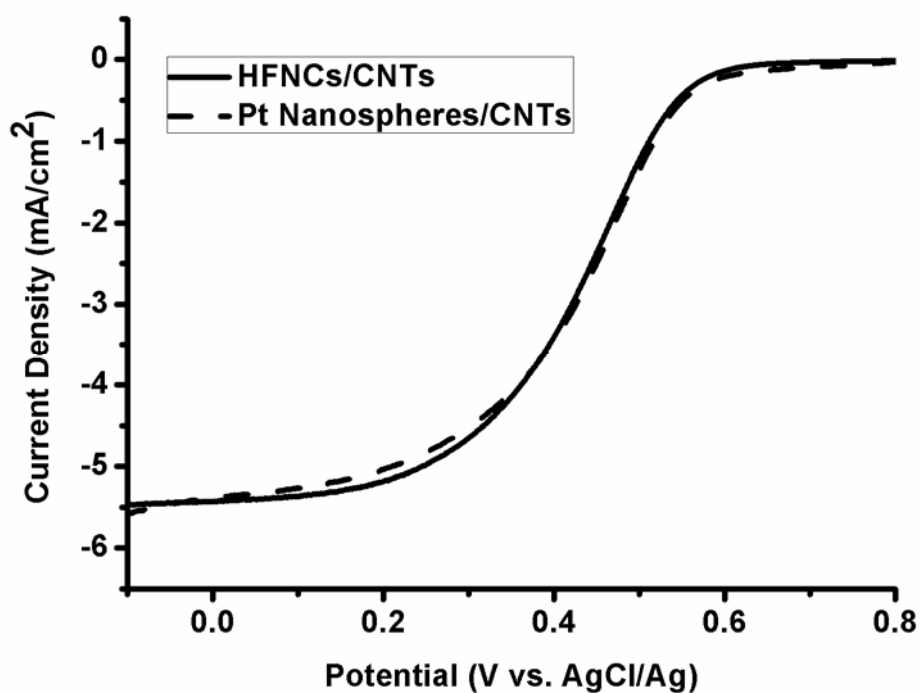


Figure S7. ORR polarization curves recorded at room temperature with a scanning rate of 5 mV/s in O₂-saturated HClO₄ solution (0.1 M), the rotation speed is 1600rpm.

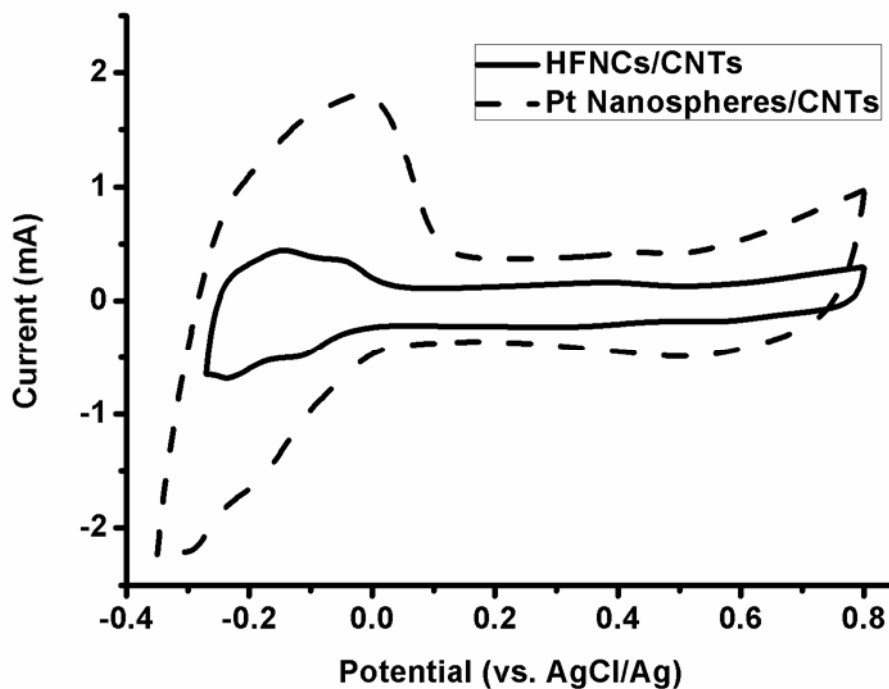


Figure S8. Cyclic voltammograms with a scanning rate of 100 mV/s in N₂-saturated HClO₄ solution (0.1 M).

5. HFNCs/CNTs as catalysts for selective oxidation of glycerol

Oxidation of glycerol was carried out at atmospheric pressure in a thermostat glass reactor (100 cm³) equipped with magnetic stirrer, thermocouple, and gas supply system. About 40 cm³ of 2 wt% of glycerol solution and 0.025 g catalyst were added into the reactor. Constant flow of oxygen (65 cm³/min) was introduced into the suspension when the temperature reached 60 °C. The aqueous solution was separated by filtration and analyzed using a high-performance liquid chromatography with photodiode array detector (PAD) and Alltech OA-1000 column (HPLC, Shimadzu LC-20A series). All products were confirmed by the UV spectra and retention times of the standard products purchased from Alfa SIGMA, Aesar and TCI.

References

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