Supplementary Information:

One-Step and Rapid Synthesis of "Clean" and Monodisperse Dendritic Pt Nanoparticles and Their High Performance Toward Methanol Oxidation and *p*-nitrophenol Reduction

Jun Wang, Xin-Bo Zhang, Zhong-Li Wang, Li-min Wang, Wei Xing, and Xiang Liu School of Chemical and Material Engineering, Jiangnan University, State Key Laboratory of Rare Earth Resource Utilization and State Key Laboratory of Electro-Analytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 130022 Changchun, China

1. Chemicals and materials

Chloroplatinic acid (H₂PtCl₆·6H₂O, Sino-Platinum Metal Co. LTD, Pt \geq 37.0%), potassium tetrachloroplatinate (K₂PtCl₄, Sino-Platinum Metal Co. LTD, Pt \geq 46.8%), methanol (CH₃OH, Beijing Chemical Works, >99.9%), ethanol (CH₃CH₂OH, Beijing Chemical Works, >99.7%), ascorbic acid (C₆H₈O₆, Beijing Chemical Works, >99.7%), sodium hydroxide (NaOH, Beijing Chemical Works, >99%), *p*-nitrophenol (C₆H₅NO₃, Aladdin Reagent, >99%), sodium borohydride (NaBH₄, Beijing Chemical Works, \geq 98%), polyvinylpyrrolidone (PVP, Aldrich, MW=360000), commerical carbon supported platinum catalyst (Pt/C, Johnson Matthey (JM) PLC, 20 wt %), activated carbon (Vulcan XC-72R, Cabot Corp.), Al₂O₃ powder (Aldrich, 0.5 and 3 µm), and Nafion solution (Sigma-Aldrich, 5 wt %) were used as received. Ultrapure water with the specific resistance of 18.2 MΩcm was obtained by reversed osmosis followed by ion-exchange and filtration. Glassy carbon electrode (GC, 5 mm in diameter) was purchased from Tianjin AidaHengsheng Tech. Co., China.

2. Preparation of dendritic Pt nanoparticles (DPNs)

In a typical synthesis, DPNs were synthesized just by mixing H_2PtCl_6 (2 mL, 18.9 mM), ascorbic acid (0.2 mL, 1 M) and NaOH (30 µL, 5 M) together in a beaker which contains 18 mL H₂O. After heating in water bath at 60 °C for only 10 min, the brown suspension containing monodisperse and well-defined DPNs was obtained. While different control experiments were performed, the total volume of the solution maintains 20.23 mL.

3. Catalytic reduction of *p*-nitrophenol

The aqueous solutions of *p*-nitrophenol (0.1 M) and NaBH₄ (1.5 M) were freshly prepared. 0.1 mL of *p*-nitrophenol solution and 1 mL of NaBH₄ solution were added into a quartz cuvette. Then, 0.05 mL of the brown suspension containing DPNs and 3.85 mL of H₂O were injected into the cuvette to start the reaction with the *n* (*p*-nitrophenol)/*n* (DPNs) ratio of 107. The intensity of the absorption peak at 400 nm was monitored by UV-vis spectroscopy as a function of time.

4. Preparation of the thin-film working electrode

29.5 mg XC-72R carbon dispersed in 10 mL ethanol was added into the as-prepared brown suspension. After durative sonication and agitation for 24 h, DPNs/XC-72R (20 wt %) was collected by consecutive washing/centrifugation cycles for three times with water. The collected product was then dried at 60 $^{\circ}$ C for 12 h.

The GC electrode was sequentially polished with 3 and 0.5 μ m Al₂O₃ paste (mixed with Al₂O₃ powder and ultrapure water). After the mechanical pretreatment, the electrode was cleaned by sonication in ultrapure water. To prepare the working electrode, 5 mg of the DPNs/XC-72R was dispersed in diluted Nafion alcohol solution which contained 1000 μ L ethanol and 50 μ L Nafion, and was sonicated for 1 h to obtain a uniform suspension. Next, 10 μ L of the suspension was pipetted onto the flat glassy carbon electrode. The coated electrode was then dried at room temperature for 30 min. The Pt loading was 0.0485 mg/cm².

5. Instrumentation

Powder X-ray diffraction (XRD) measurements were performed on a

Rigaku-Dmax 2500 diffractometer with Cu K α radiation ($\lambda = 0.15405$ nm). The morphology and dimensions of as-prepared samples were obtained using a field emission scanning electron microscopy instrument (Hitachi S-4800), operating at an accelerating voltage of 10 kV. Specimens for SEM were prepared by dispersing as-prepared product in ethanol by sonication for about 10 min, and then depositing the sample onto an ITO glass, attached to a SEM brass stub. Transmission electron microscope (TEM) and selected area electron diffraction (SAED) patterns were performed using a FEI Tecnai G2 S-Twin instrument with a field emission gun operating at 200 kV. Samples for all of these TEM experiments were prepared by dispersing the samples in ethanol with sonication for 30 min to ensure adequate dispersion of the nanostructures, and evaporating one drop of the solution onto a 300 mesh Cu grid, coated with a lacey carbon film. UV-Vis spectra were collected on a UV5800 modal spectrophotometer. XPS spectra were obtained with an ESCALABMKLL X-ray photoelectron spectrometer using an Al Ka source. Dynamic light scattering (DLS) data was obtained by Nano-ZS Zetasizer ZEN3600 (Malvern Instruments Ltd., U.K.). Fourier transform infrared spectroscopy (FT-IR) is obtained with BRUKER Vertex 70 FT-IR spectrometer. The electrochemical tests were carried out with a BioLogic VMP3 station. Raman spectrum was collected with a Renishaw 2000 model confocal microscopy Raman spectrometer with a CCD detector and a holographic notch filter at ambient conditions.



Fig. S1. Size distribution histograms for (A) DPNs and (B) the primary Pt nanoparticles. Their mean particle sizes are 31.1 and 3.7 nm, respectively.



Fig. S2. Dynamic light scattering plot of the obtained DPNs sample. The measured particle size is around 34.03 nm.



Fig. S3. XRD profile of the as-prepared DPNs.



Fig. S4. TEM images of Pt nanostructures prepared by (A) 0.5, (B) 1, and (C) 4 mL of the precursor solution of H_2PtCl_6 (18.9 mM) with other conditions unchanged.



Fig. S5. TEM images of Pt nanostructures prepared at different temperature with other conditions unchanged: (A) 0, (B) 30, and (C) 90 $^{\circ}$ C.



Fig. S6. TEM images of Pt nanostructures prepared (A) without or with (B) 20 and (C) $40 \ \mu$ L of the aqueous solution of NaOH (5 M) keeping other conditions unchanged.



Fig. S7. (A) FT-IR spectra of ascorbic acid and the DPNs after washing and drying, and (B) Raman spectrum of the DPNs.



Fig. S8. (A) XPS results of (a) PVP-directed DPNs after a consecutive centrifugation and washing cycle with water and ethanol for many times {the product is synthesized according to reference 10 [b] and the inset is the corresponding TEM image}, and (b) DPNs prepared with our strategy after washing with water twice, and (B) FT-IR spectrum of PVP-directed DPNs.



Fig. S9. SEM image of DPNs deposited on XC-72R carbon.



Fig. S10 (A) Cyclic voltammetry of DPNs/XC-72R, DPNs-PVP/XC-72R and commercial Pt/C catalyst taken in 0.5 M deaerated H_2SO_4 solution and (B) the corresponding ECSAs calculated by integrating hydrogen adsorption/desorption charges.



Fig. S11. Stable CV curves obtained for the DPNs/XC-72R, DPNs-PVP/XC-72R, and commercial Pt/C catalyst in the electrolyte of 0.5 M H_2SO_4 and 0.5 M CH_3OH at the sweep rate of 50 mV/s.



Fig. S12. The chronoamperometric curves of (a) DPNs/XC-72R and commercial Pt/C catalyst recorded at 0.67 V in 0.5 M H_2SO_4 and 0.5 M CH_3OH deaerated solution at room temperature.