

Supporting Information

Monodispersed Platinum Nanocubes for Enhanced Electrocatalytic Properties in Alcohol Electrooxidation

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Synthesis of Pt nanocubes. The Pt nanocubes were prepared by reducing Pt salt in organic-based solution. All chemicals used were of analytical grade. For solution of dissolved Platinum acetylacetonate salt ($\text{Pt}(\text{acac})_2$, Aldrich), the 5 mL 1-octadecene solution containing 2 mM $\text{Pt}(\text{acac})_2$ and 25 mg PVP was prepared in a 30 mL vial. For perfect dissolution of Pt salt, the mixture solution were dissolved with continuous stirring and kept for 30 min at 70 °C. On the other hand, the 10.78 mL 1-octadecene ($\text{C}_{18}\text{H}_{36}$, Aldrich) solution containing 9.22 mL oleylamine ($\text{C}_{18}\text{H}_{37}\text{N}$, Aldrich), 12.6 mg oxalic acid ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, Johnson Matthey Co.) and 25 mg poly(vinyl pyrrolidone) (PVP, MW=29,000, Aldrich) was prepared in a three-neck flask (50 mL) under a nitrogen atmosphere. The mixed solutions were raised by 7 °C min^{-1} and kept for 1 h at 250 °C. The dissolved Pt salt solution with yellow color was injected into heating solvent with continuous string and kept for 2 h at 250 °C until Pt salts were completely reduced under a nitrogen balnket. The resulting colloid solution was rapidly cooled into hexane and black colloid was observed indicating the formation of Pt nanoparticles.

Preparation of carbon-supported Pt nanocube catalyst. The carbon (Vulcan XC-72R) powder was stirred in 5 M HCl solution at 50 °C for 12 h and then washed with water and ethanol several times to remove impurity and HCl. The 50 mL colloid solution containing as-synthesized Pt nanocubes (120.4 mg) was putted to 30 mL of acetic acid (2 M) and 20 mL acetone for well-depositd Pt on carbon black and removed the organic materials. The Vulcan XC-72R (481.6 mg) as supports were added to the solution and mixed with continuous stirring at 70 °C for 12 h. The resulting powder was precipitated and washed with acetone, ethanol, and water to remove surfactant and impurity. For comparison of effect of the PVP as an additive agent, the Pt NPs synthesized in absence of PVP in same experimental condition.

Structural analysis. For the structure analysis of the catalysts, X-ray diffraction (XRD) analysis was carried out using a Rigaku X-ray diffractometer with Cu K_α ($\lambda = 0.15418$ nm) source with a Ni filter. The source was operated at 40 kV and 100 mA. The 2θ angular scan from 20° to 80° was explored at a scan rate of 5° min^{-1} . For all the XRD measurement, the resolution in the scans was kept at 0.02°. The

morphology and size distribution of the catalysts were characterized by field-emission transmission electron microscopy (TEM) using a Tecnai G2 F30 system operating at 300 kV. TEM samples were prepared by placing drops of catalyst suspension dispersed in ethanol on a carbon-coated copper grid.

Electrochemical analysis. Electrochemical properties of the catalysts were measured in a three-electrode cell at 25 °C using a potentiostat (CH Instrument, CHI 700C). A Pt wire and Ag/AgCl (in saturated KCl) were used as a counter and reference electrode, respectively. The catalyst ink was prepared by ultrasonically dispersing catalyst powders in an appropriate amount of Millipore water and 5 wt% Nafion[®] solution (Aldrich). The catalyst ink was contained to 2 mg metal of all catalysts, 150 μ L of Millipore water, 57.2 μ L of 5 wt% Nafion[®] solution, and 500 μ L of 2-propanol solution (C₃H₈O, Sigma). The catalyst ink was dropped onto a glassy carbon working electrode (area \sim 0.0706 cm²). After drying in 50 °C oven, total loading of catalyst was 20 μ g cm⁻². To compare electrocatalytic properties of the catalysts, cyclic voltammograms (CVs) were obtained between -0.2 to +1.0 V in Ar-saturated 0.1 M HClO₄ solution with a scan rate of 50 mV s⁻¹ at 25 °C. The electrochemical active surface areas of these catalysts were determined by integrating hydrogen adsorption/desorption areas of the CVs. The EASAs measured by integrating the charges in the hydrogen desorption regions were 71.7 and 98.9 m²·g⁻¹ for cubic Pt/C and spherical Pt/C, respectively. To evaluate electrocatalytic activities of the as-prepared catalysts, CVs were obtained between -0.2 to +1.0 V in Ar-saturated 0.1 M HClO₄ + 2 M CH₃OH, 0.1 M HClO₄ + 2 M CH₃CH₂OH, and 0.1 M HClO₄ + 2 M HCOOH with a scan rate of 50 mV s⁻¹ at 25 °C, respectively.

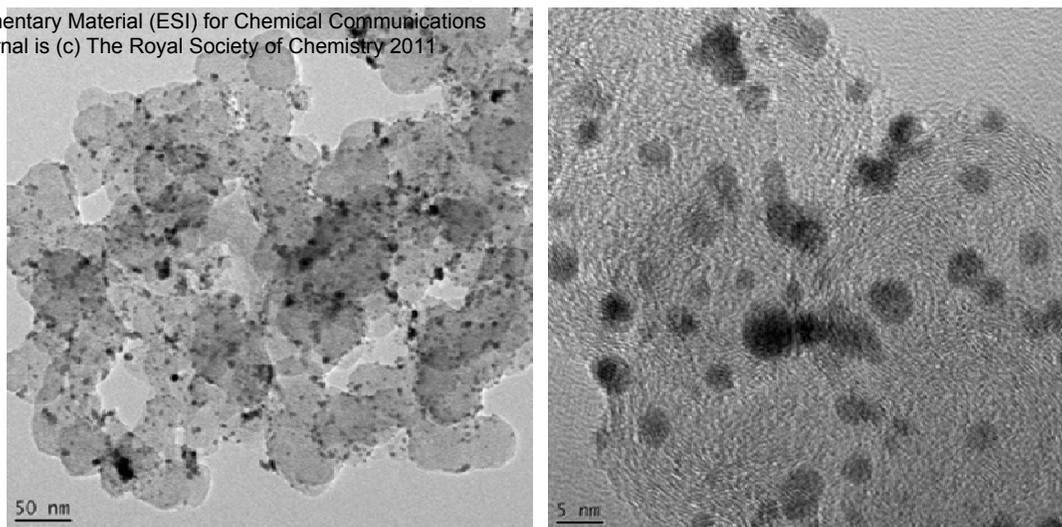


Figure S1. TEM and HR-TEM images of spherical Pt/C (E-TEK, Co.).

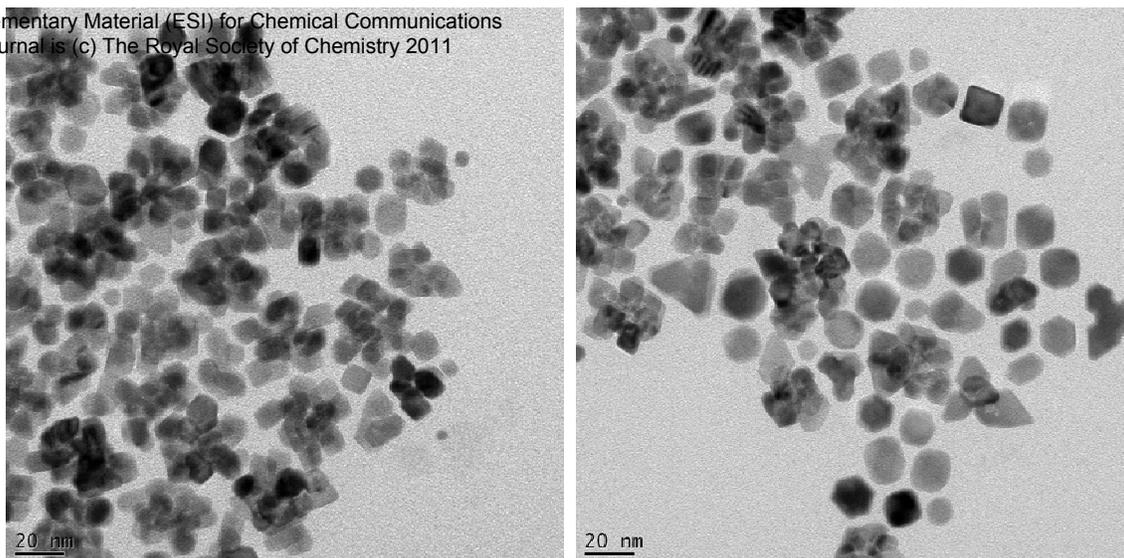


Figure S2. Field-emission transmission electron microscopy (FE-TEM) images of Pt nanoparticles prepared in the absence of PVP.

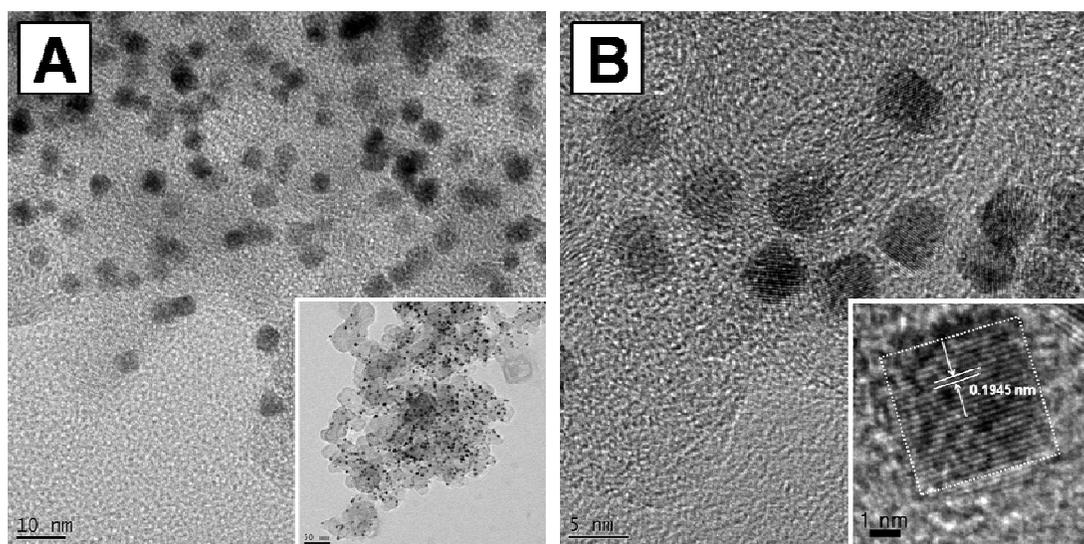


Figure S3. (A) Field-emission transmission electron microscopy (FE-TEM) and (B) high-resolution transmission electron microscopy (HR-TEM) images of as-synthesized Pt nanocubes deposited on Vulcan XC-72R.

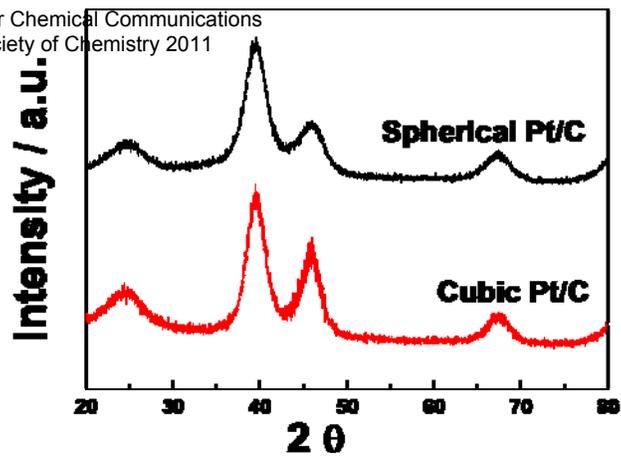


Figure S4. X-ray diffraction patterns (XRD) of Pt nanocubes deposited on carbon black (Vulcan XC-72R) and spherical Pt/C.