Supporting Information

Interfacial Synthesis of Two-Dimensional Dendritic Platinum Nanoparticles Using Oleic Acid-in-Water Emulsion

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Materials and Methods

Chemicals and Materials

Chemicals including Chloroplatinic (IV) acid hydrate ($H_2PtCl_6 \cdot xH_2O$, ≥99.9%), Oleic acid (90%), Pluronic F-127, Sodium borohydride ($NaBH_4$, ≥98%), and Perchloric acid (70%) were purchased from Sigma-Aldrich Inc. Sulfuric acid (95%), Methyl alcohol (99.5%) was purchased from Samchun. Commercially available carbon-supported platinum catalyst was purchased from Alfa Aesar (20 wt% Pt, HiSPECTM 3000, Johnson Matthey). All chemicals were used without further purification. Deionized (DI) water with a resistivity of 18 M Ω-cm was used in all cases. All glassware were treated with a piranha solution (H_2SO_4:H_2O_2 = 7:3 v/v, warning: this solution is a very harmful and strong acidic oxidant) for 30 min, and rinsed with DI water for several times.

Interfacial synthesis of 2D dendritic platinum nanoparticle

2D dendritic platinum nanoparticle was synthesized in a 30 ml glass vial. 5.0 ml chloroplatinic (IV) acid hydrate ($H_2PtCl_6 \cdot xH_2O$, 2.0 mg/ml) aqueous solution containing 0.2 mM Plurionic F127 was prepared in vial, and 5.0 ml of aqueous sodium borohydride ($NaBH_4$, 5 mM) was added to the solution with stirring. Under vigorous stirring, 8 ml of oleic acid immediately was introduced into the solution to create oleic acid-in-water emulsions. The reaction in the emulsion mixture was allowed to proceed for 30 min while it was stirred continuously with a magnetic stirrer. After 10 min the stirring was stopped and the mixture was separated into water and oleic acid, and aqueous phase was collected. The synthesized nanoparticles in aqueous solution were isolated by centrifugation (10,000 rpm, 20 min) and three times washed with DI water.

Characterization of the synthesized nanoparticle

The morphological properties of the synthesized nanoparticles were characterized by transmission electron microscopy (TEM) and atomic force microscopy (AFM). 10 μl of solution was dropped onto a carbon-coated 300 mesh TEM grid (Inc. Ted Pella) and allowed to remove the solution by using filter paper within 1 min and repeated 5 times.

TEM images were obtained with a Carl Zeiss LIBRA 120 electron microscope operating at an acceleration voltage of 120 kV. AFM images were obtained with a NX10 (Park sytstems). High resolution TEM studies were performed in a JEOL JEM-2100F electron microscope operating at an acceleration voltage of 200 kV. Energy-dispersive X-ray spectroscopy (EDS) analysis was performed by JEOL JEM-3010 electron microscope with Oxford Instruments EDS operating at an acceleration voltage of 300 kV.

Electrochemical activity measurements

All electrochemical catalytic activities of platinum nanoparticles were characterized using an Iviumstat workstation in a three-electrode cell. Rotating disk electrode was used for the measurement. A catalyst loaded the glassy carbon electrode (GCE, 5 mm diameter), an Ag/AgCl electrode (KCl saturated) and a platinum electrode served as working, reference and counter electrodes, respectively. 8.0 μl of catalyst droplet containing 3 μg of platinum nanoparticle was dropped onto GCE and dried at room temperature. The linear sweep voltammetry was performed between 0.0 and 1.0 V with a scan rate 50 mV s^{-1} in O_2 saturated 0.1 M $HClO_4$ aqueous solution at 1600 rpm. Cyclic voltammetry was conducted between -0.2 and 1.0 V in N_2 saturated 0.5 M H_2SO_4 aqueous solution in the presence of 1.0 M methanol at a scan rate of 50 mV s^{-1}.

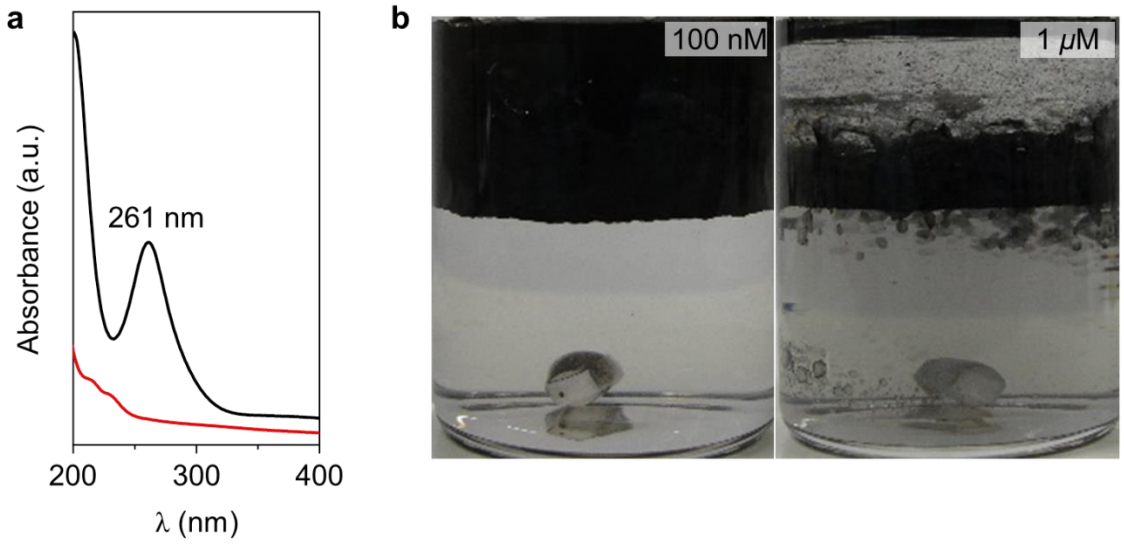

Figure S1. (a) UV-visible spectrum of the reaction solution at 0 min (black) and after 30 min of reaction (red). (b) Photographs of the reaction solutions after stopping stirring. Note that the colour of oleic acid is changed to be black at 100 nM (left) and 1 μM (right) of the block copolymer concentration, indicating the transfer of nanoparticle to the oleic acid layer.

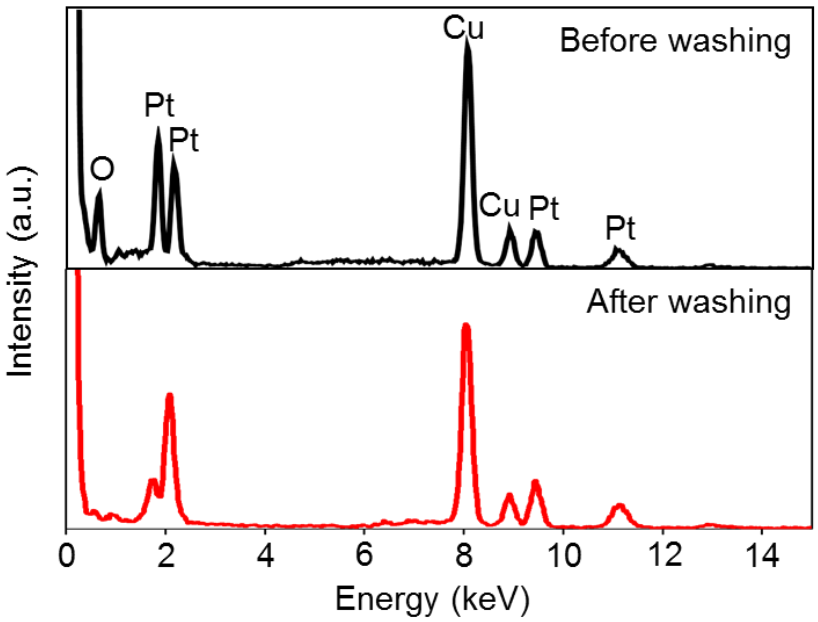

Figure S2. EDS spectra of 2D dendritic platinum nanoparticle before and after washing with ethanol.

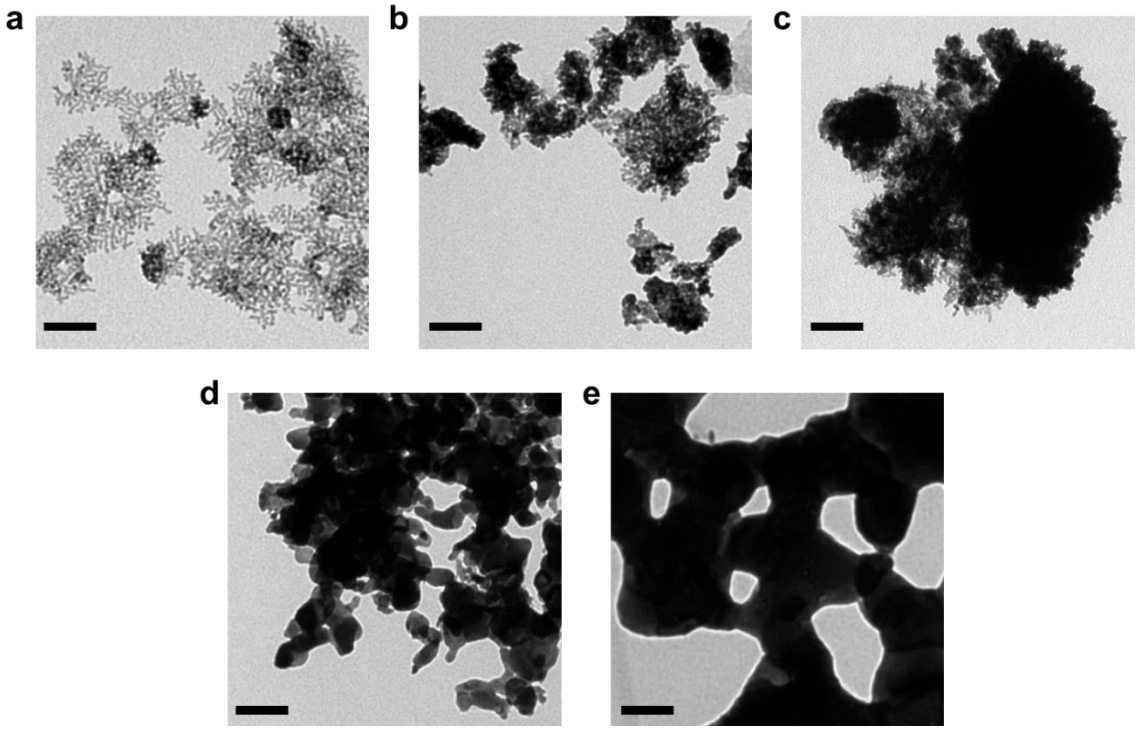

Figure S3. TEM images of 2D dendritic platinum nanoparticle in case of (a) without heat treatment, (b) at 200 °C, (c) at 300 °C, (d) at 400 °C and (e) at 500 °C for 1 hr annealing. Note that the shape of nanoparticle changes from dendrites to aggregates. Scale bar = 50 nm.

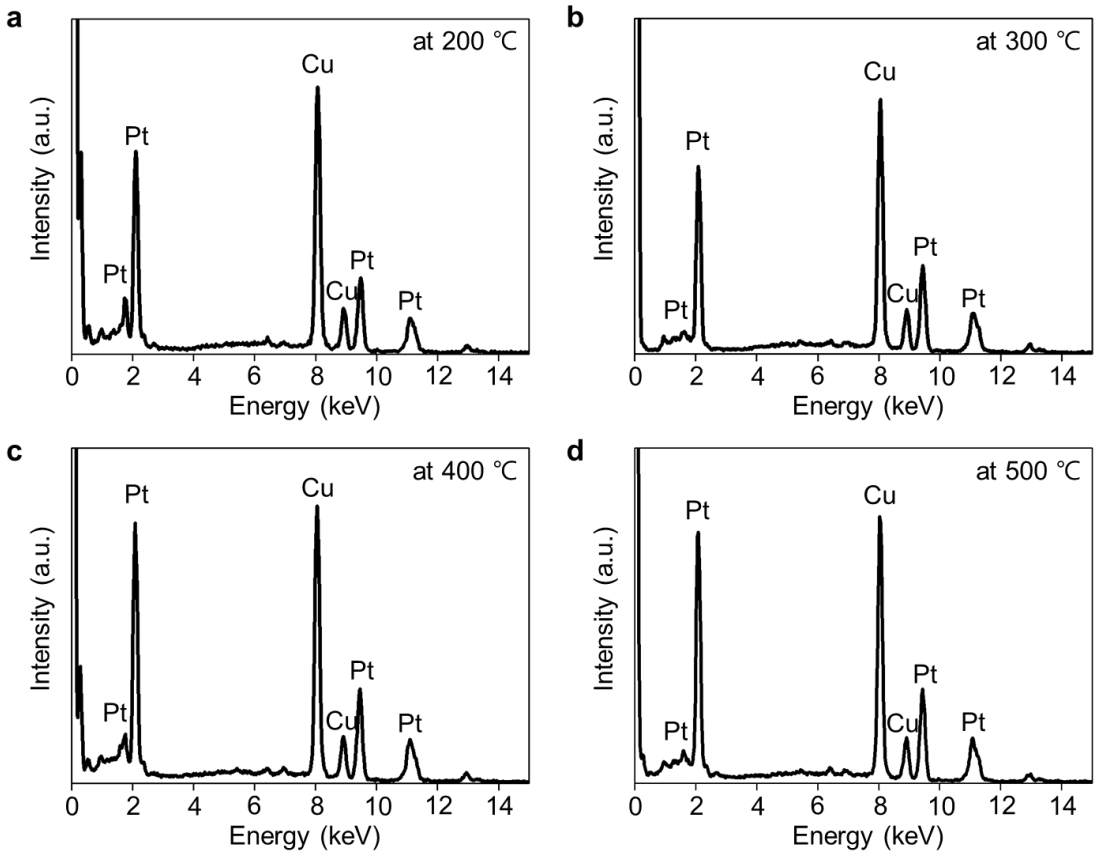

Figure S4. EDS spectra of 2D dendritic platinum nanoparticle for 1 h annealing (a) at 200 °C, (b) at 300 °C, (c) at 400 °C, and (d) at 500 °C, respectively.

	Electrochemical active surface area (EASA) (m^2/g)
2D dendritic Pt nanoparticle before washing with ethanol	14.26
2D dendritic Pt nanoparticle after washing with ethanol	71.24

Table S1. Calculated electrochemical active surface area of 2D dendritic platinum nanoparticle before and after washing with ethanol.