# Supporting Information for

## Controlling and Self Assembling of Monodisperse Platinum Nanocubes as Efficient Methanol Oxidation Electrocatalysts

Xiuhui Sun, Xing Zhu, Nan Zhang, Jun Guo, Shaojun Guo, Xiaoqing Huang\* Email: hxq006@suda.edu.cn

#### 1: Materials and methods

- 1.1 Chemicals: Platinum(II) acetylacetonate (Pt(acac)<sub>2</sub>, 97%) and cetyltrimethylammonium chloride (CTAC, AR) were purchased from Sigma-Aldrich. FeCl<sub>3</sub> 6H<sub>2</sub>O, CoCl<sub>3</sub> 6H<sub>2</sub>O, NiCl<sub>2</sub> 6H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub> 9H<sub>2</sub>O, NaCl, formaldehyde aqueous solution (40%), PVP (K30, AR), and benzyl alcohol (AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the chemicals were used as received without further purification. The water (18 MΩ/cm) used in all experiments was prepared by passing through an ultra-pure purification system (Aqua Solutions).
- 1.2 Preparation of monodisperse Pt nanocubes: In a typical preparation of monodisperse Pt nanocubes, Pt(II) acetylacetonate (Pt(acac)<sub>2</sub>, 10.0 mg), poly(vinylpyrrolidone) (PVP, MW=30000, 200.0 mg) and 2.5 mL formaldehyde solution (40%) were mixed together with 10 mL benzyl alcohol. The resulting homogeneous yellow solution was transferred to a 20-mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 150 ℃ for a 10 h before it was cooled to room temperature. The black nanoparticles were precipitated by acetone, separated via centrifugation and further cleaned by an ethanol-acetone mixture.
- 1.3 Preparation of Pt nanocube assemblies: In a typical preparation of monodisperse Pt nanocubes, Pt(II) acetylacetonate (Pt(acac)<sub>2</sub>, 10.0 mg), poly(vinylpyrrolidone) (PVP, MW=30000, 200.0 mg), ferric chloride hexahydrade (FeCl<sub>3</sub> 6H<sub>2</sub>O, 6.75 mg) and 2.5 mL formaldehyde solution (40%) were mixed together with 10 mL benzyl alcohol. The resulting homogeneous brown-yellow solution was transferred to a 20-mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 150 °C for a 10 h before it was cooled to room temperature. The black nanoparticles were precipitated by acetone, separated via centrifugation and further cleaned by an ethanol-acetone mixture.
- 1.4 Characterizations: Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were conducted on an FEI Tecnai F20 transmission electron microscope at an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) images were taken with a Zeiss scanning electron microscopy. The samples were prepared by dropping ethanol dispersion of samples onto carbon-coated copper TEM grids using pipettes and dried under ambient condition. Powder X-ray diffraction (PXRD) patterns were collected on a Shimadzu XRD-6000 X-ray diffractometer. The concentration of catalysts was determined by the inductively coupled plasma atomic emission spectroscopy (710-ES, Varian, ICP-AES).

#### 1.5 Methanol electro-oxidation measurements:

A three-electrode cell was used to do the electrochemical measurements. The working electrode was a glassy-carbon Rotating Disk Electrode (RDE) (diameter: 5 mm, area:  $0.196 \text{ cm}^2$ ) from Pine Instruments. Ag/AgCl (3 M Cl<sup>-</sup>) was used as reference electrode. Pt wire was used as counter electrode. 10 µL Ethanol dispersion of Pt catalysts (2.5 mg Pt/mL for Pt nanocube assemblies and 2.3 mg Pt/mL for Pt nanocubes) was deposited on a glassy carbon electrode to obtain the working electrodes after the solvent is dried naturally. The electrochemical active surface area (EASA) measurements were determined by integrating the hydrogen adsorption charge on the cyclic voltammetry (CV) at room temperature in nitrogen saturated 0.1 M HClO<sub>4</sub> solution. The potential scan rate was 50 mV/s for the CV measurement. Before cyclic voltammetry measurements, 50 cycles of potential sweeps between 0.05 V and 1.26 V *vs* reversible hydrogen electrode (RHE) were applied. Methanol electrooxidation measurements were conducted in a 0.1 M HClO<sub>4</sub> + 0.2 M CH<sub>3</sub>OH solution. The scan rate for methanol electrooxidation was 50 mV/s. For comparison, Commercial Pt black were used as the baseline catalysts, and the same procedure as described above was used to conduct the electrochemical measurement, except that the Pt loadings were 30 µg Pt for commercial Pt black.

### 2: Supplementary Figures



Figure S1. Additional Low-magnification TEM images for the monodisperse Pt nanocubes.



**Fig. S2.** TEM image of the Pt nanocrystals obtained from the reaction with the same condition used in the synthesis of monodisperse Pt nanocubes but (a, b) in the absence of formaldehyde, (c, d) in the presence of 0.4 mL formaldehyde , (e, f) in the presence of 4.0 mL formaldehyde, and (g. h) by changing DMF with benzyl alcohol.



**Fig. S3.** Additional low-magnification (a, b) SEM, (c) TEM and (d) HAADF-STEM images for the unique Pt nanocube assemblies. (e) SEM-EDX for the Pt nanocube assemblies. There was  $\sim$ 3% of Fe in the Pt nanocube assemblies.



**Fig. S4.** (a) TEM image of an individual Pt nanocube assembly and (b) its corresponding SAED image. (c) HRTEM image on the edge of an individual Pt nanocube assembly.



**Fig. S5.** Additional TEM images of Pt nanostructures prepared using the standard procedure for the preparation of Pt nanocube assemblies, except for the use of different amount of FeCl<sub>3</sub>: (a) 1.35 mg, (b) 2.7 mg and (c) 13.5 mg. TEM images of Pt nanostructures prepared using the standard procedure for the preparation of Pt nanocube assemblies, except for changing FeCl<sub>3</sub> with (d) NaCl, (e) MnCl<sub>2</sub> and (f) CoCl<sub>3</sub>.



**Fig. S6.** TEM image of the Pt nanocrystals obtained from the reaction with the same condition used in the synthesis of unique Pt nanocube assemblies but changing  $FeCl_3$  with  $Fe(NO_3)_3$ .



Fig. S7. Typical TEM images of the commercial Pt black.



**Fig. S8.** Cyclic voltammograms (1st, 100th and 250th cycle) of (a) Pt nanocubes and (b) commercial Pt black for methanol oxidation. Potential was continuously scanned between 0.05 and 1.26 V *vs* reversible hydrogen electrode (RHE) for 250 cycles at 50 mV s<sup>-1</sup> in 0.1 M HClO<sub>4</sub> + 0.2 M methanol.