

# Electronic Supplementary Information

## **Large-scale template-free synthesis of ordered mesoporous platinum nanocubes and their electrocatalytic property**

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## **Experimental details**

### **Chemicals**

Hexachloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ), ethylene glycol (EG, >99%) and polyvinylpyrrolidone (PVP,  $M_w \approx 55000$ ) from Sigma-Aldrich; Hydrochloric acid (HCl, 37wt %), all other solvents (acetone, hexane and ethanol) and commercial Pt black (with an average size less than 10nm) from Aladdin, China were used for the synthesis of the Pt mesocrystals. All the chemicals were used as received without further purification.

### **Synthesis of mesoporous Pt nanocubes**

In a typical synthesis, 2.5 mL ethylene glycol (EG) was firstly refluxed for 5 min at 170°C in the flask. Then 1.7 mL of 35wt% HCl solution was added under vigorous stirring. Subsequently, 3.2 mL of PVP 0.375 M and 1.5 mL of 0.625M  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  in EG were added into the above solution for 32 times during a 16 min period. After the addition of the reactants, the solution was further heated for 20 min at 170°C. The product was collected by centrifugation and washed several times using acetone, ethanol and hexane. Finally, the Pt NCs were dispersed in ethanol solution. To study the effect of reaction time, Pt NCs under different reaction time were collected.

### **Characterizations:**

Transmission electron microscope (TEM) and high resolution TEM images were taken by using a JEOL JEM-2100F microscope at the accelerating voltage of 200 kV. High-angle annular dark-field scanning TEM (HAADF-STEM) images and Scanning electron microscopy (SEM) images were obtained using a Magellan 400 microscope

at the accelerating voltage of 30 kV. Wide-angle and low-angle powder X-ray diffraction (XRD) profiles were recorded with a D8 ADVANCE diffractometer with Cu K $\alpha$  radiation.

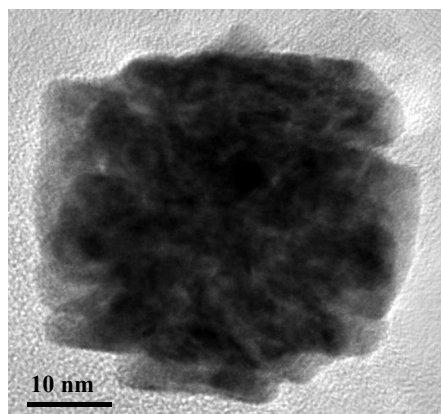
### **Electrochemical analysis:**

Cyclic voltammograms (CVs) curves were achieved by using a CHI 600C electrochemical analyzer (CH Instrument, USA). A conventional three-electrode cell was used, including an Ag/AgCl electrode as a reference electrode, a platinum wire as a counter electrode, and a glassy carbon electrode (GCE, 3 mm in diameter) modified by catalyst as a working electrode. Prior to the surface coating, the GCE was polished carefully with 0.05  $\mu\text{m}$  alumina powder and rinsed with deionized water and then dried at room temperature. After being carefully cleaned, the samples were coated on the surface of GCE at the loading of 4 $\mu\text{g}$ . Therefore, the Pt loading was 56.6  $\mu\text{g}/\text{cm}^2$ . Then, Nafion solution (2.0  $\mu\text{L}$ , 1wt%) was coated on the surface and was dried completely at room temperature. The electrochemical active surface area (ECSA) 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 50mV/s for the CV measurement. Methanol oxidation reaction (MOR) measurements were carried out in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing 1.0 M methanol. Formic acid oxidation reactions (FOR) measurements were carried out in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing 0.5 M formic acid. The scan rate for MOR and FOR measurement was 50mV/s. For comparison, Commercial Pt black (Aladdin) were used as the baseline catalysts, and the same procedure as

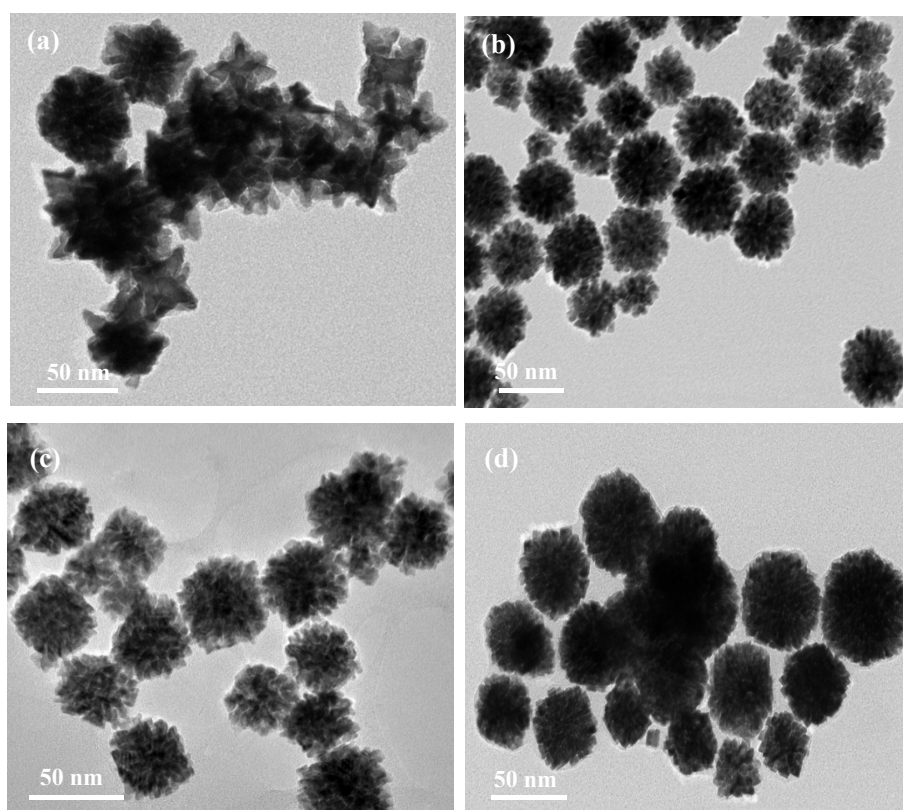
described above was used to conduct the electrochemical measurement, except that the Pt loadings were  $70.7 \mu\text{g}/\text{cm}^2$  for Pt black catalysts.

**Movie S1**

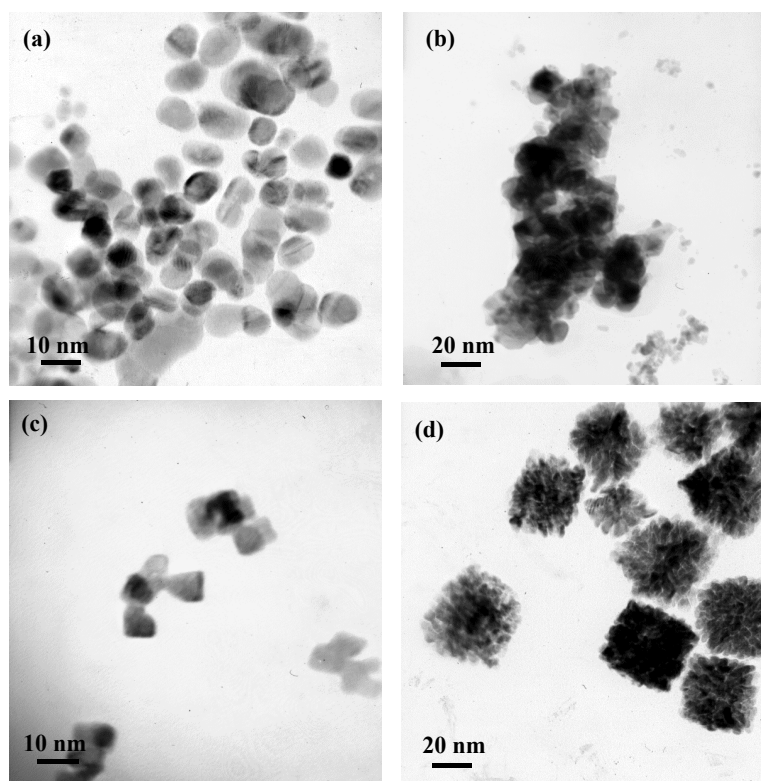
Three-dimensional TEM images of the ordered mesoporous Pt NC.



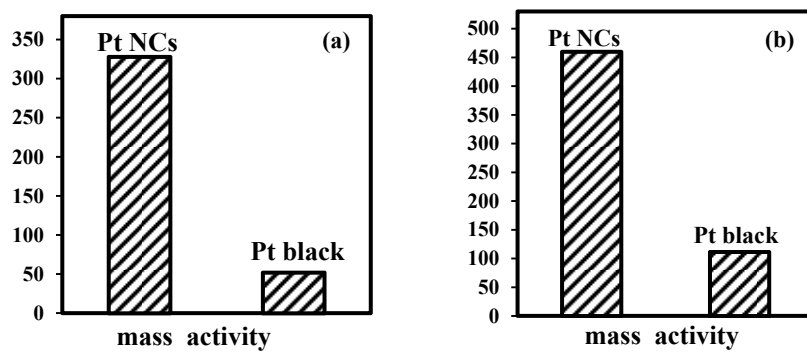
**Figure S0.** TEM image of Pt nanoparticles obtained by reacting for 40 min.



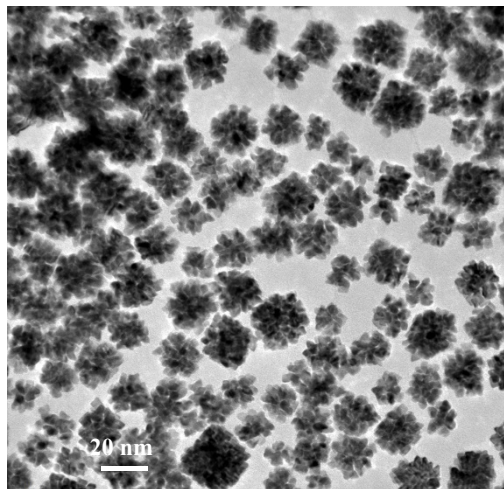
**Figure S1.** TEM images of Pt nanoparticles obtained by adding PVP with different concentrations (a) without PVP, (b) 0.1875 M PVP, (c) 0.375 M PVP and (d) 0.75 M PVP.



**Figure S2.** TEM images of Pt nanoparticles obtained by adding (a) no additive, (b) NaOH, (c) HNO<sub>3</sub>, and (d) HCl.



**Figure S3.** The mass activities of Pt mesocrystals and commercial Pt black (a) in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1.0 M methanol solution, (b) in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M HCOOH solutions. The scan rate was 50 mV/s.



**Figure S4.** TEM image of mesoporous Pd nanocubes.