

## Supporting information:

# The Role of Anisotropic Structure and Its Aspect Ratio: High-Loading Carbon Nanospheres Supported Pt Nanowires and Their High Performance Toward Methanol Electrooxidation

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### 1. Chemicals and materials

Chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , Sino-Platinum Metal Co. LTD, Pt > 37.0%), formic acid (HCOOH, Aldrich, >97%), methanol ( $\text{CH}_3\text{OH}$ , Burdick & Jackson Crop., >99.9%), ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ , Beijing Chemical Works, China, >99.7%), commercial carbon supported platinum catalyst (Pt/C, Johnson Matthey (JM) PLC, 60 wt %), activated carbon (Vulcan XC-72R and Vulcan XC-72, Cabot Corp.),  $\text{Al}_2\text{O}_3$  powder (Aldrich, 0.5  $\mu\text{m}$  and 3  $\mu\text{m}$ ), and Nafion solution (Sigma-Aldrich, 5 wt %) were used as received. Ultrapure water with the specific resistance of 18.2  $\text{M}\Omega \cdot \text{cm}$  was obtained by reversed osmosis followed by ion-exchange and filtration. Glassy carbon electrode (GC, 4 mm in diameter) was purchased from Tianjin AidaHengsheng Tech. Co., China.

### 2. Preparation of the high-loading carbon nanospheres supported single-crystal Pt nanowires

### (NWs) catalysts

In a typical synthesis, 15 mg Vulcan XC-72R nanospheres employed as the support were dispersed in 40.5 mL ultrapure water under ultrasonication condition for 30 min. 6.08 mL H<sub>2</sub>PtCl<sub>6</sub> solution (0.02 M) and 3 mL HCOOH were added to the carbon containing water. Another process in ultrasonication was carried out for 30 min to ensure the dispersion. The obtained mixture was then stored at room temperature for 72 h. After the reduction, the products were washed with ultrapure water and dried at room temperature. A sample of Pt NWs on Vulcan XC-72 nanospheres was prepared using the same procedure except Vulcan XC-72 was employed.

To investigate the dependence of morphology of Pt NWs on the reaction temperature and time, control experiments at room temperature for different reaction times (12, 24, 36, 48, and 60 h) and at different reaction temperatures (40 and 60 °C) for 10 and 20 h were carried out.

### 3. Preparation of the thin-film working electrode

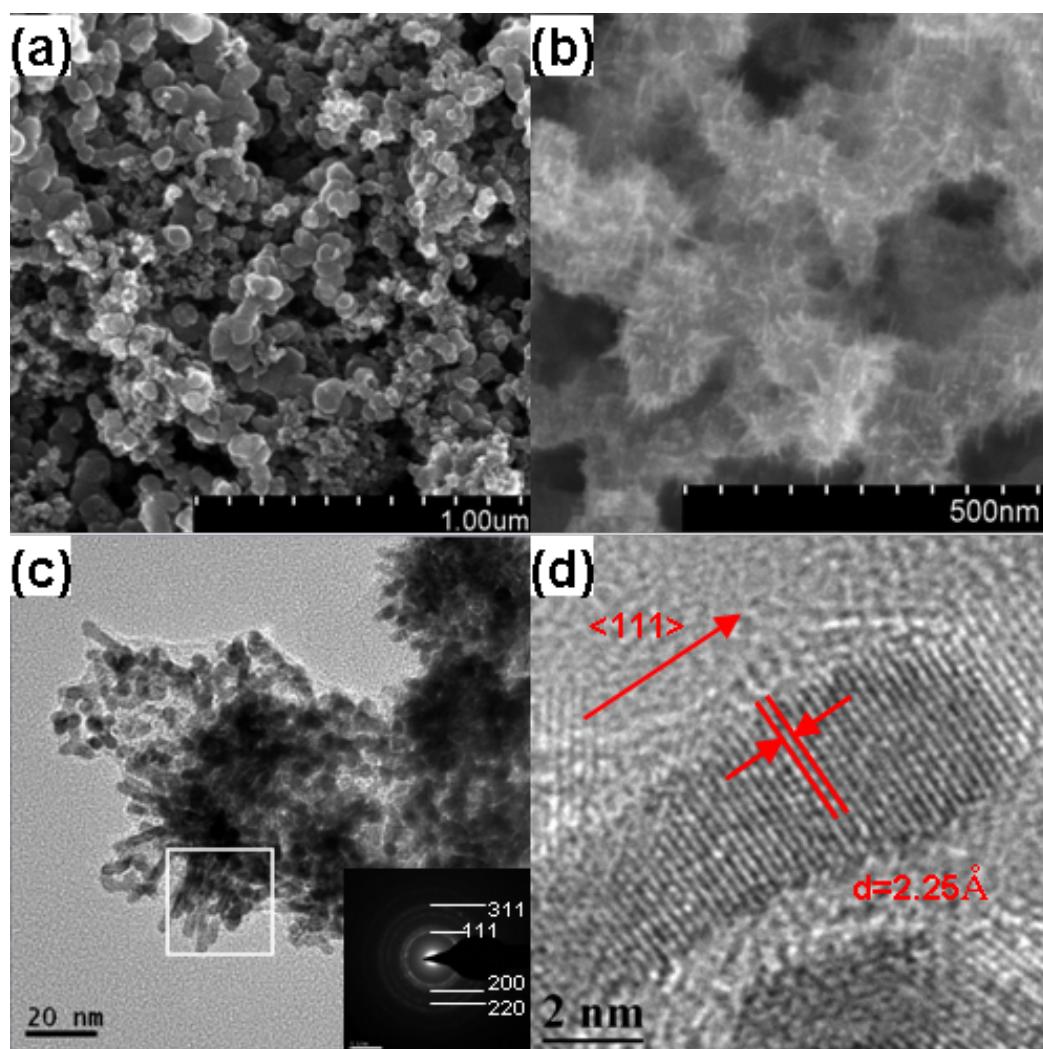
The GC electrode was sequentially polished with 3 µm and 0.5 µm Al<sub>2</sub>O<sub>3</sub> paste (mixed with Al<sub>2</sub>O<sub>3</sub> powder and ultrapure water). After the mechanical pretreatment, the electrode was cleaned by sonication in distilled water and finally rinsed by ultrapure water.

To prepare the working electrode, 5 mg of the catalyst was dispersed in diluted Nafion alcohol solution which contained 1000 µL ethanol and 50 µL Nafion solution (Aldrich, 5 wt % Nafion), and was sonicated for 30 min to obtain a uniform suspension. Next, 10 µL 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 0.08 mg/cm<sup>2</sup>.

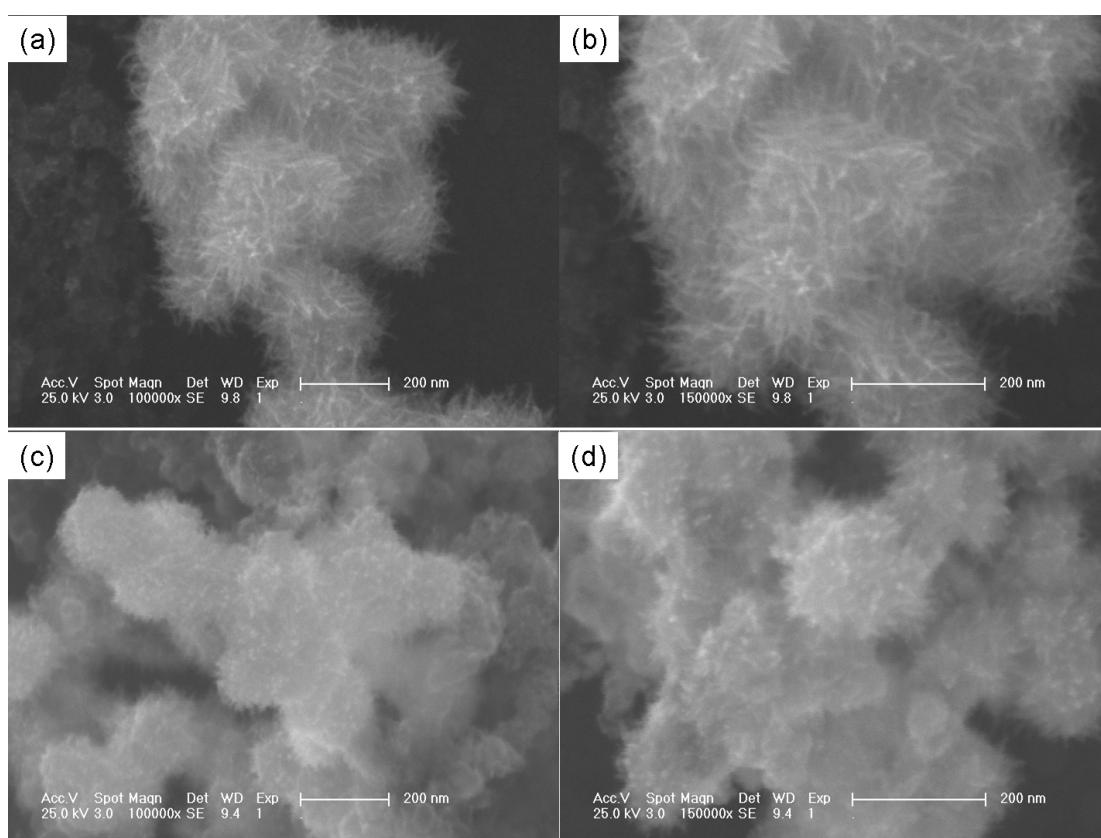
### 4. Catalyst characterization

#### 4.1 Scanning electron microscopy (SEM) and transmission electron microscope (TEM)

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 sonicating for about 1 min, and then depositing the suspension onto a piece of ITO glass, attached to a SEM brass stub.



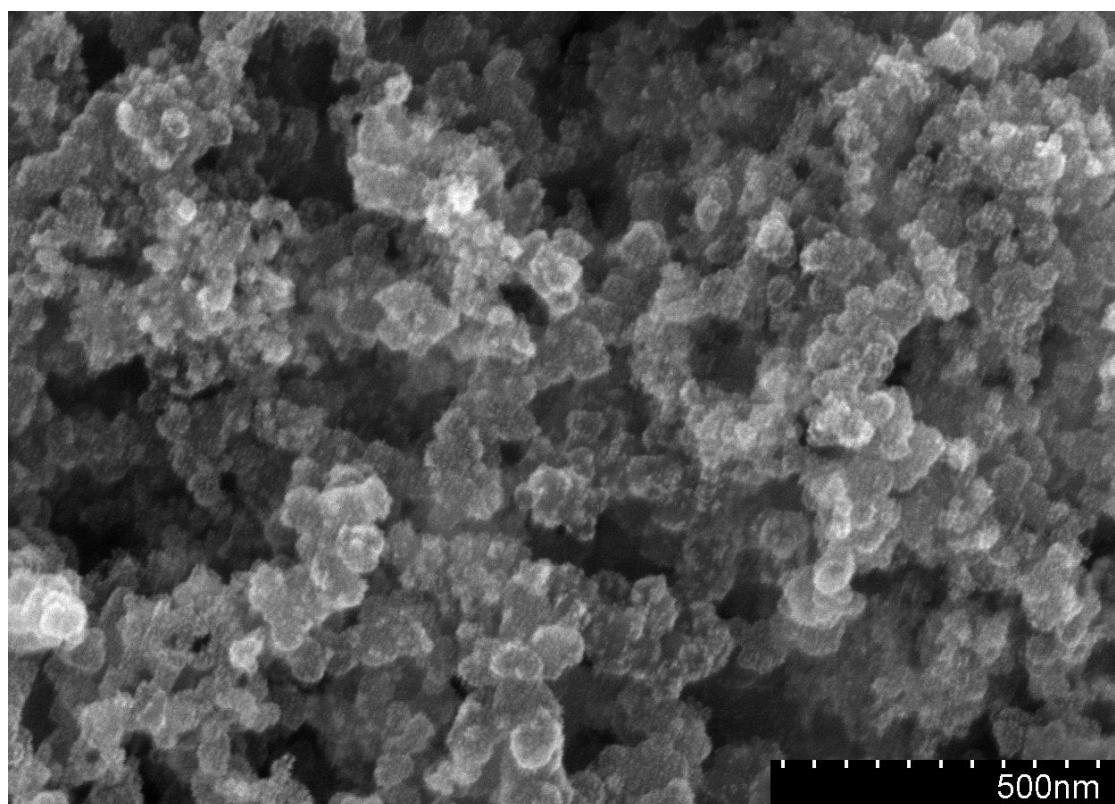
**Figure S1.** SEM images of Vulcan XC-72 carbon nanospheres (a) before, (b) after growth of Pt NWs (60 wt %), (c) low and (d) high magnification TEM micrographs of the Pt NWs/XC-72 nanostructures. The inset in (c): SEAD of the Pt NWs.



**Figure S2.** SEM images with different magnifications of Pt NWs/ Vulcan XC-72R: (a) and (b); Pt NWs/ Vulcan XC-72: (c) and (d).

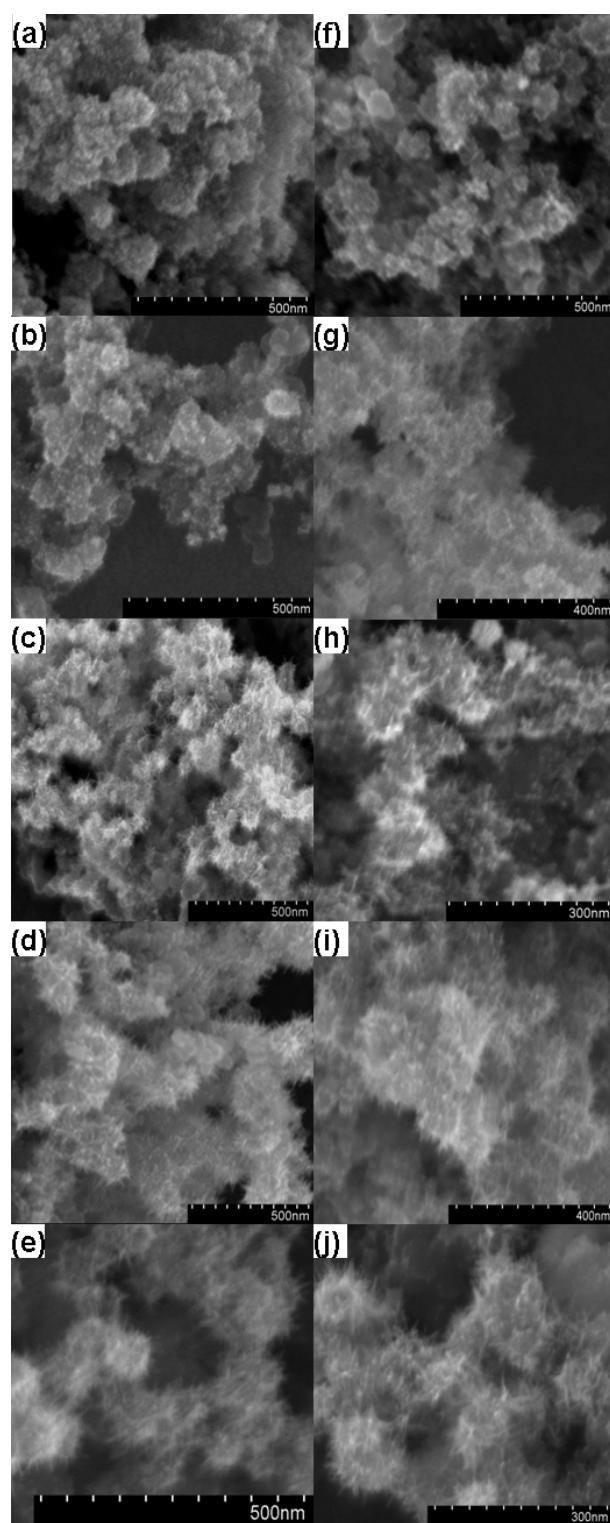
Low- to high-resolution transmission electron microscopy and selected area electron diffraction (SAED) patterns were performed using a FEI Tecnai G2 S-Twin instrument with a field emission gun operating at 200 kV, and images were acquired digitally on a Gatan multipole CCD camera. Specimens for all of these TEM experiments were prepared by dispersing the samples in ethanol, sonicating for 2 min to ensure adequate dispersion, and evaporating one drop of the suspension onto a 300 mesh Cu grid, coated with a lacey carbon film.

The SEAD of the sample infers that as-synthesized Pt NWs are crystallized in a phase similar to the bulk Pt. In addition, the HRTEM indicates that the Pt NWs is a single crystal with a lattice spacing 0.225 nm, implying the growth direction along the <111> axis.



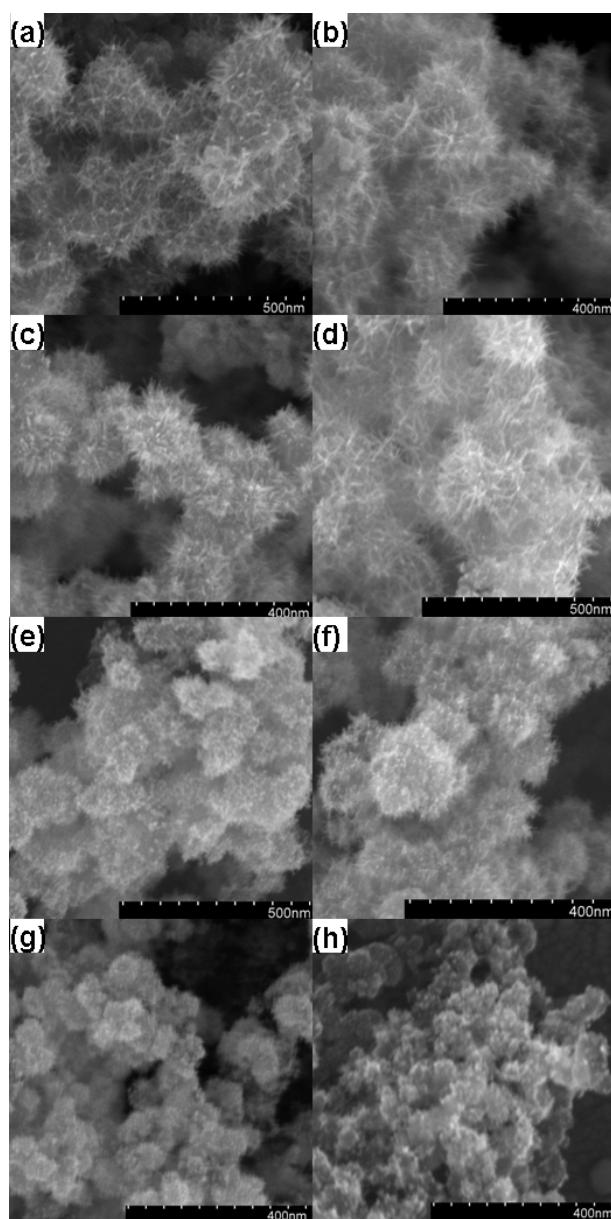
**Figure S3.** SEM micrograph of commercial Pt catalyst (Pt 60 wt %, JM PLC).

This image shows that Pt nanoparticals uniformly dispersed on the carbon nanospheres.



**Figure S4.** SEM images of Pt/C nanostructures (Pt 60 wt %) collected at various times at room temperature on different supports: (a-e) Pt NWs/XC-72R, 12, 24, 36, 48, 60 h, respectively (f-j) Pt NWs/XC-72, 12, 24, 36, 48, 60 h, respectively.

It is found that the density of Pt NWs on both kind of carbon supports increases gradually with the increase of reaction time, indicating the feasibility of handily control of morphology and Pt loading by reaction time.

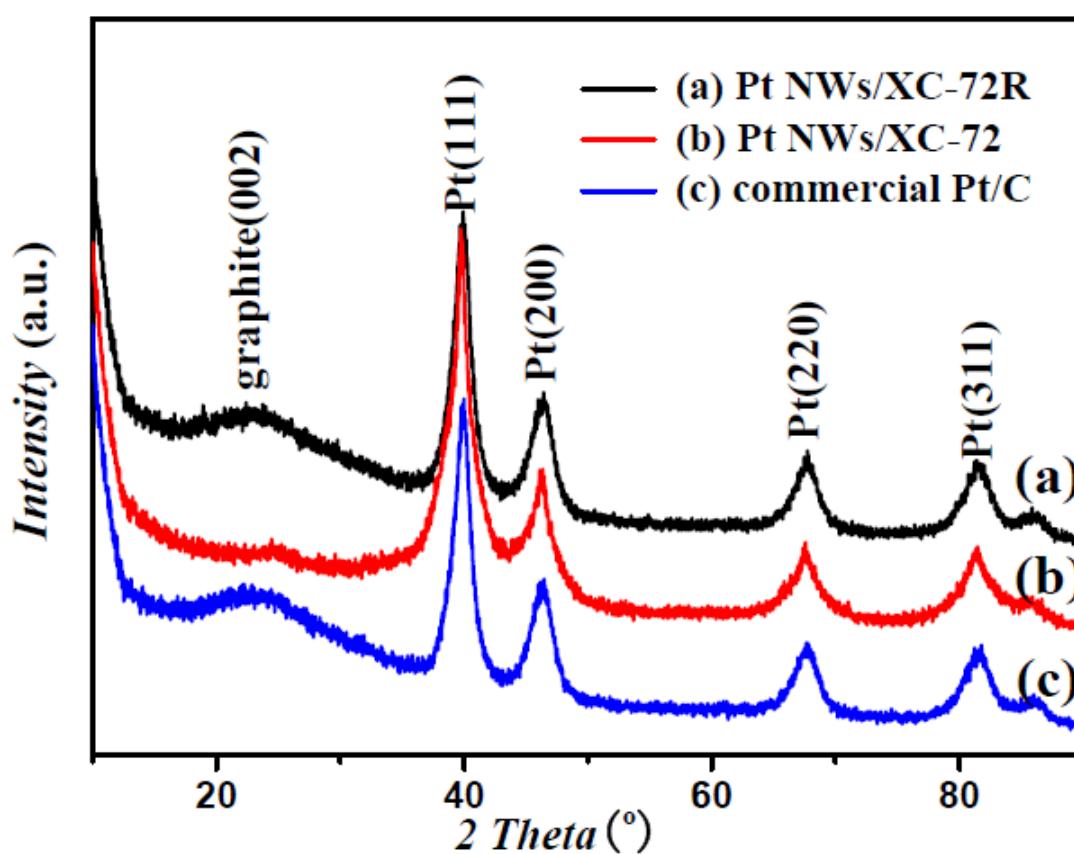


**Figure S5.** SEM micrographs of Pt/C nanostructues (Pt 60 wt %) collected at different temperatures: (a-b) Pt NWs/XC-72R, 40 °C, 10 h and 20 h; (c-d) Pt NWs/XC-72, 40 °C, 10 h and 20 h; (e-f) Pt NWs/XC-72R, 60 °C, 10 h and 20 h; (g-h) Pt NWs/XC-72, 60 °C, 10 h and 20 h.

The images show that dense Pt NWs can also be obtained at 40 °C although some nanoparticles generated simultaneously. However, the length of the Pt NWs is much less than that of the corresponding samples obtained at room temperature. When the temperature increased to 60 °C, the carbon supports were nearly covered by Pt nanoparticles with only little short Pt NWs found.

These control experiments indicate that the low temperature and prolonged reaction time play key roles for the growth of dense and long Pt NWs on carbon support, which might be due to the necessary quasi-steady-state reduction process for Pt NWs growth can only be obtained at low temperature.

#### 4.2 Powder X-ray diffraction (XRD)



**Figure S6.** X-ray diffraction patterns of Pt NWs grown on (a) Vulcan XC-72R, (b) Vulcan XC-72, and (c) commercial Pt/C. Both of the Pt NWs/C catalysts were synthesized at room temperature for 72 h with Pt loading 60 wt %.

XRD measurements were performed on a Rigaku-Dmax 2500 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.15405$  nm) from 10 to 90 degree at a scanning rate of 5 degree per minute. The samples were grinded and flattened in a piece of glass with a hole.

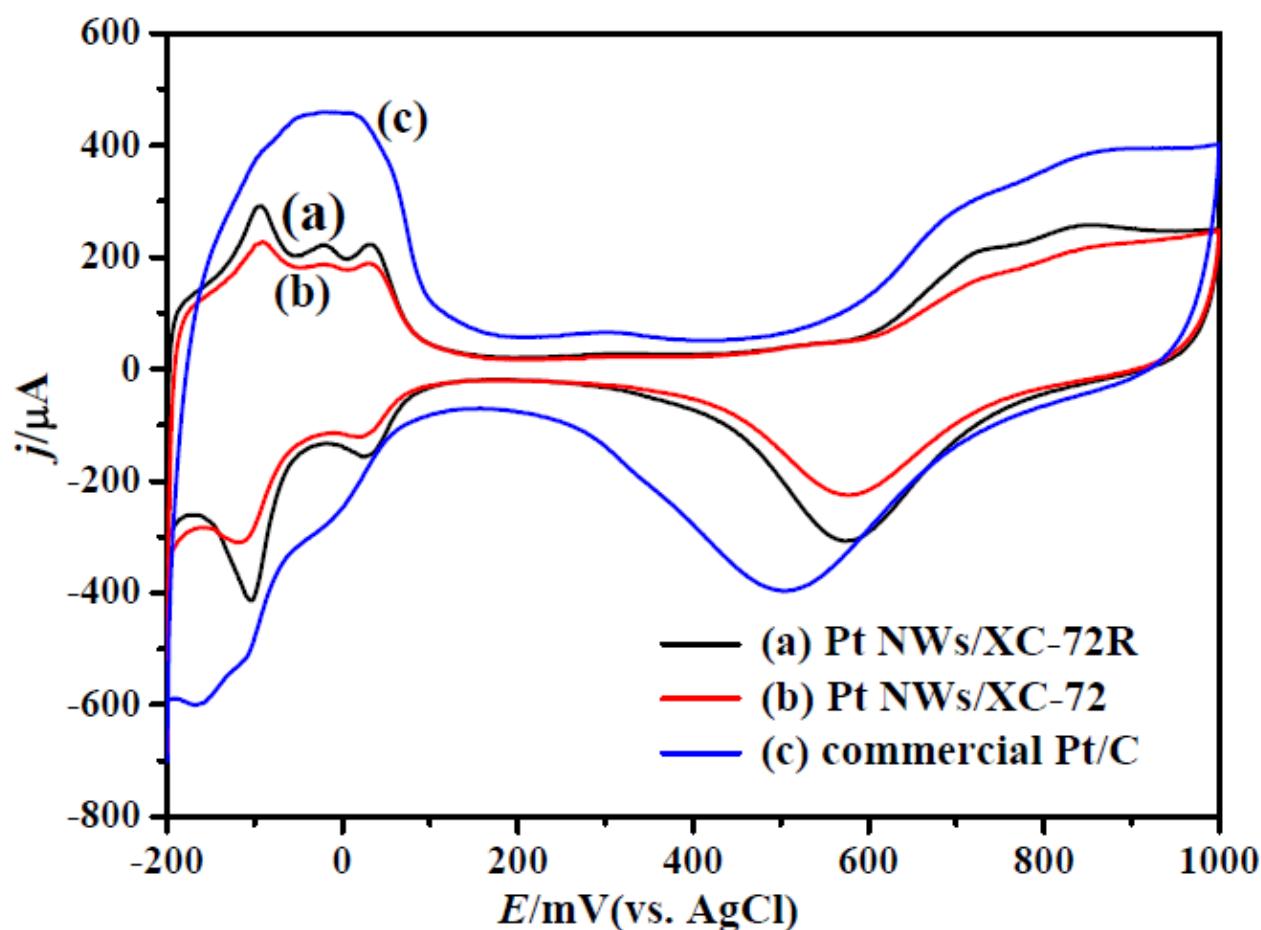
#### 4.3 Electrochemical characterization

Electrochemical experiments were carried out in a standard three-electrode cell at room temperature (about 298 K). The working electrode was the thin-film electrode with catalysts. Pt foil and Ag/AgCl were used as the counter and reference electrodes, respectively. All potentials in this report referred to Ag/AgCl. All electrolyte solutions were deaerated with high-purity nitrogen for at least 20 min prior to any measurement. Electrode potential was controlled by an EG&G (model 273) potentiostat/galvanostat system.

The Pt NWs/C catalysts in the electrochemical characterization were synthesized at room temperature for 72 h with Pt loading 60 wt %.

##### 4.3.1 Electrochemical surface area (ECSA)

An important parameter for Pt-based electrocatalysts is the electrochemical surface area (*ECSA*,  $m^2/g_{Pt}$ ). The ECSA was estimated from the charge transfer of H adsorption/desorption cyclic voltammetry (CV) of the catalysts taken in 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution (sweep rate 20 mV/s). The three-electrode cell was purged with nitrogen for 20 min prior to CV tests. All electrochemical measurements were taken at room temperature. The potential range was from -0.2 to 1.0 V.



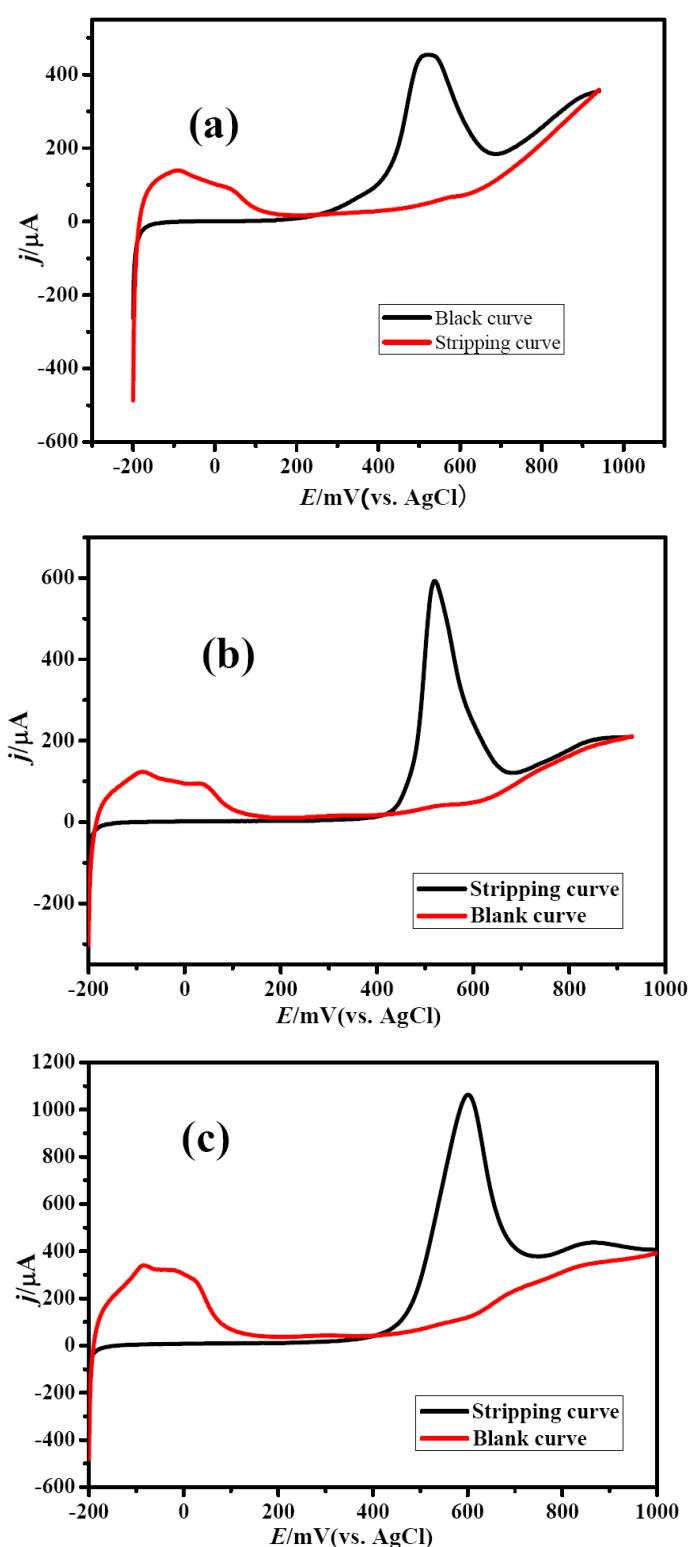
**Figure S7.** Cyclic voltammetry in deaerated 0.5 mol/L  $\text{H}_2\text{SO}_4$  and solution with a sweep rate of 20 mV/s at room temperature: (a) Pt NWs/XC-72R, (b) Pt NWs/XC-72, and (c) commercial Pt/C.

**Table S1.** The electrochemical surface area (ECSA) of the samples calculated from Figure S7.

	$S, \text{cm}^2$	$ECSA, \text{m}^2/\text{g}_{\text{Pt}}$
Pt NWs/XC-72R	11.57	91.11
Pt NWs/XC-72	11.39	89.67
commercial Pt/C	19.45	153.2

CO stripping voltammetry is also employed to evaluate the ECSA of the catalysts as well as their anti-poison ability. CO was purged into 0.5 M  $\text{H}_2\text{SO}_4$  solution for 30 min to allow complete adsorption of CO onto the electrocatalyst, while maintaining a constant potential at 0.12 V (the potential of the double-layer). Excess CO was then purged with  $\text{N}_2$  for 30 min. The amount of

$\text{CO}_{\text{ads}}$  was evaluated by integrating the  $\text{CO}_{\text{ads}}$  stripping peak (electrode potential scan rate: 20 mV/s), corrected for electric double-layer capacitance. The specific surface area of Pt was estimated using two assumptions: (1) there was a monolayer of linearly adsorbed CO and (2) the Coulombic charge required for oxidation was  $420 \mu\text{C}/\text{cm}^2$ .



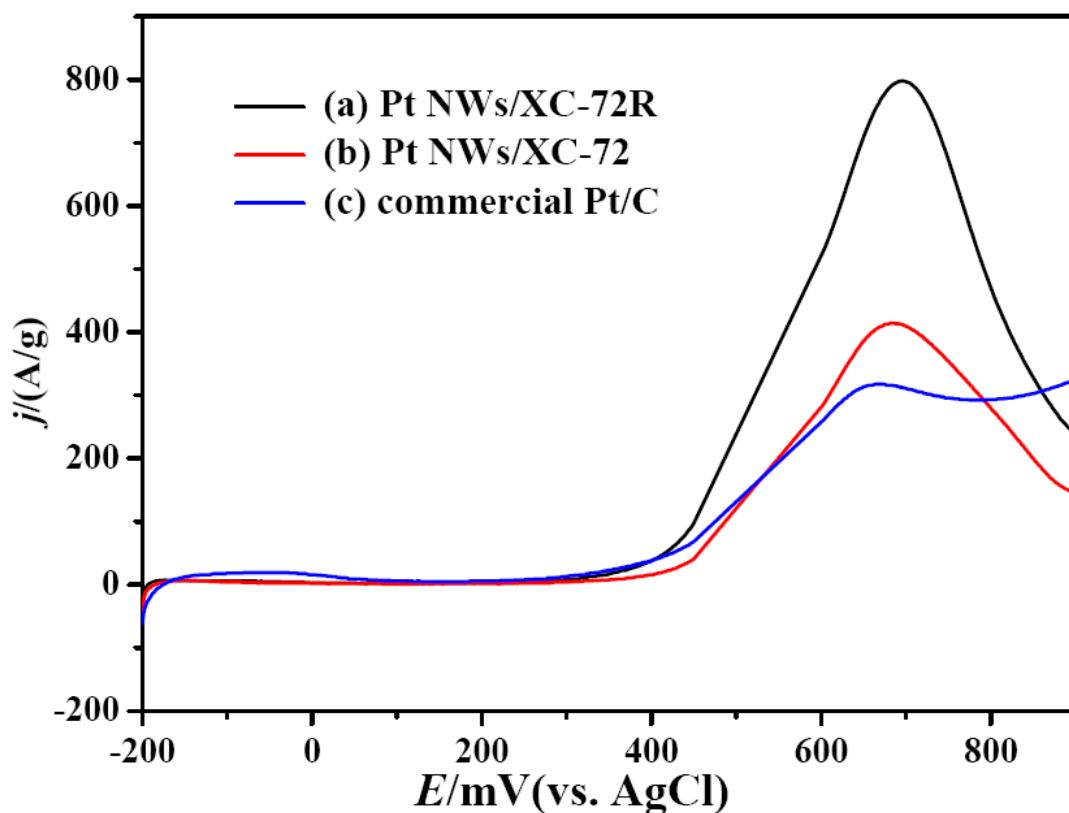
**Figure S8.** The  $\text{CO}_{\text{ad}}$  stripping voltammograms in deaerated 0.5 mol/L  $\text{H}_2\text{SO}_4$  solution with a sweep rate of 20 mV/s, at room temperature: (a) Pt NWs/XC-72R, (b) Pt NWs/XC-72, and (c) commercial Pt/C.

**Table S2.** The CO oxidation peak potentials and the corresponding ECSA of the samples calculated from [Figure S8](#).

	$V_p$ , mV	$S$ , cm <sup>2</sup>	ECSA, m <sup>2</sup> /g <sub>Pt</sub>
Pt NWs/XC-72R	523	9.70	73.09
Pt NWs/XC-72	520	6.97	52.48
commercial Pt/C	601	17.07	128.64

#### 4.3.2 Catalytic activity

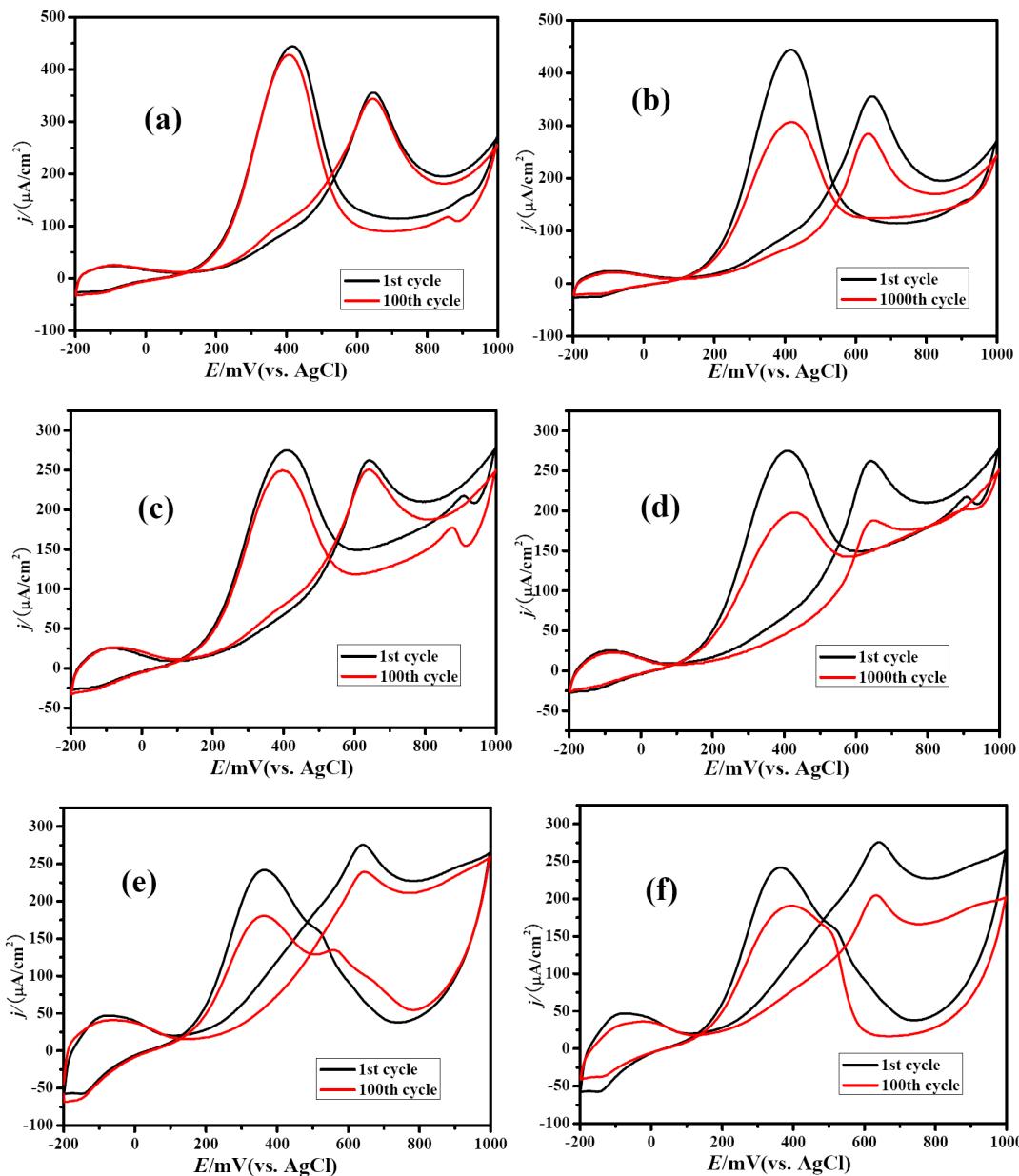
To evaluate the catalytic activity of the electro-oxidation towards methanol, CVs tests were performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing 0.5 M CH<sub>3</sub>OH at a scan rate of 20 mV/s. The potential range was from -0.2 to 1.0 V.



**Figure S9.** Linear sweep voltammetry (mass activities) in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M CH<sub>3</sub>OH deaerated solution with a sweep rate of 20 mV/s at room temperature: (a) Pt NWs/XC-72R, (b) Pt NWs/XC-72, and (c) commercial Pt/C.

### 4.3.3 Catalyst stability

The cycle stability tests of the samples were done at the same condition as the catalytic activity at a scan rate of 100 mV/s.

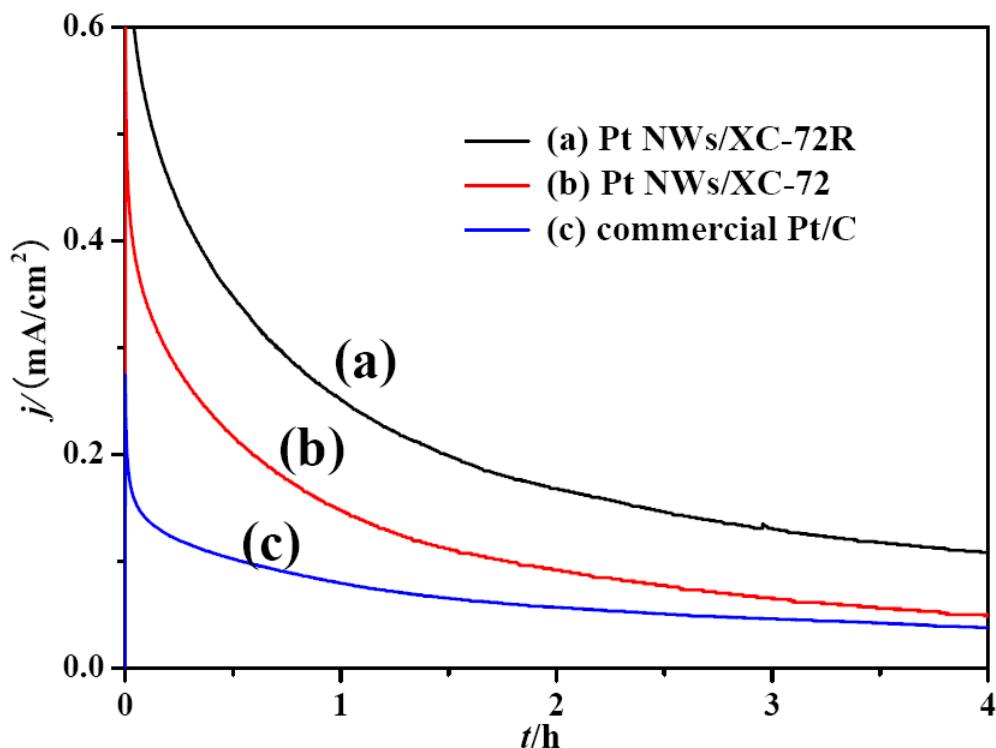


**Figure S10.** The cycle stability tests of the samples measured at a scan rate of 50 mV/s, in deaerated 0.5 mol/L  $\text{H}_2\text{SO}_4$  and 0.5 mol/L  $\text{CH}_3\text{OH}$  solution at room temperature: (a-b) Pt NWs/XC-72 R; (c-d) Pt NWs/XC-72; (e-f) commercial Pt/C.

**Table S3.** The peak currents and the calculated reduced radios obtained from the 1st, 100th and 1000th cycles of the cycle stability tests in Figure S10.

	1 <sup>st</sup> cycle	100 <sup>th</sup> cycle		1000 <sup>th</sup> cycle	
	$i_p$ , ( $\mu\text{A}/\text{cm}^2_{\text{Pt}}$ )	$i_p$ , ( $\mu\text{A}/\text{cm}^2_{\text{Pt}}$ )	reduced ratio	$i_p$ , ( $\mu\text{A}/\text{cm}^2_{\text{Pt}}$ )	reduced )
Pt NWs/XC-72R	355	344	3.16%	284	19.9%
Pt NWs/XC-72	262	251	4.34%	188	28.4%
commercial Pt/C	276	239	13.1%	205	25.7%

Chronoamperometric curves were obtained in 0.5 M  $\text{H}_2\text{SO}_4$  solution containing 0.5 M  $\text{CH}_3\text{OH}$  at the potential of 0.667 V (peak potential of the NWs samples) for 4 h.



**Figure S11.** Chronoamperometric curves in deaerated 0.5 M  $\text{H}_2\text{SO}_4$  solution containing 0.5 M  $\text{CH}_3\text{OH}$  at the potential of 0.67 V for 4 h at room temperature: (a) Pt NWs/XC-72R, (b) Pt NWs/XC-72, and (c) commercial Pt/C. The order of the stable value: (a) > (b) > (c).

**Table S4.** The initial currents, the stable currents and the calculated reduced ratios obtained from [Figure S11](#).

	$i_0/S,$ (mA/cm <sup>2</sup> <sub>Pt</sub> )	$i_{4h}/S,$ (mA/cm <sup>2</sup> <sub>Pt</sub> )	reduced ratio
Pt NWs/XC-72R	0.689	0.0908	86.8%
Pt NWs/XC-72	0.367	0.0307	91.6%
commercial Pt/C	0.241	0.0334	86.1%