

Supporting information for

Hanging Pt Hollow Nanocrystal Assemblies on Graphene Resulting in an Enhanced Electrocatalysts

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Experimental Section

Preparation of catalysts:

Chemicals and materials. Natural graphite (SP-1) was purchased from Bay Carbon, MI. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, NaBH_4 , $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, KMnO_4 , H_2O_2 and citric acid were from Beijing Chemical Reagent Ltd., Beijing.

Synthesis of graphene oxide (GO). GO was synthesized from purified natural graphite by the modified Hummers method. H_2SO_4 (50 mL) was added into the 250 mL flask filled with graphite (2 g) at room temperature, followed by addition of solid KMnO_4 (7 g) slowly at 0 °C (ice bath). After increase of temperature to 35 °C, the mixture was stirred by magnetic stirring bar overnight. Excess water was added into the mixture at 0 °C (ice bath) and then H_2O_2 (30 wt% in water) was added until there was no gas produced. Filtration with glass filter afforded brown powder (GO) and the GO powder was dried in the vacuum at room temperature for 12 h.

Graphene functionalization. The reduced graphene was obtained by treating GO in H_2/Ar gas mixture (H_2 volume was 5%) at 800 °C in a tube furnace for 2 hours. After heat treatment, 50 mg graphene and 20 mL concentrated nitric acid were mixed together and refluxed for 3 h, followed by rinse and dry process to obtain functionalized graphene.

Synthesis of graphene supported Pt hollow nanospheres (Pt-H-G) and supportless Pt hollow nanospheres (Pt-H). 4.8 mg functionalized graphene was dispersed in 50 mL ultra-pure water and ultrasonicated for 1 h. 0.1 mL CoCl_2 (0.4 M) and 0.5 mL (20 mg/mL) citric acid were then added. After stirring the suspension for half an hour, freshly prepared NaBH_4 (24 mg in 10 mL water) was added. H_2 was evolved during the reaction and continued for several minutes. When gas evolution ceased, the solution was immediately added to a stirred solution of H_2PtCl_6 (13mg $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in 30 ml water, corresponding to 4.9 mg Pt) at room temperature. The as-prepared

catalysts were centrifuged and washed with water and ethanol for several times and redispersed in ethanol solution. Supportless Pt hollow nanospheres were prepared by the same procedure as graphene supported Pt hollow nanospheres but without using any graphene.

Characterization of catalysts:

Scanning electron microscopy (SEM) samples were prepared by drying a drop of catalyst dispersion on Si surface. SEM images were taken on a Hitachi S-4800 microscope, operating at 15 kV. Tunneling electron microscopy (TEM) and high resolution TEM (HRTEM) images were obtained on a JEOL-2010, working at an accelerating voltage of 200 kV. Powder X-ray diffraction (XRD) pattern was recorded with a Regaku D/Max-2500 diffractometer equipped with a Cu K α 1 radiation ($\lambda=1.54056$ Å). Raman spectrum was collected on a DXR SmartRaman Spectrometer from Thermo Fisher Scientific with a laser wavelength of 632.8 nm. X-ray photoelectron spectroscopy (XPS) data were measured on an ESCALab220i-XL electron spectrometer from VG Scientific. The base pressure was about 3×10^{-9} mbar. The binding energies for all spectra were referenced to C1s line at 284.8 eV. The catalyst loading in terms of Pt content was measured via an inductively coupled plasma emission spectrometer (ICP-AES, Shimadzu) analysis. The PerkinElmer Thermogravimetric Analyzers (Pyris 1 TGA) was used to record the TGA curve and confirm the content of Pt hollow nanostructure on graphene.

Electrochemical measurements:

All cyclic electrochemical measurements were carried out on a CHI 660D electrochemical analyzer (CH Instrument, TX, USA). A standard three-electrode cell system was used with a catalyst modified glassy carbon (GC) electrode as the work electrode, a saturated calomel electrode (SCE) as reference electrode and a Pt wire as counter electrode. All measurements were done at room temperature. For preparation of working electrode, a certain amount of catalyst paste with given loading of catalyst was drop-casted on pretreated GC electrode. After drying the electrode at room temperature, 5 μ L of 0.1 wt.% Nafion (Alfa Aesar) in ethanol was spread on the surface of catalysts and dried in air. Pt black (Alfa Aesar) and Pt/C (40 wt% of Pt nanoparticles (< 3.5 nm) supported on activated carbons, Johnson Matthey) were used for comparison in measurement. Based on the results of ICP measurement, the Pt loadings of catalysts for MOR measurement are 13 μ g for Pt-HG, 12 μ g for Pt-H, 10 μ g for Pt/C, and 14 μ g for Pt black, respectively. Before the electrochemical measurements, the catalyst modified working electrodes were first cycled between -0.25 V and 1.0 V (vs SCE) in N₂-purged 0.5 M H₂SO₄ to produce a clean electrode surface.

Cyclic voltammetry (CV) measurement. CV measurements were performed by cycling the potential between -0.25 V and 1.0 V (vs SCE) with sweep rate of 50 mV s⁻¹ in N₂-purged 0.5 M H₂SO₄ at room temperature. The electrochemical surface areas (ECSA) of catalysts by measuring the charge associated with hydrogen adsorption between 0 and 0.37 V (vs RHE (Reversible Hydrogen Electrode)) after double-layer correction and assuming a value of 0.21 mC cm⁻² for the adsorption of a hydrogen monolayer, corresponding to a surface density of 1.3×10^{15} Pt atoms per cm², which is generally accepted for polycrystalline Pt electrodes. ECSA was measured for each catalyst-modified electrode for methanol oxidation.

Methanol oxidation reaction measurement (MOR). Methanol oxidation experiments were

conducted by recording steady MOR current between 0 V and 0.9 V (vs SCE) in fresh-prepared 0.5M H₂SO₄ and 0.5 M CH₃OH at room temperature. Mass activity and specific activity for MOR was calculated through dividing MOR current by ECSA and mass of the used catalysts, respectively.

Figure S1. Energy dispersed spectrum (EDS) of Pt-H-G, taken on catalyst dispersed on Si. Si signal is from Si substrate for SEM. A trace amount of Co signal is from the residue of Co source.

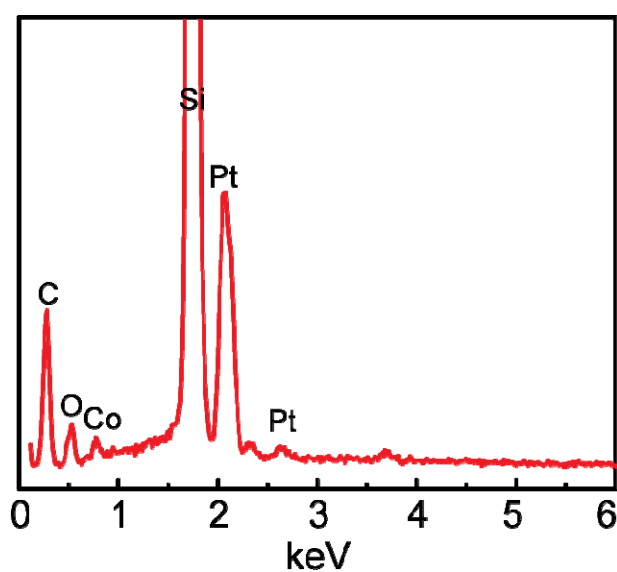


Figure S2. Low-magnification SEM image of Pt-H-G, showing Pt-H are well dispersed and intercalated in graphene layers.

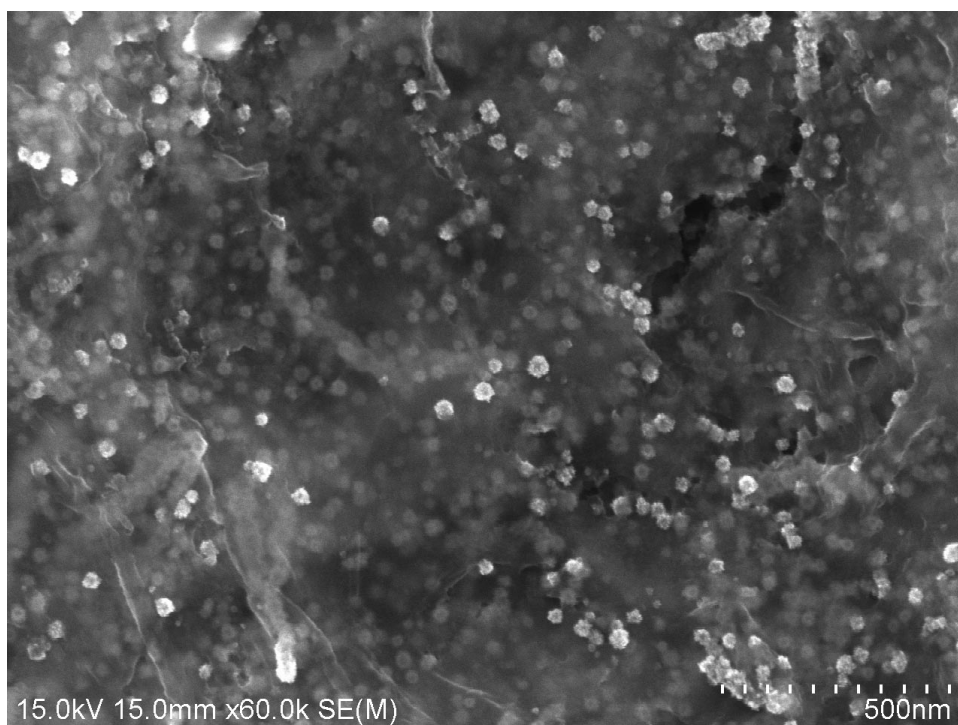


Figure S3. The selected-area electron diffraction (SAED) pattern taken on Pt-H-G, matching well with the diffraction patterns of fcc Pt crystals.

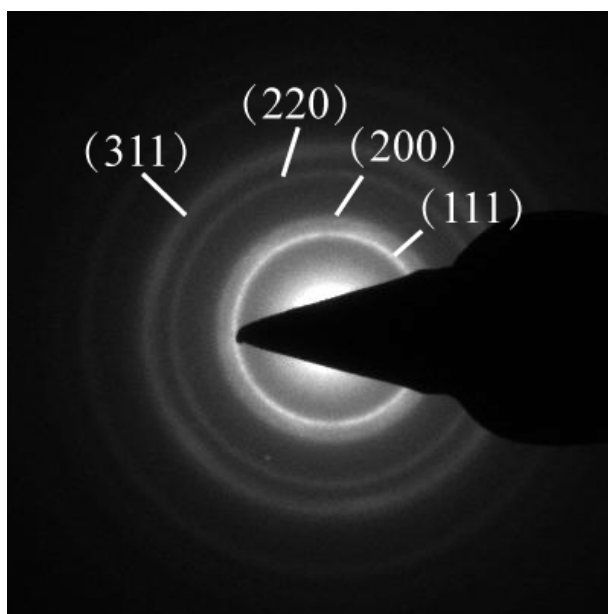


Figure S4. The TEM image and the selected-area electron diffraction (SAED) pattern of supportless Pt-H catalysts, side-by-side prepared under the same condition as that for Pt-H-G but without the addition of graphene, which indicates Pt-H has similar morphology and structure to Pt hollow nanoparticle assemblies in Pt-H-G but without graphene support.

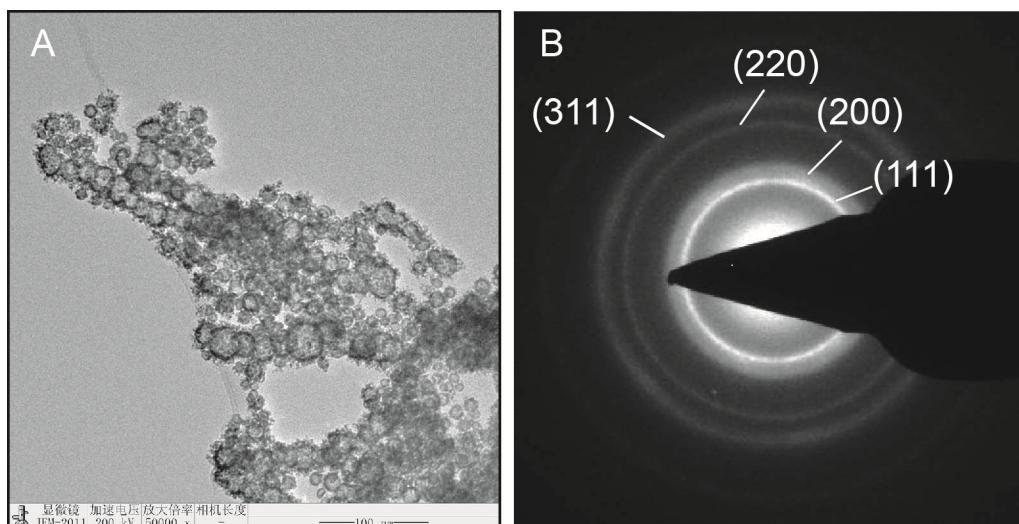


Figure S5. TGA curve of Pt-H-G

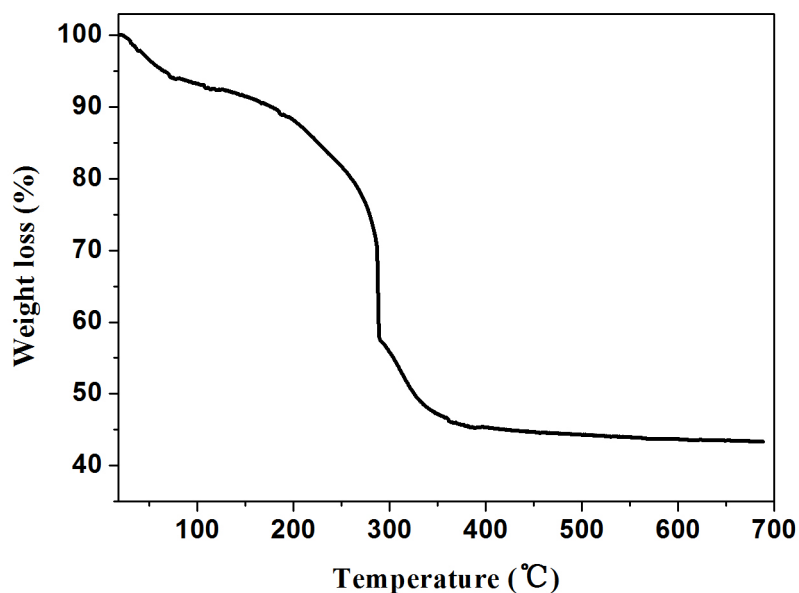


Figure S6. Cyclic voltammetry curves obtained by cycling the potential between -0.25 V and 1.0 V (vs SCE) with sweep rate of 50 mV s^{-1} in N_2 -purged $0.5 \text{ M H}_2\text{SO}_4$ at room temperature.

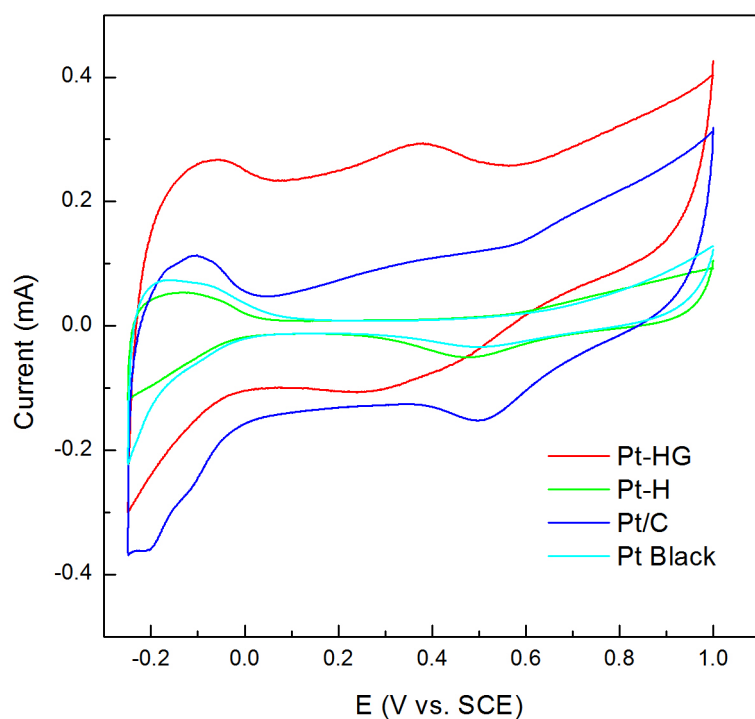


Figure S7. Cyclic voltammograms curve for MOR catalysed by graphene alone in an aqueous solution containing $0.5 \text{ M H}_2\text{SO}_4$ and 0.5 M methanol.

