

Electronic Supplementary Information (ESI)

**Core-shell Hierarchical WO₂/WO₃ Microsphere as an
Electrocatalyst Support for Methanol Electrooxidation**

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Experimental Section

Preparation of Pt-WO₂/WO₃ electrocatalyst:

All chemical reagents were analytical grade. In a typical synthesis, hollow ammonium metatungstate microspheres (HAMT) precursor was prepared by spray drying previously reported by our group.¹⁻² The as-prepared precursor was then put into a ceramic boat and sent into a tube furnace that had been purified with a mixture of CO and CO₂ for 0.5 h. The temperature of the furnace was raised to 673 K and held for 1 h, and then raised to 973 K for 2 h, while a mixture of CO and CO₂ at a ratio of 10:1 was passed through the furnace. The flow rates of CO and CO₂ were 200 mL min⁻¹ and 20 mL min⁻¹, respectively. The sample was cooled to room temperature under an atmosphere of nitrogen. The as-prepared product was designated as WO₂/WO₃.

Subsequently, Pt-WO₂/WO₃ catalyst was prepared through the improved liquid phase reduction method. In a typical procedure, 50 mg of the as-prepared WO₂/WO₃ support and 11.4 mL of 5 mM H₂PtCl₆ solution was dispersed in 50 mL of water by sonication. Then, after the pH was adjusted to nearly 9 using 1 M NaOH solution, a freshly prepared 10 mL of 0.1 M NaBH₄ solution was added to the solution, followed by stirring for 2 h. The resulting solution was filtered, washed, and dried at 85 °C for 10 h in a vacuum oven, yielding 20 wt % Pt loading on the supports. A commercial 20 wt % PtRu/C (JM PtRu/C) was purchased from Johnson Matthey Co., Ltd. and used as contrast samples.

Preparation of Pt/h-WO₃ electrocatalyst:

The as-prepared HAMTS was in a furnace at 973 K for 2 h in air and the sample was cooled to room temperature naturally. The as-prepared product was denoted as h-WO₃. For comparison, Pt supported on h-WO₃ catalyst with the same Pt loading amounts was prepared by the same procedure above, which was denoted as Pt/h-WO₃.

Electrochemical Measurements:

The electrochemical measurements were performed using a three-electrode cell with an Ivium electrochemical workstation at room temperature. For electrode preparation, 5 mg of electrocatalysts were ultrasonically mixed in 200 μ l of ethanol-water solution to form a homogeneous ink followed by dropping 2 μ l of the electrocatalyst ink onto the surface of a glassy carbon electrode (GCE, with a diameter of 3 mm), and 5 μ l of Nafion solution of 1.0% (DuPont, USA) in ethanol was added to fix the electrocatalyst on the GCE surface. Glassy carbon (GC) disk electrode served as the substrate for the support. Prior to use, the GC electrode was polished using aqueous alumina suspension. And then the catalyst suspension was pipetted using a micropipettor onto the GC surface to make a Pt loading of about 0.2 mg cm⁻². A Pt foil and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The electrocatalytic activity of the catalysts on the oxidation of methanol was studied in 0.5 M H₂SO₄ aqueous solution containing 1.0 M CH₃OH at a scan rate of 50 mV s⁻¹.

Characterization:

The phases present in the synthesized materials were identified using XRD (Panalytical X'Pert Pro, Cu K α 1 radiation source ($\lambda = 0.1541$ nm), voltage of 40 kV, current of 40 mA). The morphology and structure of the products were characterized using FE-SEM (Hitachi S-4700 II) and TEM (Tecnai G2 F30) with Energy-dispersive X-ray spectroscopic (EDS). Thermogravimetric analysis (TGA) was performed with TA Q600 at a heating rate of 10 °C min⁻¹ from room temperature to 800 °C under air flow (100 mL min⁻¹). XPS was carried out on Kratos AXIS Ultra DLD. All XPS spectra were corrected using the C 1s line at 284.6 eV. Curve fitting and background subtraction were accomplished.

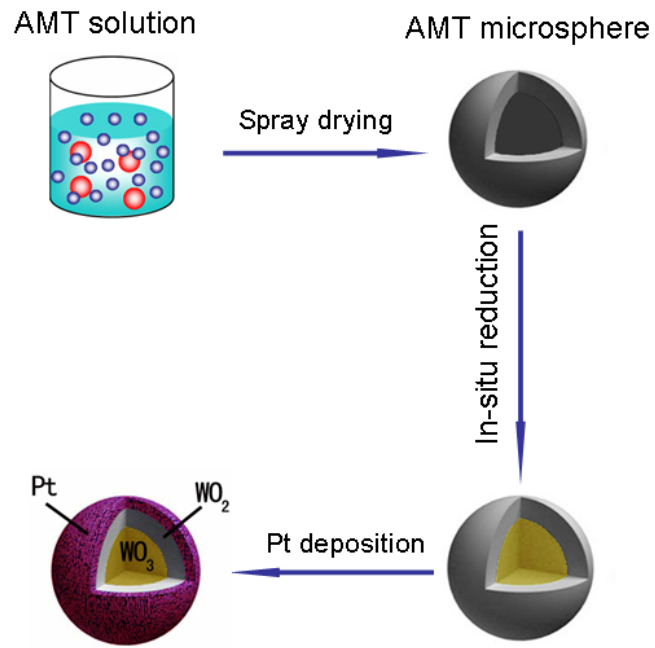


Figure S1. Schematic illustration of the synthetic procedure of Pt-WO₂/WO₃

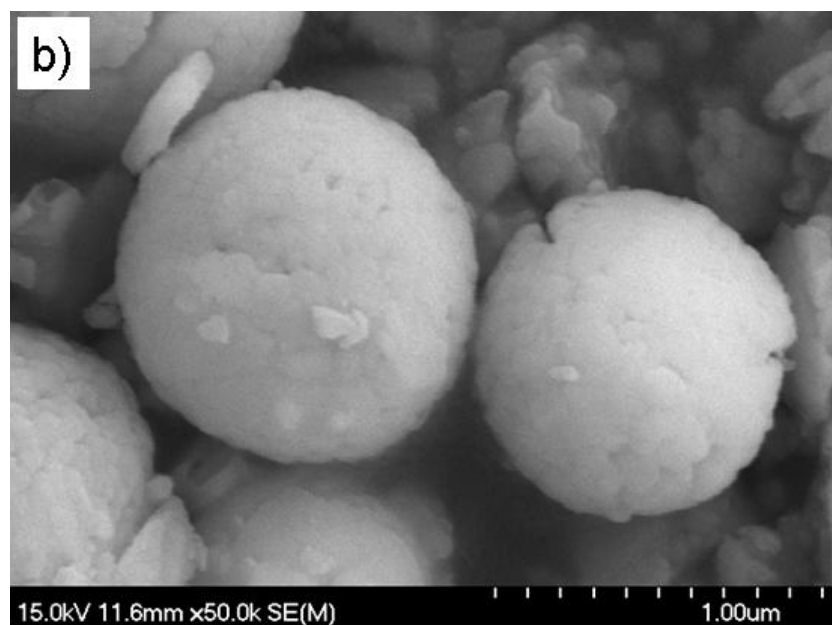
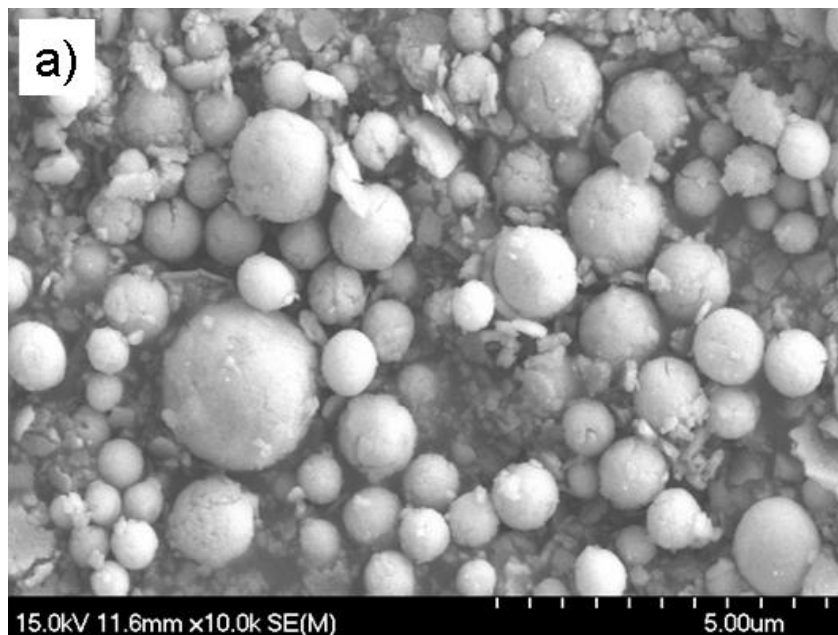


Figure S2. a) and b) SEM of h-WO₃

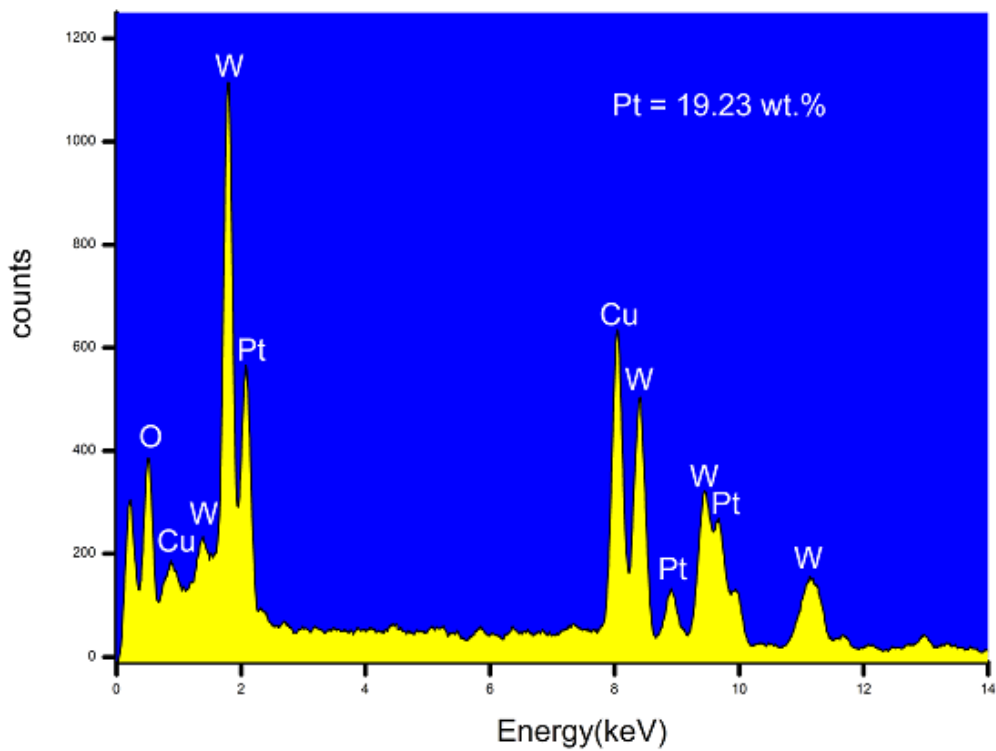


Figure S3. EDS spectra of Pt-WO₂/WO₃ catalyst

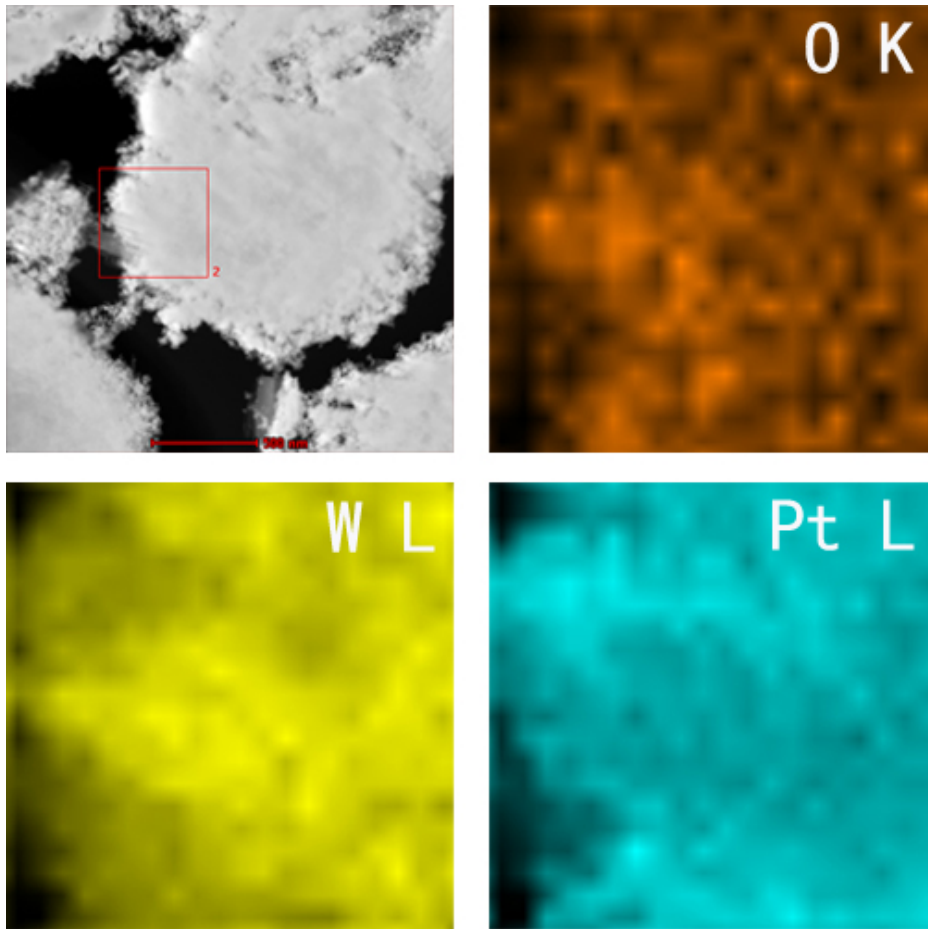


Figure S4. Element mapping of Pt-WO₂/WO₃ catalyst

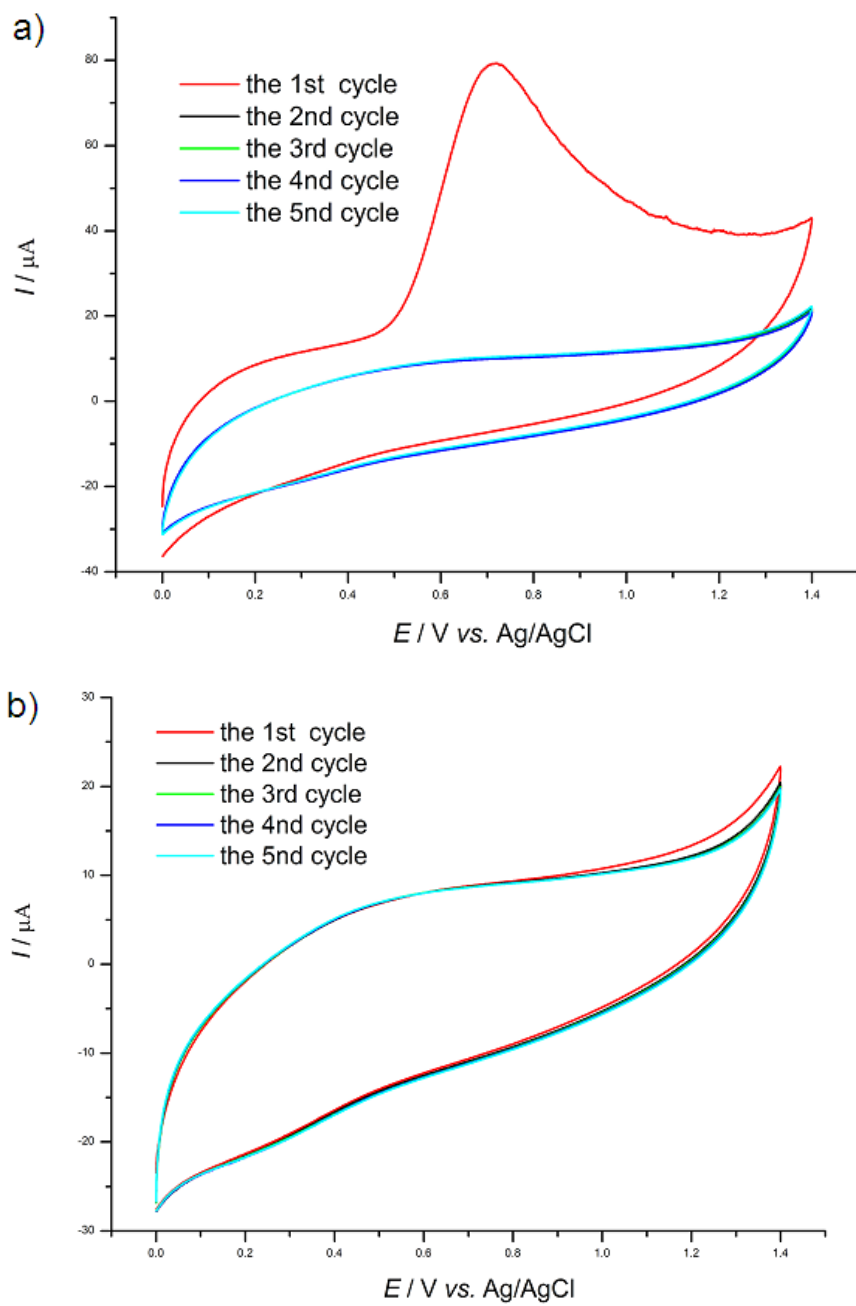


Figure S5. Cyclic voltammetric curves of a) WO_2/WO_3 and b) WO_3 in 0.5 M H_2SO_4 at the scan rate of 50 mV s^{-1} ;

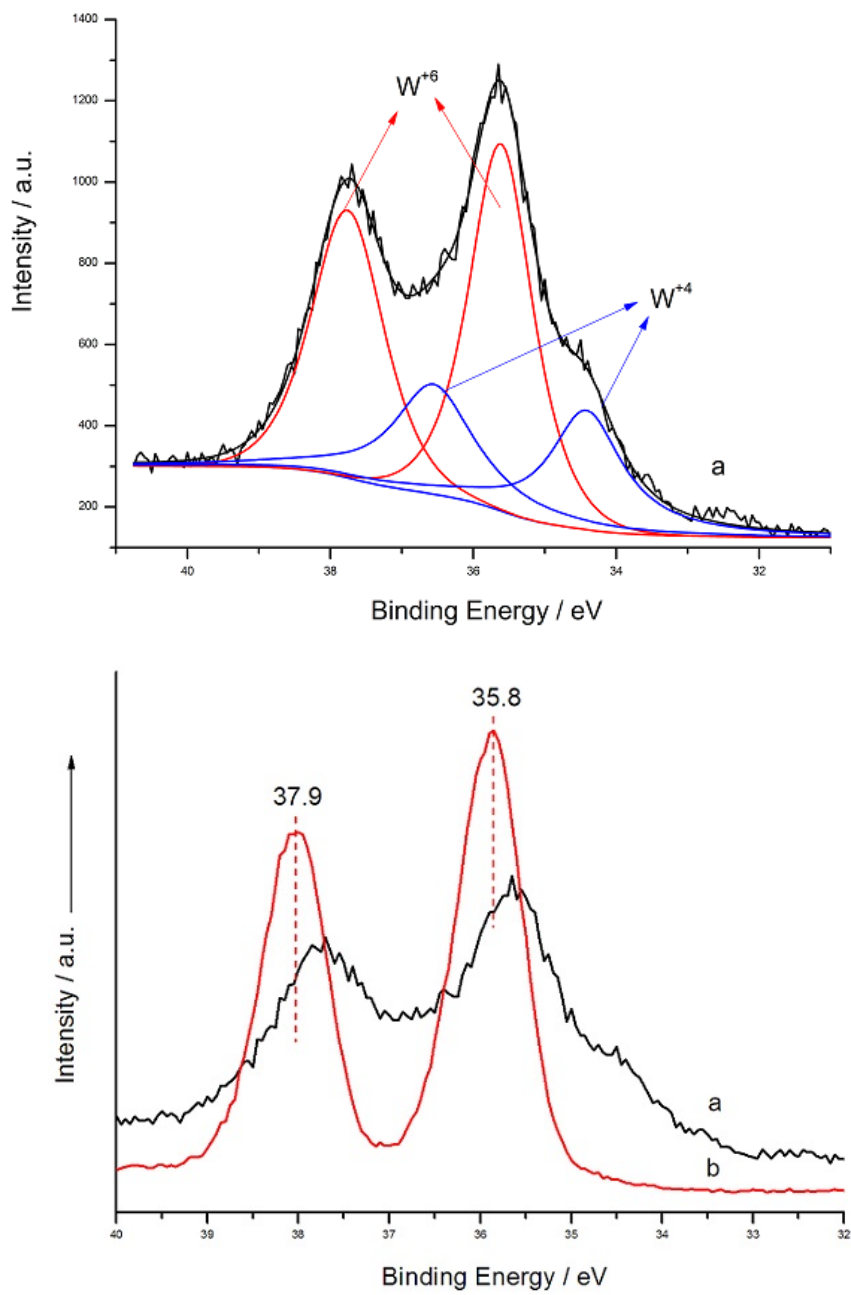


Figure S6. The W 4f XPS Spectra of a) WO_2/WO_3 ; b) h-WO_3

References

- [1] Y. Zhou, X. Hu, Y. Xiao, Q. Shu, *Electrochimica Acta* 2013, **111**, 588.
- [2] Y. Zhou, X. C. Hu, L. Q. Li, X. R. Chen, *Acta Physico-Chimica Sinica* 2014, **30**, 83.