

Supporting Information
for
Hierarchical Carbon Coated Molybdenum Dioxide Nanotubes as
High Activity and Durability Electrocatalytic Support for
Methanol Oxidation

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Experimental section

Synthesis of MoO₃ nanorods: 0.7 g of ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, Aladdin) was dissolved in 20 mL of mixed solution of 65% HNO₃ and deionized H₂O (Millipore, 18.2 MΩ cm) with a volume ratio of 1:5. The uniform solution after stirring was transferred into a contraposition polyphenyl lined stainless-steel autoclave

(50 mL capacity) and heated at 200 °C for 20 h. After cooling down to ambient temperature, the slurry was taken out from the autoclave, washed with ultrapure water and ethanol several times. The product was dried at 70 °C for 12 h.

Synthesis of hierarchical MoO₂@C nanotubes: In a typical synthesis of hierarchical MoO₂ nanotubes, 100 mg of the as-prepared MoO₃ nanorods was added into 20 mL of deionized H₂O followed by an ultrasonic treatment for 15 min to obtain a homogeneous dispersion. 200 mg of (NH₄)₆Mo₇O₂₄·4H₂O and 50 mg of dopamine hydrochloride (C₈H₁₁NO₂·HCl, Aladdin) were dissolved into the above solution completely to form the Mo-dopamine complex at room temperature. Then 40 mL of ethanol was emptied into the orange-red slurry. After stirring for another 5 min, 0.15 mL of 28~30 % NH₃·H₂O (Sigma) was poured into the above reaction solution fast and the mixed solution reacted for 120 min with stirring uniformity. Finally, the orange-red precipitate was obtained by centrifugation, washed two times with 30 mL of ethanol and dried in vacuum at ambient temperature. To realize the MoO₂@C phase, the as-synthesized Mo-polydopamine precursor was then annealed at 750 °C under a H₂/Ar gas flow for 16 h with a heating rate of 5 °C min⁻¹.

Preparation of Pt-based catalysts: Pt-based catalyst was synthesized by the microwave-assisted ethylene glycol process (MAPP) [1]. A calculated amount of support was dispersed in the mixed solution containing ethylene glycol (EG) and isopropyl alcohol (v/v = 4:1) under an ultrasonic treatment for 1 h to form a uniform slurry. Then H₂PtCl₆-EG solution was added into the suspension with a gentle stirring for 3 h. The ink was adjusted to pH 12.0 with NaOH-EG (1 mol L⁻¹) solution and the suspension was heated for 55 s under the argon saturated atmosphere by a microwave oven. After the suspension cooling cooled down to

ambient temperature, the pH value of solution was adjusted to 2-3 by adding HNO₃ aqueous solution. The mixture was stirred for 12 h and washed with deionized water and dried under vacuum at 80 °C for 5 h.

Materials Characterization: X-ray diffraction (XRD, D/max-RB) was performed on a Rigaku SmartLab X-ray diffractometer using a Cu K α X-ray as the radiation source and scanning from 10° to 90°. The composition and morphology of samples were characterized on a field emission transmission electron microscope (TEM, Tecnai F30, Philips-FEI). Elemental mapping over the selected regions of the photocatalyst was conducted by an energy-dispersive X-ray spectrometer (EDX) attached to TEM FEI Tecnai F30. Brunauer-Emmett-Teller (BET) surface area of the sample was examined via nitrogen adsorption experiments at 77 K by using a QUADRASORB SI analyzer and X-ray photoelectron spectroscopy (XPS, PHI 5700, Physical Electronics) measurements with an Al K α X-ray source operating at 250 W.

Preparation of the working electrode: The catalyst ink was prepared by ultrasonically processing 2.0 mg sample in 2.0 mL ethanol for 20 min. Then, a quantity of 10 μ L suspension was deliberately carefully dripped to the pre-cleaned glassy carbon electrode (GCE, 4 mm diameter) and 5 μ L of a 5 wt% Nafion[®] solution (Dupont) was added onto the surface of the catalyst layer. After drying, the working electrode was used for test.

Electrochemical measurements: All the electrochemical measurements were evaluated in a classic three-electrode cell with a saturated Hg/Hg₂SO₄ electrode (MSE, 0.68 V vs. RHE) as the reference electrode, a platinum foil (1.0 \times 1.0 cm²) as the counter electrode, and the as-prepared GCE as the working electrode. The solution of an Ar-saturated 0.5 mol L⁻¹ H₂SO₄

solution was used for electrochemical active surface area (ESA) test and an Ar-saturated 0.5 mol L⁻¹ H₂SO₄ containing 0.5 mol L⁻¹ CH₃OH solution was applied in the methanol electrooxidation test. All potentials of cyclic voltammograms (CV) were recorded from -0.63 to 0.52 V (vs. MSE) at a sweeping rate of 0.05 V s⁻¹. Formula $ESA_{Pt} = Q_H / (0.21M_{Pt})$ was adopted to calculate the ESA of platinum, wherein Q_H stands for the current integration during hydrogen adsorption/desorption (H_{ads}/H_{des}) process in the hydrogen region of CV curve [2]. Electrochemical impedance spectroscopy (EIS) was recorded at a frequencies range from 100 kHz to 0.01 Hz under the condition of onset potential overlapped with a 5 mV AC signal. The stability of the catalyst was evaluated by the accelerated potential cycling test (APCT) which was conducted within the potential range of -0.63 to 0.52 V (vs. MSE). CO stripping voltammograms were obtained after bubbling CO gas into the three electrode system for 10 min at 0.08 V, followed by Ar purging (30 min) to remove the excess of dissolved CO. The voltammetry was carried out in 0.5 mol L⁻¹ H₂SO₄ with a scanning rate of 50 mV s⁻¹. All the measurements were performed under ambient temperature.

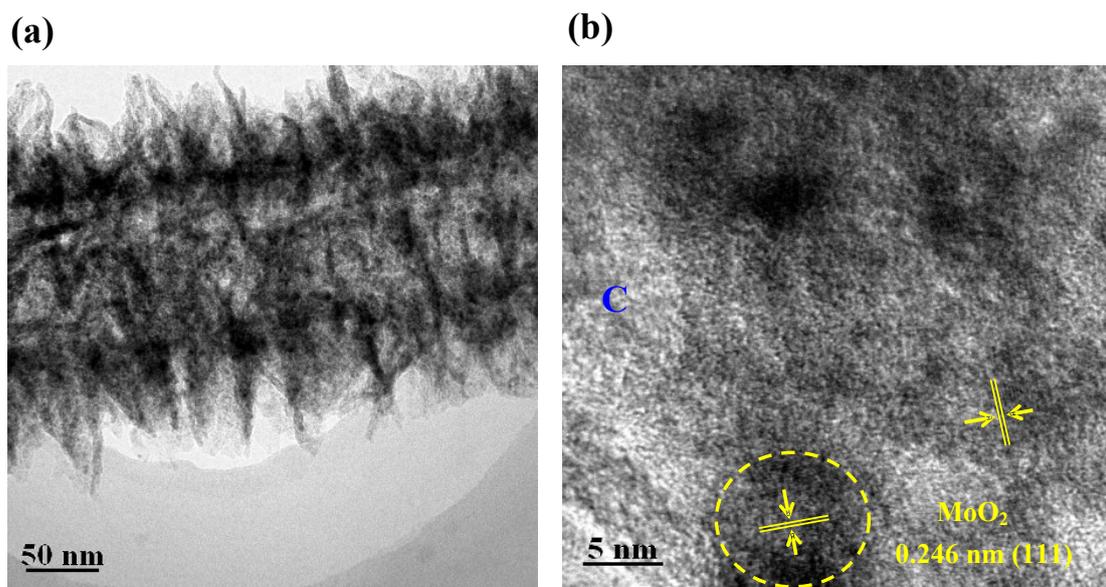


Figure S1

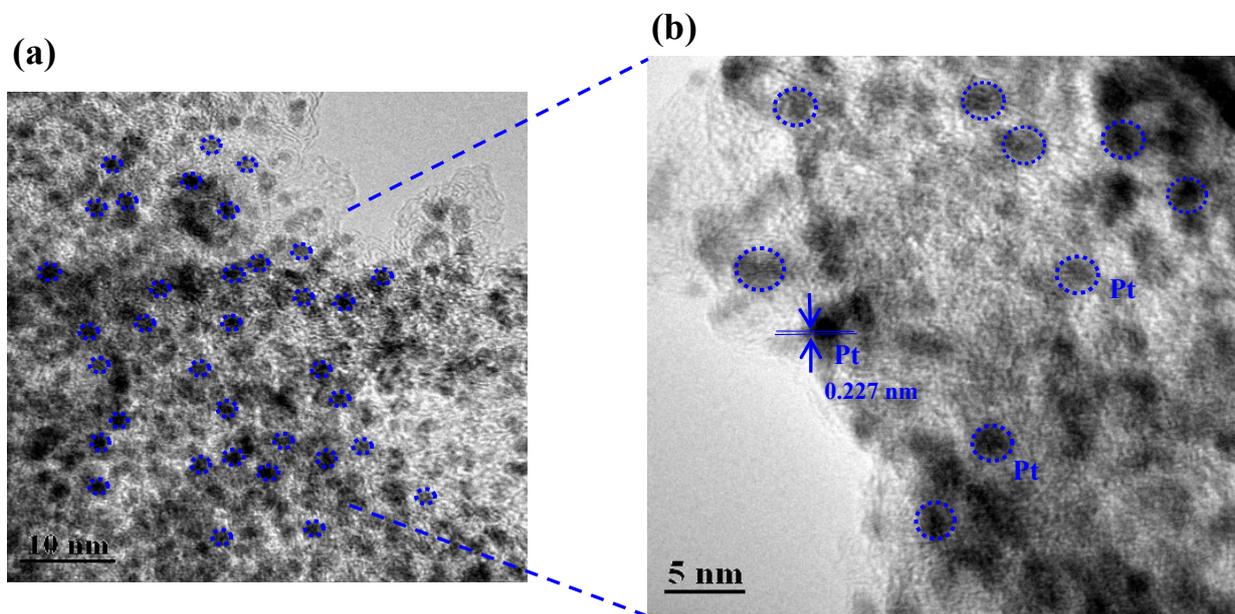


Figure S2

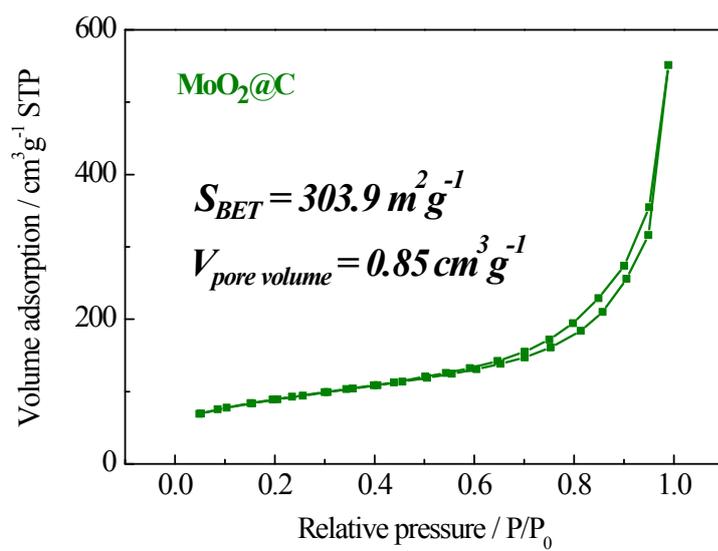


Figure S3

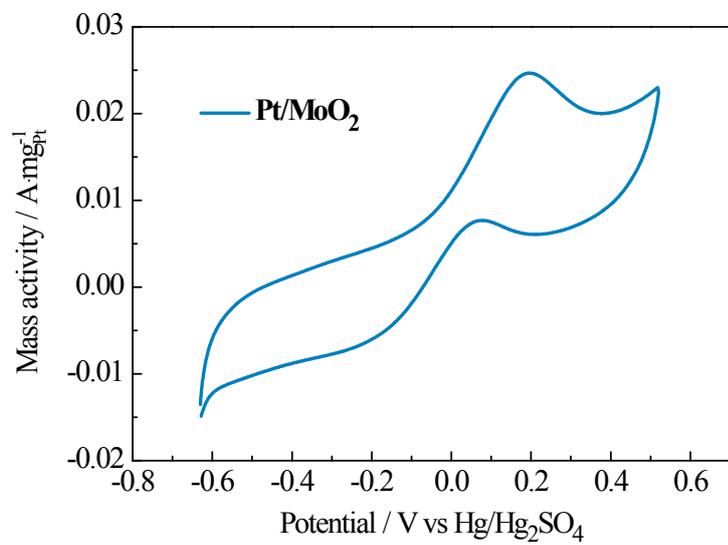


Figure S4

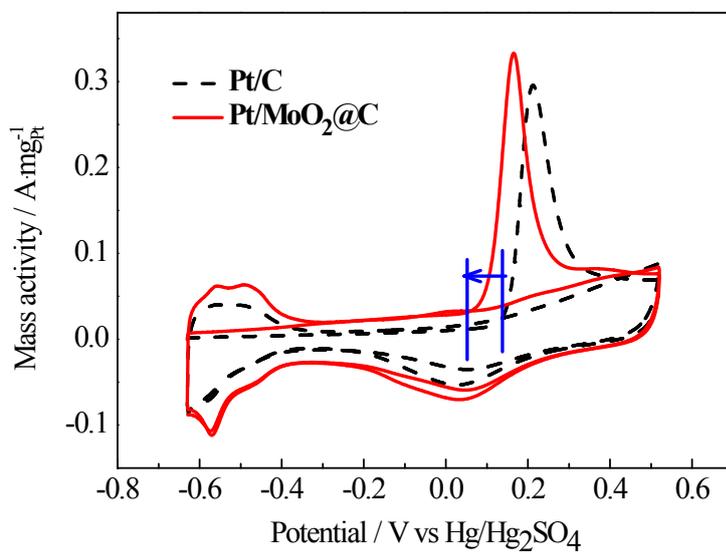


Figure S5

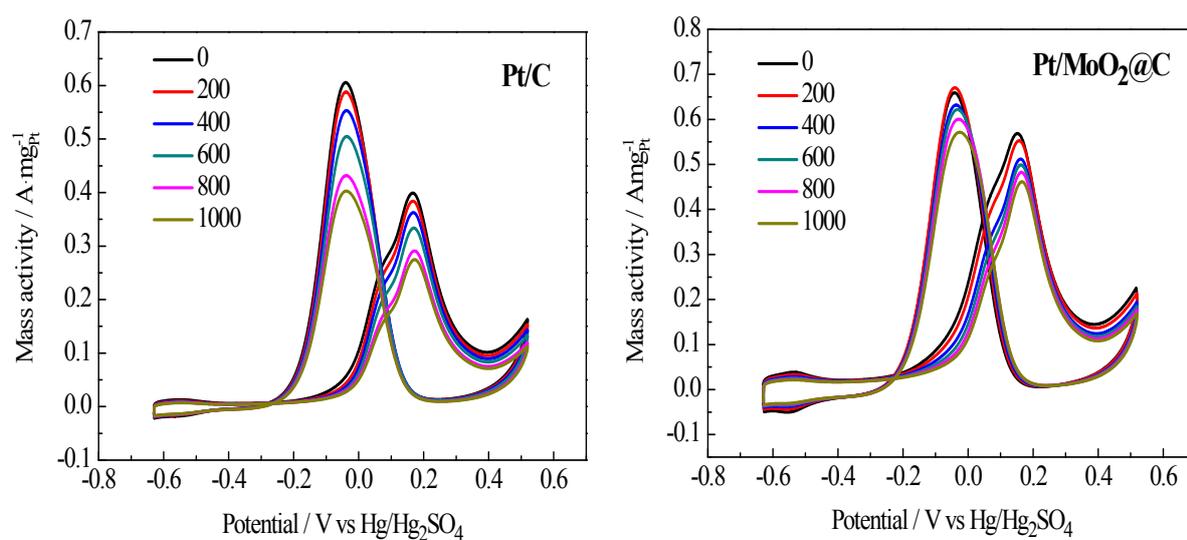


Figure S6

Table S1. Comparison of MOR performance in acidic media of hierarchical Pt/MoO₂@C nanotubes with some representative MOR electrocatalysts

Catalyst	ESA _{Pt} / m ² g ⁻¹	Mass activity/ mA mg ⁻¹
Pt/ETEK [3]	54.1	0.36
Pt/Ir-CNT [4]	51	0.058
Pt/B-G [5]	58.8	0.386
Pt/Ppy-C [6]	60.9	0.55
Pt/MoO ₂ @C (our work)	91.3	0.57

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