

Electronic Supplementary Information

Highly dispersed MoO_x on carbon nanotube as support for high performance Pt catalyst towards methanol oxidation

Zhiming Cui ^{a,b}, San Ping Jiang ^c and Li Changming ^{a,b*}

^a Institute for Clean Energy & Advanced Materials, Southwest University, Chongqing 400715, P.R. China

^b School of Chemical & Biomedical Engineering & Centre for Advanced Bionanosystems, Nanyang Technological University, 70 Nanyang Drive, Singapore 637457

^c Curtin Centre for Advanced Energy Science and Engineering, Curtin University, Perth, WA 6845, Australia

Experimental

Materials: H₂PtCl₆ (Sigma-Aldrich). Multi-walled carbon nanotubes (CNTs, 20-40 nm in diameter and 5-15 μm in length, Shenzhen Nanotech Port Co., Ltd., China.). The as-purchased CNTs were surface oxidized by H₂SO₄-HNO₃ mixture (8.0 M for each acid) for 4h in an ultrasonic bath. Poly(diallyldimethylammonium chloride) (PDDA, 20 wt% in water, MW = 5000–40000, Sigma-Aldrich), Phosphomolybdic acid (H₃PMo₁₂O₄₀, Keggin-type, Sigma-Aldrich)

The preparation of MoO_x/CNTs: 50 mg of carbon nanotubes were initially suspended in 50 ml 10 mg ml⁻¹ PDDA solution by ultrasonication. After stirring for one night, the solution was centrifuged and washed with deionized water for several times. PDDA-CNTs were then sonicated in 50 ml 10 mg ml⁻¹ HPMo solution. After stirring for 24h, the solution was filtered and washed with deionized water for several times and then dried at 60 °C to obtain HPMo-PDDA-CNTs. Then the HPMo-PDDA-CNTs were calcined at 600 in N₂ for 6 h to give a decomposition product of MoO_x/CNTs.

The deposition of Pt nanoparticle on MoO_x/CNTs and CNTs: Firstly, 50 mg of MoO_x/CNTs (or CNTs) was suspended in 50 ml of ethylene glycol solution, and an appropriate amount of H₂PtCl₆ solution was added. Then the mixture was heated at 150 °C for 3 h. Subsequently, the suspension was filtered and washed with deionized water, and then dried at 80 °C for 6 h to obtain the Pt-MoO_x/CNTs catalysts (or Pt/CNTs).

Physicochemical characterization of catalysts: The zeta potentials of the samples were measured using a zeta potential analyzer (Brookhaven Instruments Co., USA). The size and morphology of Pt-MoO_x/CNTs catalysts and Pt/CNTs catalysts were characterized by TEM (JEOL JEM 2010). X-ray diffraction spectra were measured with a Shimadzu XRD-6000 X-ray diffractometer with a Cu K α radiation. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Kratos XSAM-800 spectrometer with an Mg K α radiator.

2.4. Electrochemical Measurements

Electrochemical measurements were carried out with a potentiostat/galvanostat (Autolab model PGSTAT30) and a conventional three-electrode test cell. The catalyst ink was prepared by ultrasonically dispersing the mixture of 5 mg catalysts, 1 mL ethanol, and 50 μ L 5 wt. % Nafion solutions. 10 μ L catalyst inks was pipetted and spread on the glassy carbon disk. A Pt foil and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. For Polarization current vs. time the potential was fixed at 0.6 V. The CO stripping voltammograms was measured by oxidation of pre-adsorbed CO (CO_{ad}) in the 0.5M H₂SO₄ solution at a scan rate of 20 mV s⁻¹. CO was purged into the 0.5 M H₂SO₄ solution for 30 min to allow the complete adsorption of CO onto the catalyst when the working electrode was kept at 0 mV vs Ag/AgCl electrode. Excess CO in the electrolyte was then purged out with N₂ for 10 min. The amount of CO_{ad} was evaluated by integration of the CO_{ad} stripping peak.

Results

1. Zeta potential test

The zeta potential of the MWCNTs changes significantly after treated in PDDA and HPMo solutions. The positive zeta potential for PDDA-CNTs is clearly due to the functionalization of CNTs by the positively charged PDDA, while the negative zeta potential for HPMo-PDDA-MWCNTs indicates the successful assembly of HPMo on PDDA-CNTs.

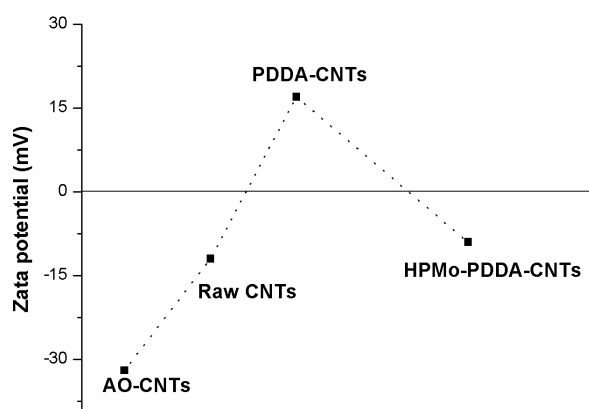


Fig. S1. Zeta potential of AO-CNTs, Raw-CNTs, PDDA-CNTs and HPMo-PDDA-CNTs.

2. EDX test

Table S1. The weight percent of elements for Pt-MoO_x/CNTs and MoO_x/CNTs by EDX.

<i>samples</i>	C (%)	O (%)	Mo (%)	Pt (%)
Pt-MoO _x /CNTs	65.85	8.58	4.54	21.03
MoO _x /CNTs-1	81.05	10.93	8.02	-
MoO _x /CNTs-2	69.2	14.67	16.13	-
MoO _x /CNTs-3	58.58	18.84	22.58	-

Different bilayer of PDDA and HPMo (1, 2 and 3) were formed on CNTs, and these composites were calcined in N₂ to get MoO_x/CNTs-1, MoO_x/CNTs-2 and MoO_x/CNTs-3. It can be observed that Mo loading of MoO_x/CNTs increase linearly with self-assembly layers. Here MoO_x/CNTs-1 was used to prepare Pt-MoO_x/CNTs.

3. TGA test

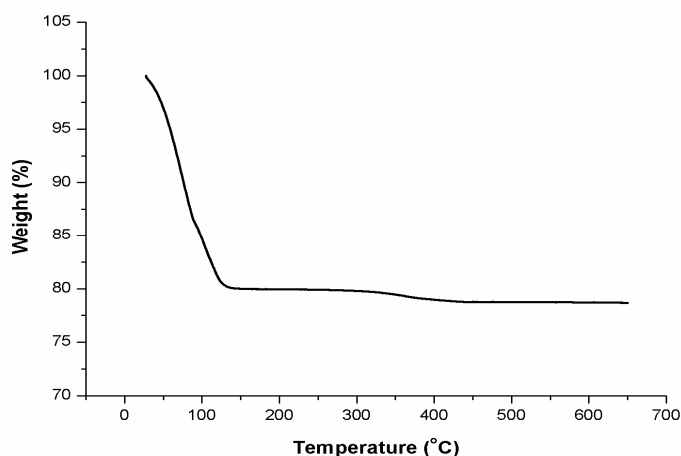


Fig. S2 TGA diagrams of HPMo

Thermogravimetric analysis (TGA) of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (HPMo) was performed at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under N_2 atmosphere. As shown in Fig.S2, HPMo loses crystalline water up to $250\text{ }^{\circ}\text{C}$. The decomposition of HPMo above $300\text{ }^{\circ}\text{C}$ is believed to occur as (Masayuki Nogami et al, Chem. Mater. 2007, 19, 3604-3610):



It's well known that P_2O_5 will sublime at $\sim 340\text{ }^{\circ}\text{C}$. Thus, the final products is MoO_3 , which is also further confirmed by the following XRD.

4. XRD test

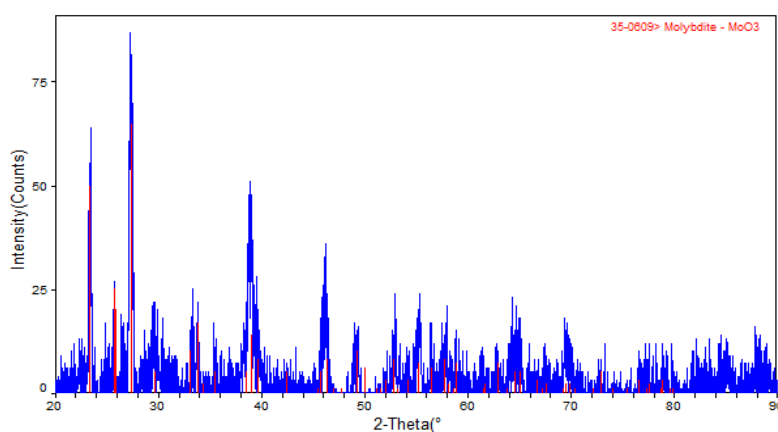


Fig. S3 XRD patterns of the final decomposition product of HPMo

As shown in Fig.S3, The diffraction peaks at 23.3° , 25.7° , 27.3° , 29.6° , 33.7° and 49.2° can be assigned to the 110, 040, 021, 130, 111 and 002 lattice reflections based on orthorhombic MoO_3 (PDF #35-0609). No other diffraction peaks are observed except for the diffraction peaks of MoO_3 .

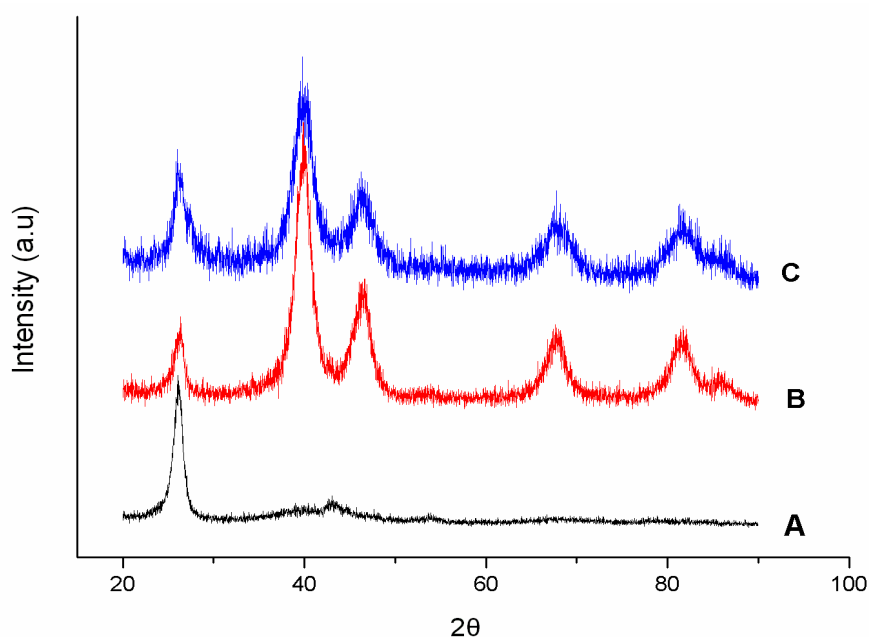


Fig. S4 XRD spectrum of MoO_x/CNT (A), $\text{Pt-MoO}_x/\text{CNT}$ (B) and Pt/CNTs (C).

As shown in Fig. S4, the XRD pattern of MoO_x/CNTs (A) showed mainly graphite diffraction peaks corresponding to the carbon support. This indicated that most of the molybdenum species in MoO_x/CNTs did not form crystalline aggregate. The Pt/CNTs and $\text{Pt-MoO}_x/\text{CNTs}$ exhibit characteristic patterns of Pt face-centered cubic (fcc) diffraction.

5. XPS

PDDA is a quaternary ammonium and polyelectrolyte. Its structure is shown in Fig.1. PDDA may undergo pyrolysis and carbonization process with increasing temperature to 600°C under N_2 atmosphere. Therefore, PDDA is not responsible for the shift of binding energy of Pt 4f. EDX shows that Mo loading is 4.54 wt.% in $\text{Pt-MoO}_x/\text{CNTs}$, which confirms the existence of molybdenum oxides. The shift of binding energy of Pt 4f can be attributed to the interaction between Pt particles and MoO_x/CNTs support.

6. TEM test

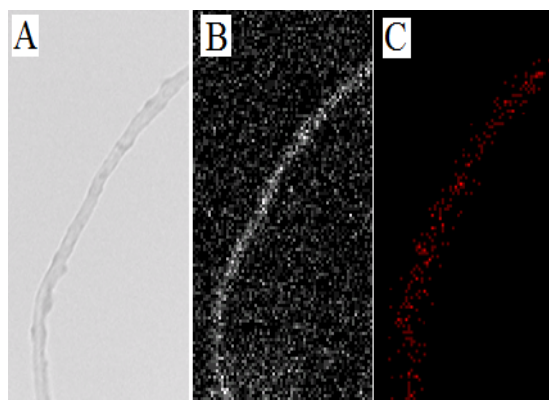


Fig. S5 TEM image of (A) HPMo-PDDA-CNTs and element distributions of (B) C and (C) Mo

The TEM image of HPMo-PDDA-CNTs (A) corresponds well with the EDS mapping of C and Mo elements (B and C). This shows that HPMo molecules were uniformly assembled onto the PDDA-MWCNTs, forming HPMo-PDDA-CNT catalyst support.

7. Electrochemical test

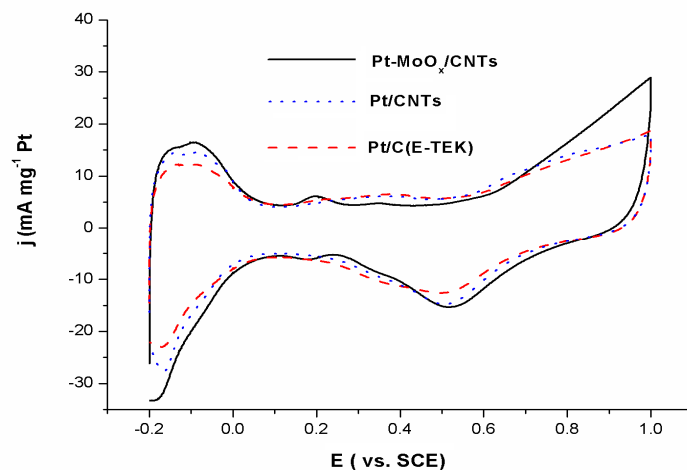


Fig. S6. Cyclic voltammograms recorded in 0.5M H₂SO₄ solution at a scan rate of 20 mV s⁻¹.

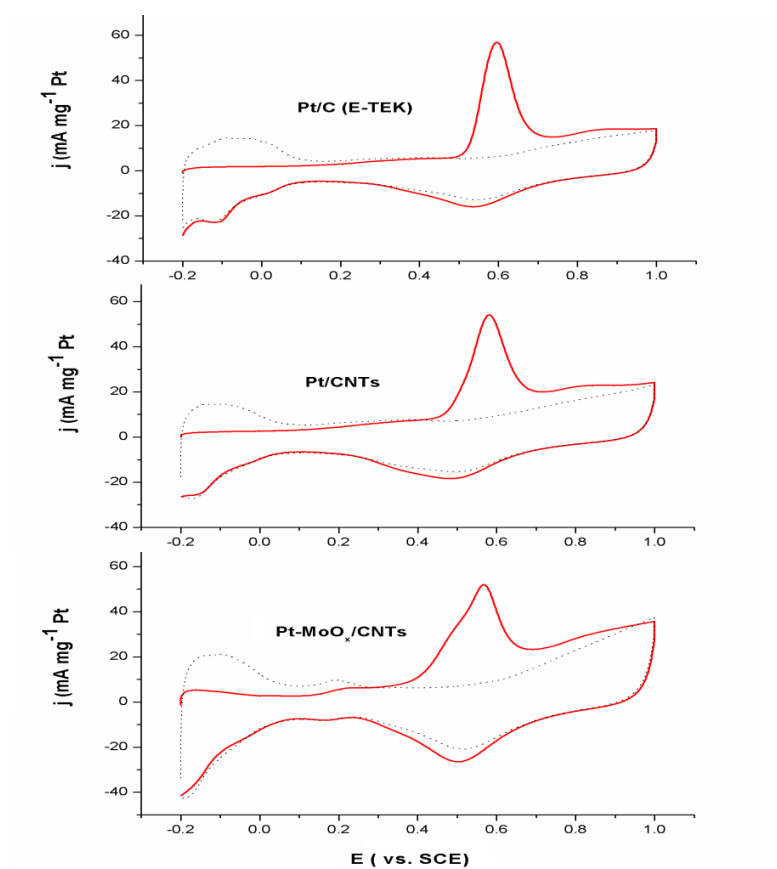


Fig. S7. CO_{ad} stripping voltammograms for Pt/C (E-TEK), Pt/CNTs (b) and Pt-MoO_x/CNTs.