Electronic Supplementary Information

Probing Synergetic Effects Between Platinum Nanoparticles Deposited via Atomic Layer Deposition and Molybdenum Carbide Nanotube Support through Surface Characterization and Device Performance

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Thermogravimetric Analysis

TGA was carried out on bare Mo₂C samples to qualitatively determine free carbon percentages. As shown in Figure S1, an obvious weight loss in the temperature range of approximately 690 to 750 K could be attributed to oxidation of some amorphous carbon (around 6.4wt% calculated from the decrease in weight) remaining in the samples. When the temperature was raised above 750 K, an increase in weight % was observed and could be attributed to the oxidation of the Mo₂C samples to molybdenum trioxide and carbon dioxide. The weight gain was observed until 960K and the decrease in weight from 960K could be attributed to the evaporation of MoO₃.



Figure S1. Thermogravimetric analysis of Mo₂C under air at the heating rate of 10°C/min.







Figure S3. (a) Pt 4f spectra (b) Pt 4f BE shift for different Ar sputtering time of 100 Pt/Mo₂C (c) C1s XPS peak of 15, 50 and 100 Pt/Mo₂C.

Cyclic Voltammogram of 15 Pt/Mo₂C per Pt mass

Based on the most conservative Pt loading estimation using the number of ALD cycles and Pt loading in 100 cycles of ALD, Pt wt% for 15 Pt/Mo₂C comes out to be 0.66%. LSV and CV for 15 Pt/Mo₂C per Pt mass was obtained below (Fig. S4) from the estimated Pt wt% for 15 Pt/Mo₂C.



Figure S4. (a) LSVs (b) CVs of 15 Pt/Mo₂C and 20% Pt/C where current normalized to Pt loading. Inset: Current normalized to Pt loading at -144mV vs. RHE.

Effect of potential cycling on Pt/Mo₂C



Figure S5. Linear sweep voltammograms (LSV) after 3000 potential cycling from -0.4 to 0.6 V of (a) 100 Pt/Mo₂C (11.9 μ g Pt/cm²_{disk}), (b) 50 Pt/Mo₂C (2.9 μ g Pt/cm²_{disk}), (c) 20% Pt/C (54.3 μ g Pt/cm²_{disk}) with the scan rate of 2 mV/s in N₂ Saturated 0.1M HClO₄ solution.



Figure S6. Preliminary device data with Pt loading of 0.4mg cm⁻² on the anode for both 100 Pt/Mo₂C and 20% Pt/C. Cathode is made of commercial 20% Pt/C with Pt loading of 0.4 mg Pt cm⁻². OCV in insets stands for open circuit voltage.



Figure S7. Device data on 100 Pt/Mo₂C in anode using different fabrication techniques. Pt loadings in anode for Ultrasonic Spray: 0.015 mg cm⁻²; for Brush Paint: 0.02 mg cm⁻². Cathode is made of commercial 20% Pt/C with Pt loading of 0.4 mg Pt cm⁻².

Schematic of D-band center shift due to increased lattice spacing

According to Ruban et. al. when a metal with smaller lattice spacing is deposited on top of another metal with higher lattice spacing, the d-band width of the overlayer metal is lowered due to the reduced local electron density causing the upward shift of the d-band center as can be seen from Figure S5.



Figure S8. Schematic diagram of d-band center shift as a result of tensile strain on metal over layer.

Electrochemically Active Surface Area Calculation:

ECSA calculation was performed using the concept reported by Rodríguez et. *al.*¹ Here the charge of monolayer hydrogen adsorption was used to determine the ECSA. This charge is associated with the area shown in Fig. S9 for 50 Pt/Mo₂C. Equation S1 is used to determine total charge Q associated for the hydrogen adsorption,

Ean S1

$$Q = \int_{t_i}^{t_f} I dt$$
 Eqn S1
where t_i

is the

time when H^+ starts getting adsorbed on the surface, t_f is the time when a monolayer of hydrogen atom is formed and just before hydrogen evolution (shown in the shaded area in Fig. S9) and I is the current density of the reaction. However, from the CV curve the limits are in potential. These potential limits can be converted into time by equations S2 and S3. Specifically, in the reverse sweep potential is varied according to equation S2,

$$V = V_0 - vt$$
 Eqn S2

where V_0 is the initial potential, v is the scan rate and V is the potential at time t. Using equation S2, the initial and final time was obtained from the respective potentials using CV curves,

$$t_{i} = \frac{V_{0} - V_{i}}{v}$$
Eqn S3
$$t_{f} = \frac{V_{0} - V_{f}}{v}$$
Eqn S4

Following the conversion from potential limits to time, I vs. t curve can be obtained using equation S2. Total charge, Q, associated within the potential limits shown in the shaded area (Fig. S9) can then be determined by integration of I vs. t curve using the limits obtained by Eqn S3 and S4 via trapezoidal method. This total charge comprises double layer charge and hydrogen adsorption charge. The actual monolayer hydrogen adsorption charge Q_M can then be determined by subtracting the double layer current for the duration of $(t_f - t_i)$ from Q. Specifically, double layer charge can be written as,

$$Q_{dl} = I_{dl}(t_f - t_i)$$
Eqn S5

Therefore, the monolayer hydrogen adsorption charge will be,

$$Q_M = \int_{t_i}^{t_f} I \, dt - I_{dl}(t_f - t_i)$$
Eqn S6

Once

monolayer charge is determined, ECSA can be calculated using following equation,

the

$$ECSA = \frac{Q_M}{\Gamma L}$$
 Eqn S7

Where

the charge required to reduce a monolayer of protons on Pt, which is a constant. For Pt, Γ equals to 210 μ C cm⁻². L is the Pt loading on the electrode in g_{Pt}cm⁻².²



Figure S9. CV of 50 Pt/Mo₂C showing the region used for ECSA calculation.

References

1. J. D. Rodríguez and J. H. Melián, Journal of Chemical Education, 2000, 77, 1195.

2. K. Kinoshita and P. Stonehart, in Modern Aspects of Electrochemistry, Springer US, Boston, MA, 1977, pp. 183–266.

 Γ_{is}