SUPPORTING INFORMATION

Continuous and Ultrathin Platinum Films on Graphene using Atomic Layer Deposition: A Combined Computational and Experimental Study

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Supporting Figures (Figure S1-S7)

Figure S1. Different physisorption orientations of MeCpPtMe₃ and Pt(acac)₂ on pristine graphene [and associated binding energies] as predicted at the PBE-D3 level of theory.

Figure S2. Binding of multiple MeCpPtMe₃ precursor molecules on graphene with grain boundaries.
$2(C-O)^* + \text{MeCpPtMe}_3 \rightarrow \text{C-MeCpPtMe}_2^* + \text{C-Me}^*$

$\Delta E_a = 0.15 \text{ eV}, \Delta E_r = -2.73 \text{ eV}$.

$2(C-OH)^* + \text{MeCpPtMe}_3 \rightarrow \text{C-MeCpPtMe}_2^* + \text{CH}_4$

$\Delta E_a = 0.05 \text{ eV}, \Delta E_r = -3.42 \text{ eV}$.
Figure S3. PBE-D3 level energetics (from CI-NEB computations) corresponding to MeCpPtMe3 binding on graphene with (top) epoxided and (bottom) hydroxylated grain boundaries. Here, the first points (physisorbed species) are (top) -0.40 eV and (bottom) -0.49 eV with respect to the respective separated species (MeCpPtMe3 and graphene).
(b) Epoxydated GO (double-sided)
(d) Hydroxylated GO (double-sided)
Figure S4. Ball-and-stick representation of the lowest-energy (left) physisorbed and (right) chemisorbed species of MeCpPtMe3 and Pt(acac)2 on selected graphene oxide models considered in current DFT calculations. Relative chemisorption energies are given in brackets. Color code, C: brown; O: red; H: pink-white; Pt: Gray.
2(C-O)* + MeCpPtMe₃ → C-O-MeCpPtMe₂* + C-O-Me*
\[ \Delta E_a = 0.15 \text{ eV}, \Delta E_r = -3.65 \text{ eV}. \]

**Figure S5.** Minimum energy path of MeCpPtMe₃ binding on GO mixture via methyl transfer release mechanism as predicted by PBE-D3 level of theory.
$2(C-O)^* + \text{MeCpPtMe}_3 \rightarrow C-O-\text{MeCpPtMe}^* + \text{Me}_2^*$

$\Delta E_a = 1.59 \text{ eV}, \Delta E_r = -0.71 \text{ eV}$.

**Figure S6.** Minimum energy path of MeCpPtMe3 binding on GO mixture via Me2 release mechanism as predicted by PBE-D3 level of theory.

**Figure S7.** SEM images (with 20k X and 50 k X magnifications) showing the Pt ALD coverage after 1000 ALD cycles using MeCpPtMe3 as the Pt precursor on graphene oxide obtained by a 5-min O2 plasma treatment.