Epitaxial and Atomically Thin Graphene-Metal Hybrid Catalyst Films: The Dual Role of Graphene as the Support and the Chemically-Transparent Protective Cap

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Supporting Information

Experimental Section

Synthesis

In this study, Pt monolayers are electrochemically grown on 50 nm thick Au (111) thin films grown by electron beam evaporation, supported on glass substrates, using surface limited redox replacement (SLRR) as the primary synthesis method. Detailed methodology about Pt monolayer synthesis and Au films PVD are published elsewhere. The study embodies three main sample architectures to examine the incorporation of graphene with Pt monolayers as a catalyst system. The first sample case consists of Pt monolayers grown without graphene (Pt_ML). The second case includes Pt monolayers grown on a graphene template (Pt_ML/GR), and the third sample case includes Pt monolayers covered with a single-layer graphene placed on top (GR/Pt_ML).

Electrochemical oxygen reduction reaction (ORR) probing

ORR was probed through linear sweep voltammetry (LSV) for two sample sets with and without a single-layer graphene cap (i.e. GR/Pt_ML and Pt_ML, respectively) in O$_2$-saturated 0.1 M H$_2$SO$_4$. ORR polarization curves were generated by linearly sweeping voltage negatively from 800 mV to -100 mV (vs. Ag/AgCl). The resulting current achieved during the potential sweep has been attributed to the oxygen reduction reaction. By taking the first derivative of the ORR polarization curves, the peak position represents the inflection point of the current reaction curve and can be used to evaluate the required overpotential needed to catalyze the ORR. Since a negative potential sweep (i.e. cathodic reaction probing) was used,
the higher the reported potential values are for the first derivative peak position, the lower the required overpotential is for the ORR to take place. An overlay of the original ORR curves can be seen in Figure 2S of Supporting Information.

Figure S2: ORR polarization curves for 1-5 MLs obtained by linear sweep voltammetry in O2-saturated 0.1 M H2SO4. a.) GR/Pt_ML and b.) Pt_ML samples. The sweep rate is 20 mV/s. Reference electrode used was Ag/AgCl.

Figure S2 shows ORR polarization curves for Pt_ML samples with 1 - 5 ML thick surface shells. This data is the same as used for the first derivatives as seen in Figure 4-b, left inset.
Figure S3 shows the XPS spectra for both the GR/Pt_ML and Pt_ML sample sets. The positions of these peak features are found in Figure 4-b, right inset.

Pt monolayer catalyst durability testing

To investigate how graphene affects the durability of Pt catalyst over time, a subset samples were cycled from 400 mV to 750 mV (vs. Ag/AgCl), under harsh condition in oxygen-saturated 0.1 M H$_2$SO$_4$ at room temperature for 1000 cycles. CV sweeps tested the Pt MLs electrochemical active surface area (ECSA) to monitor surface Pt-catalyst loss. A characterization CV curve from 0 V to 1.20 V was taken in nitrogen-saturated 0.1 M H$_2$SO$_4$ at three intervals (i.e. before ADT, after 500 cycles and after 1000 cycles) in order to examine the changes in Pt reduction peaks ~0.4 V, as the surface undergoes cycling protocols.

Raman spectroscopy was used to verify the state of the graphene during cycling, and these results are shown in Figure S4, which compares a single-layer graphene deposit Pt_ML sample both before and after ORR cycling experiments. The two most intense features seen are the so-called G band at ~1580 cm$^{-1}$, which originates from in-plane vibration of sp$^2$ carbon atoms,$^{[6,7]}$ and the 2D band at 2700 cm$^{-1}$ (historically named G$'$), which arises from second-order phonons.$^{[8]}$ Single-layer graphene is known to exhibit an intense Lorentzian-shaped 2D peak and a 2D:G ratio of ~2 or greater.$^{[9]}$ As shown in Figure 11, the 2D:G intensity ratio is seen to be 1.110. After undergoing cycling experiments, the 2D feature shifted only 2 cm$^{-1}$, and the 2D:G intensity ratio reduces to 1.007. Shifting of the 2D feature positions and an increase of the FWHM can be seen as an indication of either strain or charge transfer between the graphene and Pt/Au.$^{[10]}$
The reduction of the 2D:G ratio is known to be a clear indication of charge transfer. A combination of strain and charge transfer is consistent with the observed charge transfer by XPS and observed strain by EXAFS. While changes to the 2D and G band are observed, no significant D band at ~1350 cm\(^{-1}\) is observed indicating defects in the graphene remain negligible even after 1000 cycles.

*Figure S4: Raman shift spectra for GR/Pt_ML before cycling and after cycling experiments.*
Pt-capped graphene monolayers ORR activity was evaluated against Pt-carbon commercial nanoparticles that are available readily in the market. Results, in terms of mass activity, showed similar ORR activity. Five atomic layers of Pt capped with graphene (GR/Pt_5ML) showed enhancement in electrochemical surface area (ECSA) and catalyst durability after 1000 cycles by 43% and 170%, respectively, when compared to its Pt-carbon commercial counterpart. Results are shown in Figure S5.

![Figure S5: Comparison between Pt-carbon commercial nanoparticles (Pt-XC Commercial) and 5 atomic layer thick Pt capped with graphene (GR/Pt_ML). For each comparison, Pt-XC commercial was set as a reference with 100% performance and GR/Pt_ML was evaluated accordingly.](image)

Samples with graphene cap showed extensive durability, surviving Pt-monolayers catalysts ECSA. XPS and CV data comparisons are shown in Figure S5 & S6 provide insights about Pt monolayers thickness and associated ECSA, before and after ADT. Graphene capped samples preserved their Pt coverage on the surface while graphene-free samples suffered dramatic loss Pt surface coverage.
Figure S6: Pt 3 atomic layers thick, the Pt 4f\(^{7/2, 5/2}\) pair and the Au 4f\(^{7/2}\) XPS spectra for GR/Pt_ML samples and Pt_ML samples are shown before and after ORR cycling.

Figure S7: Cyclic Voltammetry sweeps before and after ADT for 4 ML Pt thick with and without graphene capping.
Figure S8: Dark atom contrast TEM image of Pt ML on pristine graphene, with an inset of Fast Fourier Transform (FFT) of TEM image with highlighted diffraction spots of graphene in red and {100} Pt in blue. TEM image showing templated Pt ML on graphene (the growth front outlined by the yellow dotted line). A single-atom thick row of atoms is highlighted between the dashed turquoise and dotted yellow lines. Beyond that row, the stacking of the second layer atoms occupies atop positions over the first layer atoms. The superimposed red graphene lattice shows the Pt/GR registry with Pt occupying bridge sites (yellow for would-be and blue for actual locations) on graphene, along the zigzag and the armchair directions.
Sources


