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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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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ABSTRACT

In this study, we demonstrate dual roles for graphene, as both a platform for large-area, fully-wetted growth of two-dimensional Pt films that are one monolayer to several multilayers thick, while also serving as a 'chemically transparent' barrier to catalytic deactivation wherein graphene does not restrict the access of the reactants but does block Pt from dissolution or agglomeration. Using these architectures, we show that it is possible to simultaneously achieve enhanced catalytic activity and unprecedented stability, retaining full activity beyond 1000 cycles, for the canonical oxygen reduction reaction (ORR). Using high resolution TEM, AFM, x-ray photoemission/absorption spectroscopy (XPS/XAS), Raman, and electrochemical methods, we show that, due to intimate graphene-Pt epitaxial contact, Pt_ML/GR hybrid architectures are able to induce a compressive strain on the supported Pt adlayer and increase catalytic activity for ORR. With no appreciable Pt loss or agglomeration observed with the GR/Pt_ML catalysts after 1000 ORR cycles, our results open the door to using similar graphene-templated/graphene-capped hybrid catalysts as means to improve catalyst lifetime without a necessary compromise to their activity. More broadly, the epitaxial growth made possible by the room-temperature, wetted synthesis approach, should allow for efficient transfer of charge, strain, phonons and photons, impacting not just catalysis, but also electronic, thermoelectric and optical materials.

INTRODUCTION

The prospect of a graphene-metal epitaxy is tantalizing, since such a material architecture would have a broad and immediate impact on the science and technology of surfaces and interfaces. Properties of metal-graphene interfaces that are currently being investigated, for example, from the point of view of reduced electron/phonon scattering [1] and enhanced surface-state passivation [2] can, with epitaxy, be imagined to reach theoretical limits. Similarly, the practically impermeable graphene to the transport of most atoms and standard small molecules, [3] means that the metal-graphene epitaxial interface has the promise of near-infinite corrosion resistance. With the recent demonstration of roll-to-roll synthesis of continuous monolayer graphene films with millimeter-sized domains under industrially safe conditions, [4] it is also quite timely to realize graphene-metal epitaxial systems that may be ready for scale-up.

If metals can be deposited on the graphene as continuous, atomically-thin films, then one obvious area that such an architecture will impact is catalysis. Improving the catalyst activity, material utilization, and durability is essential to a wide array of energy applications, where expensive catalysts based on Pt

still set the benchmark of performance. Epitaxial graphene-metal catalysts can potentially transcend the activity-stability dilemma; atomically thin epitaxial films render nearly every catalyst atom in an active surface site while the bonds from the epitaxy can also provide increased stability against detachment [5] or Ostwald ripening. While there have been schemes to increase stability by increasing the interaction energy with either alloyed-in high melting temperature metals that can induce compressive strain on Pt atoms,[6, 7] or with the catalyst supports,[8] these approaches necessarily compromise on the activity and on the compositional range of the catalyst/support architecture.

Another intriguing prospect of graphene-metal epitaxy is the possibility of catalysis from the graphene side, with the catalyst film sandwiched between the graphene and the support. While several groups have investigated using graphene as a support material for long-term durability,[9-14] incorporating graphene as a protective barrier has not been thoroughly studied. A true epitaxy should involve a shared electronic structure between the graphene and the catalyst, and, as a result, one can imagine that reactions on the graphene side of the hybrid structure would have activity comparable to that of catalyst side. However, now that the catalyst is trapped between the graphene and the support, it would be expected to have unprecedented stability.
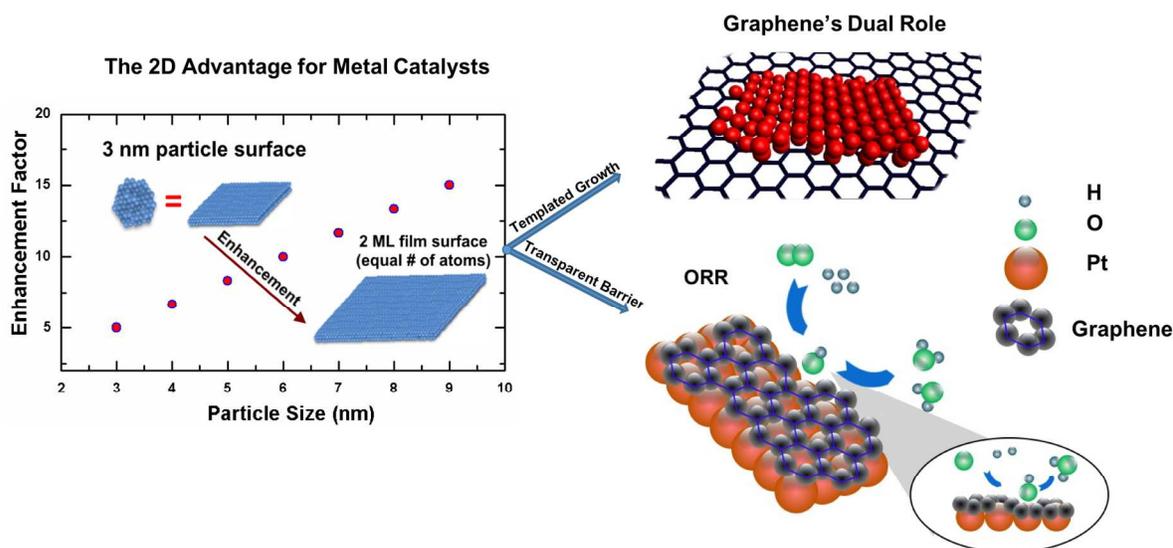

Figure 1: The enhancement factor of surface sites available for catalysis when the number of atoms in a nanoparticle are redistributed as a 2 ML film is shown (left). The dual roles of graphene are illustrated, as the platform for 2D growth (upper right) and as a protective, 'chemically transparent' barrier in catalytic reactions such as ORR (lower right). (Inset) The nearest vicinity between Pt and OH- through graphene.

These concepts of graphene (GR) playing a dual role, both as a template for epitaxial growth and as a protective cap against catalyst loss, for monolayer to few multilayer Pt films (Pt_ML) are captured in Figure 1. The first role, for example, translates to nearly an order of magnitude enhancement in the number of surface atoms, when comparing 2 Pt_ML to a 5 nm particle. The second role translates to a potentially 'chemically transparent' barrier to catalysis, such as in the canonical oxygen reduction reaction (ORR).

In a previous study,[15] we demonstrated that room temperature layer-by-layer synthesis of Pt_ML/GR/Au is possible, and that, in such cases, a sizeable compressive strain is transferred to the Pt atoms from the GR. At the same time, the hybrid electronic structure of this architecture allows charge transfer between the Au ligand to the Pt surface through the sandwiched GR. In this study, we first investigate the nature of the Pt/GR interaction and, if epitaxial, the details of the atom-atom registry.

We further posit that the inherent strength of the sp^2 bonding in graphene should not only provide structural integrity against its own (carbon) chemical corrosion but, as an atomically intimate cap over the catalyst, it should also act as a barrier preventing catalyst loss. Furthermore, we expect that a reaction fundamental to (electro)catalytic energy conversion, ORR, can take place on the graphene side of the hybrid catalyst without compromise to activity over a large number of reaction cycles.

We investigate these proposed ideas using layer-by-layer synthesized low-dimensional Pt films for which the stability and the electrochemical activity toward the ORR are studied in the presence/absence of graphene and as a function of the vicinity of surface Pt atoms to the graphene. This study embodies a fundamental first look at incorporating single-layer graphene into low dimensional Pt catalysts as both a support template (Pt_ML/GR) and as a protective surface cap (GR/Pt_ML), as shown in Figure 2. Surface coverage, catalytic activity, electronic and atomic structure were measured using a complementary suite of electrochemical and x-ray spectroscopic methods.
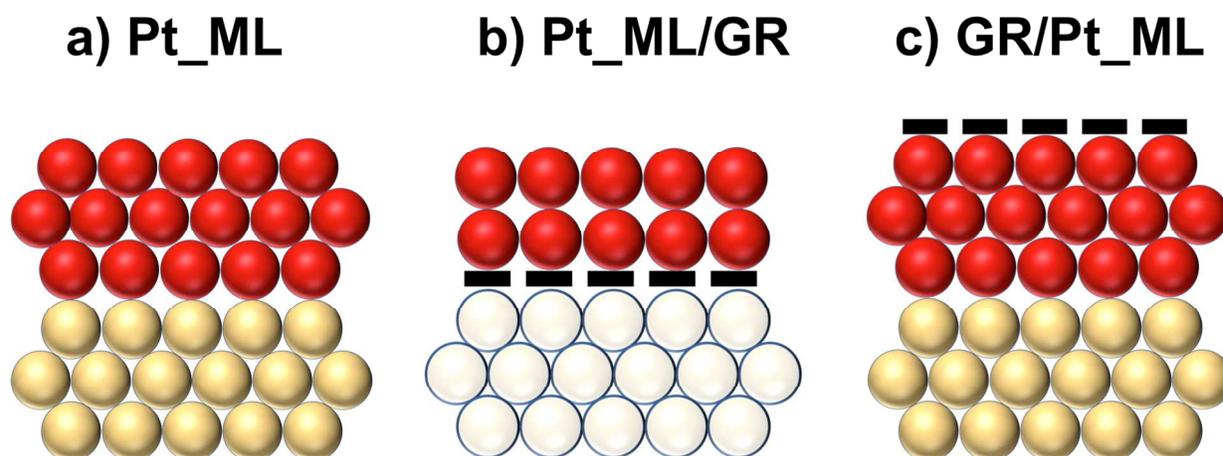

Figure 2: Studied samples architectures: a) Graphene-free Pt monolayers (red) electrochemically grown on an Au film (yellow) supported on a glass substrate, b) Pt monolayers grown on a graphene template with flexible underlying substrate: freestanding (i.e. no substrate), metal oxides, metal nitrides, pure metal films (e.g. Au as in 2a), and non-conductive glass, c) single-layer graphene capping Pt monolayers.

RESULTS AND DISCUSSIONS

Structural Analysis

In previously published work by this group, we found that wetted Pt monolayers can be deposited on a graphene template supported by an Au substrate, in a wetted, layer-by-layer, fashion.[15] Here we explore the morphology at different length scales of the Pt_ML/GR structure using atomic force microscopy, AFM, (Figure 3a) and high resolution transmission electron microscopy, HRTEM, and associated simulations (Figure 3b-h).

Surface roughness was measured by AFM for 3, 5 and 8 Pt monolayers (MLs) thick, electrochemically grown on a graphene monolayer supported on a glass substrate. Samples with surface thicknesses of 3 through 8 MLs showed an increase in the average root mean squared (rms) roughness from 2.6 to 3.1 nm. All AFM scans showed a fully wetted conformal coating of Pt MLs on the graphene surface. Taking the starting roughness of the graphene and glass substrate into account, the actual rms roughness of our 5 ML Pt film was found to be about ± 0.2 nm. In other words, the layer-by-layer growth on graphene

is smooth to about ± one atomic layer of Pt over at least 4 µm^2 regions (Figure 3-a). The change in surface roughness from 3 to 8 MLs confirmed the 2D wetted growth that avoids island formation or agglomeration (i.e. Ostwald ripening). Figure 3-i shows cyclic voltammograms (CV) of Pt_ML/GR sample case. Once the overlayer is around 4 ML in thickness, the Au reduction peak disappears in CV, which indicates an eventual total coverage of Pt over graphene. This observation shows that an ultrathin layer of Pt at 4 ML – roughly equivalent to ~1 nm thick, is able to fully mask the graphene template, i.e. pinhole free. The epitaxy with graphene further increases the activity of the monolayer catalyst for ORR (Figure 3-j). To our knowledge, this is the first reported full coverage of a metal on graphene at such low dimension over macroscopic surfaces areas (i.e. 1 cm^2),[15] and is believed to be directed by a graphene epitaxy. The finding opens the door to host potential applications beyond catalysis, such as in property-tunable transparent electrodes and atomically thin interconnects.
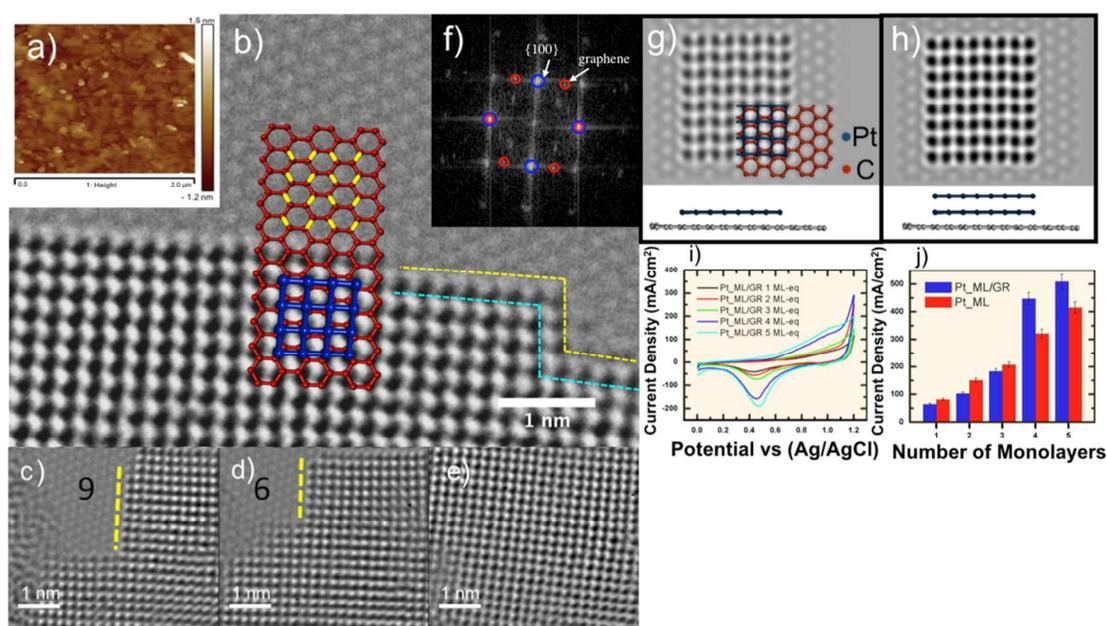

Figure 3: a) AFM over 2x2 µm for 5 ML of Pt on single layer graphene. b-e) Dark atom contrast TEM image of Pt ML on pristine graphene. b) TEM image of templated Pt ML on graphene (the growth front outlined by the yellow dotted line). A single-atom thick row of atoms is highlighted between the dashed 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. c-e) Pt growth evolution with the leading-edge transitioning between 9 (c) through 6 (d) to zero (e) empty rows. f) Fast Fourier Transform (FFT) of TEM image with highlighted diffraction spots of graphene in red and {100} Pt in blue. g&h) Simulated phase contrast images of 1 and 2 ML thick Pt on graphene, respectively, in {100} stacking. i) CV sweeps of Pt_ML/GR samples show the layer-by-layer evolution of Pt reduction peak ~0.45V and diminishing of Au reduction peak ~0.95 V with successive Pt MLs. j) ORR current density comparison of Pt MLs grown with or without graphene (i.e. Pt_ML/GR and Pt_ML, respectively), and the activity enhancement due to a graphene-induced compressive strain on Pt MLs.

HRTEM analysis of the Pt ML architecture on single-layer graphene provides insight into the Pt-GR bonding and the resulting epitaxial growth of Pt MLs. The dotted yellow line in Figure 3-b illustrates the atomically sharp edges and corners of the Pt growth-front that the graphene templating provided. The simulated red graphene lattice was overlaid on the graphene in Figure 3-b to illustrate how the Pt-GR registry was maintained throughout the Pt ML. The Pt atoms were seen to stabilize on the bridge site of above every other C-C bond in the zigzag direction and over each C-C bond in the armchair direction. These C-C bonds were highlighted in yellow and an example of Pt lattice that sits over these bonds is shown in blue.

Based on phase contrast simulation, the contrast difference between a carbon with different number of Pt atoms on top (e.g. one and two Pt atomic-layer thick on top of a single-layer graphene, as shown in Figure 3-g&h, respectively) was established. Atoms in regions of one-layer thick (e.g. atoms between yellow and turquoise lines) can be differentiated form those in double layer stacking (e.g. beyond turquoise line). Beyond that row, the second layer atoms maintain the template of the first layer by occupying atop positions. This stacking was seen over a mixed zone of 1-2 ML thick for 2-3 rows away from the growth front, beyond which a continuous 2 ML thick of Pt is observed over the remaining Pt layer imaged.

Figure 3-f shows the reciprocal space information obtained by an FFT of TEM image shown in Figure 3-b. The graphene diffraction pattern aligns with the Pt {100}, supporting observation from Fig. 3-b that graphene provides an epitaxial template for Pt atoms growth. Though the more efficiently-packed {111} planes, when stacked, would evolve the bulk face-centered cubic (FCC) structure of Pt, a marked absence of {111} diffraction spots were observed for one and two Pt monolayers thick. Due to epitaxial stabilization from graphene, the first two layers of Pt resist a transition away from the {100} stacking even at the cost of having lower Pt-Pt coordination (4 and 5 for single and double layers, respectively) relative to the close-packed {111} arrangement (6 and 9 for the single and double layers, respectively). Our Pt_ML/GR architecture opens the door to grow atomic-thin and wetted metal layers on 2D or 3D (i.e. foam-like) graphene with and without support, that can be transferred to a plethora of substrates [16] for various applications.

Structure-property relationship

In order to investigate the role of graphene capping on the catalytic activity of Pt monolayers catalysts, electrocatalytic activity towards ORR was investigated. Details about the experimental setup can be found in the supporting information.

For GR/Pt_ML samples, despite the Pt overlayer surface being fully capped by graphene, it was able to catalyze the ORR with no additional energy barrier. A reflection of the energy barrier is the onset potential of ORR. The description of the method for identifying the onset potential is provided at supporting information. In both the GR/Pt_ML and Pt_ML cases, the onset potential shifted positively as the number of Pt MLs increase, which is equivalent to a lower overpotential required to catalyze the ORR. For 1, 2, and 3 Pt MLs, the onset potential value of the GR/Pt_ML samples lies at a higher positive potential than corresponding Pt_ML samples. At 4 and 5 MLs, the two samples share similar overpotential values. This indicates that the presence of graphene at the surface of the Pt has either a beneficial or no harmful effect on the required overpotential towards catalyzing the ORR. Results are depicted by blue triangles in Figure 4-b. GR/Pt_ML sample of 5 atomic layer thick showed showed similar ORR current density, however, with a slight negative overpotential than state of the art Pt-carbon commercial catalyst. This can be attributed to difference in samples nature. Pt-carbon commercial ink contained nafion which is widely known to enhance ORR activity due to better

conductivity and contact of ORR species with the catalyst active sites, however GR/Pt_ML was tested for ORR without nafion.

In order to further investigate the surface chemistry of the monolayer catalyst platforms, X-ray photoelectron spectroscopy (XPS) was used to evaluate the electronic state of Pt MLs. Noticeable shifts can be seen in the binding energies of the Pt $4f_{7/2}$ photoemission for both sample sets as seen in Figure 4-b. The Pt_ML sample set showed a slight shift towards lower binding energies with increasing number of Pt monolayers, flattening out within a .05 eV margin of error at around 71.15 eV. On the other hand, GR/Pt_ML samples exhibited significantly lowered binding energies in all cases. The lowest binding energy is at ~70.8 eV for the 1 ML sample (~0.4 eV lower than its graphene-less counterpart), but this energy shifts higher with the addition of Pt, as seen in Figure 4-b insets. This decrease in binding energy for GR/Pt_ML samples can be explained by considering charge transfer. With this architecture, it is expected that graphene will have a net donation of electron density to Pt.[17] Such a transfer would affect the electron charge of the Pt monolayer shell, which creates a negative shift in its effective binding energy (i.e. to lower binding energy values), as measured in XPS. When only a single Pt ML is present, this negative shift was most significant as seen in Figure 4-b. As the Pt layer grew in thickness, the cumulative effect of this electron density transfer was diminished and nearly vanish by the 5th monolayer. XPS spectra of the Pt $4f_{7/2}$ photoemission for all samples can be found in Figure S3 of Supporting Information.

These binding energies for GR/Pt_ML samples can correlate with the advantage in ORR overpotential as discussed earlier. Lower Pt 4f binding energies indicate a metal *d* band shift towards the Fermi level, which can lead to higher activity by enhancing the kinetics for ORR.[18] Others have shown that changes in the d-band structure can be obtained indirectly using shifts in XPS core-level binding energies that are sensitive to d-band structure [19, 20], but we take it further a step further. We show that the shifts in Pt 4f binding energies, directly controlled by the dimensionality of Pt_ML catalysts in the presence/absence of graphene, and corresponding shifts in ORR overpotentials can be made. Figure 4-b shows how for each monolayer sample comparison, lower binding energy correlates to a positive shift in ORR overpotential, as depicted in green squares. Since adsorption of oxygen species plays a major role in determining the kinetics of ORR at Pt electrodes, maintaining access of Pt atoms to the electrolyte is necessary. Our data shows that the epitaxy between graphene and Pt allow the Pt atoms to be in sufficient electronic intimacy through the graphene with the incoming ORR reactant species, and the graphene-Pt hybrid surface is able to catalyze oxygen at an overpotential advantage when compared to a bare Pt surface.
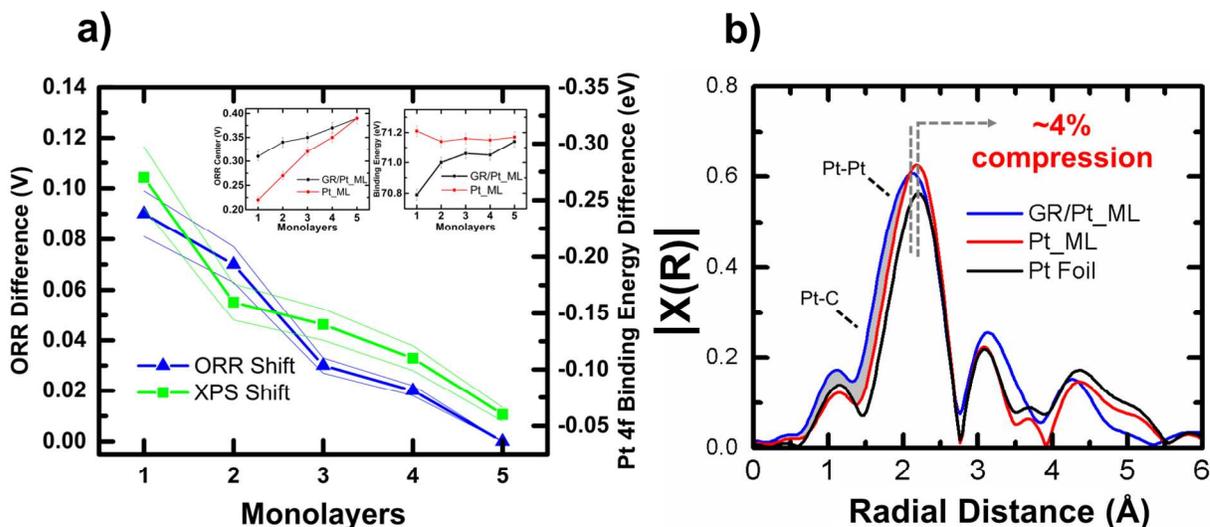
Figure 4: a) The difference in Pt 4f binding energy (blue triangles) plotted with the difference in ORR overpotential (green squares) between GR/Pt_ML and Pt_ML samples. Outer thin lines indicate a 10% margin of error. 4-a Left inset) XPS binding energy for each sample. 4-a Right inset) ORR overpotential for each sample. b) Real-space EXAFS spectra comparing 5 MLs of Pt with and without a single-layer graphene cap to that of a reference bulk Pt foil. The local structure of the GR/Pt_ML and the Pt/ML samples matches that of FCC Pt (Pt foil), with the former showing a compressive strain of ~4% and also exhibiting a shoulder due to Pt-C bonds (marked grey).

Strain tuning of Pt monolayers, particularly inducing compressive strain on Pt-Pt atomic bond, has been of a great interest due to its associated electrocatalytic enhancement, especially for ORR. Two major research routes have been under investigation to engineer the strain induced on Pt adatoms: first, alloying Pt with other metals (e.g. first row transition metals[21, 22] or Lanthanides[6]). Second, modifying the catalyst support (e.g. graphene[15], metal-oxide[23,24], metal-nitride[25,26]). Eelectrocatalytic enhancement following those two routes can be attributed to crystal mismatch between Pt and its vicinity through dictating Pt growth following the underlayment substrate epitaxy, respectively. Extended x-ray absorption fine-structure (EXAFS) was used to measure the average local atomic structure around Pt atoms. In Figure 4-a, bulk Pt (i.e. Pt foil) exhibited an observed nearest Pt-Pt nearest neighbor (nn) Pt-Pt distance, which was well aligned at the same position for Pt-Pt nn of 5 Pt_ML sample. However, for the GR/Pt_ML samples, the nn peak was shifted towards a lower value that translated to a compressive strain of the Pt-Pt nn by ~4%. ur previous work showed that compressive strain can positively affect Pt catalytic. There was also a widening of GR/Pt_ML peak on the lower-distance side (shaded in grey) where the Pt-C bond is expected, as an indication about Pt-graphene chemical bonding. This bonding can be the source of the observed strain as the Pt followed the graphene templated epitaxy.[15] The structure beyond the nn peak is still very similar to that of Pt foil indicating that Pt MLs overall strive to obtain a face centered cube-like close-packed structure.

Catalyst Durability

Catalyst platforms were subjected to accelerated durability tests (ADT),[27, 28] experimental details can be found in supporting information. XPS spectra of the samples before and after 1000 cycles were taken

to evaluate the surface architecture of each sample. Because our sample architecture is that of a Pt-Au core-shell, by comparing the relative photoemission intensity of the Pt overlayer to the underlying Au photoemission, the relative average thickness of the Pt shell can be determined. Figure 5-a shows a comparison of before/after ADT of GR/Pt_ML and their Pt_ML counterparts. After 1000 cycles, the XPS spectra for the GR/Pt_ML samples were almost identical to their spectra prior to ADT, as the peak intensity for the Pt 4f was unchanged relative to that of the Au 4f. This indicates the Pt atoms remain pinned to their original lattice on average, resulting in high resistance to both dissolution but ripening. On the other hand, Pt_ML samples without graphene clearly showed dramatic reduction in Pt peak intensity relative to Au. This indicates that, in the Pt_ML case, the Pt overlayer was on average much thinner (i.e. a large amount of Pt loss and/or ripening occurred due to ADT). The results here clearly show that the graphene cap works to effectively lock the Pt atoms in place, and dramatically improves the retention of Pt at a variety of monolayer thicknesses.
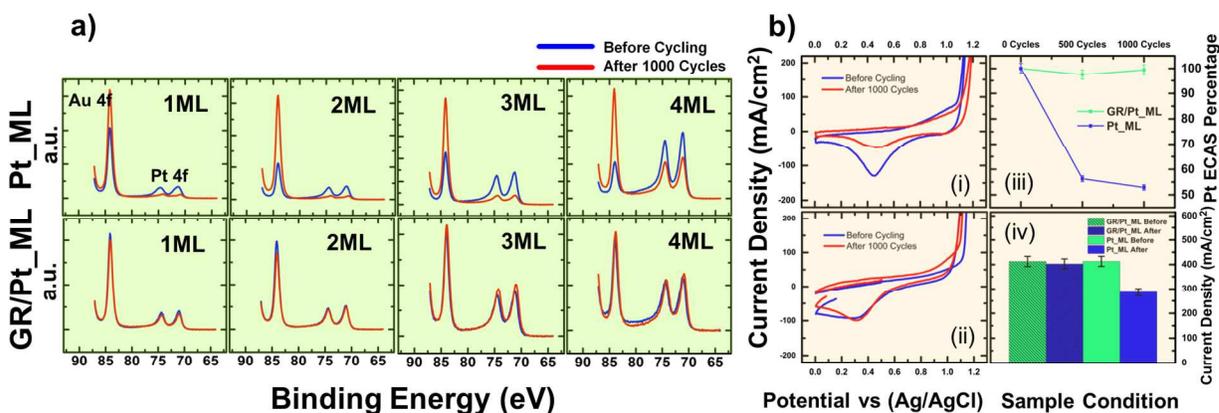

Figure 5: a) The Pt 4f$_{7/2,\ 5/2}$ pair and the Au 4f$_{7/2}$ XPS spectra for GR/Pt_ML samples and Pt_ML samples are shown before and after ORR cycling. b) (i & ii) CV sweeps before and after cycling for 4 ML GR/Pt_ML and 4 ML Pt_ML sample, respectively. (iii) ECSA percentage of Pt monolayers depicted from CV scans represented in (i&ii). (iv) current density obtained from LSV sweeps before and after 1000 cycles, indicates Pt monolayer activity towards ORR.

Integrating the Pt reduction peaks from cyclic voltammetry (CV) scans provided a representation of the amount of active Pt on the surface.[28-31] GR/Pt_ML samples showed enhancement of ECSA and catalyst durability after 1000 cycles by 43% and 170%, respectively, compared to Pt-carbon commercial catalyst (results summary are depicted in figure S5). Results for the 4 ML sample are shown in Figure 5-b. GR/Pt_ML samples showed that the reduction peak of Pt was maintained during 1000 cycles, however, Pt_ML samples showed significant decrease of the peak area, indicating a significant amount of electrochemical active surface area (ECSA) loss due to Pt dissolution into the electrolyte. ADT test was performed in H_2SO_4 acidic medium, which is known to promote an indirect two-electron ORR mechanism with H_2O_2 as intermediate species that degenerates the Pt electrode.[32] Despite the presence of this corrosive environment, graphene showed excellent protection to Pt with minimal or no loss up to 1000 cycles. These initial harsh cycling results show a promise for using graphene-capped as a protection for extended ADT. Linear potential sweeps investigating the ORR also showed about a 30% decrease in current for the 4 ML Pt_ML samples after cycling, while GR/Pt_ML counterpart maintained its ORR current as seen in Figure 5-b (iv). In corroboration with the XPS results shown in Figure 5-a, it is clear that the graphene acting as a transparent catalytic barrier for Pt monolayers dissolution. Raman

spectroscopy was used to verify the defects state of the graphene during ADT. Graphene showed very similar structure before and after ADT (results are shown in Figure S4).

We have demonstrated a new paradigm for graphene-templated, wetted, dimensionally-tunable, atomically-thin catalyst system that is support-flexible in design. We show systems with monolayer to few multilayers of Pt (Pt_ML) sharing an interface with single-layer graphene (GR), and find that epitaxial nature of the interface imposes a compressive strain on the Pt that lowers the required overpotential for ORR at thinner Pt loading (4 ML or less). At the same time, the epitaxy renders the Pt_ML/GR or GR/Pt_ML system to be one electronically-coupled catalyst system that exhibits no sacrifice in activity when reactants approach from the GR end. From the perspective of the reactants, the GR capping layer is 'chemically transparent' that provides 'infinite' resistance to activity loss from Pt dissolution, agglomeration through Ostwald ripening, and carbon corrosion (graphene, in our case), as evidenced by no activity loss within 1000 ORR cycles (within measurement errors). These combined results show obvious promise for incorporating graphene as a template at various catalyst interfaces as a catalyst support and as a surface cap that restrains catalyst loss down to negligible amount that can help transcend the activity-stability dilemma. The room-temperature, fully-wetted, epitaxial synthesis approach for a metal that is demonstrated here creates, more broadly, a new frontier for the nature of metals themselves, where they can be rendered in 2D films that are atomically thin and are supported on a movable, electronically coupled substrate (graphene). Such metal/graphene or graphene/metal architectures will impact not just catalysis, but also electronic, thermoelectric and optical materials.

ASSOCIATED CONTENT

Supporting Information.

 Supporting Information Available: Experimental setup including synthesis and characterization details. XPS spectra and LSV probing the ORR. Raman analysis of graphene before and after ADT.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. τ contributed equally.

Notes

The authors declare no competing financial interest

Sources

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Broader Context

Improving the catalyst activity, material utilization, and durability is essential to a wide array of energy applications, where expensive catalysts based on Pt still set the benchmark of performance. We have demonstrated a new paradigm for graphene-templated, epitaxial, dimensionally-tunable, atomically-thin catalyst system that is support-flexible in design. This epitaxial graphene-metal system is a platform that transcends the activity-stability dilemma in catalysis since atomically-thin films render nearly every catalyst atom in an active surface site while the bonds from the epitaxy also provide increased stability against catalyst deactivation. Our graphene-Pt catalyst exemplifies this effect by providing a 'chemically transparent' barrier with 'infinite' resistance to activity loss from Pt dissolution and agglomeration in 1000 cycles the canonical oxygen reduction reaction. The room-temperature, fully-wetted, epitaxial synthesis approach for a metal creates, more broadly, a new frontier for the nature of metals themselves, where they can be rendered in 2D films that are atomically thin and are supported on a movable, electronically coupled substrate (graphene). Such metal/graphene or graphene/metal architectures will impact not just catalysis, but also electronic, thermoelectric and optical materials with broad energy and environmental implications and applications.