Highly Active Bifunctional Oxygen Electrocatalytic Sites Realized in Ceria–Functionalized Graphene

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The development of efficient, durable, and cost-effective bifunctional electrocatalysts for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) is essential in the advancement of solar fuels, metal–air batteries, and unitized regenerative fuel cells. This work demonstrates an effective approach of activating 2D carbon for highly efficient bifunctional oxygen reactions without N-doping, let alone a transition metal–nitrogen (TM–N) moiety, the usual component needed for high oxygen electrocatalytic activities. A solvothermally synthesized ceria (CeO$_2$)–hydroxylated graphene hybrid catalyst shows excellent bifunctional ORR/OER activities both in alkaline and acidic solutions. Density functional theory calculations reveal that the activation of graphene occurs via topmost oxygens on ceria surface, but only when low coverage of hydroxyl groups is present on graphene. Furthermore, catalytically active forms of graphene share similar hydroxylated structural motifs. Finally, a simple approach of dramatically enhancing durability even in acidic media is demonstrated.

1. Introduction

The oxygen reduction reaction (ORR) and oxygen evolution reactions (OER) lie at the heart of sustainable electrochemical systems such as fuel cells, electrolyzers, water splitting, and metal–air batteries.$^{[1–3]}$ However, due to the sluggish kinetics of these reactions, the discovery of efficient catalytic platforms is essential to improve device performance.$^{[4]}$ The widely accepted benchmark catalysts use noble metals: Pt for ORR and IrO$_2$ or RuO$_2$ for OER. Since these materials are good catalysts for one reaction, not for both, they are not suitable for metal–air batteries$^{[5,6]}$ or unitized regenerative fuel cells (URFCs)$^{[7]}$ that require efficiency for both ORR and OER in each given device. Furthermore, their limited availability, high cost, and poor operational stability prohibit them from widespread commercial applications.$^{[2,7]}$ Since materials and configurations tuned for ORR are not optimal for OER, the development of high-performance bifunctional oxygen electrocatalysts remains an ongoing challenge.$^{[8]}$

As an alternative to noble-metal-based catalysts, carbon nanostructures have been intensively explored for oxygen electrocatalysis. Two categories of carbon are widely considered to be highly active. One is metal-free heteroatom-doped carbons (most notably, N-doped carbon), and the other is metal and nitrogen co-doped carbon (M–N–C structure).$^{[8,9]}$ In a recent report, we suggested alternative approach of activating 2D carbon: incurring chemical coupling with metal oxides.$^{[10]}$ A number of studies employed metal oxide (MO)/carbon hybrid systems for ORR and OER by using MOs with decent oxygen electrocatalytic activity such as Co$_3$O$_4$,$^{[11–13]}$ Mn$_2$O$_4$,$^{[14–16]}$ and Fe$_2$O$_4$.$^{[17,18]}$ In this case, the hybridization is targeted to use the carbon structure as a high-surface-area backbone to achieve a better electronic conduction and stable dispersed anchoring of MO nanoclusters (NCs).$^{[19–21]}$ These hybrid MO/carbon materials sometimes demonstrate a synergistic effect and achieve an unexpectedly high catalytic activity.$^{[22–25]}$ However, the MOs used in our prior study (TiO$_2$ and ZrO$_2$) were inert against oxygen evolution catalysts,

Inspired by our results with inert metal oxide/graphene (G), we now use ceria (CeO$_2$) as the MO to be interfaced with 2D carbon for bifunctional oxygen electrocatalysts. The facile transitions between Ce$^{3+}$ and Ce$^{4+}$ provide surface redox capability, reversible oxygen exchange, and high oxygen storage capacity, all of which are expected to enhance catalytic activity.$^{[26,27]}$ While the use of CeO$_2$ as an oxygen electrocatalysis is much less common than other transition MOs (e.g., CoO$_x$, MnO$_x$, and FeO$_x$), it was
recently employed as the ORR/OER catalyst in combination with hydroxides[28,29] and carbon,[30–32] or as a support of noble metal catalyst to extend oxygen storage capacity.[33–35] Given these promising properties for electrocatalysis, an even higher catalytic activity was anticipated. In this report, we demonstrate that an appropriate functionalization of graphene oxide (GO) prior to interfacing CeO2 NCs results in hybrid CeO2/graphene catalysts with excellent ORR and OER performance, comparable to or even better than that of noble-metal-based benchmark catalysts. Most notably, this enhancement is observed even in acidic media, not limited to alkaline media. A mechanistic interpretation of the surprising performance is also presented through a combination of experimental analyses and density functional theory (DFT) calculations. We identify a common structural motif of the activated graphene responsible for bifunctional activity. While it is widely known that most non-noble metal oxide and/or carbon-based catalysts degrade readily in acidic conditions,[3,36] we additionally demonstrate that our hybrid catalyst can operate in acidic environment with excellent stability if mixed with an acid-treated activated carbon (AC).

2. Results and Discussion

2.1. Physical Characterization of CeO2–Functionalized GO Variants

Three different kinds of functionalized GOs (fGOs)—as-synthesized GO (eG; graphene functionalized mostly with epoxy group), hydroxylated GO (hG), and carboxylated GO (cG)—were prepared before anchoring CeO2 NCs onto them. The basal planes of chemically exfoliated graphene oxides (named as eG in this report) are decorated with mostly epoxy groups ([37,38]). hG was prepared by treating eG with hydrobromic acid to convert the epoxy groups into hydroxyl groups, and cG was prepared by further adding oxalic acid, which converted hydroxyl groups into carboxyl groups.[10,39] A quantification by the titration method[40] (see Supporting Information for details) indicates that hG has the largest amount of hydroxyl group, and eG and cG have the highest content of epoxy and carboxyl groups, respectively (see Table S1 in the Supporting Information). Additionally, a nuclear magnetic resonance (NMR)[41] characterization was performed on eG having negligible OH content (0.001 mmol g−1) while hG and cG having larger (0.853 and 0.875 mmol g−1, respectively) OH content (see Supporting Information for procedure; Figure S1 in the Supporting Information). The high OH content of cG is reasonable considering that each carboxyl group has a hydroxyl group in it. The Fourier transform infrared spectroscopy (FT-IR) peak intensities of R–OH and R=O of CeO2–fGO hybrid samples (Figure 1a) are significantly lower than those without CeO2 incorporation (FT-IR on fGOs in ref. [10]), suggesting that the graphene sheets were highly reduced by losing most of their oxygen-containing functional groups during the hydrothermal reaction. It is also noted C-hG showed distinct Ce–O bond stretching (~1300 cm−1; indicative of CeO2 incorporation on graphene[42]) unlike the other two hybrids.

![Figure 1](attachment:figure1.png)

Figure 1. a) FT-IR and b) XRD spectra of C-eG, C-hG, and C-cG. Co Kα radiation (λ = 1.78897 Å) was used for XRD. Both C-eG and C-cG show the (200) diffraction of graphene sheet restacking at 26.5°, which is missing from C-hG. c) XPS Ce 3d and d) O 1s spectra of CeO2–fGO hybrid catalysts.
The X-ray diffraction (XRD) spectra in Figure 1b show peaks characteristic to CeO₂ in a cubic structure including the (111) fringe at 33.5°. An important observation is that C-eG and C-cG show a distinct carbon (002) peak at 26.5° while the peak is absent from C-hG. Since its appearance is ascribed to graphene sheet restacking, the absence of (002) peak from C-hG suggests that the binding of CeO₂ particles on the basal plane of graphene is likely strong enough to deter the restacking of graphene flakes, which makes it advantageous to widen the accessible catalytic sites. The conjecture is in agreement with the electrochemically active surface areas (ECSA) that are separately quantified. The measured ECSA values of C-eG, C-hG, C-cG, and bare Ni foam were 9.4, 19.5, 10.3, and 4.5 cm² (see the procedure and data in Figures S2 and S3 in the Supporting Information), confirming that C-hG exhibits the largest surface area.

Figure 2. a–c) HRTEM images of a) C-eG, b) C-hG, and c) C-cG, revealing lattice fringes of cubic (111) and (220) planes in the majority of imaged CeO₂ nanoclusters. d) A zoomed-out TEM image of C-hG and e–g) their corresponding EFTEM elemental map of Ce, O, and C, respectively.

The X-ray photoelectron spectroscopy (XPS) spectra of the samples. The survey spectra (Figure S4, Supporting Information) show O 1s, C 1s, and Ce 3d peaks. The Ce 3d level (Figure 1c) has two series of peaks, v and u, corresponding to the 3d₅/₂ and 3d₇/₂ spin–orbit pairs, respectively. The doublet (v', u') corresponds to Ce³⁺ and all the other peaks are assigned to Ce⁴⁺. By applying Maslakov et al.’s approach, the molar ratios of Ce³⁺ with respect to the sum of Ce³⁺ and Ce⁴⁺ in C-eG, C-hG, and C-cG were quantified to be 13.8%, 29.8%, and 23.3%, respectively (see “Deconvolution of XPS spectra” and Table S4 in the Supporting Information). The oxidation states of Ce can be alternatively quantified from O 1s core level spectra (Figure 1d). Three peaks were considered for deconvolution: 529.4 eV for O–Ce⁴⁺, 531.5 eV for O–Ce³⁺, and 532.4 eV for adsorbed oxygen molecules or hydroxyl species. C-eG has mostly O–Ce⁴⁺ (85.2%) with a small presence of O–Ce³⁺, whereas C-hG and C-cG have a much larger amount of O–Ce³⁺ bonding (C-hG: 82.5% and C-cG: 80.8%) than O–Ce³⁺. This trend is overall aligned with the result from Ce 3d peaks in that C-hG and C-cG have much higher Ce³⁺ species than C-eG. On the other hand, the atomic ratios of Ce per C are quantified to be 29.8%, 10.3%, and 11.3% for C-eG, C-hG, and C-cG, respectively. The unexpectedly high concentration of Ce in C-eG is ascribed to a formation of ceria (C) nanoparticle clusters without necessarily interfacing with each graphene flake leading to an unclear correlation between Ce content and ECSA.

High-resolution transmission electron microscopy (HRTEM) images of the three CeO₂–fGO variants (Figure 2a–c) show that CeO₂ NCs of 2–4 nm in size are densely populated on graphene. C-eG has mostly O–Ce⁴⁺ (85.2%) with a small presence of O–Ce³⁺, whereas C-hG and C-cG have a much larger amount of O–Ce³⁺ bonding (C-hG: 82.5% and C-cG: 80.8%) than O–Ce³⁺. This trend is overall aligned with the result from Ce 3d peaks in that C-hG and C-cG have much higher Ce³⁺ species than C-eG. On the other hand, the atomic ratios of Ce per C are quantified to be 29.8%, 10.3%, and 11.3% for C-eG, C-hG, and C-cG, respectively. The unexpectedly high concentration of Ce in C-eG is ascribed to a formation of ceria (C) nanoparticle clusters without necessarily interfacing with each graphene flake leading to an unclear correlation between Ce content and ECSA.

The ORR performance of CeO₂–fGO hybrids was characterized in both alkaline (0.1 m KOH) and acidic (0.5 m H₂SO₄) media. All samples (including 20 wt% Pt/C) used a solid loading
of 0.18 mg cm\(^{-2}\). In 0.1 m KOH, C-hG shows the best performance among the CeO\(_2\)–fGO variants for both ORR and OER (Figure 3a–c). The ORR onset and half-wave potentials of C-hG (0.90 and 0.79 V vs reversible hydrogen electrode, RHE; all potentials are versus RHE hereafter) are similar to those of Pt/C (0.92 and 0.81 V), and the Tafel slope of C-hG (58 mV dec\(^{-1}\)) is even smaller than that of Pt/C (78 mV dec\(^{-1}\)). C-hG also exhibits higher current densities than Pt/C in the mass-transport-limited region (5.78 vs 5.40 mA cm\(^{-2}\) at 0.3 V). Compared to the hydroxylated version, C-eG and C-cG show worse ORR performance (much lower onset and half-wave potentials). We also note that C-hG catalysts result in a dominant 4 e\(^-\) transfer process (average \(n = 3.98\) when averaged within the potential window of 0.3–0.85 V), while C-eG and C-cG are characterized as a mixed 2e\(^-\) and 4e\(^-\) process (averaged \(n = 3.28\) and 3.55, respectively). As for OER in 0.1 m KOH solution (Figure 3b), the potential needed to reach 10 mA cm\(^{-2}\) (\(E_{10}\)) was 1.67 V for C-hG, significantly lower than the potential needed for IrO\(_2\) (1.74 V). In addition, both C-hG and IrO\(_2\) showed the OER Tafel slopes of 60 mV dec\(^{-1}\), much smaller than those measured from C-eG and C-cG.

The promising ORR/OER performance of C-hG is not limited to alkaline media. Even in an acidic solution of 0.5 m H\(_2\)SO\(_4\), C-hG exhibited excellent performance. For ORR, the onset and half-wave potentials of C-hG (0.94 and 0.83 V) are even more positive than those of Pt/C (0.92 and 0.82 V), and its Tafel slope (81 mV dec\(^{-1}\)) is nearly the same as Pt/C (78 mV dec\(^{-1}\)). Similar to the case in 0.1 m KOH, C-hG exhibited a dominant 4e\(^-\) ORR process (average \(n = 3.88\)) throughout the potential window of study (0.3–0.85 V) in the acid solution. For OER (Figure 3e,f), C-hG showed an \(E_{10}\) value of 1.58 V, significantly lower than those of IrO\(_2\) (1.70 V), C-cG (1.90 V), and C-eG (>2 V). The OER Tafel slopes of both C-hG and C-cG were quantified to be 50 mV dec\(^{-1}\), slightly larger than that of IrO\(_2\) (45 mV dec\(^{-1}\)). All linear sweep voltammetry (LSV) and corresponding Koutecky–Levich plots are provided in Figures S7 and S8 (Supporting Information), and the ORR/OER performance is summarized in Table S6 (Supporting Information). It is also noted that the ORR and OER activities of each of fGOs (i.e., eG, hG and cG) and CeO\(_2\) themselves without interfacing each other are much worse than the hybrid catalysts; LSV curves in both 0.1 m KOH and 0.5 m H\(_2\)SO\(_4\) are provided in Figure S9 (Supporting Information).

To the best of our knowledge, this level of performance (on par with noble-metal-based benchmark) with versatility (bifunctional ORR/OER activity in both alkaline and acidic media) in oxygen electrocatalysis is unprecedented. It is also noted that the excellent performance was realized without forming TM–N moieties (TM: transition metal) which has been considered almost as a prerequisite for a high-performance oxygen electrocatalysis in non-noble-metal-based systems.[46,47] To further explore the origin of enhanced activity, we performed DFT calculations as discussed in the following sections.

**2.3. Theoretical Understanding of the Activity of fGO and CeO\(_2\)–fGO Hybrid Systems**

To rationalize the observed experimental activity of the fGO and CeO\(_2\)–fGO hybrid catalysts, we consider a number of possible
electrochemically stable fGO and CeO$_2$–fGO systems as discussed further in the following sections. Given these systems, we then evaluate their theoretical ORR and OER activities (see Modeling and Computation section in the “Experimental Section”) at all possible active sites. This approach allows us to construct relative activity trends, particularly as a function of the activation groups (eG, hG, and cG), and of the ceria (C) support. The initial structures for graphene (G), epoxy-graphene (eG), and graphene hydroxide (hG) were chosen from original work of Wang et al.$^{[48]}$ The nanostructured model of mildly reduced GO (mrGO) was taken from Bukas et al.,$^{[49]}$ while ceria structural models were taken from our recent work on nickel–ceria CO$_2$RR catalysts,$^{[50]}$ both of which are included in the Catalysis-hub.org repository.$^{[51]}$ Finally, minimal cells representing the interface between GO and ceria surfaces were generated via MPInterfaces code.$^{[52]}$

The most active structural models of graphene (G), fGO, and CeO$_2$–fGO hybrid catalysts are shown in Figure 4a. This set includes two hydroxy-graphene (hG-model) and other reduced GO variants with different configurations of epoxy and hydroxyl groups: nanostripe structures, eG-edge and hG-edge. A nanostructured model of mrGO$^{[48]}$ (eG-patch) was also tested (not shown). Finally, we also highlight the structure of the “activated” form of functionalized graphene on ceria (100) (aG-C), which is a configuration where a covalent bonding is formed between ceria and fGO as discussed further in the following. Fully oxidized GO (i.e., GO fully covered with epoxy group; full eG) and fully hydroxylated GO (full hG) were also tested (not shown). To study the activity of ceria alone, the stoichiometric (O-vacancy free) (111), (110), and (100) surfaces were also considered. Additionally, the computational benchmark catalysts Pt(111) and Au(111)$^{[53]}$ for ORR and IrO$_2$ (110)$^{[54]}$ for OER were also included for direct comparison with experiments.

Since the exact nature of the CeO$_2$–fGO interface is not known experimentally, an exhaustive search of all possible interfaces, orientations, lattice mismatches, and facets is not possible, and is unlikely to provide fundamental insights. Instead, using MPInterfaces code,$^{[52]}$ we have narrowed down to the minimal common cells combining graphene variants (G, eG, and hG) and ceria (C) facets, (111), (110), and (100). Such fully relaxed interfaces between graphene, full eG and full or half hG, and a stoichiometric ceria (111) yielded very little interface formation energy and a very small charge transfer at the interface (shown in Figure S11 in the Supporting Information). Other ceria surfaces yielded similar results. For that reason, we have further investigated more reduced forms of the graphene variants supported on ceria. Particularly, for ceria (100), which had considerably better lattice matching between top-most oxygens of ceria and carbons in graphene, a covalent bond formation between ceria top-most oxygens and graphene is formed if hydroxyl groups were present. We refer to a configuration with covalently bonded functionalized graphene on ceria (100) as “activated” and name it aG-C. A number of possible combinations and coverages were tested using the surface Pourbaix analysis (see Figure S12 in the, Supporting Information). The direct oxygen bonding of ceria with graphene in all aG-C hybrid models resulted in the presence of surface Ce$^{3+}$ detected from DFT local magnetic moment analysis.

Figure 4. a) Important structural models of GO–ceria hybrid system. The picture insets show rendered atomic structures with hydrogen, carbon, oxygen, and ceria atoms are shown as pink, gray, red, and lime-green spheres, respectively. The structure labels are introduced in text as graphene (G) (with OH*), two hydroxy graphene (hG-model), hydroxylated graphene–graphene edge with OH* (hG-edge), and epoxy graphene–graphene edge with OH* (eG-edge). Supported and activated graphene structures on CeO$_2$(100) (aG-C) have either low coverage of OH* (ORR), or high-coverage of O-epoxy (OER). The ellipses highlight a common structural motif. b) Calculated ORR activity map as a function of OH* and OOH* free energies of the above models. For comparison, the results for ceria surfaces and Pt(111) and Au(111) benchmarks adapted from ref. [53] are also shown. The dashed line indicates the OOH* versus OH* linear scaling obtained in this study. c) Similarly, the calculated OER activity map as a function of O*-OH* and OH* free energies for the above models including the IrO$_2$ (110) benchmark from ref. [54]. Symbols in brackets are numerical values of the obtained theoretical overpotentials for b) ORR and c) OER based on Equations (6) and (8).
Figure 4b shows a map of calculated theoretical ORR overpotentials (see Equation (6)) as a function of the two most important descriptors of ORR activity, the adsorption free energies of OH* and OOH*. Figure 4c features a similar map calculated for OER overpotential (see Equation (8)), which is a function of O* and OOH* adsorption free energies. It is noted that while the theoretical overpotentials are always calculated explicitly from OH*, O*, and OOH*, the construction of the 2D maps takes advantage of O* or OOH* scaling versus OH* for ORR and OER, respectively.

The ORR activity map (Figure 4b) shows that energetics of all the systems (with the exception of full hG) closely follows the universal scaling relations between OOH* and OH* adsorption free energies,\[^{[55,56]}\]\[\Delta G_{\text{OOH}} = 0.9 \cdot \Delta G_{\text{OH}} + 3.29 \text{ eV}\] (shown as dotted line in Figure 4b). The main calculated trend in ORR activities is that only reduced forms of hG (hG-edge and hG-model) and the activated hybrid catalysts (aG-C) (\(\eta = 0.51 \text{ V}\)) result in theoretical activities close to or better than Pt(111) (\(\eta = 0.44 \text{ V}\)). The reduced forms of eG are predicted to perform significantly worse when compared to reduced forms of hG, followed by pure ceria surfaces that have very low affinity for OH/O* groups. It is well known that ceria readily forms oxygen vacancies, but these, in turn, bind OH* too strongly (\(> -0.5 \text{ eV}\) for single oxygen vacancy at CeO\(_2\) (111)) to be catalytically relevant.

The OER activity map (Figure 4b) shows that reduced forms of hG (hG-edge and hG-model), activated hybrid (aG-C), and eG-patch contain favorable OER active sites, and all have overpotentials lower than IrO\(_2\) (\(\eta = 0.63 \text{ V}\)). Again, we do not find pure ceria surfaces to be a viable system for OER due to low affinity for OH*/O* groups. In the presence of oxygen vacancies on ceria surface, the affinity becomes too high.

From the aforementioned observations, it is worth highlighting that the highly active two-hydroxy-graphene structural motif of the hG-model is essentially shared across all the active ORR and OER structures (highlighted with ellipses in Figure 4a). For that reason, we hypothesize that the bifunctional activity of hydroxylated CeO\(_2\)–fGO hybrid catalysts originates from the presence activated forms of reduced hG and of the hybrid aG-C (Figure 4a). For that reason, we hypothesize that the bifunctional activity of hydroxylated CeO\(_2\)–fGO hybrid catalysts originates from the presence activated forms of reduced hG and that such activation shares a common structural motif.

A direct comparison of experimentally quantified performance to predictions of our theoretical models is shown in Figure 5. The measured ORR/OER overpotentials of the three CeO\(_2\)–fGO hybrid samples and benchmark catalysts (Figure 5a; directly quantified from data in Figure 3) are compared to calculated limiting potentials (Figure 5b,c; based on the results of Figure 4). We caution that such a comparison can only be made on a relative basis, and only if the precise chemical nature of the CeO\(_2\)–fGO hybrid catalysts is known at the operational conditions. Nevertheless, for the ORR case, we find that the experimentally determined activity C-hG relative to Pt and other hybrid catalysts is well aligned with theoretical prediction based upon activated forms of reduced hG, particularly with the model of activated hybrid aG-C catalyst (Figure 5b). This is in agreement with the post e-chem analysis of C-hG samples, which indicate the presence of hydroxy groups.

For the OER case, we find that the high activity of C-hG also matches well with the theoretical prediction based upon activated forms of reduced hG and of the hybrid aG-C (Figure 5c). Under OER conditions, some epoxy surface species are present in the hybrid aG-C model (Figure S12, Supporting Information), but the presence of hydroxy groups is simultaneously required to form an activated interface between the graphene and ceria. Post OER e-chem analysis of C-hG samples also shows a high content of hydroxy groups.

2.4. Operational Durability

The operational durability of C-hG was evaluated via potential cycling measurements in both 0.1 m KOH and 0.5 m H\(_2\)SO\(_4\).
While the performance decay of C-hG during potential cycling in 0.1 m KOH was negligible (Figure 6a), a dramatic degradation was observed in 0.5 m H2SO4 (Figure 6b). The sum of ORR and OER overpotentials (E° - E°1/2) changed from 0.70 V (150 cycles) to 1.63 V (2000 cycles). This is not surprising because strong acids are expected to cause leaching of metal oxides.[57] In addition, carbon is known to degrade readily from oxidation in OER condition unless it is properly structured to resist it.[36]

To probe possible impacts on durability by incorporating other functional groups on a carbon-based substrate, a composite of C-hG and AC is considered. Since ACs have a high surface area and microporosity, they are widely used as the carbon support of oxygen electrocatalysts.[58] We mixed ACs with C-hG along with nitric acid (HNO3) and sulfuric acid (H2SO4), mainly because acid treatment of ACs is expected to create various oxygen-containing functionalities.[58,59] The addition of AC proved highly effective in improving the operational stability of C-hG for both ORR and OER, especially in the acidic solution. As evident in Figure 6, AC-mixed C-hG (namely C-hG/AC) shows little difference in the activity between the 150th and 2000th cycles. To the best of our knowledge, this is the first demonstration of MO-based oxygen electrocatalysts stable in an acidic solution. It is noted that the ORR activity of AC itself is not impressive; the onset potential is 0.72 V, and electron transfer number spans between 2.2 and 3.3 in 0.1 m KOH as shown in Figure S14a,b,c (Supporting Information). Therefore, the stability should originate from a specific type of chemical bonding between functionalized graphene and AC and/or between ceria and AC. The sulfonic group found in the AC as verified by an FT-IR scan (at ~2490 cm⁻¹; Figure S14a, Supporting Information) may be responsible for the performance and stability, because carbon with sulfonic groups acts as an active and stable heterogeneous acid catalyst.[60] To focus on the ceria–functionalized graphene as the advanced catalyst of this report, however, a detailed mechanistic study about the surprising stability of C-hG/AC is planned for a separate report.

3. Conclusion

In our previous work,[10] we demonstrated that MO/graphene hybrids can be highly ORR active even with ORR-inert MOs (TiO2 and ZrO2). We consider this behavior as an “MO-enabled activation of graphene for ORR,” which is totally different from the conventional view on MO/graphene hybrids where graphene is regarded as an MO-anchoring template to enhance electronic transport and suppress MO agglomeration. As an extension of the study, herein CeO2 is applied to the MO/graphene system with the expectation of a further enhanced performance due to its promising properties related to oxygen electrocatalysis. In this report, we demonstrate a highly active bifunctional oxygen electrocatalysis from the CeO2-activated 2D carbon. CeO2/hydroxylated graphene affords a surprisingly high ORR and OER performance, comparable to those of noble-metal-based benchmark catalysts, in both alkaline and acidic media. This work presents a new approach of activating 2D carbon for excellent ORR/OER performance even without N–C or metal–N moieties, the widely accepted essential component for high catalytic activity in carbon-structure-based systems. Our thermodynamic screening approach applied to GO, mrGO, and hybrid CeO2–fGO systems identifies the highest theoretical activities for reduced hydroxy-functionalized GO. The calculations also reveal an activation mechanism, by which ceria nanoparticles form strong interface with GO if hydroxyl groups are present. We further rationalize the bifunctionality of the CeO2–fGO hydroxylated hybrid catalyst in the presence of previously unknown hydroxy-activated graphene structural motif. Finally, we briefly demonstrate a substantially enhanced stability of CeO2/fGO hybrid catalysts in acidic media by incorporating activated carbon.

4. Experimental Section

Graphene Oxide Synthesis: GO was synthesized by a modified Hummers method. 45 mm flake graphite powder (3 g) and KMnO4 (18 g) were mixed in 0.98 m H2SO4 (360 mL) and 0.75 m H3PO4 (14 mL) for 12 h at 50 °C. Then, (400 mL) ice cubes were added to the solution. Once the ice was melted, (3 mL) H2O2 and (50 mL) deionized (DI) water were added sequentially. The resulting GO solution was then centrifuged for six times at 8000 rpm for 8 min, filtered slowly with (200 mL) 0.1 m of HCl and (200 mL) DI water, and then allowed to dry.

Preparation of Hybrid Catalyst: Hybrid catalysts made of CeO2 NCs and fGO were synthesized through a hydrothermal reaction process
at 180 °C. Three different kinds of fGOs were prepared before the hydrothermal reaction: eG, hG, and cG. For an eG sample, (30 mg) CO (3 mL) ethanol, and (27 mL) DI water were ultrasonicated for 0.5 h. Then, (2 mL) hydrobromic acid was added and stirred for 14 h. The resulting solution was filtered/washed with (200 mL) DI water and allowed to dry under a house vacuum. For a cG sample, an additional (600 mg) oxalic acid was added and stirred for 5 h after mixing HBr for 14 h. These acid treatments to generate hG and cG were intended to further create hydroxyl and carboxyl groups, respectively, in GO.[61] After these acid treatments, the GO solution was filtered, washed with DI water, and dried. The resulting (100 mg) dried GO was added to a solution made of 0.1 M of cerium(III) nitrate hydrate that was created three days prior in (100 mL) DI water. This was then heated at 80 °C for 3 h and allowed to cool at room temperature, during which (~15 mL) DI water was added to maintain the same level of water before heating. The suspension was stirred for 2 h and placed in a 90 mL Teflon-sealed dry oven for a hydrothermal reaction. The reaction was performed at 180 °C for 18 h, and the resulting CeO$_2$–fGO hybrid materials starting with eG, hG, and cG were named Ce-eG, Ce-hG, and Ce-cG, respectively. A hybrid synthesis was made using C-Hg and acid treated AC. More specifically, the (15 mg) catalyst material C-Hg with (10 mL) ethanol was sonicated for 1.5 h. In a separate container, that was made a day before C-Hg was suspended in ethanol, (3.75 mg) AC was mixed with (2 mL) a 1:1 ratio of 0.1 M HNO$_3$ and 0.1 M H$_2$SO$_4$. This was allowed to mix for 4 h, washed with (400 mL) DI water, and then dried overnight. Once dried, the acid-treated AC was mixed with the suspended C-Hg sample and stirred for 4 h at 80 °C and dried under house vacuum.

**Material Characterization:** Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images were recorded on a 200 kV FEI monochromated F20 UT Tecnai system. The STEM image was acquired with a convergence angle of 10 mrad and a detection angle of 30 mrad. EFTEM in association with STEM was used to visualize elemental distribution. Sample preparation for TEM samples included drop-casting sonicated ethanol-suspended catalyst upon a 3 mm Lacey B Carbon 400 mesh grid from Ted Pella, followed by ambient drying. XPS was performed on a PHI Quantum 2000 system using a focused, monochromatic Al K$_x$ X-ray (1486.6 eV) source for excitation and a spherical section analyzer (200 mm diameter X-ray beam incident to the surface normal; detector set at 45°). The collected data were referenced to an energy scale with binding energies for Cu 2p$_{3/2}$ at 932.7 ± 0.1 eV and Au 4f$_{5/2}$ at 84.0 ± 0.1 eV. For XPS, catalysts were dispersed in ethanol and drop-cast onto a cleaned Si wafer. XRD patterns were recorded by a PANalytical X’Pert PRO with Co K$_x$ radiation ($\lambda$ = 1.78897 Å) at a step size of 0.02° and scanning rate of 0.04° s$^{-1}$. Sample preparation for XRD included 10 mg of catalyst sonicated with 5 mL in ethanol and then drop-cast upon an aluminum disk to dry in ambient conditions. FT-IR samples were dried under vacuum for 36 h and placed on a diamond crystal. A silicon wafer was placed on top of the sample before spectra was recorded (Nicoleto 380 system, Thermo Scientific).

**Electrochemical Characterization:** The ORR and OER activities of the catalysts were evaluated in 0.5 M H$_2$SO$_4$ and 0.1 M KOH with cyclic voltammetry (CV; SP-200, Bio-Logic Science Instruments) and rotating ring-disc electrode (RRDE; RRDE-3A, ALS Co.) in a three-electrode setup, where a graphene rod and a Ag/AgCl/KCl (3.5 M) electrode were used as the counter and reference electrodes, respectively. The working electrode was prepared by drop-casting each electrode ink onto a 4 mm glassy carbon disk electrode. The ink was prepared by immersing 15 mg of CeO$_2$–fGO catalyst material into 2.21 mL of ethanol along with 3.75 mg of carbon black and 75 μL of 5 wt% Nafion (Nafion D-521, Alfa Aesar). For Pt/C and IrO$_2$ electrodes, a 15 mg mL$^{-1}$ suspension was prepared by using a commercial 20 wt% Pt supported on carbon black (Vulcan XC72) or IrO$_2$ (Alfa Aesar) instead of the CeO$_2$–fGO samples. These samples were dried under N$_2$ at 32 sccm rotating at 750 rpm. Then, O$_2$ and N$_2$ saturated environments were achieved by flowing high-purity O$_2$ (for OER) and N$_2$ gas (for OER) at 32 sccm into 80 mL of electrolyte for 30 min. For the OER cyclic durability test and the CVs for ECSA quantification, Ni foams (area: 0.5 cm$^2$; thickness: 1.6 mm) were used as the substrate. All the other electrochemical measurements were performed on glassy carbon disk electrodes. All the potentials were expressed with respect to RHE.

**Modeling and Computation:** The ORR and OER activities were computed using the thermodynamic limiting potential framework using DFT. For all systems, PBE-DFT$^{[92]}$ functional PAW potentials, 500 eV plane-wave cutoff, using the Vienna Ab initio Simulation Package$^{[63–65]}$ (VASP, version 5.4.4), and 5.3 eV Hubbard-U correction applied to f-electrons of Ce atoms were employed, as described previously.$^{[58,66,67]}$ These simulation cells for ceria surfaces contained a minimum of three layers with a 2 × 2 periodicity. The two topmost layers were always allowed to relax until the forces were lower than 0.02 eV Å$^{-1}$ using a 5 × 5 × 1 k-point mesh. Equivalent precision was also used for graphene unit cells.

The theoretical limiting potentials for ORR and OER were calculated directly from free energies of OH*, O*, and OHOO* intermediates assuming the most common four-electron associative single-site mechanism.$^{[53,68]}$ Details of this approach were presented in the recent ORR and OER reviews.$^{[53,69]}$ Less common dissociative ORR mechanism$^{[54,70]}$ which bypasses OHOO* step but also requires low barrier for binuclear bond breaking,$^{[71]}$ was not considered in this screening study. Using standard conditions ($T$ = 298.15 K, $p = 1$ bar, $pH = 0$), it requires 1.23 eV for each elementary step, and 4.92 eV in total for an ideal catalyst to perform ORR. For OER, the elementary reactions are $O_2^+ + e^- + H^+ \rightarrow HOOH^*$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O + O^* \quad (1)$$

$$O^* + (H^+ + e^-) \rightarrow OH^* \quad (2)$$

$$OH^* + (H^+ + e^-) \rightarrow H_2O + * \quad (3)$$

and the theoretical ORR limiting potentials and overpotentials are defined based upon the free energies of Equations (1)–(4) as

$$\eta_{ORR} = \max[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4]/\epsilon \quad (5)$$

$$\Delta G_1 = \epsilon \eta_{ORR} = \max[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4]/\epsilon + 1.23 V \quad (6)$$

For OER, the equivalent elementary equations for the 4e$^-$ OOH-based mechanism$^{[56,72,73]}$ can be written as the reverse of Equations (1)–(4), and the theoretical OER limiting potentials and overpotentials are again defined simply as

$$\eta_{OER} = \max[\Delta G_4, \Delta G_3, \Delta G_2, \Delta G_1]/\epsilon \quad (7)$$

$$\Delta G_1 = \epsilon \eta_{OER} = \max[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4]/\epsilon + 1.23 V \quad (8)$$

The Gibbs free reaction energies are calculated as

$$\Delta G = \Delta E + \Delta ZPE \pm T \Delta S.$$ The differences between zero-point energy, $\Delta ZPE$, and entropy, $T \Delta S$, were calculated through vibrational frequencies of adsorbates on the surface, and the adsorption energies $\Delta E$, were calculated relative to H$_2$O (g) and H$_2$ (g) references as

$$\Delta E_{OH} = E(OH\_2) - E(O\_2) - E(H_2O) - \frac{1}{2}E(H_2) \quad (9)$$

$$\Delta E = E(O\_2) - E(H\_2) \quad (10)$$

$$\Delta E_{OH} = E(OHOO\^*) - E(O\_2) - \frac{1}{2}E(2H_2O) - \frac{1}{2}E(H_2) \quad (11)$$

Whenever applicable, the coverage of the surfaces under applied voltage was incorporated by the calculation of the surface Pourbaix plots (see Figure S12 in the Supporting Information). The calculated energies involving adsorption on graphene or CO were corrected by

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Solvation corrections calculated with explicit water (see Figure S13 in the Supporting Information). Finally, all calculated ∆E were released as part of the Catalysis-hub.org repository [51] at https://www.catalysis-hub.org/publications/GrewalHighly2019.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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