**Single-sided fluorine-functionalized graphene: a metal-free
electrocatalyst with high efficiency for oxygen reduction reaction**

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Abstract. By means of density functional theory (DFT) computations, we systematically explored the potential of the single-sided chemically functionalized graphene by various functional groups as the metal-free electrocatalyst for oxygen reduction reaction in alkaline media. Our computations revealed that the spin density due to the single-sided functionalization at 12.5% ratio enhances O₂ adsorption, and the O₂ adsorption energies well correlate with the magnetic moments of C₈R graphenes. C₈F and C₈(OCH₃) graphenes with moderate magnetic moments exhibit appropriate chemical reactivity towards O₂ activation. The following ORR elemental steps prefer to proceed through a 4e⁻ associative pathway, rather than the dissociative and 2e associative pathway. Both C₈F and C₈(OCH₃) graphenes are promising ORR catalysts, and C₈(OCH₃) graphene is more efficient due to its lower overpotential. The present work provides an effective way to tune the catalytic performance of graphene for ORR by introducing a suitable spin density using its covalent functionalization.

Keywords: Graphene; covalently functionalized graphene; oxygen reduction reaction; catalyst; density functional theory computations

1. Introduction

Due to their high conversion efficiency, high power density, and no pollution, fuel cells [1], one of the most efficient electrochemical energy conversion devices, are playing an important role to meet the urgent requirement of electric vehicles of sustainable energies [2–4]. However, the current bottleneck of fuel cells lies in the sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode, which is the pivot for a fuel cell because it could greatly affect the chemical–electrical energy conversion efficiency [5–9]. Although Pt-based catalysts exhibit the highest electrocatalytic activities for ORR, their performance has been overshadowed by their high cost, scarcity, and large overpotential [2]. Hence, intensive efforts have been devoted to search for alternative electrocatalysts to substitute Pt-based catalysts, including nonprecious metal catalyst and metal free catalysts [10–19].

Graphene, a two-dimensional one-atom-thick single layer of graphite, has become a hot topic since its discovery in 2004 [20]. Due to its extraordinary properties such as large surface area, high mobility of charge carriers, excellent mechanical properties, and superior thermal conductivity, graphene could be widely used to design anode and cathode electrocatalysts in fuel cells [21–28]. Especially, graphene doped with various heteroatoms (N, S, B, P *etc.*, including dual-doping and trinary-doping) has been demonstrated to exhibit excellent catalytic performance for ORR [25, 29–39], among which N-doped graphene seems most promising to replace Pt-based catalysts for fuel cells owing to its high catalytic activity, long-term stability, and low-cost [40]. Besides the experimental investigations, some theoretical

calculations have also been employed to reveal the catalytic mechanism of different doped graphene [31, 41–45]. Generally, the energy band gap, spin, and charge density determine the electrocatalytic performance of these heteroatom-doped graphene for the ORR [21]. For example, by means of density functional theory (DFT) computations, Zhang *et al.*[41] proposed that the electrocatalytic activity of N-doped graphene is dependent on the spin density, in which the surrounding C atoms with high charge density are shown to exhibit high ORR activity. Thus, any species in the form of substitution or attachment on graphene, which can result in high asymmetric spin density and atomic charge density, and a suitable energy gap on graphene, could induce high catalytic activities for the ORR [41].

Another widely used approach to functionalize graphene is covalent functionalization [37, 46–59]. Various kinds of functional groups have been chemically anchored to graphene, and the corresponding ratios can be easily tuned [37, 46, 48], leading to a diversity of graphene-based nanocomposites with wide applications. Very recently, Dou *et al.* experimentally successfully attached nitrobenzene to graphene, and found that the functionalized graphene with the mass ratios of 20:1 exhibited the highest catalytic performance for the ORR in alkaline media due to the charge transfer effect [60]. The covalently functionalized graphene possesses several advantages over the Pt-catalysts: it exhibits excellent fuel selectivity and durability; the synthesis is relatively easy with low energy consumption and ready for large-scale production; this doped graphene with higher functionalization ratio allows more catalytic sites for ORR.

Dou *et al.*'s work [60] inspires us to consider the following questions: can the experimentally available functionalized graphenes by other functional groups be utilized as promising catalysts for ORR? If yes, how can the type and coverage of the functional groups affect the catalytic performance of graphene?

To address these questions, we systemically studied the adsorption of O₂ molecule and the subsequent ORR reaction steps on the single-sided functionalized graphenes by several representative functional groups, including F, CN, OCH₃, and NH₂ groups that exhibit different electron-accepting or -donating ability. The single-sided functionalized graphenes with 12.5% modification ratio are chosen since typically they exhibit spin density [61], which favors ORR reaction. Our computations showed that both C₈F and C₈(OCH₃) graphenes are promising ORR catalysts, and C₈F graphene is more efficient due to moderate O₂ binding strength, low reaction barrier, and comparable limiting potential to Pt-based catalyst in alkaline media.

2. Computational methods

The spin-polarized DFT computations employed an all-electron method within a generalized gradient approximation (GGA) for the exchange-correlation term, as implemented in the DMol³ code [62, 63]. The double numerical plus polarization (DNP) basis set and PBE functional were adopted [64]. The accuracy of DNP basis set is comparable to that of Pople's 6-31G** basis set [65] and exhibits excellent consistency with experiments.[66, 67] Especially, to accurately describe the

long-range electrostatic interactions of ORR species with catalysts, the PBE+D2 method with the Grimme vdW correction was employed [68]. Self-consistent field (SCF) calculations were performed with a convergence criterion of 10^{-6} a.u. on the total energy and electronic computations. To ensure high quality results, the real-space global orbital cutoff radius was chosen as high as 4.7 Å in all the computations. A conductor-like screening model (COSMO) was used to simulate a H₂O solvent environment throughout the whole process [69]. The dielectric constant was set as 78.54 for H₂O solvent. All data were obtained under this method unless mentioned otherwise.

We set the x and y directions parallel and the z direction perpendicular to the plane of these functionalized graphenes, and adopted a supercell length of 20 Å in the z direction. A 3×3 supercell is employed, which consists of 72 carbon atoms. The Brillouin zone was sampled with a $5 \times 5 \times 1$ k points setting in geometry optimizations, and a $12 \times 12 \times 1$ grid was used for electronic structure computations. Linear synchronous transition/quadratic synchronous transit (LST/QST) [70] method in DMol³ was employed to investigate the minimum energy pathway for the ORR on single-functionalized graphenes. This method involves linear synchronous transit (LST) maximization, followed by repeated conjugated gradient (CG) minimizations, and then quadratic synchronous transit (QST) maximizations and repeated CG minimizations until a transition state is located.

The change in free energy (ΔG) of a reaction step on the functionalized graphenes was calculated based on a computational hydrogen electrode (CHE) model suggested

by Nørskov et al [72-74]. In detail, free energy change was determined by $\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + \Delta G_{\text{pH}} + \Delta G_{\text{U}}$, where ΔE is the reaction energy directly obtained from DFT calculations. For example, the adsorption energy of O_2 (E_{ads}) on C_8F graphene was defined as: $E_{\text{ads}} = E_{\text{C}_8\text{F-O}_2} - E_{\text{C}_8\text{F}} - E_{\text{O}_2}$, where $E_{\text{C}_8\text{F-O}_2}$, $E_{\text{C}_8\text{F}}$, and E_{O_2} are the DFT total energies for the O_2 adsorbed C_8F graphene, free C_8F graphene, and O_2 molecule, respectively. E_{ZPE} is the zero-point energies, T is temperature (298.15 K), and ΔS is the change in entropy. $\Delta G_{\text{U}} = -neU$, where n is the number of electrons transferred and U is the electrode potential. ΔG_{pH} is the correction of the H^+ free energy by the concentration $\Delta G_{\text{pH}} = k_{\text{B}}T \times \ln 10 \times \text{pH}$, where k_{B} is the Boltzmann constant and $\text{pH} = 14$ in alkaline conditions. Zero-point energies and entropies of the ORR intermediates were calculated from the vibration frequencies. The entropies and vibrational frequencies of molecules in the gas-phase are taken from the NIST database [72], while the vibrational frequencies of adsorbed species were calculated to obtain ZPE contribution in the free energy expression. Only adsorbate vibrational modes were calculated explicitly, while the functionalized graphene sheets are fixed (assuming vibrations of the functionalized graphene sheets are negligible) as done in previous theoretical studies [74-77]. In basic conditions, the equilibrium reduction potential for O_2 to OH^- at $\text{pH} = 14$ is 0.40 V versus Standard Hydrogen Electrode (SHE) following the direction four-electron pathway [14]. Since some of the elementary steps are uphill at equilibrium potential (U_0), an applied potential U is required to overcome the positive free energy change, the overpotential (η) is computed as $\eta = U_0 - U$.

3. Results and discussion

3.1. O₂ adsorption on single-sided functionalized graphene.

O₂ adsorption on the catalyst surface is the most important step for initiating the whole ORR, a suitable O₂ binding energy is essential for sufficiently activate O₂ molecules. Thus, we first examined the O₂ adsorption on graphenes single-sided functionalized by several monovalent functional groups with different electron-accepting or -donating ability, namely F, CN, OCH₃, NH₂, and H groups, in order to screen appropriate functional groups. We began our screening process by computing the O₂ adsorption on C₈F graphene, and then extended our computations to other functionalized graphenes.

Figure 1 presents the optimized structure of C₈F graphene in a 3×3 supercell, in which all F atoms locate on the same side of graphene. Each unit cell contains eight C atoms and one F atom, and the C–F bond length is 1.57 Å. The C₈F graphene has a spin-polarized ground state with the magnetic moment of 0.42 μ_B , which is consistent with previous report [61].

To obtain the lowest-energy configuration for O₂ adsorption, two possible configurations were considered by placing O₂ on different sites of C₈F graphene, including end-on and side-on configurations. Our computations revealed that O₂ molecule prefers to chemically adsorb on the C1 atom via a side-on configuration (Figure 2a), in which the adsorbed O₂ molecule and F atoms locate on different sides of graphene, and two C–O bonds (1.50 Å) are formed. Note that this lowest-energy configuration, i.e. the O₂ chemisorption, can be transferred from the O₂ physisorption

(with the exothermicity of 0.36 eV) by crossing a small activation barrier of 0.47 eV (Figure S3). According to the Hirshfeld charge population analysis [78], there is about 0.19 e charge transfer from C₈F graphene to the chemisorbed O₂ molecule. The partial density of states for O₂ adsorbed C₈F surface (Figure 2b) clearly shows an obvious hybridization between the O₂-2*p* orbitals and C-2*p*, and the O₂-2*π** state largely accounts for the activation of O₂ molecule, as evidenced by the elongation of the O-O bond from 1.21 Å to 1.33 Å. The computed O₂ adsorption energy (-0.49 eV) is very close to that on Pt(111) surface [79–81]. This reaction step can be written as: O₂(g) → O₂^{*}, where the asterisk ^{*} denotes an adsorption site on catalyst surface. In comparison, for C₄F, C₁₈F, or pristine graphenes without spin density [61], the interactions with O₂ molecule (-0.10, -0.15, and -0.18 eV, respectively) are rather weak (Figure S1 in Supporting Information), indicating that these two fluorinated and pristine graphenes cannot promote the ORR.

To further confirm the stability of the O₂ chemisorption, we performed first-principles molecular dynamics (MD) simulations of C₈F graphene with chemically adsorbed O₂. At the 300 K temperature, the variation of O-O bond length is always less than 0.1 Å during the 3 ps simulation period (Figure S2), indicating the good stability of O₂ molecule on C₈F graphene.

We also computed the ORR on the functionalized side. In general, the O₂ adsorption on the functionalized side is very weak. For example, in C₈F graphene, it is not energetically favorable for the O₂ adsorption to the C atoms, the O₂ adsorption energy on the F atoms is only -0.07 eV (Figure S4), suggesting only rather weak

physisorption.

Our above analyses show that the C_8F graphene can sufficiently activate O_2 , can other single sided–functionalized graphenes with 12.5% modification ratio (C_8R graphenes) be utilized as the ORR electrocatalyst? To answer this question, we examined the energetics of O_2 adsorption on other C_8R graphenes, where R includes methoxy (OCH_3), amine (NH_2), and cyano (CN) groups as well as hydrogen (H) and chlorine (Cl) radicals, respectively. However, the single–functionalized chlorinated graphene was not further considered because in this configuration Cl atoms will form Cl_2 molecules and escaped [82].

Similar to C_8F graphene, these C_8R materials are magnetic materials with the magnetic moment of 0.50, 0.84, 0.73, and $0.79 \mu_B$, respectively for OCH_3 , NH_2 , CN , and H additions. As a result, these C_8R graphenes exhibit high chemical reactivity toward O_2 molecule (Figure S5). The adsorption energies of O_2 molecule on $C_8(OCH_3)$, $C_8(NH_2)$, $C_8(CN)$, and C_8H graphenes are -0.84 , -1.27 , -1.10 , and -1.25 eV, respectively.

To illustrate the relationship between the magnetic moments of C_8R graphenes and O_2 adsorption energies, we plotted the variation of O_2 adsorption energies with the magnetic moments of C_8R graphenes (Figure 3). Clearly, the O_2 adsorption becomes more favorable with increasing the magnetic moment of C_8R . According to the Sabatier principle [83, 84], an ideal catalyst should bind with the reaction species not too strongly nor too weakly (which prevents reaction intermediates from drifting away from the catalytic center). Thus, though O_2 molecule can also be activated,

$C_8(NH_2)$, $C_8(CN)$, and C_8H could be unsuitable for catalyzing for ORR due to their too strong binding strength with O_2 molecule (-1.27 , -1.10 , and -1.25 eV, respectively), while C_8F and $C_8(OCH_3)$ are good candidates as ORR catalysts according to the screening based on the O_2 adsorption.

3.2. Oxygen reduction reaction paths.

Following the O_2 adsorption, the ORR at cathodes in alkaline solutions can be written as: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ with three possible reaction pathways (one dissociative and two associative) as illustrated in Scheme 1 [85]. The first step is O_2 adsorption, followed by two pathways: the adsorbed O_2 is **(I)** directly dissociated to yield two O^* species (i.e. dissociative mechanism), or **(II)** hydrogenated by accepting a proton from H_2O (i.e. associative mechanism). The pathway **II** also includes two different pathways: one is the associative $2e^-$ pathway, in which O_2 is reduced to OOH^- and OH^- (named **II-2e⁻**), and the other is the associative $4e^-$ pathway, in which O_2 is reduced to $4OH^-$ (named **II-4e⁻**). Generally, ORR can proceed in Langmuir–Hinshelwood (LH) or Eley–Rideal (ER) mechanisms. In LH mechanism, the proton is adsorbed on the catalyst surface, the same as other species, such as O , OOH , and OH . In comparison, in ER mechanism, the proton comes directly from the electrolyte [43, 44, 86].

Our O_2 adsorption energy computations screened out two promising ORR catalysts, C_8F and $C_8(OCH_3)$ graphenes. In the following section, we will examine both LH and ER mechanisms for these two monolayers.

ORR pathways on C_8F : Firstly, we investigated the LH mechanism under an alkaline

environment, both the dissociative pathway and associative pathway were considered.

Providing that the ORR follows the dissociative pathway **I**, the dissociation of the adsorbed O₂ molecule on the C₈F surface should occur. Note that this mechanism is preferred on the Pt surface according to previous theoretical studies [87]. However, our computations showed that the O₂ dissociation on C₈F is endothermic by 0.98 eV and should overcome an energy barrier of 1.46 eV (Figure S6), thus, O₂ dissociation is not expected at the working temperature of alkaline fuel cell (approximately 350 K) on C₈F graphene.

Providing that the ORR follows the associative pathway **II**, the adsorbed O₂ molecule will interact with H₂O to form either (OOH⁻ + OH⁻) in the associative 2e⁻ pathway (**II**-2e⁻), or first to (2OH⁻ + O^{*}) and finally to 4OH⁻ in the associative 4e⁻ pathway (**II**-4e⁻).

In the **II**-2e⁻ pathway in the LH mechanism, the formed OOH and OH species locate at different hexagonal rings, which the distance of OOH or OH with C₈F graphene is 1.47 Å (Figure 4). Meanwhile, a weak hydrogen bond with a distance of 2.42 Å is formed between the H atom in OOH^{*} and the O atom in OH^{*}. However, the reaction, O₂^{*} + H₂O → OOH^{*} + OH^{*}, is endothermic by 0.33 eV, accompanying with a high energy barrier of 1.67 eV (Figure 4). Thus, it is energetically unfavorable for the adsorbed O₂ to convert into OOH species by interacting with H₂O, and the **II**-2e⁻ pathway is not favored.

In the **II**-4e⁻ pathway, for the O₂^{*} + H₂O → O^{*} + 2OH^{*} step, the calculated reaction energy and barrier are -0.09 and 0.82 eV (Figure 5a), respectively, which

indicates that it is rather facile for the adsorbed O_2 molecule to dissociate into O and OH species with the help of H_2O . Subsequently, the O^* is hydrogenated by accepting a hydrogen atom from the second H_2O molecule, leading to the formation of another two separated OH species on the C atoms with high spin density (Figure S7). Moreover, this elementary step, $O^* + H_2O \rightarrow 2OH^*$, is exothermic by -0.99 eV and has a small barrier of 0.48 eV (Figure 5b).

Overall, the ORR on the C_8F graphene in alkaline solution in LH mechanism prefers to proceed through the $II-4e^-$ pathway via three elemental steps, $O_2(g) \rightarrow O_2^*$, $O_2^* + 2H_2O \rightarrow O^* + 2OH^*$, $O^* + H_2O \rightarrow 4OH^*$ (Figure 5c). The $O_2^* + H_2O \rightarrow O^* + 2OH^*$ step has the largest activation barrier of 0.82 eV, thus is the rate-determining step. The high selectivity of $4e^-$ reduction pathway over $2e^-$ reduction pathway is a big advantage for C_8F graphene as ORR electrocatalyst because the reduction of O_2 via $2e^-$ pathway affords only about half of the energy compared to the $4e^-$ reduction pathway.

Secondly, we analyzed the ORR process on C_8F graphene following ER mechanism, in which the proton comes directly from the electrolyte. The Gibbs free energy (ΔG) of each elementary step at different electrode potentials was calculated by using the method developed by Nørskov *et al* [72-74]. According to the free energy diagram (Figure 6a), at $U = 0$, the first step $O_2 \rightarrow O_2^*$ (Scheme 1) is an endothermic reaction with a free energy change of $\Delta G_1(U_0) = 0.27$ eV, while the second step to form chemisorbed O^* and the third step to form OH^* are all exothermic with $\Delta G_2(U_0) = -0.58$ eV and $\Delta G_3(U_0) = -1.24$ eV, respectively. The last electron

transfer step, OH^* desorption, has a small free energy change $\Delta G_4(U_0) = -0.20 \text{ eV}$. Therefore, $\Delta G_1(U_0)$ is the largest one among the free energy changes of these four reaction steps, which indicates that the $\text{O}_2 \rightarrow \text{O}_2^*$ step is the most sluggish one (namely limiting step) and represents the highest resistance for the whole ORR.

Since the overpotential (η) of ORR is an important criterion to evaluate the catalytic activities a catalyst [72], we calculated the overpotential for the ORR on C_8F graphene. An ideal catalyst should be able to promote ORR just above the thermodynamic equilibrium potential with zero overpotential. However, the ideal case cannot be achieved because of the adsorption energies of the ORR species are correlated [72]. Therefore, thermodynamically, the lower the overpotential, the higher the catalytic activity of a catalyst for the ORR [88]. For the ORR on C_8F graphene in alkaline medium, the energy levels of each elementary step would be shifted at a given U . At the equilibrium potential ($U_0 = 0.40 \text{ V}$), $\text{O}_2^* + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{O}^* + 2\text{OH}^-$ and $\text{OH}^* \rightarrow \text{OH}^-$ are uphill in the free energy profile. The highest potential value at which all reduction steps were still downhill was 0.20 V (Figure 6a). Since the reaction of $\text{O}_2 \rightarrow \text{O}_2^*$ is not influenced by the applied potential (there is no electron transfer), the whole overpotential of ORR on C_8F graphene is $[0.27 + (0.40 - 0.20)] = 0.47 \text{ V}$.

ORR pathways on $\text{C}_8(\text{OCH}_3)$: Similarly, we examined the other promising ORR catalyst, $\text{C}_8(\text{OCH}_3)$ graphene. For the LH mechanism, our computations demonstrated that the energy barriers of $\text{O}_2^* + 2\text{H}_2\text{O} \rightarrow \text{O}^* + 2\text{OH}^*$ and $\text{O}^* + 2\text{OH}^* + \text{H}_2\text{O} \rightarrow 4\text{OH}^*$ were 1.55 and 1.23 eV (Figure S8), respectively, suggesting that the two pathways are

kinetically unfavorable. For the ER mechanism, the corresponding free energy profiles at different electrode potentials were analyzed (Figure 6b). Our DFT results indicated that the onset potential of ORR on C₈(OCH₃) graphene is 0.14 V (OH^{*} + e⁻ → OH⁻), corresponding to an overpotential of $\eta = 0.26$ V. Thus, C₈(OCH₃) graphene also exhibits good catalytic performance for ORR, and it is more efficient than C₈F graphene ($\eta = 0.47$ V) in the alkaline media. Remarkably, the predicted overpotential values of ORR on C₈F (0.47 V) and C₈(OCH₃) (0.26 V) are comparable (even lower) than the other widely studied doped graphene-based materials (for example, 0.28 V on B-doped graphene) [89] and the theoretically identified best catalysts (~0.45 V on Pt) [72]). Thus, the C₈F and C₈(OCH₃) graphenes have superior high catalytic activity toward ORR processes.

Overall, the covalent attachment of any species to the surface of graphene that could cause a suitable spin density could result in a good catalytic performance of graphene for the ORR. Remarkably, the single-sided covalent functionalization of graphene with various functional groups can be easily achieved [90, 91]. For example, Stine *et al.* demonstrated the synthesis of single-sided fluorinated graphene with tunable C/F atomic ratio, such as C₄F, C₈F, C₁₀F, C₁₆F, and C₂₀F by varying XeF₂ exposure times [92].

4. Conclusions

In summary, our spin-polarized DFT calculations have demonstrated that spin density can be induced into graphene through single-sided functionalization with

various functional groups with the 12.5% ratio. The resulting C_8F and $C_8(OCH_3)$ graphenes can moderately activate the O_2 molecule and promote the subsequent ORR through a more efficient 4e associative pathway, suggesting that the two catalysts possess good catalytic performance for ORR. Compared to $C_8(OCH_3)$ graphene, C_8F graphene has an even higher catalytic activity due to its smaller activation barrier and lower overpotential. Our theoretical results indicated that the catalytic activity of graphene can be tuned by causing a suitable spin density through appending some functional groups to the surface of graphene. The high feasibility of single-sided functionalized graphenes and the ease to choose functional groups distinguish these 2D ORR catalysts. We hope that our studies could encourage more experimental and theoretical studies on exploring the potential of the functionalized graphene with various groups as metal-free catalysts for ORR.

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Scheme 1. Reaction scheme of ORR on catalyst in alkaline solution [43, 83].

FIGURE CAPTIONS

Figure 1. Optimized geometric structure of C₈F graphene in a 3×3 supercell. The red dotted lines indicate a unit cell. The gray and blue balls represent C and F atoms, respectively.

Figure 2. (a) The top and side views of the lowest-energy configuration of O₂ on C₈F surface, and (b) its projected density of states (PDOS). The Fermi level is set as zero in red dashed line. The gray, blue, and red balls represent C, F, and O atoms, respectively.

Figure 3. The variation of O₂ adsorption energy (E_{ads}) with the magnetic moments of various C₈R graphenes (μ_B).

Figure 4. The pathway of $\text{O}_2^* + \text{H}_2\text{O} \rightarrow \text{OOH}^* + \text{OH}^*$ on C₈F graphene and the involved stationary points along the pathway. The gray, blue, red, and green balls represent C, F, O, and H atoms, respectively.

Figure 5. Minimum energy pathways for ORR elemental steps in alkaline media on the C₈F graphene at zero potential *via* LH and ER mechanisms.: (a) $\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{O}^* + 2\text{OH}^*$, (b) $\text{O}^* + \text{H}_2\text{O} \rightarrow 2\text{OH}^*$, and (c) schematic energy profile.

Figure 6. Schematic energy profiles for the ORR pathways in alkaline media at different potentials catalyzed by the (a) C₈F graphene and (b) C₈(OCH₃) graphene.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6