Single Si-Doped Graphene as a Catalyst in Oxygen Reduction Reactions: An In Silico Study

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ABSTRACT: Single Si-doped graphene C_{53}H_{18}Si with one carbon atom replaced by a three-coordinate silicon atom is studied by density functional theory (DFT) calculations as a catalyst for the oxygen reduction reactions (ORRs) in both acidic and alkaline media. The active sites for oxygen adsorption were determined from the distribution of the charge density difference analysis. At the equilibrium electrode potential, the most stable intermediate was found to have the structure HO*O*−C_{53}H_{18}Si with both oxygen atoms bound to the support, one of them being incorporated in between Si and C atoms, corresponding to the transfer of one hydrogen atom [H+ + e−]. The 2e ORR mechanism is shown to be very unlikely because the alternative 4e ORR pathway occurring via intermediates with a broken O−O bond is much more exothermic. In addition to the commonly adopted ORR mechanism, new reaction pathways have been discovered and shown to be potentially preferable over the traditional mechanism. The new proposed four-electron ORR route was predicted to proceed spontaneously in acidic media at U < 0.99 V and in alkaline media at U < 0.22.

INTRODUCTION

Fuel cells are known as highly efficient sources of clean energy used in various devices and act on the basis of the oxygen reduction reaction (ORR) at the cathode.1 The main challenge on this way to clean and renewable power sources is the slow kinetics of ORR at the cathode.2 The most efficient Pt-based catalysts for ORR suffer from such drawbacks as high cost, low durability, and chemical poisoning.3−5 In recent years, many efforts have been made to create noble metal-free or even totally metal-free catalysts for ORR, in particular, nanocarbon materials (NCMs) doped with different heteroatoms.6−8 Of special interest among NCMs are graphene and nanotubes doped with boron, nitrogen, phosphorus, sulfur, selenium, and other heteroatoms. All of these heteroatoms can be easily embedded in the center or on the periphery of the graphene sheet without distorting its planar structure.9−11

The behavior of a dopant embedded in carbon nanomaterials is distinct from that of the same dopant nanoparticles or mononuclear compounds in which extraordinary catalytic activity, selectivity, and stability in various reactions, including ORR, were demonstrated and attributed to the low-coordination environment of the dopant atom (three-coordinate silicon in our case) as well as the high atom utilization and improved strong dopant-support interactions.12 Such a new class of catalysts termed single-atom catalysts, in which catalytically active dopant atoms are anchored to the support, can exhibit optimal atom utilization, with all dopant atoms being exposed to reactants and available for catalytic reactions.13

As compared to other heteroatoms, much less attention has been paid to silicon-doped materials, although a very high oxophilicity of the silicon atom is a good prerequisite for the Si-containing materials to act as ORR catalysts, provided that the silicon atom is retained in the structure of the catalyst during the whole catalytic cycle. In this connection, the work of Chisholm et al.14 should be mentioned, who proved experimentally that the silicon atoms incorporated in the graphite layers do not react with molecular oxygen by forming SiO2 and thus be removed from the carbon support. The observed oxidation resistance in conjunction with high oxophilicity favoring oxygen adsorption of the Si-doped nanocarbon support makes these materials promising in catalytic applications, including ORR electrocatalysis.

In this context, noteworthy is the experimental study of the synthesis of Si-doped single-walled carbon nanotubes15−17 (and of their high electrocatalytic activity and long-term stability for ORR),17 or Si-doped graphene as a high-performance substance18 and new anode material.19

The number of theoretical studies on the role of Si-doped carbon nanomaterials in ORR is limited. The study of a series
of metal-doped (including Si-doped) graphenes with respect to the possible migration of the doping element from the surface of the solid to the bulk dissolution medium showed that the binding energy in the support is higher than the cohesive energy in the reaction environment, which proves the stability of these materials as possible ORR catalysts.

Thus, the adsorption and dissociation of the O2 molecule (the initial step of ORR) on pristine and Si-doped graphenes were shown to proceed exothermally via [2 + 1] or [2 + 2] cycloaddition followed by the dissociation of the adsorbed O2 by different mechanisms. Note that the barrier to dissociation of adsorbed O2 on the Si-doped graphene is ~16 times less than that on the pristine graphene. Si-doped graphenes were examined theoretically as possible catalysts for CO oxidation by N2O or O2 and for NO reduction to N2O. In both papers, graphene was simulated by a truncated sheet of nine-membered rings. In relation to ORR, only a few recent works can be mentioned; in the latest one, a rather exotic structure with the silicon atom surrounded by four nitrogens, all five atoms lying in one plane, is considered; the analysis of such structures is beyond the scope of our study.

Most relevant to our study is the work of Bai et al. who carried out density functional theory (DFT) calculations of ORR on the Si-doped graphene and showed that the kinetically preferred pathway includes O2 dissociation and HOO* hydrogenation into O* + H2O (*—the catalyst support). A conclusion was made that Si-doped graphene may serve as a good catalyst for ORR. However, there are a number of concerns that deserve to be addressed. Leaving aside the use of the projector augmented wave (PAW) pseudopotential method for analyzing an infinite periodic structure of small Si-doped graphene motifs, the most principal question is how the silicon atom is incorporated into the graphene sheet. Bai et al. replaced one C–C bond by the four-coordinate silicon atom forming the structure with attenuated aromaticity, as shown in Figure 1, left. In contrast to that, we constructed the Si-doped sheet C53H18Si with a three-coordinate silicon atom, in which the aromaticity is retained, as shown in Figure 1, right.

Figure 1. Model Si-doped graphenes with a four-coordinate (left) and a three-coordinate silicon atom (right).

The propensity of three-coordinate silicon to chemisorption of oxygen should be larger than that of four-coordinate silicon due to the high instability of hypovalent silicon. Another issue, which was not discussed so far, is the mechanism in alkaline media, whereas most ORRs are experimentally performed in alkaline solutions. All of this may (and, as will be shown below, does) result in substantially different interaction of the oxygen-containing intermediates with silicon in the Si-doped graphene, and even to the realization of a new, previously unknown, reaction pathway. Indeed, our analysis allowed us to reveal an alternative, previously not described, mechanism of the oxygen reduction reaction on Si-doped graphene.

Numerous studies on the ORR mechanism showed it to proceed via a 2e or 4e pathway or both, finally leading to H2O2 (2e pathway) or 2H2O (4e pathway). ORR includes the steps of (i) oxygen adsorption on the active site of the catalyst, (ii) hydrogenation of covalently bonded O2* (or O*O*) molecule to form HOO* or HO*O*, (iii) second hydrogenation to form H2O2 via the 2e pathway or HO*HO* or O* + H2O via the 4e pathway, (iv) third hydrogenation to form HO* + H2O, and (v) final fourth hydrogenation to form two H2O molecules. Formation of different intermediates and their relative energies in steps (ii–v) are crucial for effective ORR catalysis, whereas step (i) is a necessary (but not sufficient) precondition for the catalyst to be active toward the ORR. The overall reaction potential varies depending on the media; thus, for the aqeous acidic solution, it is equal to 0.695 V (for 2e ORR) or 1.229 V (for 4e ORR). It was concluded that the advantage of ORR in alkaline media is due to enhanced activation of the peroxide intermediate that enables the 4e-transfer process.

In view of this, in the present paper, we will concentrate on the mechanism of ORR, both in regard to thermodynamics and kinetics, on the Si-doped graphene C53H18Si by analyzing the elementary steps of the catalytic cycle and taking into account the results of works. The influence of acidic or alkaline media on the energetics of ORR will be examined and the rate-determining steps will be defined. Note, that the effect of pH was not especially analyzed, despite the fact that ORRs are usually studied experimentally in alkaline media.

RESULTS AND DISCUSSION

Structural Analysis of Si-Doped Graphene. The model Si-doped graphene includes 19 six-membered-ring graphene carbon sheets of C64H18 composition, in which the central phenyl ring is surrounded by two belts of phenyl rings and one of the carbons in the central ring is replaced by a silicon atom (C64H18Si, Figure 2). This is the optimal size of the support for analyzing the doping effects because a network of smaller size would not allow to adequately describe these effects due to larger constraints upon doping with a heteroatom, whereas the introduction of a fourth belt will impermissibly increase the computational costs.

The introduction of silicon into the structure of graphene C64H18, as predicted by B3LYP/6-311+G(d), gives planar structure C64H18Si (1a), as depicted in Figure 2. Due to the larger size of silicon as compared to that of carbon, the internal angles at the Si atom are distorted so that \( \angle_{CSiC} = 114.3^\circ \) and all three Si–C bond lengths are equal to ~1.68 Å. Fuzzy bond order analysis showed the Si–C bond order to be 1.24–1.28, indicating their aromatic character. However, planar structure 1a is only a local minimum on the potential energy surface (PES) since a deviation of the silicon atom from the plane by 0.67 Å (Figure 2, 1b) lowers the energy by 0.60 eV with respect to 1a. The formation energy \( E_f \) of 1b according to eq 3 is 7.62 eV (in both DFT methods), the energy gap \( E_{gap} = 2.42 \) eV (5.29 eV at wB97XD), which is ~0.4 eV lower than that of pristine graphene C64H18. It is worth noting that the planar structure was not located when using the wB97XD functional. In the global minimum 1b, all three angles \( \angle_{CSiC} \) are equal to ~108°, and the Si–C bonds fall in the range 1.75–1.76 Å and have a bond order of 1.18–1.23. These geometric parameters indicate the preference of sp2 hybridization by Si in graphene.
and less aromatic or even nonaromatic character of this part of the molecule, whereas the rest of structure 1b remains aromatic. The preference for Si sp$^3$ hybridization in the Si-doped graphene is in agreement with the reported structure.

The value of 0.60 eV is, therefore, the difference between the aromatic 1a and nonaromatic Si-doped graphene 1b. Looking ahead, the approach of the oxygen molecule to the silicon atom in 1a distorts its planar structure and gives the same “atop” O$_2$*–C$_{53}$H$_{18}$Si adducts as in the case of O$_2$ adsorption on 1b.

**Charge Density Difference (CDD) Analysis.** In the next step, we have analyzed charge density difference (CDD) in 1b since this parameter serves as a measure of the ORR catalyst activity. The CDD map for the first excited state is presented in Figure 3, and those for higher-lying states are available in the Supporting Information (Figure S1). As is clearly seen from Figures 3 and S1, there is charge accumulation on the silicon and neighboring carbon atoms for the first four excited states, while on the peripheral carbons, charge depletion occurs. An analysis of the $\Delta r$ index value (0.635 Å), the integral of overlap of the hole–electron distribution ($S = 0.614$), and the distance between the centroid of the hole and electron ($D = 0.549$ Å) for the first excited state allows us to assume that it represents local excitation rather than charge transfer, as was stated for the Si-doped nitrogen-coordinated graphene.

**Structure and Energy of ORR Intermediates.** According to CDD analysis, the most probable sites for oxygen adsorption are the silicon atom, the neighboring carbon atoms, and the carbon atom in the “para” position to the Si atom, where charge accumulation occurs, Figure 3. Indeed, the adsorption of the O$_2$ molecule on silicon in C$_{53}$H$_{18}$Si was found to proceed barrierless, giving exclusively atop intermediate 2a ($E_{ads} = -2.40$ eV, Figure 4 and Table 1) as proved by the absence of the corresponding transition state (TS). It is worth noting that being formed by the addition of the O$_2$ molecule to the three-coordinate silicon, the spatial structure of the O$_2$SiC$_3$ coordination knot in 2a is unique and principally different from the classical trigonal bipyramidal structure of pentacoordinate silicon compounds with two axial electronnegative atoms and an equatorial SiC$_3$ plane.

Other possible O$_2$*-containing species in which O–O bond is also retained are “bridge” (2b, $E_{ads} = -2.46$ eV) and para O$_2$* (2c, $E_{ads} = -1.74$ eV) intermediates. However, the most stable O$_2$* species are those in which the O–O bond is broken, that is, the [O*O*]-containing species: “epoxy” [O*O*] (2d, $E_{ads} = -2.80$ eV) and 2e ($E_{ads} = -4.83$ eV). Thus, the stability of O$_2$* species increases in the order 2c < 2a < 2b < 2d < 2e. The obtained adsorption energies of O$_2$*-containing species are consistent with those obtained previously by Chen et al., who computationally studied transformations in the series of O$_2$*-containing species adsorbed on pristine and Si-doped graphene. Therefore, below, we present a brief discussion of transformations between intermediates 2a–e and a detailed analysis of the ORR mechanism including intermediates 1–6 and transition states (TS).

The strong exothermic effect of dioxygen molecule adsorption ($E_{ads}$) is a manifestation of high oxophilicity of three-coordinate silicon, whereas four-coordinate silicon demonstrates 10 times lower affinity toward dioxygen molecule. For comparison, the adsorption of O$_2$ on pristine graphene C$_{44}$H$_{18}$ is predicted to be endothermic by 0.65 eV at the same level of theory.
As stated, the elongation (and, hence, loosening) of the O–O bond in the O$_2^*$ intermediate increases the activity of the adsorption site for ORR. The variation in the O–O distances in the O$_2^*$ species.
Table 1. Si–O Bond Lengths (Å), Adsorption Energies ($E_{ads}$, eV), and Free Energies ($\Delta G^\circ$, eV) of Oxygen-Containing Species Involved in ORR on Si-Doped Graphene C$_{53}$H$_{18}$Si

| Intermediate | B3LYP $E_{ads}$ | $\Delta G^\circ$ | wB97XD $E_{ads}$ | $\Delta G^\circ$ |
|--------------|----------------|----------------|----------------|----------------|
| atop O$_2^*$ (2a) | 1.708 | −2.40 | −1.19 | 1.695 | −2.45 | −1.13 |
| bridge O$_2^*$ (2b) | 1.701 | −2.46 | −1.16 | 1.695 | −2.81 | −1.12 |
| para O$_2^*$ (2c) | 1.738 | −1.74 | −0.45 | 1.730 | −2.12 | −0.65 |
| epoxy [O*O*]$^*$ (2d) | 1.562 | −2.80 | −1.55 | 1.551 | −3.08 | −1.63 |
| [O*O*]$^*$ (2e) | 1.545 | −4.83 | −3.57 | 1.536 | −4.95 | −3.52 |
| HOO* (3a) | 1.469 | −2.56 | −1.32 | 1.694 | −2.85 | −1.47 |
| HOO* (3b) | 1.653 | −3.42 | −2.16 | 1.645 | −3.89 | −2.43 |
| HOO* (3c) | 1.658 | −3.46 | −2.16 | 1.650 | −4.08 | −2.61 |
| HOO* (3d) | 1.647 | −5.10 | −3.80 | 1.639 | −5.47 | −4.03 |
| HOO* (4a) | 1.674 | −6.02 | −4.25 | 1.664 | −6.70 | −2.70 |
| HOO* (4b) | 1.657 | −6.09 | −2.31 | 1.648 | −6.79 | −2.77 |
| HOO* (4c) | 1.706 | −5.64 | −1.96 | 1.752 | −6.05 | −2.15 |
| O* (5a) | 1.564 | −6.93 | −1.82 | 1.554 | −6.92 | −1.70 |
| O* (5b) | 1.564 | −6.93 | −1.82 | 1.554 | −6.92 | −1.70 |
| O* (5c) | 1.567 | −6.48 | −1.33 | 1.652 | −6.78 | −1.49 |
| HOO* (6) | 1.665 | −4.10 | −2.29 | 1.665 | −4.41 | −2.53 |

$\Delta G$ refers to the electrode potential $U = 1.23$ V in acidic media corresponding to $[4H^+ + e^-] + O_2 = 2H_2O$ equilibrium. $\Delta G$ and zero-point energy (ZPE) values are calculated at method/6-311G(d,p)// method/6-311+G(d). Calculated as $E_{ads}(4) = E(4) - E(1b) - E(H_2O_2)$.

### 1$\text{a}$-c in both methods in Table 1 is nearly the same: atop (2a) $\approx$ bridge (2b) < para (2c), all being significantly larger than that of the ordinary O–O bond (1.49 Å in H$_2$O$_2$). The Si–O bond length in 2d is 1.562 Å (1.545 Å in 2e), the second oxygen atom being remote from the Si atom to form the epoxide at the C$_{53}$Si bond of graphene near the Si atom. In the most stable isomer 2e, the second oxygen atom is inserted into the Si–C bond to form a Si–O–C fragment, Figure 4.

Less evident is the relationship between the catalytic activity and the energy $E_{ads}$ (or free energy $\Delta G$) of adsorption. On the one hand, the process of adsorption must be exothermic enough to allow the process to occur. On the other hand, too strong adsorption would not allow the adsorbed species to diffuse from the electrode to the bulk solution; therefore, neither of the two extremes is good for efficient catalysis.

In view of the possibility of the formation of several O$_2^*$–C$_{53}$H$_{18}$Si isomers, the ORR may follow different paths. Thus, protonation of one oxygen in the atop isomer O$_2^*$–C$_{53}$H$_{18}$Si 2a by [H$^+$ + e$^-$] affords HOO$^*$–C$_{53}$H$_{18}$Si 3a through TS$_{2a}$–TS$_{3a}$ (vide infra), where the O–O bond is retained, although significantly weakened, Figure 4. Adducts 3a–e have $E_{ads}$ decreasing in the order 3a > 3b > 3c > 3d > 3e from −2.56 to −5.10 eV (B3LYP) or from −2.85 to −5.47 eV (wB97XD, Table 1). Within the series of the singly protonated isomers HOO$^*$O$^*$–C$_{53}$H$_{18}$Si, 3e is the most energetically favorable one, lying 2.54 eV (2.62 eV, wB97XD) lower than 3a. The latter is the key intermediate, whose protonation can result in the undesirable H$_2$O$_2$ formation via the 2e ORR. As will be shown below, an attempt to protonate the Si–O oxygen atom in HOO$^*$ 3a leads to the rupture of the O–O bond and conversion of 3a into the HO$^*$HO$^*$ 4c intermediate, rather than to elimination of the hydrogen peroxide molecule from silicon.

In the case of isomers HO$^*$O$^*$–C$_{53}$H$_{18}$Si 3b–e, the protonation leads to the formation of diols HO$^*$HO$^*$–C$_{53}$H$_{18}$Si 4a and 4b, Figure 4, with high adsorption energies $E_{ads}$ of the two HO groups, which, again, strongly decreased on going to $\Delta G$ values. A reorientation of the hydroxyl groups in 4a by 180° gives 4b and lowers the energy by ~0.08 eV. Structure 4b is distinct from 4a by a slightly extended HO–HO hydrogen bond and contracted Si–O bond. It should be noted that diols 4a, 4b, and especially 4c, are stable with respect to nonreacting system 2b + H$_2$O$_2$ by 3.48–3.85 eV (3.78–4.52 eV, wB97XD), again indicating the preference of 4c over the 2c mechanism for ORR. Further protonation of O* 5a, 5c, or HO*HO* 4b, 4c results in the intermediate HO* 6, with the HO group attached to the silicon atom and $E_{ads} = −4.10$ eV (~4.41 eV, wB97XD). Final protonation leads to the release of the second H$_2$O molecule, regenerating the catalyst and completing the 4e ORR catalytic cycle.

The highly negative adsorption energy $E_{ads}$ of O* 5a, 5c is, apparently, due to the instability of atomic oxygen (in 5a) or the electron-donating effect of silicon (in 5c). For this reason, the values of $E_{ads}$ of compounds 5 in Table 1 are given not only as calculated from eq 5 (see the Experimental Section) but also by the following equation

$$E_{ads}(S) = E(S) + E(H_2O) - E(1b) - E(H_2O_2)$$

However, the high values of $E_{ads}$ are substantially outbalanced (for O* 5a, 5c) or even overbalanced (O* 5b) by the entropy loss so that the corresponding $\Delta G$ values are only moderately negative or even positive, Table 1.

The obvious question arising is whether ORR on the Si-doped graphene proceeds via the 2e or 4e pathway, or both? On the one hand, after the first protonation of O**, the O–O bond may be retained, making the 2e pathway feasible. On the other hand, the hypothesis that ORR on the Si-doped graphene proceeds predominantly as the 4e process is supported not only by the absence of HOO$^*$ 3a → H$_2$O$_2$ transition state (vide infra) but also by the analysis of the Si–O bond lengths and energetics of adsorption. Structure HOO$^*$ 3a in Figure 4 is a point of bifurcation on the PES because its protonation with retention of the O–O bond would direct the reaction along the 2e pathway, whereas protonation with breaking of the O–O bond would mean the 4e mechanism of ORR. We failed to find any structure HOHO$^*$ 4 with the retained O–O bond; the geometry optimization led to its rupture in all structures 4a–c, Figure 4. Moreover, the adsorption energy $E_{ads}$, which is an indicator of stability, decreases in the order O* (−6.92 eV) > HO$^*$ (−4.41 eV) > HOO$^*$ (−2.85 eV), indicating that the species related to the 4e ORR, that is, O* and HO*, are the most stable intermediates. Therefore, keeping in mind the elongated O–O bond in HOO$^*$ (up to its cleavage to form HO$^*$HO$^*$) and its relative stability with respect to other intermediates, we conclude with high probability that the ORR proceeds via the 4e pathway. This conclusion is consistent with the
hypothesis that the selectivity of the catalyst toward H2O2 or H2O is determined by its propensity to break the O−O bond, which in turn is set by the binding strengths of the intermediates of the 4e pathway, namely, O* and HO*.37

**Effect of Electrode Potential and Mechanism of ORR.**

As stated above, due to the possibility of the formation of various O2* and [O*O*] intermediates 2a–e, the ORR may follow different mechanistic pathways. A tentative catalytic cycle for ORR on Si-doped graphene C53H18Si 1b is proposed in Figure 5. It starts from the catalyst 1b barrierless chemisorption of the O2 molecule to form atop O2* 2a intermediate with a free energy ΔG gain of 1.19 eV calculated hereinafter at electrode potential U = 1.23 V in acidic media (Figure 5, Tables 1 and S1). Further protonation of O2* 2a leads to slightly more stable HOO* 3a intermediate; however, such transformation needs to overcome the barrier of 1.68 eV (1.57 eV, wB97XD, Table S1). Another possible route for atop O2* 2a isomerization is the formation of para O2* intermediate 2c, Figure 4. It has the barrier of ΔG = 0.81 eV (0.89 eV, wB97XD). However, energetically, the equilibrium 2a ⇌ 2c is strongly shifted to the left, Figure 5, Tables 1 and S1, so structure 2c was omitted from further consideration not only because of its low content but also because there was no alternative pathway for the conversion of O2* 2c into other intermediates of ORR. Finally, the most kinetically favored transformation of O2* 2a is its isomerization into bridge O2* 2b through TS2a−2b having the barrier of only 0.49 eV. B3LYP predicts the equilibrium 2a ⇌ 2b to be negligibly shifted to 2a (0.03 eV), while wB97XD gives 2b to be more stable by 0.24 eV. Thereby, in accordance with the ΔG values of TSs, the probability of transformation of atop O2* 2a to other intermediates increases in the order 3a < 2e < 2c < 2b.

Returning to transformations of the key HOO* intermediate 3a, it should be mentioned that the further course of the reaction after bifurcation depends on which oxygen in 3a is protonated: the Si−O oxygen leading to the formation of H2O2 and the 2e mechanism or the HO oxygen leading to the 4e mechanism via the formation of O* 5a, Figure 6. Search for a saddle point for the former route resulted in only TS3a−4c, Figures 4 and 5 and Table S1, whose structure is indicative of concerted protonation of Si−O oxygen and the O−O bond rupture, thus canceling the 2e ORR mechanism on the Si-
doped active site. The transformation $3a \rightarrow 4c$ requires overcoming the barrier of 2.64 eV (2.99 eV, wB97XD). The latter route is less favorable and goes via transition state $TS_{3a-5a}$, Figure 5 and Table S1, with the barrier of 2.79 eV (3.27 eV, wB97XD). It should be noted that the equilibrium $4c \rightleftharpoons 5a$ is shifted to the left by 0.14 eV (0.45 eV, wB97XD) due to the instability of species $O^*$ containing atomic oxygen. Transformation $5a \rightarrow 4c$ through $TS_{4c-5a}$ involves climbing the barrier of 0.66 eV (0.56 eV, wB97XD), which is lower than that for protonation of $O^*$ $5a$ to $HO^*$ $6$ via transition state $TS_{5a-6}$ having a $\Delta G$ barrier of 2.04 eV (1.85 eV, wB97XD). Final $[H^+ + e^-]$ transfer to $6$ resulting in the release of the second water molecule and the catalyst regeneration is also high energy-consuming, with the corresponding $TS_{6-1b}$ of $\sim$3.2 eV.

However, this is only an apparent problem. First, in the solution, the barriers must be smaller due to solvation of the corresponding TS. Second, while the release of $H_2O$ from the support is unfavorable energetically ($E_{\text{desorb}}$ = 0.35 eV and 0.61 eV at the B3LYP and wB97XD levels, respectively), the corresponding $\Delta G$ values are negative ($\Delta G = -0.22$ and $-0.01$ eV at the B3LYP and wB97XD levels, respectively). Third, and most important, is that to complete the catalytic cycle one has to consider not the process of water release from the support but a homodesmotic reaction, eq 2

$$H_2O^* + O_2 = O_2^* + H_2O \quad (2)$$

The homodesmotic reaction is exothermic by 2.04 (B3LYP) or 1.84 eV (wB97XD), and free energy is more favorable by 1.40 (B3LYP) or 1.08 eV (wB97XD) under the equilibrium conditions. Thus, the energy gain from the homodesmotic reaction can be a driving force for the recovery of the catalyst activity and hence for completing the catalytic cycle.

Intermediate $[O^*O^*]_{2e}$, as a result of atop $O_2^*$ isomerization, is one of the most stable oxygen-containing structure in whole ORR on Si-doped graphene $C_{33}H_{18}Si$ $1b$. Nevertheless, it can undergo two possible transformations. The first one, to epoxy $O_2^*$ $2d$ is highly unlikely due to exothermicity of the reverse isomerization, $2d \rightarrow 2e$, Figure 5. The second one is the transfer of $[H^+ + e^-]$ to $[O^*O^*]_{2e}$ to form the most stable $HO^*O^*$ $3e$ intermediate, Figures 4 and 5. The free energy $\Delta G$ of $3e$ is $-3.80$ eV ($-4.03$ eV, wB97XD) at $U = 1.23$ V, while the $2e \rightarrow 3e$ transformation requires to overcome the barrier of 2.23 eV (2.12 eV, wB97XD). The latter value is 0.65 eV (1.00 eV, wB97XD) lower than that of $2e \rightarrow 2d$. Although protonation of epoxy $O_2^*$ $2d$ is endothermic, Figure 5, it may follow the route $2d \rightarrow 3d \rightarrow 3c \rightarrow 3e$ as the most energetically favorable, again leading to the most stable intermediate $[HO^*O^*]$ $3e$, Figure 5.

Further ORR evolution of $[HO^*O^*]$ $3e$ is to be converted into diol $HO^*HO^*$ $4a$ surmounting the barrier of $\sim$3.95 eV through $TS_{3e-4a}$ after protonation or, following a more energetically favorable route, to form $O^*5c$ and $H_2O$ through transition state $TS_{3e-5c}$ which is $\Delta \Delta G = 0.15$ eV (0.45 eV,

![Figure 6](image-url) Conventional mechanism of the oxygen reduction reaction (ORR).

![Figure 7](image-url) Free energy plots for the possible 4e ORR pathways on Si-doped graphene, at $U = 1.23$ V in acidic media: common route via $HOO^*$ ($3a$) $\rightarrow$ $O^*$ ($5a$) (A), alternative route via $HOO^*$ ($3a$) $\rightarrow$ $HO^*HO^*$ ($4c$) (B), and route via $O$--$O$ bond rupture after $O_2$ adsorption and oxygen atom insertion into the graphene sheet (C).
Intermediate 5c can further isomerize into the more stable isomer 5a via the transition state TS5c−5a with the barrier of as low as 0.18 eV (0.36 eV, wB97XD). Further ORR evolution of 5a is described above.

Therefore, the meticulous investigation of the ORR mechanism on the single Si-doped graphene C_{35}H_{18}Si_{1b} as the catalyst revealed at least three possible 4e reaction pathways. The first is the commonly adopted route via protonation of HOO• to form O•• (3a → 5a); the second one including protonation of HOO• to form HO•HO• (3a → 4c) is new and slightly preferable over the former (0.15 eV at B3LYP and 0.28 eV at the wB97XD level). Finally, the third pathway is also new; it includes oxygen insertion into the Si−C bond (2a → 2e) and is the longest but energetically most favorable (by 0.5 eV at B3LYP and 1.09 eV at the wB97XD level under the same conditions). The free energy plots for all three pathways at U = 1.23 V in acidic media are presented in Figure 7.

A careful analysis of Figure 7 allows us to conclude that route 1 (1b → 2a → 3a → 5a → 6 → 1b) at equilibrium in the acidic media will reach the local minimum corresponding to intermediate HO•• 6 with the transfer of three out of four required electrons. The overall barrier corresponds to the transition state for protonation of the hydroxyl oxygen atom in the intermediate HOO• 3a to O•• 5a and release of one H₂O molecule, ΔG° = 1.47 eV (1.80 eV at wB97XD). Route 2 (1b → 2a → 3a → 4c → 6 → 1b) is similar, except that the rate-limiting step is the protonation of Si−O in HOO• 3a to HO•HO• 4c, ΔG° = 1.32 eV (1.52 eV at wB97XD). The longest route 3 (1b → 2a → 2e → 3e → 5c → 5a → 4c → 6 → 1b) passes through the global minimum on the PES, corresponding to intermediate HO•O• 3e and the transfer of one electron with high energy gain, Figure 7C.

For routes 1 and 2, the effect of electrode potential in acidic media is similar; that is, at any U, the intermediate HO•• 6 will be most energetically favorable (Figure 8A,C). In alkaline media, the decrease of the electrode potential will determine
the ease of the fourth electron transfer (HO* + e− → HO− + *); the lower the $U$, the smaller the energy gap between the intermediate and the product (Figure 8B,D,E). Along route 3, two local minima are found (HO*O* 3e and HO 6) depending on $U$ both in acidic and alkaline media (Figure 8E,F). Thus, in acidic media at $U < 0.4$ V, the system prefers to be in the local minimum HO 6, corresponding to the transfer of three out of four possible electrons, whereas at $U > 0.4$ V, HO*O* 3e becomes preferable, resulting in the transfer of only one electron and decreasing the effectiveness of ORR (Figure 8E). In alkaline media at $U > -0.4$ V, one electron is transferred with the formation of stable intermediate HO*O* 3e. Further proceeding of ORR along route 3 at this electrode potential is determined by the barrier of transformation 3e → 5c (HO*O* → O*, Figure 8F). A further decrease of $U$ facilitates ORR, and the minimum corresponds to HO* 6.

The principal question to be answered is at which electrode potential the processes represented by routes 1–3 of ORR on the Si-doped graphene would proceed spontaneously? To answer this question, we compared the free energies for the initial system and the most highly lying transition states for all three routes both in acidic and alkaline media at different electrode potentials. It turned out that route 1 (1b → 2a → 3a → 5a → 6 → 1b) can proceed spontaneously in acidic media at $U < -0.33$ V, whereas in alkaline media, it occurs at $U < -0.33$ V. Route 2 (1b → 2a → 3a → 4c → 6 → 1b) can proceed spontaneously at $U < 0.57$ V in acidic media and at $U < -0.26$ V in alkaline media. Route 3 (1b → 2a → 2e → 3e → 5c → 5a → 4c → 6 → 1b) proceeds spontaneously in acidic media at $U < 0.99$ V and in alkaline media at $U < 0.22$ V. As the electrode potential $U$ is connected with the onset potential (the lowest potential for the reaction to occur), the latter value of $U$ seems promising since it is indicative of the ORR at $U = 0$ with respect to the standard hydrogen electrode potential.

## CONCLUSIONS

The conventional and newly proposed mechanisms of oxygen reduction reactions (ORRs) on the single Si-doped graphene C53H18Si with one carbon atom replaced by a three-coordinate silicon atom are studied theoretically using DFT calculations. Three-coordinate silicon demonstrates 10 times higher ability to O2 adsorption forming the adduct with atop configuration than the four-coordinate one. A new mechanism includes the rupture of the O–O bond and insertion of an oxygen atom in the catalyst support. Further protonation leads to the most stable intermediate HO*O*+, thus proving the 2e route of ORR via the formation of H2O2 to be thermodynamically unfavorable. An independent search for the transition state on the way to H2O2 led to the HO*HO*× intermediate, which contained two OH groups attached to the Si atom. Therefore, the mechanism through the HOO* → HO* × key intermediate step was found to be kinetically ~0.2 eV more favorable than the conventional scheme via the HOO* → O* + H2O transformation. The second, HO*O* → O* + H2O, alternative 4e-route of ORR was found to be 0.55 eV (1.09 eV at wB97XD) kinetically preferable over the conventional mechanism. The rate-determining step for this alternative is the second H2O molecule formation, which requires to overcome the overall barrier of 0.97 eV (0.71 eV at wB97XD), which is by ~0.6 eV less than the barrier predicted by Bai et al.26 There are two local minima (HO*O* + and HO*) along this new alternative route, depending on $U$ both in acidic and alkaline media. Thus, in acidic media at $U < 0.4$ V, the system prefers passing via the local minimum HO*, corresponding to the transfer of three out of four electrons, whereas at $U > 0.4$ V, HO*O* 3e becomes preferable, resulting in the transfer of only one electron and decreasing the effectiveness of ORR. In alkaline media at $U > -0.4$ V, one electron is transferred with the formation of stable intermediate HO*O* 3e. At $U < -0.4$ V, intermediate HO* 6 formed by the transfer of three electrons becomes the global minimum. A comparison of the Gibbs free energies for the reactants and the highest-lying transition state for the proposed new 4e ORR mechanism on Si-doped graphene revealed that the reaction proceeds spontaneously in acidic media at $U < 0.99$ V and in alkaline media at $U < 0.22$ V. Based on the performed analysis, the three-coordinate Si-doped graphene can be considered to be efficient ORR catalysts.

## EXPERIMENTAL SECTION

All calculations were performed with full geometry optimization with the Becke’s three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP) employing the 6-311+G(d) basis set.18 For all stationary points, second derivatives of the energy with respect to the Cartesian nuclear coordinates were calculated using the B3LYP/6-311+G(dp) basis set to obtain thermochemistry data and to check whether they are minima or transition states on the potential energy surface (PES). To achieve better accuracy, the ORR mechanism on Si-doped graphene was also studied using a long-range corrected DFT functional that includes empirical dispersion correction, wB97XD39 with the same basis sets. All calculations were performed using the Gaussian 09 suite of programs.40 The ChemCraft 1.8 program was used for structure visualization.41 Charge density difference (CDD) analysis was performed using Multiwfns 3.5 software.42 To investigate the stability of Si-doped graphene (Si−Gr), the formation energy $E_f$ was estimated as suggested15

$$E_f = (E_{Si-Gr} - E_{Gr}) - (E_Si - E_C)$$

(3)

where $E_{Si-Gr}$, $E_{Gr}$, $E_Si$, and $E_C$ are total energies of Si-doped graphene, pristine graphene, and silicon and carbon atoms respectively. To assess the charge injection ability, the highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) gap ($E_{gap}$) was used.

$$E_{gap} = E_{LUMO} - E_{HOMO}$$

(4)

To study the stability of various O2 adsorbates along with O2 protonated species involved in ORR on Si−Gr, the adsorption energy ($E_{ads}$) at the B3LYP/6-311+G(d) level of theory was evaluated as follows:

$$E_{ads} = E_{adsorbate-Si-Gr} - E_{adsorbate} - E_{Si-Gr}$$

(5)

where $E_{adsorbate-Si-Gr}$ and $E_{Si-Gr}$ are gas-phase total energies of adsorbate together with Si-doped catalyst C53H18Si, isolated adsorbate and the catalyst, respectively. The negative value of $E_{ads}$ indicates exothermicity of the adsorption process. The 2e and 4e mechanisms of ORR on the Si-doped graphene were investigated. In acidic media, the following ORR steps should be considered (* = catalyst). For 2e ORR

$$O_2 + * + 2[H^+ + e^-] \rightarrow O_2* + 2[H^+] + e^-$$

(6)

$$O_2* + 2[H^+ + e^-] \rightarrow HOO* + [H^+ + e^-]$$

(7)
HOO* + [H+ + e−] → H2O2 + *  
overall: O2 + 2[H+ + e−] → H2O2  
(8)

For 4e ORR:

O2 + * + 4[H+ + e−] → O2* + 4[H+ + e−]  
O2* + 4[H+ + e−] → HOO* + 3[H+ + e−]  
or O2* + 4[H+ + e−] → HO*O* + 3[H+ + e−]  
HOO* + 3[H+ + e−] → O* + H2O + 2[H+ + e−]  
(11a)

or HOO* + 3[H+ + e−]  
→ HO*HO* + H2O + 2[H+ + e−]  
(12a)

HO*O* + 3[H+ + e−] → HO*HO* + 2[H+ + e−]  
O* + 2[H+ + e−] → HO* + H2O + [H+ + e−]  
HO*HO* + 2[H+ + e−] → HO* + H2O + [H+ + e−]  
HO* + H2O + [H+ + e−] → 2H2O + *  
overall: O2 + 4[H+ + e−] → 2H2O  
(13)

In alkaline media, each step for 4e ORR is defined as follows

O2 + * + 2H2O + 4e− → O2* + 2H2O + 4e−  
O2* + 2H2O + 4e− → HOO* + H2O + HO− + 3e−  
or O2* + 2H2O + 4e−  
→ HO*O* + H2O + HO− + 3e−  
(19a)

HOO* + H2O + HO− + 3e− → O* + 2HO− + 2e−  
(20a)

or HOO* + H2O + HO− + 3e−  
→ HO*HO* + 2HO− + 2e−  
(20b)

HO*O* + H2O + HO− + 3e−  
→ HO*HO* + 2HO− + 2e−  
(21)

O* + 2HO− + 2e− → HO* + 3HO− + e−  
HO*HO* + 2HO− + 2e− → HO* + 3HO− + e−  
HO* + 3HO− + e− → 4HO− + *  
overall: O2 + 2H2O + 4e− → 4HO−  
(25)

Finally, the free energy diagrams of 2e and 4e ORR pathways were estimated in accordance with the method proposed by Nørskov et al. by the following equation44

\[ \Delta G = \Delta E + \Delta ZPE - T \Delta S + \Delta G_U + \Delta G_{\text{ph}} \]  
(26)

where \( \Delta E \) is the energy difference between the products and reactants, eqs 6–25; \( \Delta ZPE \) and \( \Delta S \) are the zero-point energy corrections to the total energy and entropy; \( T \) is the temperature (298.15 K); \( \Delta G_U = -neU \), where \( n \), \( e \), and \( U \) are the number of electrons in the reaction, the electron charge, and the electrode potential with respect to the standard hydrogen electrode, respectively; \( \Delta G_{\text{ph}} = k_B T \ln 10 \times \text{pH} \), where \( k_B \) is the Boltzmann constant. In this study, \( \text{pH} = 0 \) (\( \Delta G_{\text{ph}} = 0 \) eV) and \( \text{pH} = 13 \) (\( \Delta G_{\text{ph}} = 0.77 \) eV) were assumed for the acidic and alkaline media, respectively. The total energy and entropy of H2O in bulk water were calculated in the gas phase under the pressure of 0.035 bar (the equilibrium vapor pressure of H2O at 298.15 K). The free energy of O2 was obtained as the free energy of the reaction \( O_2 + 2H_2 \rightarrow 2H_2O \) equal to \(-4.92\) eV, and the free energy of H2O2 was taken from the reaction \( O_2 + H_2 \rightarrow H_2O_2 \) to be \(-1.39\) eV, both under standard conditions. The free energy of \([H^+ + e^-]\) in the solution, according to the computational hydrogen electrode model, was estimated as the energy of \( 1/2H_2 \) under standard conditions. The free energy of HO− was obtained from the dissociation of water, \( H^+ + HO^- = H_2O \), which was \(-0.03\) eV under standard conditions. The entropies and vibrational frequencies of the molecules in the gas phase were taken from the National Institute of Standards and Technology (NIST) database.45 The ZPE correction to the total energies and entropies of the species excluding those with Si-doped graphene were calculated from the vibrational frequencies. Throughout the text, geometric and energy parameters refer to the B3LYP functional if not stated otherwise.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01303.

Charge density difference plot for higher than first excited states of Si-doped graphene C53H18Si, adsorption and free energies along with absolute energies and geometries of all studied oxygen-containing species involved in ORR (PDF)

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**Notes**

The authors declare no competing financial interest.

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REFERENCES

(1) Song, C.; Zhang, J. Electrocatalytic Oxygen Reduction Reaction. PEM Fuel Cell Electrocatalysts and Catalyst Layers; Springer: London, 2008; pp 89–134.

(2) Gasteiger, H. A.; Koche, S. S.; Sompalli, B.; Wagner, F. T. Activity Benchmarks and Requirements for Pt, Pt-Alloy, and non-Pt Oxygen Reduction Catalysts for PEMFCs. Appl. Catal., B 2005, 56, 9–35.

(3) Zhang, Y.; Zhang, X.; Liu, M.; Liu, Y.; Huang, H.; Lin, S. One-Step Synthesis of an Octahedral MnOx/rGO Composite for Use as an Electrocatalyst in the Oxygen Reduction Reaction. J. Solid State Electrochem. 2018, 22, 2159–2168.

(4) Nie, Y.; Li, L.; Wei, Z. Recent Advancements in Pt and Pt-Free Catalysts for Oxygen Reduction Reaction. Chem. Soc. Rev. 2015, 44, 2168–2201.

(5) Shao, Y.; Yin, G.; Gao, Y. Understanding and Approaches for the Durability Issues of Pt-Based Catalysts for PEM Fuel Cell. J. Power Sources 2007, 171, 558–566.

(6) Higgins, D.; Zamani, P.; Yu, A.; Chen, Z. The Application of Graphene and Its Composites in Oxygen Reduction Electrocatalsysis: A Perspective and Review of Recent Progress. Energy Environ. Sci. 2016, 9, 357–793.

(7) Wang, D.-W.; Su, D. Heterogeneous Nanocarbon Materials for Oxygen Reduction Reaction. Energy Environ. Sci. 2014, 7, 576–591.

(8) Chen, N.; Huang, X.; Qu, L. Heterotatom Substituted and Decorated Graphene: Preparation and Applications. Phys. Chem. Chem. Phys. 2015, 17, 32077–32098.

(9) Wang, X.; Sun, G.; Routh, P.; Kim, D.-H.; Huang, W.; Chen, P. Heteroatom-Doped Graphene Materials: Syntheses, Properties and Applications. Chem. Soc. Rev. 2014, 43, 7067–7098.

(10) Zhu, C.; Dong, S. Recent Progress in Graphene-Based Nanomaterials as Advanced Electrocatalsysts Towards Oxygen Reduction Reaction. Nanoscale 2013, 5, 1753–1767.

(11) Shao, Y.; Sui, J.; Yin, G.; Gao, Y. Nitrogen-Doped Carbon Nanostructures and Their Composites as Catalytic Materials for Proton Exchange Membrane Fuel Cell. Appl. Catal., B 2008, 79, 89–99.

(12) Cheng, N.; Zhang, L.; Doyle-Davis, K.; Sun, X. Single-Atom Catalysts: From Design to Application. Electrochem. Energy Rev. 2019, 2, 539–573.

(13) Yang, X.-F.; Wang, A.; Qiao, B.; Li, J.; Liu, J.; Zhang, T. Single-atom catalysts: a new frontier in heterogeneous catalysis. Acc. Chem. Res. 2013, 46, 1740–1748.

(14) Chisholm, M. F.; Duscher, G.; Windl, W. Oxidation Resistance of Reactive Atoms in Graphene. Nano Lett. 2012, 12, 4651–4655.

(15) Campos-Delgado, J.; Maciel, I. O.; Cullen, D. A.; Smith, D. J.; Jorio, A.; Pimenta, M. A.; Terrones, H.; Terrones, M. Chemical Vapor Deposition Synthesis of N-, P-, and Si-Doped Single-Walled Carbon Nanotubes. ACS Nano 2010, 4, 1696–1702.

(16) Kaukonen, M.; Krasheninnikov, A. V.; Kauppinen, E.; Nieminen, R. M. Doped Graphene as a Material for Oxygen Reduction Reaction Activity of Metal-doped Graphene by Density Functional Theory. Appl. Surf. Sci. 2016, 379, 291–295.

(17) Kong, X. Metal-free Si-doped graphene: A New and Enhanced Anode Material for Li Ion Battery. J. Alloys Compd. 2016, 687, 534–540.

(18) Chen, X.; Chen, S.; Wang, J. Screening of Catalytically Active Metal-doped Graphene by Density Functional Theory. Appl. Surf. Sci. 2016, 379, 291–295.

(19) Chen, Y.; Yang, X.-c.; Liu, Y.-j.; Zhao, J.-x.; Cai, Q.-h.; Wang, X.-z. Can Si-doped graphene activate or dissociate O2 molecule? J. Mol. Graphics Modell. 2013, 39, 126–132.

(20) Shao, Y.; Yin, G.; Gao, Y. Understanding and Approaches for the Durability Issues of Pt-Based Catalysts for PEM Fuel Cell. J. Power Sources 2007, 171, 558–566.

(21) Shao, Y.; Yin, G.; Gao, Y. Understanding and Approaches for the Durability Issues of Pt-Based Catalysts for PEM Fuel Cell. J. Power Sources 2007, 171, 558–566.
J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

(41) Chemcraft—Graphical Software for Visualization of Quantum Chemistry Computations. https://www.chemcraftprog.com.

(42) Lu, T.; Chen, F. A Multifunctional Wavefunction Analyzer. J. Comput. Chem. 2012, 33, 580–592.

(43) Wang, Y.; Jiao, M. G.; Song, W.; Wu, Z. J. Doped Fullerene as a Metal-Free Electrocatalyst for Oxygen Reduction Reaction: A First-Principles Study. Carbon 2017, 114, 393–401.

(44) Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jonsson, H. Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. J. Phys. Chem. B 2004, 108, 17886–17892.

(45) http://webbook.nist.gov/chemistry/ (accessed 4 April, 2019).