



Probing the activity of pure and N-doped fullerenes towards oxygen reduction reaction by density functional theory



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ABSTRACT

Fullerene can be potentially used as the electrocatalyst for oxygen reduction reaction (ORR) due to its curvature and pentagon defect. In this study, the ORR mechanisms and catalytic abilities of pure and N-doped fullerenes were investigated via DFT computations. Four different sized fullerenes, C₂₀, C₄₀, C₆₀, and C₁₈₀, with respectively the diameter of approximately 0.4, 0.6, 0.7, and 1.2 nm, were utilized to investigate the size effect on the ORR performance. The results reveal that the smallest (C₂₀ and N-doped one) and the largest (C₁₈₀ and C₁₇₉N) fullerenes are not effective ORR catalysts candidates in view of their unsuitable adsorption strength to the ORR species. In contrast, N-doped C₄₀ and C₆₀, with the adsorption energy much close to those on Pt(111), manifest high ORR activity potentials. Further analysis of the relative energy diagram shows that the ORR process on C₁₉N and C₁₇₉N is completed through a H₂O₂ dissociation mechanism, while on C₃₉N and C₅₉N it will undergo an OOH dissociation pathway. In addition, the C₃₉N has the largest decreased energy of rate-determining step in the relative energy profile, suggesting its ORR activity is the best among all the different sizes of fullerenes that we studied.

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1. Introduction

In view of the upcoming exhausting of traditional energies, it is increasingly imperative to find new energies as replacement. Fuel cell has attracted much attention in recent years due to its high power density, high energy conversion efficiency, and non-pollution property [1–3]. The oxygen reduction reaction (ORR) occurring at cathode side dictates the performance of fuel cells. As is well known, metal platinum (Pt) is the best in catalyzing the ORR compared with other materials [4], however, with its scarcity, expensiveness and easily being poisoned by CO hampering its broad applications. To resolve this problem, much efforts have been devoted to develop inexpensive and renewable metal-free catalysts as substitutions [5].

As one kind of metal-free catalysts, carbon-based materials, such as graphene, carbon nanotube, and fullerene, have been broadly studied due to their unique structures and properties. Numerous studies have shown that these materials, especially the chemically doped structures with heteroatoms, present excellent ORR performance [6–9], which is attributed to their modulated

electronic characteristics, such as the atomic spin, charge densities, band structure, and electronic states of the studied complexes [10–12]. Furthermore, their surface and local chemical properties can also be improved by doping [13–15].

This paper focuses on the ORR catalyzed by fullerene due to its curvature and pentagon defect compared with graphene and carbon nanotube, which might make fullerene a better choice for ORR [16–18]. Wang et al. theoretically predicted that N-doped C₆₀ fullerene (C₅₉N) shows better catalytic activity compared with other heteroatom-doped fullerenes (C₅₉B, C₅₉P, C₅₉Si, and C₅₉S) [19], which was further experimentally validated by others [20]. Therefore, in this work, we selected element N as the dopant, and further investigated the size effect of pure and doped fullerenes on the ORR activity, since the catalytic activity can be largely controlled by the catalyst size [21]. Four different sized fullerenes, namely, C₂₀, C₄₀, C₆₀, C₁₈₀, with respectively the diameter of approximately 0.4, 0.6, 0.7, 1.2 nm, were utilized to investigate the size effect.

2. Computational details

All spin-polarized DFT calculations were performed by using DMol³ code [22,23]. The exchange-correlation functional was

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described by the generalized gradient approximation (GGA) of the BLYP functional [24]. The double numeric quality basis set (DNP) and effective core potentials (ECPs) were utilized throughout all calculations. A Fermi smearing of 0.005 Ha to the orbital occupation was applied to improve computational performance. The convergence tolerance for energy change, max force, and max displacement were 2×10^{-5} Ha, 0.004 Ha \AA^{-1} , and 0.005 \AA , respectively.

For reaction energy calculation in the whole ORR process, we used the method proposed by Nørskov et al. [4]. In their model the chemical potential for the reaction ($\text{H}^+ + \text{e}^-$) can be related to that of $1/2\text{H}_2$ in the gas phase by use of the standard hydrogen electrode.

3. Results and discussion

3.1. Stability of N-doped fullerenes

The primary prerequisite for a material utilized as an ORR catalyst is its stability. The doped fullerene structures are prepared by substituting one C atom in fullerene with N atom. We evaluated the stability of doped fullerenes by formation energy (E_f), which is defined as $E_f = E_{\text{N-surface}} + E_{\text{C}} - E_{\text{surface}} - E_{\text{N}}$, where $E_{\text{N-surface}}$, E_{surface} , E_{C} , and E_{N} are the total energy of the N-doped fullerene, fullerene, the energy of atomic C in fullerene, and the energy of atomic N, respectively. A negative E_f suggests doped fullerene can stably exist. As clearly shown in Fig. 1, all doped fullerenes possess much larger negative E_f values, indicating they are stable based on reaction thermodynamics. Furthermore, the E_f value does not change monotonically with the size of N-doped fullerenes increase. In other words, the structure of C_{39}N has an abnormal larger E_f value of -4.64 eV, which may be originated from the distinctive symmetry of C_{40} (D_2) compared with the other three others (I_h).

3.2. Charge distributions on pure and doped fullerenes

As is well known, for carbon-based materials, the positively charged site is more favorable in adsorbing O_2 . In order to determine the active centers for ORR, the charge distributions were calculated for all pure and doped fullerenes (C_{20} , C_{19}N , C_{40} , C_{39}N , C_{60} , C_{59}N , C_{180} , and C_{179}N), with only the charge on C_{20} and C_{19}N shown in Fig. 2 for the sake of clarity. For C_{19}N , due to the high electronegativity of doped N atom, more positive charge is induced onto its three neighboring carbon atoms when compared with pure C_{20} . The most positively charged carbon atom carries the charge of $+0.164$, and this carbon is selected as the reaction site for ORR.

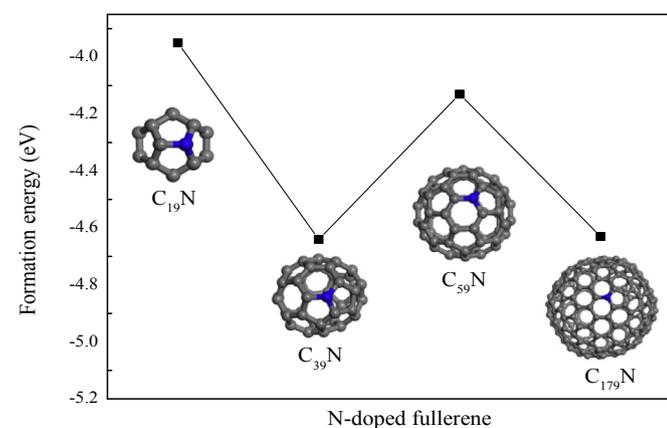


Fig. 1. Calculated formation energies of N-doped fullerenes. (A colour version of this figure can be viewed online.)

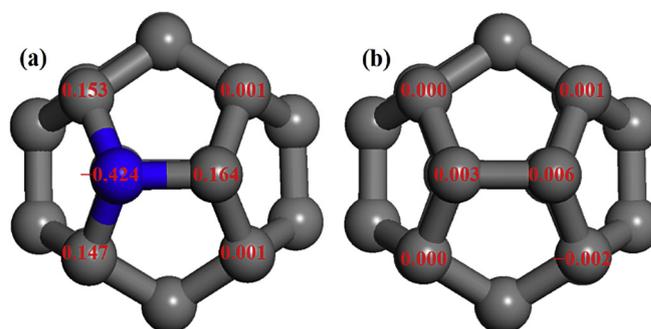


Fig. 2. Charge distributions on (a) C_{19}N and (b) C_{20} . (A colour version of this figure can be viewed online.)

The ORR sites on other studied structures are also determined by this method.

3.3. Adsorption properties of ORR species

Adsorption of ORR species plays a key role for the investigation of ORR mechanism and catalytic activity. The adsorption stability of the ORR species (O_2 , OOH , O , OH , and H_2O) on fullerenes and doped ones was estimated by the adsorption energy (E_{ads}), which is defined as $E_{\text{ads}} = E_{\text{total}} - E_{\text{surface}} - E_{\text{X}}$, where E_{total} , E_{surface} and E_{X} are the total energy of the fullerene (or N-doped fullerene) with an adsorbed X species, fullerene (or N-doped fullerene), and isolated adsorbed species, respectively. The calculated E_{ads} of the most stable adsorption configurations are listed in Table 1. The E_{ads} values on Pt(111), which were calculated at the same computational level with the current paper, are cited from our recent work [25].

As is clearly shown in Table 1, the pristine C_{20} fullerene has mighty larger E_{ads} of ORR species compared with Pt(111). Such strong adsorption suggests that the desorption of ORR species is very difficult and the catalytic reactions are hard to proceed. Unfortunately, the doping of nitrogen even makes the E_{ads} stronger, especially for the atomic O intermediate (-6.15 eV). As shown in Fig. 3, where gives the most stable adsorption configurations of all ORR species on C_{19}N fullerene (the adsorption structures on C_{20} are not given because they are similar to those on C_{19}N), the C–N bond is largely elongated after O adsorption, indicating the structure of C_{19}N fullerene might not be stable. The above analysis reveals that the ORR activity of C_{20} fullerene becomes lower after nitrogen doping, which is different from the cases of most of the carbon-based materials, for which the doping of nitrogen can largely enhance the catalytic activity. This is mainly attributed to the too small size of C_{19}N fullerene that the resulted hoop strain will significantly bend the C–C and C–N bonds, in which case the strong adsorption of ORR species is unavoidable [26].

For C_{40} fullerene, although the adsorption configurations of the ORR species (Fig. 4) are similar with those on C_{20} , the E_{ads} are quite

Table 1
Adsorption energies (E_{ads} , eV) of ORR intermediates.

Species	O_2	OOH	O	OH	H_2O
C_{20}	-1.85	-2.34	-4.56	-3.63	-0.10
C_{19}N	-1.75	-2.68	-6.15	-3.98	-0.19
C_{40}	-0.63	-1.04	-3.06	-2.34	-0.06
C_{39}N	-0.60	-1.22	-3.88	-2.56	-0.06
C_{60}	0.25	-0.38	-3.38	-1.66	-0.05
C_{59}N	-0.12	-1.51	-3.61	-2.79	-0.08
C_{180}	0.62	0.15	-2.66	-0.89	-0.06
C_{179}N	0.43	-0.67	-2.68	-1.93	-0.09
Pt(111)	-0.45	-1.10	-3.66	-2.04	-0.27

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