Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Self-assembled nitrogen doped fullerenes and their catalysis for fuel cell and rechargeable metal-air battery applications

Seung Hyo Noh,[a] Choah Kwon,[a] Jeemin Hwang,[a] Takeo Ohsaka,[b] Beom-Jun Kim,[c]
Tae-Young Kim,[c] Young-Gi Yoon,[c] Zhongwei Chen,[d] Min Ho Seo,[c*] and Byungchan Han,[a**]

[a] *Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul, 03722, Republic of Korea*
[b] *Research Institute for Engineering, Kanagawa University. 3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama, Kanagawa, 221-8686, Japan*
[c] *Hydrogen & Fuel Cell Center, New & Renewable Energy Research Division, Korea Institute of Energy Research (KIER), 20-41, Sinjaesaengeneogi-ro, Haseo-myeon, Buan-gun, Jellabuk-do, Korea*
[d] *Department of Chemical Engineering, Waterloo Institute for Nanotechnology, Waterloo Institute of Sustainable Energy, University of Waterloo, 200 University Ave. W, Waterloo, ON, N2L 3G1, Canada*

* Corresponding author
Tel: +82-063-581-1681
Fax: +82- 063-581-1630
E-mail address: foifrit@kier.re.kr

** Corresponding author
Tel: +82-2-2123-5759
Fax: :+82-2-321-6401
E-mail address: bchan@yonsei.ac.kr

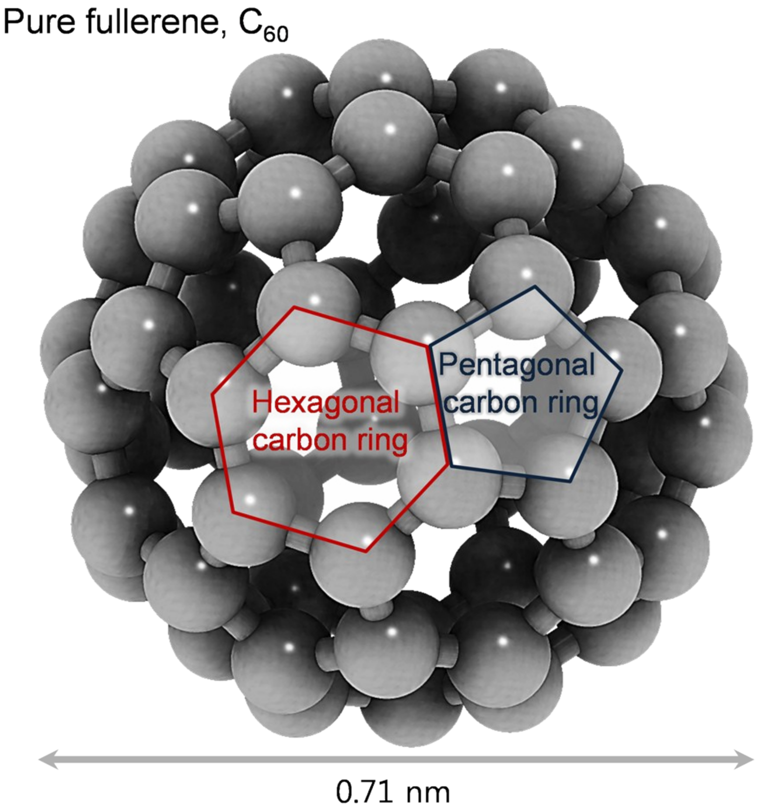

Fig. S1 Model system of a pure fullerene (C_{60}) consisting of hexagonal and pentagonal carbon rings alternatively.

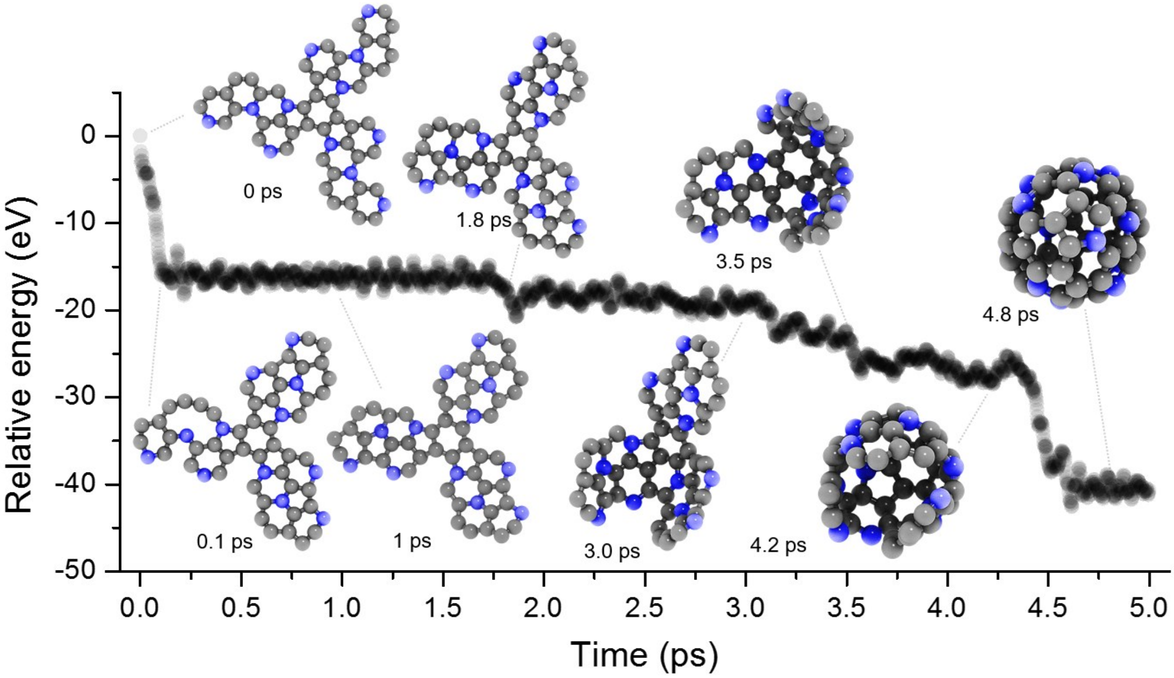

Fig. S2 Ab-initio molecular dynamics simulations describing self-assembling of a N-fullerene with 20 at.%. N from molecular N-doped carbon fragments at 750 K over 5 ps.

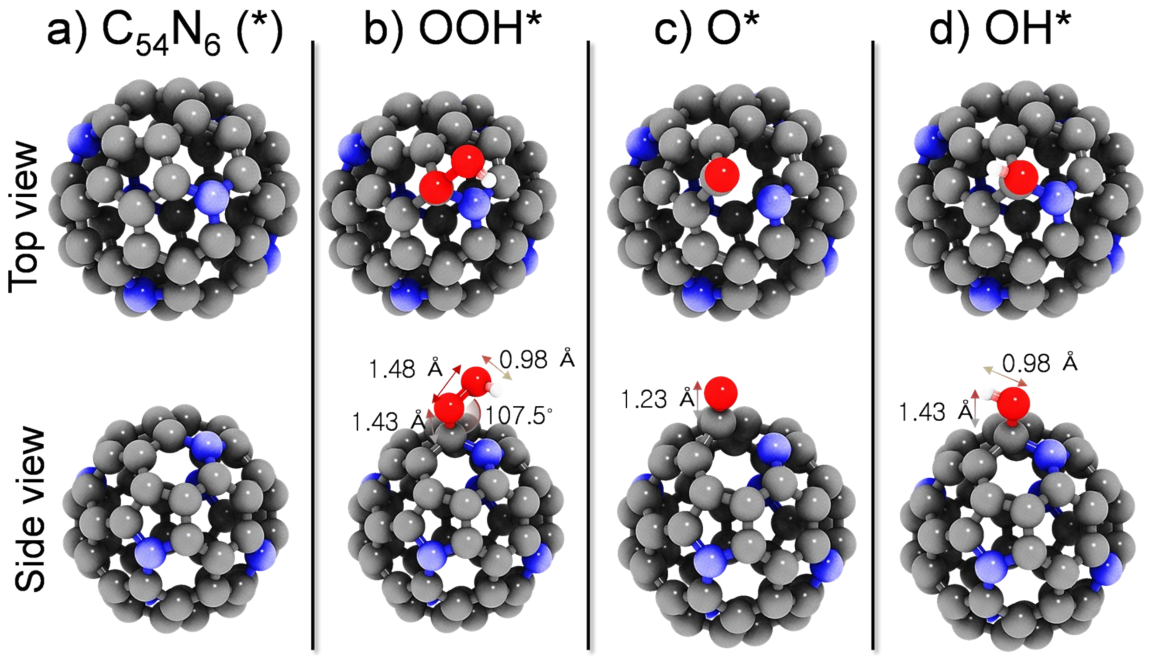

Fig. S3 N-fullerenes with 10 at.% N adsorbed by oxygen-contained intermediates in ORR and OER.

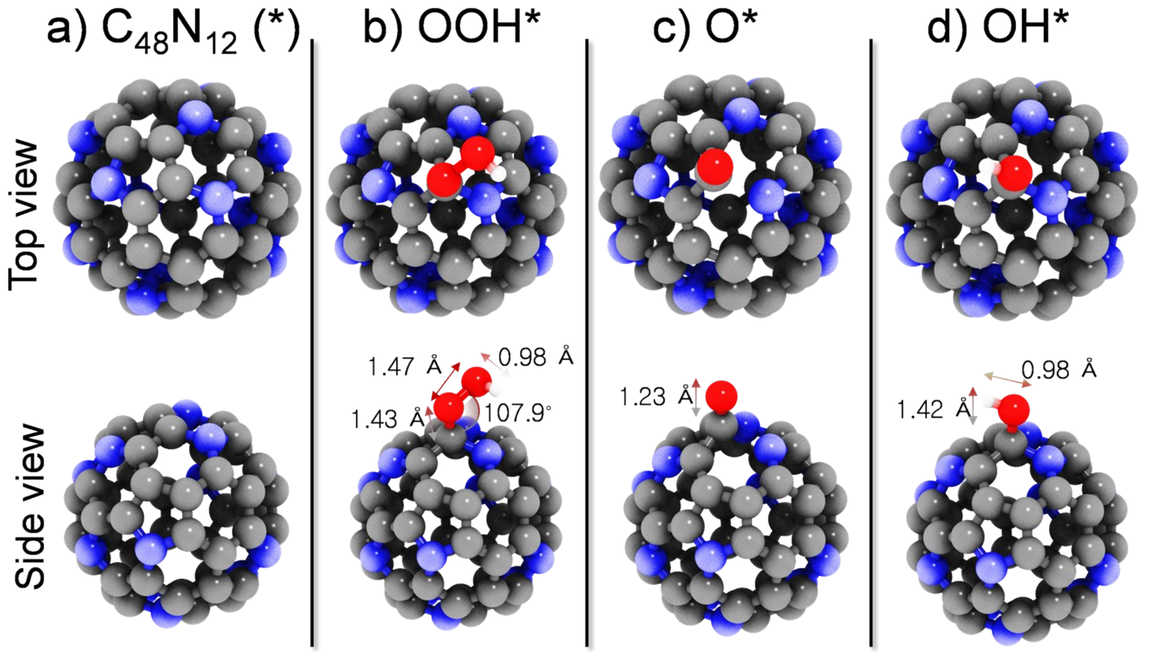

Fig. S4 N-fullerene with 20 at.% N adsorbed by oxygen-contained intermediates in ORR and OER

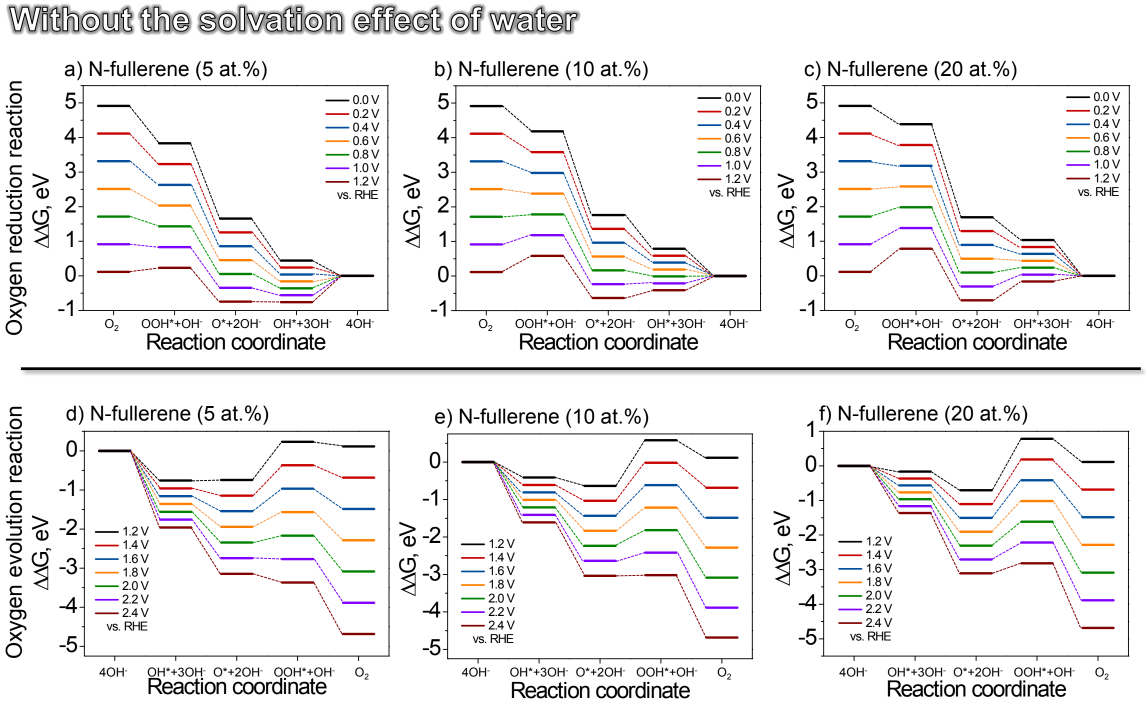

Fig. S5 Free energy diagrams for N-fullerene toward a-c) ORR and d-f) OER as a function of N-doping level (5, 10 and 20 at.% N) and with thermodynamic potential step of 0.2 V. Effect of solvation by water on the mechanisms was not considered.

The exothermic ORR potentials (E_{ORR}) of a bulk Pt(111) surface, which was known to be the best catalyst for a pure metal, were already reported by other groups as 0.75 V and 0.78 V vs. SHE with and without correction of an electric field effect, respectively.[1, 2] In our work, the E_{ORR} of the azafullerene (0.73 V vs. SHE for 10 wt.% of N) catalyst is quite comparable with that of the bulk Pt (111) surface, evaluating the. Hence, we proposed that it is a promising catalyst on the aspects of the lower material cost as well as the ORR catalytic performance.

Table S1 Solvation energy of ORR/OER intermediates (E_{solv}, eV).

	OOH*	O*	OH*
N-fullerene (5 at.%)	-0.16	-0.27	-0.12
N-fullerene (10 at.%)	-0.18	-0.30	-0.13
N-fullerene (20 at.%)	-0.20	-0.47	-0.16

Solvation effect by water on ORR/OER activity was calculated using DFT calculations as implemented implicit method in VASPsol[3]. The solvation energy was calculated by equation S1.

$$E_{solv} = E_{solvent} - E_{vac} \qquad \text{(S1)}$$

where E_{sol} is the solvation energy, $E_{solvent}$ is the total energy of adsorbate on catalyst by an implicit solvent model, and E_{vac} is the total energy of adsorbate on catalyst under vacuum environment. Accordingly, a negative E_{solv} implies the given structure is more stabilized in the water against the vacuum.

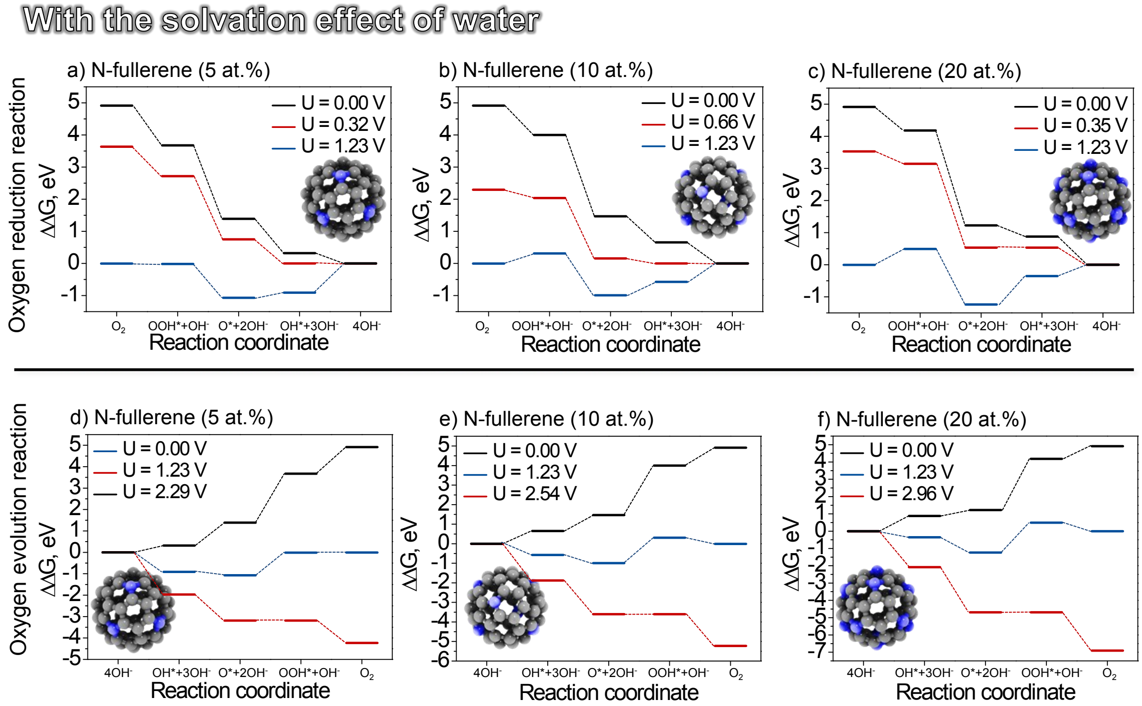

Fig. S6 Free energy diagrams for N-fullerene toward a-c) ORR and d-f) OER as a function of N-doping level (5, 10 and 20 at.% N). Solvation effect on the mechanisms was considered using calculated data provided in table S1.

Our results indicate that all reaction intermediates are stabilized by the solvation in water but with differently depending on the N-doping level as agreeing with previous results.[4] In particular, O* species are strongly adsorbed in the N-fullerenes. Hence, the rate-determining step of N-fullerene (20 at.%) in Fig. S6c is shifted to O* → OH* unlike at the non-solvent model system shown in Fig. 4c.

With the solvation effect of water

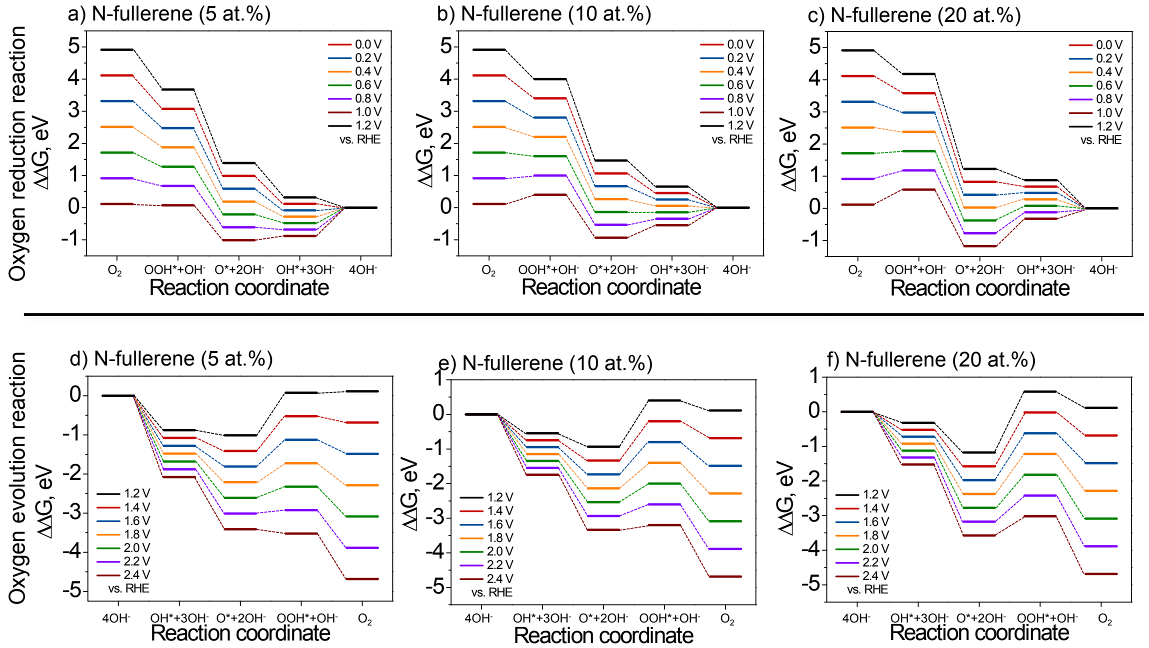

Fig. S7 Free energy diagrams for ORR and OER[5] in alkaline medium as a function of N-doping level with thermodynamic potential step 0.2 V. Effect of solvation in water was considered using calculated data provided in table S1.

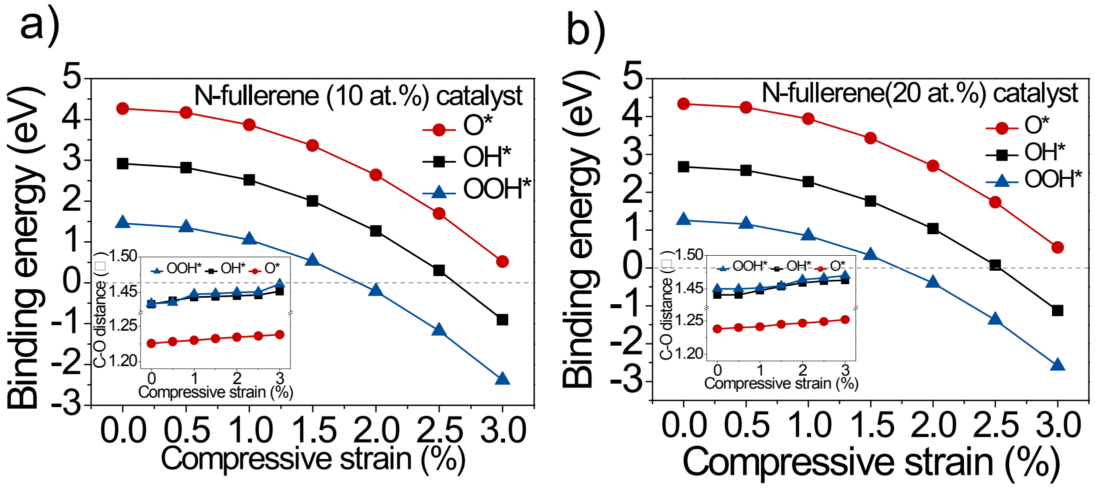

Fig. S8 Binding energies of intermediates, O, OH and OOH in a) N-fullerene (10 at.% N) and b) N-fullerene (20 at.% N) with varying extent of the compressive strain. Insets shows bond distances of C-O in the fullerene and intermediates.

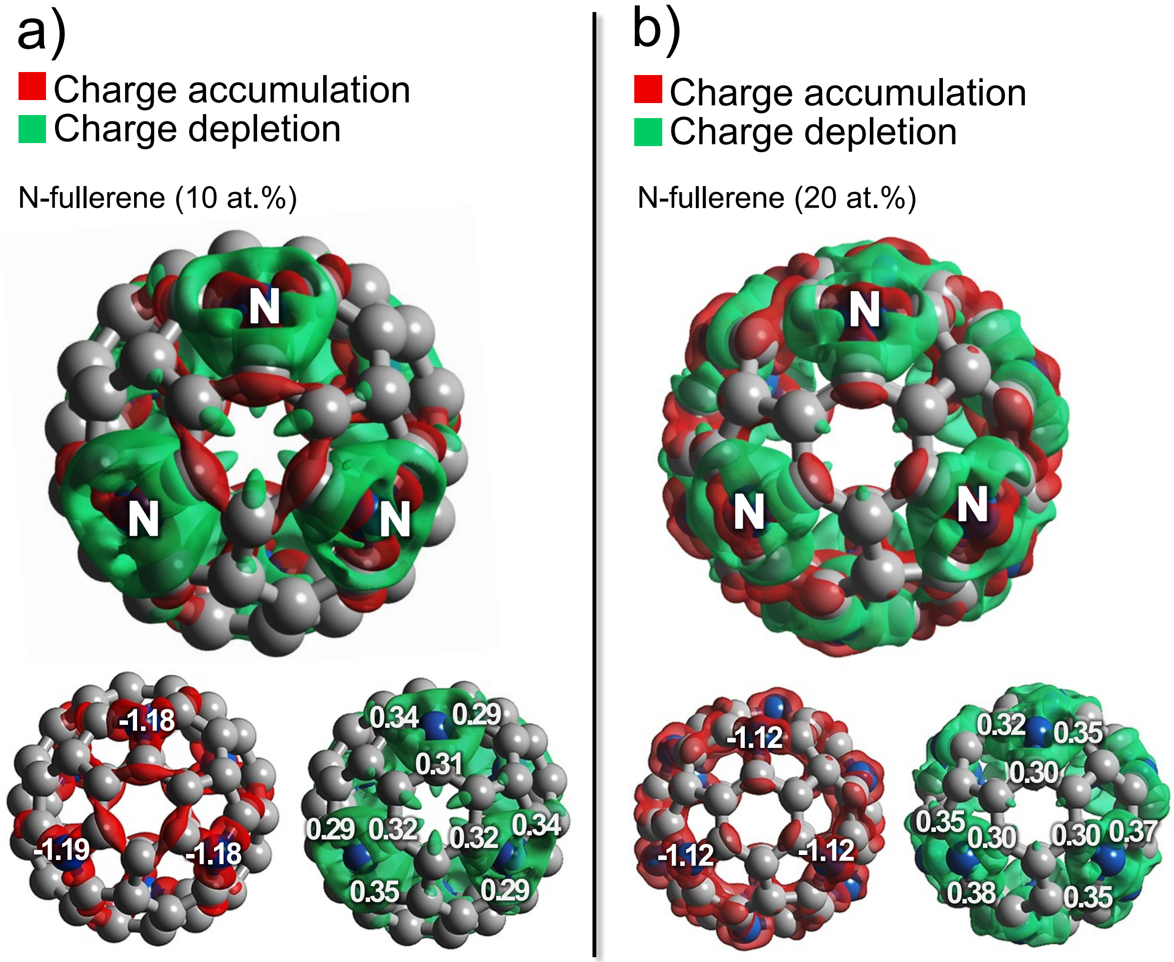

Fig. S9 Charge distribution of a) N-fullerene (10 at.% N) and b) N-fullerene (20 at.% N) in ORR/OER catalysis. Red (green) colors indicate the charge accumulated (depleted) regions.

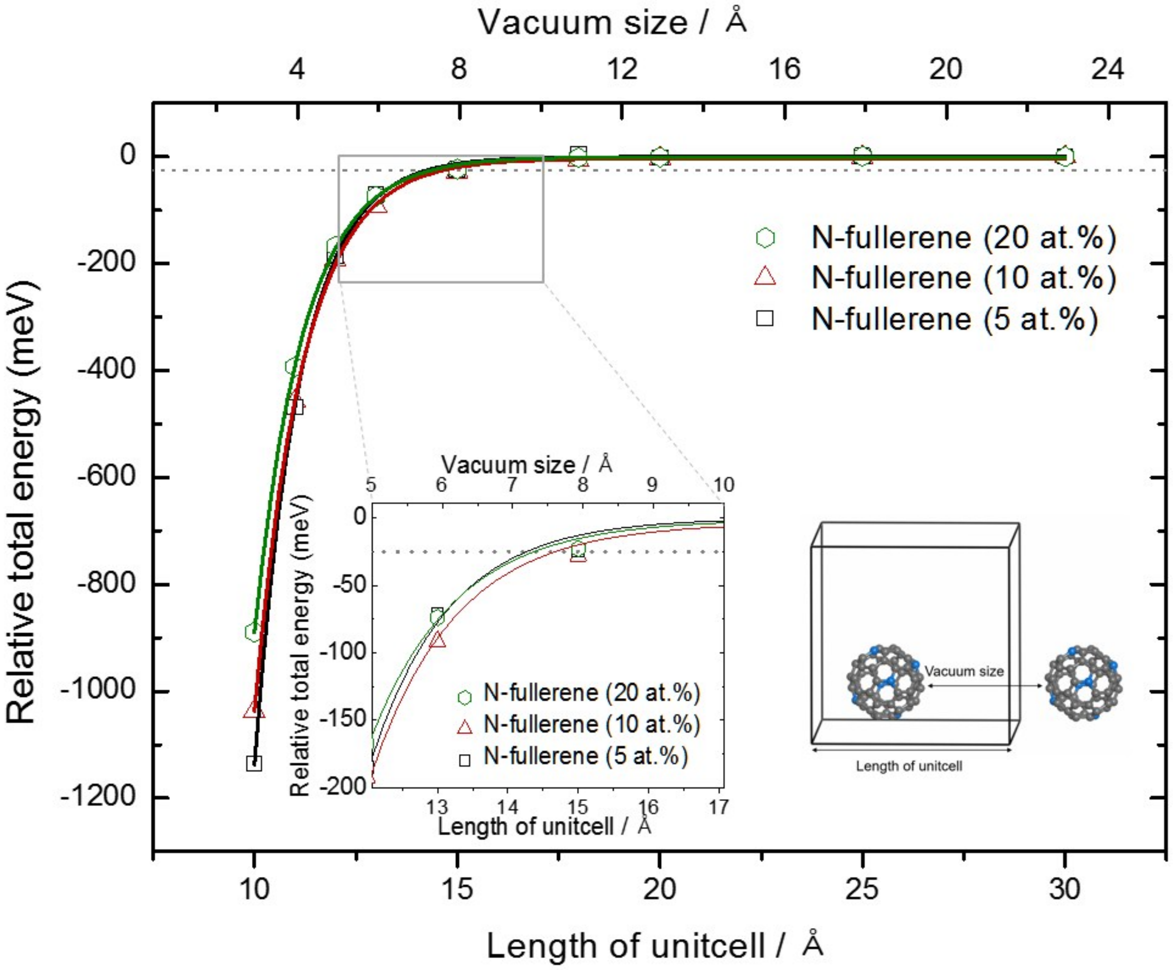

Fig. S10 Vacuum size test. The relative total ground state energy of N-fullerene (5, 10 and 20%) nanoparticles with varying vacuum sizes. (Inset) the definition of vacuum size and length of unitcell.

We identified optimum vacuum size (the larger vacuum size the higher computational cost) for less computational cost but without losing the accuracy at the same time. Our results indicate that total energies calculated at 8 Å and 23 Å are essentially the same (difference less than 25 meV) for the models of fullerenes with 5, 10 and 20% of N-doping levels.

Carbon corrosion from thermodynamic calculations

For the calculation of graphite and pure fullerene

$$C_s(s) + 2H_2O(l) \leftrightarrow CO_2(g) + 4H^+ + 4e^- \tag{S2}$$

$$U = \frac{1}{4} \times [(\Delta G^o_{CO_2(g)} + 2\Delta G^o_{H_2,(g)}) - (\Delta G^o_{C(s)} + 2\Delta G^o_{H_2O(l)}) - 0.059pH] \tag{S3}$$

For the calculation of N-doped fullerenes (e.g., N-fullerene (5 at.%)

$$C_{57}N_3 + 57(2H_2O(l)) \leftrightarrow 57CO_2(g) + 227(H^+ + e^-) + HN_3(g) \tag{S4}$$

$$\Delta G_f = 57 \times \Delta G^o_{CO_2(g)} + 227(\Delta G^o_{H^+} + \mu^o_e) - 227eU + \Delta G^o_{HN_3(g)} - \Delta G^o_{C_{57}N_3(g)} - 114 \times \Delta G^o_{H_2O(l)} + 227 \times 0.059pH \tag{S5}$$

$$U = \frac{1}{227e}[57 \times \Delta G^o_{CO_2(g)} + 227\frac{\Delta G^o_{H_2(g)}}{2} + \Delta G^o_{HN_3(g)} - \Delta G^o_{C_{57}N_3(g)} - 114 \times \Delta G^o_{H_2O(l)}] - 0.059pH \tag{S6}$$

Table S2. Corrosion potential of a variety of carbon materials at pH = 0 and 25 ℃.

Materials	U (V vs. RHE), corrosion potential
Graphite	0.207
C_{60} (Fullerene)	0.086
$C_{57}N_3$ (N-fullerene (5 at.%))	0.161

References

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