Electronic Supplementary Information

Enhanced electrocatalytic activity of nitrogen-doped olympicene/graphene hybrids for oxygen reduction reaction

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Computational methods

Spin-polarized DFT calculations were performed using the DMol^{3}code.[1,2] The well-known Perdew-Burke-Ernzerhof (PBE) functional with generalized gradient approximation (GGA) is used as the exchange-correlation functional.[3] The core electrons are described by the all electron relativistic (AER) core treat method.[4] The double numerical plus polarization (DNP) is chosen as the atomic orbital basis set.[1] A smearing of 0.005 Ha is applied to the orbital occupation. The real-space global orbital cutoff radius is set to 3.7 Å in our calculations. The convergence tolerances of energy, maximum force and displacement are 1.0×10^{-5} Ha, 0.002 Ha/Å, and 0.005 Å, respectively. The DFT-D2 method of Grimme is employed to includethe van der Waals (vdW) interaction in our computationss.[5] A conductor-like screening model (COSMO) is used here to describe the water solvent environment, and the dielectric constant is set as 78.54.[6] To quantify the robustness of our computational settings, we carried out sysmematically tests for basis set and functionals. We also calculated the ORR process on N_A-olympicene based on triple numerical plus polarization (TNP), double numerical plus *d*-functions (DND), and hybrid functional B3LYP. As shown in Figure S7, the overpotential of ORR on N_A-olympicene are determined to be 0.79, 0.84, and 0.75 V from GGA/PBE/TNP, GGA/PBE/DND, and B3LYP/DNP, which are close to that obtained from GGA/PBE/DNP (0.70 V).

The E_{ad} of ORR intermediates on N-olympicenes was determined as $E_{ad} = E_{mol} + E_{N\text{-}Oly} - E_{mol\text{-}N\text{-}Oly}$, where E_{mol}, $E_{N\text{-}Oly}$ and $E_{mol\text{-}N\text{-}Oly}$ are the electronic energies of an isolated adsorbed molecule, N-olympicenes, and the adsorption systems, respectively.[7,8] By this definition, the positive E_{ad} values correspond to the exothermic stably adsorption processes.

The free energy diagram was calculated based on the computational hydrogen electrode (CHE) model developed by Nørskov *et al.*[9,10] The reaction free energies (ΔG) of every elemental step are calculated at standard conditions and defined as: $\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_{pH} + \Delta G_U$, where ΔE is the DFT reaction energy, ΔZPE is the difference in zero-point energy, T is the temperature (298.15K), ΔS is the change in the entropy, ΔG_{pH} and ΔG_U are the free energy contributions related to the pH value and electrode potential U. The important effect of the electrode potential on ΔG is quantified by $\Delta G_U = neU$, where U is the electrodepotential, and n is the number of electrons transferred in each elementary step. Note that n equals to 1 for single coupled proton and electron transfer step.[9,11] $\Delta G_{pH} = k_B T \ln 10 \times \text{pH}$, where k_B is Boltzmann's constant. pH is set as 0 in this work. The free energy of $O_2(g)$ is derived as $G_{O2(g)} = 2G_{H2O(l)} - 2G_{H2} - 4.92$ eV, because the high-spin ground state of O_2 molecule cannot be well described in the framework of DFT calculations. The free energy of $H_2O(l)$ is calculated as $G_{H2O(l)} = G_{H2O(g)} + RT \times \ln(p/p_0)$, where R is the ideal gas constant, $T = 298.15$ K, $p = 0.035$ bar, and $p_0 = 1$ bar.[12] $G_{H2O(g)}$ can be directly obtained by DFT calculations.

Table S1. Formation energies (E_f) of substitutional N atom in olympicene.[a] The corresponding substitutional sites are shown in Fig.S1. All results are in the unit of eV.

graphitic-type	Site	A	B	C	D	E	
	E_f	1.06	1.45	1.46	1.06	1.27	
pyridine-type	Site	F	G	H	I	J	K
	E_f	1.09	0.42	0.51	0.44	0.46	0.47

[a] The nitrogen substitution formation energy (E_f) can be determined by $E_f = E_{N\text{-}Oly} + E_C + mE_H - E_{Oly} - E_N$, where $E_{N\text{-}Oly}$ and E_{Oly} are the total energies of N-doped olympicene and pristine olympicene, respectively. E_C, E_H, and E_N are the total energies of single atom in graphene, hydrogen molecule, and nitrogen molecule, respectively. m equals 0 or 1 for graphitic-type or pyridine-type N-doped olympicenes. Based on these definitions, the smaller the E_f, the more energy favorable for nitrogen atom substituted.

Table S2. Adsorption energies(E_{ad}) of OOH, O, OH, and CO on N-olympicenes and N-olympicene/graphene hybrids and *p*-band center (ε_p) of N-olympicene and N-olympicene/graphene hybrids. All results are in unit of eV.

	OOH	O	OH	CO	ε_p
N_A-olympicene	1.24	3.32	2.54	0.14	–8.315
N_A-olympicene/Graphene	0.77	2.92	2.05	0.11	–8.487
N_D-olympicene	1.71	3.78	3.01	0.15	–7.946
N_D-olympicene/Graphene	1.27	3.51	2.58	0.08	–8.168
N_G-olympicene	0.04	2.88	1.36	0.07	–6.384
N_G-olympicene/Graphene	–0.03	2.79	1.28	0.07	–6.441

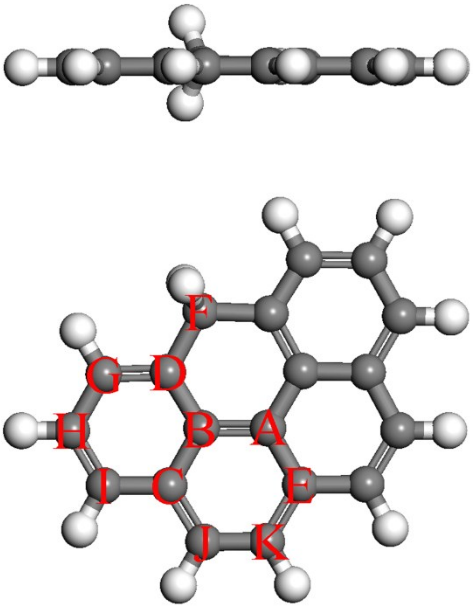


Fig.S1. Atomic structures of pristine olympicene.

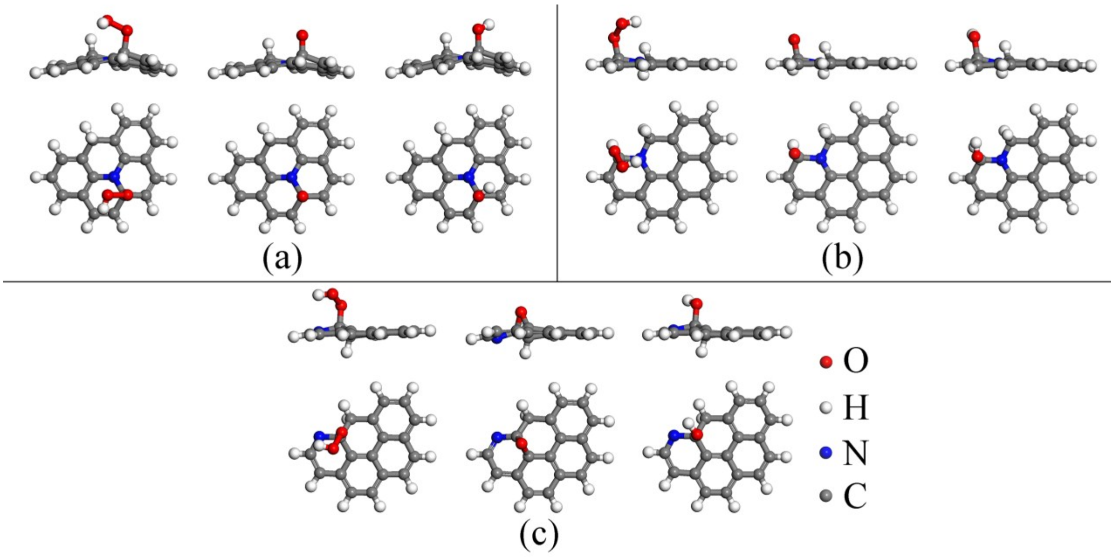


Fig. S2. Preferred adsorption structures of ORR intermediates on N_A-olympicene (a), N_D-olympicene (b), and N_G-olympicene (c).

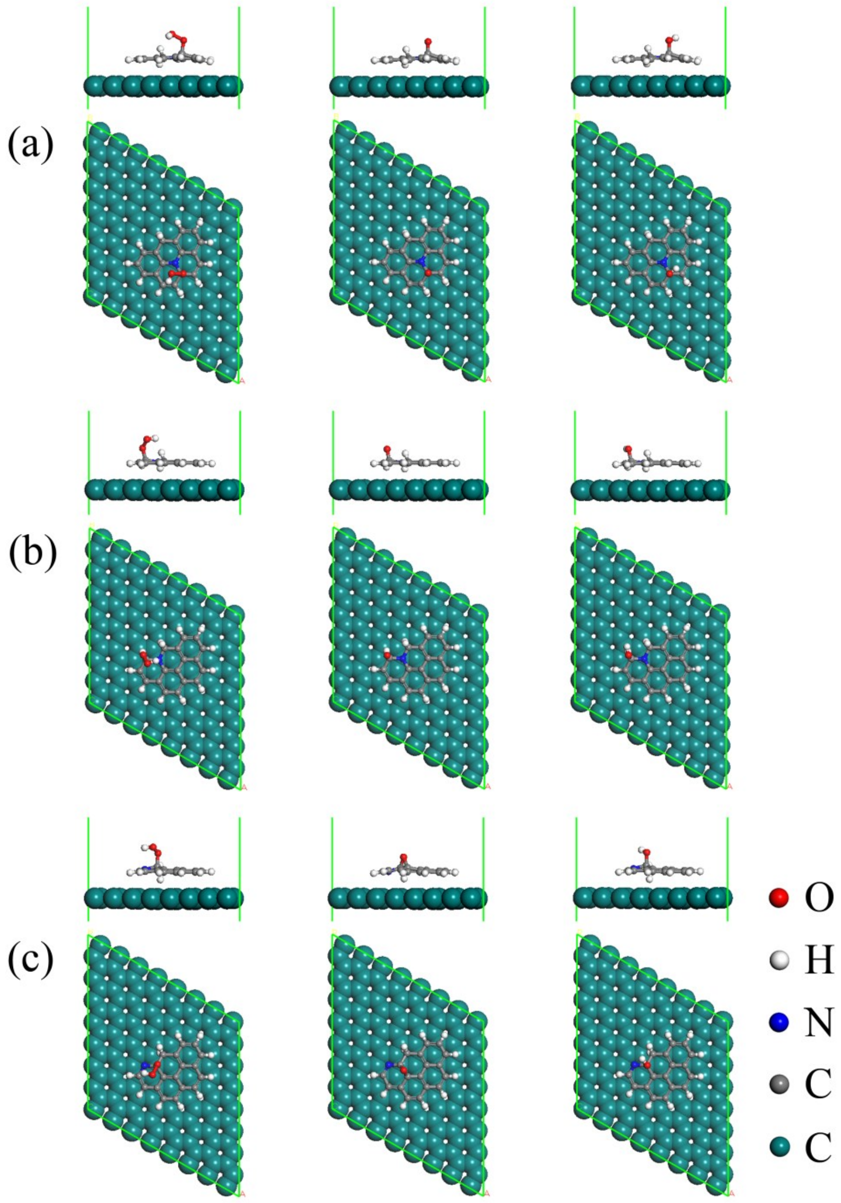


Fig. S3. Preferred adsorption structures of ORR intermediates on N_A-olympicene/graphene (a), N_D-olympicene/graphene (b), and N_G-olympicene/graphene (c).

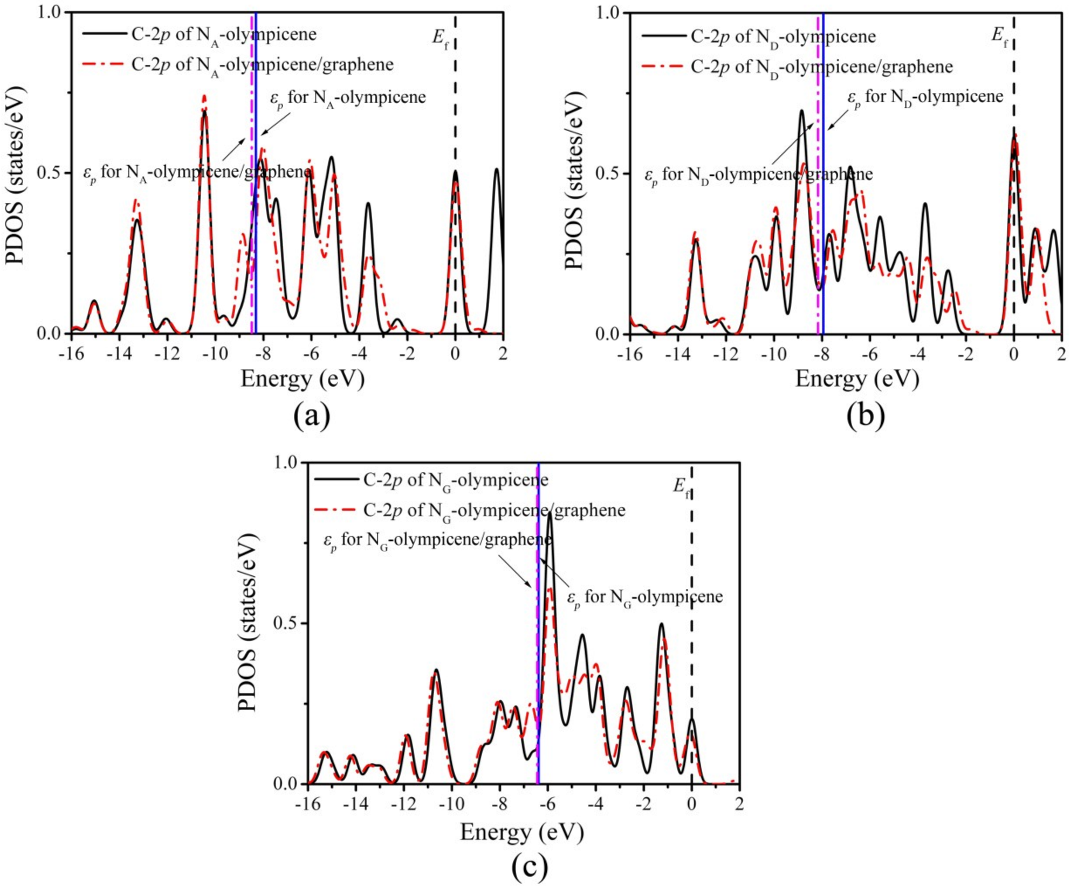
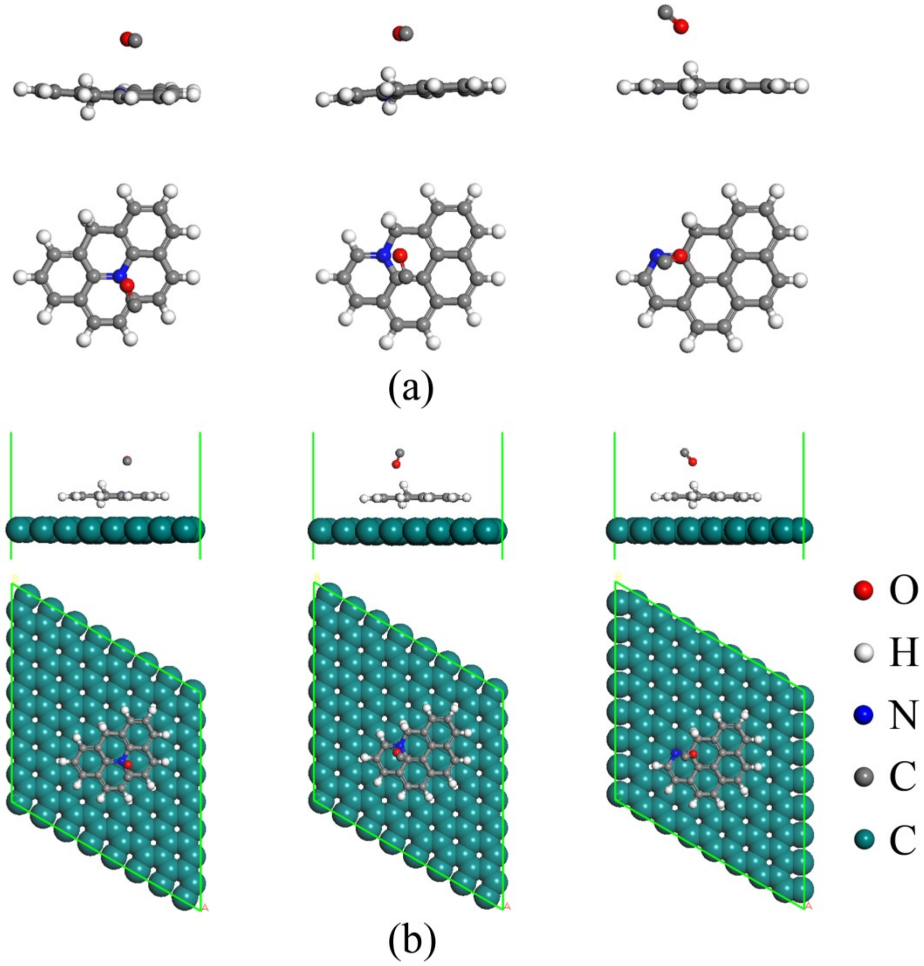


Fig. S4. Partial density of states (PDOS) for C atom near doped N atom in N-olympicenes and N-olympicene/graphene hybrids. E_f and ε_p are Fermi energy level and *p*-band center.



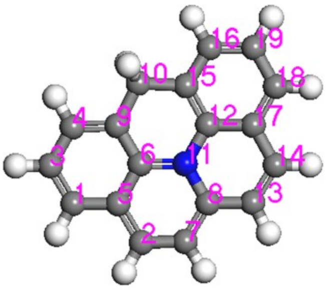
(a)

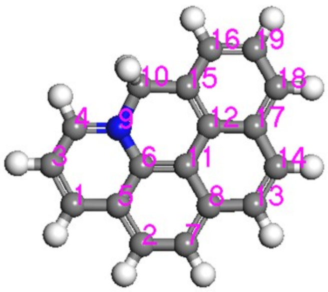
(b)

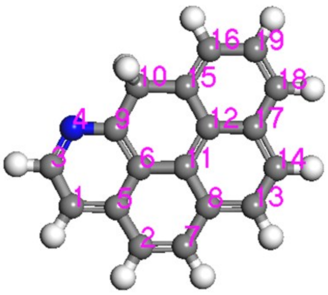
Fig. S5. Adsorption structures for CO on N-olympicenes (a), and N-olympicene/graphene hybrids (b).

Table S3. The number of occupied p-electrons for C atom in N-olympicenes. All results are based on integrated partial density of states. The atomic indexes are shown below. N_A-oly, N_A-oly/Gra, N_D-oly, N_D-oly/Gra, N_G-oly and N_G-oly/Gra stand for N_A-olympicene, N_A-olympicene/Graphene, N_D-olympicene, N_D-olympicene/Graphene, N_G-olympicene, and N_G-olympicene/Graphene.

Atom index	N_A-oly	N_A-oly/Gra	N_D-oly	N_D-oly/Gra	N_G-oly	N_G-oly/Gra
1	2.919	2.898	2.936	2.951	2.866	2.855
2	2.917	2.927	2.921	2.901	2.864	2.848
3	2.898	2.877	2.908	2.885	2.756	2.751
4	2.901	2.888	***2.785***	***2.806***	3.839	3.803
5	2.807	2.799	2.801	2.793	2.801	2.784
6	2.657	2.659	2.641	2.645	2.830	2.810
7	2.899	2.876	2.894	2.866	2.905	2.882
8	***2.686***	***2.720***	2.822	2.816	2.775	2.757
9	2.840	2.824	3.891	3.892	***2.660***	***2.660***
10	2.999	3.003	2.861	2.862	3.025	3.019
11	3.924	3.927	2.852	2.819	2.721	2.727
12	2.657	2.659	2.788	2.779	2.824	2.801
13	2.899	2.876	2.895	2.873	2.886	2.868
14	2.917	2.927	2.917	2.891	2.808	2.803
15	2.840	2.824	2.829	2.814	2.730	2.740
16	2.901	2.888	2.909	2.885	2.854	2.847
17	2.807	2.799	2.806	2.789	2.839	2.811
18	2.919	2.898	2.908	2.880	2.804	2.802
19	2.898	2.877	2.902	2.878	2.891	2.877







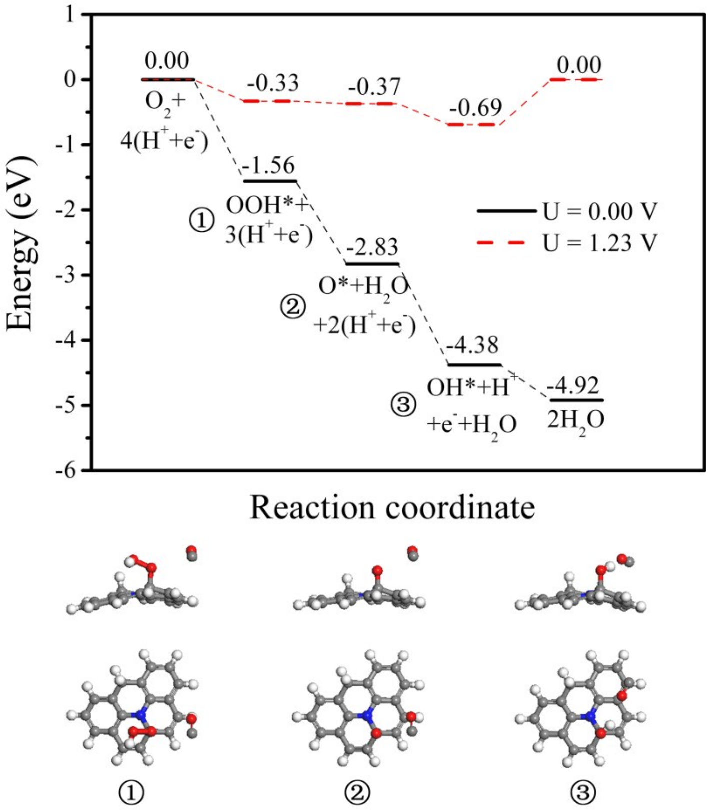


Fig. S6. Schematic free energy diagrams of ORR on N_A-olympicene with the existing of one CO molecule. Selected intermediate structures are also shown.

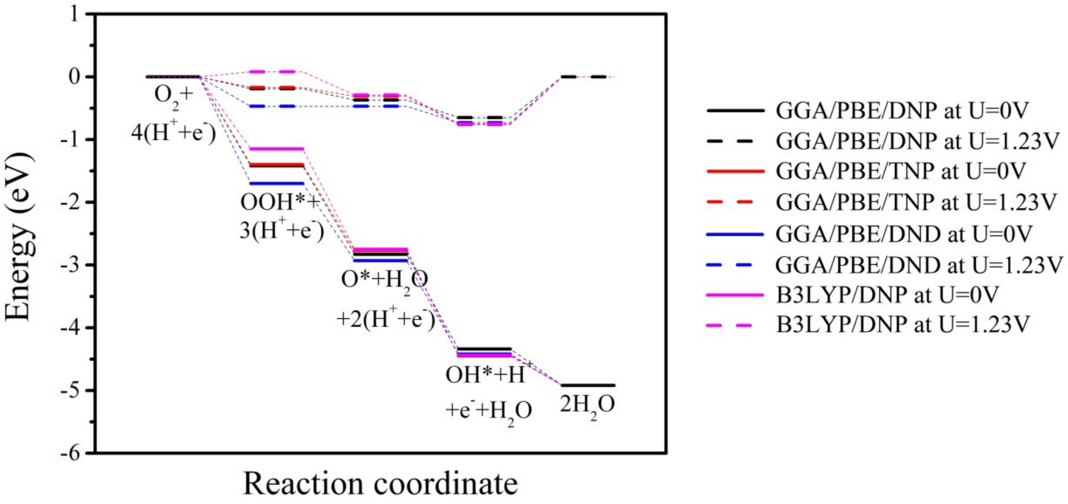


Fig. S7. Schematic free energy diagrams of ORR on N_A-olympicene with different basis sets and functionals.

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