Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Nitrogen-doped carbon nanotube as a potential metal-free catalyst for CO oxidation

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Table S1. Calculated adsorption energies (eV) and Bader charges (*e*; in parentheses) of O_2 species adsorbed on various sites of N-doped graphene.

Materials\site	C–N	C–C-1	C–C-2
N-graphene	–0.38 (–0.28)	0.50 (–1.10)	0.91

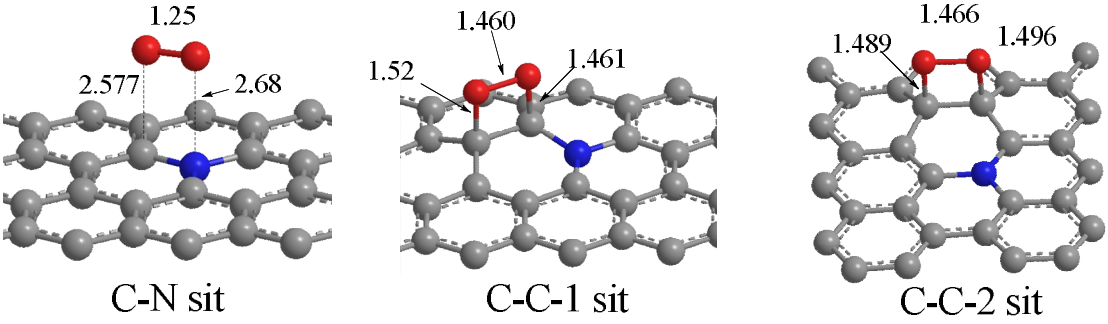

Figure S1. Optimized structures of O_2 adsorption on N-doped graphene. Gray, blue, and red spheres represent C, N, and O, atoms, respectively.

Oxygen reduction reaction (ORR) processes on C–C-1 site of N-doped carbon materials and O_2 diffusion from C–N site to C–C-1 site on the N-doped carbon materials

We also studied the oxygen reduction reaction (ORR) process on the C–C-1 site of (3, 3)-NCNT, (4, 4)-NCNT, and (5, 5)-NCNT. As shown in Figure S2, gas-phase O_2 molecule is placed at the C–C-1 site with the distance of ~4.0 Å as the reactant. The NEB calculation reveals that this process needs to overcome a significant activation energy barrier of 0.42, 0.13, and 0.52 eV to be adsorbed and reduced on the C-C-1 site for (3, 3)-, (4, 4)-, and (5, 5)-NCNTs.

We also investigated the O_2 diffusion from C–N site to C–C-1 site on the N-doped carbon nanotubes and the minimum energy path of this process has been depicted in Figure S3. The diffusion barriers of this process are predicted to be 0.04, 0.25, and 0.49 eV for (3, 3)-, (4, 4)-, and (5, 5)-NCNTs, respectively.

As a comparison, there is no energy barrier in the minimum energy paths for ORR on the C–N sites and the O_2 diffusion from C–N site to C–C-1 site needs to overcome energy barriers. Therefore, we rule out the possibility of CO oxidation process on the C–C-1 site. However, the calculation results for CO oxidation on the C–C-1 site are still discussed and presented in Supporting Information (Figures S7~S9).

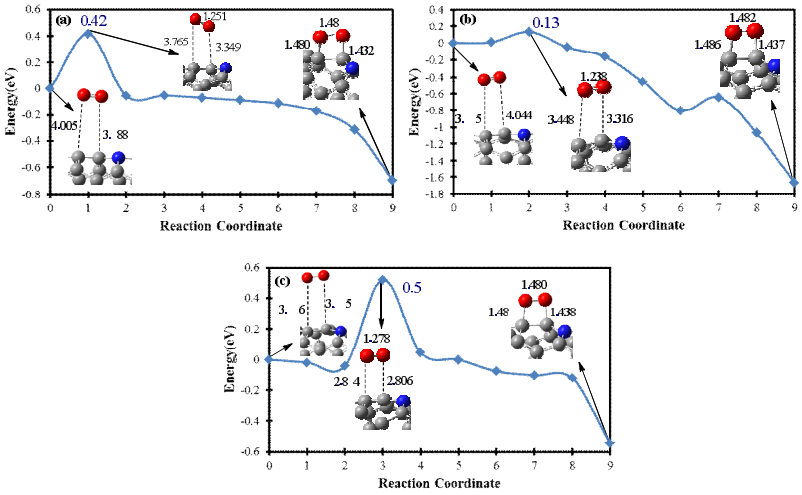

Figure S2. Calculated minimum energy paths of O_2 adsorption and reduction on the C–C-1 sites of (a) (3, 3)-NCNT, (b) (4, 4)-NCNT, and (c) (5, 5)-NCNT.

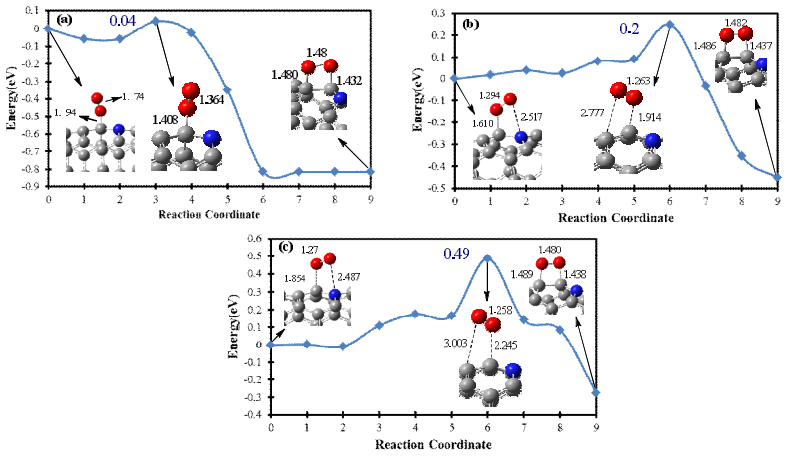

Figure S3. Calculated minimum energy paths of O_2 diffusion from C–N site to C–C-1 site on (a) (3, 3)-NCNT, (b) (4, 4)-NCNT, and (c) (5, 5)-NCNT.

Ab initio molecular dynamic (ABMD) trajectory of O_2 reduction reaction process

Similarly to the case of (3, 3)-NCNT, O_2 molecule is placed on the top of the C–N site with a distance of 3.5~4.0 Å. An obvious drop in the beginning of the potential energy in the interval of 0 ~ 144 fs and 0 ~ 86 fs for the case of (4, 4)- and (5, 5)-NCNTs, respectively, see Figure S4. In this time interval, O_2 molecule gradually approaches and binds to the C–N site via the end-on configuration of O_2 adsorption. Then the O_2 diffusion from the C–N site to the C–C-1 site with side-on configuration takes place in the time-step interval of 156 ~ 478 fs and 86 ~ 500 fs for (4, 4)- and (5, 5)-NCNTs accompanying a hill at 144 and 134 fs in the energy profile.

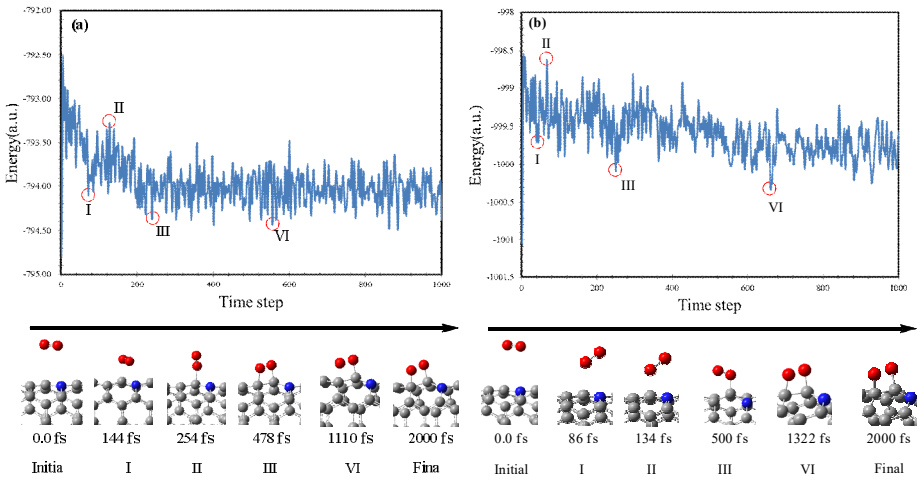

Figure S4. Ab initio molecular dynamic (ABMD) trajectory of O_2 reduction reaction process with some snapshots of intermediate at different times: (a) (4, 4)-NCNT and (b) (5, 5)-NCNT.

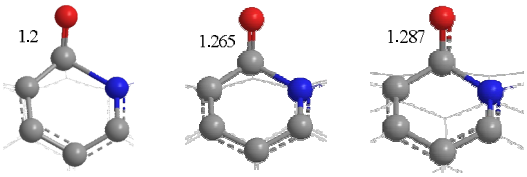

Figure S5. Optimized structures of O adsorption on (3, 3)-, (4, 4)-, and (5, 5)-NCNTs.

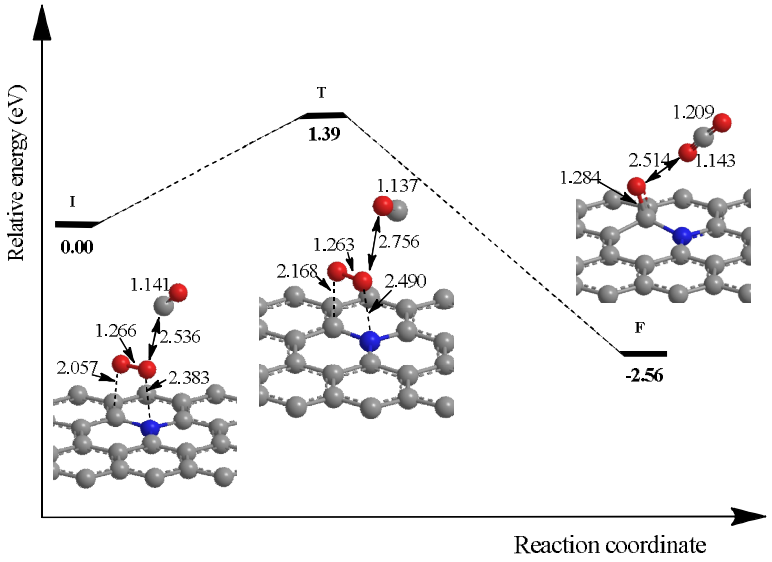

Figure S6. Optimized structures of initial states (reactants), transition states, and final states (products) for CO oxidation on C–N site of N-doped graphene and the related energy diagrams of CO oxidation reaction.

CO oxidation reaction processes on C–C-1 site of N-doped carbon nanotubes.

We also studied the CO oxidation processes on the C–C-1 site. This reaction starts from the CO and O_2 co-adsorption (initial state) in which the O_2 is adsorbed at C-C-1 site via the side-on configuration. The CO and O_2 co-adsorption energy is computed to be –1.63, –1.04, –0.62 and 0.49 eV for (3, 3)-, (4, 4)-, (5, 5)-NCNTs, and N-doped graphene, respectively, which are slightly higher than those of O_2 side-on adsorption. As showed in Figures S7 and S9, the distance between C_{CO} and 1O is predicted to be 4.401, 3.853, 3.910, and 2.786 Å for (3, 3)-, (4, 4)-, (5, 5)-NCNTs, and N-doped graphene, respectively. The bond length of C–O in CO and O–O in O_2 is predicted in the range of 1.135 ~ 1.137 and 1.460 ~ 1.489 Å. As depicted in Figure S8, CO starts moving to approach the side-on adsorbed O_2 and active the adsorbed O_2 at the transition state, TS1. The O–O bond distance is lengthened to 2.745, 3.018, 2.701, and 1.791 Å in the TS1 for (3, 3)-, (4, 4)-, (5, 5)-NCNTs, and N-doped graphene, respectively, indicating the dissociation of the O–O bond of the O_2 adsorbed to two O atoms adsorbed on the NCNTs. The calculated barrier at TS1 for this step is 0.04, 0.12, 0.15, and 1.99 eV for (3, 3)-, (4, 4)-, (5, 5)-NCNTs, and N-doped graphene, respectively. The process continues to generate a carbonate-like intermediate (MS) with an exothermicity of 5.36, 5.23, 5.14 and 4.31 eV. The C_{CO}–O_{CO}, C–O_{1O}, and C–O_{2O} bond length in MS are 1.260, 1.275, and 1.270 Å for N-doped graphene. Those are 1.190, 1.369, 1.353, and 1.194, 1.365, 1.347 and 1.191, 1.364, 1.347 Å for the case of (3, 3)-, (4, 4)- and (5, 5)-NCNTs. The final state including CO_2 and adsorbed O atom is produced from MS by overcoming a very high barrier of 1.56, 1.35, 1.36, and 0.83 eV for (3, 3)-, (4, 4)-, (5, 5)-NCNTs and N-doped graphene. In the TS2, the cleavage of Cco-O_{1O} and C_{2C}-O_{2O} bonds increases to 1.519 ~ 2.072 and 2.252 ~ 2.642

Å while the C_{1C}-O_{1O} bond decreases to 1.161 ~ 1.238 Å. The overall reaction is predicted to be exothermic by 3.85, 3.90, 3.93, and 4.66 eV for (3, 3)-, (4, 4)-, (5, 5)-NCNTs, and N-doped graphene, respectively. The desorption of CO_2 molecule from FS is easy to occurs due to the small adsorption energy (The adsorption energy of CO_2 is calculated to be–0.04, –0.03, and 0.01 eV for (3, 3)-, (4, 4)-, and (5, 5)-NCNTs, respectively).

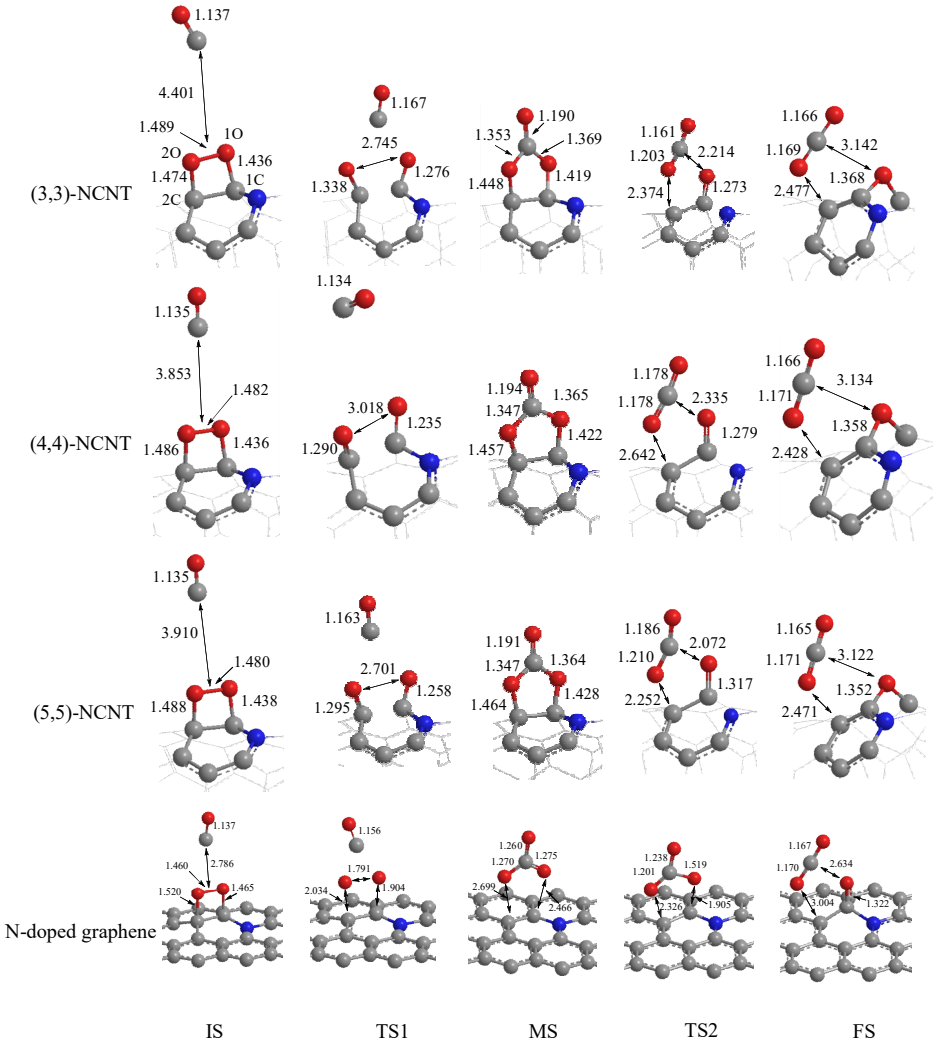

Figure S7. Optimized structures of initial states (reactants), transition states, intermediates (MS) and final states (products) for CO oxidation on C–C-1 site of (3, 3)-, (4, 4)-, (5, 5)-NCNTs, and N-doped graphene.

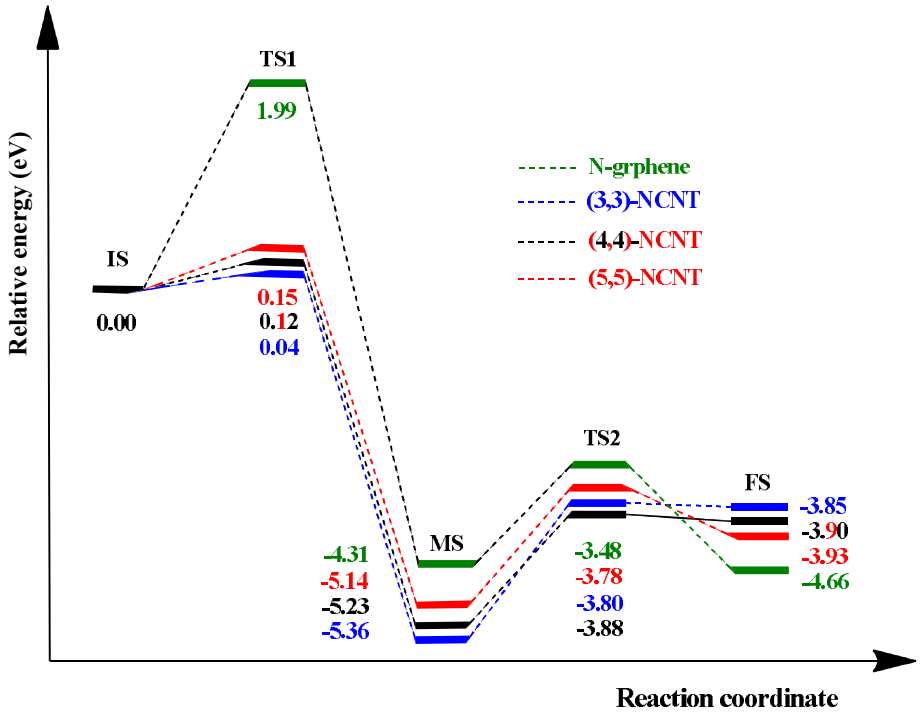

Figure S8. Energy diagrams of CO oxidation reaction on C–C-1 site of (3, 3)-, (4, 4)-, (5, 5)-NCNTs, and N-doped graphene.