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Electronic Supplementary Information for

Mechanisms of the oxygen reduction reaction on B- and/or N-doped carbon nanomaterials with curvature and edge effects

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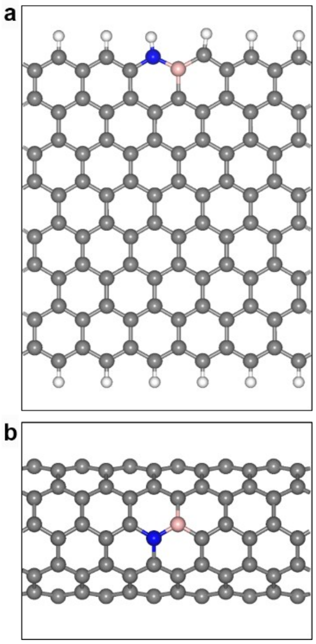

Fig. S1. Unit cells for GNRs and (5, 5) CNTs, taking BN cooping as an example.

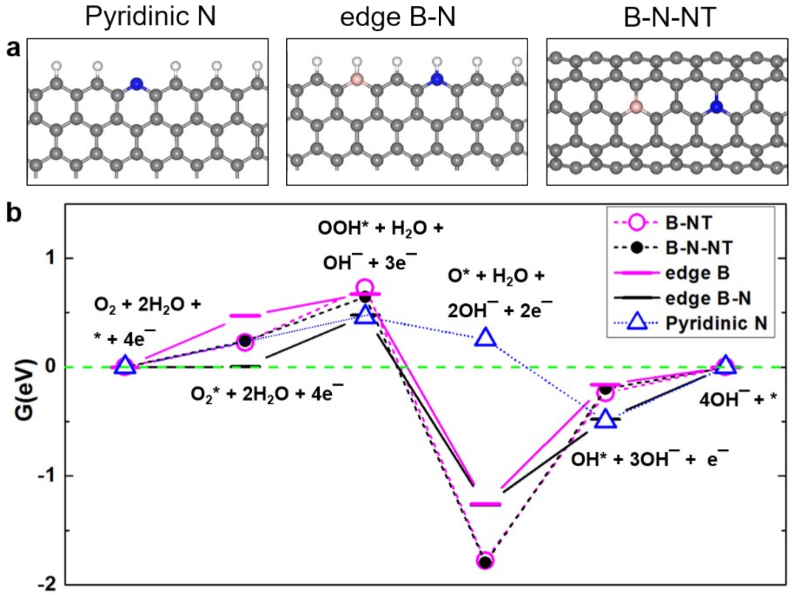

Fig. S2. (a) Structural models for pyridinic N, separate BN doped graphene edge and CNTs with high concentration. (b) Free energy diagram for ORR on three models in (a) under the conditions of pH = 14 and the maximum potential allowed by thermodynamics. The results for B doped graphene edge and CNTs at low concentration are included for comparison.

In the main text, we have considered graphitic N and pyridinium N with H saturated at the edges. For comparison, we further consider pyridinic N without H saturation as shown in Fig. S2a. The overpotential determined from the thermodynamic free energies is 0.5 eV, which is slightly lower than the BN coped GNRs (0.55 eV). However, it should be noted that pyridinic N could not adsorb O_2 chemically, which might reduce the ORR kinetics. The high-performance of pyridinic N on ORR activities is consistent with recent experiments based on HOPG model catalysts and nitrogen-doped graphene nanosheets catalysts.[1]

To understand the influences of distance between B and N atoms, we consider separate B and N dual-doped graphene edge and (5, 5) CNT with the distance between B and N about 4.9 Å, shown as edge B-N and B-N-NT in Fig. S2a. If B and N atoms distribute uniformly with such distance, the doping atom ratio would be around 12%. For comparison, the distance between dopants in isolated B doping cases (edge B and B-NT) considered in the manuscript is about 14.8 Å, which corresponds to doping atom ratio of 1-2%. Thermodynamic diagrams for these four doping cases (edge B-N, B-N-NT, edge B and B-NT) are shown in Fig. S2b. For doped CNTs, B-NT and B-N-NT show negligible difference on energies of intermediate states. For doped edges, the adsorption free energies of $*O_2$, *OOH and *OH on edge B-N is higher than on edge B, while that of *O is similar on these two sites. Accordingly, the barrier for the rate-determining hydrogenation of *O is lower to 0.8 eV, which is similar to edge N case. Nevertheless, it is still significantly higher than that of BN coped graphene edge (0.55 eV). Since the doping atom ratio in this model is quite high and difficult to achieve in experiments, the effects of distance between B and N atoms would not play a key role in determining the ORR performance in most cases.

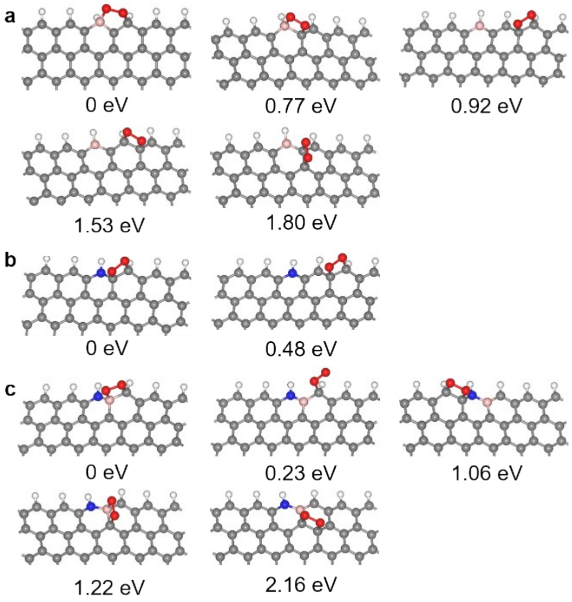

Fig. S3. Different optimized configurations and their relative energies for chemically adsorption of O_2 on (a) B, (b) N, and (c) BN doped GNRs.

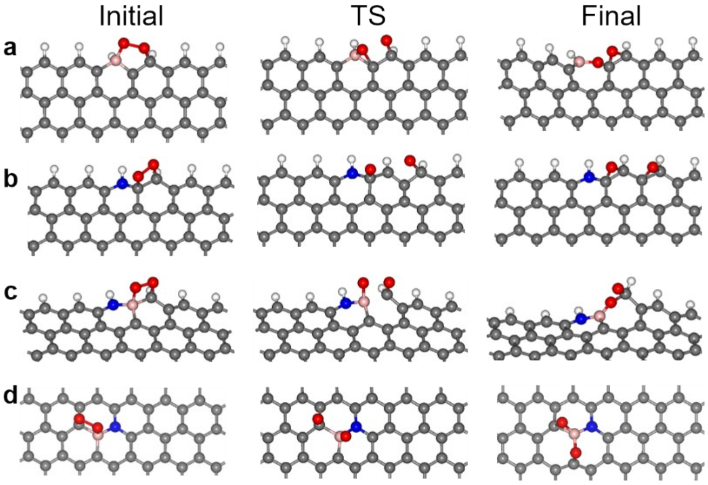

Fig. S4. Initial, transition-state, and final structures for the O_2 dissociation process on (a) B, (b) N, (c) BN doped GNR edges as well as (d) BN codoped graphene.

References

1. D. H. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo and J. Nakamura, *Science*, 2016, **351**, 361-365.