

Supporting Information

Unraveling the Mechanisms of S-doped Carbon Nitride for Photocatalytic Oxygen Reduction to H₂O₂

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Table S1. Zero-point energy (E_{ZPE}) and entropic correction (TS) at $T = 298.15$ K for relevant species in ORR. The entropy (S) of H_2 is taken from the NIST database. The vibrational frequencies of OOH^* , O^* and OH^* species are calculated on the most stable adsorption configurations, and they give similar results for E_{ZPE} . Thus, constant values of E_{ZPE} are used for the oxygenated intermediates adsorbed on various model.

Species	E_{ZPE} (eV)	TS (eV)
H_2O	0.56	0.67
H_2	0.28	0.40
*OOH	0.47	--
*O	0.11	--
*OH	0.40	--

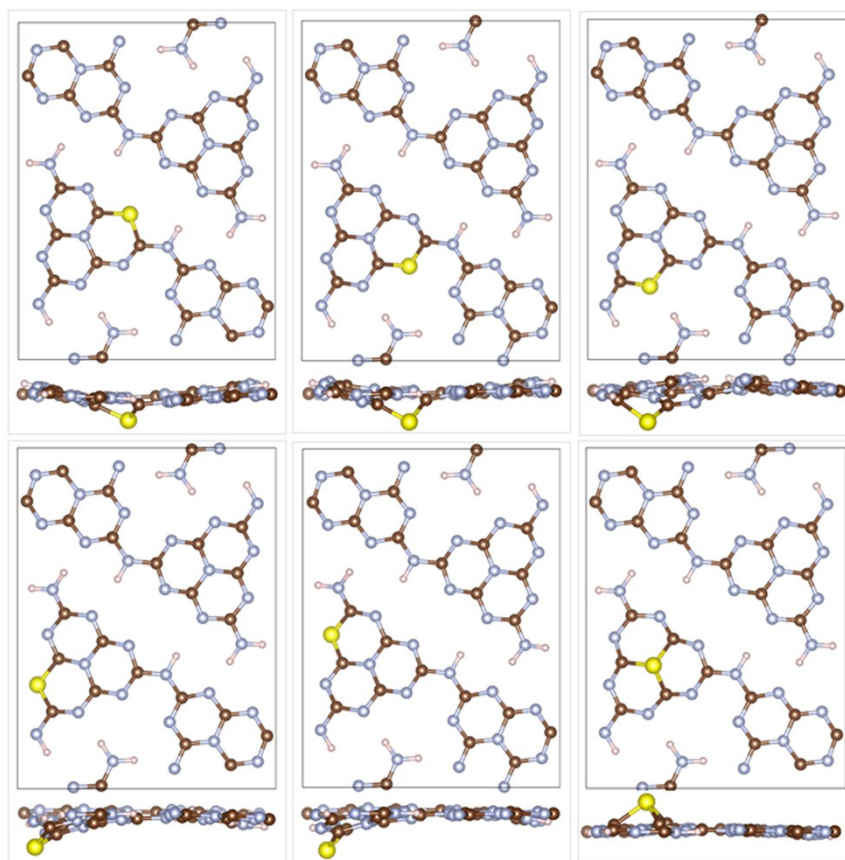


Figure S1. Top and side views of geometric structure S-doped melon-based CN of the possible doping sites (N2, N3, N4, N5, N6, N7). The brown, gray, light pink and yellow balls represent C, N, H and S atoms, respectively.

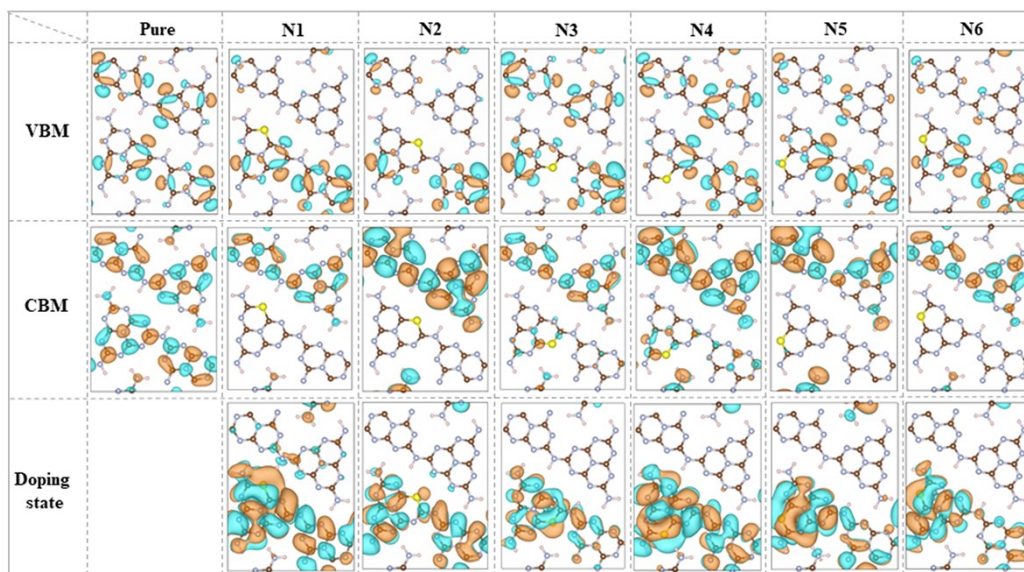


Figure S2. The orbital diagrams of VBM, CBM and Doping state of melon-based CN and S-doped melon-based CN. The orbitals with orange and cyan colors represent the positive and negative values of the molecular orbitals (MOs, ψ). The brown, gray, light pink and yellow balls represent C, N, H and S atoms, respectively.

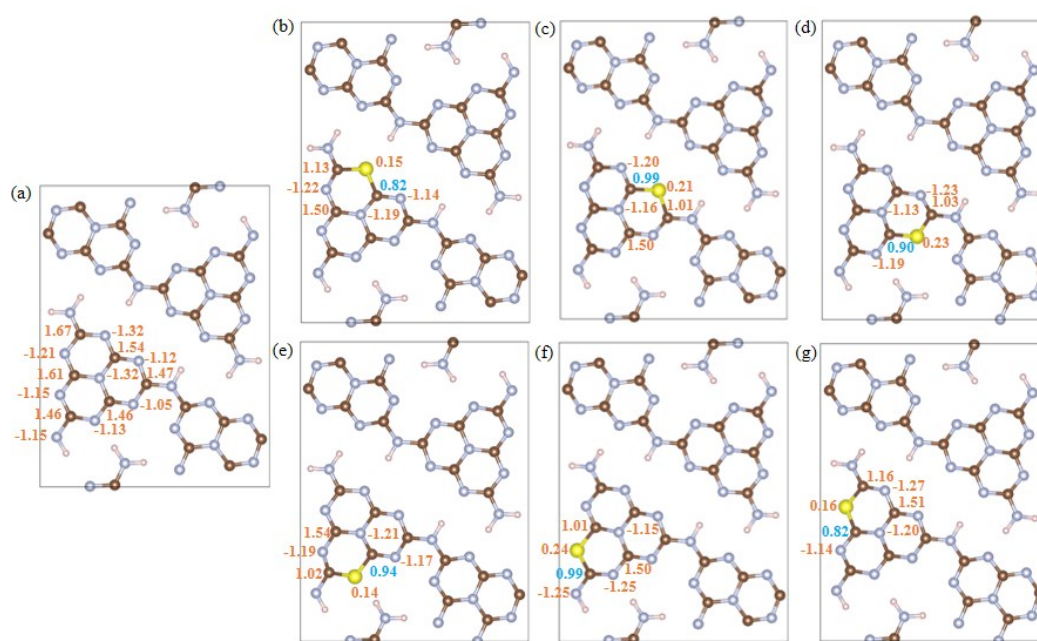


Figure S3. Bader charge of (a) melon-based CN, (b) N1, (c) N2, (d) N3, (e) N4, (f) N5 and (g) N6 site S-doped melon-based CN. The brown, gray, light pink and yellow balls represent C, N, H and S atoms, respectively.

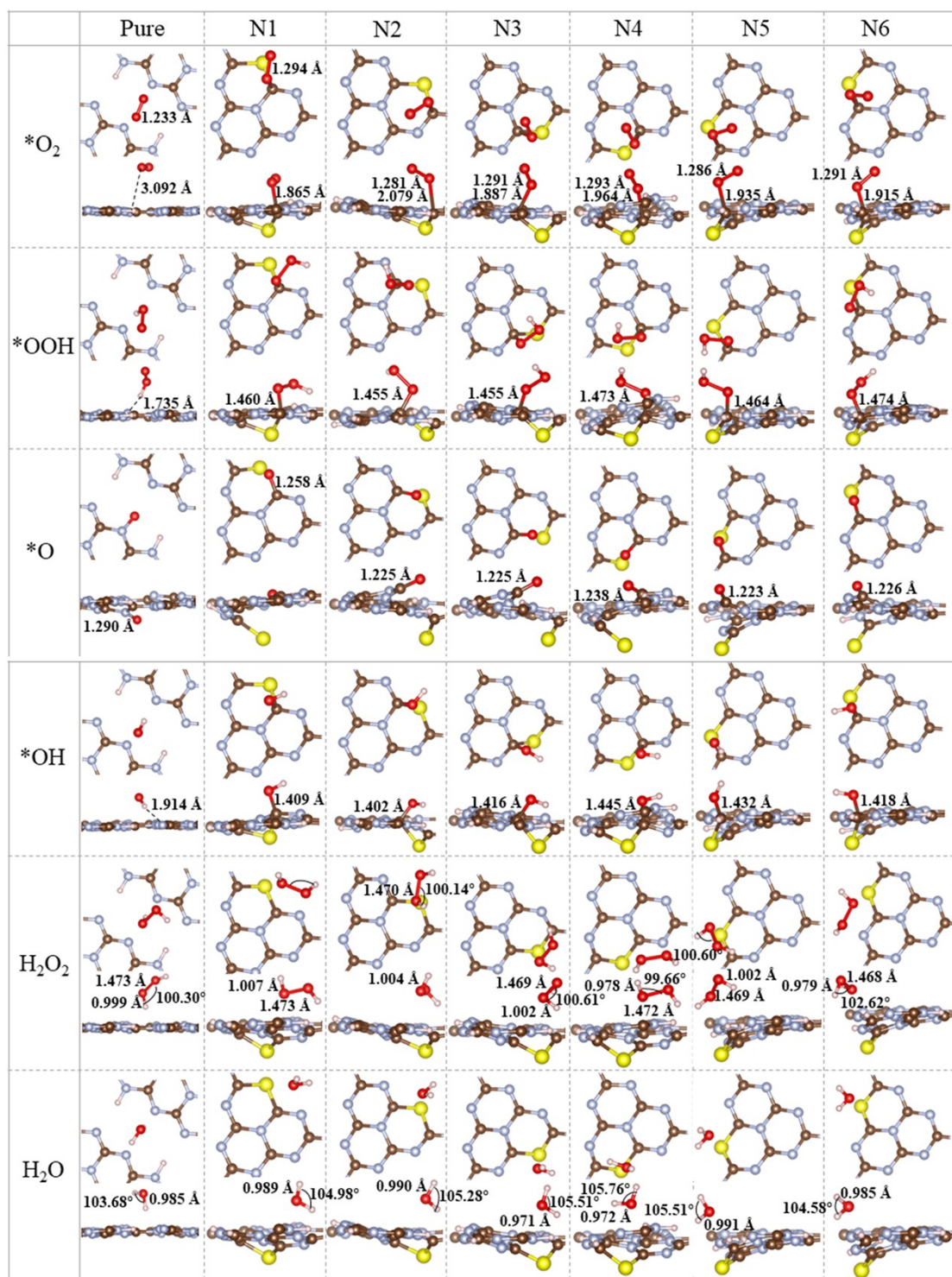


Figure S4. The most stable adsorption configurations of relevant species during ORR on melon-based CN and S-doped melon-based CN. The brown, gray, light pink, yellow and red balls represent C, N, H, S and O atoms, respectively.