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## **Fe and Co adatoms on bilayer borophene as single-atom catalysts for oxygen reduction reaction: A DFT study**

Energy conversion technologies like water electrolyzers, rechargeable metal-air batteries, and proton-exchange membrane fuel cells require high-performance catalysts to minimize reaction kinetic barriers of critical processes like the oxygen reduction reaction (ORR). Developments of efficient non-precious metal ORR electrocatalysts are keys to advancing these technologies. Single-atom catalysts (SAC) represent promising types of catalysts, consisting of isolated metal atoms dispersed on suitable support materials. SACs offer several advantages over conventional catalysts, including atomic precision at specific coordination environments, resistance to deactivation due to their unique atomic-scale structure, and aggregation prevention, which can significantly enhance activity and selectivity. However, suitable substrates for SACs require strong anchoring of metal atoms to prevent demetallation while preserving the metal's electronic characteristics. In this respect, two-dimensional materials like graphene and borophene have emerged as promising substrates for SACs due to the lack of 3d orbitals, avoiding interfering with the active site, the metal center. Indeed, bilayer borophene has been recently synthesized on Ag(111), and Cu(111) [1-2], where the hexagonal structure found is consistent with two covalently bonded AA-stacking alpha-borophene layers containing hollow hexagons.

This work employs DFT calculations to investigate Fe and Co adatoms on free-standing bilayer borophene (BB) as single-atom catalysts for ORR. Our results indicate that BB is a semiconducting material with a bandgap of 0.7 eV. The metal adatoms strongly bind to the BB surface at the hollow sites, exhibiting binding energies higher than 2 eV, inducing metallicity and facilitating charge transport during electrocatalysis. Concerning the pristine BB, we observe that the metal incorporation reduces the work function by more than 1 eV. Increasing the adatom coverages further reduces the work function, thereby enhancing its charge transfer characteristics. Next, we examine the adsorption and dissociation of O<sub>2</sub> and OOH molecules on the metal adatoms for different metal coverages. Upon adsorption of O<sub>2</sub> and OOH, we find dissociation energy barriers of around 1.0 and 0.6 eV, respectively, where lower activation energies would be associated with a high-spin configuration for the metal-molecule adduct. The O<sub>2</sub> and OOH activation energies are lower than those previously reported on Fe/N/C catalysts [3], approaching those found on the Pt(111) surface, the most efficient ORR electrocatalyst.

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## References

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