

ABSTRACT

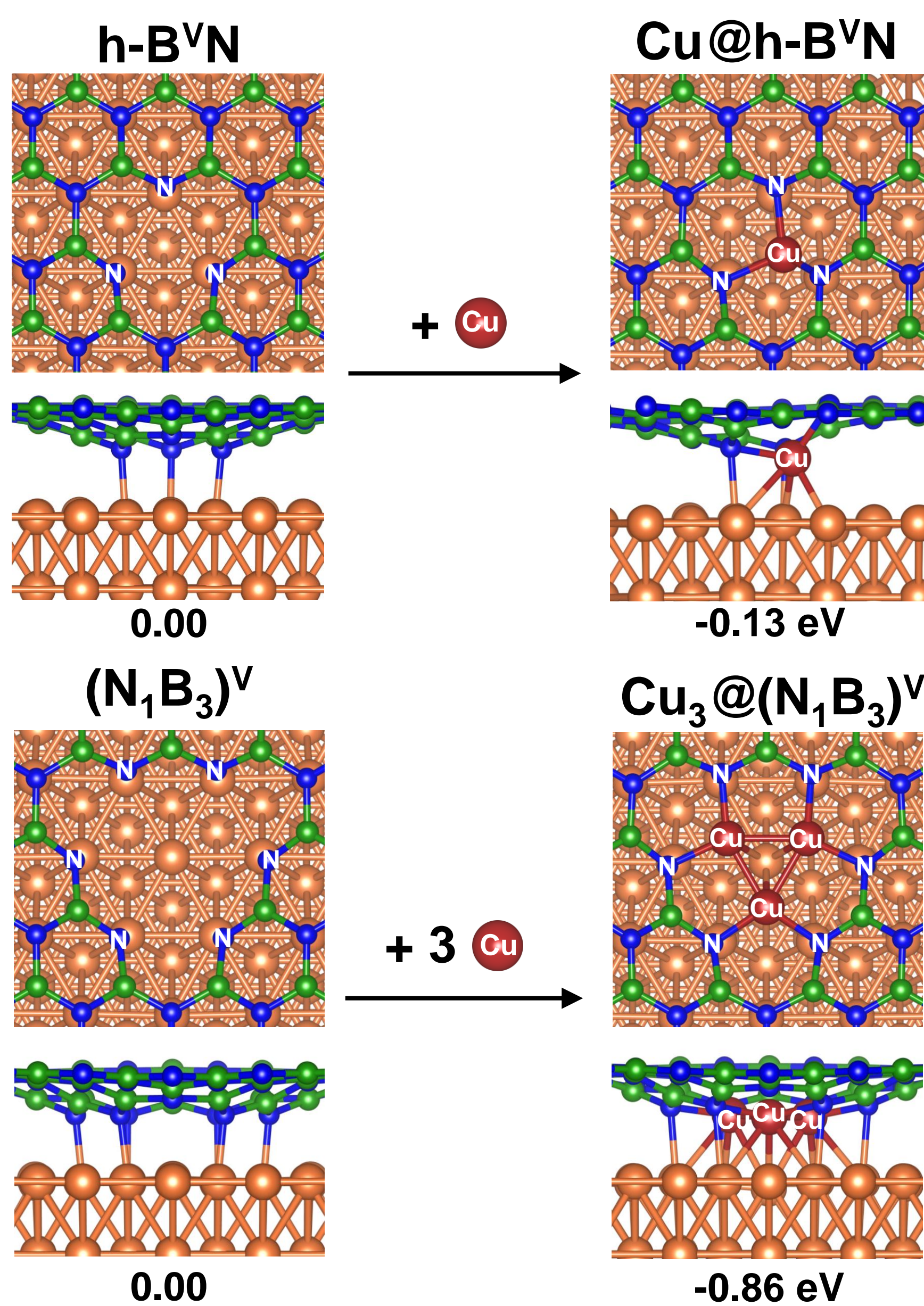
Metal-doped and metal-supported two-dimensional materials are attracting a lot of interest as potentially active electrocatalysts for reduction and oxidation processes.^[1] When a non-regular 2D h-BN layer was grown on a Cu(111) surface, metal adatoms were found to spontaneously emerge from the bulk to fill the atomic holes in the structure and become available for surface catalysis.^[2] Herein, computational electrochemistry is used to investigate and compare the performance of Cu-doped and Cu-supported pristine and defective h-BN systems for the electrocatalytic water oxidation reaction (OER).^[3] For the various model systems, the intermediate species of this multistep oxidation process are identified and the free-energy variations for each step of reaction are computed, even for those steps that do not involve an electron or a proton transfer.

Small Cu clusters (tetramers) trapped in the h-BN defective lattice on a Cu(111) support are found to be very active for the water oxidation reaction since such systems are characterized by a low overpotential and by a small energy cost for O₂ release from the catalyst, which is often observed to be a major limit for other potential electrocatalysts.

COMPUTATIONAL DETAILS

- Quantum ESPRESSO package (QE) / vdW-DF2^{C09x} functional (DFT)
- 8×8 supercell for h-BN / 4-layer (8×8) cell for Cu (111)
- The electrochemical cell, together with the effect of an applied external potential, has been simulated with the methodology originally proposed by Nørskov and co-workers.^[4]

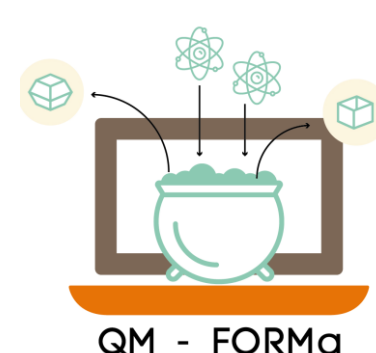
Cu TRAPPING STRUCTURES



- We studied if Cu metal adatoms can spontaneously pop up from the bulk to fill the holes in the h-BN structure.
- Defective h-BN, exposing N-terminated edges, behaves like a multi-N-donor macrocyclic ligand that can encapsulate Cu atoms as a consequence of a huge stabilization deriving from the Cu-N bond formation.

ACKNOWLEDGMENTS

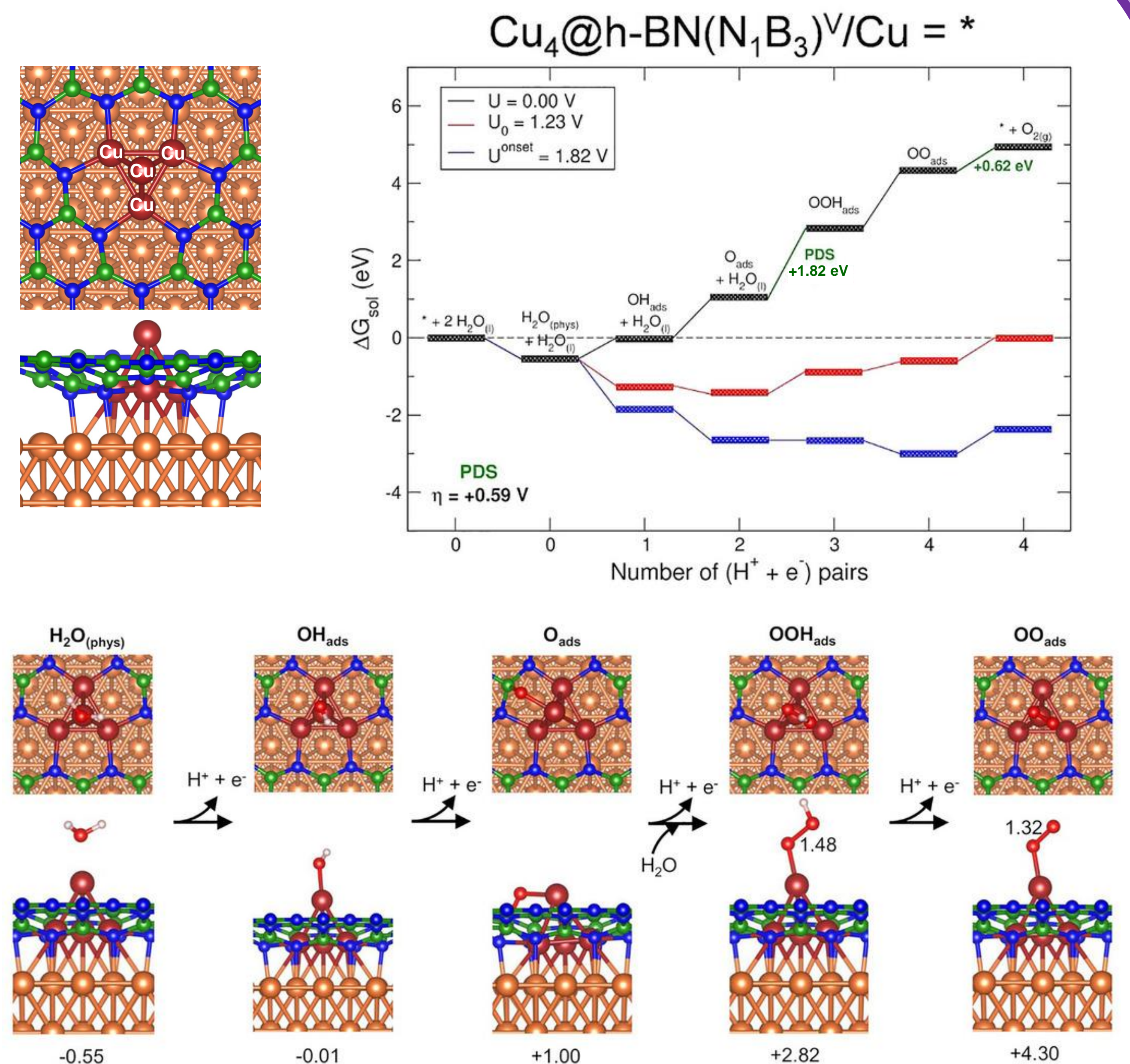
QM-FORMa: Designing New Materials with Quantum Mechanics



QM-FORMa is a network of world leading material scientists who perform accurate Quantum Mechanics calculations to help in designing new materials from a bottom-up perspective.

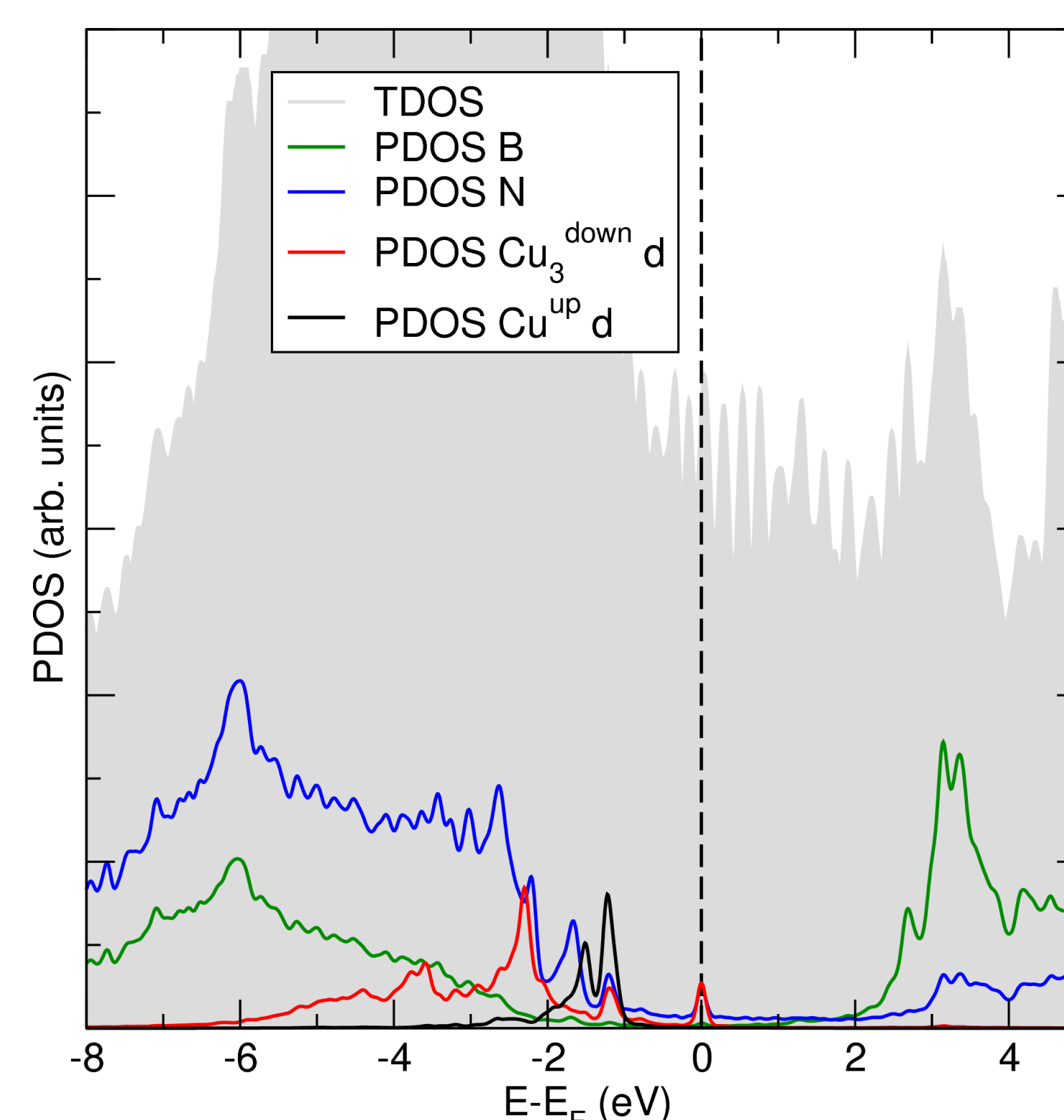
<https://eitrawmaterials.eu/project/qmforma/>

REACTION MECHANISM



- Among all the Cu trapping structures, the Cu tetramer is found to be the best electrocatalyst for the OER.
- The consecutive steps of reaction have a uniform increase in free energy, with a PDS that is just slightly higher than the other steps. The computed theoretical overpotential is reasonably low (0.59 V).
- The last step of O₂ release costs only +0.62 eV, because the end-on superoxo species is not too strongly bound to the Cu on the pyramid vertex.

ELECTRONIC PROPERTIES



The d states associated to the Cu atom at the vertex of the Cu₄ pyramid do not lie in the proximity of the Fermi energy but at least -1 eV below. Therefore, only the Cu atom at the Cu₄ vertex is not electron rich, that is, is not prompt in donating d electrons to any bound chemical species. We consider this the reason that this system is the best electrocatalyst for the water oxidation reaction. Being an oxidation reaction, it is required that the electron is removed from the water species and not from the Cu atoms. A confirmation of the poor electron donor properties of the trapped Cu₄ systems comes from the fact that the adsorbed OO species before O₂ release is a superoxo (with one extra electron), whereas in all other cases of trapped Cu atoms it is a peroxo (with two extra electrons). The O₂ release from a stabilized side-on -(O-O)²⁻ species is energetically more demanding than that from an end-on -(O-O)⁻ species.

CONCLUSIONS

We performed a computational electrochemistry analysis based on DFT calculations to establish the performance of Cu-doped and Cu-supported defective h-BN as an electrocatalyst for the water oxidation reaction.

We considered the possibility of small Cu clusters filling larger lattice defects in the h-BN lattice. **Trapped Cu tetramers**, in the form of pyramids, expose one Cu atom toward the vacuum, which becomes available for catalysis. Such systems have a relatively **low overpotential** (0.59 V) and a **low free-energy cost** (0.62 eV) for the final step of O₂ release. These results pave the way for a rational engineering of the interface between two dimensional materials and the underlying metal support for preparation of active electrocatalysts for O₂ evolution reaction (OER), discussed in this work, but also for other oxidation or reduction processes.