

Noble Metals Supported Hexagonal Boron Nitride for Oxygen Reduction Reaction: A DFT Study

Seoin Back and Samira Siahrostami*

SUNCAT Center for Interface Science and Catalysis, Department of Chemical Engineering,

Stanford University, Stanford, CA 94305, United States

* Corresponding author: samiras@stanford.edu

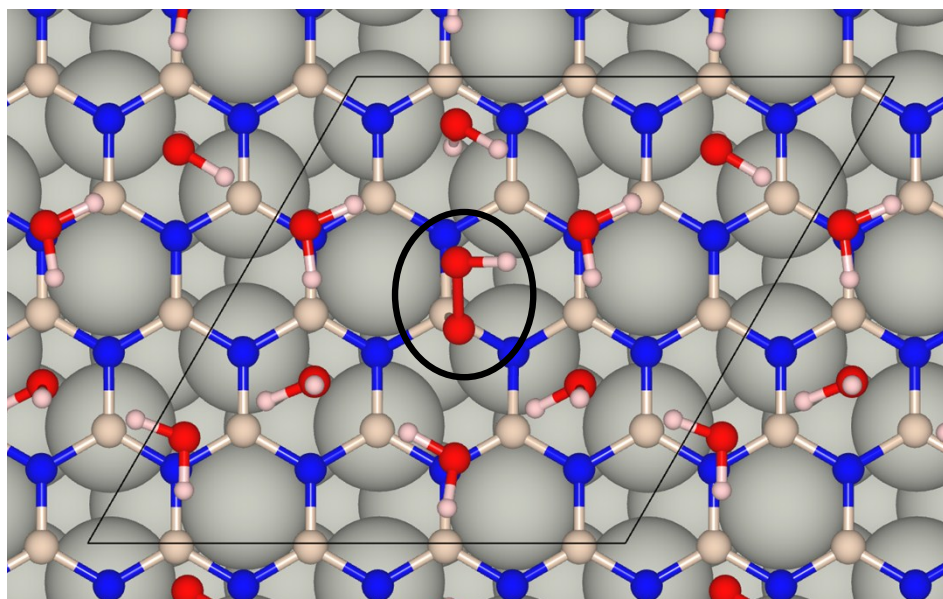


Figure S1. The optimized geometry of *OOH on *h*-BN@Pd in the presence of eight H₂O molecules in the supercell.

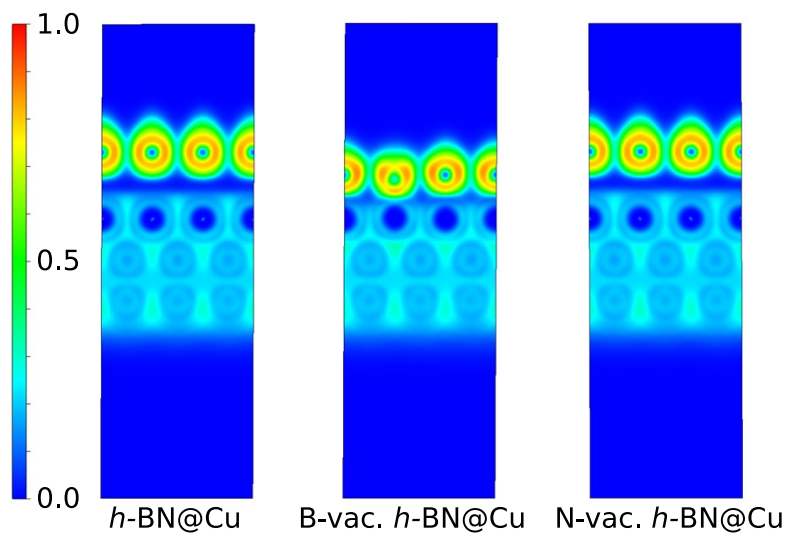
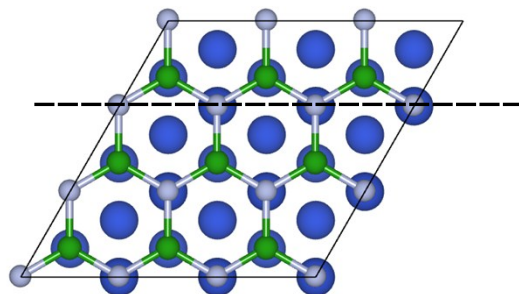
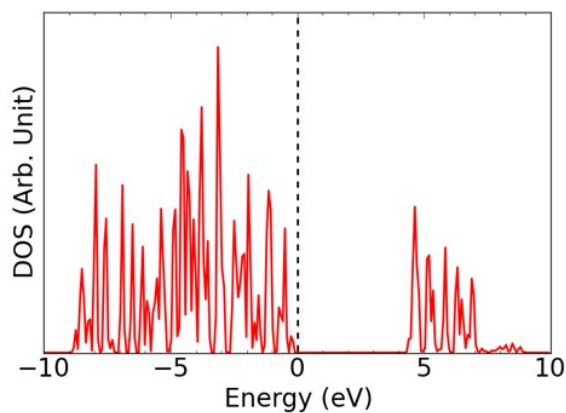
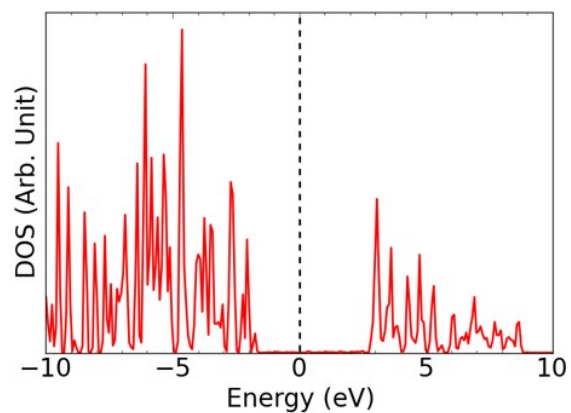


Figure S2. The electron localization function (ELF) through the plane perpendicular to the dotted line.

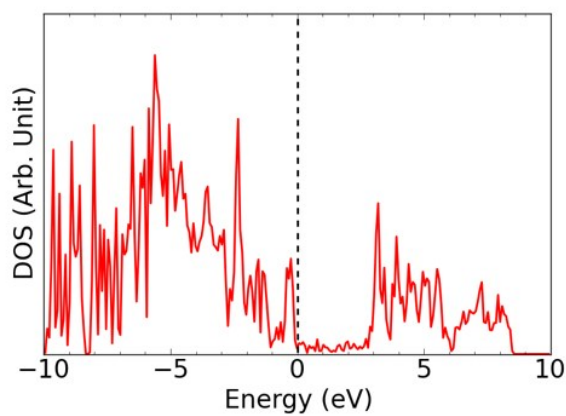
A. Unsupported *h*-BN



B. *h*-BN@Ag



C. B-vac. *h*-BN@Ag



D. N-vac. *h*-BN@Ag

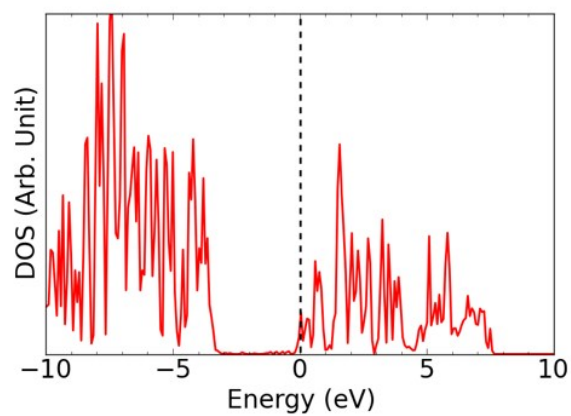
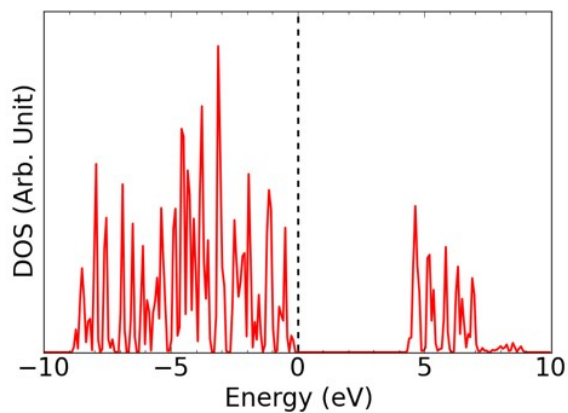
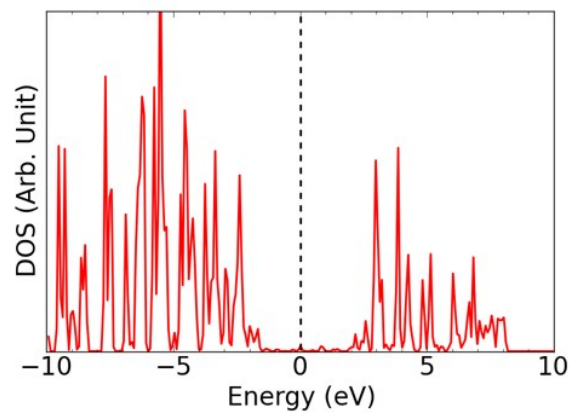


Figure S3. Projected density of states (PDOS) of the *p*-orbitals of B and N for (A) freestanding *h*-BN, (B) Ag supported *h*-BN without vacancy, (C) with B vacancy and (D) with N vacancy. The vertical dashed line represents the position of the Fermi level at 0 eV.

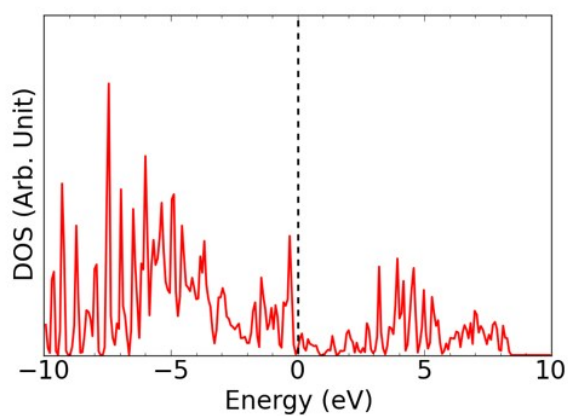
A. Unsupported *h*-BN



B. *h*-BN@Cu



C. B-vac. *h*-BN@Cu



D. N-vac. *h*-BN@Cu

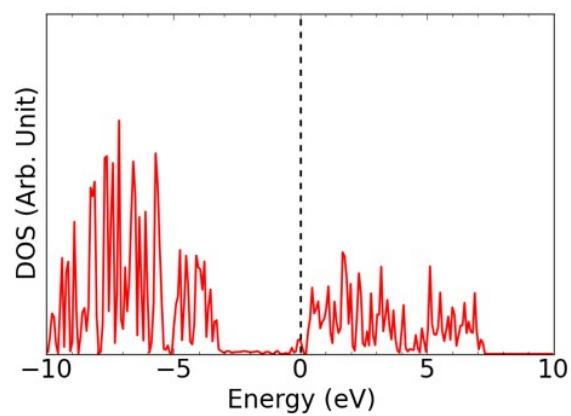
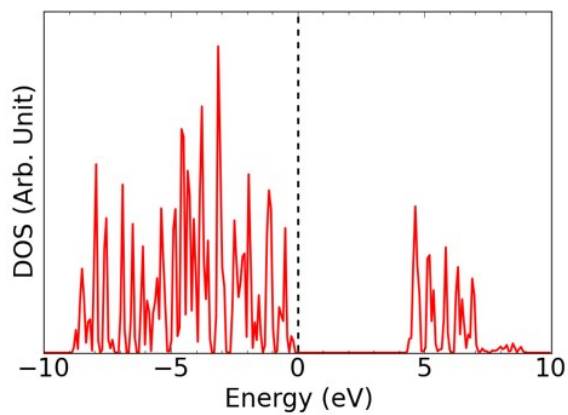
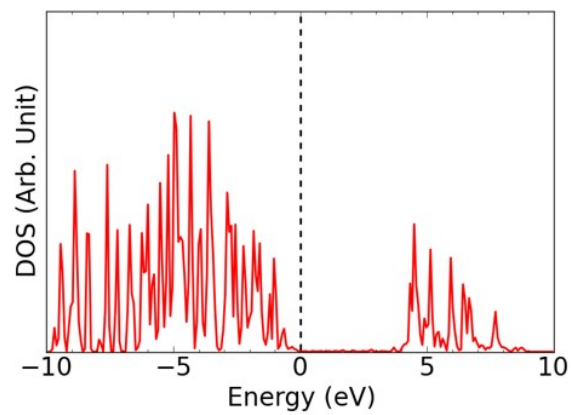


Figure S4. Same as Figure S1, but for Cu support.

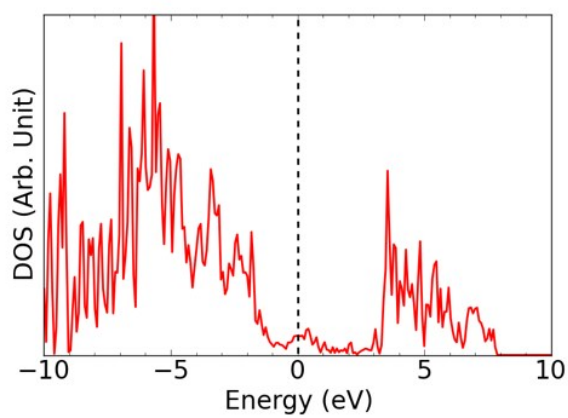
A. Unsupported *h*-BN



B. *h*-BN@Pt



C. B-vac. *h*-BN@Pt



D. N-vac. *h*-BN@Pt

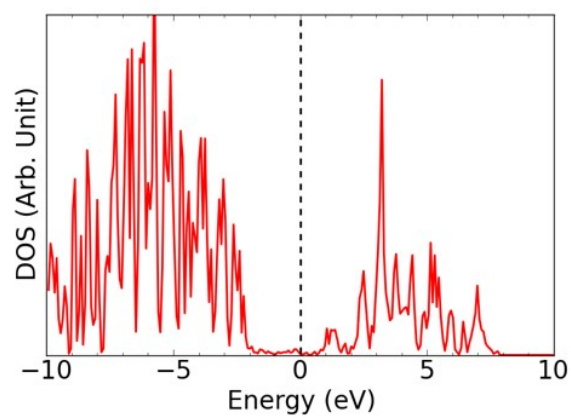


Figure S5. Same as Figure S1, but for Pt support.

Supplementary Note 1: Constructing Surface Pourbaix Diagrams

During electrochemical reactions, catalyst surface can be covered by several reaction intermediates depending on binding strength of the surface and electrochemical potential. Using the CHE model, a potential dependence of binding energies can be taken into account. In this model, the chemical potential of hydrogen gas is equivalent to that of a proton-electron pair, ($0.5\mu(H_2) = \mu(H^+ + e^-)_{U=0V}$). The chemical potential of the proton-electron pair is potential dependent, $\mu(H^+ + e^-)_U = \mu(H^+ + e^-)_{U=0V} - eU$. Using this relation, we can obtain free energy change of proton electron transfer reaction at potential U.

For example, the potential dependence of the free energy changes of OH* ($H_2O + * \rightarrow *OH + H^+ + e^-$) and O* ($H_2O + * \rightarrow *O + 2H^+ + 2e^-$) intermediates can be expressed as Eq. 1 and 2, respectively.

$$\Delta G(*OH)_U = \Delta G(*OH)_{U=0} - eU \quad (\text{Eq. 1})$$

$$\Delta G(*O)_U = \Delta G(*O)_{U=0} - 2eU \quad (\text{Eq. 2})$$

For all surfaces we considered several possibilities of surface terminations including one and two adsorbates, and generated the surface pourbaix diagram. Using this technique, the most stable coverage at the surface at certain potential can be determined (Figure S6 to S8).

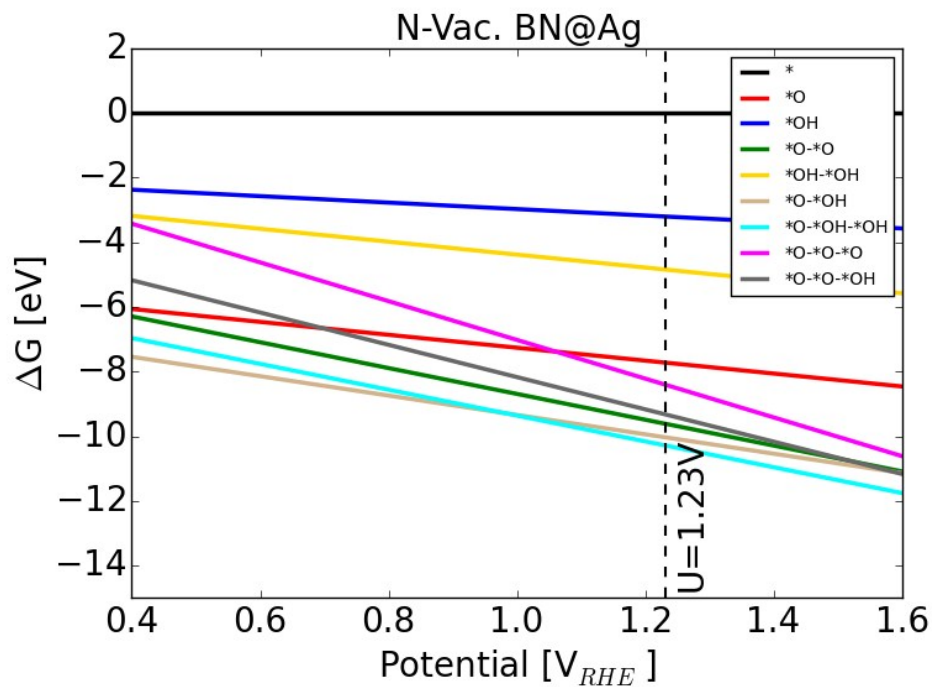


Figure S6. Surface pourbaix diagram of N-vac. *h*-BN@Ag.

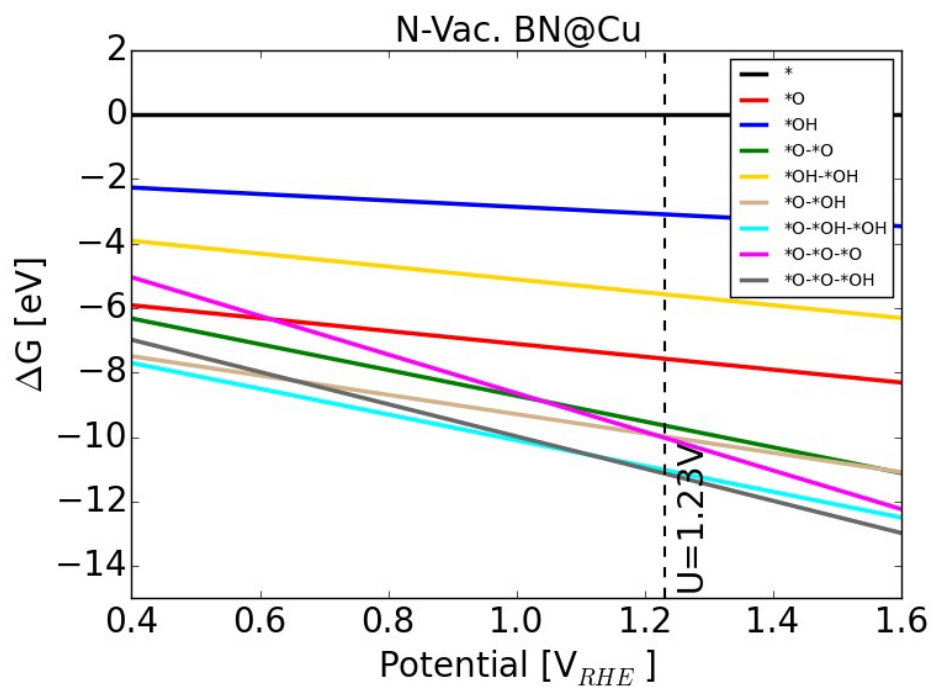


Figure S7. Surface pourbaix diagram of N-vac. *h*-BN@Cu.

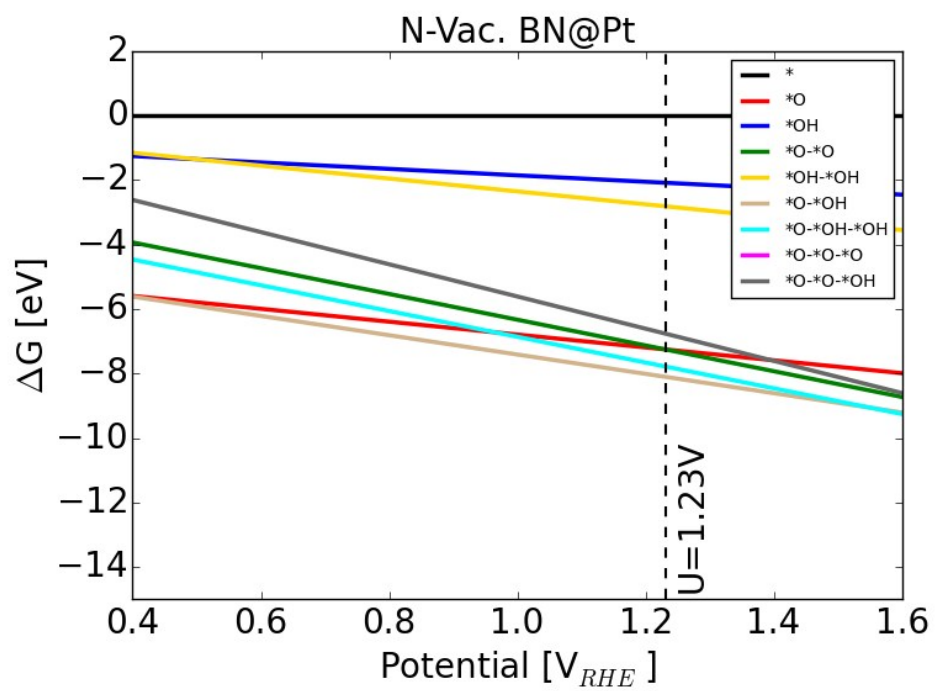


Figure S8. Surface pourbaix diagram of N-vac. *h*-BN@Pt.