

Two-Dimensional Materials as Catalysts for Energy Conversion

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Abstract Although large efforts have been dedicated to studying two-dimensional materials for catalysis, a rationalization of the associated trends in their intrinsic activity has so far been elusive. In the present work we employ density functional theory to examine a variety of two-dimensional materials, including, carbon based materials, hexagonal boron nitride (*h*-BN), transition metal dichalcogenides (e.g. MoS₂, MoSe₂) and layered oxides, to give an overview of the trends in adsorption energies. By examining key reaction intermediates relevant to the oxygen reduction, and oxygen evolution reactions we find that binding energies largely follow the linear scaling relationships observed for pure

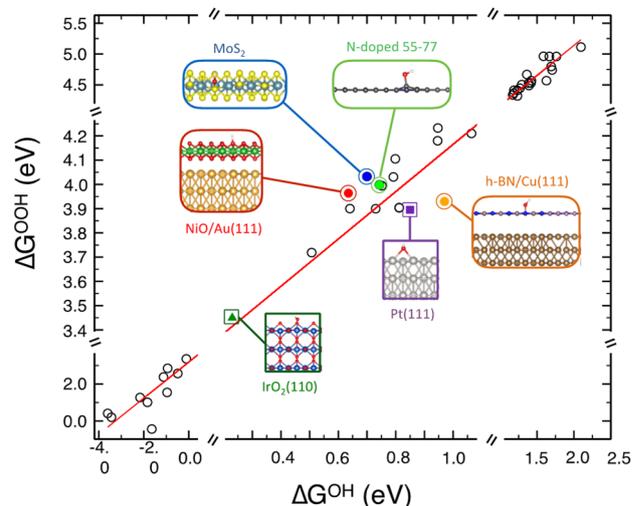
metals. This observation is very important as it suggests that the same simplifying assumptions made to correlate descriptors with reaction rates in transition metal catalysts are also valid for the studied two-dimensional materials. By means of these scaling relations, for each reaction we also identify several promising candidates that are predicted to exhibit a comparable activity to the state-of-the-art catalysts.

Graphical Abstract Scaling relationship for the chemisorption energies of OH* and OOH* on various 2D materials.

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Inspired by the success of graphene in a broad range of electronic and energy applications [1–7], novel classes of layered two-dimensional (2D) materials have been intensively studied in the past few years [8–14]. Structurally modified graphene, hexagonal boron nitride (*h*-BN), transition metal dichalcogenides (e.g. MoS₂, MoSe₂) and layered transition metal oxides, are some of the 2D materials that have found

broad applications due to their high surface area to volume ratio, and desirable electrical, mechanical and thermal properties [15–18]. Because of their low cost and ability to form a wide range of nanostructures, these 2D materials are also being increasingly considered for electrochemical energy conversion and storage [19, 20], and they represent a promising class of alternatives to replace the commercial precious-metal catalysts [5–7].

In their pristine state, most 2D materials do not exhibit any chemical activity. However, their properties can be tailored by introducing dopants [19, 21, 22], generating defects [23] and by supporting them on transition metals [24–26]. Nitrogen doped graphene, for instance, has been shown to catalyze the electrochemical reduction of oxygen to water and the oxygen reduction reaction, (ORR) [22, 27–34]. Other dopants such as boron [35], sulfur and phosphorous [21, 36] have been also proven to be interesting. Likewise, *h*-BN, an otherwise inert material, becomes a promising ORR catalyst when supported on transition metals such as Au [24] and Cu [25]. Layered transition metal dichalcogenides, such as molybdenum sulfides and selenides, are active catalysts for the hydrogen evolution reaction (HER) and CO₂ reduction reaction [18, 37–40], and their activity can be further improved by introducing defects and transition metal dopants [41–43]. Layered oxides based on earth-abundant transition metals such as nickel, iron, or cobalt, have been reported to be highly active materials for the oxygen evolution reaction (OER), specially the multimetallic oxides based on these elements [44–46]. Some of these catalysts have shown a comparable (or even better) performance in alkaline media than that of the state-of-the-art Ir and Ru based catalysts [47, 48], and therefore, they are particularly promising.

Recently, it has been shown that graphene based catalysts are able to catalyze both ORR and OER reactions [30–32]. This bifunctionality is particularly remarkable as it points out the great potential of these materials for a wide variety of applications. It is, however, not yet known whether other related two-dimensional materials exhibit the same versatility. Although the reaction conditions for the ORR and OER differ substantially, both processes involve the hydroxyl (OH*) and hydroperoxo (OOH*) intermediates, and the corresponding calculated chemisorption energies have been successfully employed to describe the ORR and OER reactivities [49, 50]. Furthermore, the energetics of these two intermediates have been found to be correlated through linear scaling relations on transition metal [51] as well as transition metal oxide surfaces [52], thus making it possible to establish volcano-type relationships for both ORR and OER [49, 53].

Herein, we seek to investigate trends in chemisorption energies for a wide range of different 2D materials (details and structures in Supplementary Information) in order to draw comparisons with currently known catalysts and evaluate their predicted activity for the ORR and OER reactions.

We find that the linear scaling relations between the adsorption energies of key intermediates of the ORR and OER reactions, i.e., OH* and OOH* [54], can be used to rapidly assess the catalytic activity of a material for ORR and OER. Our results also show that 2D materials represent an especially interesting class of catalysts offering a promising alternative to the commercial ones based on precious metals.

We employ density functional theory (DFT) calculations to study the chemisorption energies of OH* and OOH* on the selected 2D materials (SI). Calculations for the carbon based and chalcogenides were performed using the QUANTUM ESPRESSO program package [55] and the atomic simulation environment (ASE) [56]. The Bayesian Error Estimation Functional with van-der-Waals correction (BEEF-vdW) [57] was used, and the electronic wave functions were expanded in plane waves up to a cutoff energy of 500 eV, while the electron density was represented on a grid with an energy cutoff of 5000 eV. Core electrons were approximated with ultrasoft pseudopotentials. Calculations on the layered nickel oxide supported on gold (NiO_x/Au(111)) were performed using the Perdew–Burke–Ernzenhof (PBE) exchange correlation functional, as implemented in the VASP [58, 59]. For a better description of the Co(3d), Ni(3d) and Ce(4f) electrons, the Hubbard effective terms $U_{eff}(\text{Co})=3.32$ eV, $U_{eff}(\text{Ni})=6.45$ eV and $U_{eff}(\text{Ce})=4.5$ eV were added to the PBE functional through the rotationally invariant approach proposed by Dudarev et al. [60]. All periodic slab calculations were carried out using a plane wave kinetic energy cutoff of 500 eV and a vacuum spacing of at least 15 Å. Further details on the slab setups and the *k*-point sampling used in calculations can be found in the references.

Although all materials studied herein present a 2D structure, their relevant active sites differ significantly. For graphene and *h*-BN, these sites are carbon and boron atoms, respectively. For MoS₂ and MoSe₂, the basal plane has been shown to be inert, and adsorbates bind to under-coordinated chalcogen atoms on the edges. On the other hand, for nickel and cobalt oxide films supported on gold (NiO_x/Au(111)), both edge and basal plane sites contribute to the OER activity [61].

Figure 1 displays the scaling relationship for the adsorption energies of the OH* and OOH* on the different studied 2D structures. The Pt(111) surface is depicted for comparison and the optimal ORR catalyst should have an OH* binding energy approximately 0.2 eV weaker than Pt(111) [53]. As can be seen in Fig. 1, all the computed adsorption energies follow the same scaling relation with.

$$\Delta G^{\text{OOH}} \approx \Delta G^{\text{OH}} + 3.2 \text{ eV} \quad (1)$$

We note that this scaling relation is identical to that found for transition metal surfaces exposing the (111) facet [51,

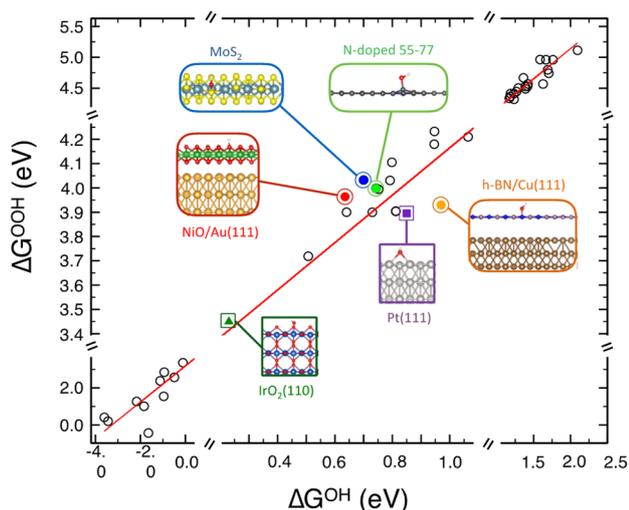


Fig. 1 Scaling relationship for the chemisorption energies of OH* and OOH* for various 2D materials. Pt(111) and IrO₂(110) data adapted from Refs. [49, 62] are shown for comparison in *purple* and *dark green*, respectively. OH and OOH adsorption energies are reported relative to liquid water and gas phase hydrogen using H₂O(l) + * → OH* + 1/2H₂(g) and 2H₂O(l) + * → OOH* + 3/2H₂(g), respectively. *h*-BN/M and NiO_x/Au are adapted from Refs. [25, 61], respectively. Color code: C (*gray*), N (*blue*), O (*red*), H (*white*), B (*pink*), S (*yellow*), Mo (*cyan*), Cu (*brown*), Ni (*green*), Au (*orange*), Pt (*silver*), Ir (*light blue*)

[54, 63] and similar to the values obtained for metal-oxides [52, 64]. This linear scaling therefore suggests that the same descriptor based prediction of activity also holds for the 2D materials considered in this study. Interestingly, Fig. 1 also shows that there is a wide range of binding energies on the various materials, demonstrating the tunability of 2D materials. Thus, despite the wide variety of 2D materials, with different active sites and compositions, their scaling behavior is consistent with each other, and with the transition metals and metal oxides. This finding, however, also points to the fact that the herein studied 2D materials are unlikely to lead to major improvements in catalytic efficiency resulting from deviations from scaling relations.

Among all the investigated materials, we identify several 2D structures that have similar OH and OOH binding energies as Pt(111), and thus they are expected to be potential candidates for efficient ORR. These materials include the N-doped version of Stone Wales defect in graphene (N-doped 55–77), MoS₂, and *h*-BN/Cu(111) (Fig. 1). In fact *h*-BN/Cu(111) has been found to be a reasonably good catalysts for ORR [25], while NiO_x/Au(111) has been both experimentally and theoretically proven to be active for OER [61]. The performance of this latter catalyst has been also shown to improve considerably through a synergistic effect that arises from using cerium as a dopant and gold as a metal support [61].

In summary, we have studied a large number of 2D materials involving a diverse range of chemical and geometrical

structures and modifications, and showed that all the calculated adsorption energies follow the same scaling relations as established for transition metal surfaces. The existence of scaling relationships for these 2D materials suggests that the same simplifying assumptions used for predicting and evaluating new transition metal catalysts are also valid for this class of materials. Volcano-type analyses established for transition metals can thus be used for high-throughput screening of materials similar to those studied herein. Also important is the fact that the adsorption energies vary significantly depending on the type of active site, allowing for a wide range of possible activities, even within the same type of materials. For ORR some of the 2D-materials considered herein exhibit structures that provide adsorption energies similar to Pt, one of the best ORR catalysts. However, the fact that the scaling relations for 2D materials are identical to those of pure metals, suggest that scaling limitations will also inhibit further improvements in their potential catalytic activity.

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