Non-Monotonic Trends of Hydrogen Adsorption on Single Atom Doped g-C₃N₄

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Abstract: To estimate the reaction free energies of the hydrogen evolution reaction (HER) on under-coordinated metallic sites, density function theory (DFT) calculations are usually employed to calculate the hydrogen adsorption energy with an “only-one-hydrogen-adsorption” model, assuming that adsorption with one hydrogen is the most thermodynamically favorable situation during catalysis. In this brief report, we show that on many single atom sites, adsorption of more than one hydrogen is sometimes even more thermodynamically favorable, with the presence of two or three hydrogens resulting in lower adsorption energies. These interesting non-monotonic trends indicate that modeling HER and other hydrogen-related reactions on under-coordinated sites should also consider the numbers of hydrogen being adsorbed at the same site, otherwise the results could deviate from real experimental situations.

Keywords: hydrogen; non-monotonic trends; single atom; adsorption; catalysis; graphitic carbon nitride (g-C₃N₄)

1. Introduction

Under-coordinated materials have shown promising performance for catalysis, especially for the electrochemical reduction of carbon dioxide (CO₂) [1,2] and nitrogen (N₂) [3,4]. For CO₂ and N₂ electro-reductions, the hydrogen evolution reaction (HER) is a competing reaction [5,6]. To theoretically understand the activity and selectivity of the reactions, density functional theory (DFT) is a powerful quantum-mechanical computation method used to calculate the reaction energies of these reactions, showing good agreements with many catalytic systems [7–11]. A widely-accepted theory to explain the promising selectivity of CO₂ and N₂ electro-reductions at under-coordinated sites is that these under-coordinated sites adsorb hydrogen too strongly, leading to high up-hill energy that needs to be overcome during HER [4,6], which in turn, weakens the activity of this unwanted competing reaction.

Under-coordinated materials are one of the most commonly studied materials in science. During recent years, a large number of these materials and their various functions and applications have been reported [12–17]. To calculate the reaction free energies of HER on under-coordinated metallic sites, many previous studies have employed DFT to calculate the hydrogen adsorption energy with an “only-one-hydrogen-adsorption” model [18–22], assuming that adsorption with one hydrogen is the most thermodynamically favorable situation. However, in this brief report, we show that this sometimes under-estimates the binding strengths of the site-hydrogen interaction and that there could
be more thermodynamically favorable adsorption by adsorbing with more than one hydrogens at the same site.

During recent years, carbon-related nanomaterials has become popular due to their unique catalytic, mechanical, and electric properties [23–28]. In particular, carbon nitrite has shown interesting properties which enable it to form a thermodynamically-stable under-coordinated single-metal site for catalysis [29,30]. For this reason, using single atom transition elements (Ir, Os, Pd, Pt, Re, Rh, and Ru) doped on graphitic carbon nitrite (g-C₃N₄) [31] as a case study, we show that there are several non-monotonic trends that indicate stronger hydrogen adsorption energies happening with the presence of two or three hydrogens at one single atom catalytic site. These results suggest that when modeling HER on under-coordinated catalytic sites like a single atom, adsorption with more than one hydrogen should be carefully considered in order to avoid uncertainty in the theoretical conclusions. Better understanding of the HER mechanism is not only beneficial to N₂ and CO₂ reduction, but could also be beneficial in addressing the pressing challenges of hydrogen production and storage that the world faces [32–36].

2. Results and Discussion

Figure 1 shows the DFT-optimized structures of hydrogen adsorbed at a single atom site of a g-C₃N₄ structure, using Os as an example. It can be seen that for a transition metal element such as Os, more than one hydrogen were able to be adsorbed on a single atom site. This is consistent with the theoretical intuition that compared to orderly-packed surfaces, under-coordinated sites have stronger adsorption capacities that can accommodate more than one adsorbate on a catalytic site.

![Figure 1](image_url)

Figure 1. Hydrogen adsorption on an Os doped on g-C₃N₄. Brown, light blue, blue, and white spheres represent C, N, Os, and H, respectively.

To evaluate the hydrogen adsorption energies on single atom sites, Figure 2 shows the DFT-calculated hydrogen adsorption energies on seven types of single atom elements, with varying numbers (from one to four) of hydrogen adsorbed at the site. Interestingly, most of the studied transition metal elements show non-monotonic trends of hydrogen adsorption energy with the increasing number of adsorbed hydrogen. This surprising result is somewhat different from many previous conclusions that increasing the number of adsorbates on higher-coordinated surfaces (in other words, increasing the adsorbate coverage) monotonically weakens the calculated adsorption energy. It can be seen from Figure 2 that on many single atom elements like Ir, Os, Pd, Pt, and Ru, the (thermodynamically) most favorable number of adsorbed hydrogen is larger than one (as summarized in Table 1). Interestingly, these unusual trends show that most of these elements can favorably adsorb two hydrogens, except Ir (which favorably adsorbs three hydrogens), and Re and Rh (which favorably adsorb one hydrogen). Because the bond length usually correlates well with the adsorption energy [37], we also examined the potential correlation between the H-metal bond length and the calculated hydrogen adsorption energies. Table 1 summarizes the (average) bond lengths between H and the single atom element. Interestingly, no clear correlation can be found between the bond length and
adsorption trend. For example, adsorbing two hydrogens on Os should lead to the tightest adsorption (Figure 2), however, the average hydrogen-metal bond length on Os is unexpectedly shortened with the increased number of adsorbed hydrogen.

![Figure 2](image-url)

**Figure 2.** Hydrogen adsorption energy on a single atom doped on g-C$_3$N$_4$. The vertical black dashed line represents the optimal adsorption for hydrogen evolution ($-0.24$ eV).

**Table 1.** Optimized H-metal bond lengths (unit: Å) and the most thermodynamically favorable adsorbed hydrogen number on different single atom elements doped on g-C$_3$N$_4$.

<table>
<thead>
<tr>
<th>Element</th>
<th>H-Metal Bond Length (with 1H)</th>
<th>H-Metal Bond Length (with 2H)</th>
<th>H-Metal Bond Length (with 3H)</th>
<th>H-Metal Bond Length (with 4H)</th>
<th>Number of Favorable Adsorbed H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir</td>
<td>1.597</td>
<td>1.604</td>
<td>1.591</td>
<td>1.589</td>
<td>3</td>
</tr>
<tr>
<td>Os</td>
<td>1.660</td>
<td>1.648</td>
<td>1.636</td>
<td>1.627</td>
<td>2</td>
</tr>
<tr>
<td>Pd</td>
<td>1.571</td>
<td>1.552</td>
<td>1.653</td>
<td>1.689</td>
<td>2</td>
</tr>
<tr>
<td>Pt</td>
<td>1.575</td>
<td>1.563</td>
<td>1.595</td>
<td>1.596</td>
<td>2</td>
</tr>
<tr>
<td>Re</td>
<td>1.736</td>
<td>1.700</td>
<td>1.641</td>
<td>1.670</td>
<td>1</td>
</tr>
<tr>
<td>Rh</td>
<td>1.585</td>
<td>1.579</td>
<td>1.631</td>
<td>1.613</td>
<td>1</td>
</tr>
<tr>
<td>Ru</td>
<td>1.631</td>
<td>1.620</td>
<td>1.615</td>
<td>1.641</td>
<td>2</td>
</tr>
</tbody>
</table>

* These are the average bond length values

To evaluate the theoretical HER activity with the results shown in Figure 2, we used the famous catalytic model developed by Nørskov et al. to estimate the HER free energy ($G_H$) with zero-point energy and entropic corrections by $G_H = E_{Adv} + 0.24$ eV. The volcano-like activity plot for HER was developed using the adsorption energy of hydrogen as the reaction descriptor, showing excellent agreement with previous experiments [38]. The free energy values higher or lower than zero would lead to an additional barrier that should be overcome during the reaction. Therefore, $G_H = 0.00$ eV (or $E_{Adv} = -0.24$ eV) represents the theoretically optimal HER activity (Figure 2, black dashed line) [39]. It can be clearly seen that the theoretical conclusions on the HER activity are significantly different from these single atom elements with adsorbing more than one hydrogen. For example, while a doped single Ru looks promising for HER when adsorbed with only one hydrogen, its more favorable hydrogen adsorption mode makes it less favorable for HER (Figure 2, light green). These results indicate that in studying HER on under-coordinated catalytic sites (like the single atom), an only-one-hydrogen-adsorption model (which is the model commonly used in previous theoretical calculations) might not be adequate for evaluating real experimental situations. Also, it is worth noting that developing an adsorption phase diagram can be a rational strategy for evaluating competing adsorption among multiple adsorbates with varying chemical potential and pressure and for understanding the selectivity of the reaction.
that is completed by HER [40,41]. Experimentally, multiple HER active sites might be detected using state-of-the-art techniques [42,43], since the polycondensation reaction could be terminated at the intermediate step with a non-negligible hydrogen content, as indicated from previous combined theoretical and experimental studies [44,45]. Nevertheless, since this brief report mainly discusses the unusual hydrogen adsorption trends, we do not include further results on the g-C$_3$N$_4$ substrate.

Interestingly, a recent study published by Jiang et al. [38] also found a similar non-monotonic trend for hydrogen adsorption on ligand-capped Au$_{22}$ nanocluster system. Similarly, they found that adsorbing two hydrogens could lead to the most thermodynamically favorable adsorption configuration. Behaving like hydride, the electron of hydrogen was found to be delocalized into the system, therefore, the free electron count was found to be a plausible explanation for such an unusual adsorption trend [38]. Although our study investigated very different systems, we expect that this could also be a plausible explanation for the discovered non-monotonic trends.

3. Methods

All the ab initio calculations performed to calculate hydrogen adsorption used the Vienna ab initio simulation package (VASP) [46]. A generalized-gradient approximation method with Perdew–Burke–Ernzerhof functionals was employed for electron exchange and correlation [47,48], with the kinetic energy cutoff of 400 eV. Electron-core interactions were described via a projector-augmented wave method [49]. Kohn–Sham orbitals were used and expanded on a plane-wave basis [50]. All the adsorption geometries were considered optimized after all the forces were lower than 0.05 eV/Å. The Brillouin zone was sampled by a $(3 \times 3 \times 1)$ $k$-point mesh [51].

The element-doped g-C$_3$N$_4$ models were modeled as a single atom element X (X = Ir, Os, Pd, Pt, Re, Rh, and Ru) bound with the nitrogen of a one-layer g-C$_3$N$_4$. For each doping element, the doping was modeled as having the three nitrogen pointing towards the transition metal ion with equal N-metal distances. Interestingly, after relaxing most of the geometries, the element X clearly coordinates with three nitrogen, with one of the nitrogen being “pressed down” and the other two are still in the 2-D plane. All these optimized geometries (in the form of POSCAR) can be found in the Supplementary Materials. To evaluate the hydrogen adsorption on these single atoms, different numbers of hydrogen (from one to four) were modeled to be adsorbed on the metal sites. The hydrogen adsorption energies $E\text{Ads}$ were calculated using the energy of the H$_2$ molecule in vacuum as the reference:

$$E\text{Ads} = \left( E\text{Total} - E\text{Bare} - \frac{n}{2} E\text{H}_2 \right) / n,$$

where $E\text{Total}$ is the total energy of the adsorption system, $E\text{Bare}$ is the total energy of the system without adsorbed hydrogen, $E\text{H}_2$ is the total energy of a H$_2$ molecule in vacuum, and $n$ is the number of the adsorbed hydrogen (from one to four).

4. Conclusions

In this brief report, we have shown the interesting non-monotonic trends of hydrogen adsorption on under-coordinated transition metals. Using the single atom model (Ir, Os, Pd, Pt, Re, Rh, and Ru) doped on g-C$_3$N$_4$ as an example, we have shown that on many of these elements, adsorbing more than one hydrogen results in more thermodynamically favorable energies. These counterintuitive results indicate that theoretical catalytic modeling could be more reliable if they consider the favorable numbers of adsorbate on the under-coordinated sites. Given that these trends are not fully correlated with the well-known $d$-band theory [52], future studies on understanding these non-monotonic trends (e.g., spin density variation and spin multiplicity) would be valuable to physically explain the origins of these adsorption trends found from DFT. We expect that this study could also be valuable for many HER-related applications such as CO$_2$ and N$_2$ capture and utilization [5,53]. Also, it is expected that similar trends could be found in other reactions (e.g., oxygen reduction [54–57], oxygen
evolution [58], and organic oxidation [59–61]) and in various types of advanced under-coordinated material systems [62–71].

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4344/9/1/84/s1, important coordinates used for DFT calculations.

**Author Contributions:** All the authors participated in the research and writing of this study. The majority of this work was done before H.L. left Sichuan University. Both H.L. and Z.Z. came up with the original idea together and did the majority of this work in the year of 2014. Z.L. participated in the important additional calculations in this manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

**Nomenclature**

- g-C$_3$N$_4$: graphitic carbon nitrite
- HER: hydrogen evolution reaction
- H: Hydrogen
- C: Carbon
- O: Oxygen
- Ir: Iridium
- Os: Osmium
- Pd: Palladium
- Pt: Platinum
- Re: Rhenium
- Rh: Rhodium
- Ru: Ruthenium
- $E_{\text{Ads}}$: adsorption energy, eV
- $E_{\text{Tot}}$: total energy of the adsorption system, eV
- $E_{\text{Bare}}$: total energy of the bare system, eV
- $E_{\text{H}_2}$: total energy of a hydrogen molecule in vacuum, eV
- n: number of adsorbed hydrogens
- $G_{\text{H}}$: reaction free energy of hydrogen evolution reaction, eV

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