Enhancing the Hydrogen Activation Reactivity of Nonprecious Metal Substrates via Confined Catalysis Underneath Graphene

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ABSTRACT: In the hydrogen evolution reaction (HER), the reactivity as a function of the hydrogen adsorption energy on different metal substrates follows a well-known volcano curve, peaked at the precious metal Pt. The goal of turning nonprecious metals into efficient catalysts for HER and other important chemical reactions is a fundamental challenge; it is also of technological significance. Here, we present results toward achieving this goal by exploiting the synergistic power of marginal catalysis and confined catalysis. Using density functional theory calculations, we first show that the volcano curve stays qualitatively intact when van der Waals attractions between a hydrogen adatom and different metal (111) surfaces are included. We further show that the hydrogen adsorption energy on the metal surfaces is weakened by 0.12–0.23 eV when hydrogen is confined between graphene and the metal surfaces, with Ni exhibiting the largest change. In particular, we find that the graphene-modified volcano curve peaks around Ni, whose bare surface already possesses moderate (or marginal) reactivity, and the corresponding HER rate of graphene-covered Ni is comparable to that of bare Pt. A hydrogen adatom has high mobility within the confined geometry. These findings demonstrate that graphene-covered Ni is an appealing effective, stable, and economical catalytic platform for HER.

KEYWORDS: density functional calculations, heterogeneous catalysis, hydrogen evolution reaction, confined catalysis, graphene

H
drogen is an ideal fuel with zero emission of pollutants or greenhouse gases. The hydrogen evolution reaction (HER) using metal catalysts is an efficient way to produce hydrogen; in this reaction, protons from solution combine with electrons at metal electrodes to form atomic H and then combine with each other to become H₂ via associative desorption. The ability of a given metal to catalyze HER is usually measured experimentally by the exchange current density, iₜ. In the Tafel equation, iₜ is defined as the current at zero overpotential, which is the rate of hydrogen evolution per surface area of the electrode when the electrode potential is at equilibrium of the reaction. In a seminal study, it was pointed out that the measured exchange current as a function of the calculated hydrogen adsorption energy (ΔEₜ) follows a volcano-shaped curve, peaked at the precious metal Pt. Furthermore, the adsorption free energy of hydrogen (ΔGₜ) was identified as a good descriptor for HER, based on the fact that the binding between a H adatom and the metal surface cannot be too strong or too weak for the reaction to proceed. If the binding is too strong, the chemisorbed H will poison the catalytic surface against sustainable reactivity; if the binding is too weak, hydrogen will not be readily captured from its dissolved phase by the catalyst. Among the various conceptual approaches for catalyst design, confined catalysis is attracting increasing attention. In the present work, confined catalysis refers to a situation where confinement of the whole or parts of the catalyst, reactants, and products in a restricted space, enhances the reactivity due to modification of the relevant electronic states by the boundary conditions. In particular, the discoveries of an ever-increasing number of different classes of two-dimensional (2D) materials offer new opportunities for optimizing confined catalysis, as demonstrated experimentally for CO oxidation in the confined geometry formed by a layer of graphene or hexagonal boron nitride on Pt(111). Confined catalysis using 2D materials has the added advantage that typically the 2D overlayer is highly

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selective in its permeability, allowing small atoms and molecules to permeate while blocking other undesirable species that are likely to poison the catalyst.

In these areas and more broadly in surface chemistry, a fundamental challenge is how to convert nonprecious metals or materials into efficient catalysts for reactions of industrial significance. Given the recent advances in confined catalysis, it is particularly intriguing to explore whether the proper choice of a 2D overlayer would be able to convert a nonprecious metal into an effective catalyst for important chemical reactions such as HER or CO oxidation. Toward this goal, we exploit the concept of marginal catalysis, that is, a catalyst with moderate reactivity becoming more reactive through controlled variations of the reaction conditions or environments. In what concerns HER, nonprecious metal candidates for marginal catalysts are those located close to the peak of the volcano curve. As a compelling example, a recent study has shown that Ti-doping turns Al into a noble-metal-like catalyst for low-temperature activation of molecular hydrogen.14

In this Letter, we investigate the catalytic performance of graphene-covered metals for HER, using density functional theory (DFT) calculations. We explore several representative transition and noble metals, including Ni, Pd, Rh, Pt, Cu, Au, and Ag. We first revisit the previously established volcano curve of HER on metal (111) surfaces by including van der Waals (vdW) corrections, which are now readily available in computational modules. We confirm that the volcano curve is qualitatively unchanged when we include vdW interactions, a natural contribution to the energy, between the H adatom and the metal substrates. Next, we calculate the adsorption free energies of hydrogen at the interfaces between a graphene layer and the metal substrates. We find that the graphene layer generally weakens the H binding energy by different amounts for different metals, thereby introducing significant variations in the expected volcano curve. In particular, the Ni surface, which exhibits moderate HER rate in bare form, shifts to be close to the peak of the graphene-modified volcano curve. We also confirm that the high mobility of H on bare Ni(111) is largely preserved in the confined geometry, a necessary requirement in the proposed reaction scheme. These findings show that graphene-covered Ni is an effective, stable, and economical catalytic platform for HER.

For the DFT calculations, we used the Vienna ab initio simulation package (VASP)15 with the projector-augmented wave (PAW) pseudopotentials16,17 and the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE)18 to treat the exchange-correlation potential of electrons. For the vdW corrections, we used the DFT-D2 method,19,20 which has been shown to yield a reasonable description of the graphene/metal (Gr/M) interactions.21,22 We chose a cutoff energy of 400 eV to expand the electron wave functions in a plane-wave basis set and a \( \sqrt{7 \times 7 \times 1} \) Monkhorst–Pack k-point grid23 to achieve sufficient accuracy in the total energy. We obtained the lattice constants of the metals and monolayer graphene via structural optimization. We modeled the metal substrates by slabs of five atomic layers, with the bottom two layers fixed in their respective bulk positions and all the other atoms fully relaxed until the forces on each atom were smaller in magnitude than 0.01 eV/Å. We modeled the Gr/M system by placing a monolayer of graphene on top of the metal surface, with the lattice of graphene adjusted to match that of the metal. We used a vacuum region of more than 16 Å to eliminate the couplings between neighboring slabs. In the present study, all the calculations were spin polarized. We used the climbing image nudged elastic band (CI-NEB) method24 to determine the potential energy barriers of the hydrogen diffusion processes, with five intermediate images constructed along each pathway, and performed proper convergence tests to ensure that the central findings are robust.

In order to minimize the lattice mismatch between graphene and metals, we adjusted the lattice constant of a \((2 \times 2)\) supercell of graphene to match that of a \((2 \times 2)\) supercell for Ni and Cu, or a \((\sqrt{3} \times \sqrt{3})\) supercell for Pd, Rh, Pt, Au, and Ag25,26 as illustrated in Figure 1. This treatment ensures that the hydrogen coverages per surface area are essentially equivalent for each investigated system. The range of the lattice mismatch between graphene and metal substrates is 0.0—5.4%. The most stable contact geometries were obtained by structural optimization of many different initial configurations. For Cu(111) and Ni(111) surfaces, the carbon atoms in graphene are located at the atop and hollow sites of the metal substrates, whereas for the rest of the metals, the atop and bridge sites are preferred. To find the most stable adsorption site of H on each metal substrate in the absence or in the presence of a graphene layer, we consider different high-symmetry positions, including the fcc hollow, hcp hollow, atop, and bridge sites of the metal substrate. The hydrogen adsorption energy on a bare metal is defined by

\[
\Delta E_H = E(\text{metal} + H) - E(\text{metal}) - \frac{1}{2}E(H_2)
\]

(1)

where \(E(\text{metal}+H)\) and \(E(\text{metal})\) are the total energies of metal plus a H adatom and bare metal, respectively, and \(E(H_2)\) is the total energy of a hydrogen molecule in the gas phase. Here, we have taken the limit of low hydrogen coverage, with only one H adatom in the supercell system. However, the volcano curve is not expected to change when higher coverages are considered.2

The corresponding adsorption free energy is calculated as

\[
\Delta G_{H^*} = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H = \Delta E_H + 0.24 \text{ eV}
\]

(2)

where \(T\) is the surface temperature, \(\Delta E_{ZPE}\) is the difference in zero point energy of hydrogen vibration between the adsorbed state and gas phase, and \(\Delta S_H\) is a measure of the corresponding
entropy change, with $\Delta E_{\text{ZPE}} - T\Delta S_H = 0.24 \text{ eV}$ at $T = 300 \text{ K}$, a reasonable, well established approximation. When the metal surface is covered by a graphene layer, eq 1 is modified to

$$\Delta E_{\text{H}/Gr} = E(\text{Gr/metal + H}) - E(\text{Gr/metal}) - \frac{1}{2}E(H_2)$$

and the corresponding adsorption free energy in the presence of the graphene overlayer is calculated as

$$\Delta G_{\text{H}/Gr} = \Delta E_{\text{H}/Gr} + \Delta E_{\text{ZPE}} - T\Delta S_H = \Delta E_{\text{H}/Gr} + 0.24 \text{ eV}$$

(4)

In the present study, we first calculate the hydrogen adsorption energy on different bare metal (111) surfaces with and without vdW interactions, and the corresponding $\Delta G_{\text{H}/Gr}$, shown in Figure 2a and b, respectively. The vdW corrections generally enhance the binding between H and metal, and the overall volcano curve is shifted to the left in the $\Delta G_{\text{H}/Gr}$ scale, with the new peak still located at the most reactive metal Pt ($\Delta G_{\text{H}/Gr} = -0.21 \text{ eV}$) as established experimentally. The values of the exchange current density $i_0$ are from the experimental data, and the fitted relationship between log $i_0$ and $\Delta G_{\text{H}/Gr}$ can now be described as

$$i_0 \propto \exp(-|\Delta G_{\text{H}/Gr} - (-0.21 \text{ eV})|/kT)$$

(5)

where $k$ is the Boltzmann constant and the peak is positioned at Pt. Clearly, the classic volcano curve stays qualitatively intact when the vdW interactions are included. In particular, the relative locations of the different metals are essentially unaffected.

Next, we explore the HER reactivity of each metal covered by a layer of graphene, with the H adatom confined at the interface of the Gr/M system. The adsorption free energies $\Delta G_{\text{H}/Gr}$ in the Gr/M structures are shown in Figure 2c. Generally, the graphene overlayer weakens the adsorption free energy of hydrogen on the metal surfaces by about $0.12-0.23 \text{ eV}$, with Ni showing the largest shift to the right in the $\Delta G_{\text{H}/Gr}$ scale, changing its relative location with respect to its neighbors. The hydrogen adsorption free energies in the Gr/M systems show pronounced differences from those in Figure 2b, strongly indicating that the Gr/M systems will possess distinctly different HER rates from the bare metal systems.

Experimental values of HER rates for the Gr/M systems are not available, and we expect that the HER rates are predominantly determined by the $\Delta G_{\text{H}/Gr}$ values. We use the established volcano curve shown in Figure 2b for the bare metal systems to estimate the exchange current densities in the Gr/M systems, with the optimal adsorption free energy of H and the prefactor approximately unchanged. Such approximations are reasonable, because (a) the graphene cover is unlikely to change the fundamental qualitative nature of the HER mechanism on the metal surface, leading to the optimal adsorption free energy of H essentially unchanged; (b) the HER rate depends less sensitively on the prefactor, whose influence by graphene is even further limited due to the much stronger interaction of H with metal than with graphene. The results are shown in Figure 2c. The Gr/M systems with M = Ni, Pd, and Rh are located near the peak of the volcano curve, that is, highly reactive for HER, with comparable exchange current densities. We expect the absolute values of the peaked HER rates for Gr/Ni, Gr/Pd, and Gr/Rh to be comparable to that of bare Pt, which is no longer the most reactive substrate for HER underneath a graphene overlayer. Among these three candidates, Ni is the only nonprecious metal, thereby fulfilling our goal of finding an efficient and nonprecious-metal catalyst for HER by exploiting the synergistic power of marginal

![Figure 2](image-url)

**Figure 2.** Fitted volcano-shaped dependence of log($i_0$) in HER on the calculated adsorption free energy of hydrogen on different catalytic metal (111) surfaces (a) without and (b) with vdW corrections, respectively. The volcano curve in (c) indicates the anticipated HER rates when the H adatom is confined underneath a graphene layer. A schematic view of the system considered is shown on the right of each curve. It is notable that the log($i_0$) data in the top two subfigures are from experimental measurement, while that in the bottom are from theoretical prediction.

<table>
<thead>
<tr>
<th>Table 1. Structural and Energetic Parameters for the Bare Metals and Gr/M Systems$^a$</th>
<th>Ni</th>
<th>Pd</th>
<th>Rh</th>
<th>Pt</th>
<th>Cu</th>
<th>Au</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{\text{Gr-metal}}$ w/o H (Å)</td>
<td>2.14</td>
<td>2.96</td>
<td>3.05</td>
<td>3.07</td>
<td>2.98</td>
<td>3.14</td>
<td>3.07</td>
</tr>
<tr>
<td>$d_{\text{Gr-metal}}$ w/ H (Å)</td>
<td>3.14</td>
<td>3.13</td>
<td>3.23</td>
<td>3.20</td>
<td>3.21</td>
<td>3.22</td>
<td>3.25</td>
</tr>
<tr>
<td>$\Delta G_{\text{H}/Gr} - \Delta G_{\text{H}/H}$ (eV)</td>
<td>0.23</td>
<td>0.13</td>
<td>0.13</td>
<td>0.14</td>
<td>0.13</td>
<td>0.19</td>
<td>0.12</td>
</tr>
<tr>
<td>$\Delta E_{\text{H}/M}$ (eV)</td>
<td>0.16</td>
<td>0.04</td>
<td>0.04</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>$\Delta E_{\text{H}/M}$ (eV)</td>
<td>0.07</td>
<td>0.09</td>
<td>0.09</td>
<td>0.12</td>
<td>0.10</td>
<td>0.17</td>
<td>0.09</td>
</tr>
</tbody>
</table>

$a$ $d_{\text{Gr-metal}}$ w/o H is the distance between graphene and metals without H at the interfaces; $d_{\text{Gr-metal}}$ w/ H is the distance between graphene and metals with H at the interfaces; $\Delta G_{\text{H}/Gr} - \Delta G_{\text{H}/H}$ is the difference between the hydrogen adsorption free energies without and with a graphene overlayer, which can be decomposed into the changes in Gr/M interactions ($\Delta E_{\text{Gr/M}}$) and those in M/H interactions ($\Delta E_{\text{H/M}}$).
catalysis and confined catalysis. We also note that Ni will stay as the only most reactive nonprecious metal for HER even if the $\Delta G^\circ_{\text{H}}$ value for the maximal rate deviates by $\sim \pm 0.1$ eV from the experimentally determined value of $-0.21$ eV for bare metals (Figure 2b). These analyses collectively characterize the Gr/Ni system as an appealing effective and economical catalytic platform for HER.

In the following, we examine the underlying mechanisms for the weakened adsorption of hydrogen in the Gr/M systems. First, the weakened adsorption of H at the Gr/M interface is partly due to the energy penalty caused by lifting the graphene overlayer to establish enough space for the adsorbed H. Table 1 shows that the vertical distance between a carbon atom in the graphene overlayer and the top layer of a given metal substrate, $d_{\text{Gr-metal}}$, is increased when a H adatom is trapped at the interface. The vertical distances are in the range of 3.13–3.25 Å when H is present at the Gr/M interface, and the changes in this distance from the structures without H range from 0.08 to 1.00 Å. In particular, because of the stronger attraction between graphene and Ni, the distance between graphene and Ni without H adsorption is much shorter than the other systems, and the distance increase between graphene and Ni due to H adsorption is much larger (1.00 Å). Accordingly, the change in the Gr/M interaction of the Gr/Ni system (0.16 eV) is also the largest among all the Gr/M systems considered (Table 1).

Second, the chemical binding between hydrogen and the metal surface is also weakened by the graphene overlayer, which can be illustrated through detailed structure and charge density analysis. The essence of a catalytic process is that a catalyst assists the bond breaking or formation involved in a chemical reaction during which the changes in the electrostatic force and sharing or transfer of electrons associated with the presence of the catalyst play an important role. Although we find that the interaction between graphene and H is quite weak (H is separated from graphene by 2.29 Å) in the Gr/H/Ni system, the graphene overlayer alters the interaction between H and the underlying metal surface. Figure 3a shows the adsorption configuration and charge density difference of H on Ni(111), calculated by the total charge density of H on Ni(111) subtracting the charge density of the isolated hydrogen atom and that of the bare Ni(111) substrate. Figure 3b shows the corresponding structure and charge density difference of H in Gr/Ni. In both cases, electrons are found to transfer from the H adatom to the first-layer Ni. By comparing the most stable adsorption structures of H with and without graphene, we observe that the presence of graphene changes H from the fcc site (favored in H/Ni) to the originally unfavorable hcp site (favored in Gr/H/Ni). Furthermore, we notice that graphene pushes H to be closer to Ni by about 0.07 Å, a structural change also reflected in the slightly more significant charge depletion around H in Figure 3b. The closer contact between H and Ni increases their mutual overlap of electron clouds, resulting in the enhanced repulsion part of the interaction. Additionally, we find that the nature of the weakened H–metal bond by graphene is generic for all the metals investigated here.

The volcano curve in HER suggests that the interaction between the H adatom and a metal catalyst has to be optimal for achieving high reactivity, that is, this interaction cannot be too strong or too weak. Hydrogen is quite strongly adsorbed on the bare Ni surface with adsorption energy $-0.41$ eV (relative to a H molecule in the gas phase), a value reduced to $-0.18$ eV in graphene-covered Ni. As a consequence, the interplay between graphene, hydrogen, and Ni interactions leads to the optimization of hydrogen adsorption, rendering the composite Gr/Ni system an effective nonprecious-metal catalyst for HER. Here we note that within the framework of the volcano curve, we have implicitly assumed that the Tafel mechanism is the dominant mechanism for H2 production under the graphene cover. This assumption is made more valid because larger reaction intermediates favoring other production mechanisms are more difficult to penetrate into the confined space between graphene and metal.

In addition to the beneficial modifications that an overlayer graphene produces on the relevant HER processes, another significant advantage is the protection of the highly reactive catalytic metal surfaces from being poisoned by other atomic or molecular species present in the environment. As a related matter, likely poisoning effects of graphene on metal catalysts have also been considered in previous studies, due to its chemical inertness and physical blockage. However, structural imperfections in graphene, including island edges, grain boundaries, and wrinkles are inevitable during growth or transfer processes. These imperfect structures provide fast channels for the diffusion of molecules into the Gr/M interfaces, which is a prerequisite for confined catalysis to occur. Furthermore, a recent experimental study reported that small atoms and molecules such as protons can easily penetrate through the one-atom-thick graphene, making the Gr/M systems permeable for potential HER processes. Our detailed calculations also indicate that hydrogen adsorption at the subsurface sites of Gr/Ni is energetically less stable than that at the interface by 0.62 eV per H. Therefore, H strongly prefers to stay at the interface rather than to diffuse into the subsurface or bulk sites. Given these considerations, an important issue in considering the Gr/Ni catalyst for HER is whether hydrogen atoms can diffuse rapidly at the Gr/Ni interface. To address this question, we calculate the diffusion barriers of a H adatom on the bare Ni surface and at the Gr/Ni interface. The results are shown in Figure 4, where the H adatom moves between an hcp hollow and an fcc hollow site. The diffusion barrier is 0.15 eV on the bare Ni surface and 0.20 eV at the Gr/Ni interface, respectively, slightly increased by the graphene overlayer. By closely examining the detailed structures, we observe that the graphene overlayer pushes the H atom toward Ni by about 0.07 Å at the hcp and fcc sites while pulling it away from the surface by about 0.04 Å at the saddle point of the diffusion. Such variations of the H vertical positions are caused by the confinement effect and the potential energy surface overlap.
Because the graphene overlayer is impermeable to H under the graphene overlayer. The fast diffusion of H through the smaller atomic radius of H atom. The state with two H2 fast to the active sites for rapid H2 formation and desorption. We demonstrated that a H adatom has a very small binding energy, which is reasonable given the atomic level of C at the Gr/Ni interface, which is reasonable given the smaller atomic radius of H atom. Therefore, predict that the condensed phase transition barrier in the presence of graphene. In a recent study, we have shown fast diffusion of carbon atoms at the interfaces of Gr/Cu(111) and of Gr/Ni(111), thereby facilitating catalytic growth of the second-layer graphene underneath the first layer. Here, we find that H diffuses even faster than C at the Gr/Ni interface, which is reasonable given the smaller atomic radius of C atom. The state with two individually adsorbed H atoms is energetically more stable than H2 underneath the graphene overlayer. The fast diffusion of H thus enables a continuous H supply around the structurally imperfect sites of graphene, where the H–H coupling and subsequent H2 desorption occurs more efficiently. Collectively, H ions are able to penetrate into the confined region, and the activated H atoms underneath graphene are also able to diffuse fast to the active sites for rapid H2 formation and desorption. Because the graphene overlayer is impermeable to H2 molecules, the structural imperfections that exist inevitably and usually abundantly in graphene are the active sites for H2 desorption.

In the field of surface catalysis, novel catalysts are structurally designed and modified from their elemental materials in many different ways, such as alloying and coating, to enhance their catalytic performance for desirable reactions. In most situations, the reaction mechanisms need to be unaffected upon the structural change of the elemental catalyst, which means that the tuning capacity of catalysis is generally quite limited. Therefore, in the design of new catalysts, the elemental materials should be selected among those showing at least some noticeable (or marginal) catalysis. As demonstrated in our present case study, because the reaction rate depends exponentially on the adsorption energy, a relatively moderate tuning of the adsorption strength by the graphene overlayer is able to turn Ni (with marginal catalysis) into a highly reactive catalyst for HER.

To conclude, our systematic study has identified the graphene-covered Ni surface as an effective nonprecious-metal catalyst for HER. The graphene overlayer weakens the adsorption free energy of a H adatom on the metal surface, shifting Ni to be close to the peak of the volcano curve for HER. We demonstrated that a H adatom has a very small diffusion barrier at the interface of the Gr/Ni system. We therefore predict that the confined space between the Ni(111) surface and graphene overlayer will have high catalytic performance for HER. The present study introduces an appealing new catalytic system to produce hydrogen, which we expect to stimulate experimental validations and promote related technological developments in green energy. The approach to tune the reactivity of metal catalysts using graphene could also be applicable by using transition metal dichalcogenides (TMDs) or other 2D materials. In particular, it has been shown that enhanced H binding can be achieved on top of a MoS2 overlayer adsorbed on different metal substrates, favoring enhanced HER processes. It would be interesting to examine how the corresponding HER rates will change underneath such a TMD overlayer and to investigate whether a different nonprecious metal could be tuned to be most reactive for HER in that case.

### References


