Theoretical insights into the electroreduction mechanism of \( \text{N}_2 \) to \( \text{NH}_3 \) from an improved \( \text{Au(111)}/\text{H}_2\text{O} \) interface model†

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An improved H coverage-dependent \( \text{Au(111)}/\text{H}_2\text{O} \) electrochemical interface model is proposed in this paper, which is firstly used to study electroreduction mechanisms of \( \text{N}_2 \) into \( \text{NH}_3 \) at the thermodynamical equilibrium potential in cooperation with electronic structure analysis. The results show that the associative mechanism is more favorable on \( \text{Au(111)} \) and therein alternating and distal pathways may be able to parallelly occur in gas phase and the present simulated electrochemical interface. The initial \( \text{N}_2 \) reduction into the \( \text{N}_2\text{H} \) intermediate is the rate determining step, which may be able to be regarded as the origin of the observed experimentally high overpotential during \( \text{N}_2 \) electroreduction. The presence of an electrochemical environment can significantly change the \( \text{N}_2 \) reduction pathway and decrease the barrier of the rate determining step, which can be ascribed to the significant electron accumulation and interaction between \( \text{N}_2 \) molecules and \( \text{H}_2\text{O} \) clusters. The theoretical results display excellent consistency with the available experimental data, confirming the rationality of the present proposed electrochemical model. The comparison of the barrier between the hydrogen evolution reaction and rate determining step well explains why the activity of \( \text{Au} \) electrodes is usually unsatisfactory. Accordingly, a single descriptor can be proposed, in which an ideal electrocatalyst should be able to reduce the barrier for initial \( \text{N}_2 \) electroreduction into \( \text{N}_2\text{H} \). In this way, \( \text{N}_2 \) electroreduction pathways can be facilitated and the yield of \( \text{NH}_3 \) can be enhanced. We believe that the present study can represent progress to study \( \text{N}_2 \) electroreduction mechanisms from an improved electrochemical model.

1. Introduction

\( \text{NH}_3 \) as a promising carbon-free alternative energy carrier can be employed in fertilizers, production of important chemicals, \( \text{NH}_3 \) fuel cells and indirectly hydrogen fuel cells.\(^*\) At present, \( \text{NH}_3 \) is synthesized primarily by reaction of \( \text{N}_2 \) with \( \text{H}_2 \) on an \( \text{Fe}/\text{Ru} \)-based catalyst through the industrial Haber–Bosch (HB) process under harsh conditions such as high temperatures and pressures,\(^*\) which is an energy intensive chemical process and consumes ca. 2% of annual global energy because of the stability and chemical inertness of \( \text{N}_2 \) molecule.\(^*\) By contrast, the electrochemical reduction of \( \text{N}_2 \) into \( \text{NH}_3 \) with proton and electron transfer in an aqueous environment is more energy efficient and attracts extensive interest in recent years since it can be operated at ambient conditions and powered by renewable electricity.\(^*\)† Unfortunately, the required large overpotential and competing hydrogen evolution reaction lead to low faradaic efficiency and poor selectivity for \( \text{N}_2 \) electroreduction into \( \text{NH}_3 \) on most electrocatalysts, thus impeding its practical applications.\(^*\) The poor activity of the cathode electrocatalyst may put a major limitation on production of \( \text{NH}_3 \) product in significant yields at ambient conditions. To achieve the rational design of more selective and active electrocatalysts, the system understanding on electroreduction mechanism of \( \text{N}_2 \) into \( \text{NH}_3 \) is extremely urgent and essential.

Although tremendous efforts in recent years, \( \text{N}_2 \) electroreduction mechanism remains elusive. The present most studies on \( \text{N}_2 \) electroreduction reaction primarily focus on the synthesis of electrocatalysts including metals such as \( \text{Pt}, \text{Ru}, \text{Fe}, \text{Au}, \text{Pd}, \text{Rh}, \text{Fe}, \text{Ni}, \text{Mo} \) and \( \text{Bi},\) alloys such as \( \text{Pt–Ru},\) metal nitrides and sulfides,\(^*\) and carbon-based materials.\(^*\) However, these reported electrocatalysts suffer from low \( \text{NH}_3 \) faradaic efficiency and \( \text{N}_2 \) electroreduction reaction is still plagued. Based on these previous studies, the development of more active and selective electrocatalysts is highly desired but remains challenging. Study of \( \text{N}_2 \) electroreduction reaction mechanism will help design electrocatalysts with high activity and selectivity. In the most recent reviews from Shao et al. and
Zhang et al.,15,40 N₂ electroreduction mechanisms and reaction intermediates that obtained in experiments by various spectroscopy techniques are summarized. Currently, it is generally accepted that there are two main reaction mechanisms for N₂ electroreduction into NH₃, namely, dissociative pathways and associative pathways. N≡N bond in N₂ molecule is broken to form N atoms on electrocatalyst surface before hydrogenation in dissociative mechanism, whereas the hydrogenation of N₂ molecule occurs before N≡N bond is broken in associative mechanism. It is currently believed that the dissociative mechanism is dominant in the HB process of N₂ reduction into NH₃.15,41 An associative distal or alternating mechanism may be followed during N₂ electroreduction into NH₃ through experimental identification of some intermediates. For example, using surface-enhanced infrared absorption spectroscopy, Shao et al., studied for the first time N₂ electrochemical reduction reaction mechanism on Au thin film, in which the adsorbed NₓHᵧ (1 ≤ y ≤ 4) species was detected at potentials below 0 V (vs. RHE),43 thus indicating that N₂ electroreduction may follow the associative alternating and distal mechanisms on Au surface. Combining surface-enhanced infrared absorption spectroscopy with electrochemical measurements, the adsorbed NₓHᵧ (0 ≤ x ≤ 2) species was detected at potentials below 0.2 V (vs. RHE) on Ru thin film in the subsequent study from Shao et al., and notably increased coverage of NₓHᵧ was observed as the potential decreasing from 0.2 to −0.4 V, thus the associative distal mechanism may be able be concluded.43 By performing isotope-labelled experiments, Yin et al., found only a trace amount of NₓHᵧ intermediate during N₂ electroreduction on bismuth surface, suggesting that associative distal mechanism may be more favorable.43 Despite of understanding of N₂ electroreduction reaction mechanism is of importance for rationally designing more efficient electrocatalysts, the experimental studies are very rare at present in this area since low selectivity makes experimental determination of mechanism rather difficult.

Because of the experimental limitations to identify intermediates and complexity of N₂ electroreduction process involving 6 elementary reaction steps, theoretical calculations have become a powerful tool for studying electrocatalytic reactions by employing density functional theory (DFT).43–44 DFT calculations can give mechanistic information that is not accessible based on experiments alone and identify favored reaction intermediates. Theoretical work by Skulason et al. and Montoya et al. thermodynamically indicated that the associative distal mechanism would be more favorable since more positive reaction free energies are expected for the associative alternating mechanism by combining DFT calculations with the computational hydrogen electrode model.15,45 Their findings had shown that the potential limiting step is N₂ reductive protonation to the adsorbed NₓHᵧ species on the transition metal surface with relatively weak N adsorption such as Pt, Pd, Ag, Au, Ni, Co and Ru during N₂ electroreduction into NH₃, whereas the potential limiting step is determined by the protonation of the adsorbed NH into NH₂ species for more reactive transition metals, such as Mo. On the basis of DFT-based computational hydrogen electrode model, the electrocatalytic activity of various binary transition metals are systematically examined in recent theoretical work from Zhao et al.,46 and the binary FeRh catalyst was thought to have the optimal catalytic performance due to its lowest limiting potential and best suppressing effect on hydrogen evolution reaction during N₂ electroreduction reaction. Furthermore, their study indicated that N₂ reduction reaction prefers to proceed through associative distal mechanisms than alternating pathways on the FeRh catalyst. These above theoretical studies assumed that activation barriers of reaction pathways is related with reaction free energies on different transition metal surfaces and only considered various elementary step thermodynamics, whereas the potential-dependent kinetic barriers that predicting catalytic activity were not further calculated. Most recently, Janik et al. calculated explicitly the potential-dependent activation barriers for elementary electroreduction reactions included in associative distal and alternating pathways during N₂ electroreduction using their previously developed method,53–56 and concluded that the alternating mechanism by direct surface hydrogenation may be more favorable on late transition metals due to smaller barriers at 0 V (vs. RHE).50,51 in which N₂ electroreduction into N₂H species is rate determining step of overall reaction. However, despite various theoretical efforts, N₂ electroreduction mechanisms are still not systematically understood and mechanistic inconsistencies remain exist. Furthermore, the key factor such as solvent effect was not included in previous theoretical studies on N₂ electroreduction mechanisms. Thus, the modeling of electrocatalytic reaction systems occurred at the complex electrode/aqueous interfaces remains a subject of ongoing discussion.

In the present paper, Au electrocatalyst is selected due to its excellent durability, relatively high faradaic efficiency and low hydrogen evolution reaction activity in N₂ electroreduction. Furthermore, electrocatalytic N₂ reduction reaction on the Au surface is indeed possible under ambient conditions.55,56 Our previous validated explicit solvation model with two relaxed H₂O bilayer structure is employed to simulate solvent effect,53–55 which allows us to better model the interactions among adsorbates, surface and solvents and determine the kinetic barriers for various elementary reaction steps. Thus, an improve H coverage-dependent Au(111)/H₂O electrochemical interface model is proposed, by which the electroreduction mechanisms of N₂ into NH₃ can be identified. Simultaneously, solvation effect on N₂ reduction mechanisms is also considered in this work. Our present used model is differentiated from previous theoretical work on N₂ electroreduction into NH₃. The available experimental results on Au electrodes will be used to examine whether the currently employed computational model is enough accurate by comparing with our present theoretical study.

2. H coverage-dependent Au(111)/H₂O interface model

2.1 Determination method of equilibrium potentials

Surface and solvation model, and computational parameters included in computational details have been represented in detail in ESI (see Fig. S1).† It is known that the hydrogen evolution reaction and proton-coupled electron transfer usually occur during N₂ electroreduction on the Au electrodes, thereby
Thus, the H coverage-dependent equilibrium potential $E$ can be determined at Au(111)/$\text{H}_2\text{O}$ interface when the Gibbs free adsorbed H atoms and $D$ surface adsorbed H atoms, calculated equilibrium potentials (eqn (1)) can be obtained during $\text{N}_2$ electroreduction by following eqn (1):

$$H^+ + e^- \rightarrow \frac{1}{2} \text{H}_2 \rightarrow H^* \quad (1)$$

At different H coverage conditions, the Gibbs free energy of eqn (1), $\Delta G(\theta)$ can be calculated by eqn (2) on the basis of the methodology proposed by Nørskov et al., Chen et al. and Strasser et al. for oxygen reduction, hydrogen evolution and CO$_2$ electrochemical reduction reactions$^{56,59-63}$ in which $\Delta E(\theta)$, $\Delta S(\theta)$, $\Delta ZPE$ and $k_b T \ln(\theta/1 - \theta)$ represent the differential adsorption energy of surface adsorbed H atoms, entropy change, zero-point energy change and the contributions of configuration entropy to $\Delta G(\theta)$, respectively. Herein, coverage $\theta = n/N$, in which $n$ is the number of surface adsorbed H atoms and $N$ is the total number of surface Au atoms. Thus, the H coverage-dependent equilibrium potential $U$ (vs. RHE) can be determined at Au(111)/$\text{H}_2\text{O}$ interface when the Gibbs free energy, $\Delta G(\theta)$ is equal with zero.

$$\Delta G(\theta) = \Delta E(\theta) + eU - T \Delta S(\theta) + \Delta ZPE + k_b T \ln(\theta/1 - \theta) \quad (2)$$

According to eqn (3), the differential adsorption energy of surface adsorbed H atoms, $\Delta E(\theta)$ can be calculated, where $E(\theta)_{\text{M}_{\text{H}_2}}$ is the total energy of the Au surface with different coverage of adsorbed H atoms.

$$\Delta E(\theta) = \frac{\partial E(\theta)_{\text{M}_{\text{H}_2}}}{\partial n} \theta n - \frac{1}{2} E_{\text{H}_2}$$

$$= \frac{\partial E(\theta)_{\text{M}_{\text{H}_2}}}{\partial \theta} N \theta - \frac{1}{2} E_{\text{H}_2} \quad (3)$$

The contributions from ZPE and entropy changes together to $\Delta G(\theta)$ are estimated to be ca. 0.24 eV at standard temperature (298 K) based on the available data from previous literature.$^{64}$ Therefore, combining eqn (2) with eqn (3), the eqn (4) can be obtained. The values of $E(\theta)_{\text{M}_{\text{H}_2}}$ and $E_{\text{H}_2}$ is directly available via DFT calculations. A series of values of $E(\theta)_{\text{M}_{\text{H}_2}}$ can be calculated by changing the coverage of surface adsorbed H atoms on Au(111). At the different coverages, the values of $\Delta G(\theta)$ can be obtained by differentiating the plots of $\partial E(\theta)_{\text{M}_{\text{H}_2}}/\partial \theta$ against $\theta$ on the basis of eqn (3).

$$\Delta G(\theta) = \left[ \frac{\partial E(\theta)_{\text{M}_{\text{H}_2}}}{\partial \theta} - N \theta - \frac{1}{2} E_{\text{H}_2} - eU \right] + 0.24 + k_b T \ln(\theta/1 - \theta) \quad (4)$$

### 2.2 Relationship between H coverage and equilibrium potentials

In the present study, we consider various possible surface adsorption configurations of H atoms and coverage dependence. It is observed that H atoms prefer to adsorb at 3-fold face-centered cubic hollow (fcc) sites on Au(111) so that they can stay away from each other in order to minimize the repulsive interactions among adsorbed H atoms. Fig. 1(a) exhibits a reasonable polynomial relationship between the differential adsorption energy of surface adsorbed H atoms, $\Delta E(\theta)$ and $\theta_\text{H}$, indicating that the Langmuir adsorption isotherms may be followed on Au(111). Thereby, $\Delta E(\theta)$ can be calculated at any $\theta_\text{H}$ through polynomial fitting of $\Delta E(\theta) \sim \theta_\text{H}$ data. We can calculated the equilibrium potentials ($U$) based on the eqn (4) at any $\theta_\text{H}$ and then the polynomial relationships between $\theta_\text{H}$ and $U$ can be obtained on Au(111). It is found that the more negative equilibrium potentials can be obtained with the increasing H coverage, as shown in Fig. 1(b). In fact, the previous theoretical study from Skulason et al. also showed that most surfaces will be fully covered with the adsorbed H atoms at more negative

![Fig. 1](image-url) (a) The relationship between the differential adsorption energy of H atoms and H coverage ($\theta_\text{H}$), $\Delta E(\theta)$; (b) the relationship between the calculated equilibrium potentials ($U$) and H coverage ($\theta_\text{H}$).
Our present study will focus on the electroreduction mechanisms of N$_2$ into NH$_3$ at the thermodynamical required equilibrium potential. The equilibrium potential is calculated as ca. $-0.22$ V (vs. RHE) for N$_2$ electroreduction under ambient conditions, which is the closest to the thermodynamical value of ca. $-0.06$ V (vs. RHE) for N$_2$ electroreduction under ambient conditions, thus being regarded as the thermodynamical equilibrium potential. Our present study will focus on the electroreduction mechanisms of N$_2$ into NH$_3$ at the thermodynamical required equilibrium potential with the aim of applying the present proposed H coverage-dependent Au(111)/H$_2$O electrochemical interface model to some degree. The equilibrium potential with the aim of applying the present proposed H coverage-dependent Au(111)/H$_2$O electrochemical interface model to some degree. The equilibrium potential with the aim of applying the present proposed H coverage-dependent Au(111)/H$_2$O electrochemical interface model to some degree. The calculated potential-dependent N$_2$ electroreduction mechanisms will be further studied in our future work.

3. Results and discussion

3.1 N$_2$ reduction mechanism on Au(111) in gas phase

For comparison and consideration of solvation effect on N$_2$ reduction mechanisms, we firstly present calculated results of N$_2$ reduction to NH$_3$ via dissociative and associative mechanisms on Au(111) in gas phase. In dissociative mechanism, N$_2$ is initially dissociated to form the adsorbed N atoms on Au(111) with an extremely high activation barrier of ca. 6.02 eV, as can be seen in Fig. 2. Subsequently, the adsorbed N atoms are further reduced to form NH$_3$ molecules via serial surface hydrogenation steps with corresponding barriers of ca. 0.40, 0.47 and 0.57 eV, respectively. By comprehensively scrutinizing the overall energy pathway diagram of N$_2$ reduction into NH$_3$ in gas phase, N$_2$ dissociation pathway is rate determining step of overall reaction in dissociative mechanism on Au(111).

Fig. 3 shows the overall energy pathway diagram of N$_2$ reduction into NH$_3$ via associative alternating and distal mechanisms in gas phase. In these both mechanisms, the activation barrier is calculated as ca. 2.10 eV for the first hydrogenation step of N$_2$ molecule into the adsorbed N$_2$H species. Beginning with the further reduction of N$_2$H, there may be two possibilities to occur. One is N$_2$H hydrogenation to form the surface adsorbed NHNH species, which is defined alternating pathways; another is N$_2$H hydrogenation to form the surface adsorbed NNH species, being defined as distal pathways. The required barrier for the formation of NNH species is ca. 0.17 eV in alternating pathways. NNH species can further be reduced to form the adsorbed NNH$_2$ species with an activation barrier of ca. 0.26 eV. Two possibilities are considered for NNH$_2$ subsequent further reduction, the adsorbed NH$_2$NNH species and NNH$_2$H species may be formed via surface hydrogenation. The corresponding barrier is 0.31 and 0.21 eV, respectively, which is extremely low and surmountable at room temperature, indicating that NNH$_2$ further reduction into NH$_2$NNH and NNH$_3$ species may be parallel pathways in alternating pathways. NH$_2$NNH further reduction to form the first NH$_3$ molecule may be able to be separated into two elementary reaction steps, namely, NH$_2$NNH species surface hydrogenation into the adsorbed NH$_2$NNH species, and subsequent formation of the adsorbed NH$_3$ species and NH$_3$ product via N–N bond cleavage. The calculated barrier is ca. 0.37 and 1.66 eV, respectively, as shown in Fig. 3(a). Surface hydrogenation of NH$_2$ intermediate can finally leads to production of the second NH$_3$ molecule.

In distal pathways, surface hydrogenation of NH$_2$ intermediate is possible to form the adsorbed NNH$_2$ and NNH$_3$ species. However, the significant higher barrier for formation of
Table 1 Activation barriers (\(\Delta E_{\text{act}}, \text{eV}\)) and reaction energies (\(\Delta E_{\text{reac}}, \text{eV}\)) for the possible elementary reaction steps involved in \(\text{N}_2\) reduction pathways on \(\text{Au}(111)\) in gas phase

<table>
<thead>
<tr>
<th>Elementary reaction steps*</th>
<th>(\Delta E_{\text{act}}, \text{eV})</th>
<th>(\Delta E_{\text{reac}}, \text{eV})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{N}_2 + * \rightarrow \text{N}^* + \text{N}^*)</td>
<td>6.02</td>
<td>5.67</td>
</tr>
<tr>
<td>(\text{N}^* + \text{H}^* \rightarrow \text{NH}^*)</td>
<td>0.40</td>
<td>-1.87</td>
</tr>
<tr>
<td>(\text{NH}^* + \text{H}^* \rightarrow \text{NH}_2^*)</td>
<td>0.47</td>
<td>-1.52</td>
</tr>
<tr>
<td>(\text{NH}_2^* + \text{H}^* \rightarrow \text{NH}_3^*)</td>
<td>0.57</td>
<td>-2.05</td>
</tr>
<tr>
<td>(\text{N}_2 + \text{H}^* \rightarrow \text{N}_2\text{H}^*)</td>
<td>2.10</td>
<td>1.75</td>
</tr>
<tr>
<td>(\text{NH}_2^* + \text{H}^* \rightarrow \text{NNH}_2^*)</td>
<td>0.17</td>
<td>-0.79</td>
</tr>
<tr>
<td>(\text{N}_2\text{H}^* + \text{H}^* \rightarrow \text{NNH}^*_2)</td>
<td>0.22</td>
<td>-0.48</td>
</tr>
<tr>
<td>(\text{NNH}^<em>_2 + \text{H}^</em> \rightarrow \text{NNH}_2\text{H}_2^*)</td>
<td>0.26</td>
<td>-0.92</td>
</tr>
<tr>
<td>(\text{NNH}_2^* + \text{H}^* \rightarrow \text{NNH}_2^*)</td>
<td>0.24</td>
<td>-1.23</td>
</tr>
<tr>
<td>(\text{NNH}_2^* + \text{H}^* \rightarrow \text{NNH}_2)</td>
<td>0.72</td>
<td>0.48</td>
</tr>
<tr>
<td>(\text{NNH}_2) (\rightarrow \text{N}^* + \text{NH}_2^*)</td>
<td>0.21</td>
<td>-1.52</td>
</tr>
<tr>
<td>(\text{NH}_2\text{H}^* + \text{H}^* \rightarrow \text{NH}_3\text{H}_2^*)</td>
<td>0.37</td>
<td>-0.40</td>
</tr>
<tr>
<td>(\text{NNH}_2^* + \text{H}^* \rightarrow \text{NH}_3\text{H}_2^*)</td>
<td>0.24</td>
<td>-1.37</td>
</tr>
<tr>
<td>(\text{NNH}_2) (\rightarrow \text{NH}^* + \text{NH}_2^*)</td>
<td>0.65</td>
<td>-1.23</td>
</tr>
<tr>
<td>(\text{NH}_2\text{H}^* + \text{H}^* \rightarrow \text{NH}_2\text{H}_2^*)</td>
<td>1.66</td>
<td>-1.38</td>
</tr>
</tbody>
</table>

* The asterisk (*) indicates that the species is adsorbed on the \(\text{Au}(111)\) surface.

\(\text{NHNH}_2\) than \(\text{NNH}_2\) is observed (0.72 eV vs. 0.24 eV), indicating that the \(\text{NHNH}_2\) formation is kinetically inhibited, as shown in Fig. 3(b). Starting with \(\text{NNH}^*_2\) further reduction, the first \(\text{NH}_3\) molecule may be produced via two elementary reaction steps involving hydrogenation into the adsorbed \(\text{NHNH}_3\) species and its subsequent N–N bond scission with the formations of the adsorbed \(\text{NH}_2\) species and \(\text{NH}_3\) product, and the corresponding barrier is calculated as \(ca. 0.21\) and 0.65 eV. The adsorbed \(\text{NH}_2\)\(\text{NH}_2\) intermediate is also possible to be formed through \(\text{NNH}^*_2\) surface hydrogenation with the surmountable barrier of \(ca. 0.31\) eV at room temperature in distal pathways. As above elaborated, \(\text{NH}_2\)\(\text{NH}_2\) species can further be reduced into the adsorbed \(\text{NH}_2\) species and the first \(\text{NH}_3\) molecule via surface hydrogenation and N–N bond scission. The adsorbed \(\text{NH}_2\) and \(\text{NH}_3\) intermediates can finally lead to the second \(\text{NH}_3\) molecule via surface hydrogenation in distal pathways. However, we note that the extremely high barrier is required for N–N bond cleavage in \(\text{NNH}_3\) species to form \(\text{NH}_3\) product (\(ca. 1.66\) eV) in associative alternating and distal mechanisms, thereby it can be concluded that \(\text{NH}_2\)\(\text{NH}_2\) species is only a spectator during \(\text{N}_2\) reduction in gas phase due to its easy formation \(via \text{NNH}_3\) and \(\text{NH}_2\)\(\text{NH}_2\) hydrogenation. The corresponding energetics of for the possible elementary reaction steps involved in \(\text{N}_2\) reduction pathways on \(\text{Au}(111)\) in gas phase are summarized in Table 1.

By scrutinizing the overall energy pathway diagram of associative alternating and distal mechanisms (see Fig. 3), \(\text{N}_2\) hydrogenation into \(\text{N}_2\)\(\text{H}\) species is rate determining step with the barrier of \(ca. 2.10\) eV, suggesting that both alternating and distal pathways may be parallel and operable on \(\text{Au}(111)\) in gas phase. It is found that the barrier of rate determining step for the associative mechanism is notably lower than that of dissociative mechanism by comparing the barriers between these both mechanisms (\(ca. 2.10\) eV vs. 6.02 eV), suggesting that the associative mechanism including the adsorbed \(\text{NNH}_2\)\(\text{NH}_3\), \(\text{NH}_2\)\(\text{NH}_2\), \(\text{NNH}_3\) and \(\text{NH}_2\)\(\text{NH}_3\) intermediates is more favorable.

![Fig. 4](image-url)  
Fig. 4 The optimal associative mechanisms on \(\text{Au}(111)\) in gas phase: (a) alternating pathways \(via \text{NNH}_3\) species; (b) distal pathways \(via \text{NNH}_2\) species (* represents surface adsorption).
The optimal associative mechanisms including alternating and distal pathways on Au(111) in gas phase are summarized in Fig. 4. Images of reactants, products and transition states for N₂ reduction into NH₃ via the optimal associative mechanisms are included in ESI, as shown in Fig. S3–S13.† However, we also note that the required barrier for initial N₂ hydrogenation is extremely high, which may be able to ascribed to weakly bonded N₂ molecule on Au(111) with the adsorption energy of ca. –0.03 eV. Furthermore, N≡N bond length of N₂ on Au(111) is almost identical with that of isolated N₂ molecule, ca. 1.11 Å.

3.2 N₂ electroreduction mechanism at Au(111)/H₂O interface

Our present proposed H coverage-dependent Au(111)/H₂O electrochemical interface model is utilized to simulate N₂ electroreduction pathways, including dissociative and associative mechanisms. The present calculated thermodynamically required equilibrium potential of ca. –0.22 V (vs. RHE) when θH is equal with zero is focused. Fig. 1 shows the overall energy pathway diagram of N₂ electroreduction into NH₃ through dissociative mechanism. The largest barrier for this mechanism is initial N≡N bond scission to form the adsorbed N atoms with an activation barrier of ca. 4.90 eV at –0.22 V (vs. RHE), thus being rate determining step of overall reaction. Although the barrier for N₂ dissociation is significantly decreased at Au(111)/H₂O electrochemical interface by comparing with that in gas phase (4.90 eV vs. 6.02 eV), it is still extremely high and difficult to be overcome. An activation barrier of ca. 1.75 eV is required for initial N₂ electroreduction into N₂H species at the present simulated Au(111)/H₂O interface in associative mechanisms, as can be seen in Fig. 5. The barrier for N₂H further electroreduction into the surface adsorbed NNH and NH₂ species in alternating and distal pathways is calculated as ca. 0.22 and 0.01 eV, respectively, suggesting that both NNH and NH₂ species are possible key intermediates during N₂ electroreduction on Au(111) because of extremely low formation barriers.

Beginning with NNH further electroreduction in alternating pathways, we find that the adsorbed NNH₂ species is unstable at Au(111)/H₂O interface, which can be spontaneously electrochemically reduced to form the surface adsorbed NH₂NH₃ species by proton-coupled electron transfer with the surmountable barrier of ca. 0.24 eV at room temperature, as shown in Fig. 5(a). The first NH₃ molecule can be produced by further electroreduction of NNH₂NH₃ species through two elementary reaction steps including NH₂NH₃ formation and its subsequent N–N bond scission. The corresponding barrier is calculated as ca. 0.48 and 0.69 eV, respectively. It is noted that the barrier for NH₂NH₃ further electroreduction into the adsorbed NH₄ species and NH₃ product is significantly decreased at Au(111)/H₂O interface compared with that in gas phase (0.69 eV vs. 1.66 eV), suggesting that the presence of electrochemical interface may be able to alter N₂ reduction mechanisms. The formed NH₄ species can finally lead to production of the second NH₃ molecule with an activation barrier of ca. 0.56 eV. Starting with NNH₂ intermediate formed in distal pathways, it is found that the adsorbed NNNH₂ and NNH₃ species observed in gas phase are unstable at Au(111)/H₂O interface, which can be also spontaneously electrochemically reduced to form the surface adsorbed NH₂NH₃ and NNH₃ intermediates by proton-coupled electron transfer process. The required barrier for NH₂ electroreduction into NH₂NH₂ and NH₂NH₃ is calculated as only ca. 0.11 and 0.05 eV, respectively, as shown in Fig. 5(b), suggesting that NH₂NH₃ and NNH₃ species is possible intermediate in distal pathways. Similarly, NH₂NH₃ intermediate can be further electrochemically reduced to form the adsorbed NH₄ species and the first NH₃ molecule via abovementioned two elementary reaction steps. Two possibilities are also considered for further electroreduction of NNNH₂ intermediate at Au(111)/H₂O interface, one is NH₂NH₃ formation, and another is formation of the adsorbed NH species and production of the first NH₃ molecule via N–N bond scission. It is found that the required barrier for the former is notably lower than that of the latter (0.24 eV vs. 0.94 eV), indicating that NH₂NH₃ formation is more favorable. Thus, we can concluded that the first NH₃ molecule is possible to be produced by N–N bond scission of NH₂NH₃ species at Au(111)/H₂O interface, rather than NNH₂ species as observed in gas phase, again suggesting that the influence of electrochemical interface containing solvation effect on N₂ reduction pathways. The corresponding energetics of for various possible reaction steps involved during

Fig. 5 Overall energy pathway diagram of N₂ electroreduction into NH₃ via associative mechanism at the present proposed Au(111)/H₂O interface: (a) alternating pathways; (b) distal pathways.
Table 2: Activation barriers (ΔE_{act}, eV) and reaction energies (ΔE_{react}, eV) for various possible reaction steps involved in N₂ electroreduction pathways at Au(111)/H₂O interface

<table>
<thead>
<tr>
<th>Reaction steps</th>
<th>ΔE_{act}, eV</th>
<th>ΔE_{react}, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂ + * → N* + N*</td>
<td>4.93</td>
<td>4.92</td>
</tr>
<tr>
<td>N* + (H + e⁻) → NH*</td>
<td>0.33</td>
<td>-1.37</td>
</tr>
<tr>
<td>NH* + (H + e⁻) → NH₂*</td>
<td>0.73</td>
<td>-1.78</td>
</tr>
<tr>
<td>NH₂* + (H + e⁻) → NH₃*</td>
<td>0.56</td>
<td>-1.51</td>
</tr>
<tr>
<td>N₂ + * + (H + e⁻) → N₂H*</td>
<td>1.75</td>
<td>1.65</td>
</tr>
<tr>
<td>N₂H* + (H + e⁻) → NHNHNH*</td>
<td>0.22</td>
<td>-1.30</td>
</tr>
<tr>
<td>N₂H* + (H + e⁻) → NH₂NHNH₂*</td>
<td>0.01</td>
<td>-0.75</td>
</tr>
<tr>
<td>NHNHNH* + 2(H + e⁻) → NH₂NHNH₂*</td>
<td>0.24</td>
<td>-1.25</td>
</tr>
<tr>
<td>NHNHNH₂* + 2(H + e⁻) → NH₂NHNH₂*</td>
<td>0.11</td>
<td>-1.80</td>
</tr>
<tr>
<td>NHNHNH₂* + (H + e⁻) → NH₂NHNH₂*</td>
<td>0.05</td>
<td>-1.34</td>
</tr>
<tr>
<td>NHNHNH₂* + (H + e⁻) → NH₂NHNH₂*</td>
<td>0.48</td>
<td>-0.85</td>
</tr>
<tr>
<td>NHNHNH₂* + NH₂ + NH₂*</td>
<td>0.24</td>
<td>-1.31</td>
</tr>
<tr>
<td>NHNHNH₂* + NH₂ + NH₂*</td>
<td>0.94</td>
<td>-0.21</td>
</tr>
<tr>
<td>NHNHNH₂* + NH₂ + NH₂*</td>
<td>0.69</td>
<td>-0.68</td>
</tr>
</tbody>
</table>

* The asterisk (*) indicates that the species is adsorbed on the Au(111) surface.

N₂ electroreduction at Au(111)/H₂O interface are summarized in Table 2.

By scrutinizing the overall energy pathway diagram, our present simulation results reveal that the rate determining step for N₂ electroreduction into NH₃ via associative alternating and distal mechanisms at Au(111)/H₂O interface is N₂ electroreduction into form the adsorbed N₂H species, suggesting that these both mechanisms may be able to parallelly occur. The corresponding barrier is significantly lower than that of rate determining step in the dissociative mechanism (1.75 eV vs. 4.90 eV). Thus, it can be concluded that the associative mechanisms are more facile to occur at the present simulated Au(111)/H₂O interface. The optimal associative alternating and distal mechanisms are summarized in Fig. 6. Images of reactants, products and transition states for N₂ electroreduction into NH₃ via the optimal associative mechanisms at the present simulated Au(111)/H₂O interface are included in ESI, as shown in Fig. S14–S23.

Our present calculated N₂ electroreduction mechanisms at Au(111)/H₂O electrochemical interface are partially inconsistent with the previous theoretical study from Janik et al., in which only alternating pathway via NHNHNH species is favorable on late transition metals at 0 V (vs. RHE) with rate determining step of N₂ electroreduction into N₂H species by calculating explicitly the potential-dependent barriers for elementary electro-reduction reactions (see Fig. 7). Furthermore, the predicted NHN₂H species on late transition metals at 0 V (vs. RHE) is found to be unstable at Au(111)/H₂O interface, which can be spontaneously reduced to form adsorbed NH₂NH₂ species by proton-coupled electron transfer with the surmountable barrier at room temperature. The difference of interface model may lead to partially inconsistent N₂ electroreduction mechanisms, in which only a H₂O molecule is employed to simulate solvent effect in previous theoretical work from Janik et al., being insufficient to model interactions among solvent, adsorbates and surface. However, our present theoretical results can be confirmed by the most recent experimental study from Shao et al., in which the adsorbed intermediates such as N₂H, NHN₂H, NH₂NH₂, NH₂NH₂H, and NH₂ may be able to be formed during N₂ electroreduction on the Au electrodes at potentials of ca. −0.10 V (vs. RHE) or lower due to detected N₂H₄ (1 ≤ y ≤ 4) reaction species using the surface-enhanced infrared absorption spectroscopy technique, further validating the rationality of our present employed Au(111)/H₂O interface model. Simultaneously, we also note that the presence of electrochemical interface makes the barrier of rate determining step in the associative mechanisms decrease compared with that in gas phase (1.75 eV vs. 2.10 eV), indicating that the presence of solvent effect could help stabilize the adsorbed N₂H species and lower the corresponding barrier value to ca. 1.75 eV. Even so, barrier of 1.75 eV is still high for N₂ electroreduction, making
this process be still challenging, which may be able to be regarded as origin of experimentally observed high overpotential. The almost not changed $\text{N} \equiv \text{N}$ bond length of $\text{ca.} 1.11 \text{ Å}$ at Au(111)/$\text{H}_2\text{O}$ interface again shows weakly adsorbed $\text{N}_2$ molecule compared with that of isolated $\text{N}_2$ molecule.

The potential of the hydrogen evolution reaction is very approximate to the thermodynamically required potential for $\text{N}_2$ electroreduction under ambient conditions. Therefore, overcoming the undesirable hydrogen evolution reaction competition may become the critical challenge during $\text{N}_2$ electroreduction at present, which can greatly reduce the faradaic efficiency of reaction. Herein, the barrier of hydrogen evolution reaction is evaluated by using our present proposed H coverage-dependent Au(111)/$\text{H}_2\text{O}$ interface model at $-0.22 \text{ V (vs. RHE)}$ and compared with that of rate determining step for the optimal associative mechanisms during $\text{N}_2$ electroreduction into $\text{N}_2\text{H}$ species at the present simulated electrochemical interface. As can be seen in Fig. 8, the calculated activation barrier of $\text{ca.} 0.24 \text{ eV}$ is remarkably lower than that of initial $\text{N}_2$ electroreduction into $\text{N}_2\text{H}$ intermediate ($\text{ca.} 1.75 \text{ eV}$). Furthermore, we also observe that the formed $\text{N}_2\text{H}$ intermediate may be unstable, which can be facile to back to $\text{N}_2$ molecule with extremely low barrier of $\text{ca.} 0.10 \text{ eV}$. The present comparison and analysis can well explain why the catalytic activity of Au electrodes is usually unsatisfactory although the relatively high faradaic efficiency can be achieved experimentally during $\text{N}_2$ electroreduction. Accordingly, the single descriptor may be able to be proposed to scale catalytic activity of electrocatalysts for $\text{N}_2$ electroreduction, in which an ideal electrocatalyst should be able to reduce barrier for initial $\text{N}_2$ electroreduction into $\text{N}_2\text{H}$ intermediate. In this way, $\text{N}_2$ electroreduction pathways can be facilitated and the yield of $\text{NH}_3$ can be enhanced.

3.3 Origin of solvation effect on $\text{N}_2$ reduction mechanisms

As above discussed, the presence of electrochemical interface including solvation effect could change $\text{N}_2$ reduction mechanism, especially it can reduce the barrier of rate determining step. To ascertain the origin of difference of $\text{N}_2$ reduction mechanisms at gas phase and the present simulated electrochemical interface on Au(111), the charge density difference analyses are carried out in our present work taking example for $\text{N}_2$ adsorption on Au(111). It is observed that there is almost not significant electron accumulation and interaction between $\text{N}_2$ molecule and surface Au atoms under gas- and aqueous-phase environment, as shown in Fig. 9, confirming the above-mentioned weakly binding $\text{N}_2$ molecule on Au(111) and almost identical $\text{N} \equiv \text{N}$ bond length compared with isolated $\text{N}_2$ molecule, thus explaining why high barrier is required for initial $\text{N}_2$ reduction. However, the significant electron interactions are found between $\text{N}_2$ and $\text{H}_2\text{O}$ cluster at the present simulated electrochemical interface. The existence of $\text{H}$ bonds and interactions of $\text{N}_2$ with $\text{H}_2\text{O}$ molecules at the Au(111)/$\text{H}_2\text{O}$ interface may lead to easier initial $\text{N}_2$ electroreduction, as observed decreased barrier value.

Based on the above conclusions, we can conclude that the decreased barrier for rate determining step may be able to be ascribed to electronic interactions between $\text{N}_2$ and $\text{H}_2\text{O}$ cluster. Therefore, the quantitative analysis of electronic structures will facilitate well understanding the origin of solvation effect on $\text{N}_2$ electroreduction mechanisms. According to projected electron densities of states, the Löwdin charge (the number of valence electron) of $\text{N}_2$ can be obtained from Löwdin population analyses on Au(111) in gas phase and at the present simulated electrochemical interface. Table 3 gives the electron gains ($\Delta q$) for $\text{N}_2$ molecule, respectively, which could be obtained by subtracting the Löwdin charge of isolated $\text{N}_2$ molecule from that in the optimized structure. Simultaneously, $\Delta q$ of $\text{H}_2\text{O}$ cluster at the present simulated electrochemical interfaces are also given in Table 3 compared with that of free $\text{N}_2$ adsorbed Au(111)/$\text{H}_2\text{O}$ interface. A positive value of $\Delta q$ will imply a gain of electron by the component. It can be found that only slight electron transfer occurs between $\text{N}_2$ molecule and Au(111) surface in gas phase due to little electron gains of total, s and p orbitals of $\text{N}_2$, as
found weakly bonded N₂ molecule on Au(111) with the adsorption energy of only ca. 0.03 eV, confirming the above observed no significant electron accumulation and interaction based on the charge density difference analyses. However, we notice that the nature of electronic interactions at the Au(111)/H₂O interface is practically not the same as that observed in gas phase. The significant electron transfer occurs between N₂ molecule and H₂O cluster, namely, the total net electrons of H₂O cluster are positive because s orbital can gain more electrons although p orbital loses electrons, whereas the total net electrons of N₂ is negative, in which s orbital loses electrons and p orbital gains electrons. Thus, it can be concluded that the notable different electron interactions on Au(111) in gas phase and at the electrochemical interface may result in the difference of N₂ reduction mechanisms.

4. Conclusions

In the present paper, an improved H coverage-dependent Au(111)/H₂O electrochemical interface model is proposed, which is firstly used to study electroreduction mechanisms of N₂ to NH₃ at the thermodynamical equilibrium potential cooperated with electronic structure analysis. The calculated results show that the associative mechanism is more favorable on Au(111) and therein alternating and distal pathways may be able to parallelly occur in gas phase and the present simulated electrochemical interface. The initial N₂ reduction into N₂H intermediate is rate determining step, which may be able to be regarded as the origin of observed experimentally high over-potential during N₂ electroreduction. However, the presence of electrochemical environment can significantly change N₂ reduction pathway and decrease the barrier of rate determining step, in which NHH₂ and NH₃ species observed in gas phase are unstable at Au(111)/H₂O interface, which can be spontaneously electrochemically reduced to form adsorbed NHH₂ and NH₃ intermediates by proton-coupled electron transfer process. The significant electron accumulation and interaction between N₂ molecule and H₂O cluster may result in different N₂ electroreduction pathways and the decreased barrier of rate determining step. The theoretical results display excellent consistency with the available experimental data, confirming the rationality of the present used Au(111)/H₂O interface model. The comparison of barrier between hydrogen evolution reaction and rate determining step well explains why the catalytic activity of Au electrodes is usually unsatisfactory although the relatively high faradaic efficiency can be experimentally achieved. Accordingly, the single descriptor may be able to be proposed, in which an ideal electrocatalyst should be able to reduce barrier for initial N₂ electroreduction into N₂H intermediate. In this way, N₂ electroreduction pathways can be facilitated and the yield of NH₃ can be enhanced. We believe that the present study represents a progress to systematically study N₂ electroreduction mechanisms based on an improved electrochemical interface model.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Key Program of Education Department of Hunan Province (Grant No. 19A337); Hunan Provincial Natural Science Foundation of China (Grant No.
2018JJ2273); Key Program of Hunan University of Arts and Science (192D006) and National Natural Science Foundation of China (Grant No. 21303048).

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