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The critical role of interface electrons in modulating the sensing behavior of Au/Pd and Pt/Pd resistive hydrogen sensors

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Abstract Due to the advantages of scalability and cost-effectiveness, Palladium (Pd) has demonstrated great promise in developing high-performance H₂ gas sensors. However, poor stability and reliability remain obstacles. In this work, we theoretically devised Pd-based heterostructures Au/Pd(111) and Pt/Pd(111) for high-performance H₂ gas sensing. The density functional theory (DFT) calculations for H₂ response mechanism of Pd unambiguously elucidate that the rate-determining step dominating the response performance of Pd-based hydrogen sensors is the surface dissociative adsorption of H₂, rather than the subsequent bulk diffusion of dissociated H atoms. By integrating reaction kinetics energy barrier calculations with Bader charge analysis, we found that the electron redistribution at the Au/Pd(111) and Pt/Pd(111) heterointerface forms targeted negatively charged Au and Pt active sites, respectively, which can effectively activate the H-H bond and reduce the H₂ dissociation energy barrier. The climbing image nudged elastic band (CI-NEB) calculations confirm that the H₂ dissociative adsorption barrier at the Au/Pd(111) and Pt/Pd(111) heterointerface is lowered by 0.32 eV and 0.85 eV relative to Pd (111), which indicates that Pt/Pd(111) heterostructure can drastically accelerate the H₂ dissociative adsorption rate and increase the Pd surface H coverage, thus producing more β -phase PdH_x and greatly shortening the sensor's response time to H₂ gas. The H₂ desorption barrier at the Au/Pd(111) and Pt/Pd(111) heterointerface is lowered by 1.02 eV and 0.93 eV compared with Pd (111). It demonstrates that the sensing response of Au/Pd(111) and Pt/Pd(111)-based sensor can swiftly revert to its original baseline performance once the H₂ atmosphere is replaced by air.

Key words: Resistive H₂ sensors, Pt/Pd(111) heterointerface, Interfacial electronic modulation, DFT calculation, CI-NEB

1. Introduction

As a clean and renewable energy source, hydrogen (H_2) is crucial for realizing the goals of carbon peak and carbon neutrality.[1-3] However, its highly explosive nature has raised significant safety concerns.[4, 5] Therefore, developing highly sensitive gas sensors is crucial for the fast and accurate monitoring of trace H_2 or hydrogen leakage detection.

Compared with catalytic, optical or electrochemical gas sensors, resistance gas sensors have the advantages of simpler structures, low fabrication cost, and excellent adaptability to diverse application scenarios.[6, 7] Resistive H_2 sensors utilize the principle that exposure of the sensing material to H_2 will cause a change in the resistivity of the material to detect hydrogen. When the ambient hydrogen concentration changes, the resistance of the sensing material is measured to obtain the hydrogen concentration, and the relationship is approximately linear. With the booming development of low-carbon manufacturing and hydrogen energy emerging industries, high-performance resistive H_2 sensors with high sensitivity, short response time, and high stability, have become a research hotspot in recent years.[8-10] For now, much research efforts explored numerous materials for hydrogen-sensitive sensors. Among these, palladium (Pd) metal emerged as an optimal choice for fabricating hydrogen sensors, owing to its exceptional sensitivity and selectivity towards H_2 . [11, 12] Nevertheless, single Pd materials for H_2 sensors suffer from several non-negligible drawbacks: i) oxygen-driven baseline resistance shift in air, ii) active site deactivation due to surface contamination and poisoning, iii) the strong affinity of H_2 on Pd limits the H desorption, resulting in unsatisfied response, and iv) the formation of α -phase PdH_x that changes the volume of Pd, leading to unstable sensing performances.

Recently, numerous research groups and industrial teams widely employ palladium (Pd)-based functional materials to develop and fabricate high-performance advanced H_2 sensors. They adopted various strategies, such as morphology modulation, alloying, and heterostructure construction, for the Pd surface modification to enhance H_2 sensing performances.[6, 7, 13] For example, Kim et al. prepared thin film of PdAu alloy with optimized composition ($Pd_{0.62}Au_{0.38}$) as a resistive sensor, which exhibits excellent durability for repeated operation (>35 h) in 5% H_2 and resistance to humidity and carbon monoxide.[13] The detection lower limit of this sensor can be as low as 2 ppm and a fast response time of 9.5 s at room temperature. Anasthasiya et al. deposited Ag nanoparticles on the Pd thin film, which is stable for repeated cycling of 4% hydrogen with a lower detection limit

of 800 ppm as compared to pure Pd having the detection limit of 1.6% H₂ in argon.[14] The interface between nanoparticles of Ag and Pd facilitates the interaction with hydrogen. Through precise surface decoration and interfacial engineering of Pd sensing layers, the inherent drawbacks of Pd hydrogen sensors can be remarkably alleviated, leading to significantly improved long-term operational stability.

In this work, we theoretically designed stable atomic configurations of Au/Pd and Pt/Pd heterostructures to protect the underlying Pd surface from contamination, and simultaneously exploit the interfacial electronic effect to reduce the reaction energy barriers of H₂ adsorption and desorption, further enhancing the intrinsic detection sensitivity and shortening the recovery time of the H₂ sensor. Our computational investigations revealed the regulation effect of heterointerfaces on the H₂ dissociation-diffusion process, and clarified the microscopic mechanism behind the performance enhancement of Au/Pd(111) and Pt/Pd(111) heterostructures. Through the kinetic simulation of H₂ dissociation and diffusion at Au/Pd(111) and Pt/Pd(111) heterogeneous interfaces, the discrepancies in chemisorption activity of different adsorption sites were uncovered, and the influence of local charge distribution on the H₂ dissociation behavior was further elucidated combined Bader charge analysis.

2. Computational Methods

All calculations were performed using VASP 5.2, employing projector augmented wave (PAW) pseudopotentials to model electron-ion interactions.[15, 16] The Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was chosen for our simulations.[17] A plane-wave cutoff energy of 400 eV and a 3×3×1 Monkhorst-Pack k-point mesh[18] were used for the geometry optimizations. The convergence criteria were specified at 0.02 eV/Å for geometry optimizations and 10⁻⁵ eV for electronic structure calculations. The transition states (TS) for all reaction pathways were searched using the climbing image nudged elastic band (CI-NEB) method.[19]

We utilized four-layer atomic models with a 4×4 supercell to simulate Pd (111) surface and a 15 Å vacuum was introduced between adjacent layers to eliminate interactions. Au and Pt particles are modeled with Au cluster and Pt cluster including 10 Au atoms and 10 Pt atom, respectively. For the structure of Au/Pd(111) and Pt/Pd(111), Au cluster and Pt cluster were set onto the surface of Pd (111) model, respectively. The surface formation energy of Pd (111) $E_{f-Pd111}$ is computed using the

formula:

$$E_{f-Pd111} = (E_{Pd111} - n \cdot E_{Pd}) / S_{sur} \quad (1).$$

In this equation, E_{Pd111} is the energy of Pd (111) surface with n Pd atoms, E_{Pd} denotes the calculated average energy per Pd atom in the bulk Pd lattice, and S_{sur} is the surface area of the Pd (111) slab model used here. The interface formation energies for Au/Pd(111) and Pt/Pd(111) were defined as

$$E_{f-Au/Pd111} = (E_{Au/Pd111} - E_{Pd111} - E_{Au}) / S_{sur} \quad (2),$$

$$E_{f-Pt/Pd111} = (E_{Pt/Pd111} - E_{Pd111} - E_{Pt}) / S_{sur} \quad (3),$$

$E_{Au/Pd111}$ and $E_{Pt/Pd111}$ denote the total energy of Au/Pd(111) and Pt/Pd(111) interface, respectively; E_{Au} and E_{Pt} denote the total energy of Au and Pt cluster, respectively.

3. Results and Discussions

The hydrogen dissociation-diffusion mechanism for Pd-based sensing elements is described as follows: when the Pd metal is placed in the hydrogen environment, the first step is the chemisorption of hydrogen on the Pd surface, followed by dissociation of H_2 ; and the second step is the diffusion of dissociated hydrogen atoms into the interstitial sites of the Pd lattice, resulting in the formation of PdH_x compounds. When the concentration of H_2 in the environment decreases, H atoms will desorb and dissociate from Pd atoms. In the following, we first performed systematic density functional theory (DFT) calculations to elucidate the fundamental hydrogen sensing mechanism of Pd, covering the elementary step of H_2 dissociative adsorption and atomic H diffusion in Pd bulk. Afterward, we further investigated the thermodynamic stability of Au/Pd(111) and Pt/Pd(111) heterostructures, analyzed interfacial charge distribution, and described how this information affects the hydrogen dissociation-diffusion process. Finally, we presented a systematical analysis for the potential hydrogen dissociation kinetics mechanisms and elucidated the impacts of distinct active sites on the dissociation kinetics process.

3.1 Hydrogen dissociation kinetics mechanism on Pd (111)

The performance of hydrogen sensors is fundamentally determined by two critical kinetic processes: the dissociative chemisorption of H_2 on the sensing material surface and the subsequent diffusion dynamics of atomic H into the sensitive layer. We elucidated the full H_2 dissociation kinetic mechanism on Pd (111), and further compared the kinetic barrier profiles of H_2 dissociation process and H_2 diffusion process, consequently pinpointed the rate-determining kinetic step that dictates the complete H_2 response trajectory on Pd active sites. In previous investigations, two dynamical

models have been proposed to describe H_2 activated dissociation on Pt surface: the hydrogen dissociation invokes a preequilibrium and diffusion toward defects (model 1), and the direct and local reaction (model 2). By combining a curved surface approach and supersonic molecular beam methods, Juurlink et al. verified that H_2 dissociation on Pt (111) does not require physisorption and diffusion to defect sites, and the direct and local reaction mechanism is identified as the dominant kinetic mechanism for hydrogen dissociation on Pt (111).[20] In our following discussion, we primarily concentrate on the direct and local reaction mechanism in hydrogen dissociation process on Pd (111), Au/ Pd (111), and Pt/ Pd (111).

As shown in **Figure 1a**, the gaseous H_2 molecule is defined as the initial state (IS), and in the final state (FS) two atomic hydrogen species are anchored on the Pd surface via a bridge adsorption geometry, where each H atom is stably bonded between three adjacent Pd surface atoms. The hydrogen dissociation process undergoes a well-defined transition state (TS). At this critical point, the H-H bond is significantly elongated and weakened, while the bonding interaction between the H atom and adjacent Pd atoms gradually strengthens. The H-H bond in TS is lengthened from 0.751 Å to 1.222 Å, and the distance between H and adjacent Pd atoms lies between 2.610 Å ~ 2.728 Å, which is below the conventional van der Waals interaction regime. The calculated minimum energy path, as shown in **Figure 1b**, confirms that the H_2 must overcome a high kinetic barrier (1.36 eV) to pass through this TS before finally forming two H adatoms that are stably adsorbed at the bridge sites. This kinetic feature directly determines the overall dissociation rate of H_2 , and further exerts a decisive influence on the response speed of the palladium-based hydrogen sensor.

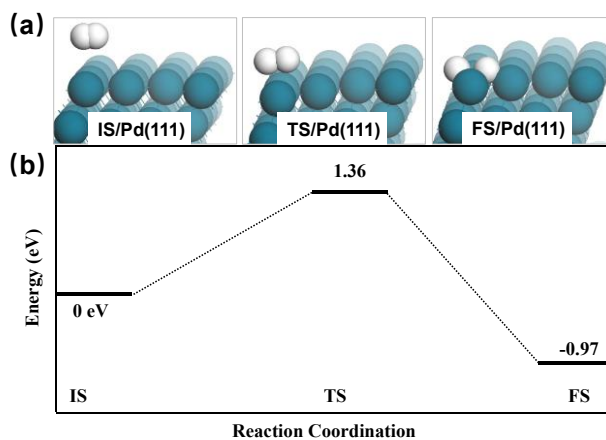


Figure 1. (a) Optimized geometry structures of the H_2 initial state IS/Pd(111), transition state TS TS/Pd(111), and final state FS/Pd(111) on Pd (111), and (b) H_2 dissociation reaction pathway on Pd(111) surface.

3.2 H atom diffusion kinetics in bulk Pd

The diffusion process of hydrogen atoms from the Pd surface into the bulk lattice is the core determinant of the H₂ response behavior of Pd materials. In this section, we computationally investigate the kinetic process of hydrogen atom diffusion from the Pd surface into the bulk Pd, by explicitly considering the migration pathway and corresponding energy barriers along the surface-to-bulk penetration trajectory. According to our CI-NEB calculations, the kinetic process of H atoms migrating from the topmost Pd surface into the subsurface lattice only needs to overcome an activation energy of 0.52 eV (see **Figure 2c**), making it thermally accessible under mild reaction conditions. The geometry structures of initial reactant (R1), transition state (TS1) and intermediate product (P1) are shown in **Figure 2a**. In R1, the H atom occupies the three-fold hollow site, residing directly above the equilateral triangle defined by three adjacent surface Pd atoms, with the calculated H-Pd bond distances of 1.811 Å. The H atom in the P1 is located below the Pd equilateral triangle, occupying the octahedral interstitial site in the Pd subsurface layer. As the H atom migrates from the three-fold hollow adsorption site into the octahedral interstitial site, it needs to surmount the energy penalty induced by the steric repulsion effect and the surface structural distortion triggered by the H transfer process. In TS1, the Pd-H bonds shortened from 1.811 Å in R1 to 1.623~1.629 Å, which demonstrates short-range interatomic repulsive interaction between the migrating H atom and the lattice Pd during its penetration into the subsurface; at same time, the three Pd-Pd bonds of Pd equilateral triangle are lengthened from 2.797 Å in R1 to 2.814 Å in TS1, suggesting the local displacement of the three Pd atoms that form the initial three-fold coordination shell around H.

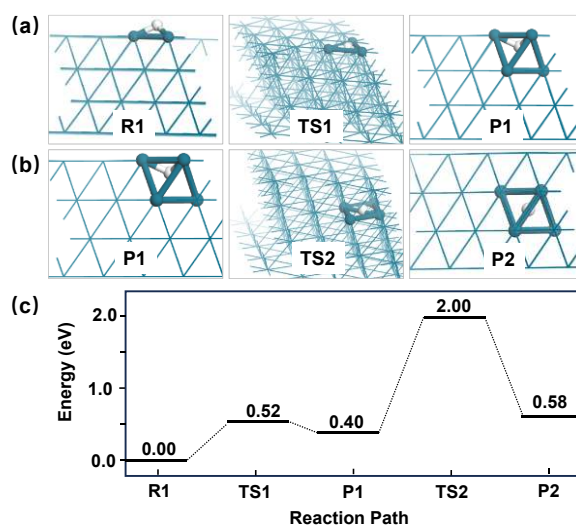


Figure 2. (a) optimized geometry structures of the initial reactant R1, transition state TS1, and intermediate product P1; (b) optimized geometry structures of the transition state TS2, and final product P2; and (c) H diffusion pathways from the topmost Pd surface layer into the subsurface lattice (R1→P1) and from the subsurface lattice into deep

subsurface lattice (P1→P2).

Due to the reduced coordination number of the topmost Pd atoms, the interatomic bonding constraints in the topmost Pd surface are significantly weakened. When interacting with H atoms, these surface atoms exhibit distinct lateral and normal lattice relaxation. In comparison, the subsurface Pd layer is defined by a bulk-like coordination environment, in which each Pd atom is surrounded by a greater number of adjacent Pd neighbors, thus the subsurface Pd layer exhibit higher structural rigidity than the topmost Pd surface. Under this circumstance, the diffusion energy barrier of H atoms is strongly modulated by the geometric shape and effective opening size of the diffusion windows that bridge different interstitial sites in the lattice. As a face-centered cubic (FCC) metal, bulk Pd possesses two distinct interstitial configurations, namely octahedral and tetrahedral interstices. The octahedral interstitial site provides a larger free volume than the tetrahedral counterpart. Consequently, H atoms accommodated in the octahedral interstice gain a lower total energy and a more thermodynamically stable configuration. When interstitial H atoms undergo lattice diffusion in bulk Pd, two elementary reaction pathways can be identified. The pathway 1 corresponds to direct H atom hopping between two adjacent octahedral interstitial sites without any intermediate trapping state, in this case, the migrating H atom needs to penetrate a parallelogram-structured diffusion window that is defined by four surrounding Pd atoms. The pathway 2, by contrast, adopts a stepwise mechanism: the H atom first diffuses from the starting octahedral site to a nearby tetrahedral interstitial site as a metastable intermediate, and subsequently hops from this tetrahedral site to the next adjacent octahedral site in the Pd crystal lattice. In both elementary hopping steps, the H atom needs to pass through a triangular interstitial window, which is fully enclosed by three adjacent Pd atoms in the Pd lattice. We computationally simulated the two reaction pathways for H atoms to traverse the Pd subsurface layer. The calculated minimum-energy path for pathway 1 shows that the diffusion barrier for this direct octahedral-to-octahedral migration is 1.60 eV, as shown in **Figure 2c**. Along this H diffusion pathway, the adsorbed H atom penetrates the parallelogram planar hollow site bounded by four Pd atoms, yielding a linear Pd–H–Pd activated complex that corresponds to the first-order saddle point on the potential energy surface. The local Pd lattice undergoes minor elastic distortion to accommodate the migrating H species, and the distance between Pd and H in TS2 is 1.376 Å and 1.414 Å, respectively, as shown in **Figure 2b**. This calculated Pd-H interatomic distance is far smaller than the equilibrium bond length in the

octahedral interstitial site. The extreme structural compression introduces a strong Pauli repulsion between the Pd d-orbitals and H 1s orbital, leading to a substantial energy increase of the TS2. The poor structural stability of the TS2 leads to a higher migration barrier.

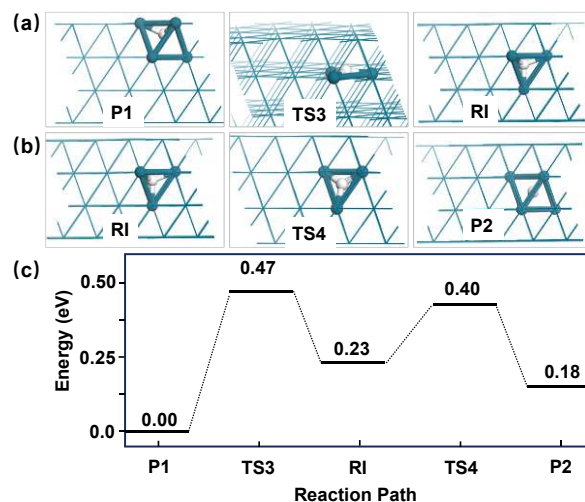


Figure 3. (a) optimized geometry structures of the initial reactant P1, translation state TS3, and reaction intermediate RI; (b) optimized geometry structures of the translation state TS4, and final product P2; and (c) H diffusion pathways from the subsurface lattice into deep subsurface lattice (P1→RI), and from tetrahedral interstitial site to octahedral interstitial site (RI→P2).

In pathway 2, the H atom in the octahedral interstice (P1) moves across the trigonal planar window formed by three surrounding Pd atoms to access the adjacent tetrahedral interstice (reaction intermediate RI), and then traverses a second equivalent trigonal Pd window to transfer to a distinct octahedral interstice in the Pd lattice (P2). The H atoms initially located at an octahedral interstice transfer to the nearby tetrahedral interstice through the transition state TS3. At the TS3, the Pd-H bonds exhibit a pronounced bond length contraction, decreasing from ~ 1.81 Å in the P1 to ~ 1.65 Å in the TS3, leading to a Pauli repulsion between the Pd d-orbitals and H 1s orbital. The activation energy for interfacial hydrogen spillover process is 0.47 eV. After the TS3, the RI is produced, as shown in **Figure 3b**. The H further transfers to a new octahedral interstice via the transition state TS4 in the consequent step to form P2. In TS4, the three contracted Pd-H bonds exhibit bond lengths in the range of 1.63–1.68 Å, showing a geometric structure similar to that of TS3. The calculated activation energy is only 0.17 eV. This is mainly because the energy of the RI is approximately 0.23 eV higher in energy than that of the P1. In Pathway 2, the rate determining step is the H atom initially located at an octahedral interstice passing through a triangular hollow site defined by three Pd atoms to occupy the nearby tetrahedral interstice. Through systematic analysis of multiple H atom

diffusion trajectories in the Pd lattice, we quantitatively demonstrate that the H diffusion energy barrier along the minimum-energy path is significantly lower than the activation energy required for H₂ dissociative adsorption on the Pd surface. This finding unambiguously identifies the surface H₂ dissociation kinetics as the rate-determining step governing the overall H₂ response process of Pd-based sensing materials.

3.3 Thermodynamic stability and charge distribution of Au/Pd(111) and Pt/Pd(111)

The surface formation energy of Pd (111) ($E_{f-Pd(111)}$) was derived from the total energy difference between the surface model and the corresponding bulk phases. The $E_{f-Pd(111)}$ value was estimated to be 1.51 J/m², which is in good agreement with the reported theoretical results. It indicates that the calculation method is reasonable and applicable. With the same rational calculation method, we performed full structural relaxation on the constructed Au/Pd(111) and Pt/Pd(111) interface models, as shown in **Figure 4a** and **4b**, and quantitatively calculated their interfacial formation energies according to the formula (2) and (3), thus their intrinsic thermodynamic stability is systematically assessed. As depicted in the **Figure 4c**, the interfacial formation energy of the Au/Pd(111) and Pt/Pd(111) interface was calculated to be -1.36 J/m² and -1.85 J/m², respectively. The ultralow interface formation energy suggests that the Au/Pd(111) and Pt/Pd(111) interface can form spontaneously in a regular laboratory environment. Quantitatively, the interface formation energy of Pt/Pd(111) is significantly lower than that of Au/Pd(111). This energetic difference unambiguously suggests that the Pt/Pd(111) heterointerface is much more prone to form spontaneously during the interfacial construction process. The distribution of Au-Pd and Pt-Pd bond lengths at the heterogeneous interface are shown in **Figure 4d**, the new formed Au-Pd bond length falls in the range of 2.68 Å to 2.83 Å, and Pt-Pd bond length in Pt/Pd(111) interface falls in the range of 2.59 Å to 2.73 Å. The Pt-Pd bond is approximately 0.1 Å shorter than Au-Pd bond, whereas the atomic radius difference between Au atom and Pt atom is on the order of 0.05 Å. It demonstrates that the Pt-Pd bond has shorter equilibrium bond length and correspondingly higher bond energy compared to the Au-Pd bond. This result is consistent with the preceding formation energy analysis.

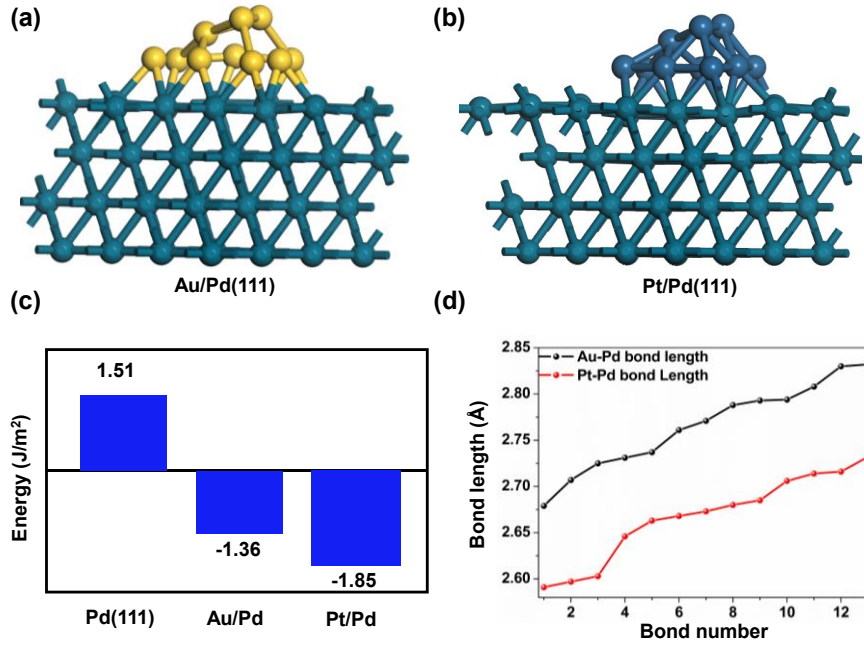


Figure 4. Optimized geometry structures of Au/Pd(111) interface (a) and Pt/Pd(111) interface (b); the formation energies for Pd (111) surface, Au/Pd(111) and Pt/Pd(111) interface (c); and Au-Pd bond length at Au/Pd(111) interface and Pt-Pd bond length at and Pt/Pd(111) interface (d).

Based on the optimized Au/Pd(111) and Pt/Pd(111) interface, the 3D isosurfaces of the charge density difference (CDD) are depicted in **Figure 5**. The CDD isosurface of Au/Pd(111) clearly shows significant electron depletion around interfacial Au and Pd atoms and obvious electron accumulation between Au metallic overlayer and Pd metallic layer. It demonstrates that the electrons depleted from interfacial Au and Pd atoms are predominantly involved in the formation of Au-Pd metallic bonds at the Au/Pd(111) interface. Notably, the distinct electron accumulation region is also visualized on a subset of Au atoms located in the topmost Au surface layer, beyond the expected charge redistribution zone that is strictly confined at the Au-Pd contact plane. This unexpected electronic feature unambiguously demonstrates that a portion of the transferred electrons does not localize merely at the buried interface, but further migrates upwards from the interfacial region to the top-surface Au atoms. In the CDD isosurface of Pt/Pd(111), we can see that the electron accumulation zone is also delocalized in Pt/Pd(111) interface and in good agreement with the formation of Pt-Pd bonds. This distribution characteristics is nearly identical to that of Au/Pd(111). In sharp contrast to the Au/Pd(111) system, the electron accumulation and charge depletion regions at the Pt/Pd(111) interface exhibit much more pronounced delocalization features, and a considerable portion of the electron accumulation regions are precisely distributed in the spatial domain of the Pt-Pt bonding orbitals and nonbonding orbitals localized on the boundary Pt atoms.

These low-lying electronic states are occupied by the redistributed interfacial electrons, which will accelerate the H₂ dissociation process through electron injection into the antibonding orbitals of H₂. Furthermore, the Bader charge analysis was performed to quantitatively characterize the charge transfer in the Au/Pd(111). The Bader charge calculation results show that approximately 0.19 electron is transferred from the Pd metallic layer to the Au metallic overlayers. This charge transfer direction is perfectly aligned with the relative Pauling electronegativity values of Au and Pd, where Au ($\chi = 2.54$) possesses a stronger electron-attracting capability than Pd ($\chi = 2.20$). The spontaneous charge redistribution at the Au/Pd(111) interface results in the observation that the interfacial Pd atoms donate electrons and become partially positively charged, while the Au atoms accept electrons and carry partial negative charges. The negatively charged Au atoms will provide excess electrons to populate the H₂ antibonding orbital, accelerating H₂ dissociation. Further analysis uncovers that the Au atomic layer at the interface bears a negative charge of 0.02 |e|, whereas its adjacent Au atomic layer possesses a much higher negative charge of 0.17 |e|. This significant charge discrepancy will inherently give rise to disparate dissociative adsorption performance. Site-specific dissociative behaviors of different Au layers will be thoroughly discussed in part 3.4. The Bader charge calculation results of Pt/Pd(111) show that only 0.04 electron is transferred from the Pd metallic layers to the adjacent Pt metallic overlayers, which is much lower than the case of Au/Pd(111). It is primarily attributed to the small electronegativity difference between Pd (Pauling scale, $\chi = 2.20$) and Pt (Pauling scale, $\chi = 2.28$). Most intriguingly, the Pt metallic layer at the interface bears a negative charge of 0.18 |e|, while its adjacent Pt atomic layer possesses a positive charge of 0.14 |e|. It means that the electrons localized in the neighboring Pt atomic layer spontaneously transfer and accumulate on the interfacial Pt atomic layer in the process of Pd-Pt bond construction at the bimetallic interface. The positive and negative charge states of Pt layers produce diametrically opposed impacts on H₂ dissociation, and this remarkable distinction in dissociative adsorption behavior will be thoroughly addressed in the part 3.5.

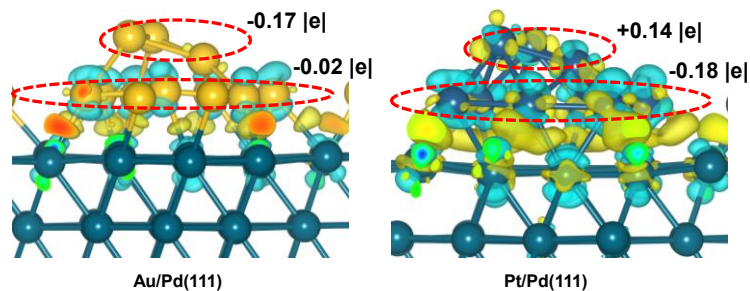


Figure 5. 3D isosurface of the charge density difference with an isovalue of 0.005 e/bohr³ for Au/Pd(111) and Pt/Pd(111); and the Bader charges for different Au layers and Pt layers.

3.4 Hydrogen dissociation kinetics mechanism on Au/Pd(111)

When the Pd surface is decorated with supported Au atoms, three new types of Au active sites are newly generated in Au/Pd(111) interface: Au atoms located at the interface (IF-Au), Au atoms located at the lateral Au surface (LS-Au), and Au atoms located on the upper Au facet (UP-Au), as shown in **Figure 6** and **7**. We first examined the H₂ dissociative adsorption process over the IF-Au. The CI-NEB calculations confirm that the direct dissociation of gas-phase H₂ into two H atoms follows a one-step pathway, with the TS connecting the intact molecular reactant directly to the dissociated atomic products. The TS and FS are shown in **Figure 6a**. The H-H bond at the TS is

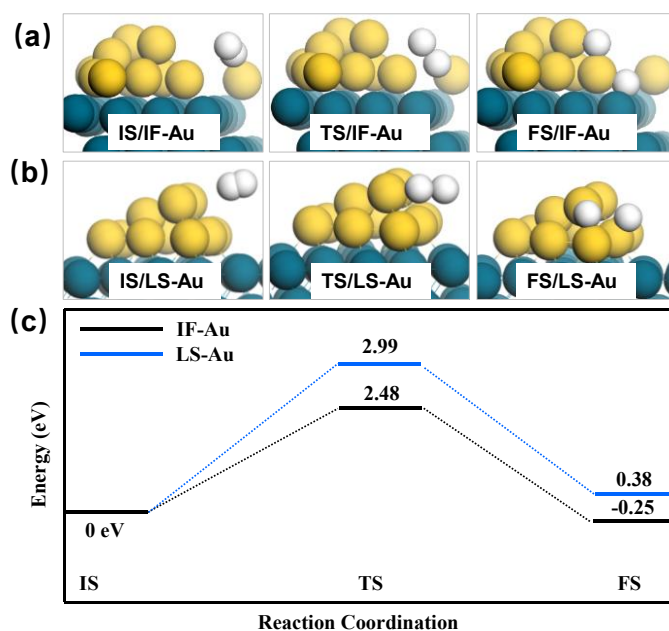


Figure 6. (a) Optimized geometry structures of the H₂ initial state IS/Pd(111), transition state TS/Pd(111), and final state FS/Pd(111) on Pd (111); (b) optimized geometry structures of the H₂ initial state IS/IF-Au, transition state TS/IF-Au, and final state FS/IF-Au on Au atoms located at the interface; (c) optimized geometry structures of the H₂ initial state IS/LS-Au, transition state TS/LS-Au, and final state FS/LS-Au on Au atoms located at the lateral Au surface; and (d) H₂ dissociation reaction pathways on different sites.

lengthened from 0.740 Å to 1.572 Å and the distance between the geometric center of H-H bond

and Au (2.324 Å) is shortened to below the van der Waals interaction distance (~ 3.701 Å), indicating the formation of a substantial orbital overlap beyond non-covalent interactions. In FS, the two dissociated H atoms exhibit distinct bonding configurations: one occupies a bridge site between two adjacent Au atoms with dual covalent interactions (Au-H-Au), while the other H anchors at the Au-Pd bimetallic interface, forming a covalent linkage with one interfacial Au and one interfacial Pd atom simultaneously (Au-H-Pd). The activation energy for H₂ dissociation process on IF-Au is 2.48 eV (see **Figure 6c**). The high energy barrier severely suppresses the occurrence of the H₂ dissociation process on IF-Au center.

We further examined the elementary reaction mechanism of H₂ dissociation at the LS-Au active center. As gas-phase H₂ molecules approach the Au surface, they first enter a shallow physisorption well at a distance of 3.701 Å between the H₂ center and the nearest-neighbor Au atom, where weak van der Waals interactions slightly elongate the H–H bond from its gas-phase equilibrium length of 0.74 Å to 0.753 Å. Traversing the TS located at the top of the reaction barrier, the molecule enters a larger molecular chemisorption well with more efficient kinetic energy dissipation, where the H–H bond fully cleaves to form two adjacent surface-bound Au–H-Au and Au-H hydride species. In the TS, the H-H bond is broken and two H move to the LS-Au sites. The H-H distance is lengthened from 0.753 Å to 1.845 Å, while the distance of H-Au is shortened from 3.326 Å to 2.071 Å. The calculated activation energy is 2.99 eV. The prohibitively high reaction energy barrier unambiguously reveals that the contribution of this pathway to the H₂ dissociation process is practically negligible under the normal reaction conditions.

Finally, we systematically investigated the elementary mechanism of H₂ dissociation at the UP-Au active center and the further migration process of the adsorbed H species at topmost Au surface to the Pd surface. The H₂ molecule spontaneously dissociates into two individual H adatoms following a single-step transition state (TS1) without metastable molecular adsorption precursor, and the H adatoms are stably anchored on the top facet of the topmost Au surface (RI), as shown in **Figure 7a**. At TS1, the H-H bond is lengthened from 0.740 Å to 1.421 Å, and the distance between H and adjacent Pd atoms lies between 1.797 Å $\sim$ 1.847 Å, which indicates that the H-H bond is in the process of dissociation, while the Au-H bonding interaction is being established. The activation energy for hydrogen dissociation process is 1.04 eV, which is much lower than the ones for the reaction pathways on IP-Au and LS-Au active centers. After this elementary H₂ dissociation step,

the absorbed H on topmost Au surface further migrate across the bimetallic boundary to the Pd surface. This H migration process requires crossing an activation energy barrier of 1.06 eV, which corresponds to transition state TS2. As shown in **Figure 7b**, the H-Au bond is broken and H establishes chemical bonding interactions with the Pd. The H-Au distance is lengthened from 1.788 Å to 2.586 Å, while the distance of H-Pd is shortened from 4.460 Å to 3.490 Å in TS2. By quantifying site-specific reactivity of Au surface, it demonstrates that UP-Au sites exhibit a higher catalytic activity for H₂ dissociation than IF-Au and LS-Au sites, with the reaction barrier reduced by 1.43 eV and 1.94 eV, respectively. The remarkable distinction in H dissociation behavior is quantitatively and directly correlated with the accumulated negative charge amount on the different Au atoms, as verified by the previous Bader charge analysis.

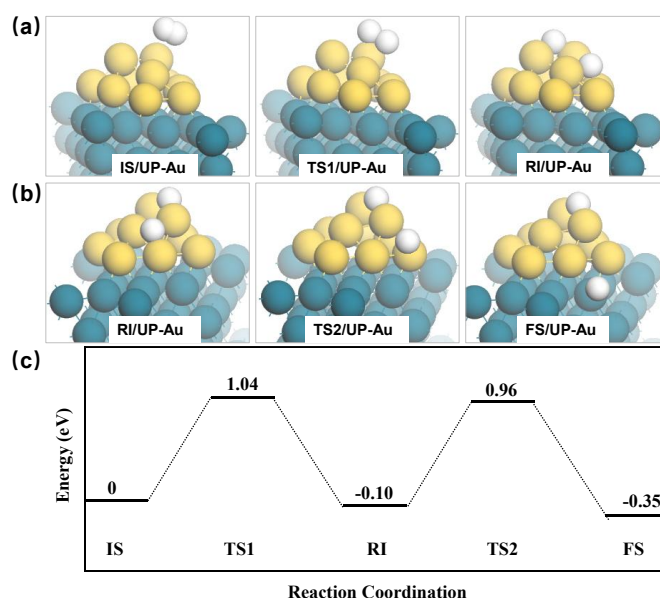


Figure 7. (a) optimized geometry structures of the H₂ initial state IS/UP-Au, transition state TS1/UP-Au, and reaction intermediate RI/UP-Au on Au atoms localized at the upper Au facet; (b) optimized geometry structures of the transition state TS2/UP-Au, and final state FS/UP-Au on Au atoms located on the upper Au facet; and (c) H₂ dissociation reaction pathway and H diffusion pathway.

3.5 Hydrogen dissociation kinetics mechanism on Pt/Pd(111)

Based on density functional theory (DFT) calculations, we also resolve the site-specific dissociation dynamics of H₂ molecules across a series of distinct catalytic sites of **Pt/Pd(111)**, quantifying the site-dependent reactivity and unveiling the fundamentally different dissociation mechanisms. Similar with **Au/Pd(111)**, we computationally investigated three structurally distinct Pt active sites on **Pt/Pd(111)**: IF-Pt, LS-Pt, and UP-Pt, as shown in **Figure 8** and **9**. For the active site IF-Pt, our CI-NEB calculations suggest that the gas-phase H₂ dissociation process that directly splits the H-H

bond to form two H atoms is a barrier-mediated single-step pathway (activation energy barrier $E_a = 0.60$ eV), where TS acts as the only saddle point connecting the molecular H_2 and the dissociated atomic H. Following the dissociative cleavage of H_2 , the generated two H atoms adsorb on the surfaces of Pd and Pt, respectively. The geometry structures of IS, TS and FS are depicted in **Figure 8a**. At TS, the H-H bond is lengthened from 0.740 Å to 1.245 Å, one H atom resides at the Pt-Pt bridge site, with H-Pt bond lengths of 2.325 Å and 2.311 Å to the two neighboring Pt centers, and the other H specie occupies the Pd-Pd bridge site, exhibiting a shorter H-Pd distance of 2.321 Å and 1.940 Å to each of the two adjacent Pd atoms. In the FS, the H atom adsorbed on the Pt surface exhibits an asymmetric dual-site bonding mode, forming two Pt-H bonds of 1.691 Å and 1.835 Å, which reflects the unique electronic interaction between the H adatom and the Pt surface; in comparison, the other H atom adsorbed on the Pd surface exhibits the symmetric dual-site bonding mode, forming two Pd-H bonds of 1.821 Å and 1.824 Å. The H atoms residing on the Pd surface can readily migrate across the Pd surface and penetrate into the interstitial sites of the Pd crystal lattice, forming subsurface or bulk hydrogen phases. Relative to the IF-Au active sites, the IF-Pt sites acting as the key reaction centers drastically lower the kinetic energy barrier for H_2 dissociative cleavage. This effect significantly accelerates the surface hydrogen activation kinetics, and ultimately enhances the H_2 response rate of the chemiresistive sensors.

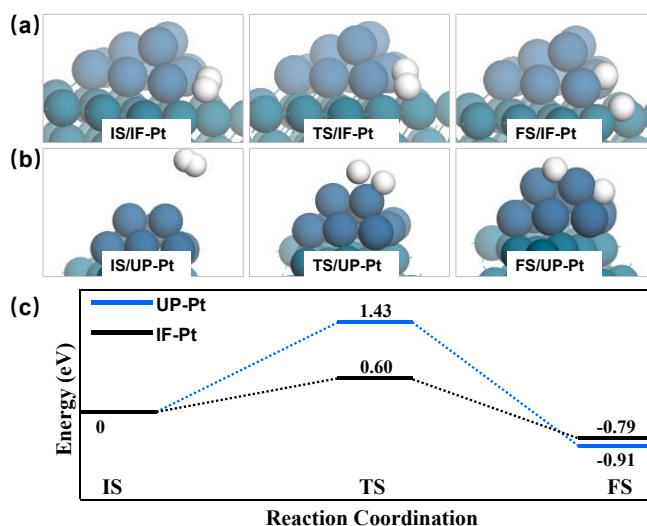


Figure 8. (a) optimized geometry structures of the H_2 initial state IS/IF-Pt, translation state TS/IF-Pt, and final state FS/IF-Pt on Pt atoms located at the interface; (b) optimized geometry structures of the H_2 initial state IS/UP-Au, translation state TS/UP-Au, and final state FS/UP-Au on Pt atoms located on the upper Pt facet; and (c) H_2 dissociation reaction pathways on different Pt sites.

On the UP-Pt sites, H_2 can undergo direct one-step dissociation from the gas phase and forms two

surface Pt-H hydride species, with no stable physisorbed molecular state identified on the reaction pathway, as shown in **Figure 8b** and **8c**. At the TS, the H-H bond is lengthened from 0.740 Å to 1.869 Å, and the distance between Pt and H is shortened to 1.769 Å. The H₂ dissociation barrier on UP-Pt site is calculated to be as high as 1.43 eV, which is much higher than the case of IF-Pt. As verified by Bader charge analysis, such a significantly increased dissociation energy barrier is essentially derived from the excessive positive charges accumulated on the topmost Pt layer, which suppresses the electron donation to the H₂ σ^* antibonding orbital. Furthermore, we investigated the LS-Pt site as an active center. Upon successive approach of H₂ molecules toward the Pt lateral facet, molecular H₂ undergoes spontaneous dissociation and yields two isolated H adatoms chemisorbed on the Pt side surface. As shown in **Figure 9a**, one H atom occupies a bridge site between two adjacent Pt atoms with dual covalent interactions (Pt-H-Pt), and the other H form a covalent bond with neighboring Pt atom (Pt-H) in the product intermediate (RI). This kinetically favorable process exhibits a much low reaction energy barrier (0.40 eV), and the geometric configuration of its TS is presented in the **Figure 9a**. The H-H bond is lengthened from 0.740 Å to 1.280 Å, and two distinct Pt-H bonds exhibit optimized bond lengths of 1.873 Å and 1.896 Å, respectively, which unambiguously demonstrates the cleavage of the H-H bond, accompanied by the concurrent formation of nascent H-Pt bonds on the LS-Pt site.

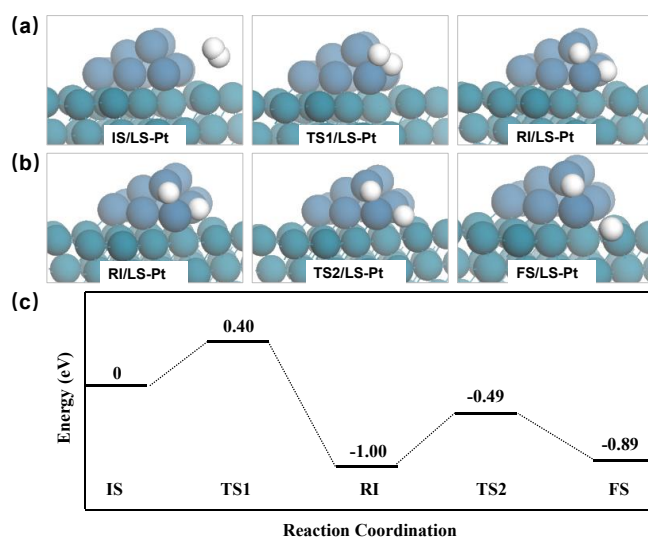


Figure 9. (a) optimized geometry structures of the H₂ initial state IS/LS-Pt, translation state TS1/LS-Pt, and reaction intermediate RI/LS-Pt on Pt atoms localized at the upper Au facet; (b) optimized geometry structures of the translation state TS2/LS-Pt, and final state FS/LS-Pt on Pt atoms located at the lateral Au surface; and (c) H₂ dissociation reaction pathway and H diffusion pathway.

We further performed computational simulations on the diffusion dynamics of H adatoms on Pt

surface migrating across the Pt-Pd interface to the Pd surface. The geometries of the initial state (RI), TS and FS are illustrated in **Figure 9b**. The diffusion kinetic barrier extracted from the optimized climbing-image nudged elastic band (CI-NEB) pathway is approximately 0.51 eV, which falls well within the typical energy range for thermally activated surface H migration. It indicates that the H diffusion from the Pt terrace to the Pd surface does not suffer from significant kinetic limitation. The low barrier also implies that the H adatom will not be stably confined at the initial Pt adsorption site, but can rapidly traverse the Pt-Pd interface to reach adsorption sites on the Pd side, and then diffuse deeper into the Pd metallic bulk lattice. Combined with the low reaction energy barrier of H₂ dissociation, we can reasonably deduce that the Pt/Pd (111) possesses outstanding H₂ response activity, far superior to that of pure Pd (111) facet.

4. Conclusion

In this study, Pd-based heterostructures Au/Pd(111) and Pt/Pd(111) are theoretically designed toward enhanced H₂ sensing performances. Density functional theory (DFT) calculations reveal that the constructed Au/Pd(111) and Pt/Pd(111) heterointerfaces lead to considerable negative charge population on partial Au and Pd atoms, generating high-activity chemisorption centers. This electronic effect greatly facilitates the dissociative adsorption of H₂ molecules, and increases the surface coverage of hydrogen adatoms on the Pd lattice.

The CI-NEB calculation results confirm that the H₂ dissociative adsorption energy barrier is significantly reduced with the elevated negative charge accumulation at the active adsorption centers. For the Au/Pd(111) heterointerface, the redistributed negative charge is dominantly populated on the UP-Au atomic plane with a value of -0.17 |e|. This electronic effect significantly decreases the H₂ dissociative adsorption energy barrier on UP-Au sites by 1.63 eV compared with LS-Au sites. On the contrary, at the Pt/Pd(111) heterointerface, the negative charge primarily accumulates in the inner interfacial Pt atomic layer (-0.18 |e|), whereas the outermost UP-Pt atomic plane is partially positively charged (+0.14 |e|), which consequently makes the H₂ dissociation barrier on the UP-Pt plane 1.03 eV higher than that on the LS-Pt plane. Moreover, our DFT calculation results unambiguously elucidate that the rate-determining step dominating the response performance of Pd-based hydrogen sensors is the surface dissociative adsorption of H₂, instead of the subsequent bulk diffusion of dissociated H atoms into the Pd lattice interior.

Our findings highlight the precise modulation of the interfacial charge redistribution on accelerating

hydrogen spillover and could provide theoretical and experimental guidance for developing a high-efficiency H₂ sensor. In the future, the universality of this strategy should be further investigated for the development of heterointerface-engineered sensing materials.

Notes

The authors declare no competing financial interest.

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