

Surface Adsorption to Bulk Storage: Integrating Experimental and Theoretical Insights into Hydrogen Behavior on Palladium

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Surface Adsorption to Bulk Storage: Integrating Experimental and Theoretical Insights into Hydrogen Behavior on Palladium

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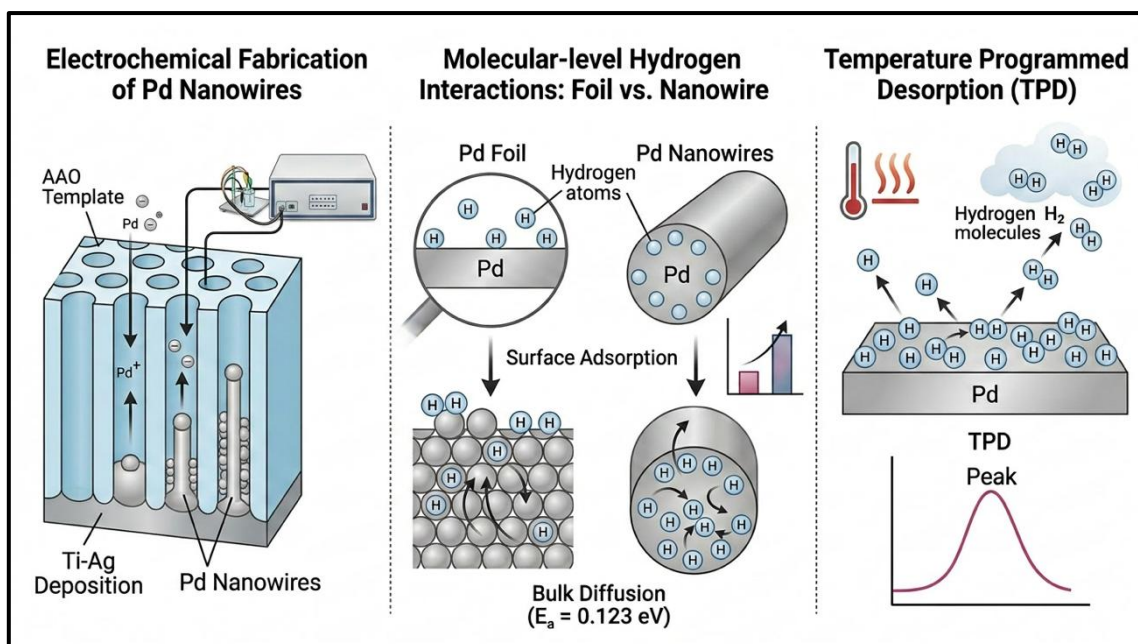
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Abstract

The interaction of hydrogen with palladium (Pd) forms the basis of numerous applications, including catalysis, biosensing, gas detection, and hydrogen storage technologies, due to the exceptional characteristics of Pd to adsorb, dissociate, and transport hydrogen. In this study, experimental and density functional theory (DFT) analyses are employed to establish a unified understanding regarding the hydrogen adsorption and bulk diffusion in Pd foils and electrochemically fabricated Pd nanowires. Pd nanowires were synthesized using anodized aluminum oxide (AAO) templates, and subsequently characterized by FE-SEM, AFM, XRD and XPS analyses to evaluate their morphology, topography,

crystallinity, and surface chemistry. Temperature programmed desorption (TPD) analysis revealed that after surface adsorption and saturation, hydrogen robustly diffuse into the Pd bulk under continuous exposure of hydrogen, with an experimentally determined diffusion barrier of 0.123 eV. However, the evolution of hydrogen is observed to follow zeroth-order kinetics. Despite the relatively rough morphology, Pd nanowires exhibited adsorption characteristics remarkably analogous to that of Pd foils, suggesting that the hydrogen uptake mechanism remains unchanged irrespective of the Pd architectures. DFT analysis provides atomistic insights into the dissociative adsorption of H₂ over Pd surface. Furthermore, calculations reveal that the migration of resulting atomic hydrogen from surface to subsurface hollow site is essentially a barrier less ($E_a \approx 0$ eV) and thermodynamically exergonic process ($\Delta G = -0.53$ eV), substantiating the experimentally observed transition from surface adsorption to bulk diffusion. Overall, this study provides a comprehensive framework for hydrogen interaction with Pd, offering guidance for the rational design of Pd-based materials for hydrogen dominated catalysis, sensing, separation, and energy storage applications.

Key words: Anodization, Pd nanowires, Pd foil, hydrogen adsorption, desorption and DFT study



Graphical abstract: Schematic diagram illustrating the template-assisted growth of Pd nanowires using anodic AAO and their surface interactions associated with hydrogen adsorption and desorption processes.

1. Introduction

Nanostructured materials have attracted significant attention due to their distinctive characteristics such as a high surface-to-volume ratio [1], [2], thermal stability [3], [4], [5], [6], and unique optical and magnetic properties. They are used in various applications including catalysis, energy storage, sensing, optics, and electronics [7], [8], [9], [10], [11]. Among these nanomaterials, metal nanowires have been extensively investigated because of their high surface-to-volume ratio, superior mechanical strength, enhanced thermal conductivity, and improved electrical conductivity [12]. In particular, Pd nanowires have gained popularity due to their short hydrogen diffusion paths and large surface area, resulting in increased sensitivity and rapid detection for hydrogen [7], [13], [14]. Palladium has many essential applications, including hydrogen gas detection [15], fuel cell catalysis [16], biosensing [17], and surface-enhanced Raman scattering [18]. Pd is a major component of three-way automotive

catalysts and is also employed as a catalyst in hydrogenation and dehydrogenation reactions [19], [20], [21], [22], [23]. Pd is also important for hydrogen storage and sensing applications [24]. Both experimental and theoretical studies have investigated how hydrogen interacts with Pd surfaces due to Pd's exceptional ability to absorb large quantities of hydrogen [19], [25], [26].

The hydrogen storage capacity of palladium is approximately 0.56 wt% at 298 K and 1 atm of H₂ [27]. The adsorption of hydrogen on Pd surfaces has been extensively studied. On the Pd(111) surface, four adsorption sites are available for hydrogen: bridge sites, on-top sites, hcp hollow sites, and fcc hollow sites. Theoretical studies show that the fcc hollow site is the most stable, followed by hcp and bridge sites [28]. Hydrogen interacts with Pd in two fundamental states: the α -state, where hydrogen dissolves into the Pd bulk, and the β -state, where hydrogen is adsorbed on the Pd surface [29]. Adsorbed hydrogen in the β -state can be classified as weakly adsorbed (physisorbed, H_w) or strongly adsorbed (chemisorbed, H_s) [30]. Hydrogen absorbed in the α -state (H_{abs}) forms palladium hydride, by the interaction with the Pd lattice [29]. Due to its high hydrogen storage capacity, Pd hydride has been extensively investigated [11], [31]. The formation of metal hydrides typically requires high hydrogen pressure or elevated temperature because dissociating hydrogen molecules requires significant activation energy [32]. However, on palladium surfaces, H₂ dissociation proceeds with minimal or no activation barrier [33]. Hydrogen uptake in Pd occurs in three steps: dissociation of H₂ molecules on the surface, diffusion of H atoms into the subsurface region, and occupation of octahedral interstitial sites to form Pd–H [19]. The interaction of hydrogen with Pd nanowires is of considerable interest because their size, morphology, and crystal orientation influence hydrogen dissociation, diffusion, and desorption. Hydrogen absorption and desorption in Pd is reversible, as the temperature changes and that makes Pd a promising material for hydrogen storage applications [34]. In this paper, we report the adsorption and absorption of hydrogen on Pd nanowires and a foil. We fabricated Pd nanowires using AAO templates and investigated the interaction of hydrogen with Pd surfaces using a temperature programmed desorption (TPD) technique. Moreover, density functional theory (DFT) is employed to

rationalize the experimental observations by comprehending energetically the adsorption configurations, diffusion, and subsequently the desorption of hydrogen at different temperature.

2. Experimental Methods

2.1. Fabrication of Pd Nanowires

Self-ordered AAO templates with pore diameters of approximately 100 nm and 60 nm were fabricated via a two-step anodization process. High-purity annealed aluminum was first electropolished in an ethanol-perchloric acid mixture (4:1) at room temperature using aluminum and graphite as the anode and cathode, respectively, under an applied voltage of 20 V for 40 s to obtain a smooth surface. Anodization was then performed in 0.3 M oxalic acid using a two-electrode configuration at constant voltages of 60 V and 45 V, while maintaining the electrolyte temperature at 3 ± 3 °C with continuous magnetic stirring. The first anodization was carried out for 2 h, followed by chemical removal of the resulting disordered oxide layer in a solution of 1.6 wt% phosphoric acid and 5 wt% chromium oxide for 12 h at ambient temperature, yielding a surface with ordered concave patterns. A second anodization under identical conditions produced highly ordered and uniform AAO templates. **Fig 1** shows the process of the Pd nanowire fabrication schematically.

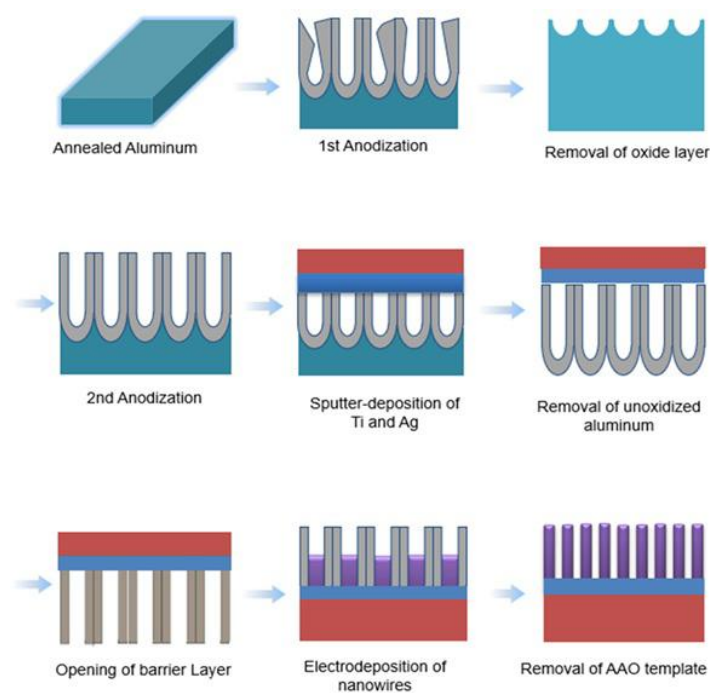


Fig. 1: Schematic diagram of the Pd nanowire fabrication process.

For nanowire growth, a Ti (20 nm)/Ag (200 nm) bilayer was sputtered onto one side of the AAO template, which was then bonded to a tantalum foil using conductive silver paste. Residual aluminum was removed using a saturated HgCl_2 solution for 4 h, and the barrier layer was dissolved in 5 wt% phosphoric acid for 3 h. Pd nanowires were electrodeposited using a three-electrode configuration with AAO as the working electrode, graphite as the counter electrode, and Ag/AgCl as the reference electrode. Electrodeposition was conducted at -0.8 V for 3600 s at room temperature in an electrolyte containing 0.05 g NH_4Cl and 0.1 g $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ dissolved in 50 mL of distilled water. In order to get free standing Pd nanowires, The AAO template was removed using the 1 M sodium hydroxide solution at room temperature, followed by a gentle wash with distilled water in order to obtain free-standing nanowires.

2.2. Computational details

First-principles density functional theory (DFT) calculations were performed using the DMol³ module in Material Studio [35]. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional within the generalized-gradient approximation (GGA) framework [36], along with the double numerical plus polarization basis set (DNP) [37], semi-core pseudopotentials [38], and Grimme's dispersion correction [39], was employed during calculations. Geometry optimizations were conducted under the fine convergence criteria and thermal smearing value of 0.005 Ha. Transition barrier was determined using the LST/QST method [40], whereas the frequency calculations were carried out to find Gibbs free energy values (G).

Adsorption energy (E_{ads}) of hydrogen on Pd(100) surface was calculated as:

$$E_{\text{ads}} = E_{\text{Pd+H}} - (E_{\text{Pd}} + nE_{\text{H}}) \quad (1)$$

where, the $E_{\text{Pd+H}}$, E_{Pd} , and nE_{H} represent ground state electronic energy of hydrogen-adsorbed Pd supercell, bare Pd supercell, and atomic hydrogen with n number, respectively.

3. Results and Discussion

3.1. AAO Template Fabrication

Pure annealed aluminum was electropolished in an electrolytic cell using an electrolyte solution of ethanol and perchloric acid, as shown in **Fig. 2a**. To obtain self-ordered AAO templates, a two-step anodization technique was employed. A 0.3 M oxalic acid solution was used to anodize the electropolished aluminum substrate. Controlled anodization of aluminum in aqueous acidic electrolytes lead to the formation of porous anodic alumina. During the first-step anodization, an oxide layer with disordered and irregular pores were produced, as illustrated in **Fig. 2b**. This irregular oxide layer was subsequently removed by chemical etching, resulting in a surface with highly regular concave patterns, as shown in **Fig. 2c**. These concave structures act as pore initiation sites during the second anodization step, enabling the formation of highly ordered, uniform, and homogeneous AAO templates [41], [42], [43], [44], [45], [46]. Important parameters governing nanoporous alumina growth include anodization voltage or current density, anodization time, electrolyte type and concentration, pH, and temperature [47], [48]. The resulting AAO template with a pore diameter of approximately 100 nm is confirmed by the FE-SEM image in **Fig. 2d**.

For nanowire electrodeposition, a metallic contact layer consisting of 20 nm Ti and 200 nm Ag was sputter-deposited onto one side of the AAO template, which was then bonded to a tantalum foil using high-temperature conductive silver paste. Metallic aluminum was removed by immersing the sample in saturated mercury chloride solution, as shown in **Fig. 2e**. The barrier layer, which inhibits electrical connectivity between the pores and the metallic substrate, was subsequently removed, as depicted in **Fig. 2f** [49], [50]. Electrodeposition of Pd nanowires was performed using a three-electrode electrochemical cell, in which AAO acted as the working electrode, graphite or platinum foil served as the counter electrode, and Ag/AgCl functioned as the reference electrode. The electrolyte solution consisted of $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ and NH_4Cl , chosen for its superior chemical stability compared to acidic or alkaline Pd electrolytes [7], [49]. **Fig. 2g** shows the Pd nanowire growth within AAO. Finally, the AAO

template was dissolved in a 2 M NaOH solution for one hour, releasing freestanding Pd nanowires on the tantalum substrate, as displayed in **Fig. 2h** [51].

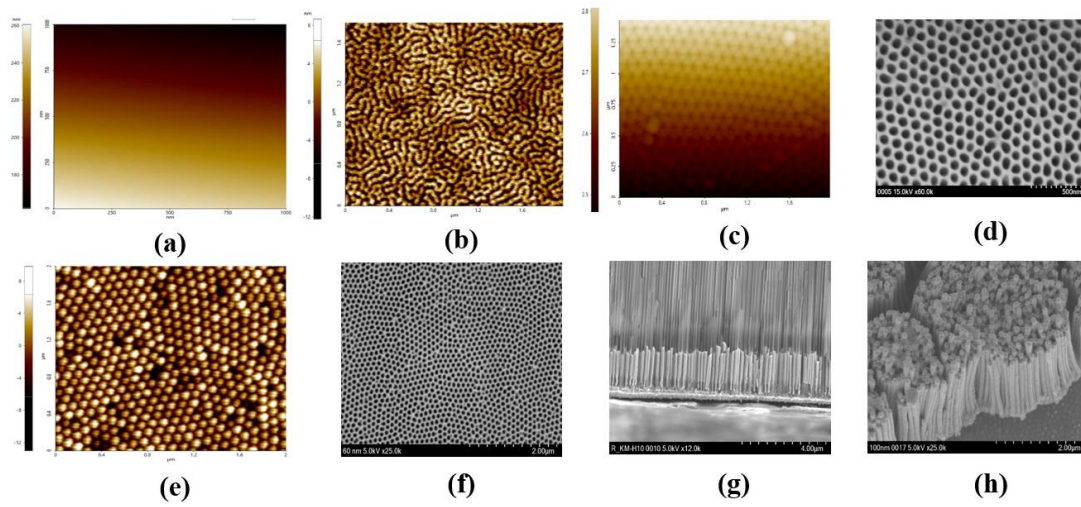


Fig. 2: AFM and FE-SEM images. (a) Electropolished aluminum surface. (b) Disordered porous alumina formed after the first anodization. (c) Highly regular concave structures. (d) Ordered AAO pores. (e) Removal of residual metallic aluminum. (f) Removal of the barrier layer to open pore bottoms. (g) Electrodeposition of Pd nanowires inside AAO pores. (h) Free-standing Pd nanowires after dissolution of the AAO matrix.

3.2. Description of the UHV system

The interaction of hydrogen with Pd nanowires was studied in ultrahigh vacuum (UHV). The chamber was featured with a manipulator, a precision leak valve for releasing hydrogen gas into the UHV chamber, a sputter ion gun for cleaning the surface, and a mass spectrometer to identify desorbing species. The chamber was pumped using a turbomolecular pump and an oil diffusion pump. The chamber's base pressure was 1.0×10^{-10} torr.

3.3. Mounting of the sample

Palladium nanowires were mounted on tantalum foil using silver paste for heating and cooling. A K-type thermocouple that was welded at the back of the tantalum foil was used to monitor the temperature

of the sample. The sample could be cooled up to 85 K using liquid nitrogen. **Fig. 3** shows the sample mounted on the manipulator.

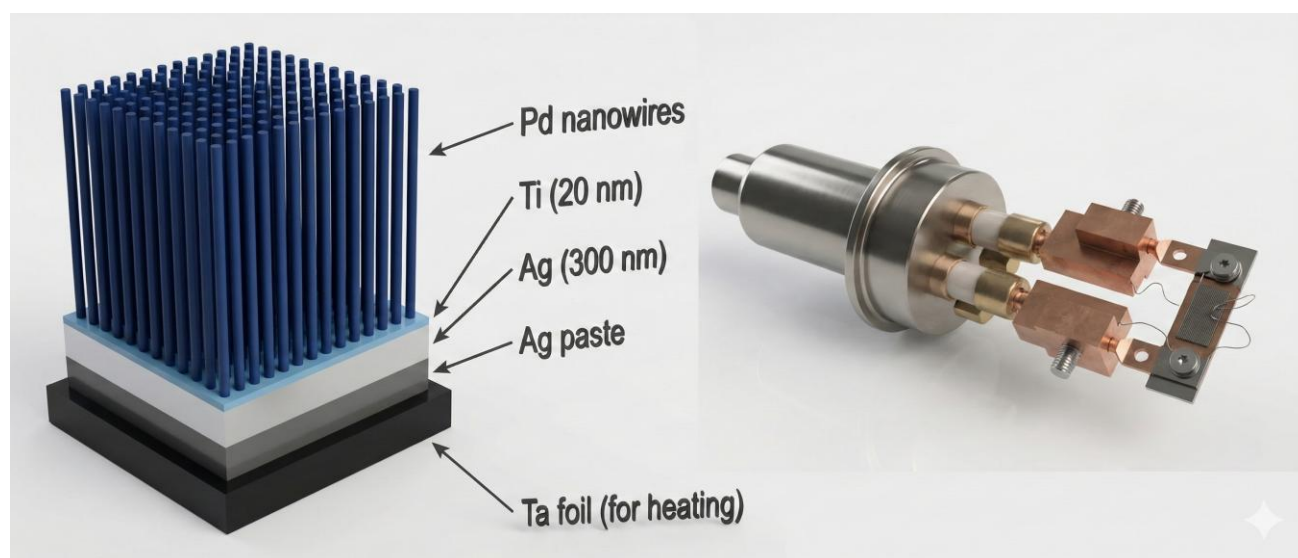


Fig. 3: Sample mounted on the sample manipulator.

3.4. X-ray Diffraction (XRD)

The crystallinity and phase identification was analyzed by employing X-ray diffraction (XRD) as shown in **Fig. 4a**. XRD diffractogram of Pd nanowires exhibits peaks at 2θ values corresponding to (111), (200), (220) and (311) planes, reflect face centered-cubic (FCC) Pd [49], reliable with a standard Pd data (JCPDS No.46-1043). The strong intense corresponding to (111) planes suggests a preferred growth orientation in this facet, which is commonly observed due to its low surface energy and thermodynamic stability [7]. Additionally, some minor peaks ascribed to Ag^+ were also observed, probably originating from underlying Ag electrode employed during deposition. The sharp and well define nature of Pd peaks reflects high crystallinity and structural order of Pd, which is related with previous reported data.

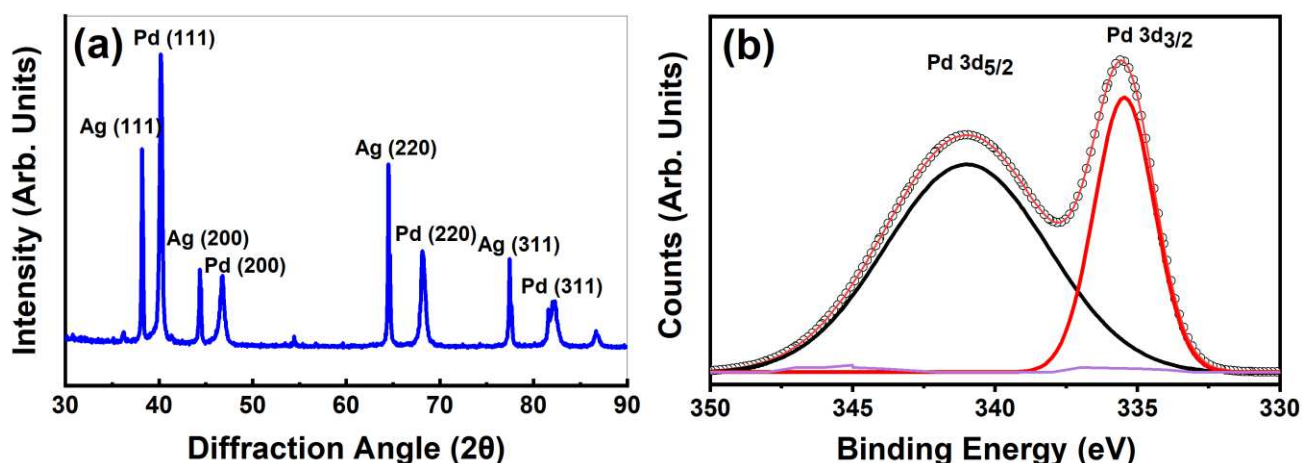


Fig. 4: (a) The XRD pattern of Pd nanowires. (b) High resolution XPS spectra of the pd nanowires.

3.5. X-ray photoelectron electron spectroscopy (XPS)

X-ray photoelectron electron spectroscopy (XPS) was used to study the surface composition and electronic state of synthesized Pd nanowires. The XPS survey spectrum of prepared Pd nanowires (**Fig. 4b**) shows the distinctive peaks corresponding to Pd 3d and carbon, C 1s. The presence of adventitious C1s on the surface of Pd nanowires is commonly observed owing of atmospheric exposure during sample handling. The high resolution spectrum of Pd 3d spectrum exhibits two prominent peaks at binding energy of approximately 335.1 eV and 340.4 eV, attributed to Pd 3d_{5/2} and Pd 3d_{3/2} levels, respectively, which is the characteristic of metallic Pd (Pd⁰) [49]. These results confirm that the prepared Pd nanowires predominantly exist in zerovalent metallic state, which is desirable electronic and catalytic application.

3.6. Adsorption and absorption of hydrogen on a Pd foil

The adsorption of hydrogen on the surface of Pd foil was investigated using the temperature-programmed desorption (TPD) technique. The formation of palladium hydrides begins with the dissociation of molecular hydrogen (H₂). Most metals, except Pd, require additional energy to overcome an activation barrier for dissociative adsorption, typically necessitating high hydrogen pressures or elevated temperatures. In contrast, palladium surfaces allow dissociative adsorption of H₂

molecules with very low activation energy barriers [52]. The TPD features of H₂ desorption from a Pd foil are presented in **Fig. 5a**. The sample surface was prepared by dosing a controlled amounts of hydrogen at 126 K. At low hydrogen exposures, a single desorption peak (labeled as the β -peak) appears at 300 K, corresponding to the recombinative desorption of chemisorbed hydrogen atoms. At higher H₂ exposures (>1 L), a second desorption feature emerges at 150 K (labeled as the α -peak). The intensity of the α -peak continues to increase with increasing hydrogen exposure. **Fig. 5b** illustrates the evolution of the α - and β -peak areas as a function of hydrogen exposure. It is evident that the β -peak saturates at approximately 5 L exposure, whereas the α -peak continues to grow with additional hydrogen dosing. The α -peak is attributed to hydrogen evolving from the bulk of palladium. This behavior indicates that hydrogen is initially adsorbed on the surface; once the Pd surface becomes saturated, hydrogen atoms begin to diffuse into the bulk of the metal [22], [53].

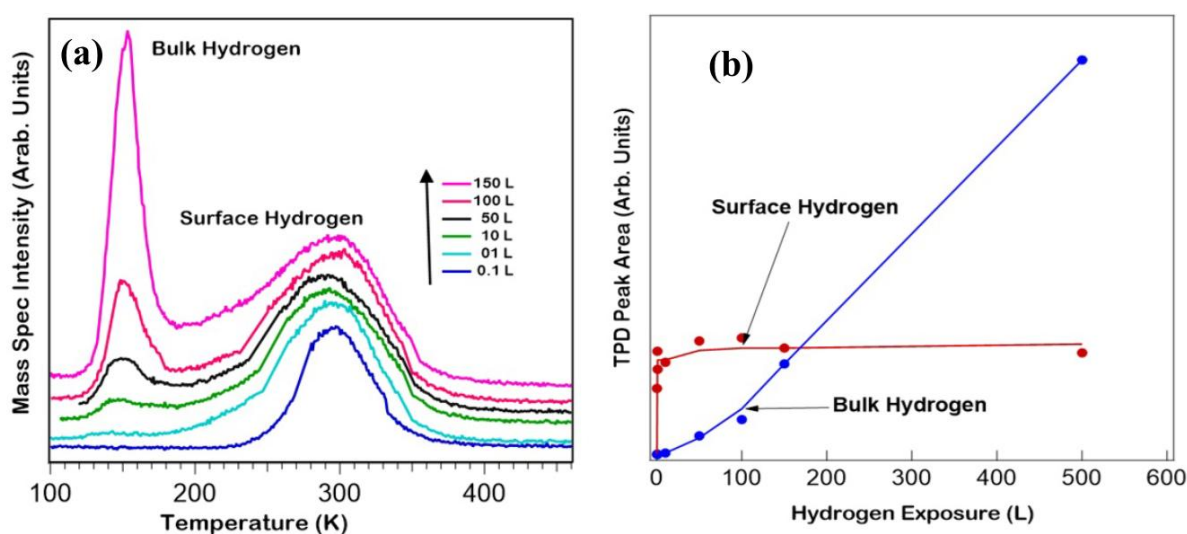


Fig. 5: (a) TPD features for H₂ after hydrogen dosing on Pd at 126 K. (b) Change of the areas of α and β peak as a function of hydrogen exposure at 126 K.

Fig. 6a shows the TPD features obtained by dosing 1,000200,000 L of hydrogen on the surface of Pd at 126 K. The bulk hydrogen desorption peak (α -peak) grows linearly and shifts to higher temperatures as the hydrogen exposure increases. Note that the leading edges of the TPD features overlap, indicating zeroth-order desorption kinetics. The zeroth-order desorption behavior implies the presence of a

hydrogen reservoir in the near surface region that can rapidly supply hydrogen to the surface. The diffusion barrier of hydrogen atoms in the Pd foil was calculated using an Arrhenius plot (**Fig. 6b**). The calculated diffusion barrier is 11.9 kJ/mol (0.123 eV), which is in good agreement with previously reported values [54].

3.7. Adsorption and absorption of hydrogen on Pd a nanowires

The interaction of hydrogen with Pd nanowires has been investigated. **Fig. 7** shows the TPD features recorded for the desorption of H₂ after dosing hydrogen on 100 nm and 60 nm Pd nanowires at 126 K. The TPD features obtained from Pd nanowires are similar in general to those from the Pd foil. Hydrogen is first adsorbed on the surface and the diffusion of hydrogen into the bulk of Pd takes place as the hydrogen exposure increases. However, the TPD peaks from nanowires are wider than that from the foil. The surface atomic structure can affect the shape of TPD features. In the case of the foil, the sample was annealed at 1100 K after Ar ion sputtering to smooth the surface. Because Pd nanowire samples were annealed at 600 K, the surfaces of nanowires might be rough compared to the surface of the Pd foil that was annealed at the much higher temperature. The absorption of hydrogen in Pd nanowires has been investigated with TPD by increasing hydrogen exposure. **Fig. 8** shows the TPD features of H₂ for the evolution of hydrogen atoms absorbed in Pd nanowires. H₂ TPD features obtained from Pd nanowires are very similar to those from the Pd foil. The leading edges of TPD peaks are superimposed when H₂ exposure is increased. Again, the evolution of hydrogen from the bulk of Pd nanowires follows the zeroth-order kinetics.

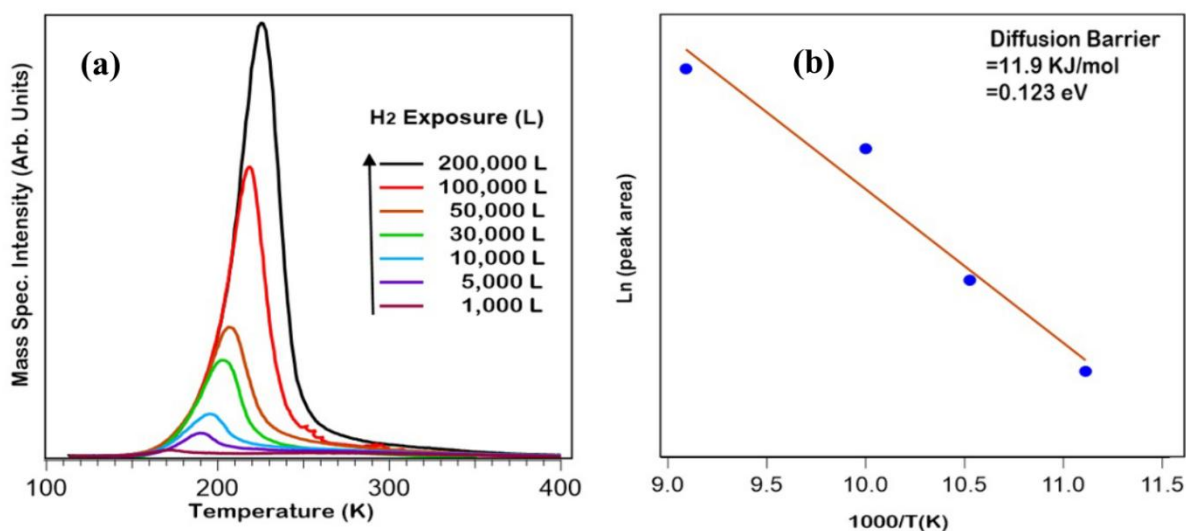


Fig. 6: (a) TPD features showing the evolution of bulk hydrogen after dosing indicated amounts of hydrogen at 126 K. (b) The Arrhenius plot that shows the change of the H₂ TPD peak area at different hydrogen dosing temperatures.

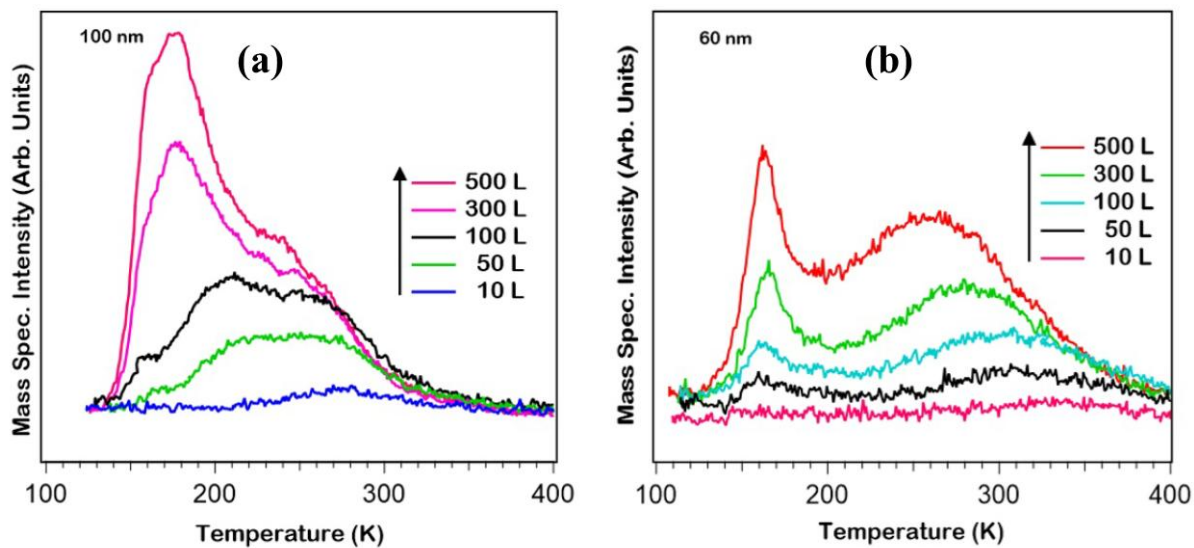


Figure 7: (a, b) TPD features of H₂/Pd nanowires after low hydrogen exposure at 126 K.

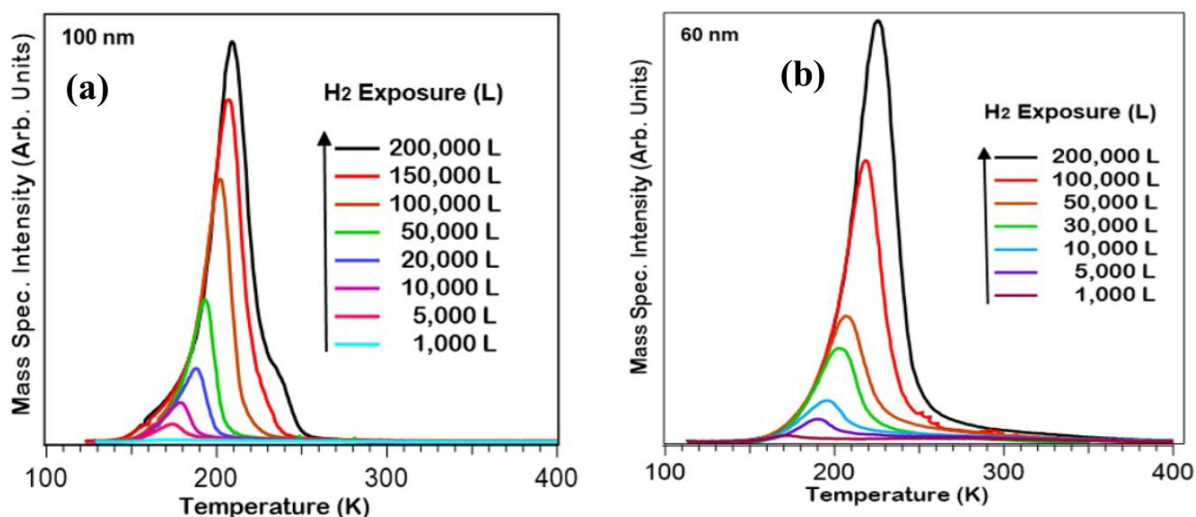


Figure 8: (a, b) TPD features of H₂/Pd nanowires after high hydrogen exposures at 126 K.

3.8. Theoretical insights

DFT analysis revealed that molecular hydrogen (H₂) adsorption on Pd(100) involves a dissociative adsorption over the surface, which can be attributed to the well-established Kubas-type interaction [55]. The H₂ adsorption, associated with E_{ads} value of -1.05 eV, is realized by backdonation of electron from the filled $d\pi$ orbital of Pd into the empty σ^* orbital of H₂, leading to weakening and subsequent homolysis of H–H bond. Such as **Fig. 9(a-b)** clearly shows that H–H bond length in the adsorption complex is elongated to 1.53 Å relative to the 0.75 Å bond length of isolated gas-phase H₂ in addition to the formation of Pd–H bond (1.74 Å). Further, Hirshfeld charge transfer analysis also corroborated this dissociation by calculating the accumulation of 0.17 e electron density on adsorbed H₂ molecule (**Table 1**), probably due to the backbonding. Similarly, the noticeable overlap of the H-1s and Pd-5s states in the valence region below the Fermi level, in the partial density of states (PDOS) plot (**Fig. 9d**), indicates a significant orbital hybridization, substantiating the electronic interaction responsible for the stable Pd–H bonding [56]. Moreover, the charge density difference (CDD) analysis (**Fig. 9c**) also supports this phenomenon, where the yellow contour across the hydrogen atoms illustrates electron density depletion, in other words H–H bond-breaking. Since the DFT analysis demonstrated

the dissociative adsorption of H_2 on Pd(100) surface, therefore atomic hydrogen was used as the adsorbate for further calculations.

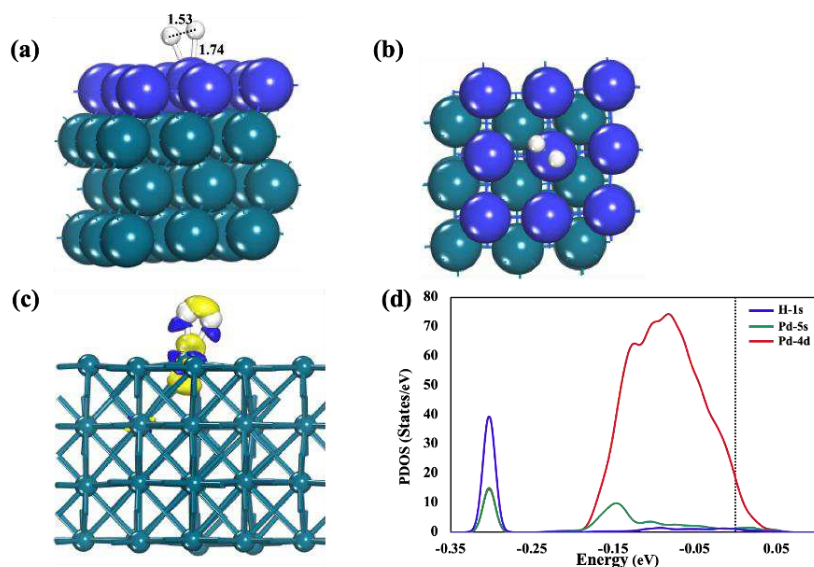


Fig. 9: Adsorption of molecular hydrogen on Pd (100) surface, (a) side view, (b) top view, (c) CDD isosurface at isovalue of 0.03 a.u., and (d) PDOS plot. Top-layer Pd atoms are in blue for clarity. Bond lengths are in Å.

To identify the energetically favorable adsorption configurations of H atom, geometry optimization and subsequent energy evaluation unveiled three distinct atomic hydrogen adsorption sites over the Pd(100) surface (**Fig. 10a**) [57]. These are: (1) top site, located directly over a Pd atom of the top layer; (2) hollow site, a cavity formed by four Pd atoms of the top layer; and (3) a bridge site, positioned between the two adjacent surface Pd atoms. The calculated E_{ads} values of the hydrogen adsorption configurations, along with the Pd–H bond lengths and Hirshfeld charge values of the adsorbed H, are summarized in **Table 1**. Comparative analysis of the adsorption sites suggested that hydrogen prefers hollow site adsorption (−1.28 eV) (**Fig. 10d**) over bridge site (−1.01 eV) (**Fig 10c**) and top site (−0.84 eV) (**Fig 10b**). The surface to subsurface ($H_{surface} \rightarrow H_{subsurface}$) migration of atomic H after dissociation is energetically realized by the energy difference (0.44 eV) between the top and hollow sites. Transition state and frequency calculation have shown that this migration is essentially a barrierless ($E_a \approx 0$ eV)

and highly exergonic ($\Delta G = -0.53$ eV) process, signifying Pd subsurface-sites as the stable reservoirs for hydrogen storage. It means that once H atoms occupy the surface, they spontaneously transition into the subsurface without requiring the thermal activation. To evaluate the maximum hydrogen loading capacity, simulation shows that the surface can be fully loaded by 18 H atoms (**Fig. 10e**), yielding a total E_{ads} value of -1.84 eV with an average value of -0.10 eV per atom. The negative energy values suggest the thermodynamic feasibility of the total adsorption. However, the lowest nature of the average value as compared to the calculated values for the three sites reflects that the penalty originates from the electronic cloud repulsion of the neighboring H atoms.

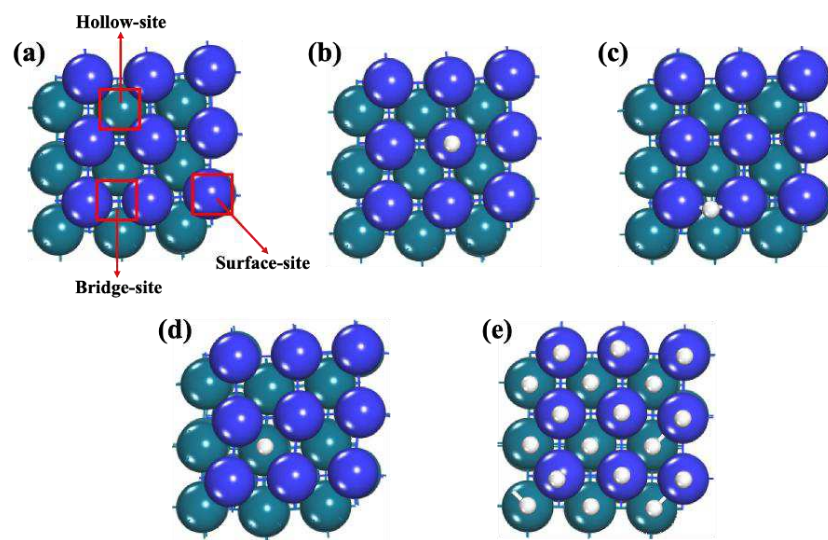


Fig. 10: (a) Atomic hydrogen adsorption sites, (b) top-site, (c) bridge-site, (d) hollow-site, and (e) fully adsorbed Pd (100) surface (top view). Top-layer Pd atoms are in blue for clarity.

Moreover, to evaluate the rate of hydrogen diffusion over the Pd(100) surface, transition state theory is applied to calculate the desorption time (τ) using the following equation: [58]

$$\tau = \nu^{-1} \exp(-E_{\text{ads}}/k_{\text{B}}T) \quad (2)$$

where ν represents a pre-exponential factor ($1 \times 10^{12} \text{ s}^{-1}$), T is the absolute desorption temperature, and k_{B} is the Boltzmann's constant.

As evident from the above equation, Table 1 shows an exponential relation of τ with E_{ads} values and an inverse relation with T . For instance, the τ values for top, bridge, and hollow sites are estimated to be 1.61×10^2 s, 1.20×10^5 s, and 4.44×10^9 s at 298 K, whereas 4.33×10^{-2} s, 6.16×10^0 s, and 1.61×10^4 s at 398 K, respectively. These values reflect the strong dependence of the desorption kinetics on both temperature and adsorption energy. Thus, the equilibrium distribution of hydrogen adsorption on Pd(100) is governed by the three sites, with the kinetic barrier for subsurface-to-surface migration directly governing the hydrogen availability for desorption. Overall, these insights emphasize the pivotal role of surface and subsurface hydrogen adsorption in dictating the hydrogen storage and catalytic characteristics of Pd as a promising hydrogen storage material.

Table 1. Hydrogen adsorption configurations with adsorption energies (E_{ads} eV), Pd–H bond length (Å), charge transferred to H (e), and desorption time (τ s) at 298 and 398 K.

Configuration	E_{ads} (eV)	$\delta d_{\text{Pd-H}}$ (Å)	Q_{H} (e)	τ @ 298 K (s)	τ @ 398 K (s)
Molecular H ₂	−1.05	1.74	−0.17	5.7×10^5	1.98×10^1
Top	−0.84	1.57	−0.1162	1.61×10^2	4.33×10^{-2}
Bridge	−1.01	1.70	−0.1309	1.20×10^5	6.16×10^0
Hollow	−1.28	2.68	−0.1495	4.44×10^9	1.61×10^4
Fully adsorbed Pd(001)	−1.84	-	-	-	-

4. Conclusion

The AAO templates with 100 and 60 nm pore diameters have been successfully fabricated. The structure of AAO templates were characterized using AFM and FE-SEM. Pd nanowires were fabricated in AAO templates by the electrodeposition method. By removing the template, free-standing Pd nanowires were prepared. The FE-SEM images show that Pd nanowires were successfully

synthesized. The composition and structure of fabricated Pd nanowires were confirmed by XPS and XRD. The adsorption and absorption of hydrogen on the Pd foil and nanowires have been investigated using the TPD method. On the Pd foil surface, hydrogen atoms are adsorbed on the surface first. As the surface is saturated with hydrogen, the diffusion of H into the bulk of Pd occurs as the exposure of hydrogen increases. DFT analysis unveils that subsurface hollow site is energetically favorable adsorption site with highest negative E_{ad} value (-1.28 eV) as compared to the bridge (-1.01 eV) and top sites (-0.84 eV), corroborating the TPD analysis. Furthermore, the frequency and Gibb's free energy calculations demonstrate that the diffusion barrier of H in Pd is a barrierless ($E_a \approx 0$ eV) and highly exergonic ($\Delta G = -0.53$ eV), which is analogously estimated to be 0.123 eV experimentally. The evolution of H from Pd follows zeroth-order kinetics. The adsorption and absorption of hydrogen on Pd nanowires are similar to those on the Pd foil even though the surfaces of Pd nanowires could be rough.

Author contributions

Umair Ali and Habib Ullah: conceptualization, software, validation and writing – original draft.

Zakir Zaman Khan: DFT calculations, writing and editing, **Aref Alshameri:** Software skills, formal analysis, **Mohsin Ali:** formal analysis and editing original draft, **Ahsan Irshad:** review and editing,

Noor Ul Islam: supervision, data curation, review and editing, **Tanveer Ali:** investigation, **Ahmad H**

Ragab: writing, review & editing, **Akif Safeen:** formal analysis and data curation, **Saeed Rehman:**

Validation

Declarations

Funding Declaration

Not applicable.

Competing Interests Declaration

The authors declare no competing interests.

Data Availability Declaration

The data will be made available upon the author's request.

Consent to Publish Declaration

Not applicable.

Consent to Participate Declaration

Not applicable.

Ethics Declaration

Not applicable.

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