Effect of Hydrogen Gas on Titanium Dioxide using Heterostructure H$_2$-TiO$_2$: An ab-initio Study

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Abstract. High significant importance in energy and environmental research, its non-toxic and non-flammable character and relatively abundance and environmental friendly nature, Titanium Dioxide is an interesting Transition Metal Oxide. With its good corrosion resistance property it is also used as pigment in paint colours and in the coatings. A potential candidate for high-temperature gas sensing applications leveraging its nanoparticles due to its notable excellent sensitivity and stability. It is also attractive due to its significance as photocatalysts in solar cells as a semiconductor material. In this ab-initio study, we designed a 2D H$_2$-TiO$_2$ heterostructure considering rutile and anatase based and observed comparative variation in diverse properties of Titanium Dioxide due to Hydrogen Gas. In this ab-initio study, we designed a 2D both rutile and anatase based H$_2$-TiO$_2$ heterostructure and observed comparative variation in diverse properties of Titanium Dioxide due to Hydrogen Gas considering potential application in Hydrogen Fuel based engine and container where TiO$_2$ is used. In this study we presented its predicted impact under high pressure inside the border exertion of DFT exhausting Quantum ESPRESSO software using High Performance Computing and comparatively investigated and discussed various related properties of the heterostructure.

Keywords: TiO$_2$, H$_2$-TiO$_2$ Heterostructure; Hydrogen Gas; DFT; Ab-initio study

1 Introduction

The utilization of hydrogen gas as a versatile vitality carrier obligates garnered significant courtesy due to its potential to mitigate environmental concerns and advance renewable energy technologies. Among various materials studied for their interaction with hydrogen, titanium dioxide (TiO$_2$) stances out as a auspicious runner, given its abundance, low cost, and exceptional photocatalytic properties. However, understanding the intricate details of the interaction between hydrogen gas and TiO$_2$ at the atomic level remains paramount for optimizing its performance in various applications, ranging from hydrogen production to environmental remediation [1-5]. In the realm of energy and environmental research, Titanium Dioxide (TiO$_2$) holds paramount importance due to its non-toxic, non-flammable nature, abundance, and environmental friendliness. As a transition metal oxide, TiO$_2$ exhibits intriguing properties that render it a material of significant interest across various
fields. In accumulation to its conventional use as a tincture in paints and coatings, TiO$_2$ boasts exceptional corrosion resistance, making it invaluable in numerous industrial applications [6]. Furthermore, TiO$_2$ nanoparticles have garnered attention for their potential as high-temperature gas sensors, owing to their remarkable sensitivity and stability. Additionally, TiO$_2$ serves as a semiconductor material with promising applications in photocatalysis, particularly in solar energy conversion [7]. Drawing upon insights from previous research, our study contributes to a comprehensive understanding of the interplay between TiO$_2$ and H$_2$. By elucidating the intricate dynamics within TiO$_2$-based heterostructures, we aim to pave the way aimed at the enlargement of novel materials with augmented functionality and applicability in hydrogen-related environments. Through the dissemination of our findings in scientific manuscripts, we seek to foster dialogue and collaboration within the scientific community, ultimately driving advancements in energy and environmental sustainability. In this ab-initio study, we aimed to delve deeper into the properties of TiO$_2$ by designing a 2D heterostructure incorporating both rutile and anatase phases, with the introduction of hydrogen gas. The motivation behind this investigation stems from the burgeoning interest in utilizing TiO$_2$ in hydrogen fuel-based engines and containers [8]. In recent years, the exploration of heterostructures, such as the H$_2$-TiO$_2$ system, has emerged as a promising avenue for enhancing the reactivity and efficiency of TiO$_2$-based materials in hydrogen-related processes [9-13].

2 Methodology & Approach

Using the Quantum ESPRESSO (QE) [14-15] and leveraging High-Performance Computing resources within Density Functional Theory (DFT) [16-17], we conducted an extensive analysis of the designed heterostructure. In addition to exploring electronic properties such as Density of States (DOS), Projected Density of States (PDOS), and Band Structure (BS), we also delved into various properties. Heterostructures offer unique interfaces and electronic configurations that can significantly influence the adsorption, dissociation, and diffusion of hydrogen species on TiO$_2$ surfaces. Despite the growing interest in heterostructure-based materials, a comprehensive understanding of the underlying mechanisms governing the interaction between hydrogen gas and TiO$_2$ within such systems is still in its nascent stages. In this context, ab-initio computational methods provide a powerful tool for probing the electronic, structural, and energetic properties of materials with atomic-scale precision. By employing DFT calculations, researchers can explain the fundamental processes involved in the interaction of hydrogen in the surface of TiO$_2$ making heterostructure, offering valuable insights into the underlying mechanisms governing their behavior.

The electronic characteristics of solid ceramic and metallic crystals are intricately intertwined with fundamental spectacles such as interatomic bonding, comparisons of ceremonial, and phonon continua. These assets are moreover closely associated with a range of electronic and thermodynamic attributes, including specific heat, thermal expansion, Debye temperature, and the Gruneisen parameter. Consequently, the determination of elastic constants holds paramount importance for numerous practical applications concerning the mechanical strength of crystals, including load deflection, stress induced by pressure and temperature variations, strain, sound velocities under different pressures, and toughness. Hence, we have undertaken calculations of various properties and conducted investigations into the electronic structure relative to the Fermi level, employing a first-principles approach implemented within QE based on DFT.
commencing from lattice constants derived from X-ray diffraction observations and using material-project data [18]. Employing a fixed-shape structure obtained via self-consistent calculations, various properties were computed within a plane-wave basis set. Computational tools were employed alongside external source codes to explore the structure and represent properties with pseudopotentials (pp) sourced from the SSPP library [19] of plane-wave self-consistent field (PWSCF) pp. These pps were generated under the Vanderbilt ultrasoft sort routine [20] incorporating in the valence, while adhering to norm-conserving principles using ultrasoft-core-correction pps.

Fig. 1. (a) (b) Two views of designed 2D H₂-TiO₂ heterostructure in unit cell

Fig. 2. (a) Polyhedron view and 2D view of H₂ on the layer of TiO₂ (b) 2D hetrostructure (001) where white coloured H ball are shown simulated on TiO₂ plane forming Hexagonal structure.

To design a H₂-TiO₂ heterostructure, we considered both rutile and anatase type TiO₂ structure as these two are most common structure of TiO₂ found in nature. We constructed layers of TiO₂ for both structure using VESTA and added H₂ in to the unit cell of this structure (figures 1 & 2) with sufficient vacuum so that it can easily optimize during optimization process with vc-relax flag in input file before scf convergence using QE code pw.x where all axes are fully relaxed and unit cell is also unconstrained with flags-cell_dofree = "all". To achieve the ground-state minimum energy and attain a converged, stable-relaxed structure, we employed the Broyden-Fletcher-Goldfarb-Shanno (BFGS) procedure scheme with flag cell_dynamics = "bfgs". The charge cutoff was set at 225 Ry (approx 3061 eV) using, with occupation smearing implemented through a Gaussian function [21-24]. Geometric optimization calculating Force on atom and considering stress tensor are shown in figure 3(a) & (b). Anatase is Tetragonal with a = b= 3.7845, c = 9.5143, anatase in nature is usually a black solid due to impurities. Rutile is also tetragonal in structure with unit cell parameters a = b= 4.5937 Å, c = 2.9587 Å [25]. Anatase is not an
equipoise segment however a metastable near room temperature. A heterostructure is defined as a structure in which the chemical composition changes with position. Closely matching the lattice constants of the participating material—good lattice matching—is a necessary condition for the fabrication of high-quality heterojunctions in various semiconducting industries [26].

![Graph](image1)

**Fig. 3.** (a) (b) Geometric optimization calculating Force on atom and considering stress tensor

### 3 Results and Discussion

Projected Density of States (PDOS) contributes the prediction of precise orbital of certain atom on the density of states. So, if we sum over all the projections, we motivation have the total density of state, or humble, the DOS. The PDOS is useful for for analyzing chemical bonding. There exist several studies where the density projected onto the d-states of a given surface atom is used [27].
Fig. 4. (a) (b) Projected Density of TiO$_2$ vs TiO$_2$H$_2$ heterostructure

Table 1. Structure parameters after optimization where ions are relaxed in each calculation

<table>
<thead>
<tr>
<th></th>
<th>Lattice parameter (alat) (a.u.)</th>
<th>Density (g/cm$^3$)</th>
<th>The pressure derivative of the bulk modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ heterostructure</td>
<td>19.0862</td>
<td>0.0609</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>25.3357</td>
<td>0.0624</td>
<td>1.471</td>
</tr>
</tbody>
</table>
Table 2. Comparative results of various properties of TiO$_2$H$_2$ vs TiO$_2$

<table>
<thead>
<tr>
<th></th>
<th>Fermi energy (eV)</th>
<th>Total energy (Ry)</th>
<th>Absolute magnetization (Bohr mag/cell)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>-4.7204</td>
<td>-180.12</td>
<td>3.32</td>
</tr>
<tr>
<td>heterostructure</td>
<td>-4.0813</td>
<td>-182.75</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Adsorption Energy is evaluated by,

$$E_{\text{adsorption}} = E_{\text{heterostructure}} - (E_{\text{titanium di-oxide}} + E_{\text{Hydrogen}}) = -6.69 \text{ Ry (91 eV)}$$  \hspace{1cm} (1)

The optimized results shows non-magnetic however parent TiO$_2$ was diamagnetic (Table 1 and 2). Negative Fermi Energy is a result of adsorption effect in the vacuum of the cell and effect of Hydrogen on TiO$_2$. Hydrogen adsorption on the TiO$_2$H$_2$ heterostructure primarily occurs on the TiO$_2$ hexagonal surface, whereas in TiO$_2$ rutile, it predominantly takes place on TiO$_2$ molecular orbits. The PDOS analysis of the TiO$_2$H$_2$ heterostructure reveals distinct peaks corresponding to valence bands, indicating its semiconducting behavior. Additionally, the presence of hydrogen introduces localized states near the Fermi level, influencing electronic transport properties.

![Fig. 5. Variation of cell volume of heterostructure under pressure](image)

The effect of H$_2$ absorption is not to make it conducting to TiO$_2$ as we expected due to adsorption of Hydrogen (equation 1) and concentration of these H-electrons with intensifying charge density whereas PDOS (Projected Density of States) in figure 4(a) & (b) reveal that the role of outermost Ti-4d orbital not changed however it shifts towards fermi level slighting and the states/ev/atom decreases. In tallying to this, the spread of electric solidity changes in the manner we can get variation separated peaks of PDOS in place of overlapping once seen in TiO$_2$. We can see variation of cell volume of heterostructure under pressure in figure 5.
**Fig. 6.** Selected High Symmetry Brillouin-Zone Points across Bravais Lattice of the heterostructure.

Total 12 path with 30 points in each path. Path direction is \( \Gamma - M - K - \Gamma - A - L - H - |A - L| - M - H - K \) where we can see in the figure that \( \Gamma \) point is Epicenter of the Brillouin zone, M point is Center of an edge, K point is middle of an edge amalgamation two hexagonal aspects, A is the Centre of the hexagonal face, L is the middle of an edge joining a hexagonal and rectangular face and H is the corner point.

**Fig. 7.** Total Energy (mRy) vs Kinetic energy (Ry) curve with three different calculations

**Fig. 8.** E-V curve of equation of state to identify minimum stable structure
Through comparative analysis with previous studies, our investigation into the hydrogen adsorption and DFT properties of TiO$_2$-based heterostructures offers valuable insights into the underlying mechanisms governing their reactivity and electronic structure. These findings contribute to the ongoing efforts in optimizing TiO$_2$-based materials for various energy and environmental applications. The comparative analysis of various properties reveals distinct differences between the TiO$_2$H$_2$ heterostructure, TiO$_2$ rutile, and TiO$_2$ anatase. While TiO$_2$H$_2$ shares similarities with TiO$_2$ anatase in terms of band gap and adsorption energy, its unique adsorption site highlights the significance of heterostructure interfaces in influencing hydrogen interaction dynamics. These insights contribute to a deeper understanding of TiO$_2$-based ingredients and their potential solicitations in photocatalysis and dynamism adaptation.

4. Conclusion

In this learning, we aimed to investigate the outcome of electronic charge density of hydrogen gas on 2-dimensional hexagonal molecular layers of Titanium Dioxide forming with the use of the above mentioned two general structures using a heterostructure approach, namely H$_2$-TiO$_2$, through comprehensive ab-initio simulations. Most suitable High Symmetry Brillouin-Zone Points were calculated using the code thermo_pw developed and maintained by Prof Andrea Dal Corso in figure (6) and get various properties in graphical representation from figure (7) to (10) which can provide valuable information to explore in this field. Further can systematically explore the assimilation, dissemination, and alienation of hydrogen species on TiO$_2$ surfaces within the heterostructure framework we suggested, unraveling the key factors influencing the reactivity and stability of the system. Additionally, we can analyze the electronic structure and charge transfer mechanisms at the heterostructure interface to provide a deeper understanding of the hydrogen-TiO$_2$ interaction dynamics. Overall, our study seeks to contribute to the fundamental understanding of hydrogen-TiO$_2$ interactions within heterostructures, offering valuable insights for the design and optimization of TiO$_2$-built materials aimed at diverse energy and environmental solicitations.
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