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 bleveraging 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 hetrostructure 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

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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.
Utilizing the self-consistent iterative approximation method within QE, we conducted structural optimization. Initially, lattice constants and ground state energy were estimated,

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.

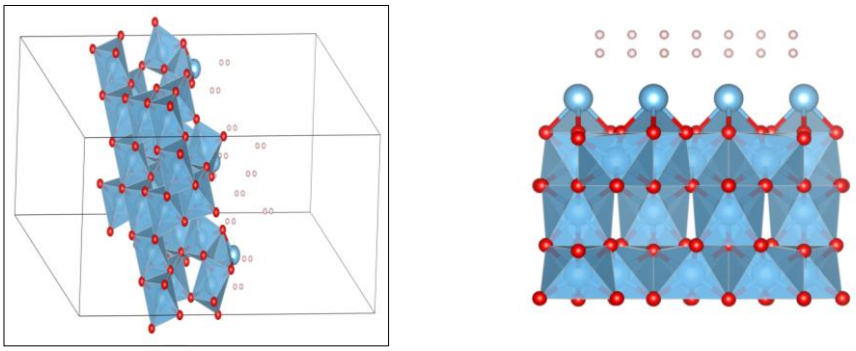


Fig. 1. (a) (b) Two views of designed 2D H_2-TiO_2 heterostructure in unit cell

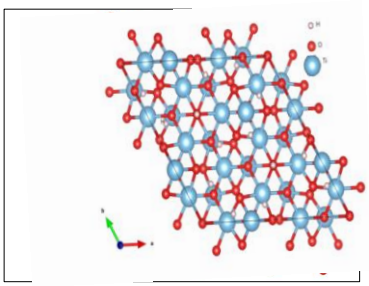


Fig. 2. (a) Polyhedron view and 2D view of H_2 on the layer of TiO_2 (b) 2D hetrostructure (001) where white coloured H ball are shown simulated on TiO_2 plane forming Hexagognal structure .

To design a H_2-TiO_2 heterostructure, we considered both rutile and anatase type TiO_2 structure as these two are most common structure of TiO_2 found in nature. We constructed layers of TiO_2 for both structure using VESTA and added H_2 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].

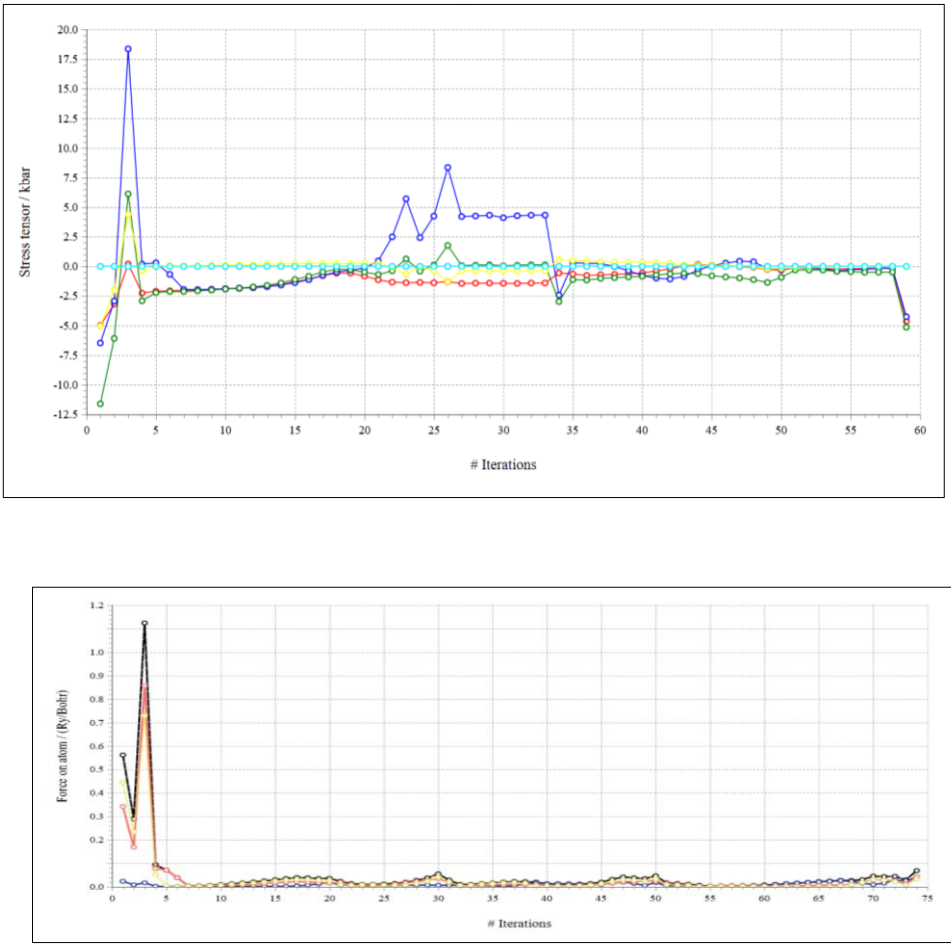
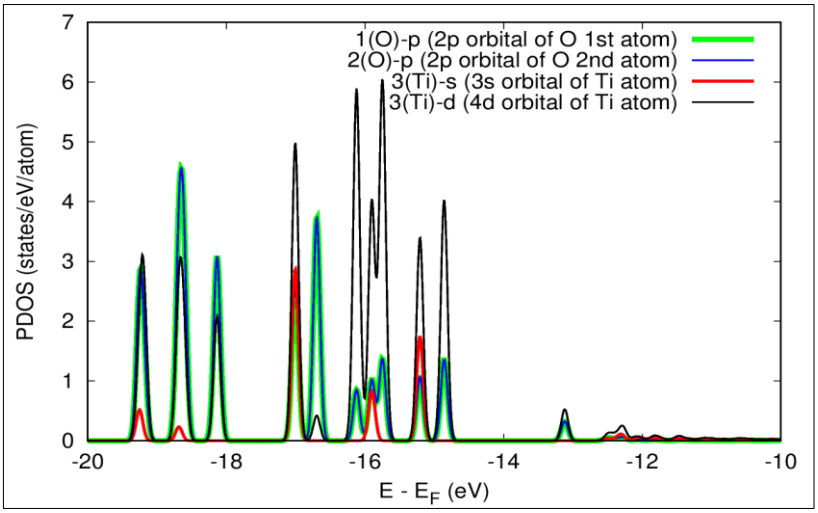


Fig. 3. (a) (b) Geometric optimization calculating Force on atom and considering stress tensor

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].



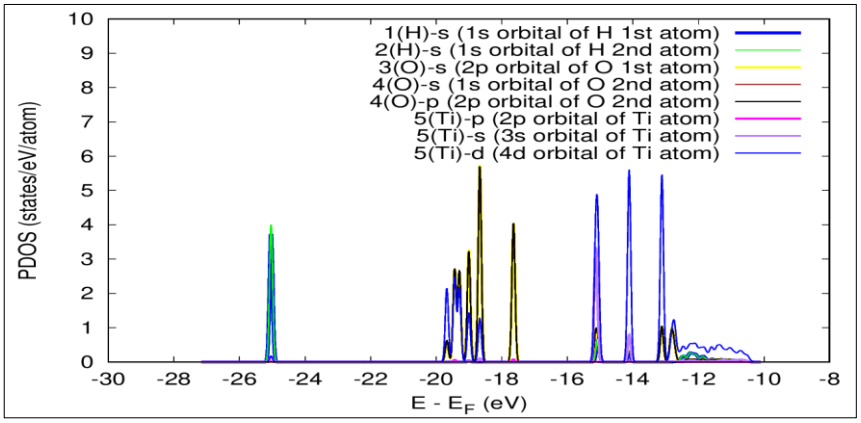


Fig. 4. (a) (b) Projected Density of TiO_2 vs TiO_2H_2 heterostructure

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

	Lattice parameter (alat) (a.u.)	Density (g/cm^3)	The pressure derivative of the bulk modulus
TiO_2	19.0862	0.0609	-
heterostructure	25.3357	0.0624	1.471

Table 2. Comparative results of various properties of TiO_2H_2 vs TiO_2

	Fermi energy (eV)	**Total energy (Ry)**	**Absolute magnetization (Bohr mag/cell)**
TiO_2	-4.7204	-180.12	3.32
heterostructure	-4.0813	-182.75	0.00

Adsorption Energy is evaluated by,

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

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_2H_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_2H_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.

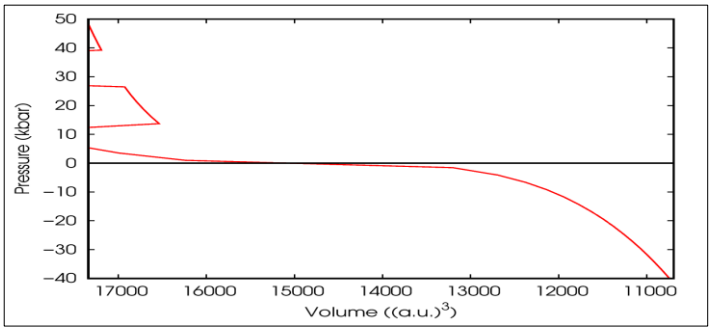


Fig. 5. Variation of cell volume of heterostructure under pressure

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.

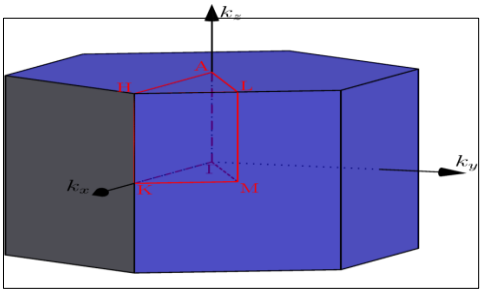


Fig. 6. Selected High Symmetry Brillouin-Zone Points across Bravais Lattice of the heterostructure.

Total 12 path with 30 points in each path. Path direction is Γ-M-K-Γ-A-L-H|A-L|M-H-K where we can see in the figure that Γ 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

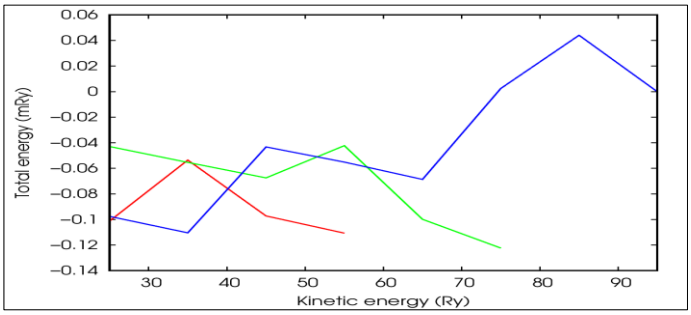


Fig. 7. Total Energy (mRy) vs Kinetic energy (Ry) curve with three different calculations

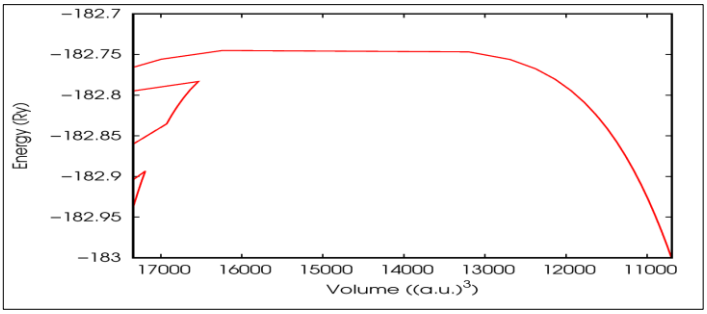


Fig. 8. E-V curve of equation of state to identify minimum stable structure

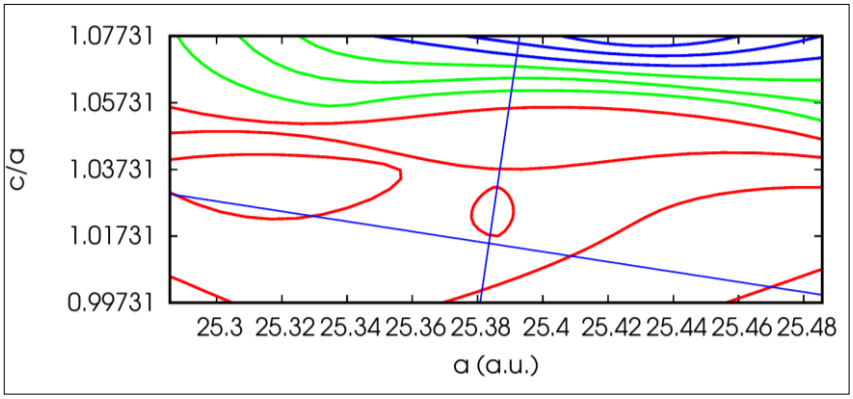


Fig. 9. c/a vs a curve to identify the stable lattice parameters

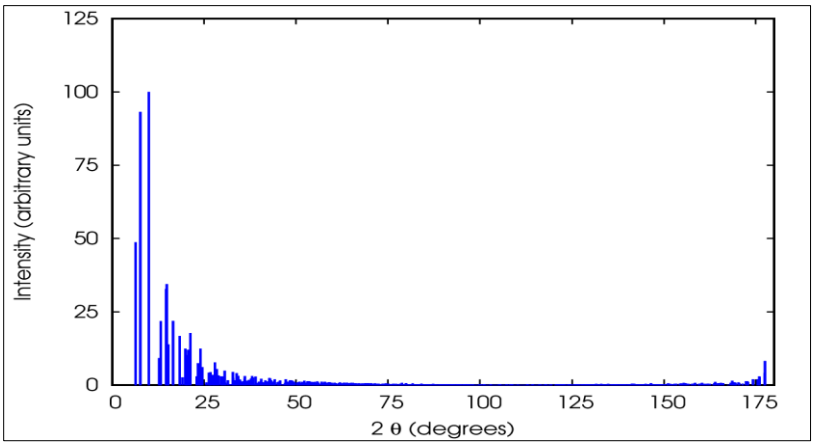


Fig. 10. Simulated XRD of heterostructure

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_2H_2 heterostructure, TiO_2 rutile, and TiO_2 anatase. While TiO_2H_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.

References

1. Shaker, L.M., Al-Amiery, A.A. & Al-Azzawi, W.K. Nanomaterials: paving the way for the hydrogen energy frontier. Discover Nano 19. 3, (2024). https://doi.org/10.1186/s11671-023-03949-8
2. Zhang, Boxue, Shengxin Cao, Meiqi Du, Xiaozhou Ye, Yun Wang, and Jianfeng Ye. Titanium Dioxide (TiO2) Mesocrystals: Synthesis, Growth Mechanisms and Photocatalytic Properties .Catalysts 9.no. 1(91), (2019). https://doi.org/10.3390/catal9010091
3. Anirban Chakraborty, Samriti, Olim Ruzimuradov, Raju Kumar Gupta, Junghyun Cho, Jai Prakash, TiO2 nanoflower photocatalysts: Synthesis, modifications and applications in wastewater treatment for removal of emerging organic pollutants. Environmental Research. Volume 212, Part D. 113550. (2022**)** .https://doi.org/10.1016/j.envres.2022.113550.
4. Dharma HNC, Jaafar J, Widiastuti N, Matsuyama H, Rajabsadeh S, Othman MHD, Rahman MA, Jafri NNM, Suhaimin NS, Nasir AM, Alias NH. A Review of Titanium Dioxide (TiO2)-Based Photocatalyst for Oilfield-Produced Water Treatment. Membranes (Basel). Mar 19; 12(3):345, (2022). https://doi.org/10.3390/membranes12030345.
5. Surender, C. Mohan, R. Kumar, –Novel modification of activated charcoal sheet with N-methylpolypyrrole and silver nanoparticles for removal of hexavalent chromium in water treatment processes" Materials Protection, vol. 64, pp 503-511, (2023). doi : 10.5937/zasmat2304503S
6. Hamidi, F.; Aslani, F. TiO2-based Photocatalytic Cementitious Composites: Materials, Properties, Influential Parameters, and Assessment Techniques. Nanomaterials . 9.1444. (2019).https://doi.org/10.3390/nano9101444.
7. Sakar, M.; Mithun Prakash, R.; Do, T.-O. Insights into the TiO2-Based Photocatalytic Systems and Their Mechanisms. Catalysts 9. 680. (2019).https://doi.org/10.3390/catal9080680.
8. D.A.H. Hanaor, M.H.N. Assadi, S. Li, A. Yu, and C.C. Sorrell, Computational Mechanics 50.(2). 185-194. (2012). https://arxiv.org/pdf/1210.7555.pdf .
9. C. Mohan, N. Kumari, J. Robinson, –Sustainable and environmental friendly energy materials" Materials Today: Proceedings, vol. 69, pp 494-498, (2022). doi : 10.1016/j.matpr.2022.09.187
10. Prasad, Tara and Shah, MC and Singh, Pankaja and Wani, Tanveer Ahmad, Ab-initio Calculations of Properties for NbB_2 Under High-Pressure Using Quantum ESPRESSO. Proceedings of International Conference on Sustainable Computing in Science, Technology and Management (SUSCOM), Amity University Rajasthan, Jaipur – India. February 26-28, (2019).http://dx.doi.org/10.2139/ssrn.3355175.
11. Aschauer, U. & Selloni, A. Hydrogen interaction with the anatase TiO2 surface. Phys. Chem. Chem. Phys. 14, 16595–16602 , (2012). https://doi.org/10.1039/C2CP42288C.
12. Chen X, Liu L, Yu PY, Mao SS. Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals. Science.746-50. (2011).https://doi.org/10.1126/science.1200448.
13. Baohuan Wei, Monica Calatayud, Hydrogen activation on Anatase TiO2: Effect of surface termination, Catalysis Today, Volumes 397–399, Pages 113-120, ISSN 0920-5861. (2022).https://doi.org/10.1016/j.cattod.2021.11.020.

14. Giannozzi, P., et al. Quantum Espresso: A Modular and Open-Source Software Project for Quantum Simulations of Materials. Journal of Physics: Condensed Matter. 21, (2009). https://doi.org/10.1088/0953-8984/21/39/395502 .
15. P Giannozzi, O Andreussi, T Brumme, O Bunau, M Buongiorno Nardelli, M Calandra, R Car, C Cavazzoni, D Ceresoli , M Cococcioni M. Schlipf; A. P. Seitsonen; A. Smogunov; I. Timrov; T. Thonhauser; P. Umari; N. Vast; X. Wu & S. Baroni Advanced capabilities for materials modelling with Quantum ESPRESSO, Journal of Physics: Condensed Matter. 29 (46): 465901, (2017).https://doi.org/10.1088/1361-648X/aa8f79.
16. Hohenberg, P. and Kohn, W. Inhomogeneous Electron Gas. Physical Review B. 136.864-871. (1964).http://dx.doi.org/10.1103/PhysRev.136.B864.
17. W. Kohn and L.J. Sham, Phys. Rev. A 140 1133, (1965). https://doi.org/10.1103/ PhysRev.140.A1133.
18. Anubhav Jain, Shyue Ping Ong, Geoffroy Hautier, Wei Chen, William Davidson Richards, Stephen Dacek, Shreyas Cholia, Dan Gunter, David Skinner, Gerbrand Ceder, Kristin A. Persson; Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. APL Mater. 1 July (2013).https://doi.org/10.1063/1.4812323.
19. G. Prandini, A. Marrazzo, I. E. Castelli, N. Mounet and N. Marzari, npj Computational Materials 4. 72, (2018). http://materialscloud.org/sssp
20. John D. Head, Michael C. Zerner, A Broyden—Fletcher—Goldfarb—Shanno optimization procedure for molecular geometries, Chemical Physics Letters. Volume 12., Issue 3.264-270, (1985). https://doi.org/10.1016/0009-2614(85)80574-1.
21. John P. Perdew, Kieron Burke, and Matthias Ernzerhof, Generalized Gradient Approximation Made Simple Phys. Rev. Lett. 77. 3865 – Published 28 October 1996. Erratum Phys. Rev. Lett. 78, (1997) https://doi.org/10.1103/PhysRevLett.78.1396.
22. Monkhorst, H.J. and Pack, J.D. Special Points for Brillouin-Zone Integrations. Physical Review B, 13, 5192, (1976)**.** http://dx.doi.org/10.1103/PhysRevB.13.5188
23. Satomichi Nishihara, BURAI, a GUI system of Quantum ESPRESSO (2018).https://burai.readthedocs.io/en/latest/
24. Andrea Dal Corso, thermo_pw: a Fortran driver for the parallel and/or automatic computation of materials properties that uses Quantum ESPRESSO (QE) routines as the underlying engine. https://dalcorso.github.io/thermo_pw/
25. D.A.H. Hanaor, W. Xu, M. Ferry, C.C. Sorrell, Abnormal grain growth of rutile TiO2 induced by ZrSiO4, Journal of Crystal Growth; Volume 359, 15 November . Pages 83-91, **(2012).**https://doi.org/10.48550/arXiv.1303.2761.
26. William R. Frensley, Chapter 1 - Heterostructure and Quantum Well Physics, Editor(s): Norman G. Einspruch, William R. Frensley, VLSI Electronics Microstructure Science. Elsevie. Volume 24. Pages 1-24, (1994).https://doi.org/10.1016/B978-0-12-234124-3.50006-9.
27. Rangel T, Rignanese GM, Olevano V. Can molecular projected density of states (PDOS) be systematically used in electronic conductance analysis? Beilstein J Nanotechnol. Jun 2.6.1247-59, (2015).https://doi.org/10.3762/bjnano.6.128