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2D नैनो-पदार्थों में प्रतिवर्ती हाइड्रोजन भंडारण का अन्वेषण: घनत्व डोपिंग एवं तनाव के माध्यम से वृद्धि

Exploring Reversible Hydrogen Storage in 2D Nanomaterials: Enhancement Through Doping and Strain

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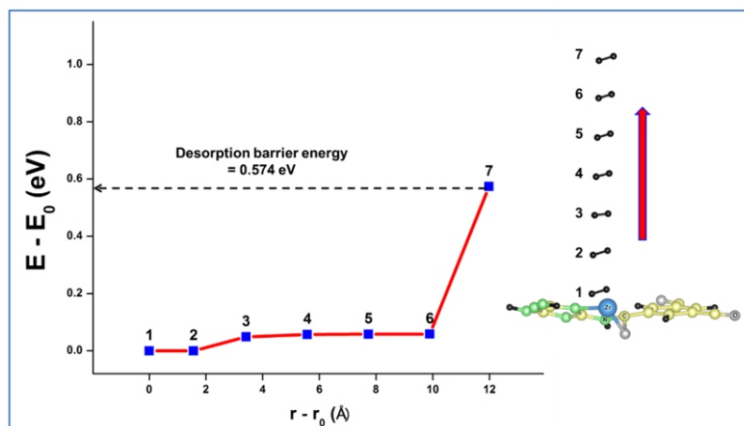
सारांश

हाइड्रोजन भंडारण एक स्वच्छ ऊर्जा वाहक के रूप में हाइड्रोजन के व्यावहारिक उपयोग और व्यापक रूप से अपनाए जाने हेतु एक महत्वपूर्ण सहायक है, जो अक्षय ऊर्जा एकीकरण को सुविधाजनक बनाता है और विभिन्न क्षेत्रों के विकास का समर्थन करता है। विभिन्न 2D नैनो-पदार्थों ने अपने उच्च सतह क्षेत्र, उच्च चालकता एवं उच्च यांत्रिक शक्ति के कारण ऊर्जा भंडारण उपकरणों के रूप में अत्यधिक ध्यान आकर्षित किया है। हालांकि H₂ भंडारण के लिए कार्बन आधारित 2D पदार्थ का पता लगाया गया है, लेकिन यह कमरे के तापमान पर H₂ को नियंत्रित नहीं कर सकता है क्योंकि अंतःक्रिया बहुत कमजोर है। यह देखा गया है कि 2D पॉलीआरामिड (2डीपीए), संक्रमण धातु (टीएम) परमाणुओं की एकल इकाई सेल को सजाकर, -0.399 और -0.480 eV की औसत बाध्यकारी ऊर्जा के साथ H₂ के 6.422 और 6.792 wt% तक के हाइड्रोजन भंडारण को क्रमशः 2DPA+Ti और 2DPA+Zr के लिए प्राप्त किया गया, जो हाइड्रोजन भंडारण उपकरणों के लिए डीओई की आवश्यकता को पूरा करता है। अध्ययन एक कुशल एवं प्रतिवर्ती हाइड्रोजन भंडारण पदार्थ के रूप में तनावग्रस्त 2D होले ग्रेफाइन की क्षमता पर भी प्रकाश डालता है।

ABSTRACT

Hydrogen storage is a crucial enabler for the practical use and widespread adoption of hydrogen as a clean energy carrier, facilitating renewable energy integration and supporting the decarbonization of various sectors. Various 2D nanomaterials have drawn immense attention as energy storage devices due to their high surface area, high conductivity and high mechanical strength. Although carbon based 2D materials have been explored for H₂ storage, it can't hold H₂ at room temperature because interaction is very weak. It has been shown that by decorating a single unit cell of 2D polyaramid(2DPA) by transition metal (TM) atoms, hydrogen storage of up to 6.422 and 6.792 wt% of H₂ with average adsorption energies of -0.399 and -0.480 eV have been obtained for 2DPA+Ti and 2DPA+Zr, respectively, satisfying DoE's requirement for hydrogen storage devices. The study also highlights the potential of strained 2D holey graphyne as an efficient and reversible hydrogen storage material.

KEYWORDS: Hydrogen storage, 2D materials, Density Functional Theory, Green economy, Strain Engineering, Kubas interactions



CI-NEB विधि का उपयोग से संगणित
2DPA+Zr+H₂ प्रणाली से हाइड्रोजन के
अवशोषण हेतु ऊर्जा बाधा।

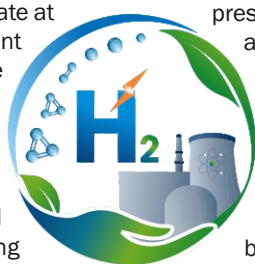
Energy barrier for desorption
of hydrogen from 2DPA+Zr+H₂
system computed using CI-NEB
Method

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Introduction

One of the major societal concerns that need to be addressed is that of the energy crisis, as the usage of fossil fuels gives rise to myriad problems. The dependence of humans on fossil fuels for energy, especially for transportation, poses immense threat to the future of human life. Not only do fossil fuels release greenhouse gases that contribute to climate change, but even the supply of fossil fuels is limited and we may soon run out of it. Thus, there is dire need to find an alternative to fossil fuels, and one that does not release harmful emissions or by-products is much desirable. Fuel cells have been touted as possible replacements for the internal combustion engine for mobile energy harnessing, and were made very popular by the Apollo Space mission when the alkaline fuel cells designed by Francis Bacon were used as an onboard energy producer, as well as water provider, given that a hydrogen-oxygen fuel cell produces water as a by-product [1]. For light vehicles however, the storage of hydrogen on the vehicle presents a major challenge. Hydrogen storage in compressed gaseous form requires large-volume, high-pressure cylinders [2], whereas storage in liquid form involves energy-intensive cryogenic liquefaction and the use of reinforced storage vessels. The storage and transportation of hydrogen in its liquid or gaseous form may be too cumbersome for an ordinary light vehicle. Instead, the adsorption of hydrogen on a solid substrate at a re-fueling site, and its desorption during requirement can be an effective solution for this issue, much like how a fuel tank operates today. Hydrogen has the highest known energy density among fuels with an achievable energy conversion efficiency of up to 65% in a stationary fuel cell-based power plant, compared to the 33–35% achieved for a conventional combustion-based thermal power plant [3]. Using hydrogen fuels emits almost no carbon and greenhouse gases, resulting in a far lower carbon footprint than that observed in conventional fuels & decreased air pollution levels.



The U.S. Department of Energy (DOE) [4] has established specific performance targets that solid-state materials must meet for practical, reversible hydrogen storage. To be viable for light-duty vehicles, current targets specify a hydrogen-substrate binding energy of -0.2 to -0.7 eV and a minimum gravimetric storage capacity of 6.5 wt%. Efficient solid-state hydrogen storage requires a balanced binding energy between physisorption and chemisorption. Developing such a material is challenging because it must simultaneously be lightweight, economical, high-capacity, and stable over thousands of cycles, while allowing effortless hydrogen release via minor temperature or pressure adjustments.

This article describes the conventional materials used for hydrogen storage, their merit and demerit. It also highlights computational design of new generation light element based 2D materials for efficient and compact storage of molecular hydrogen. It emphasizes various interaction mechanism of H_2 molecules on different materials, e.g. on pristine carbon based 2D material, transition metal doped 2D materials, strained 2D materials, non-metal substituted 2D materials etc. It also describes how to enhance hydrogen adsorption on light elements based 2D materials due to strain, doping of transition metals and substitution of non-metals.

Conventional materials used for hydrogen storage

Metal hydrides are well-explored substrates for solid-state hydrogen storage, where hydrogen atoms are incorporated into the crystalline structure of metals or metal alloys. For example, complex metal hydrides such as alanates (e.g., $NaAlH_4$) and borohydrides (e.g., $LiBH_4$) have been extensively studied [5,6]. Also, La-Ni hydride ($LaNi_5H_6$) has been explored as high capacity media for hydrogen storage. These materials can store significant amounts of hydrogen by weight but often require high temperatures for hydrogen release, limiting their practical use in certain applications. Another class of materials for solid state hydrogen storage includes porous materials such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) [7]. These materials feature large surface areas and well-defined nanoporous structures, which facilitate hydrogen adsorption through weak van der Waals (vdW) forces. MOFs like MIL-101 [8] and COFs such as COF-105 and COF-108 have shown promise due to their tuneable properties and high hydrogen storage capacities under specific conditions [9]. However, practical challenges such as slow kinetics and material degradation must be addressed for widespread commercial use. Zeolites, known for their cage and channel structures can adsorb non-polar gases through physisorption [10]. The Na-Y zeolite can provide 1.81 wt% hydrogen uptake at 77 K and pressures of 1.5 Mpa [11]; whereas, Na-X gave 2.55 wt% at 77 K and pressures of 40 bar [12]. While zeolites show rapid hydrogen adsorption-desorption, the adsorption mechanism is primarily via physisorption. Owing to the poor adsorption strength, hydrogen storage in zeolites necessitates low operating temperatures (preferably, cryogenic conditions) and high hydrogen pressures. These may be achievable for stationary storage purposes but become cumbersome for onboard hydrogen storage in transport applications.

2D Nano-materials: Next generation Hydrogen Storage Devices

2D materials are a class of crystalline solids with atomic scale thickness and lateral dimensions extending up to the nm or micron scale. Since the ground breaking discovery of graphene, extensive research has led to the identification and development of a wide variety of 2D materials, which can be classified based on their elemental composition, bonding nature, and structural

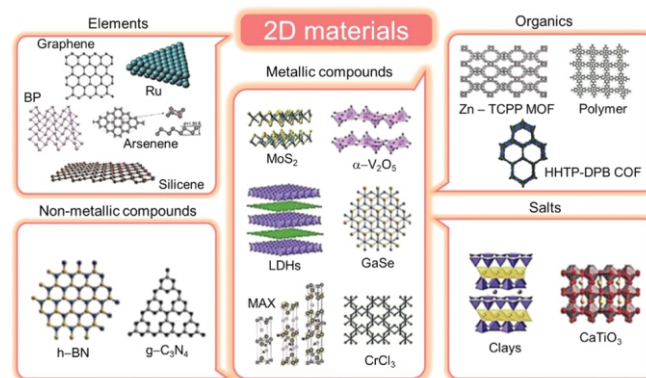


Fig.1: The atomic structures of different types of newly discovered two-dimensional material categories are schematically shown here [18].

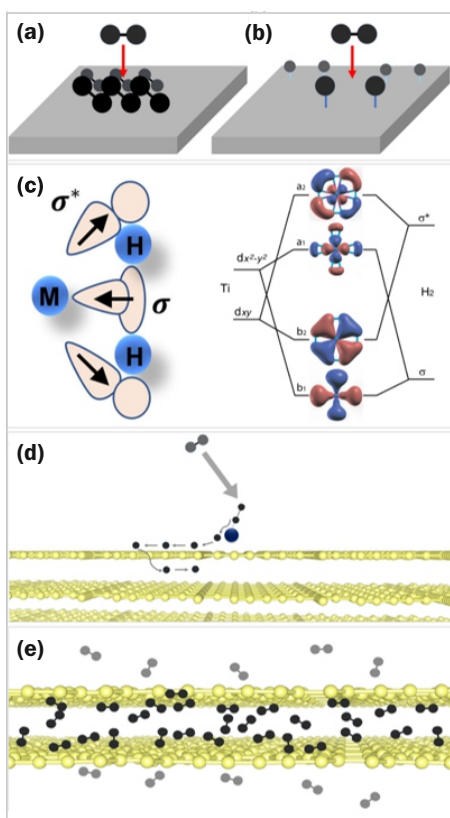


Fig.2: Mechanisms of solid-state hydrogen storage; (a) physisorption involving molecular hydrogen attracted to the substrate surface via van der Waals forces; (b) chemisorption involving dissociative adsorption of hydrogen; (c) Kubas interactions showing, in the left panel,† back donation of charge from σ^* orbitals of H_2 to the vacant d orbitals of the transition metal, and in the right panel, molecular orbital diagram showing hybridization between Ti and H_2 molecular orbitals;‡ (d) spillover mechanism of H_2 dissociating on a catalyst-embedded nanomaterial; and (e) nanopump effect in few-layer 2D materials. The yellow and black spheres denote C and H atoms, respectively; reproduced from Solid State Commun. 147, 419–422, 2008 [22].

properties. The first category includes elemental 2D materials, composed of a single type of atom arranged in a 2D lattice such as graphene (C), phosphorene (P), silicene (Si), germanene (Ge), and borophene (B) etc. These materials exhibit exceptional properties like high conductivity, flexibility, and mechanical strength. Another major category is transition metal dichalcogenides (TMDs), typically represented by the formula MX_2 , where M is a transition metal (e.g., Mo, W, Nb, Ta, Ti etc.) and X is a chalcogen (e.g., S, Se, Te) [13, 14]. TMDs exhibit semiconducting, metallic or superconducting behavior and are widely used in electronics, optoelectronics, and catalysis. Hexagonal boron nitride (h-BN), often called “white graphene,” is an insulating 2D material with excellent thermal and chemical stability [15]. In recent years, attention has also been drawn to Mxenes [16, 17], a family of transition metal carbides, nitrides, or carbonitrides with outstanding electrical conductivity and surface functionality, making them promising for energy storage, sensing, and catalytic applications. A similar but newer class is MBenes, which is a family of 2D transition metal borides derived from MAB phases, possessing high mechanical strength and favorable electronic properties for catalysis and sensor applications.

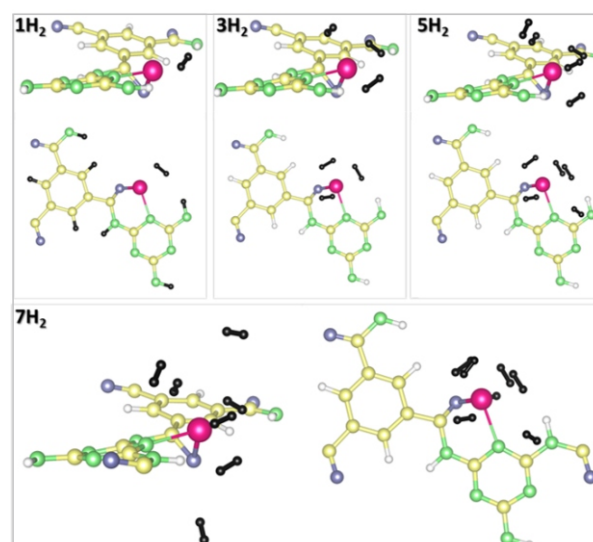


Fig.3: Structural plots in the top and side views for $2DPA+Ti+nH_2$, where $n = 1, 3, 5$, and 7 . Yellow, green, gray, white, and pink spheres represent the C, N, O, H, and Ti atoms of $2DPA + Ti$, respectively. Black spheres represent the adsorbed hydrogen molecules [29].

In last few years several graphene based 2D materials have been synthesized by modifying the elemental graphene structures with hetero-atom, different hybridized carbon atoms or incorporating different functional groups which includes graphyne, holey-graphyne, BeN_4 , biphenylene, C_6N_7 , C_5N , 2D Polyaramid etc. Fig.1 illustrates these different types of two-dimensional materials [18].

Interaction mechanism of H_2 with pristine and functionalized 2D materials

Pristine carbon nanomaterials are typically poor hydrogen adsorbers. Their electronic structure does not provide strong interactions with hydrogen molecules, leading to weak adsorption solely due to vdW forces. Modifying these materials, by introducing defects, functional groups, or doping with other elements, can alter their electronic properties and create more active sites, enhancing their hydrogen adsorption capacity. The binding of hydrogen via physisorption or chemisorption in solid substrate has been considered as a traditional mechanism [19]. As per the International Union of Pure and Applied Chemistry (IUPAC), physisorption is predominantly due to the vdW forces that arise between the adsorbate and adsorbent [18]. The electronic structure of the participating species remains unchanged in physisorption owing to the weak nature of vdW forces ($< 10 \text{ kJ mol}^{-1}$) [20]. The energy barrier for physisorption is low and typically, hydrogen physisorption has rapid adsorption/desorption kinetics. Additionally, the hydrogen storage capacity in such materials is also far too low to satisfy the DOE criteria. In contrast, chemisorption involves the introduction of atomic hydrogen into the crystal lattice of the substrate which may diffuse and occupy the interstitial sites. Consequently, the enthalpy of hydrogenation is high for hydrides, and necessitate high desorption temperatures to overcome the high energy barriers. The specific requirements for onboard reversible hydrogen storage in FCVs, and particularly in light-duty FCVs, call for a hydrogen binding mechanism that provides adsorption

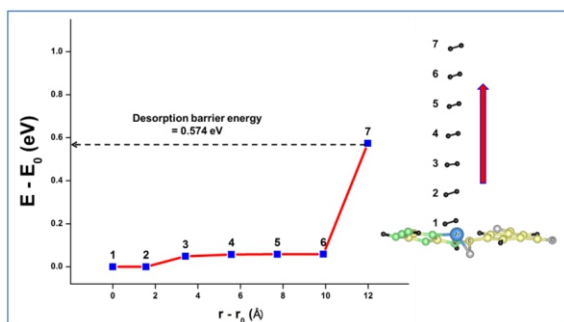


Fig.4: Energy barrier for the desorption of hydrogen from 2DPA+Zr+H₂ system computed using the climbing nudged elastic band method [29].

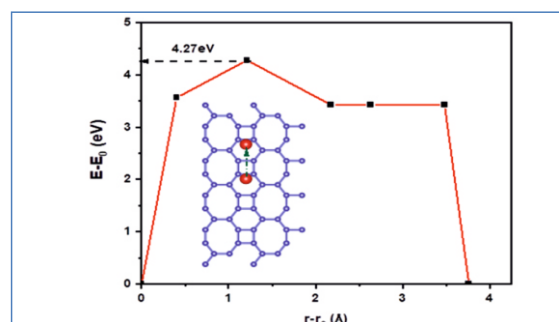


Fig.6: Diffusion Energy barrier of Bph + Nb system computed using CL-NEB Method [31].

energies intermediate to that of physisorption and chemisorption. The weak van der Waals interactions can be enhanced by introducing electric field through strain, defects or non-metal substitution. Another mechanism is Kubas interactions between transition metals and hydrogen. Kubas binding, elucidated by Gregory Kubas, describes a distinctive interaction mechanism between hydrogen molecules and TM complexes (Fig.2) [21]. In this interaction, hydrogen molecules approach the TM centre where they donate electron density from their σ -orbital the bonding orbital containing electron density to an empty d orbital or hybrid orbital of the TM. Concurrently, the TM complex back-donates electron density from its filled d orbitals or hybrid orbitals into the anti-bonding orbitals of the hydrogen molecule. This exchange of electron density creates a bond that is intermediate between chemisorption, involving strong chemical bonds, and physisorption, which relies on weaker vdW forces. The Kubas binding mechanism is notable for its ability to enhance hydrogen adsorption capacities of materials containing TMs, thereby offering potential applications in hydrogen storage technologies. The different interaction mechanisms are depicted in Fig.2 [22].

Computational Details

Theoretical simulations can provide a clear picture regarding adsorption configuration, adsorption energy, charge transfer and orbital interactions which are difficult to get in experiments. In this respect, Density Functional Theory is a rapid method in computational chemistry for computing the ground

state energy, electronic, magnetic, etc., properties of materials. In place of solving the Schrodinger equation for the wave function to obtain the energy, DFT uses the probability density of electrons, or electron density which involves lesser variables and is therefore rapid while being quite accurate.

The DFT calculations in this work have been performed using the projector-augmented wave formalism implemented in the Vienna ab initio Simulation Package (VASP) [23, 24]. Conjugate gradient methods were used for structural relaxation and the energy and interatomic force threshold for convergence was set at 10^{-5} eV and 0.01 eV/Å.

We have accounted for dispersion corrections by implementing Grimme's DFT-D3 scheme in all the calculations [26]. To find the structural stability at higher temperature, we have used Ab-initio Molecular Dynamics simulations (AIMD). The AIMD simulations utilized in these studies involved two stages. In the first stage, the system was heated from 0 K to 300 K (or higher) in an NVE ensemble in one-femtosecond timesteps for a time-period of around 5-10 picoseconds. Thereafter, the system was further equilibrated for another 5-10 picoseconds in an NVT ensemble with the temperature maintained at 300 K (or higher) using the Nose-Hoover thermostat. To find the dynamic stability, Phonon dispersion calculations were performed with increased convergence threshold values of energy cutoff (10^{-8} eV) and interatomic forces (10^{-3} eV/Å) and the Phonopy code was utilized to plot the phonon spectrum [27]. The climbing nudged elastic band (CI-NEB) method was utilized to analyze hydrogen desorption behavior.

Mechanism to Enhance Hydrogen Adsorption

For pristine light elements based 2D materials, interactions with H₂ is very weak, giving an adsorption energy around -0.10 eV/H₂, lower than DoE requirement. This adsorption is due to weak Van Der Waal's interactions and the system can't hold H₂ molecules at ambient condition. Different strategies have been adopted to increase the adsorption energy of H₂ so that system can store H₂ at ambient condition. In this article, we will discuss some of our recent work employing following strategies:

- Transition metal doping
- Applying external strain
- Non-metal substitution

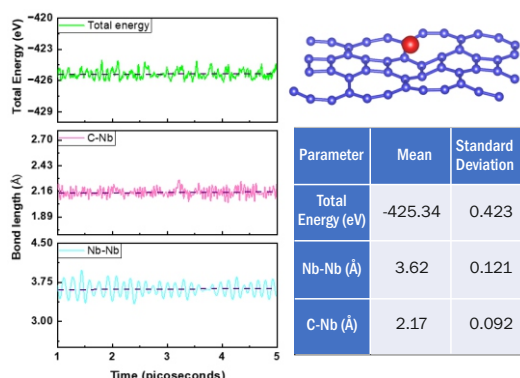


Fig.5: Time variation of Energy (top panel), and Bond lengths (bottom panels) of C-Nb and Nb-Nb bond are plotted with time (picoseconds) and distance (Å). The mean and standard deviations of the same are shown in the table [31].



Table 1: Summary of the hydrogen storage performance of 2DPA+Ti and 2DPA+Zr [29].

System	Binding energy/H ₂ (eV) with DFT-D2 corrections	
	2DPA+Ti	2DPA+Zr
2DPA+TM	-2.712	-4.122
2DPA+TM+1H ₂	-0.513	-0.544
2DPA+TM+3H ₂	-0.338	-0.509
2DPA+TM+5H ₂	-0.419	-0.555
2DPA+TM+5H ₂	-0.279	-0.429
2DPA+TM+9H ₂	NA	-0.365
Average binding energy/H ₂ (eV/H ₂)	-0.399	-0.480
Average desorption temperature (K) at 5bar	328.76	395.08

Enhancing hydrogen adsorption through Transition metal Doping

We have explored few novel 2D material to enhance their hydrogen adsorption capability by doping early transition metals(TM) with minimum unpaired electrons in the outermost shell as those TMs are good hydrogen absorber.

Titanium and zirconium decorated 2DPA nanosheet

2D polyaramid (2DPA) [28] is a porous and polymeric material which has been synthesized recently. We have studied the hydrogen storage capability of Titanium and zirconium decorated 2DPA nano sheet. By decorating a single unit cell of 2DPA with two transition metal (TM) atoms, hydrogen storage of up to 6.422 and 6.792 wt% of H₂ with average binding energies of -0.399 and -0.480 eV is predicted for 2DPA+Ti and 2DPA+Zr, respectively [29]. The binding of Ti and Zr with 2DPA is accompanied by a flow of charge (-1.474 e for Ti and -1.696 e for Zr) from the TM towards the 2DPA sheet. Table.1 represent a summary of adsorption energy for hydrogen on Ti and Zr doped 2DPA. Further, the interaction between H₂ and TM may proceed via Kubas interaction between the d orbital of the TM in 2DPA+TM and molecular orbitals of H₂, with a net flow of charge from the TM towards H₂ (-0.218 e for Ti and -0.391 e for Zr). The adsorption configurations of various H₂ molecules on 2DPA+Ti is displayed in Fig.3. The desorption of H₂ bound to 2DPA+Zr is endothermic (~0.57 eV) and close in magnitude to the binding energy of the first H₂ (~-0.544 eV) as displayed in Fig.4 where desorption energy barrier of first adsorbed H₂ has been computed using sophisticated CI-NEB method. The 2DPA+TM systems show structural and dynamic stability at high temperatures as evident from ab initio molecular dynamics simulations and phonon spectra. The movement of TM atoms across the 2DPA sheet to form clusters may be hindered by the considerable barrier energy (~4.9 eV for Ti). Through these systematic density functional theory simulations, we predict that Ti- and Zr-decorated 2DPA are high-performance hydrogen storage materials and can be explored by experimentalists.

Niobium decorated 2D Biphenylene nano-sheet

Biphenylene is a two-dimensional non-benzenoid carbon allotrope formed from a series of square, hexagonal and octagonal rings of sp² hybridized carbon atoms [30]. We have explored the hydrogen storage capability of 2D Biphenylene by decorating it with Niobium. Niobium atom gets bonded above the

bond between the octagonal and hexagonal ring with binding energy of -3.42 eV due to charge transfer from Nb d orbital to C 2p orbital. If Nb is decorated at all stable configurations, in a unitcell of biphenylene on both sides, the system will have a total of 8 Nb atoms and 40 H₂ molecules providing hydrogen uptake of gravimetric 5.76 wt% with average adsorption energy of 0.61 eV/H₂ [31].

To serve as a viable option in hydrogen storage applications, the materials should be thermally stable at higher temperatures. To analyze the thermal stability of the material, a two-step computational technique called ab initio Molecular Dynamics simulations were performed. Initially, the system was heated from 0 to 300 K over 10ps using an NVE ensemble with a 1fs time step. Subsequently, the material was equilibrated at 300K for another 5ps within an NVT ensemble employing a Nose Hoover thermostat to maintain constant temperature. The time evolution of energy as well as bond lengths are plotted in Fig.5. The negligible fluctuations in bond length and energy ensures the thermal stability of the system at room temperature.

Furthermore, the tendency of transition metals to form clusters, due to their high cohesive energy, might become a setback for their utilization in hydrogen storage application. In the hope of overcoming that, the energy required for the Nb atom to move across two equivalent positions was computed by employing the CI-NEB method. Initially the system was optimized at two equivalent positions and five images of the Nb atom at intermediate positions were generated. The maximum energy barrier, Nb atom must cross to move in the mono layer was found to be 4.27 eV (Fig.6). The high energy barrier reduces the chances of clustering making the system stable for onboard hydrogen storage.

Vanadium attached 2D Aza-triphenylene

Recently, Hao Yang et al. and Kai Niu et al. successfully synthesized a novel two-dimensional (2D) material Aza-triphenylene (Aza-COF) which represents a unique carbon-based covalent organic framework and an advanced carbon allotrope with promising structural and electronic properties [32,33]. Our DFT simulations demonstrate that vanadium-decorated Aza-triphenylene-based covalent organic frameworks (Aza-COF) are promising candidates for onboard, reversible hydrogen storage in light-duty fuel cell vehicles (FCVs). The optimal binding configuration involves vanadium atoms positioned between two nitrogen atoms at the framework edges, enabling stable adsorption of up to seven H₂ molecules per vanadium atom with an average binding energy of -0.46 eV [34], which meets the U.S. Department of Energy (DOE) requirements for hydrogen storage. The system achieves a gravimetric hydrogen uptake of 6.67wt%, approaching DOE targets, while a high diffusion barrier (~6.06 eV) prevents vanadium clustering, ensuring uniform dispersion across the COF surface. To gain deeper insights into the weak intermolecular interactions governing hydrogen adsorption and release in V-decorated Aza-COFs, a Non-Covalent Interaction (NCI) analysis was conducted [35]. As the H₂ molecules are added, the increase in green peaks in the scatter plot and iso-surface indicates dominance of weak Van der Waals interactions as shown in Fig. 7.





Titanium doped 2D - Ψ Graphene

Another advanced 2-D allotrope of carbon, called Ψ - Graphene has been theoretically predicted. It is metallic in nature and comprises of hexagonal, pentagonal and heptagonal rings of carbon [36]. Ψ - Graphene crystallizes with P_{2mg} plane symmetry and contains 12 C atoms in the unit cell having lattice constants as $a=6.70\text{\AA}$ and $b=4.84\text{\AA}$. It is known that the unique arrangement and metallic nature of Ψ - Graphene makes it thermodynamically and mechanically more stable compared to other 2-D allotropes of carbon. We presented the hydrogen adsorption of Ti decorated Ψ - Graphene (advanced 2D allotrope of carbon) using Density Functional Theory simulations [37]. Ti atom is attached strongly on Ψ - Graphene with adsorption energy of -3.39 eV due to transfer of electron from Ti 3d orbital to C 2p orbital. Titanium atom can be loaded on both side of Ψ - Graphene sheet with each Ti adsorbing maximum of 9 H_2 molecules providing gravimetric H_2 uptake of 13.14 wt%, quite higher than the prescription of 6.5 wt % by DoE's. The average adsorption energy of -0.344 eV per H_2 and an average desorption temperature TD of 438.3K provide favorable



thermodynamics for reversible hydrogen storage in fuel cell systems. The adsorption energy of H_2 is in between physisorption and chemisorptions due to Kubas interactions where H 1s orbital receives charge from metal. The interaction of Ti on Ψ - Graphene have been presented by electronic density of states analysis, charge transfer and plot for spatial distribution of charge as displayed in Fig.8. There is orbital interaction between Ti 3d and C 2p of Ψ - Graphene involving transfer of charge whereas bonding of hydrogen molecules is through Kubas type of interactions involving charge donation from σ orbitals of hydrogen molecules to the vacant 3d orbital of Ti and the subsequent back donation to σ^* orbital of hydrogen from filled 3d orbital of Ti. The system (Ψ - Graphene + Ti) was found to be stable at higher temperature by Molecular Dynamics calculations and diffusion energy barrier of 1.6 eV for Ti atom can prevent metal-metal clustering.

Strain Engineering

There are some serious limitations to the mass production of TM-decorated 2D nanomaterials, which hinder their widespread use as next-generation hydrogen-storage materials.

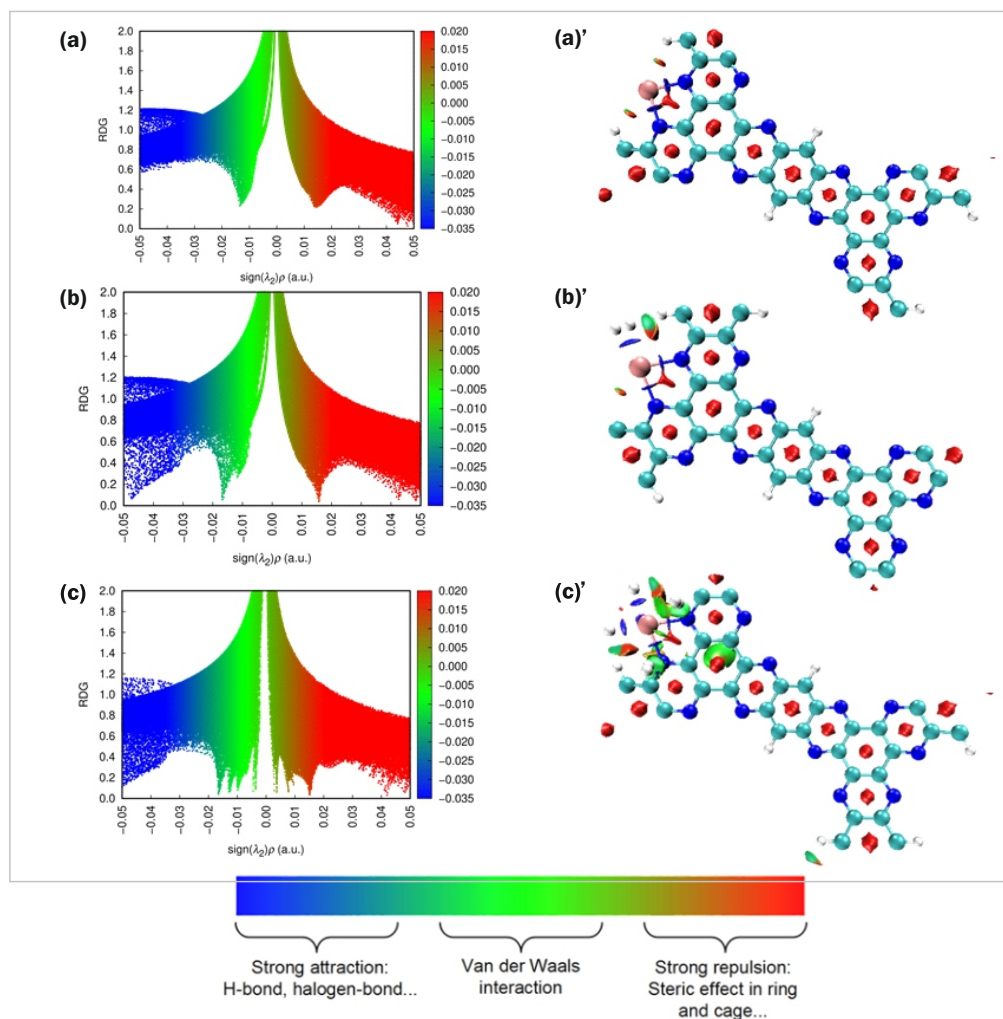


Fig.7: Reduced density gradient (RDG) iso-surfaces and corresponding scatter plots of RDG vs $\text{sign}(\lambda_2)\rho$ for (a,a') Aza-COF+V (b,b') Aza-COF+V+1 H_2 , and (c,c') Aza-COF+V+7 H_2 , respectively [34].

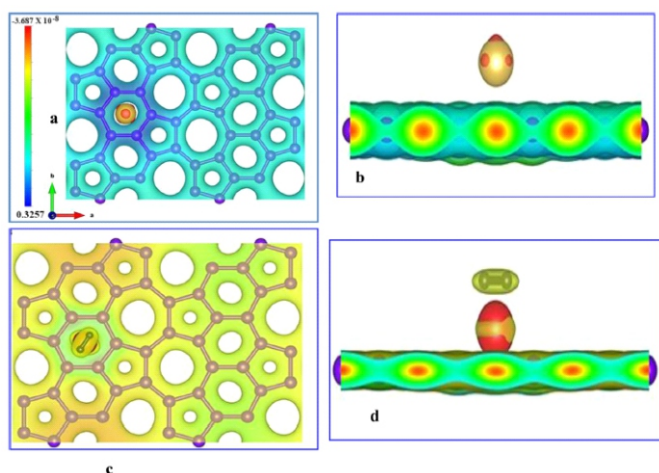


Fig.8: Electron Density plot for electron density difference between Ti-doped ψ -graphene and pristine ψ -graphene for isovalue of 0.106e; (a) top view; (b) side view; electron density plot for electron density difference between $H_2 + Ti + \psi$ -graphene and Ti doped ψ -graphene for isovalue of 0.074e; (c) top view; (d) side view. Charge loss region is indicated by red color and electron gain region by green color (less gain) and blue color (more gain) [37].

Firstly, the synthesis protocol of TM-decorated 2D nanomaterials must be designed to prevent TM aggregation into clusters. Ensuring a uniform distribution of TMs across the nanomaterial substrate is made complex owing to the high cohesive energies of TMs, particularly early TMs, driving them towards cluster formation. In addition, TMs are susceptible to oxidation due to their unique electronic structure characterized by partially filled d orbitals, which allow for multiple oxidation states to occur. Thus, their electronic configuration drives TMs to lose electrons and become cationic, driving them towards forming strong metal-oxygen bonds. These TM oxides are typically stable, making the oxidation process thermodynamically favourable. Furthermore, TMs loaded on nanomaterials exhibit a high specific surface area, increasing their reactivity and propensity for oxidation. Another significant impact of TM loading in nanostructures is the structural integrity of the host material.

Thus, alternative strategies that alter the electronic structure to enhance the substrate's reactivity and conductivity are desirable for designing efficient hydrogen-storage materials. Some of these strategies are outlined here.

Strain engineering involves applying strain in the substrate

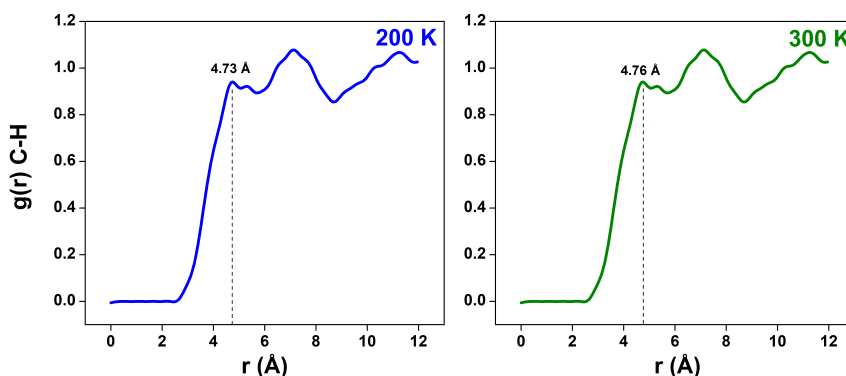


Fig.9: Radial distribution function $g(r)$ of C-H at (a) 200 K and (b) 300 K computed via AIMD simulations for hydrogen storage on HGY [38].

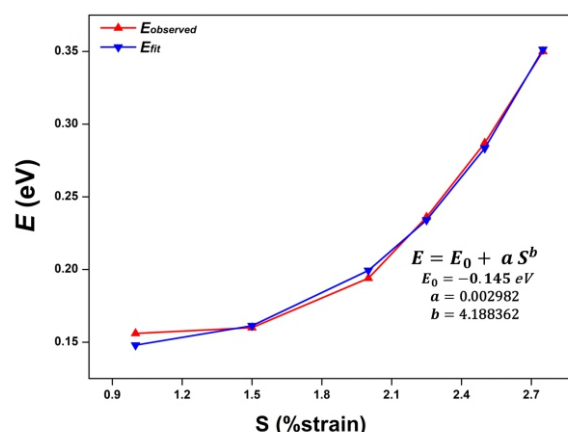


Fig.10: Variation of hydrogen adsorption energy with applied compressive biaxial strain on HGY. The results from the present simulation are compared with that of empirical fitting and the fitting equation and constants are mentioned inset (bottom-right) [38].

to modify its electronic structure without compromising on its structural stability. Applying compressive strain in nanomaterials causes an increase in charge density in the π molecular orbitals of carbon-based 2D nanomaterials. This, in turn, increases the orbitals' polarisation, which can improve their hydrogen affinity for hydrogen over that of pristine carbon-based nanomaterials. Here we describe the design of few light element based 2D materials for enhanced hydrogen storage, adopting the strain engineering technique.

Strain Engineering in 2D holey graphene (HGY)

Herein, the interaction of hydrogen with pristine and strained 2D holey graphene (HGY) has been examined. Upon subjecting HGY to biaxial compressive strain (1%–2%), linear compression of C-C bonds was noted and beyond 3% strain the structure distorted. Hydrogen adsorption on strained HGY showed enhanced adsorption energies compared to pristine HGY, peaking at -0.350 eV for 2.75% strain [38].

Based on our investigations, pristine HGY interacted with H_2 via weak van der Waals interactions, evidenced by low adsorption energies. However, under the influence of compressive strain, its electronic properties were altered and a spatial confinement was induced within HGY. The resulting increased charge polarization led to the development of an

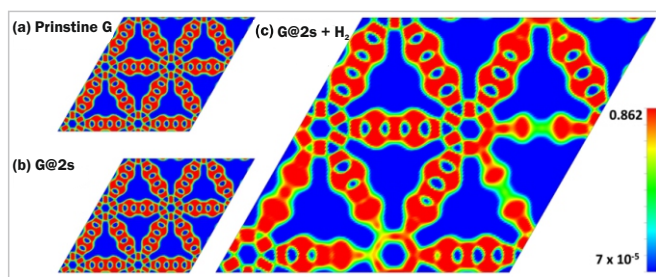


Fig.11: Electron localization function plots of (a) pristine graphdiyne, (b) G@2S, and (c) G@2S + H₂. The color legend is shown inset (bottom right)

electric field within the system, which enhanced the van der Waals interactions of the substrate with H₂. Mechanistic insights revealed that hydrogen adsorption on strained HGY occurs via an assisted van der Waals interaction mechanism. This interaction was most pronounced at 2% strain, where the work function analysis indicated increased conductivity and maximum interaction with hydrogen molecules. Furthermore, applied strain of 2.75% resulted in the highest hydrogen adsorption energy, significantly improving storage capacity. The gravimetric uptake of H₂ in 2.75% strained HGY was 5.88 wt% computed under the DFT conditions of 0 K and no applied pressure, satisfying the 2025 US DOE target for solid-state H₂ storage in light vehicles. The influence of temperature and pressure conditions on hydrogen retention by the substrate was evaluated; vapour pressure calculations revealed that at 50 bar, hydrogen delivery could occur at 342 K. The thermal stability of the strained HGY was confirmed through AIMD simulations, ensuring its viability for practical hydrogen storage applications. The first *g(r)* peak was noted at ~4.7 Å as shown in Fig.9, consistent with weak interactions between H₂ and strained HGY. Fig.10 displays the variation of adsorption energy of H₂ with the strain, fitted with an empirical formula. Thus, our findings highlight strain engineering as a promising pathway to enhance hydrogen storage in carbon nanomaterials like HGY, offering a feasible solution that avoids the limitations of metal-based approaches.

Strain Engineering in 2D graphdiyne

We have investigated the possibility of compressive strain application of synthesized 2D graphdiyne [39], an advanced member of graphene family. Under the influence of 2%

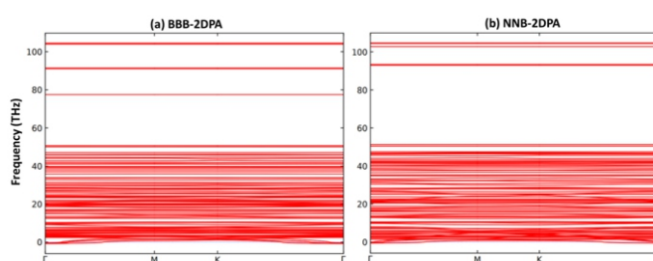


Fig.12: Phonon dispersion curves for (a) BBB-2DPA and (b) NNB-2DPA; absence of negative frequency confirms dynamic stability [42].

compressive biaxial strain (G@2S), the adsorption energy of hydrogen on graphdiyne improves to -0.224 eV/H₂ with a maximum predicted gravimetric capacity of 6.942 wt%. The mechanism of binding may be via an enhanced physisorption owing to the altered electronic structure of graphdiyne under the influence of strain. The strained system is mechanically stable at 300 K as verified by molecular dynamics simulations [40].

The electron localization function plots for graphdiyne, G@2S, and G@2S + H₂ (Fig.11) shows that the binding of hydrogen is accompanied by a reduction in local electron density near neighboring acetylenic bonds (green regions), and the C6 ring shows increased electron density (enhanced red regions). Thus, the binding interaction of hydrogen with G@2S may be due to an enhanced physisorption owing to the modified electronic structure under applied strain. Hydrogen storage in G@2S may be reversible as hydrogen vapor pressures of 12 bar can be achieved at 290 K. Based on our predictions, strain engineering in graphdiyne can be explored in experimental trials for potential hydrogen storage applications.

Strain Engineering in 2D graphene

We also reported through DFT simulations that in a 4 × 4 supercell of graphene, the application of 6% biaxial strain led to a gravimetric hydrogen uptake of 9.4% with an average adsorption energy of -0.42 eV/H₂ [41]; the enhanced hydrogen storage capacity of strained graphene was attributed to altered electronic properties of graphene under strain, leading to an enhanced charge transfer interaction between the substrate and hydrogen.

Table 2: Hydrogen adsorption energies, H-H bond length, and shortest distance between H and the substrate for the adsorbed H₂ in the doped 2DPA systems. The best performing systems are formatted in blue[42].

System	E _{ad} (eV)	Distance or bond length (Å)	
		H-H	Substrate-H
Pristine 2DPA	-0.116	0.75 (isolated H ₂)	–
N-2DPA	-0.162	0.753	2.887
NN-2DPA	-0.168	0.753	2.550
NNN-2DPA	-0.161	0.752	2.963
B-2DPA	-0.155	0.753	2.717
BB-2DPA	-0.224	0.756	2.474
BBB-2DPA	-0.234	0.757	2.053
BN-2DPA	-0.179	0.752	2.947
BBN-2DPA	-0.170	0.754	2.694
NNB-2DPA	-0.268	0.757	2.064



Non-metal Substitution

Substitutional doping with light elements such as B and N, which are similar in size to C, can lead to hole (B) or electron (N) doping in the host material. The increased conductivity of charge carriers brought about by B/N doping can enhance the substrate's interaction with hydrogen.

Non-metal Substitution in 2DPA nanosheet

We have also demonstrated the potential of non-metal substitutional doping in 2DPA as a viable strategy for enhancing its hydrogen affinity and therefore its potential towards hydrogen storage applications without the need for metal adatoms; metal adatoms cause decreased gravimetric uptakes and poor efficiency over time owing to the high likelihood of metal-clustering. A systematic doping protocol was established and B- and N-doping configurations were identified by selectively doping in a manner so as to improve the H_2 affinity of the substrate. The BBB- and NNB-2DPA systems exhibited optimal hydrogen adsorption energies within the DOE's prescribed range and showed improved H_2 -substrate interaction strength brought about by polarization-assisted van der Waals forces. B/N doping led to modifications in the electronic structure and conductivity and brought about charge polarization. This in turn improved the substrate's H_2 affinity via an assisted physisorption route. The first hydrogen adsorption energy in BBB- and NNB-2DPA was considerably enhanced (-0.234 and -0.268 eV, respectively) as compared to that in pristine 2DPA (-0.116 eV) [42]. Table.2 displays the adsorption energy on various configurations obtained by N/N substitution on 2DPA. Thermal stability studies using AIMD simulations and phonon dispersion analysis (Fig.12) confirmed the robustness of BBB- and NNB-2DPA at room temperature, making these systems viable for practical applications. The gravimetric hydrogen uptake of these substrates was found to be promising, with 4.778 wt% and 4.040 wt% obtained for BBB- and NNB-doped 2DPA, respectively. Vapour pressure calculations for a delivery pressure of 12 bar revealed desorption temperatures of 252.186 K and 275.91 K for BBB- and NNB-decorated 2DPA, respectively.

Non-metal Substitution in 2DPA nano-sheet Graphdiyne (GDY)

We have also theoretically explored the hydrogen storage capability of graphdiyne (GDY) which is an advanced member of 2D graphene family and has been synthesized. Nitrogen and boron doped graphdiyne (BCN-GDY) have also been demonstrated for hydrogen storage. Although pristine GDY exhibits weak hydrogen adsorption, strategic B/N co-doping induces charge redistribution and polarization of H_2 molecules, yielding enhanced physisorption which significantly improves its hydrogen storage capacity. BCN-GDY achieved a remarkable hydrogen weight percentage of 14.29%, which is well above the DOE target of 6.5 wt%, with an average adsorption energy of -0.23 eV/ H_2 , which falls within the optimal range of -0.2 to -0.7 eV/ H_2 [43]. The dehydrogenation temperature range is 256–331 K at 5 bar, room temperature. Overall, BCN-GDY emerges as a highly promising material for hydrogen storage applications, with superior adsorption/desorption kinetics and substantial hydrogen capacity, positioning it as a strong candidate for clean energy technologies.

Conclusions

This article uses Density Functional Theory (DFT) to investigate the interaction, charge transfer mechanisms, and hydrogen storage capacity of transition metal-decorated 2D carbon nanostructures (2D polyaramid, holey graphyne, biphenylene). The effect of strain on 2D materials for enhancing the hydrogen storage capability has also been addressed. Few systems, e.g. Ti and Zr doped 2D polyaramid, Niobium doped biphenylene and strained holey graphyne have been identified as promising materials to experimentally fabricate 2D material based hydrogen absorbing materials for next generation hydrogen storage devices.

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