Titanium-Decorated Boron Nitride Nanotube for Hydrogen Storage: A Multiscale Theoretical Investigation

Michael Rivera Mananghaya
School of Science and Engineering, Ateneo de Manila University, Katipunan Ave, Quezon City, 1108 Metro Manila, Philippines.
mikemananghaya@gmail.com, +63.947.529.8727

SUPPLEMENTARY INFORMATION

S.1 The Density Functional Theory (DFT) Calculations. The (10 ,0) BNNT cluster is shown in Fig. 1(a). It is the working model for DFT calculations. As mentioned in the methodology section, five equally spaced single B-N pair around the surface of the BNNT was replaced with an equal amount of Ti atom attached directly on the geometric center of the defect site. The terminal side of the Ti-doped BNNT was strategically filled with hydrogen to satisfy the dangling bonds. The DFT calculations of thermodynamic and electronic properties have been performed using GAMESS code. Structural relaxations and natural bond orbital (NBO) analysis were performed under the spin-unrestricted DFT gradient-corrected Perdew-Burke-Ernzerhof (PBE) functional with an empirical dispersion part in the 6–311++G (d, p) basis set. The equation for calculating the Ti binding energy ($E_{b(Ti)}$) on the nanotube surface is as follows:

$$E_{b(Ti)} = E_{Ti + BNNT} - E_{BNNT} - E_{Ti} + E_{BSSE} \qquad (1)$$

where $E_{Ti + BNNT}$ represents the total energy of the Ti atom adsorbed on the BNNTs, E_{BNNT} is the total energy of BN nanotube and E_{Ti} is the total energy of the isolated Ti atom. E_{BSSE} is the familiar basis set superposition error. For calculating the Ti binding energy on the nanotube surface with n H_2 ($E_{b(nH_2\text{-}Ti)}$) attached, we can modify the formula as follows:

$$E_{b(nH_2\text{-}Ti)} = E_{nH_2\text{-}Ti + BNNT} - E_{BNNT} - E_{nH_2\text{-}Ti} + E_{BSSE} \qquad (2)$$

$E_{nH2\text{-}Ti + BNNT}$ represents the total energy of the nH_2-Ti-BNNTs, $E_{nH2\text{-}Ti}$ is the total energy of the nH_2 attached to Ti atom. This serves as a complementary guide to access if the binding energy of Ti is greater than its cohesive energy as we add n H_2. It provides a sound basis if the Ti metals does not form clusters with each other as the proposed system approaches its H_2 saturation limit. Next, the formula for the predicted H_2 binding energy $E_{b\,(nH_2)}$ to the Ti/BNNT is as follows:

$$E_{b\,(nH_2)} = (E_{nH_2\text{-}Ti + BNNT} - E_{Ti + BNNT} - E_{nH_2} + E_{BSSE})/n \qquad (3)$$

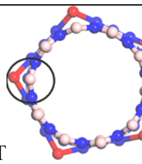
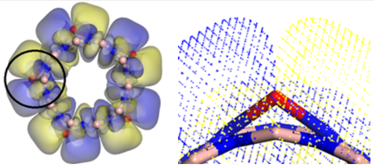
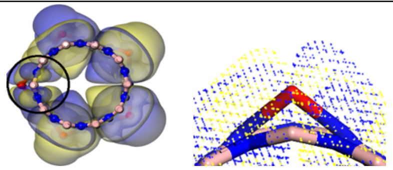
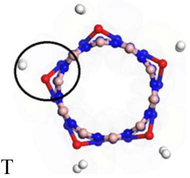
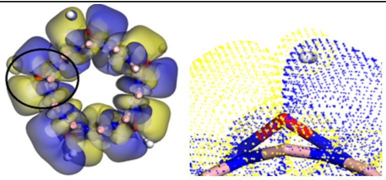
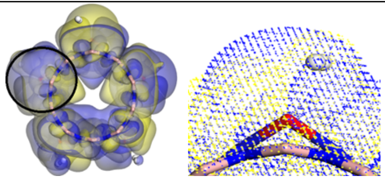
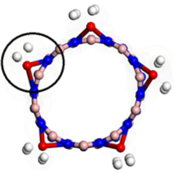
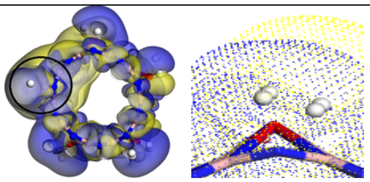
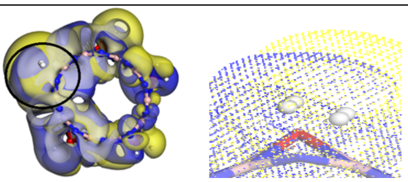
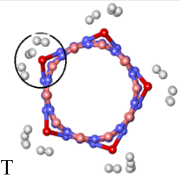
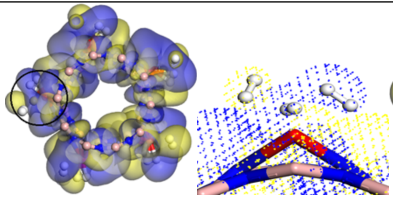
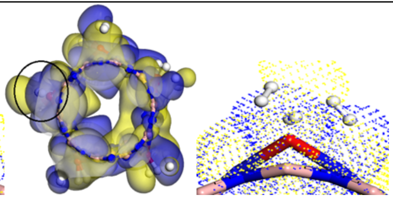
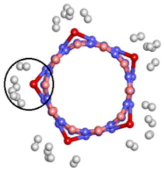
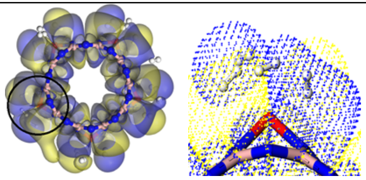
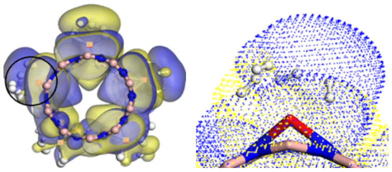
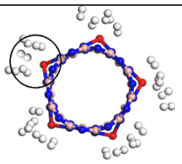
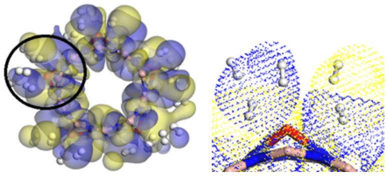
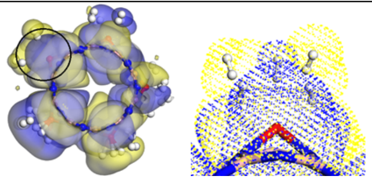
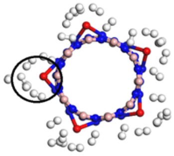
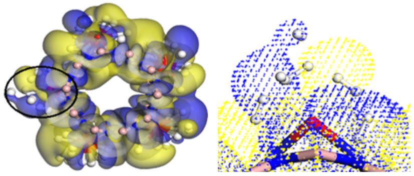
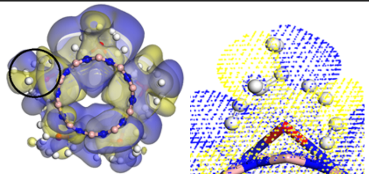
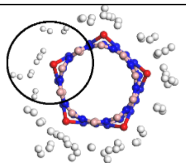
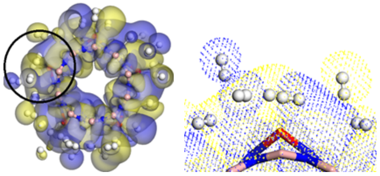
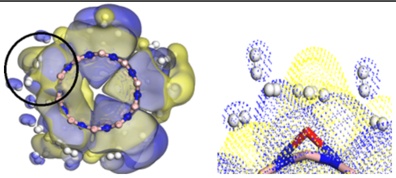
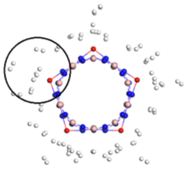
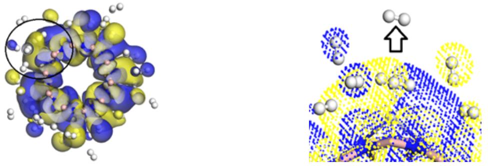
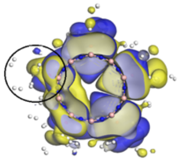
where $E_{nH_2\text{-}Ti + BNNT}$ represents the total energy of the nH_2 adsorbed on the Ti metal, $E_{Ti+BNNT}$ is the total energy of Ti/BN nanotube and E_{nH_2} is the total energy of the n H_2 adsorbed. Equation (3) is also normalized with respect to n H_2 molecules adsorbed. To ensure that the energy as H_2 is added from (n-1) to n H_2 falls within the optimal range for adsorption or desorption in the Ti/BNNT system, we need to track the energy released by the system. The formula needed to accomplish this task is

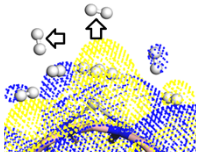
$$E_{b\,(nH_2\text{-}(n-1)H_2)} = E_{nH_2\text{-}Ti + BNNT} - E_{(n-1)H_2\text{-}Ti + BNNT} - E_{H_2} + E_{BSSE}. \qquad (4)$$

where $E_{nH_2\text{-}Ti + BNNT}$ represents the total energy of the nH_2 adsorbed on the Ti metal, E_{H_2} is the total energy of H_2 and $E_{(n-1)H_2\text{-}Ti + BNNT}$ is the total energy of the (n-1) H_2 adsorbed. In addition, the importance of DFT+dispersion corrections was assessed against reference interaction energies found in literature. The structural configurations of the isolated BNNT were fully optimized until the force on each atom during relaxation was less than 0.03 eV/Å. The established hypothesis for Fermi level (E_F) is that in a molecule it locates nearly in the average point of the HOMO and LUMO energy gap (E_g). Herein, the E_F assumed to be half the E_g.

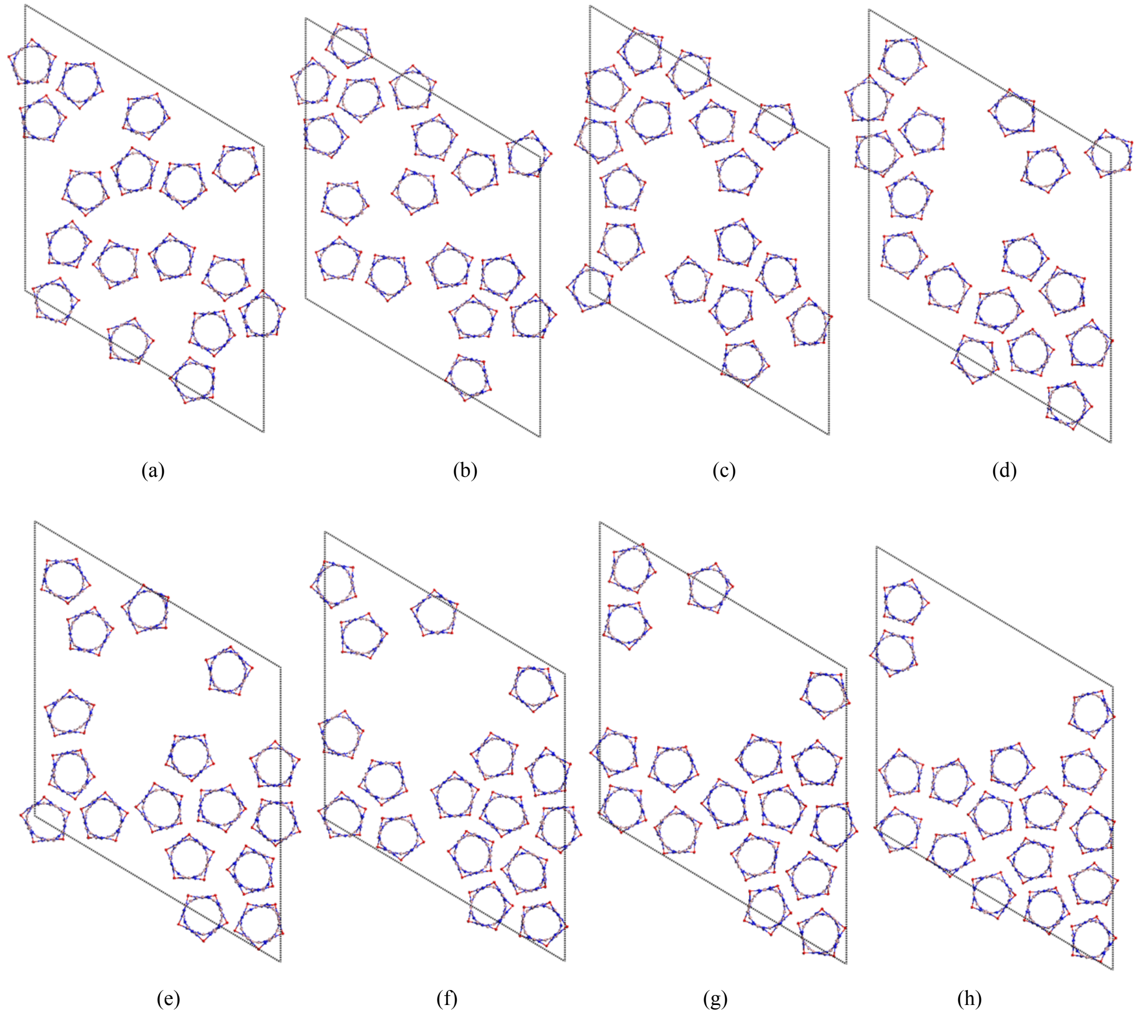
Table S1 Bond lengths of the Ti-doped BNNTs and nH_2-Ti/BNNTs.
$^*C_{nH_2}$ = charge of the nth H_2 attached.

Structure	HOMO-LUMO gap (eV)	$E_{b(nH_2\text{-}Ti)}$ (eV)	Ti–N (Å)	Ti–B (Å)	Ave Ti–nH_2 (Å)	$^*C_{nH_2}$ (e)	Average H–H (Å)
Ti/BNNT	0.517	-7.005	2.126 2.126	2.653 2.653	-	-	-
$1H_2$-Ti/BNNT	0.504	-7.539	2.088 2.088	2.086 2.086	2.263	0.005 0.008	0.793
$2H_2$-Ti/BNNT	0.420	-6.501	2.356 2.125	3.005 2.841	2.425	0.005 0.007	0.789
$3H_2$-Ti/BNNT	0.474	-7.100	2.117 2.077	2.522 2.479	2.600	0.004 0.007	0.784
$4H_2$-Ti/BNNT	0.476	-7.465	2.110 2.110	2.606 2.602	2.790	0.004 0.006	0.781
$5H_2$-Ti/BNNT	0.468	-7.555	2.105 2.110	2.615 2.608	2.991	0.004 0.005	0.774
$6H_2$-Ti/BNNT	0.467	-7.600	2.105 2.104	2.601 2.600	3.210	0.004 0.004	0.771
$7H_2$-Ti/BNNT	0.466	-7.689	2.106 2.100	2.598 2.596	3.430	0.003 0.003	0.764
$8H_2$-Ti/BNNT	0.466	-7.690	2.106 2.100	2.598 2.596	3.745	0.003 0.003	0.760

Optimized Configuration	HOMO	LUMO
 (a) Ti/BNNT		
 (b) $(1H_2)_5+Ti_5$/BNNT		
 (c) $(2H_2)_5+Ti_5$/BNNT		
 (c) $(3H_2)_5+Ti_5$/BNNT		
 (d) $(4H_2)_5+Ti_5$/BNNT		
 (e) $(5H_2)_5+Ti_5$/BNNT		
 (f) $(6H_2)_5+Ti_5$/BNNT		
 (g) $(7H_2)_5+Ti_5$/BNNT		
(h) $(8H_2)_5+Ti_5$/BNNT 		

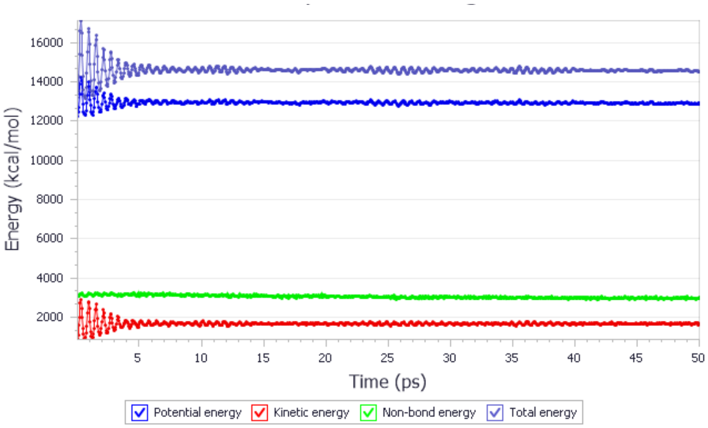
	

Supplementary Fig. S1. Relaxed configurations for the Ti/BNNTs and $(nH_2)_5$+Ti_5-BNNTs (red = Ti, pink = B, blue = N, white = H). A maximum of n=7 H_2 per Ti can populate the system. For clarity, the terminal H supplied is not visible here in the cross sectional view perpendicular to the tube axis.

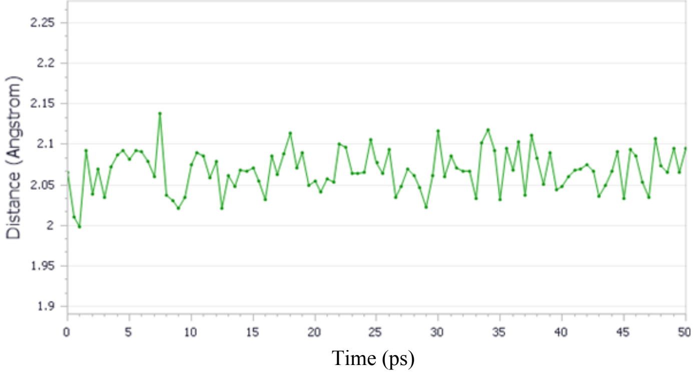

(a) (b) (c) (d)

(e) (f) (g) (h)

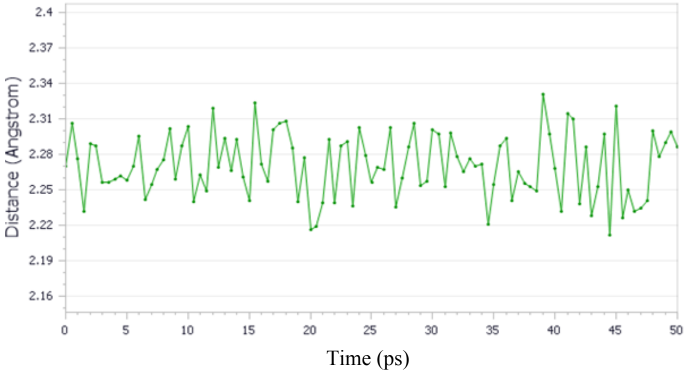
Supplementary Fig. S2. Relaxed configurations for the periodic Ti_5/BNNTs (red = Ti, pink = B, blue = N, white = H).



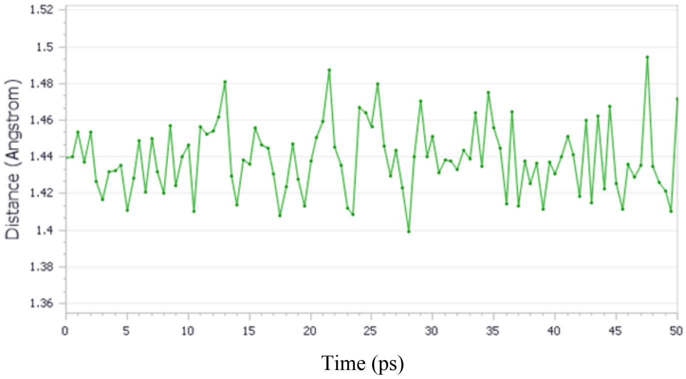
(a) Energy evolution at 50 ps.



(a) Ti-N bond evolution at 50 ps.



(c) Ti-B bond evolution at 50 ps.



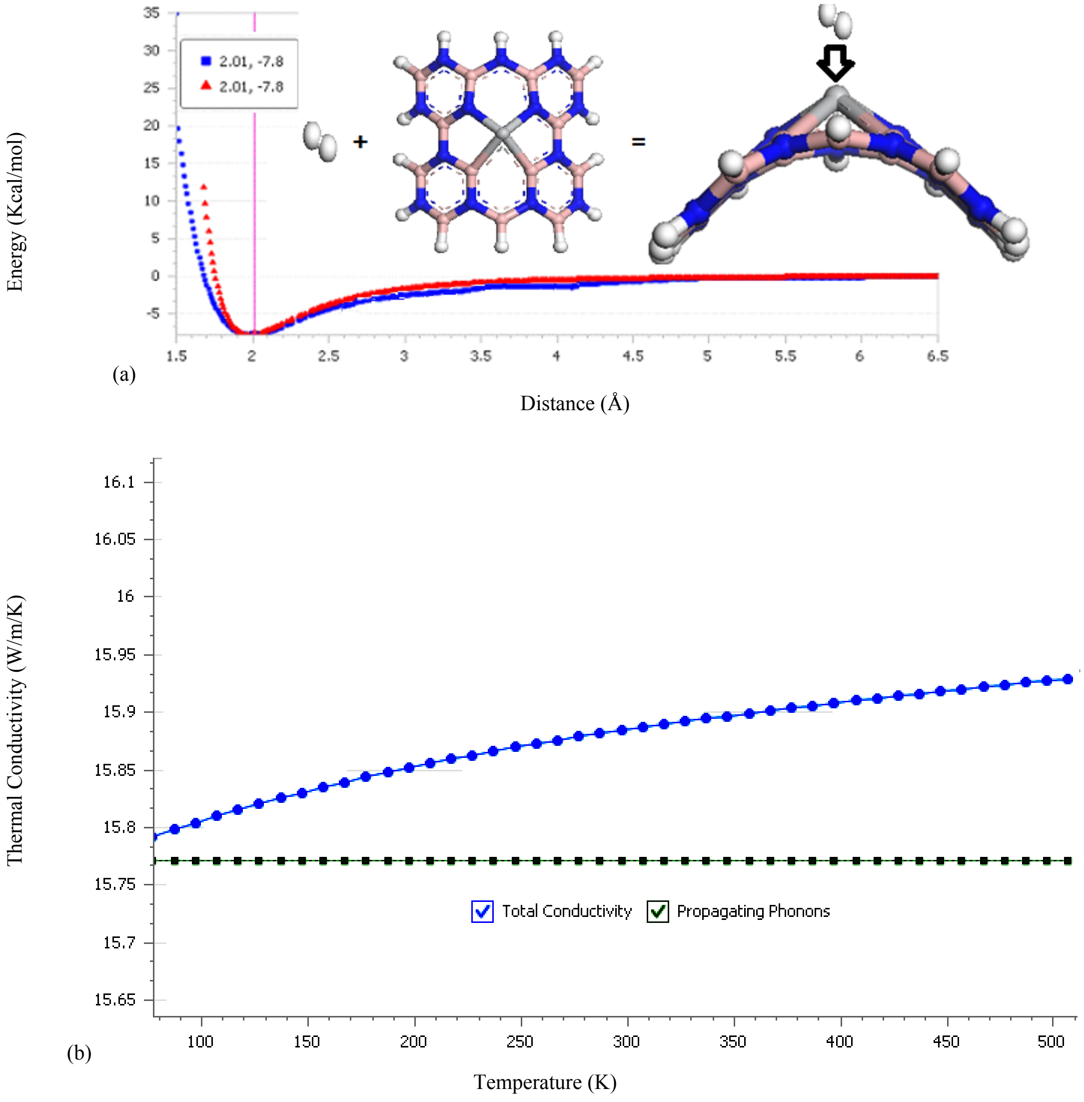
(d) B-N bond evolution at 50 ps.

Supplementary Fig. S3. The (a) energy, (b) Ti-N, (c) Ti-B and (d) B-N bond evolution as time elapses for a period of 50 ps.

S.2 The Molecular Dynamics MD simulations. The 6−12 Lennard-Jones (LJ) potential was utilized to model the H_2-Ti/BNNT bulk system. The LJ potentials is a simple mathematical model depicting the repulsive and attractive terms for approximating the interaction between H_2-Ti/BNNT, it is conveniently expressed as

$$U(r) = 4\varepsilon\,[(\sigma/r)^{12} - (\sigma/r)^{6}] \qquad (5),$$

where r is the distance between particles, ε is the depth of the potential well and σ is the distance at which the inter-particle potential is zero. As the H_2 approaches the single Ti in the $B_{13}N_{13}H_{14}$ as displayed below in Fig. S4 the LJ potential as a function of distance in Å is generated. Interestingly, Structural relaxations of a B-N ring cluster consisting of 3B and 3N similar to a benzene ring with one Ti atom above possess the same potential energy plot owing to the strong effect of Ti on H_2 adsorption. The Structural relaxations of a $B_{13}N_{13}H_{1}$ defected cluster consisting of one Ti atom attached to 2B and 2N is performed with triple zeta valence plus polarization close to basis set limit DFT using GAMESS. program. In Table S2, the LJ parameters used to construct the adsorption of H_2 on Ti/BNNT for hydrogen, boron, nitrogen, and titanium are listed. The total potential energy stored between H_2 and BNNT is written as the sum of contributions of Ti/BNNT. The parameters of interatomic interactions between H_2 and Ti/BNNT framework have implemented in a new modified DREIDING force field for H_2 gas sorption simulations. A typical simulation starting from 0.1 bar up to 100 bar included a first $1\text{x}10^7$ steps for equilibrium and the next $1\text{x}10^7$ steps for the statistical ensemble average wherein H_2 is obviously treated as a diatomic molecule. The step is summarized with three schemes: insertion of a new H_2, followed by deletion of an existing H_2 and its corresponding translation.



Supplementary Fig. S4. The (a) LJ potential as a function of distance in Å for H_2 approaching a $B_{13}N_{13}H_{14}$ cluster with one Ti atom above it at the MP2 perturbation theory (blue) and modified DREIDING (red) level. The (b) corresponding thermal conductivity and the propagating phonons obtained using the MD simulations.

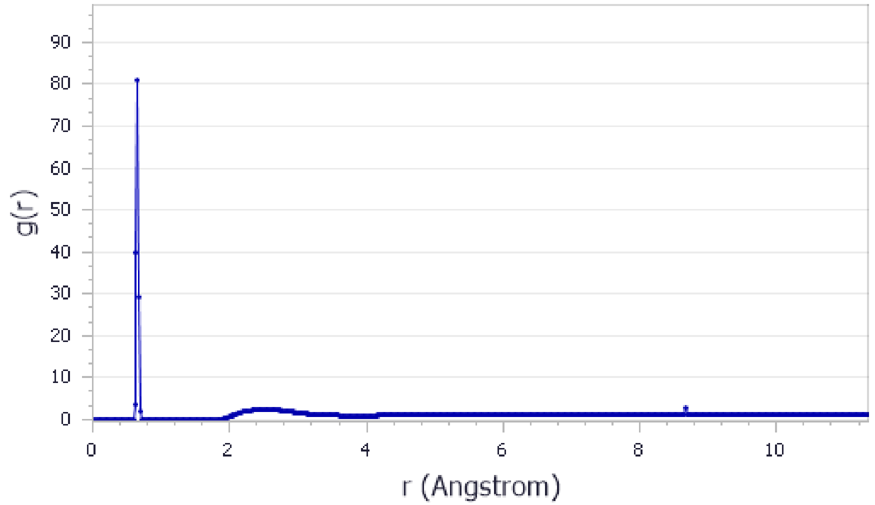
Table S2. LJ potential parameters of H_2 molecules and the entire framework atoms used in the H_2 adsorption on Ti-doped BNNTs.

Structure	ε (kcal/mol)	σ (Å)
H_2- H_2	0.025	2.312
H_2-N	0.079	3.053
H_2-B	0.052	3.133
H_2-Ti	3.124	1.785

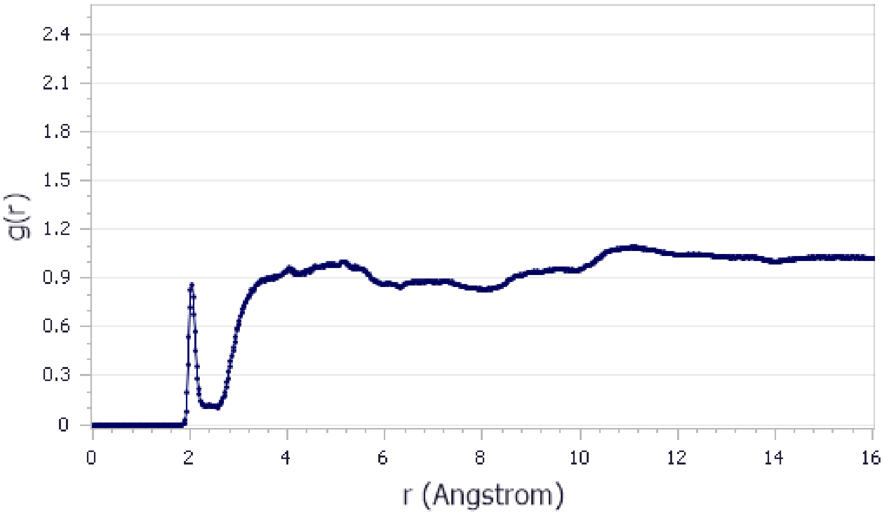
Heat transport is quantified conveniently using the thermal conductivity (κ). It is a phonon-phonon scattering dependent processes of so-called diffusons that was rigorously implemented in the GULP code. Here the phonons are calculated for a supercell and by broadening the phonon density of states. The κ can be computed conveniently using the formula: $\kappa = \frac{1}{V}\sum_{i=1}^{modes} C_i(T)D_i$. Where V is the cell volume, $C_i(T)$ is the heat capacity of mode i at temperature T and D_i is the mode diffusivity. The heat capacity has the form:

$$C_i = \frac{-\hbar\omega_i^2 \partial n_i}{VT \quad \partial\omega_i}$$

n_i is the Bose-Einstein value and its frequency ω_i is well defined. For the $(7H_2)_5$+Ti_5/BNNT system, κ is a microscopic temperature-independent definition of D_i. The mode diffusivity is an intrinsic property of the *i*th normal mode and it is an unambiguous criterion for localization. A nonzero contribution occurs by a mechanism analogous to electron hopping. The thermal conductivity and the propagating phonons are displayed conveniently above in fig S4(b).

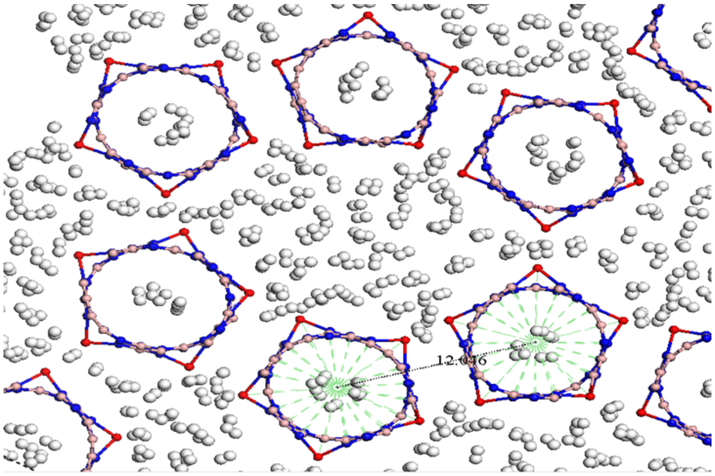


(a) Total H_2

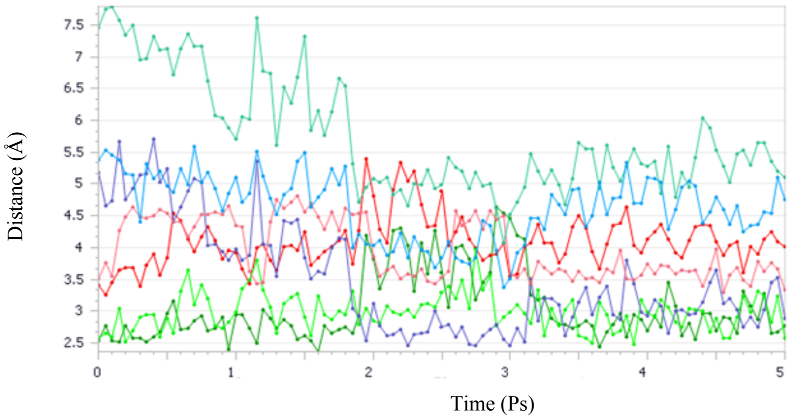


(b) Total H_2 from the Ti_5/BNNTs

Supplementary Fig. S5. The Radial distribution function of hydrogen molecules adsorbed in the Ti/BNNTs.

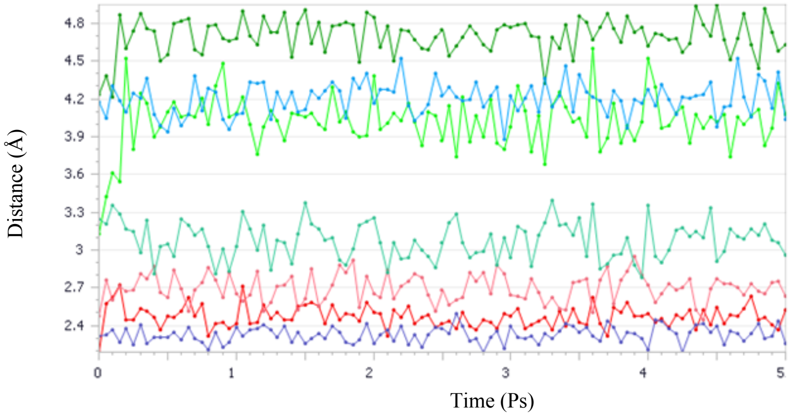


(a) Ti/BNNT to Ti/BNNT distance in Å



(b) Ti-H_2 Bond (Å)

☑ 1st H_2 ☑ 2nd H_2 ☑ 3rd H_2 ☑ 4th H_2 ☑ 5th H_2 ☑ 6th H_2 ☑ 7th H_2



(c) Ti-H_2 Bond (Å)

☑ 1st H_2 ☑ 2nd H_2 ☑ 3rd H_2 ☑ 4th H_2 ☑ 5th H_2 ☑ 6th H_2 ☑ 7th H_2

Supplementary Figure S6. Relaxed (a) Ti/BNNT to Ti/BNNT distance. The Hydrogen-Titanium adsorption distance calculated for a pressure of (b) 500 and (c) 10000 KPa at 77 K utilizing the canonical NPT ensemble.

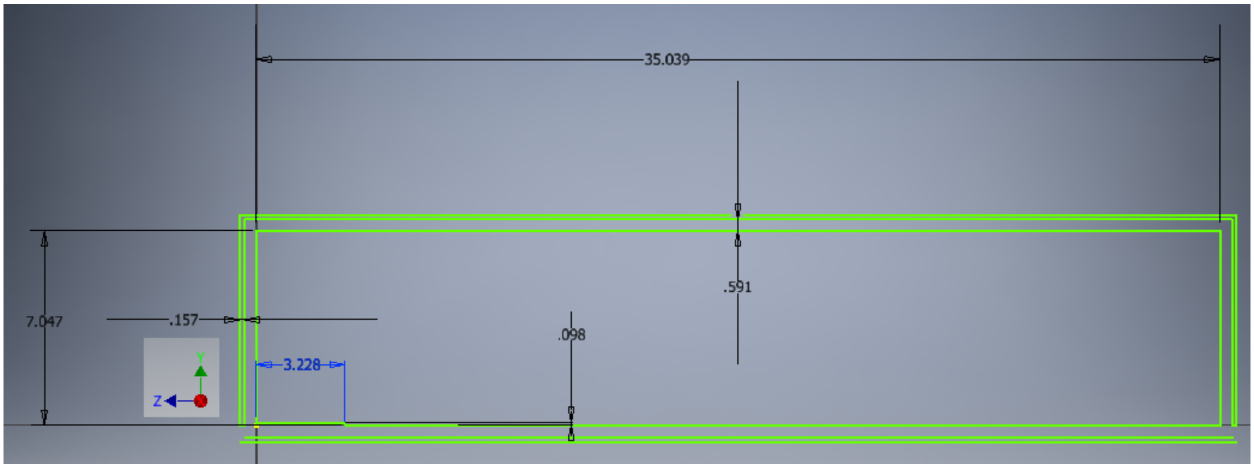
S.3 The computational fluid dynamics (CFD) subroutine. A type III H_2 cylinder with a 74L of H_2 capacity filled to up to 35 MPa has a mass of 1.8 kg. Strictly speaking, the actual flow rate required to fill the tank naturally depends on the desired fill time and the initial pressure. For stringent analysis a 10MPa initial pressure and a total fill time of 40 s was assumed in accordance to an actual experimental fill. The model is divided in several computational domains: fluid domain within the cylinder and the cylinder wall with its corresponding inlet tube. The fluid domain is filled with H_2 gas. The cylinder domain is split into the liner and laminate and its thickness is assumed to be uniform. The conservation of energy within the cylinder wall takes the form

$$\frac{\partial(\rho h)}{\partial t} = k\frac{\partial^2 T}{\partial^2 x} \qquad (6)$$

where ρ, h, T, k and t are the density (kg/m^3), specific enthalpy (J/mol), temperature (K) and thermal conductivity (W/m K) along the wall of the tube taken at time (s) at the x direction, respectively. The heat transfer is dominated by turbulent convection between the H_2 gas and the tank liner. The model employs a log law of the wall for mean temperature and the energy equation (6) is solved using the total temperature with specified initial boundary condition at the inlet representing an actual performance. This condition matches the measured pressure throughout the H_2 uptake. At the outer wall the heat transferred to the surrounding air is determined using a constant heat transfer coefficient. Further, to simplify the calculations, the temperature of the outer laminate surface of the cylinder and the ambient temperature is also assumed to be constant during uptake.

Table S3. Cylinder Tank dimensions

DESCRIPTION	VALUE
Length of the cylinder	92.8 cm (36.535 in)
Inner radius of the cylinder	17.9 cm (7.047 in)
Wall thickness of the cylinder	1.9 cm (0.748 in)
Aluminum Liner thickness	0.4 cm (0.157 in)
Carbon-fiber epoxy Laminate thickness	1.5 cm (0.591 in)
Inner radius of the gas inlet tube	0.25 cm (0.098 in)
Wall thickness of the gas inlet tube	0.20 cm (0.078 in)
Length of the tube protruding into the cylinder	8.2 cm (3.228 in)



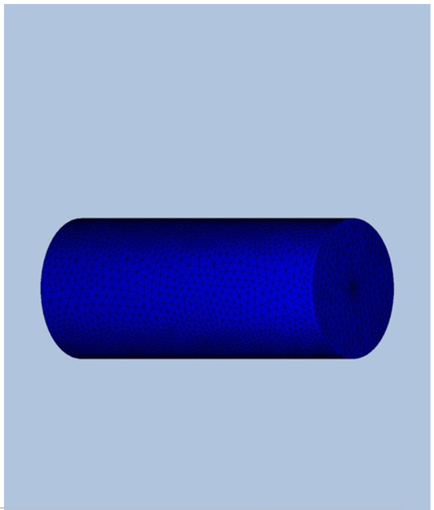
Supplementary Figure S7. Cylinder tank cross section dimensions

Table S4. Material specifications defined for a conventional cylindrical metal tank upon H_2 adsorption.

NAME	PROPERTIES	
Fiber	X-Direction	1.0 W/m-K
	Y-Direction	Same as X-dir.
	Z-Direction	Same as X-dir.
	Density	930.0 kg/m3
	Specific heat	1494.0 J/kg-K
	Emissivity	0.54
	Transmissivity	0.0
	Electrical resistivity	7.2e-05 ohm-cm
	Wall roughness	0.0 meter
Aluminum liner	X-Direction	167.0 W/m-K
	Y-Direction	Same as X-dir.
	Z-Direction	Same as X-dir.
	Density	900.0 kg/m3
	Specific heat	2730.0 J/kg-K
	Emissivity	0.54
	Transmissivity	0.0
	Electrical resistivity	7.2e-05 ohm-cm
	Wall roughness	0.0 meter
Hydrogen	Density	Equation of State
	Viscosity	8.96e-06 Pa-s
	Conductivity	0.183 W/m-K
	Specific heat	14310.0 J/kg-K
	Compressibility	1.4
	Emissivity	1.0
	Wall roughness	0.0 meter
	Phase	Vapor Pressure
Air	Density	Equation of State
	Viscosity	1.817e-05 Pa-s
	Conductivity	0.02563 W/m-K
	Specific heat	1004.0 J/kg-K
	Compressibility	1.4
	Emissivity	1.0
	Wall roughness	0.0 meter
	Phase	Vapor Pressure

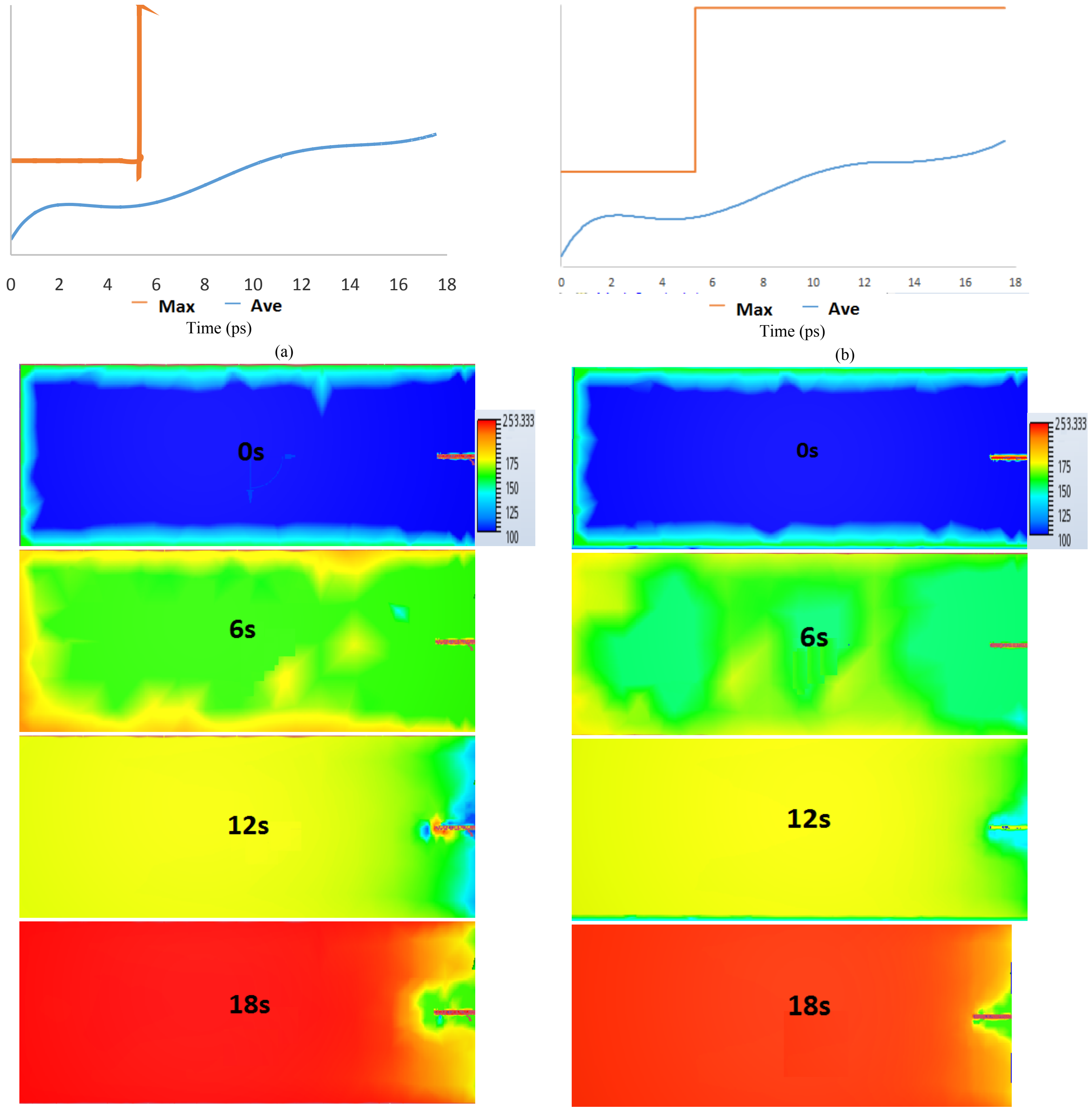
Table S5. Boundary conditions defined for a conventional cylindrical tank upon H_2 adsorption.

DESCRIPTION	VALUE
Ambient temperature, T_0/T_{in}	20/20 °C
Inlet pressure, P_{in}	100 bar
Coolant air temperature, T_c	20 °C
Reference pressure, P_{ref}	100 bar
Convective heat transfer coefficient between the cylindrical tank surface and the ambient air	10 W/m^2 K
Nominal pressure ramp rate	41.5 MPa/min



Number of Nodes	3451
Number of Elements	1170

Supplementary Figure S8. Meshed Model



(a)

(b)

Supplementary Figure S9. H_2 loading pressure in bar (a) without and (b) with the Ti/BNNT substrate.