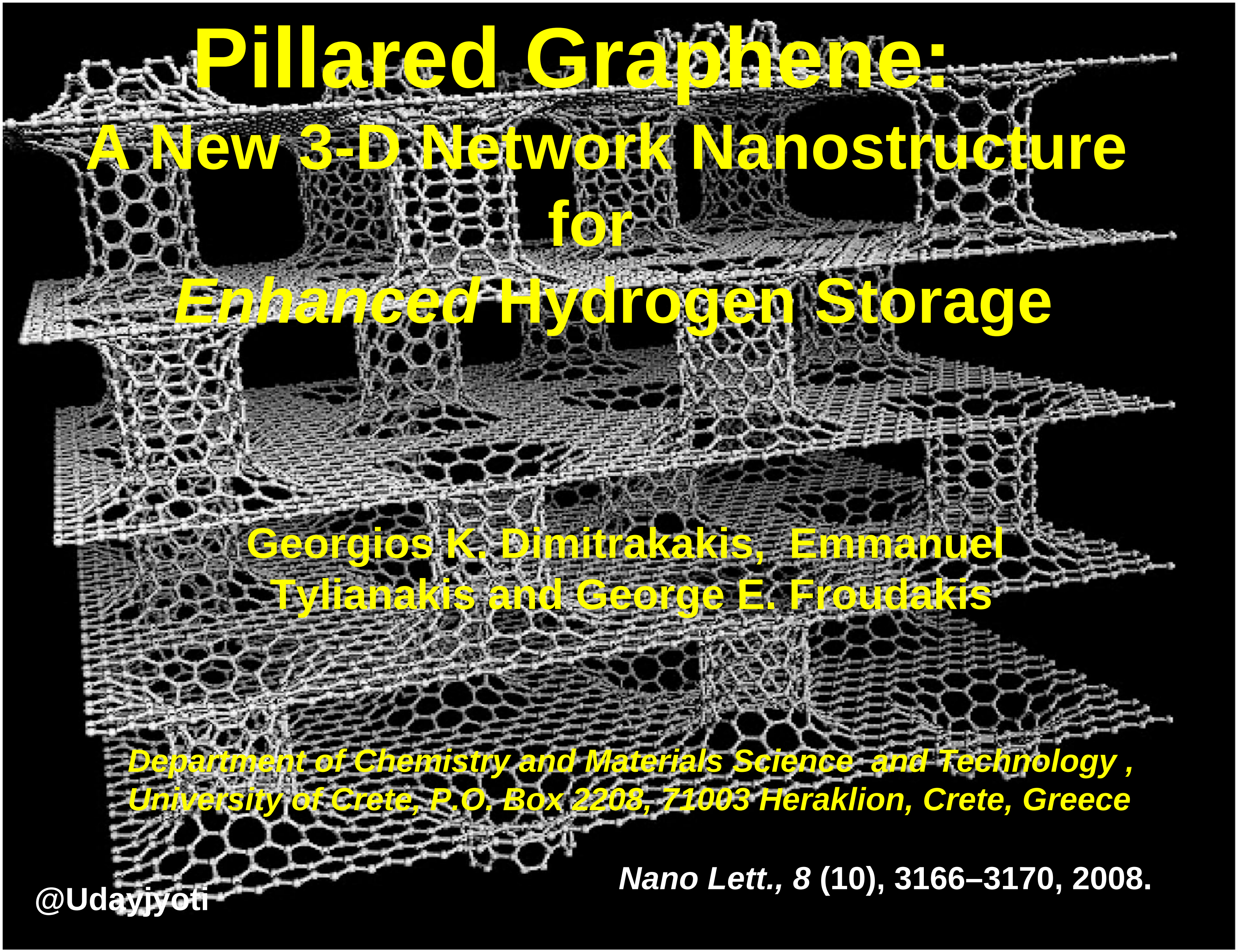

Pillared Graphene: A New 3-D Network Nanostructure for *Enhanced* Hydrogen Storage

Georgios K. Dimitrakakis, Emmanuel Tylianakis and George E. Froudakis

Department of Chemistry and Materials Science and Technology ,
University of Crete, P.O. Box 2208, 71003 Heraklion, Crete, Greece

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@Udayjyoti

Mr. Q

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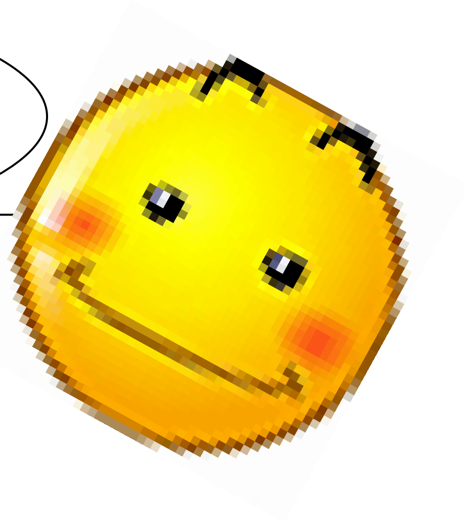
What is this paper about?

Investigation of hydrogen storage in a novel three-dimensional carbon nanostructure using a multiscale theoretical approach



Two stages

Designing of the structure

Study of interaction of the structure with hydrogen via ab- initio and grand canonical Monte Carlo calculations

Why this paper?

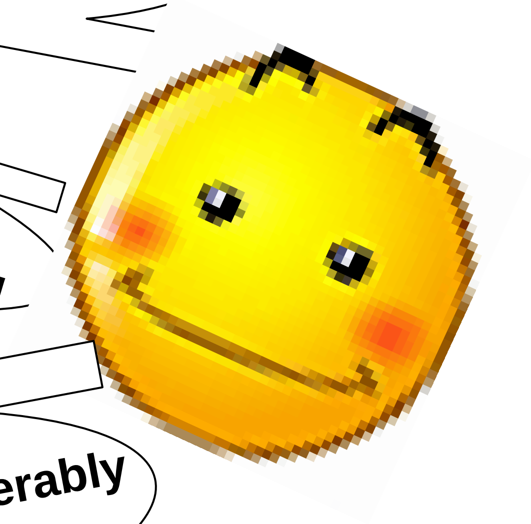
The problem as well as the result is important.

(The material + Li^+) = 41 g H_2/L, under ambient conditions

45 g H_2/L is US DOE’s aim

To synthesize the material is a challenge at this point of time

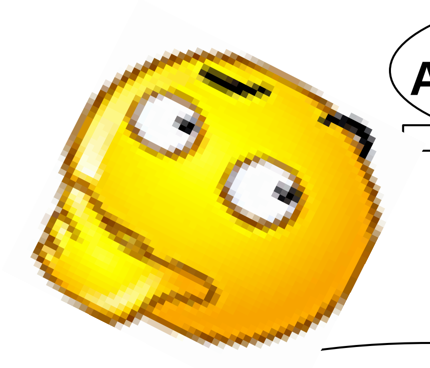
Why carbon nanostructures?



nanoporous with appropriate pore size, high surface area and light

can store hydrogen by physisorption that allows fast loading and unloading

doping CNTs with lithium atoms can considerably increase their hydrogen storage capacity



Any new system?

Are they better candidate than CNT? If yes, why?

Yes! novel nanoporous MOFs (metal organic frameworks) are recent entries.

Their high surface area combined with the increased adsorption sites leads to higher storage capacities establishing them as better candidate materials than CNTs

So, carbon based materials are out of this race?

Then, what is wrong with them?

No, no!
Carbon based materials possess a superior structural stability and amenability to a wide range of processing conditions, keeping them in the race for commercial applications

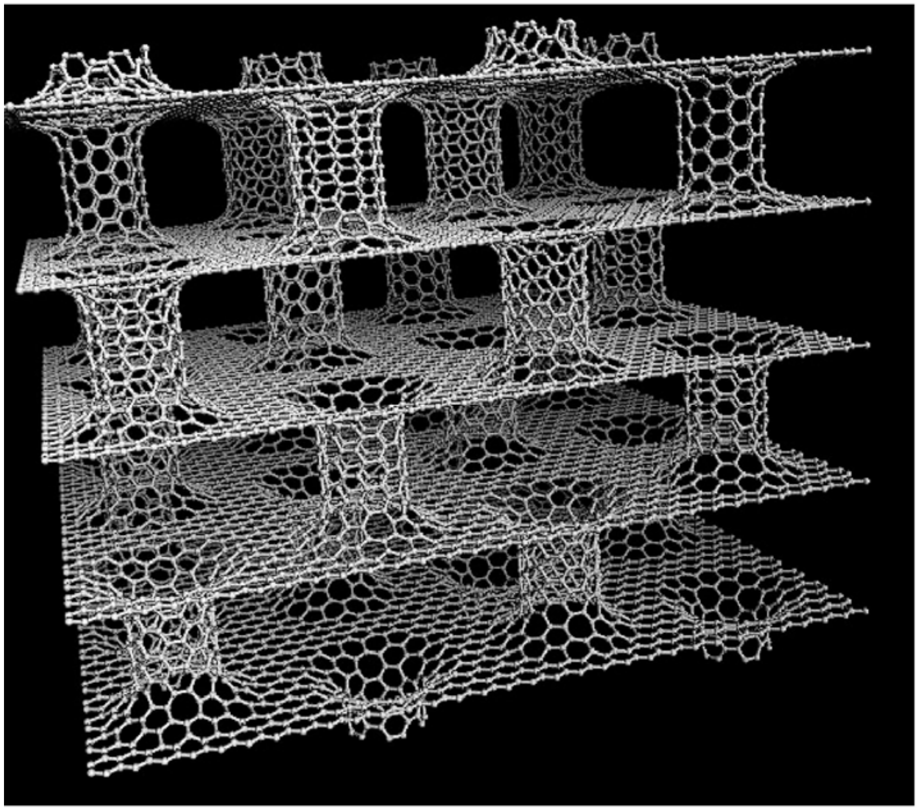
Despite the enhancement, the total amount of hydrogen stored in those structures remains far from the D.O.E. targets. We need a way to increase their storage capacity more.

How can we achieve that?

A possible route to achieve this is by synthesizing novel carbon-based architectures of large surface area, suitable for storage pores

What is the composition of the proposed structure?

It consists of parallel graphene layers at a variable distance, stabilized by CNTs placed vertically to the graphene planes

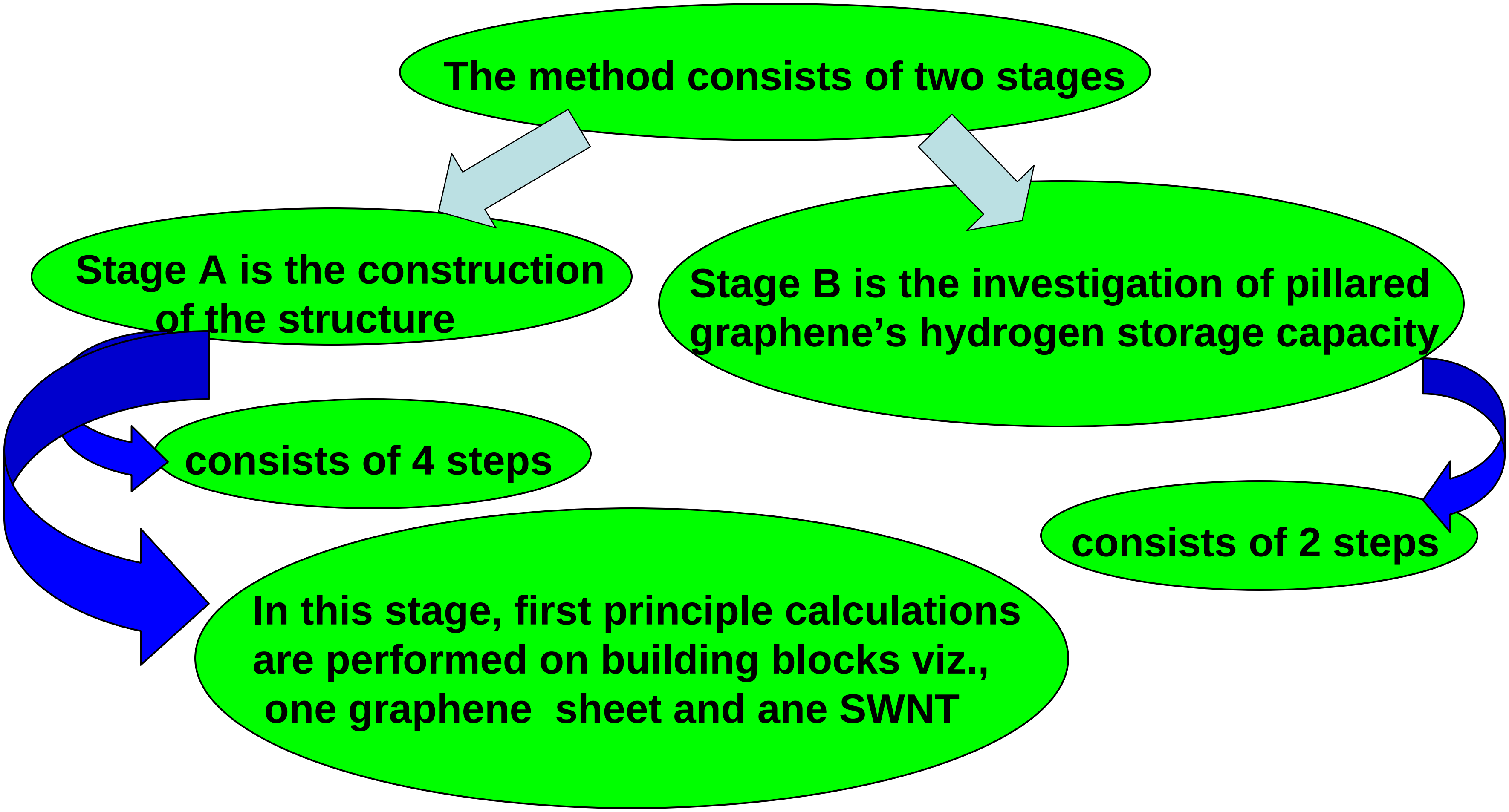


A 3-D building block

CNT are pillars

Graphene sheets are floors

Methods used to design and investigate the stability of this material



The method consists of two stages

Stage A is the construction of the structure

consists of 4 steps

In this stage, first principle calculations are performed on building blocks viz., one graphene sheet and ane SWNT

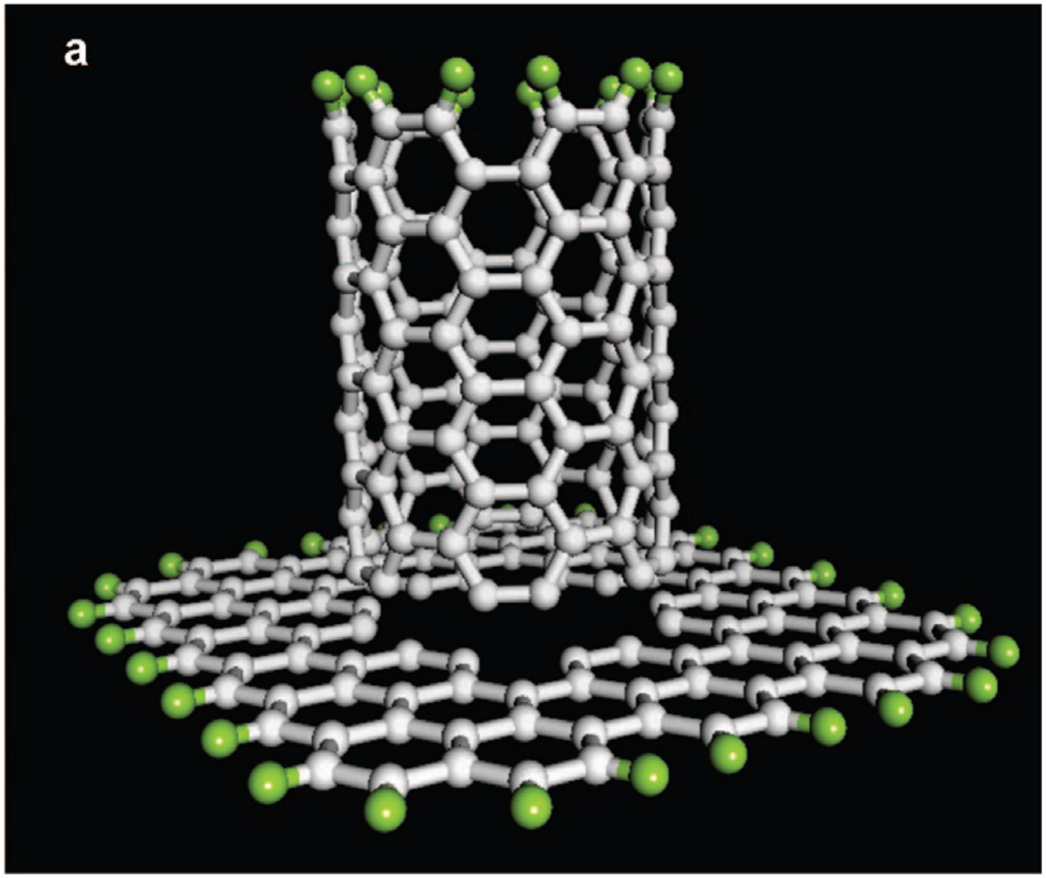
Stage B is the investigation of pillared graphene’s hydrogen storage capacity

consists of 2 steps

- ❖ ***Turbomole package to perform theoretical ab initio calculations***

First step:

Creation of one cyllindrical hole on the graphene sheet



- ***The diameter of the gap is chosen carefully to fit the selected CNT.***

Figure 2. (a) (6,6) CNT and graphene sheet ready to form a cluster. This is the initial structure which was optimized using DFT.

Second step:

Calculation of bond surplus for polygons on the surface of a closed polyhedron using generalised Eular's rule

Bond surplus is **the excess in the number of polygonal sites compared with normal value for the junction.**

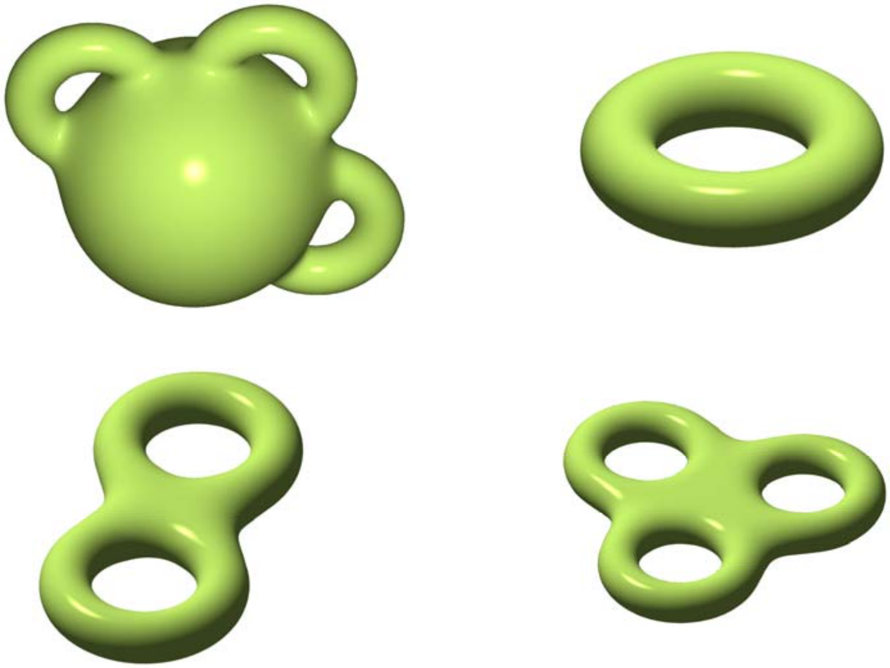
Eular's rule:

$$F + V = E + 2 - 2G$$

or

$$6(E - F - V) = 12(G - 1)$$

***F*- the number of faces,**
***V*-vertices,**
***E*- edges and**
***G*-genus.**



Third step:

Optimization of the final structure (Fig. 2b) using the resolution of identity (RI) approximation

sites under consideration

the upper hexagon

heptagon

the lower hexagon

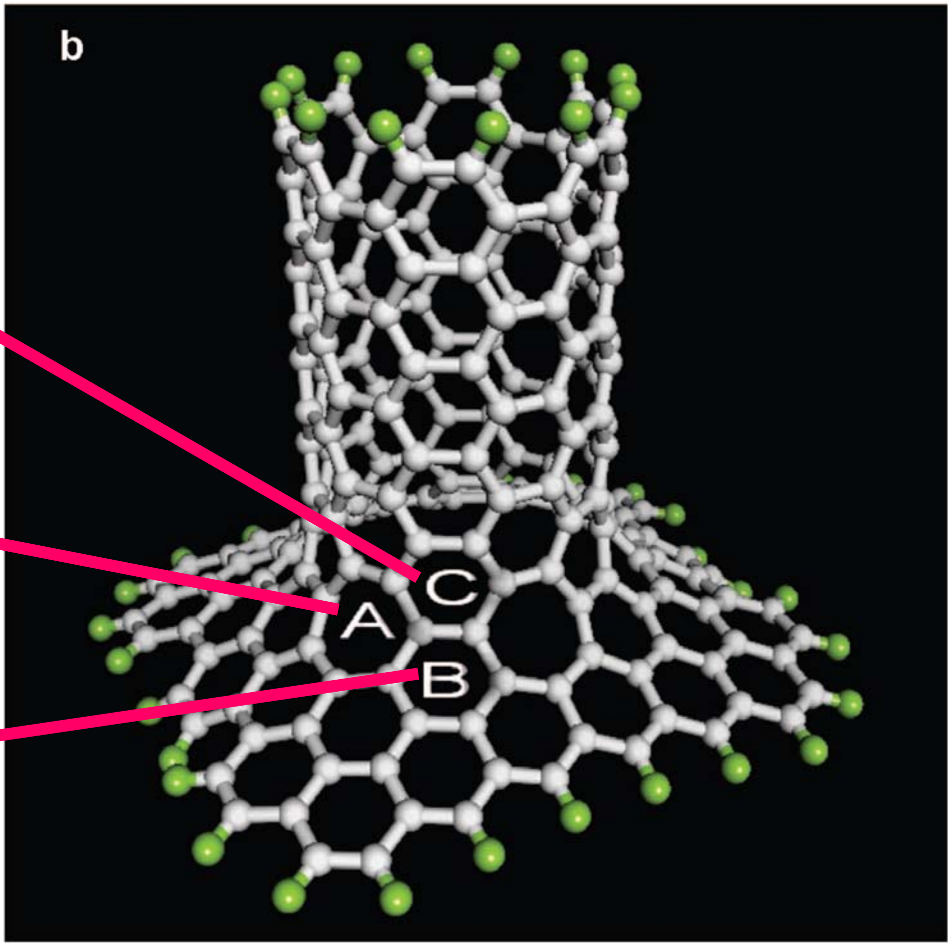
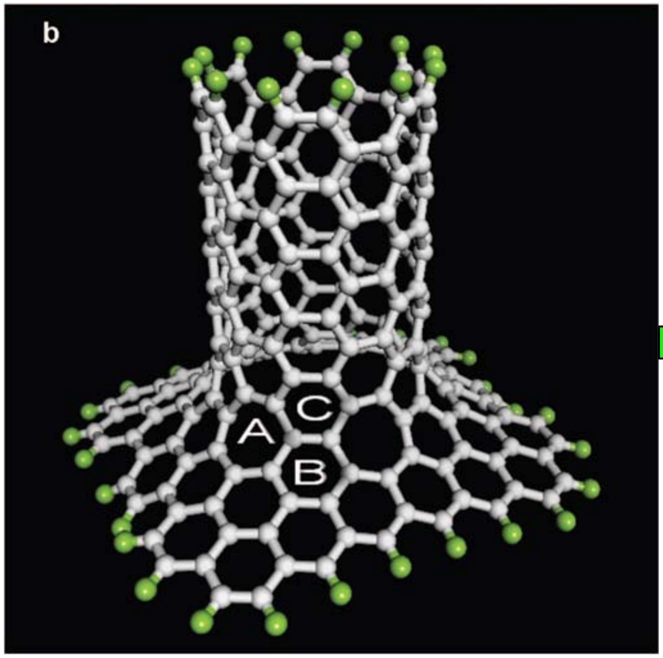


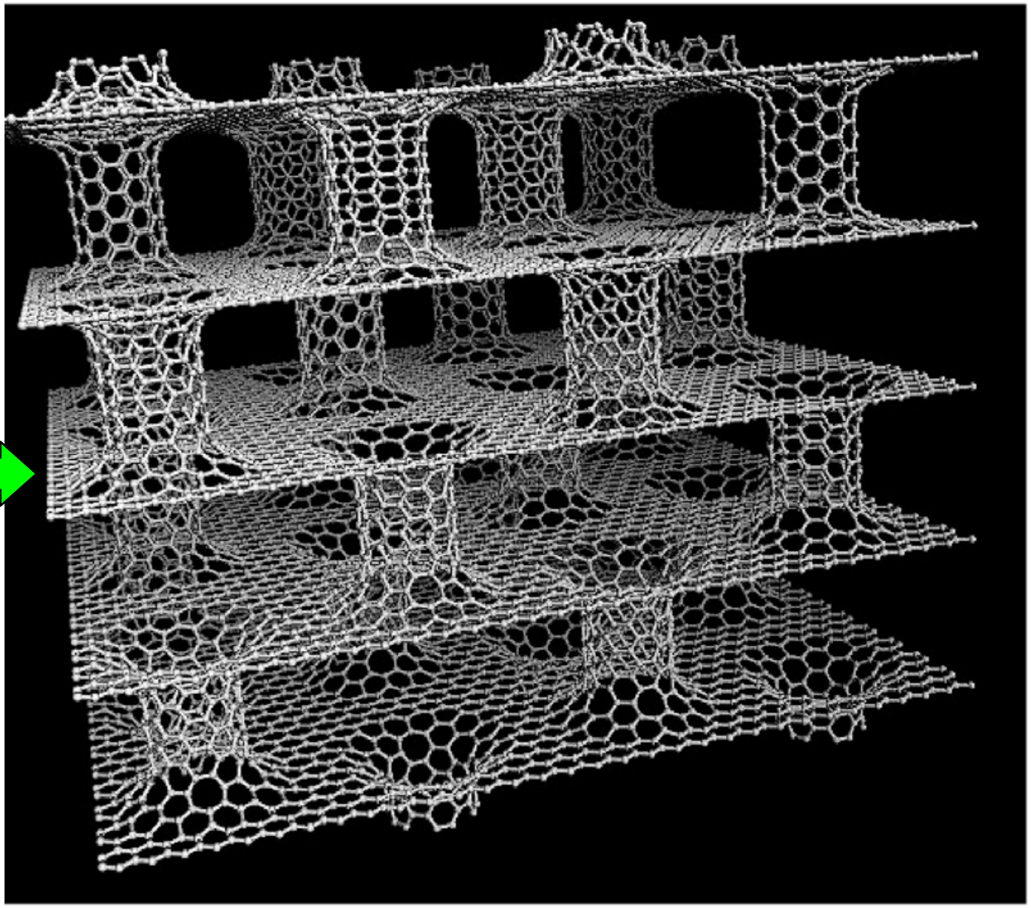
Fig. 2 (b) Optimized cluster of (6,6) CNT and graphene sheet; the beginning of the 3-D network nanostructure.

Fourth step:

Construction of an extensive periodic network on the basis of the ab initio optimized building block (Fig. 1)



Optimized building block



The 3-D network nanostructure

Stage B: *Investigation of hydrogen storage capacity of the structure*

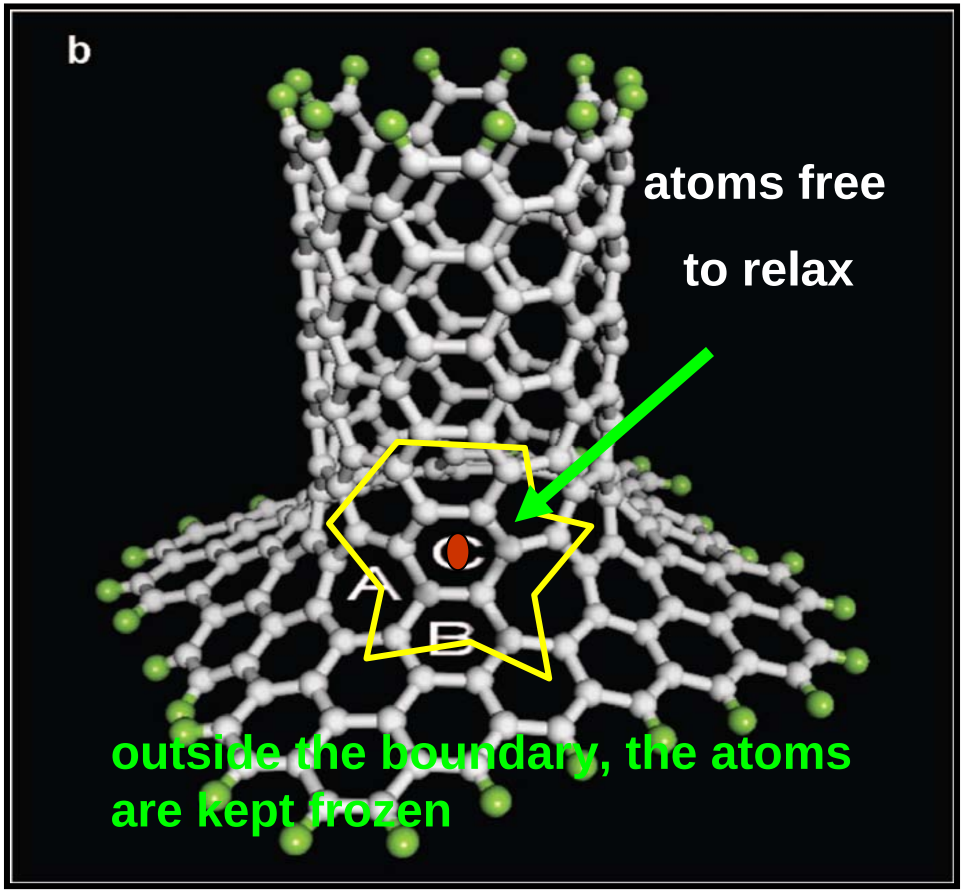
Step 1:
Assessment of the H_2 interaction with the material using first-principle quantum chemical calculation

New study of the energetics and interactions close to the junction

Correction of the calculated value of the binding energy considering basis set superposition error (BSSE) using the counterpoise (CP) method

Step 2:
Evaluation of the storage capacity by grand canonical Monte Carlo (GCMC) simulations for a variety of thermodynamic states at ambient and cryogenic temperatures

- ***Different combinations onanotube curvature,intertube and graphene sheet interlayer distances were tested, in an effort to achieve the best hydrogen uptake.***



atoms free

to relax

outside the boundary, the atoms are kept frozen

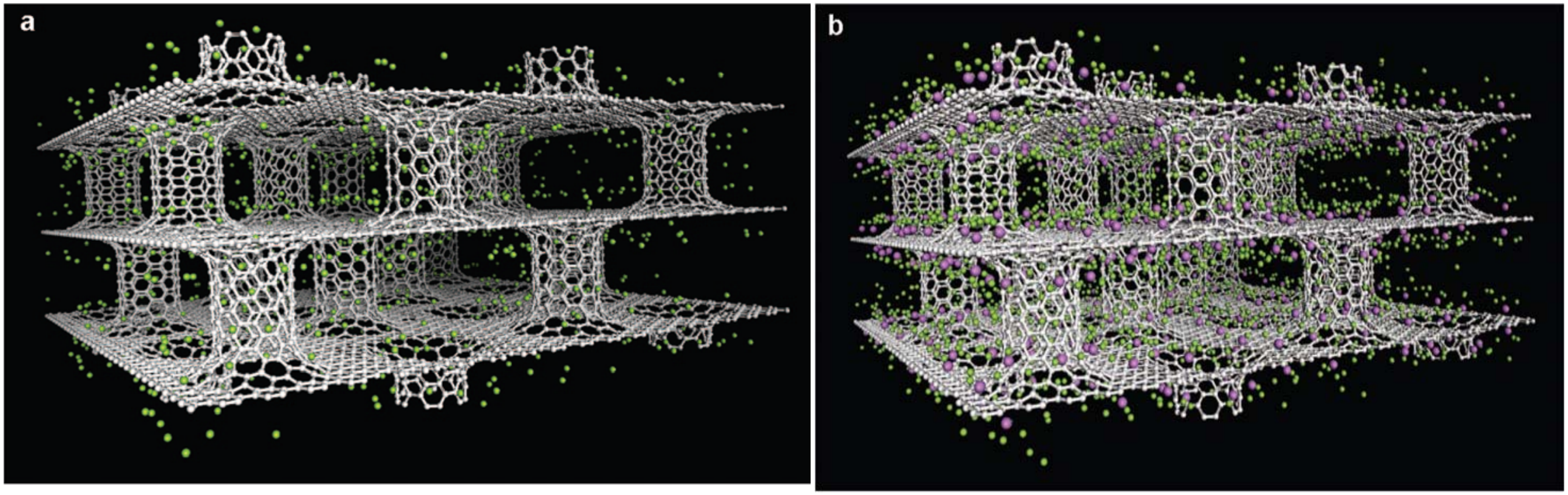


Figure 5. **Snapshots from the GCMC simulations of (a) pure pillared structure and (b) Li doped pillared structure at 77 K and 3 bar. Hydrogen molecules are represented in green, while lithium atoms are in purple.**

❖***Results are for system having intertube distance of 1.5 nm and graphene sheets with 1.2 nm interlayer distance***

Results:

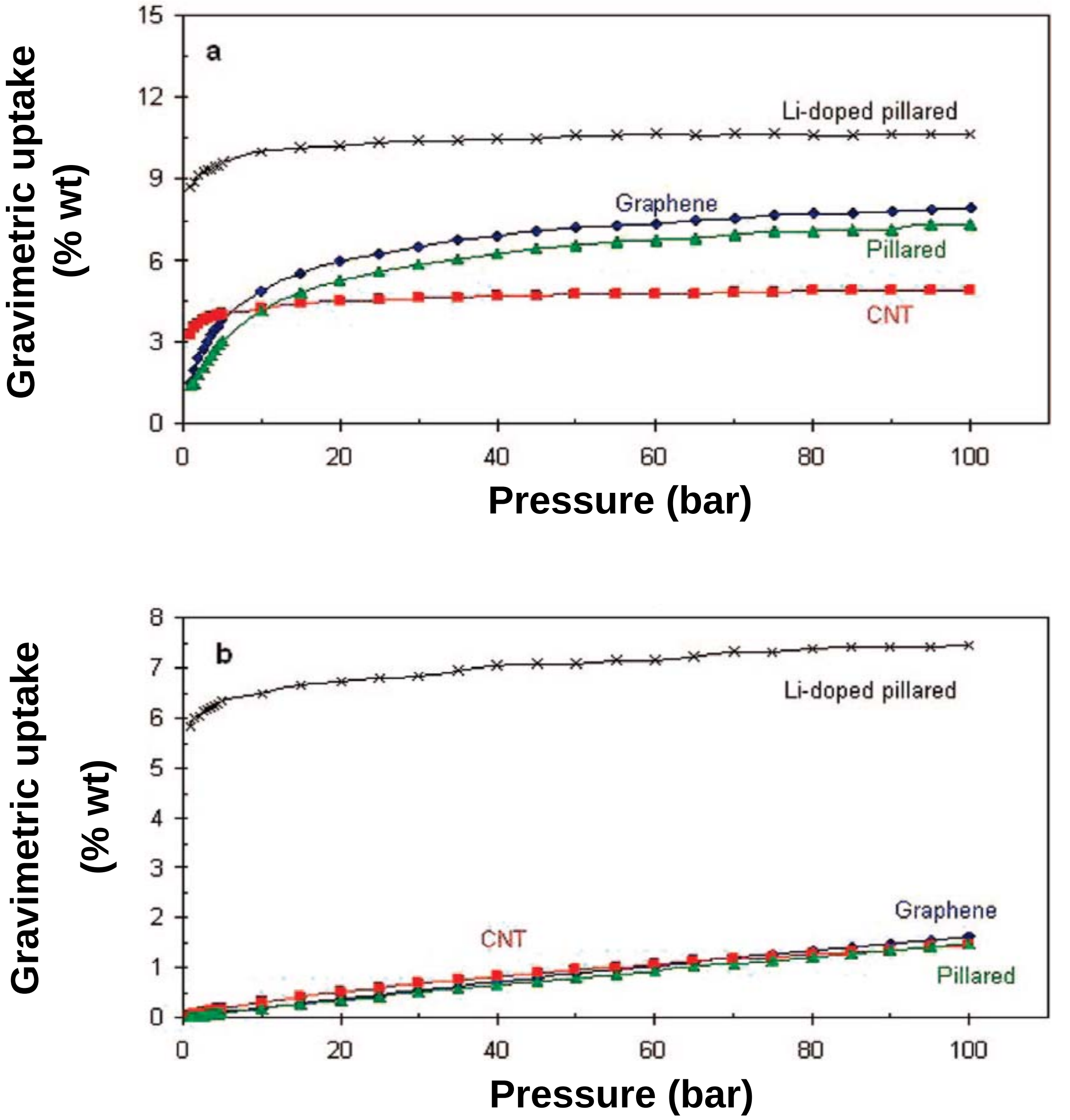


Figure 3: Gravimetric hydrogen uptake (a) 77 K and (b) 300 K.

Results:

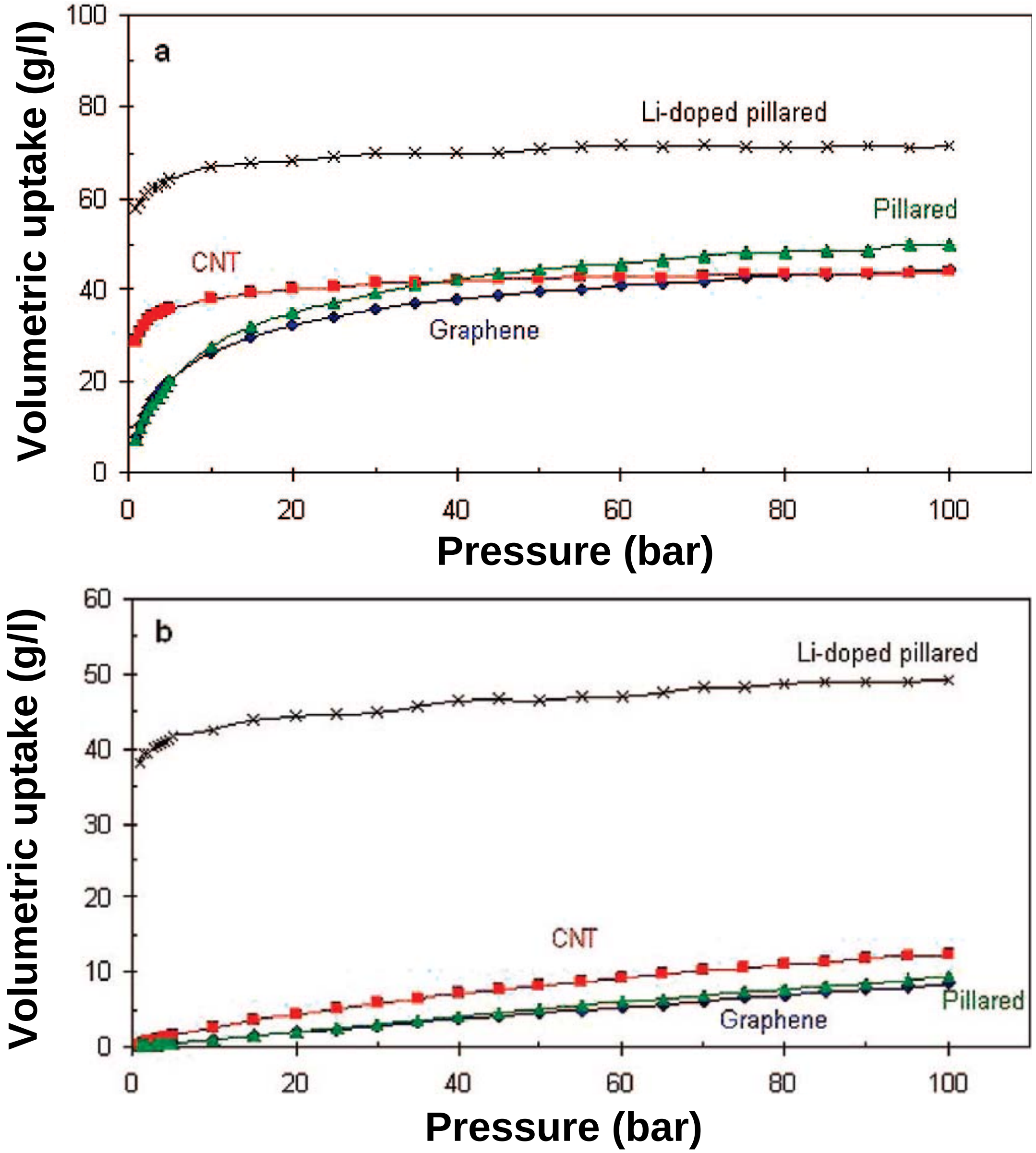


Figure 4: Volumetric hydrogen uptake (a) 77 K and (b) 300 K.

Binding energy of H_2 at the junction

System	**Binding energy of H_2 (kcal/mole)**			**Inference**
-	**Above the hexagon**		**Above the heptagon**	-
	Site A	Site B	Site C	
Pillared graphene	0.25	0.25	0.33	Interaction of H_2 with hepatgonal rings are more favourable than the hexagonal ones
Li doped pillared graphene	3.4	3.5	3.6	Enhancement on the bonding of H_2 when a Li cation is present

Results

The total storage capacity of pillared graphene was not satisfactory

Significant increase in both volumetric and gravimetric hydrogen uptake with the Li doped structure compared with the undoped case

Enhancement of , for pressures below 10 bar, the gravimetric adsorption by 76% at ambient temperature and by 88% at cryogenic; the enhancement on the volumetric adsorption is 30% and 38%, respectively.

Rapid attainment of the saturation pressure for both temperature conditions; an extra benefit since low pressure is an important safety issue in mobile applications

Conclusions

Combination of CNTs and graphene sheets is possible to form novel 3-D nanostructures capable of enhancing hydrogen storage

The material, when doped with lithium cations, can Reach D.O.E's volumetric target for mobile applications, under ambient conditions.

Even on the junction of this material, hydrogen's interaction remains weak, comparable with already known hydrogen-carbon interaction values

Experimentalists are challenged to fabricate this material and validate its storage capacity