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RESEARCH ARTICLE

# Ti-doped nano-porous graphene: A material for hydrogen storage and sensor

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Clustering of Ti on carbon nanostructures has proved to be an obstacle in their use as hydrogen storage materials. Using density functional theory we show that Ti atoms will not cluster at moderate concentrations when doped into nanoporous graphene. Since each Ti atom can bind up to three hydrogen molecules with an average binding energy of 0.54 eV/$H_2$, this material can be ideal for storing hydrogen under ambient thermodynamic conditions. In addition, nanoporous graphene is magnetic with or without Ti doping, but when it is fully saturated with hydrogen, the magnetism disappears. This novel feature suggests that nanoporous graphene cannot only be used for storing hydrogen, but also as a hydrogen sensor.

**Keywords** nano-porous graphene, hydrogen storage, hydrogen sensor

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Ideal hydrogen storage materials must meet the following criteria: They should be inexpensive and stable, store hydrogen with large gravimetric and volumetric density, and operate at near ambient thermodynamic conditions. For these, the storage materials have to be light and the binding energy of hydrogen has to be between 0.3 and 1.0 eV/$H_2$ (intermediate between physisorption and chemisorption). In spite of considerable efforts in the last decade, no materials emerged could meet these requirements. The main difficulty is that in light weight materials hydrogen is bound either weakly (van der Waals's interaction) or strongly (covalent or ionic interaction) and the thermodynamics is rather poor in both situations.

The early promise of nanoscale carbon (activated carbon [1, 2], single-wall nanotubes [3, 4] and fullerenes [5], nanofibers [6], and nanohorns [7]) as hydrogen storage materials has not materialized. It has been demonstrated [8–10] that any reported capacity of higher than 1 wt% in carbon nanotubes is a result of experimental error. Theoretical study also confirms that high hydrogen content in the pure carbon nanotubes cannot be achieved through physical sorption [11, 12]. Although recent theoretical research [13–16] has shown that doping of transition metal atoms such as Sc and Ti on carbon fullerenes and nanotubes may fundamentally change the nature of hydrogen bonding and lead to materials with hydrogen gravimetric density of up to 8 wt% [14], later calculations [17] demonstrated that transition metal atoms coated on these surfaces will cluster. This in turn would not only affect the nature of hydrogen bonding but also the amount of stored hydrogen. The clustering of transition metal atoms has also been shown to play an adverse role in transition metal doped polymers [18]. Although clustering of metal atoms can be prevented if one uses Li instead of transition metals [19, 20], the binding of hydrogen is weak and cryogenic temperatures are needed for hydrogen sorption.

Recently, because of its unique structure and electronic peoperties [21, 22], graphene has become a material of great interest. Its potential for hydrogen storage has been investigated in earlier literatures [23–25]. However, like in fullerene or carbon nanotubes, $H_2$ is weakly physisorbed on graphene. Lately, carbide-derived carbons (CDC) [26, 27] produced by high temperature chlorination of metal carbides have been investigated as promising candidates for hydrogen storage. These materials offer the following advantages: large porosity (up to 80% open volume), narrow pore size distribution tunable with better than 0.05 nm sensitivity in the range ∼0.5 to 1.5 nm, specific surface area up to 2000 $m^2/g$, and moderate cost. Unfortunately, these storage materials operate only at temperatures lower than 77 K.

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Herein we demonstrate, using first principles calculations, that the binding energy of hydrogen can be increased substantially by chemically modifying the inner surface of the carbon nanopores. In particular, we show that Ti atoms doped in graphene nanopores do not cluster at moderate concentrations and each Ti can take up to three hydrogen molecules with an average binding energy of 0.54 eV/$H_2$molecule. Thus, a tunable carbon pore, with internal surface decorated with Ti, may have the ideal properties of a hydrogen storage material. In addition, we find that carbon containing nanopores with or without Ti doping are magnetic, but magnetism disappears when the nanopores are fully saturated with hydrogen.

Spin-polarized calculations were carried out using Perdew–Burke–Ernzerhof (PBE) exchange and correlation functional [28] within the density functional theory (DFT) [29]. PBE functional is found to be slightly better that PW91 in terms of $H_2$ binding energy [30]. The projector augmented wave (PAW) [31] potentials have been used for all elements and cutoff energy we have used is 500 eV. We started with the graphite structure having lattice parameters $a$=2.461 Å and $c$=6.708 Å [32]. The structure was fully relaxed resulting in the optimized parameters, $a$=2.465 Å and $c$=6.74 Å. Using these calculated lattice parameters we constructed an 8×8×2 super cell and kept one layer to model a single graphene sheet (See Fig. 1). The volume of the cell was fixed but ion positions were allowed to be free [33]. The graphene layers were separated from each other by 13.48 Å. In all calculations, self-consistency was achieved with a tolerance in the total energy of at least 0.1 meV. Hellman–Feynman force components on each ion in the supercell were converged to 5 meV/Ångstrom. Three different pore sizes with diameters of 5.69 Å, 10.26 Å, and 14.23 Å were considered as shown in Fig. 1. The supercells corresponding to these (a) small, (b) medium and (c) large pores consist of 122, 104 and 74 atoms, respectively. Calculations were carried out in four different steps: i) First, the geometries of supercells corresponding to pure pores were optimized. ii) Hydrogen molecules were then introduced into the optimized pores to study the nature of their interaction. iii) The pores were doped with Ti atoms and their preferred binding sites were determined to examine if the atoms would prefer to cluster inside the pore or remain isolated. iv) Finally, we introduced hydrogen molecules sequentially to study the nature of hydrogen bonding and their successive binding energies.

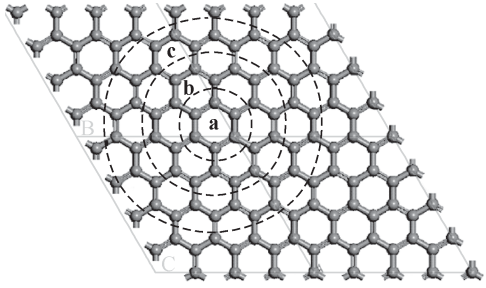



**Fig. 1** Graphene sheet containing three pore sizes: **(a)** the small pore with an inner surface diameter of 5.69 Å, **(b)** a medium pore with an inner surface diameter of 10.26 Å, and **(c)** a large pore with an inner surface diameter of 14.23 Å.

In a graphene sheet, each C atom is attached to three other C atoms to form $sp^2$ type of hybridization. At the inner surface of a pore, some of these $sp^2$ bonds break because of missing nearest neighbor C atoms. When hydrogen molecules were introduced into the pore, the molecules dissociated and the hydrogen atoms were found to attach individually to the dangling bonds of C in the inner surface of the pore. Once all the dangling bonds were saturated, subsequent hydrogen molecules did not dissociate and were physisorbed inside the pore with a binding energy of 5 meV/$H_2$. The corresponding C–H distance is 3.17 Å. This interaction is weak because there is no charge transfer between the graphene sheet and the hydrogen molecule. Although the DFT level of theory is not able to treat weak van der Waal's interaction properly, the calculated small binding energy can be used to conclude that hydrogen can be stored inside pure carbon nanopores only at cryogenic temperatures.

Next, we introduced Ti atoms into the graphene pores with varying sizes and studied their preferred binding sites. We start with the small pore [Fig. 1(a)] that has a diameter of 5.69 Å. The Ti atoms are found to bind to the C atoms in the inner pore surface so as to saturate the dangling bonds. The Ti–C distance is 2.2 Å, and moment on each Ti atom is 1.2 $\mu_B$. Hydrogen molecules were then sequentially introduced into small pore. The first two pairs of $H_2$ molecules dissociated and bound to four C atoms by saturating their dangling bonds (Fig. 2). The corresponding C–H binding energy is 2.41 eV. These hydrogen atoms are not useful from the storage point of view as they are difficult to desorb. When the next hydrogen molecule was brought to the vicinity of the Ti atom, two possibilities exist because of a minor energy difference; i) $H_2$ dissociates and binds to the Ti atom with a Ti–H distance of 1.72 Å [Fig. 2(a)]; the binding energy of hydrogen in this case is 1.02 eV/$H_2$. ii) $H_2$dissociates and binds to the two C atoms nearest to the Ti atom [Fig. 2(b)]; the corresponding binding energy is 1.01 eV/$H_2$. We were able to add two more $H_2$ molecules on the Ti atom. However, these molecules are bound associatively and the corresponding binding energies are much less, namely 0.39 eV/$H_2$ and 0.20 eV/$H_2$ [Figs. 2(c) and (d)]. In such a case, each Ti can bind to three pairs of hydrogen molecules with average binding energy of 0.54 eV/$H_2$ molecule. If zero-point energy (ZPE) correction is taken into consideration, the $H_2$ binding energy may fall into the ideal range, 20–40 kJ/mol [34] (0.2–0.4 eV).

To increase hydrogen capacity of small pores, we introduced two Ti atoms to the small pore. However, since

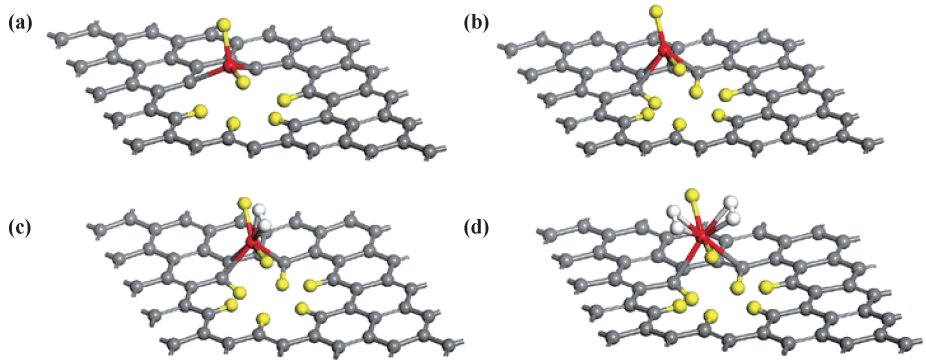



**Fig. 2** Geometries of **(a)** $H_2$, **(b)** $2H_2$, **(c)** $3H_2$ and **(d)** $4H_2$ molecules bound to Ti doped small pore.

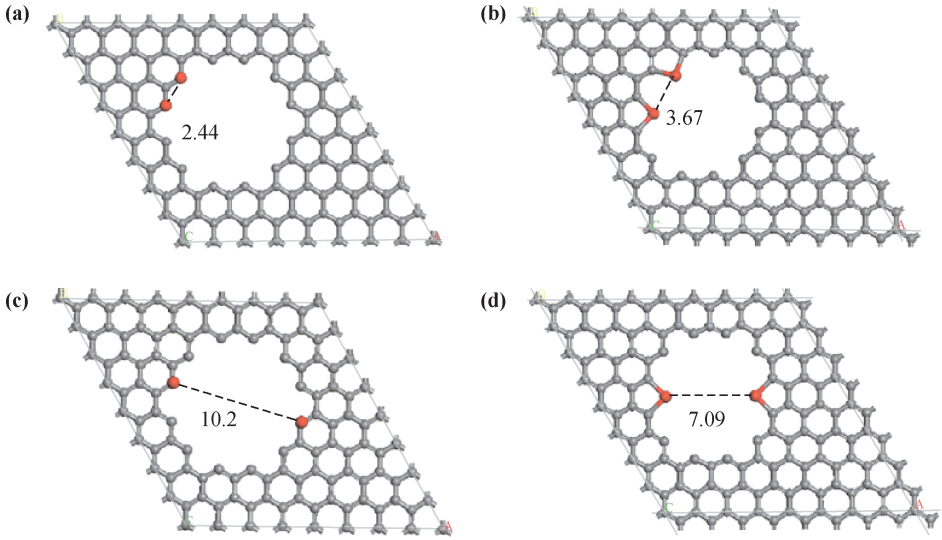



**Fig. 3** Starting configuration of two Ti atoms in the medium pore **(a)** close to each other, and **(c)** far from each other. The corresponding optimized structures are given in **(b)** and **(d)** respectively.

the pore size is small, the two Ti atoms are only 2.07 Å apart and not much room is left for storing hydrogen in such a small pore. Next we studied the medium pore [Fig. 1(b)] which has a diameter of 10.26 Å and introduced two Ti atoms. We started by placing the Ti atoms initially as nearest neighbors [Fig. 3(a)] and then isolated from each other [Fig. 3(c)]. Upon optimization, the Ti atoms were found to terminate the dangling bonds of carbon irrespective of their initial configurations. Figure 3 (b) with Ti atoms 3.67 Å apart is 0.12 eV lower in energy than that in Fig. 3(d) where the distance between the Ti atoms is 7.09 Å. Note that these distances are significantly larger than the distance in the $Ti_2$ dimer, namely 1.90 Å. Thus, we conclude that Ti atoms will not cluster inside this medium size nanopore. However, since the Ti atoms in this nanopore are only 3.67 Å apart, the hydrogen storage capacity of individual Ti atoms will be affected. We have, therefore, enlarged the pore to 14.23 Å [Fig. 1(c)]. The preferred geometries of Ti atoms were optimized by starting with two different initial structures: First, the two Ti atoms were placed 2.44 Å apart next to the two nearest neighboring carbon atoms [Fig. 4(a)]. Upon optimization the distance between the Ti atoms increased to 4.64 Å [Fig. 4(b)]. Next, the two Ti atoms were isolated at a larger distance of 5.07 Å [see Fig. 4(c)] and the system was allowed to relax. Upon optimization, the distance between the two Ti atoms increased to 5.64 Å [see Fig. 4(d)]. The configuration in Fig. 4(b) is found to be 0.14 eV *higher* in energy than the configuration in Fig. 4(d) where the Ti atoms remain isolated. Hence we conclude that Ti atoms do not cluster in carbon nanopores as long as pores are moderately large and Ti concentration is moderately low. This observation is in contrast to Ti decorated $C_{60}$ fullerene or carbon nanotube where Ti atoms prefer to cluster. The difference in this behavior can be traced to the nature of interaction between Ti and C atoms. The carbon atoms on the fullerene or nanotube surface have no dangling bonds while in carbon pores the dangling bonds interact strongly with Ti. Note that the binding energies of $Ti_2$ and TiC dimers are respectively 1.37 eV and 3.62 eV. Thus, the strong affinity of Ti to bind to C with a dangling bond prevents Ti atoms from clustering. Indeed the binding energy of Ti in the carbon pores is 7.19 eV/Ti. To complement this finding, we present the charge density distribution in the pore region in Fig. 5. We see that the $sp^2$ bonding of C atoms in the

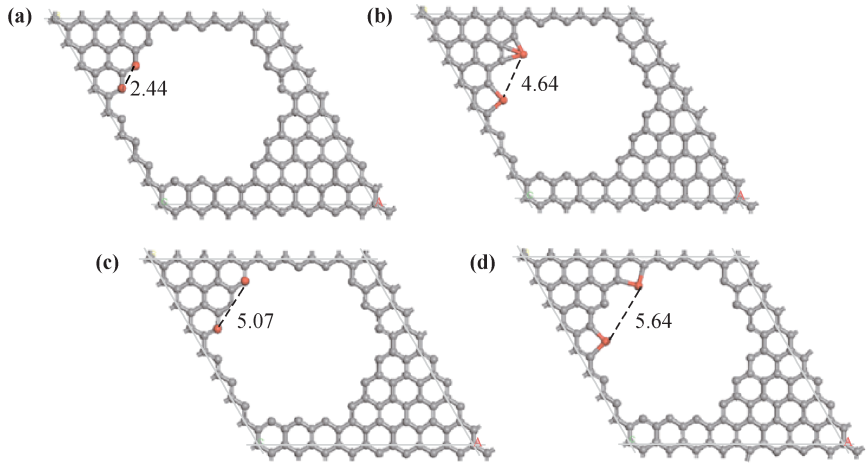



**Fig. 4** Starting configuration of two Ti atoms in the large pore **(a)** close to each other, and **(c)** far from each other. The corresponding optimized structures are given in **(b)** and **(d)** respectively.

pore region is broken. Directional bonds between Ti and two carbon atoms develop, thus saturating the dangling bonds of carbon atoms.

We know that small amount of Ti atoms in a large carbon pore will not cluster. However, we do not exclude the possibility that Ti may cluster when all carbon dangling bonds are terminated. Hence, the dopant concentration is critical for optimized gravimetric density. In the case of large pore, the critical point will be Ti/C atomic ratio 6/74 (8%). When Ti concentration is higher than the critical threshold, hydrogen gravimetric density of Ti decorated nanopore will decrease.

We next calculated the maximum number of hydrogen atoms that can be bound to each Ti atom. Here we concentrate on the largest pore [Fig. 1 (c)] decorated with 6 Ti atoms. Hydrogen molecules were then sequentially introduced into this pore. Similar to a Ti atom in the smallest pore, each Ti can bind to 3 pairs of hydrogen molecules with one pair of hydrogen dissociated; the rest C dangling bonds were terminated by H atoms. The resulting geometry is shown in Fig. 6. Thus we are able to demonstrate that by functionalizing the inner pores of graphene with Ti, we can only prevent Ti atoms from clustering at moderate concentrations but also enable each Ti atom to bind up to three $H_2$ molecules, two of them with binding energies intermediate between physisorption and chemisorption states. If two pairs of hydrogen molecules can be recycled, the weight percentage of 6Ti decorated large pore can reach 2%. Although the above results happen to a single graphene pore, we believe that the qualitative nature of hydrogen binding to carbon nanopores would remain essentially unchanged. This is because the coupling between graphite layers is weak and the inter layer distance is 3.37 Å. In comparison, the distance between the Ti atom and the $H_2$ molecule on top of the graphene pore is less than 2.05 Å.

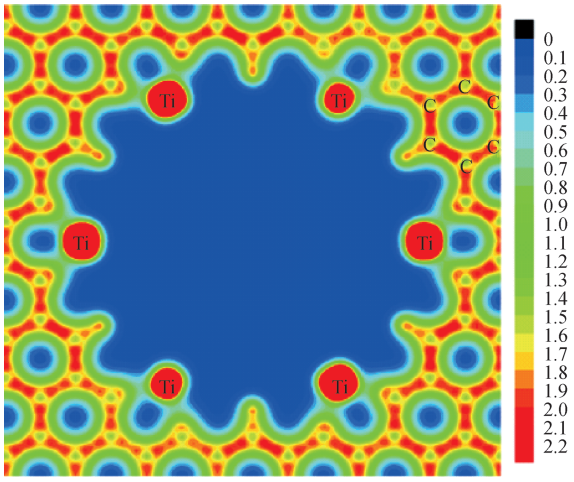



**Fig. 5** Charge density distribution in a large carbon nanopore [Fig. 1 (c)] doped with 6 Ti atoms. The dangling bonds of the six remaining C atoms were terminated with hydrogen atoms. The red and black colors correspond to the highest and the lowest electron density, respectively.

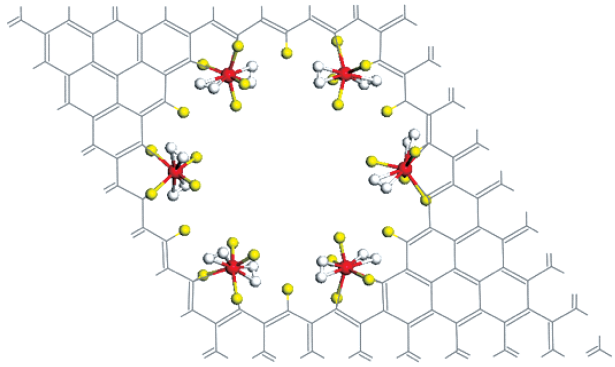


**Fig. 6** Hydrogen uptake in a large pore (diameter 14.23 Å) containing six Ti atoms. The red spheres represent Ti atoms while the yellow, and white spheres represent dissociated and associated H atoms respectively.

Our calculations also yield some other interesting results: We found nanoporous graphene to be ferromagnetic with each carbon atom at the pore surface carrying a moment of about 0.5 $\mu_B$. These moments are associated with dangling bonds of C and are consistent with earlier findings that defects in fullerenes lead to magnetism in

carbon [35]. In Fig. 5, we found all the six Ti atoms to be ferromagnetically coupled with each Ti carrying a moment of 1.2 $\mu_B$. However, the magnetism is found to disappear when the Ti decorated pores in Fig. 6 are fully saturated with hydrogen. We also studied the magnetism of Ti doped carbon nanopore by introducing only $H_2$ molecule near one of the Ti atoms in Fig. 5. While the magnetic moment of this Ti atom was completely quenched, the remaining five Ti atoms are ferromagnetically coupled with each Ti carrying a magnetic moment of 1.2 $\mu_B$.

In conclusion, we have shown that a Ti atom doped in a graphene pore can bind up to three $H_2$ molecules much the same way it does when supported on a $C_{60}$ fullerene or carbon nanotube, but with one major exception. The Ti atoms do not cluster inside the pore at moderate concentrations and hence can retain their individual hydrogen storing capability. In addition, the system is ferromagnetic with or without Ti doping. Magnetism, however, disappears when the system is fully saturated with hydrogen. This Ti doped nano-porous graphene can serve as a hydrogen sensor. It will be interesting to see if the novel interplay between magnetism and hydrogen loading is special to the nano-porous graphene system or if it is a general trend in other nano forms of carbon, such as carbon nanotubes and nano-porous graphite. It should be noted that carbide derived carbon provides a novel pathway to synthesize nanopores with tunable size and this top–down approach of creating carbon nanopores is less expensive than other carbon nanostructures created using a bottom–up approach. Thus, by incorporating Ti into porous carbide derived carbon materials, it may be possible to achieve an economical hydrogen storage material that meets the industry requirements.

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