

## Computational Investigation of Hydrogen Storage Capacity of Boron Nitride Nanocages by Newly Developed PM7 Method

SINAN SAYHAN and ARMAGAN KINAL\*

Department of Chemistry, Science Faculty, Ege University, 35100 Bornova, Izmir, Turkey

\*Corresponding author: Fax: +90 232 3888264; Tel: +90 232 3112395; E-mail: [armagan.kinal@ege.edu.tr](mailto:armagan.kinal@ege.edu.tr)

Received: 6 March 2014;

Accepted: 12 August 2014;

Published online: 10 January 2015;

AJC-16643

Employing the newly developed PM7 method, we have computationally investigated endohedral hydrogen storage capacities of boron-nitride based nanocages,  $B_mN_m$  ( $m = 12, 24, 36, 48$  and  $96$ ). The calculation results revealed that the smallest two boron-nitride nanocages,  $B_{12}N_{12}$  and  $B_{24}N_{24}$ , (their gravimetric density of hydrogen storages are 1.35 and 3.05 wt. %) are not suitable for hydrogen doping due to their rather small endohedral cavities.  $B_{36}N_{36}$ , whose hydrogen storage density is 4.96 wt. %, may not be very efficient although it has better storage capacity than the smallest two. On the other hand, the gravimetric densities of hydrogen storage inside the  $B_{48}N_{48}$  and  $B_{96}N_{96}$  nanocages are predicted to be 6.6 and 10.6 wt. %, respectively. This high weight percentage of hydrogen storage indicates that  $B_{48}N_{48}$  and  $B_{96}N_{96}$  can be considered as promising hydrogen storage materials.

**Keywords:** Boron nitride nanocages, Hydrogen storage, Endohedral doping, Semi-empirical methods, PM7.

### INTRODUCTION

World's population has been consuming tremendous amount of fossil fuels without thinking their environmental impact. Using huge amount of fossil fuels causes global warming. Therefore, scientists have been seeking for alternative, clean, renewable energy resources instead of fossil fuels. Hydrogen energy is one of these desired resources. Due to being an environment-friendly energy source, hydrogen fuel has attracted great attention both scientific and industrial communities for its potential use in vehicles, portable power application, *etc.*<sup>1-3</sup>. It is necessary that a material for being used as hydrogen storage material must have high hydrogen storage capacity in practical applications at ambient temperatures (0-100 °C). Many candidates such as metal hydrides<sup>4,5</sup> carbon-based materials<sup>6-10</sup>, metal-organic frameworks<sup>11,12</sup> and organic polymers<sup>13,14</sup> have been investigated to be able to find such material. Among these materials, it is realized that carbon nanotubes are not good for hydrogen storage since their hydrogen storage capacity is very low for mobile applications due to the very low interaction energy between hydrogen molecules and carbon atoms of carbon nanotubes<sup>15,16</sup>. At that point, boron nitride nanotube structures, discovered in 1995<sup>17</sup>, have withdrawn the attention of scientists studying on hydrogen storage materials<sup>18,19</sup>. The results of these experimental studies indicated that 4.2 wt. % of hydrogen could be stored in boron nitride nanotube at room temperature, providing that they are

better hydrogen storage materials than carbon nanotubes. Later, the reason for superior behavior of boron nitride nanotubes, explained theoretically<sup>20</sup>, is found to be the ionic character of B-N bond in boron nitride nanotubes since it rises the binding energy of hydrogen molecules on boron nitride nanotubes. In a computational study by Sun *et al.*<sup>21</sup>, density functional theory methods confirmed that a selected boron nitride nanocage structure ( $B_{36}N_{36}$ ) could store 4 wt. % of hydrogen. However, the result of molecular dynamics method performed at room temperature revealed that this weight percent could not be attained by endohedral doping due to outflow of hydrogen molecules from  $B_{36}N_{36}$ . Recently, it was stated that a porous boron nitride material called HBBN-1 could store hydrogen up to 5.6 wt. % under 3MPa pressure<sup>22</sup>. This high hydrogen storage capacity can be an indication of the fact that other boron nitride structures, especially boron nitride nanocages or boron nitride nanotubes, may store larger amount of hydrogen.

In this study, we present endohedral hydrogen storage capacities of several boron nitride nanocage ( $B_mN_m$  where  $m = 12, 24, 36, 48$  and  $96$ ) structures determined by recently developed semi empirical PM7 method that can deal with interactions between non-bonded molecules. Here, we aimed to find answers to the following questions: What is the maximum number of  $H_2$  molecules that can endohedrally be doped inside a boron nitride nanocage before the cage breaks? What is the relation between amount of hydrogen storage and

nanocage size? How geometrical changes occur in nanocage structures and hydrogen molecules within storage? Are there any thermodynamically stable  $n\text{H}_2@B_mN_m$  complexes that have lower energy than that of separated hydrogen molecules and nanocage structure?

### COMPUTATIONAL METHODS

Endohedral hydrogen molecule storage capabilities of several boron nitride nanocages have been investigated in present study. The most important challenge in these types of calculations is to be able to model noncovalent interactions, *i.e.*, nanocage atom and hydrogen molecule (B---H-H and N---H-H) interactions. We employed a new semi-empirical method called PM7 developed by Stewart<sup>23</sup>. We have chosen PM7 for two reasons: (a) to be able to model noncovalent interactions more accurately, (b) to be able to calculate relatively large systems by consuming less computational effort (especially with respect to DFT methods). PM7 is modified to improve the description of noncovalent interactions by a set of new approximations. In a recent study by Hobza *et al.*<sup>24</sup> it is shown that PM7 gives much more accurate results the unmodified PM6 method for noncovalent interactions. In addition, they indicated that PM7 has almost similar accuracy with the modified PM6 methods providing accurate description of a wide range of noncovalent interactions including dispersion, hydrogen bonding and also halogen bonding<sup>24</sup>, such as PM6-DH2, PM6-DH+, PM6-D3H4.

In this study, we used the  $B_mN_m$  ( $m = 12, 24, 36, 48$  and  $96$ ) nanocages as the hydrogen storage material. All of the host nanocages have only tetragonal and hexagonal connections in their structures. The reason for choosing these types of connections is that they have lower hydrogen escape probability than octagonal or larger connections. Initially, all these host structures were optimized and characterized as minima by utilizing harmonic vibrational analysis method at the PM7 level of theory as implemented<sup>25</sup> in MOPAC2012, semi-empirical quantum chemistry package. Then, hydrogen molecules were added inside each of these nanocages and their optimizations and frequency calculations were performed with the same method. Each nanocage was filled with hydrogen molecules until it breaks. By doing so, we obtained the hydrogen storage capacities of these nanocages.

To be able to determine thermodynamic stability of the  $n\text{H}_2@host$  complexes, their formation enthalpies at 298 K were calculated from eqn. 1:

$$\Delta H_f^{\text{complex}} = \left[ \Delta H_{f(n\text{H}_2@host)} - \left( \Delta H_{f(host)} + n \Delta H_{f(\text{H}_2)} \right) \right] \quad (1)$$

where  $\Delta H_{f(n\text{H}_2@host)}$ ,  $\Delta H_{f(host)}$  and  $\Delta H_{f(\text{H}_2)}$  are the heats of formation of the complex, host and hydrogen molecules calculated by PM7, respectively.

Within the process of determining hydrogen storage capacity, we obtained the thermodynamically most stable BN-hydrogen complexes for these nanocages. By "stable complex", we mean the complex that has a formation enthalpy lower than the sum of formation enthalpies of individual hydrogen molecules and boron nitride nanocage located at infinite separation from each other. In other words, a complex

is thermodynamically stable if it has a negative complex formation enthalpy  $\Delta H_f^{\text{complex}}$ . Formation enthalpy per added  $\text{H}_2$  molecule value,  $\Delta H_{\text{destability}}^{\text{complex}} = \Delta H_f^{\text{complex}} / n\text{H}_2$ , which may provide useful information about how much destabilization being brought to nanocage by each added  $\text{H}_2$  molecule, were also calculated with the PM7 method.

### RESULTS AND DISCUSSION

The geometries of  $n\text{H}_2@B_mN_m$  ( $m = 12, 24, 36, 48$  and  $96$ ) complexes containing maximum number of  $\text{H}_2$  molecules are depicted in Fig. 1, while the maximum  $\text{H}_2$  numbers doped inside the nanocages before they break, the formation enthalpies, the formation enthalpy per added  $\text{H}_2$  ( $\Delta H_{\text{destability}}^{\text{complex}}$ ) values and gravimetric  $\text{H}_2$  storage weight percentages (wt. % s) of these complexes are presented in Table-1. The following points about hydrogen storage capabilities of the boron nitride nanocages are to be discussed based on the PM7 results. The variation of complex formation enthalpies,  $\Delta H_f^{\text{complex}}$ , with number of hydrogen molecules are depicted in Fig. 2, revealing several important results. First of all, complex formation enthalpies have quadratic dependence on number of hydrogen molecules. There is no thermodynamically stable complex formation for the smallest two nanocages ( $B_{12}N_{12}$  and  $B_{24}N_{24}$ ). In the initial stages of endohedral hydrogen doping, however, there are some thermodynamically stable complexes (having negative complex formation enthalpies) formed up to a certain critical number of hydrogen molecules for the nanocages expect for the smallest two. PM7 predicts these critical numbers as 1, 4 and 25  $\text{H}_2$  molecules for  $B_{36}N_{36}$ ,  $B_{48}N_{48}$  and  $B_{96}N_{96}$ , respectively. After passing these critical numbers, the complexes becomes thermodynamically unstable, but kinetically stable since they cannot overcome the kinetic barrier applied by nanocage inner surface. With continued addition of hydrogen molecules, the repulsive interactions originated from both  $\text{H}_2\text{-H}_2$  and  $\text{H}_2\text{-nanocage}$  increase so as to break the weakest B-N bond of nanocage. The kinetic barrier, here, can be considered as the energy necessary to break the weakest

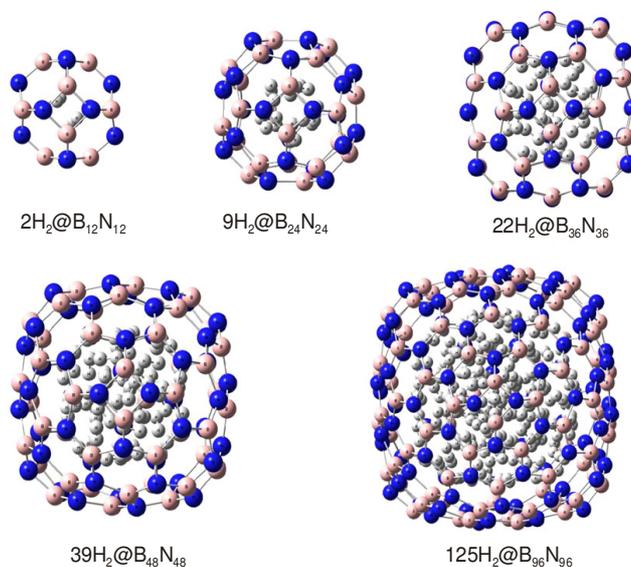


Fig. 1. Geometries of  $n\text{H}_2@B_mN_m$  complexes containing maximum number of hydrogen molecules for each nanocage obtained with PM7

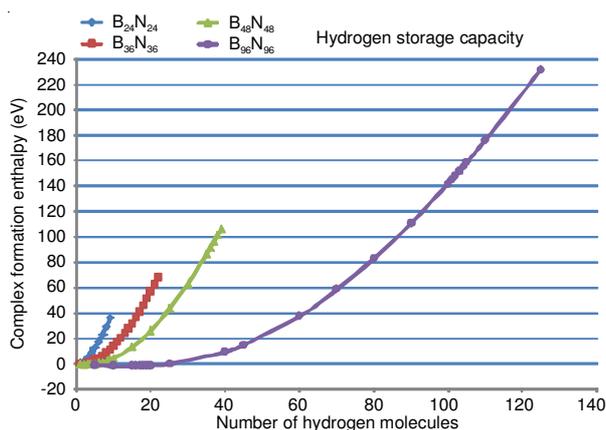


Fig. 2. Variation of complex formation enthalpies,  $\Delta H_f^{\text{complex}}$  with number of hydrogen molecules

TABLE-1  
MAXIMUM NUMBER OF H<sub>2</sub> MOLECULES DOPED, COMPLEX FORMATION ENTHALPIES, ENTHALPY PER ADDED H<sub>2</sub> MOLECULE AND WEIGHT % OF HYDROGEN STORAGE

Nanocage	Max. number of H <sub>2</sub> doped	$\Delta H_f^{\text{complex}}$ (eV)	$\Delta H_f^{\text{destability}}$ (eV/nH <sub>2</sub> )	H <sub>2</sub> storage (wt. %)
B <sub>12</sub> N <sub>12</sub>	2	17.88	8.94	1.35
B <sub>24</sub> N <sub>24</sub>	9	35.45	3.94	3.05
B <sub>36</sub> N <sub>36</sub>	22	67.81	3.08	4.96
B <sub>48</sub> N <sub>48</sub>	39	105.25	2.70	6.60
B <sub>96</sub> N <sub>96</sub>	125	229.80	1.84	10.58

B-N bond. In this case the structure of nanocage breaks down. Therefore, hydrogen storage capacity is defined as the maximum number of hydrogen molecules endohedrally doped inside nanocage whose structure is intact.

B<sub>12</sub>N<sub>12</sub> can accommodate at most two hydrogen molecules. The  $\Delta H_{\text{destability}}$  values for H<sub>2</sub>@B<sub>12</sub>N<sub>12</sub> and 2H<sub>2</sub>@B<sub>12</sub>N<sub>12</sub> are 4.90 and 8.94 eV, respectively, indicating that incorporation of second H<sub>2</sub> molecule leads to very unstable complex. This is an expected result because the B<sub>12</sub>N<sub>12</sub> nanocage is the smallest one among nanocages studied here and it has the smallest endohedral cavity that applies large repulsive force on endohedrally doped hydrogen molecules. The B<sub>24</sub>N<sub>24</sub> nanocage can be endohedrally doped by nine hydrogen molecules before its structure breaks down, leading to a hydrogen storage capacity of 3.05 wt. %. Each endohedral hydrogen molecule addition to B<sub>24</sub>N<sub>24</sub> increases formation enthalpy almost linearly and the  $\Delta H_{\text{destability}}$  value for 9H<sub>2</sub>@B<sub>24</sub>N<sub>24</sub> is found to be as 3.94 eV. Even if one hydrogen molecule is encapsulated by B<sub>24</sub>N<sub>24</sub>, the complex becomes thermodynamically unstable with a positive enthalpy of formation. On the other hand, it is not the case for the B<sub>36</sub>N<sub>36</sub> nanocage. The complex formed when one hydrogen molecule is encapsulated by the B<sub>36</sub>N<sub>36</sub> nanocage becomes thermodynamically stable with a formation enthalpy of -0.19 eV. This shows the endohedral cavity of B<sub>36</sub>N<sub>36</sub> applies an attractive force making the resultant complex more favorable. Our previous  $\omega$ B97X-D results<sup>26</sup> are in accordance with PM7 for the H<sub>2</sub>@B<sub>36</sub>N<sub>36</sub> complex. The  $\omega$ B97X-D method predicts the 2H<sub>2</sub>@B<sub>36</sub>N<sub>36</sub> complex being also stable, while the PM7 calculations shows that the 2H<sub>2</sub>@B<sub>36</sub>N<sub>36</sub> complex has very slightly positive formation enthalpy (includes all thermal

corrections at 298 K) of 0.15 eV. This difference is more likely to originate from the  $\omega$ B97X-D results not including thermal corrections in energy values (pure electronic energies). If these corrections were included in the  $\omega$ B97X-D results, most probably it would also be slightly positive. It is, therefore, safe to claim that PM7 agrees with  $\omega$ B97X-D on 2H<sub>2</sub>@B<sub>36</sub>N<sub>36</sub>. The hydrogen storage capacity of B<sub>36</sub>N<sub>36</sub> is 22 hydrogen molecules with a 4.96 wt.%. This value is close to the DOE's 2015 target of 5.5 wt. %<sup>27</sup>. Oku and Koi<sup>28</sup> reported that maximum 20 hydrogen molecules can be doped inside B<sub>36</sub>N<sub>36</sub> nanocage, confirming our findings. The small difference comes from the computational methodology. They used the PM5, earlier version of PM7, method while we employed PM7, a better semi empirical method that can model non-bonding interactions more accurately. Up to four hydrogen molecules can be stored in the B<sub>48</sub>N<sub>48</sub> nanocage so that the resulting complexes are thermodynamically stable and it is revealed that maximum 39 hydrogen molecules can be doped inside B<sub>48</sub>N<sub>48</sub>. The hydrogen storage capacity of B<sub>48</sub>N<sub>48</sub> corresponds to a wt. % of 6.60, which is above well above the DOE's 2015 target. The B<sub>96</sub>N<sub>96</sub> nanocage, the largest nanocage in this study, has rather huge hydrogen storage capacity of 10.6 wt. % since it can endohedrally hold 125 H<sub>2</sub> molecules while keeping its structure intact. As a result, the B<sub>48</sub>N<sub>48</sub> and B<sub>96</sub>N<sub>96</sub> nanocages can be promising materials for hydrogen storage.

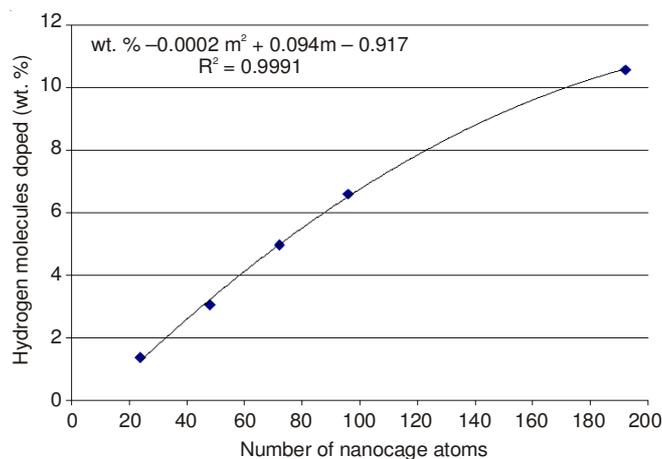


Fig. 3. Relation between hydrogen storage capacity (wt. %) vs. nanocage size

Fig. 3 gives variation of hydrogen storage capacity as wt. % with respect to nanocage size (total number B and N atoms in nanocage). The data obtained with PM7 perfectly fit to a second order polynomial function with a regression value of 0.9991. This function is given in eqn. 2:

$$\text{wt. \%} = -0.0002k^2 + 0.0948k - 0.917 \quad (2)$$

where k is the total number of B and N atoms in a nanocage. Since the coefficient of second order term is very small and first four data is very close to a linear behaviour, one can consider that as hydrogen storage capacity of boron nitride nanocages increase almost linearly with nanocage size. These results points out the possibility of finding highly effective hydrogen storage materials using boron nitride nano structures.

The  $\Delta H_{\text{destability}}$  value for each nanocage indicates energy increase by hydrogen addition. As seen from Table-2,  $\Delta H_{\text{destability}}$  decreases with increasing nanocage size. The energy needed for hydrogen storage decreases as the size of nanocage increases, explaining the increasing hydrogen storage capacity in boron nitride nanocages.

TABLE-2  
MAXIMUM PERCENT ELONGATION  
VALUES FOR B—N AND H—H BOND LENGTHS

Nanocage	B—N distance		Elongation (%)
	Average bond distance (full complex)	Average bond distance (empty nanocage)	
B <sub>12</sub> N <sub>12</sub>	1.5578	1.5076	3.33
B <sub>24</sub> N <sub>24</sub>	1.5514	1.5314	1.31
B <sub>36</sub> N <sub>36</sub>	1.5567	1.5108	3.04
B <sub>48</sub> N <sub>48</sub>	1.5659	1.5001	4.39
B <sub>96</sub> N <sub>96</sub>	1.5751	1.4831	6.20

Nanocage	H—H distance		Elongation (%)
	Average bond distance (full complex)	H <sub>2</sub> @nanocage	
B <sub>12</sub> N <sub>12</sub>	0.7644	0.7594	0.66
B <sub>24</sub> N <sub>24</sub>	0.7844	0.7594	3.29
B <sub>36</sub> N <sub>36</sub>	0.7832	0.7594	3.13
B <sub>48</sub> N <sub>48</sub>	0.7822	0.7594	3.00
B <sub>96</sub> N <sub>96</sub>	0.7762	0.7594	2.21

Table-2 gives the maximum percent elongation (% elongation) values of B-N and H-H bond lengths (in Å), calculated by employing the following average distances. The % elongation values for B-N bonds were obtained by using the difference between average B-N bond distance of the complex having maximum number of H<sub>2</sub> molecules and that of empty nanocages. Similarly, the % elongation values for H-H bond lengths were calculated by exploiting the difference between average H-H bond distances inside the complex containing maximum number of H<sub>2</sub> molecules and the H-H bond lengths of single hydrogen molecule containing nanocages. B<sub>12</sub>N<sub>12</sub> is different from other nanocages in that it reaches storage capacity with a sudden 3.3 % elongation after two H<sub>2</sub> additions due to having the smallest endohedral surface. On the other hand, the remaining nanocages show gradable trends. As nanocage size increases maximum elongation percent increases. This indicates that larger nanocages become more elastic increasing the storage capability. Upon H<sub>2</sub> addition, increase in H-H bond lengths seem an unexpected result, but this elongation decreases as nanocage size increases.

## Conclusion

In this study, endohedral hydrogen storage capacities of several boron nitride nanocage (B<sub>m</sub>N<sub>m</sub> where m = 12, 24, 36, 48 and 96) structures have been determined by newly developed semi empirical PM7 method. It is shown that the nanocages B<sub>12</sub>N<sub>12</sub> and B<sub>24</sub>N<sub>24</sub> are inadequate nano structures for hydrogen storage while B<sub>36</sub>N<sub>36</sub> might barely fulfill expectations. The B<sub>48</sub>N<sub>48</sub> and B<sub>96</sub>N<sub>96</sub> nanocages, however, that

have hydrogen storage capacities of 6.6 and 10.6 wt. %, respectively, can be considered as very promising hydrogen storage materials due to having hydrogen storage wt. % considerably higher than the 2015 target value of DOE.

In addition, the most thermodynamically stable H<sub>2</sub>-boron nitride complexes are found to be H<sub>2</sub>@B<sub>36</sub>N<sub>36</sub>, 4H<sub>2</sub>@B<sub>48</sub>N<sub>48</sub>, 25H<sub>2</sub>@B<sub>96</sub>N<sub>96</sub> and it is predicted that as nanocage size increases nanocages become more elastic leading to an increase in the storage capability.

## ACKNOWLEDGEMENTS

This study is supported Scientific Research Projects of Ege University through the project no 09/FEN/046. The PM7 calculations reported in this paper were performed at TUBITAK ULAKBIM, High Performance and Grid Computing Center (TRUBA resources).

## REFERENCES

- D.A.J. Rand and R.M. Dell, Hydrogen Energy, Challenges and Prospects (RSC Energy Series), Royal Society of Chemistry; Cambridge, UK, Ch. 5, p. 146 (2008).
- L. Schlapbach and A. Züttel, *Nature*, **414**, 353 (2001).
- A. Züttel, A. Remhof, A. Borgschulte and O. Friedrichs, *Phil. Trans. Royal Soc. A*, **368**, 3329 (2010).
- J. Zheng, X. Liu, P. Xu, P. Liu, Y. Zhao and J. Yang, *Int. J. Hydrogen Energy*, **37**, 1048 (2012).
- A. Züttel, *Mater. Today*, **6**, 24 (2003).
- W.Q. Deng, X. Xu and W.A. Goddard, *Phys. Rev. Lett.*, **92**, 166103 (2004).
- Z.X. Yang, Y.D. Xia and R. Mokaya, *J. Am. Chem. Soc.*, **129**, 1673 (2007).
- R.T. Yang, *Carbon*, **38**, 623 (2000).
- H. Kajiuura, S. Tsutsui, K. Kadono, M. Kakuta, M. Ata and Y. Murakami, *Appl. Phys. Lett.*, **82**, 1105 (2003).
- M. Ritschel, M. Uhlemann, O. Gutfleisch, A. Leonhardt, A. Graff, Ch. Täschner and J. Fink, *Appl. Phys. Lett.*, **80**, 2985 (2002).
- J.Y. Lee, C.D. Wood, D. Brandshaw, M.J. Rosseinsky and A.I. Cooper, *Chem. Commun.*, 2670 (2006).
- P.M. Budd, A. Butler, J. Selbie, K. Mahmood, N.B. McKeown, B. Ghanem, K. Msayib, D. Book and A. Walton, *Phys. Chem. Chem. Phys.*, **9**, 1802 (2007).
- J.L.C. Rowsell and O.M. Yaghi, *Angew. Chem. Int. Ed.*, **44**, 4670 (2005).
- Y.W. Li and R.T. Yang, *J. Am. Chem. Soc.*, **128**, 8136 (2006).
- G.E. Froudakis, *Nano Lett.*, **1**, 179 (2001).
- G.E. Froudakis, *Mater. Today*, **14**, 324 (2011).
- N.G. Chopra, R.J. Luyken, K. Cherrey, V.H. Crespi, M.L. Cohen, S.G. Louie and A. Zettl, *Science*, **269**, 966 (1995).
- P. Wang, S. Orimo, T. Matsushima, H. Fujii and G. Majer, *Appl. Phys. Lett.*, **80**, 318 (2002).
- R. Ma, Y. Bando, H. Zhu, T. Sato, C. Xu, D. Wu, R. Ma, *J. Am. Chem. Soc.*, **124**, 7672 (2002).
- G. Mpourmpakis and G.E. Froudakis, *Catal. Today*, **120**, 341 (2007).
- Q. Sun, Q. Wang and P. Jena, *Nano Lett.*, **5**, 1273 (2005).
- J. Li, J. Lin, X. Xu, X. Zhang, Y. Xue, J. Mi, Z. Mo, Y. Fan, L. Hu, X. Yang, J. Zhang, F. Meng, S. Yuan and C. Tang, *Nanotechnology*, **24**, 155603 (2013).
- J.J.P. Stewart, *J. Mol. Model.*, **19**, 1 (2013).
- J. Hostas, J. Rezac and P. Hobza, *Chem. Phys. Lett.*, **568**, 161 (2013).
- J.J.P. Stewart, MOPAC2012, Stewart Computational Chemistry, Colorado Springs, CO, USA (2012); <http://OpenMOPAC.net>.
- S. Sayhan and A. Kinal, *Asian J. Chem.*, **26**, 5935 (2014).
- [http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets\\_onboard\\_hydro\\_storage\\_explanation.pdf](http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage_explanation.pdf).
- N. Koi and T. Oku, *Solid State Commun.*, **131**, 121 (2004).