ATOMIC HYDROGEN ADSORPTION ON BORON NITRIDE NANOTUBE SURFACES

Margulis Vl.A.*, Muryumin E.E., Tomilin O.B.
N.P. Ogarev Mordovian State University,
Bolshevistskaya str. 68, Saransk, 430000 Russia
**E-mail: 612033@inbox.ru*

Introduction

In the last years there has been an increasing interest in the study of boron nitride nanotubes (BNNTs), which are inorganic analogues of carbon nanotubes. This interest is partly motivated by the potential significance of these systems in the field of nanotechnology. In particular, similar to carbon nanotubes, BNNTs are thought to be promising materials for applications in hydrogen storage devices. Recently, several experimental and theoretical studies on hydrogen adsorption on BNNTs have been reported [1-5]. However, the specific features of the adsorption of a single H atom on BNNTs have not been clearly understood yet. In this connection, a more systematic study concerning this problem might be useful.

In this report, we investigate the adsorption of a hydrogen atom on the outer surface of single-walled BNNTs through the semi-empirical AM1 (Austin Model) calculations. Our primary objective is to identify the preferable adsorption sites and to determine the adsorption energies for different BNNTs. We confine our consideration to the BNNTs with the chiral index (n,0), since experimental investigations have shown that BNNTs tend to have a zigzag structure during their growth.

Results and discussion

In order to carry out a meaningful computer calculation of the adsorption process of atomic H on the sidewall of the zigzag BNNTs (n,0), we have assumed that the ends of the tubes are terminated by hydrogen atoms. We have performed calculations of the quantities relevant to the adsorption on the BNNTs (n,0) with n = 5–10. The simulation tube (5,0), shown in Fig.1, contained 55 boron atoms plus 55 nitrogen atoms in the tube wall and 10 hydrogen atoms at the ends of the tube plus one H atom adsorbed on it. Thus, the smallest tube we have considered is large enough to exclude edge effects from the adatom – substrate BNNT interaction at the sites located far from the ends of the tube. This is the more so true for the largest simulation tube (10,0) considered, which contained 240 atoms. Adsorption at the centre of the B–N hexagon has not be treated, as it is not expected to be the most active site for the H adatom.

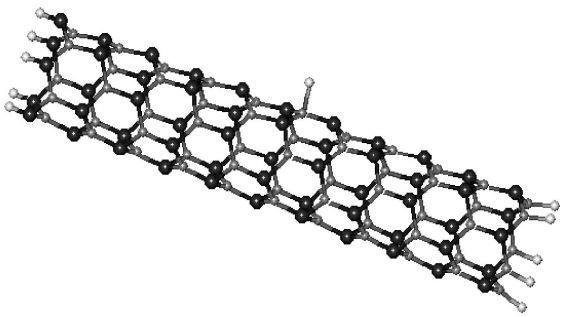

Fig.1. BNNTs (5,0) with hydrogen atom adsorbed on its surface.

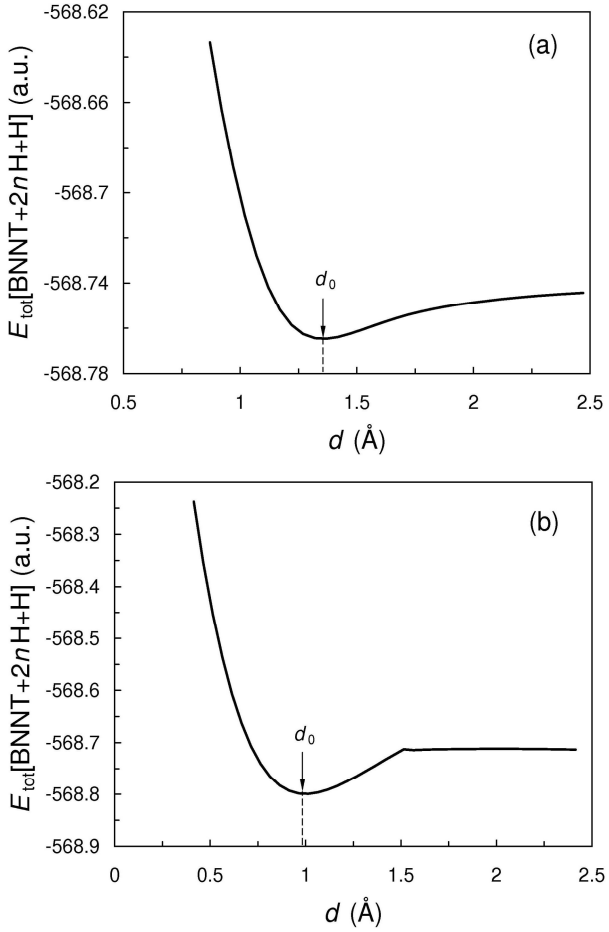

Fig.2. Total energy E_{tot} of the hydrogen-terminated BNNTs (5,0) with the adsorbed H atom on the top of the B atom (a) and on the top of the N atom (b) versus the distance d between the adatom and the tube .

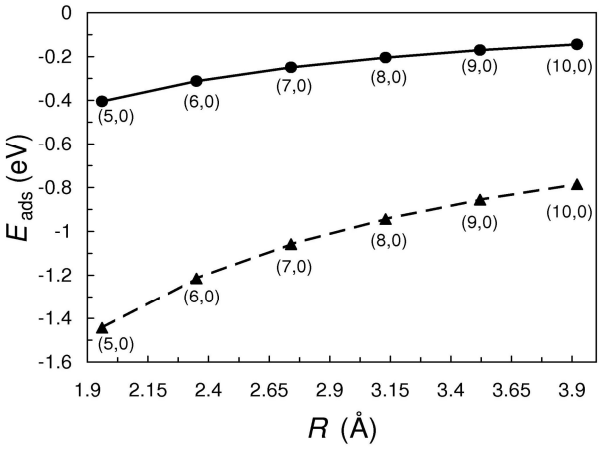

Fig.3. Calculated adsorption energies E_{ads} of a single hydrogen atom on the zigzag BNNTs (n,0) with n ranging from 5 to 10 versus the radius R of the tube. The heavy dots and triangles refer to the adsorption on the B atom and the N atom, respectively.

To examine the adsorption properties, we have first optimized the geometric structures of all the clean tubes under consideration. Secondly, for each tube we have found the optimal adsorption distance d_0 between the H atom and the tube. To do this, we have calculated the total energy $E_{tot}\left[\mathrm{BNNT}+2n\mathrm{H}+\mathrm{H}\right]$ of the hydrogen-terminated BNNTs with the adsorbed H atom on the top of the B or N atom as a function of the distance d between the adatom and the tube. As an example, in Fig. 2 we show the result of our calculations for the (5,0) tube, which is typical. The curves in this figure are characterized by the presence of the global energy minimum at the point $d = d_0$. The negative values of $E_{tot}\left[\mathrm{BNNT}+2n\mathrm{H}+\mathrm{H}\right]$ at this point indicate that the chemical bond between the H atom and the tube is formed. The comparison of the curves in Fig. 2 also shows that the adsorption on the top of the N atom is energetically more favorable than that on the top of the B atom.

The adsorption energy E_{ads} of the H atom on the surface of the BNNT (n,0) can be calculated in terms of the above-mentioned total energy $E_{tot}\left[\mathrm{BNNT}+2n\mathrm{H}+\mathrm{H}\right]$, the total energy $E_{tot}\left[\mathrm{BNNT}+2n\mathrm{H}\right]$ of the hydrogen-terminated pristine tube and the energy $E_{tot}\left[\mathrm{H}\right]$ of a single free hydrogen atom:

$$E_{ads} = E_{tot}\left[\mathrm{BNNT}+2n\mathrm{H}+\mathrm{H}\right] - \\ - E_{tot}\left[\mathrm{BNNT}+2n\mathrm{H}\right] - E_{tot}\left[\mathrm{H}\right].$$

The results of our calculations of E_{ads} are given in Fig. 3 as a function of the radius R of the tube. As the figure clearly shows, the H atom prefers to be adsorbed on the top of the nitrogen atom. The figure also shows that there is a systematic increase in E_{ads} with increasing R. Thus we have come to a somewhat surprising conclusion that in order to enhance hydrogen storage of BNNTs one should preferably use those with the smallest radii.

We have found that, as the H adatom approaches the surface of BNNT, it acquires a positive charge at the expense of the nearest-neighboring atom of the BNNT. Our calculations have shown that the largest charge transfer from the adatom to the nanotube occurs when the H atom is adsorbed on the top of the N atom (in this case its value for the nanotubes considered is about 0.23 – 0.25 of the electron charge). This is not surprising, since it is well known that nitrogen atoms are more electronegative that boron ones. Thus, we conclude that a single H atom adsorbed on the surface of BNNTs exists substantially in a cationic state.

References

1. Ma R., Bando Y., Zhu H.W., Sato T., Xu C., Wu D. Hydrogen uptake in boron nitride nanotubes at room temperature. J Am Chem Soc 2002; 124(26):7672-7673.

2. Tang C.C., Bando Y., Ding X.X., Qi S.R., Golberg D. Catalyzed collapse and enhanced hydrogen storage of BN nanotubes. J Am Chem Soc 2002;124(49):14550-14551.

3. Wu X., Yang J., Hou J.G., Zhu Q. Deformation-induced site selectivity for hydrogen adsorption on boron nitride nanotubes. Phys Rev B 2004; 69(15):153411-153414.

4. Jhi S-H., Kwon Y-K. Hydrogen adsorption on boron nitride nanotubes: A path to room-temperature hydrogen storage. Phys Rev B 2004;69(24):245407-245410.

5. Wu X., Yang J., Hou J.G., Zhu Q. Hydrogen adsorption on zigzag (8,0) boron nitride nanotubes. J Chem Phys 2004;121(17):8481-8485.