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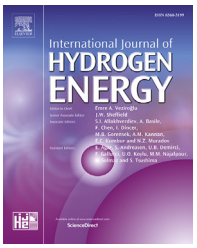

Hydrogen adsorption on graphene, hexagonal boron nitride, and graphene-like boron nitride-carbon heterostructures: A comparative theoretical study

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ABSTRACT

The results of DFT and *ab initio* calculations of the hydrogen physisorption on graphene, hexagonal boron nitride (h-BN), and a graphene-like boron nitride-carbon heterostructure (GBNCH) are discussed. PBE-D3, B3LYP-D3 as well as MP2 methods were employed in calculating the adsorption energies (*Ea*) of a hydrogen molecule to the appropriate structure and the optimal distances between them. Six adsorption sites were examined, and it is demonstrated that the 'hollow' sites are favorable for hydrogen adsorption. It was established that GBNCH exhibits increased *Ea* values in comparison with graphene and h-BN. Hydrogen adsorption isotherms at different temperatures were obtained using grand canonical Monte-Carlo simulations, and it was shown that GBNCH reveals advanced adsorption properties in comparison with its counterparts. The usage of GBNCHs for hydrogen storage is also discussed.

Introduction

The negative effects of fossil fuels consumption on the environment will facilitate the transition to the renewable energy sources. In general, molecular hydrogen is recognized as the best candidate for 'green' energetics. There are a lot of issues, however, that slow down the ultimate conversion to hydrogen-based fuels. To use the advantages of hydrogen energetics, the necessary steps are to be undertaken toward the mass hydrogen production, purification, storage, and delivery. Potential storage materials (graphene [1], carbon nanotubes [2], and other nanostructures) have earned considerable attention for their large surface area and safe nature [3,4]. Thus, for example, a vast literature exists on theoretical and experimental studies of hydrogen adsorption on one- (1D) and two-dimensional (2D) nanostructures [5–12]. In that respect, the first studies were made two decades ago [13]. The works on carbon materials were followed by the papers on the storage abilities of boron nitride nanotubes (BNNTs) and hexagonal boron nitride (h-BN) [14–17].

It was originally proposed that BNNTs are suit well for hydrogen storage owing their partially ionic character [18].

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Later, it was shown that both physisorption and chemisorption of hydrogen on h-BN and BNNTs are less favorable energetically than on carbon counterparts. BNNTs cannot adsorb hydrogen molecules effectively by the physisorption and thus are not good candidates for hydrogen storage [13,19]. After that, other 2D systems for hydrogen storage were studied [5,20,21].

Hybrid 2D materials have received enormous attention owing to their unique properties and potential applications in novel generations of nanodevices [22–24]. The comparable structures of graphene and h-BN offer the possibility of joining both materials together in a single layer, thus forming a hybrid 2D material. Graphene-like boron nitride-carbon heterostructures (GBNCHs) with different shapes of h-BN embedded in graphene and *vice versa* have been recently proposed and synthesized [25–28].

In view of our continuing interest in graphene and GBNCH [29–33], in this paper, we investigate the adsorption energy of molecular hydrogen on models of pristine graphene, h-BN, and GBNCH using dispersion-corrected density functional theory (DFT) methods (PBE-D3 and B3LYP-D3). Then, we compare the results with those obtained by the MP2 method. In our knowledge, there is only one paper dealt with this topic: Cao et al. theoretically studied hydrogen adsorption at the interface of a graphene-boron nitride hybrid atomic membrane, however, that paper focused only on hydrogen chemisorption [34]. We also simulate hydrogen adsorption isotherms for slit-pore models of graphene, h-BN, and GBNCH using the grand canonical Monte-Carlo (GCMC) method. On the base of analysis of the isotherms, we perform the additional comparison of hydrogen uptake by studied structures.

We believe that the present study can answer the following questions: (i) are the dispersion-corrected functionals reliable to estimate hydrogen adsorption energies; (ii) what is the comparative behavior of hydrogen adsorption on graphene, h-BN, and GBNCH; (iii) what is the most favorable adsorption site at boron nitride/carbon interface in GBNCH; (iv) how do the interface effects modify hydrogen adsorption energy? The answers can clarify the interface effects in GBNCHs and stimulate new experimental and theoretical investigations on hybrid nanomaterials.

Computational methods

All *ab initio* and DFT calculations were carried out using Orca 3.0.3 program package [35]. For the DFT calculations, the dispersion-corrected (as proposed by Grimme) PBE-D3 and B3LYP-D3 functionals [36–38] together with the SVP (Split Valence Polarization) basis set [39] were employed. These functionals has been demonstrated to be reliable and commonly used in the studies of adsorption phenomena [3,40]. *Ab initio* calculations were made using second-order Møller-Plesset perturbation theory (MP2) with the SVP basis set. In SVP, the inner shell atomic orbitals are described by a single basis function, two basis functions are provided for each valence shell atomic orbital, augmented by a set of polarization functions [30]. For all calculations, we employ the default convergence criteria: geometry optimization of 5×10^{-6} Hartree (E_h), self-consistent field (SCF) steps of 1×10^{-8} E_h, root mean square (RMS) force of 1×10^{-4} E_h/r_{bohr}, and minimum force of 3×10^{-4} E_h/r_{bohr}.

The coronene molecule ($C_{24}H_{12}$) is selected as a graphene model system (Fig. 1). The choice was dictated by numerous works, where coronene is regarded as the smallest molecule that resembles properties of graphene [8,41]. To obtain an h-BN model ($B_{12}N_{12}H_{12}$), we substitute carbon atoms in coronene with boron and nitrogen atoms in an alternate manner (Fig. 1 SI (Supporting Information)). As a GBNCH model ($C_{12}B_6N_6H_{12}$), we also used a coronene-like model, in which we substitute a half of carbon atoms with boron and nitrogen (Fig. 2 SI). It is worth noticing that it is not a focus of this paper to discuss the stability of the involved heterostructures but to analyze the substitution effects on *Ea* values of molecular hydrogen.

In the first step, graphene, h-BN, and GBNCH models as well as hydrogen molecules were fully optimized at the respective level of theory. The geometry of these species was then frozen. Second, we fixed the perpendicular orientation of a hydrogen molecule relatively studied systems and studied the 'hollow', 'bond', and 'top' adsorption sites (Fig. 1, left). Third, we fixed the parallel orientation of hydrogen relatively studied systems and studied the aforementioned adsorption sites (Fig. 1, right).

The distance between H_2 and all studied models is defined as the length of a perpendicular line dropped from the hydrogen center-of-mass to the plane of the studied system. Finally, we varied the distance from 5.5 to 2 Å and calculated single-point adsorption energies (*Ea*) using equation (1).

$$Ea = Etotal(model/H_2) - Etotal(model) - Etotal(H_2) \quad (1)$$

Where $Etotal(model/H_2)$ denotes single-point energy of the physisorbed system, $Etotal(H_2)$ is the total energy of hydrogen, and *Etotal(model)* is the total energy of an appropriate model.

To obtain hydrogen adsorption isotherms, we use grand canonical Monte-Carlo (GCMC) simulations following the Metropolis' sampling scheme [42,43]. The Universal force field is employed [44]. The temperatures (T) have been fixed at 77 (temperature of liquid nitrogen) and 300 K (ambient conditions). The pressures (P) have been varied from 100 kPa to 10 MPa. We use slit-shaped pore structures consisted of two parallel sheets of graphene, h-BN, or GBNCH at the distances of 15 Å. Periodic boundary conditions have been applied to all models. The in-plane cell parameters are 21.3 and 12.3 Å, while the lattice constant in the z direction is 15 Å.

Results and discussion

Hydrogen adsorption on graphene

Firstly, we take into consideration the physisorption on graphene. There are six possible configurations for hydrogen adsorption: three vertical, ('hollow' (on the center of a six-membered ring), 'bond' (on the center of a C–C bond), and 'top' (on the C atom)) and three horizontal (the same as in the previous case) positions. They are denoted as VH, VB, and VT; HH, HB, and HT for vertical and horizontal positions, respectively (Fig. 1). When the vertical orientation is

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