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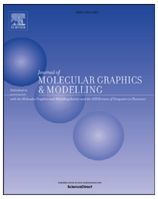

Simulations on methane uptake in tunable pillared porous graphene hybrid architectures

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A R T I C L E I N F O

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In this article, 3D pillared carbon nanotube (CNT)-porous graphene (PG) nanomesh architectures are computationally investigated as methane storage nanocontainer. The purpose of this article is to screen the configurations of 3D pillared CNT-PG materials and to select the optimal one for maximizing the methane storage capacity. Molecular mechanics (MM) calculations and MD simulations are executed to depict the structural characteristics and methane adsorption properties. The calculated structural parameters coincide well with the empirical conclusions. The methane adsorption simulations are systematic investigated as a function of geometry variables such as PG interlayer spacing, distance of CNTs, and the number of PG sheets in a wide range of pressure. The average adsorption energy of methane in different configurations is concentrated between 2 and 4 kcal mol^{-1}. The results revealed that the applications of 3D CNT-PG models can significantly enhance methane adsorption performance in comparison to pillared graphene: the maximum amount of adsorbed methane of 3D CNT-PG displays 21.3 mmol/gr (interlayer spacing of 1.2 nm and bilayer PG), which is about 25% higher than that of pillared graphene. Meanwhile, the deformation of (6, 6) carbon nanotubes can significantly improve the methane storage capacity. This provides a viable structure modification method, which is suitable for enhancement of methane storage.

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1. Introduction

Owing to its clean combustion and renewable nature, methane is widely believed as a promising energy carrier for mobile applications [1–4]. The U.S. Department of Energy (DOE) has also recently updated an ambitious methane storage standard: volumetric storage capacity of 11.741 $\mathrm{mmol/cm^3}$ ($\rho = 0.188\ \mathrm{g/cm^3}$) and gravimetric storage capacity of 0.5 $\mathrm{g}_{\text{methane}}/\mathrm{g}_{\text{adsorbent}}$ (33.3 wt %) at operational conditions [5,6]. This standard is limited to the situation where constructed containers should have high enough surface area and light enough density, so that graphene and its analogues come into view as a viable way for methane adsorption. To date a great variety of graphene-like materials have been synthesized or designed for potential application in methane storage through physical adsorption. Hassani et al. [7] investigated methane storage inside pillared graphene by hybrid molecular simulation. They found that the methane adsorption capacity on pillared graphene can reach 16.85 mmol/gr. They have also illustrated pillared graphene rather than graphene sheets enhance the adsorption of methane at a pressure of about 40 bars by approximately 22%. Zhu et al. [8] investigated methane storage with graphene sheets, activated carbon and carbon black. They found that the activated carbon has the largest methane adsorption capacity which can reach 12.52 $n_0/\mathrm{mmol\ g^{-1}}$ at 253.15 K. They also found that adsorbent with a larger specific surface area has a higher adsorption amount and a bigger isosteric heat of adsorption. Chen et al. [9] also elaborated methane adsorption with multilayer graphene nanostructures (MGNs), in which the highest methane uptake can reach 310 V (STP)/V with a graphene interlayer spacing of 0.68 nm and pressure of 35 bar. They found that MGNs is capable of acid gas separation apart from methane storage. Nonhydrocarbons in biogas can be separated with Li–MGNs before storing the main effective gas composition in MGNs with an appropriate layer distance. Methane adsorption on these graphene materials shows the prospect of high density storage. Nevertheless, the performance of methane adsorption in the previously studied graphene related nanostructures is failed to achieve the DOE's target. In this condition, PG appeared to be a more promising material due to its higher specific surface area (up to 3100 $\mathrm{m^2/g}$) and large pore volume [10].

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These outstanding materials may present entirely novel directions for highly efficient gas storage.

From the fundamental point of view, PG is nothing but a collection of graphene related functional materials with interconnected or closed nanopores in the plane. In general, PG materials include graphene nanomesh (GNM) [11,12], crumpled graphene (CG) [10,13] and graphene foam [14,15] etc. The PG materials are mainly used in the fields of energy and environmental research, for example: the storage and purification of gas [16,17]. In this article, a regular graphene nanomesh — polyphenylene superhoneycomb network which has been synthesized in Ref. [18] is chose as the main component of the research object. This superhoneycomb nanomesh is a robust two-dimensional networks with uniform sub-nanometer periodicity (pore spacing 7.4 Å) and uniform pore sizes (2.48 Å). In theory, this PG structure can be obtained by missing phenyl rings in original graphene, which remove one benzene ring from each hexagonal pore in graphene meanwhile the dangling bonds saturated with hydrogen atoms, as shown in Fig. 1. Because a part of carbon atoms are replaced by hydrogen atoms, the density of PG (0.54 mg/m^2) reduced about 30% compared to original graphene (0.77 mg/m^2), leading to the methane adsorption performance improved greatly.

In mobile applications, methane is mainly stored in materials at the temperature above 273K [19]. Gas can only form adsorption monolayer on the adsorbent surface at this temperature range, therefore it is necessary to enlarge the surface area or lessen the unit mass to achieve higher methane adsorption capability. In this case, CNTs are introduced into polyphenylene superhoneycomb network, which can lead the PG sheets packed without losing its high specific surface area. Combining the properties of PG sheets and CNTs, this framework may exhibits very high performance for methane storage. Nevertheless, gas adsorption on PG surface arises primarily from the interactions between the adsorbent and gas molecules, while for CNTs, the adsorption process is also influenced by the interactions among gas molecules given the confined space in CNTs. Under such complex circumstances, the methane adsorption process is difficult to predict. Consequently, devising and adjusting the geometric configuration of hybrid materials to comprehending and administrating the methane storage process is crucial to move it to the practical applications. To further research and predict gas adsorption properties in 3D CNT-PG frameworks, MD simulations, which have been widely used in the study of gas adsorption, are selected to discuss methane adsorption process in this hybrid system.

The purpose of this work is to assess the methane adsorption properties in 3D CNT-PG structures at 298 K. In the next section, the configurations of model and computational details employed in the simulations are elucidated. Then, methane storage performance in periodic simulation units will be presented with different simulation conditions such as pressure, PG interlayer spacing, distance of CNTs, and the number of PG sheets. Finally, conclusions are summarized in Section 4.

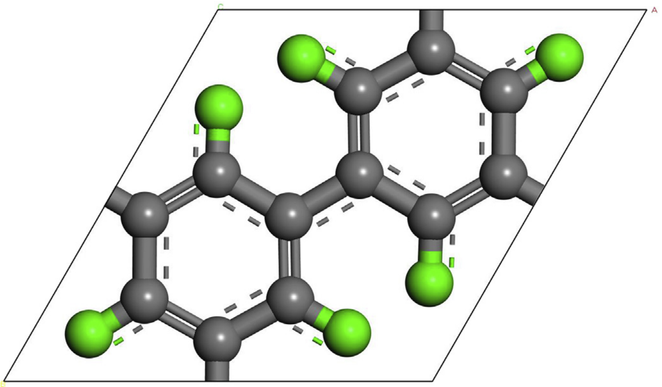

Fig. 1. Unit cell of PG sheet. (Gray balls represent carbon atom, green balls represent hydrogen atom.).

2. Models and methods

2.1. Force field

The adsorption system consists of adsorbent (3D pillared CNT-PG) and adsorbate (methane). The interatomic potentials of MD simulations are described by the reactive force fields (ReaxFF) which is an novel bond order potential for modeling larger and more complex molecular systems involving chemical reactions with higher accuracy when compared with computation intensive quantum mechanical (QM) methods [20]. ReaxFF has been used to investigate the diffusion coefficients of methane inside the C-CNT and the adsorption of methane in carbon nanochannels [21,22]. It is suitable for modeling gas adsorption with ReaxFF. In ReaxFF, the total potential energy can be written as

$$\mathrm{E_{system}} = \mathrm{E_{bond}} + \mathrm{E_{lp}} + \mathrm{E_{over}} + \mathrm{E_{under}} + \mathrm{E_{val}} + \mathrm{E_{pen}} + \mathrm{E_{coa}} + \mathrm{E_{tors}} + E_{conj}+E_{Hbond}+E_{vdWaals}+E_{Coulomb} \tag{1}$$

Where $\mathrm{E_{vdWaals}}$ and $\mathrm{E_{Coulomb}}$ are the energy of non-bonded interactions, namely the van der Waals and Coulomb interactions. In addition to $\mathrm{E_{Hbond}}$, the energy of hydrogen bond, the rest of the energy terms are the bond order dependent and account for the bonded interactions that consists of $\mathrm{E_{bond}}$, the energy of bond, $\mathrm{E_{lp}}$ for energy of lone-pairs, $\mathrm{E_{over}}$ of over-coordination, $\mathrm{E_{under}}$ of under-coordination, $\mathrm{E_{val}}$ of valence angle, $\mathrm{E_{pen}}$ of energy penalty for handling atoms with two double bonds, $\mathrm{E_{coa}}$ of coalition (three-body conjugation), $\mathrm{E_{conj}}$ of conjugated bonds (four-body conjugation), and $\mathrm{E_{tors}}$ of torsion angles.

In ReaxFF, All forces arising from bonded interactions rely on the derivate values of the bond order (BO). The functions computes the raw BOs including three exponential functions of atom pair distance and bond cut-off as shown in Eq. (2):

$$BO'_{ij} = BO'^{\,\sigma}_{ij} + BO'^{\,\pi}_{ij} + BO'^{\,\pi\pi}_{ij} = \exp\left[\mathrm{Pbo1}\cdot\left(\left(\frac{\mathrm{r^{ij}}}{\mathrm{r_o^{\sigma}}}\right)\right)^{\mathrm{Pbo2}}\right] + \exp\left[\mathrm{Pbo3}\cdot\left(\left(\frac{\mathrm{r^{ij}}}{\mathrm{r_o^{\sigma}}}\right)\right)^{\mathrm{Pbo4}}\right] + \exp\left[\mathrm{Pbo5}\cdot\left(\left(\frac{\mathrm{r^{ij}}}{\mathrm{r_o^{\sigma}}}\right)\right)^{\mathrm{Pbo6}}\right] \tag{2}$$

2.2. Models

The fundamental building unit of 3D pillared CNT-PG architectures consist of AA stacked PG sheets fixed parallelly over an armchair-type (6, 6) single-walled CNT. Similar structures of 3D pillared graphene have been designed in the previous theoretical calculations [23]. The nodes display a negative Gaussian curvature surface with six heptagons which have been elaborated by Euler's rule. Then, extensive periodic 3D CNT-PG networks which based this fundamental building unit was constructed as methane adsorption media. The model parameters of the prepared periodic 3D CNT-PG networks have been displayed in Table 1.

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