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Nanoindentation analysis of 3D-pillared carbon nanostructures used for hydrogen storage

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ABSTRACT

Molecular dynamics simulations are performed to study the mechanical behavior of hydrogen adsorption by a three-dimensional pillared nanostructure comprising graphene sheets and carbon nanotubes (CNTs). The hardness and reduced modulus of the nanostructures containing (5,5), (7,4), (9,0), and (10,10) CNTs are investigated using a nanoindentation test. Results indicate that the effects of different types of CNTs on the hardness, reduced modulus, and dissipation energy of the nanostructure are significant. In addition, the adsorption rate of the nanostructures is compared before and after nanoindentation. In the case of (7,4) CNT, the simulation showed an approximate 20% decrease in the adsorption rate of the nanostructure after nanoindentation.

Introduction

Hydrogen is a potential fuel for future applications owing to its clean combustion, high energy density, and renewable nature. It can be used in various types of power sources, such as combustion engines and fuel cells. However, hydrogen fuel has not been available for practical use due to some challenges that must be overcome. One of the major problems is the safe storage of hydrogen while maintaining sufficiently high volumetric density.

Several types of carbon nanostructure materials have been investigated for hydrogen storage through physical adsorption [1–3]. In recent years, carbon nanotubes (CNTs) and graphene have been widely studied as media for reversible hydrogen storage owing to their excellent mechanical properties and high surface area [4–8]. For example, Lee et al. [5] carried out first-principles theoretical calculations to examine the behavior of hydrogen adsorption on CNT surfaces. They found that the dissociative adsorption of H_2 molecules was severely suppressed due to the very high energy barriers of about 3 eV, whereas H atoms had low-energy barriers of less than 0.3 eV. Lamari and Levesque [6] examined the behavior of hydrogen adsorption on graphene and estimated that the excess hydrogen physisorption was approximately 7 wt% at a temperature of 77 K and a pressure of 1 MPa and decreased with an increase in temperature. Wu et al. [8] performed molecular dynamics simulations to study the adsorption of molecular hydrogen on nanostructures comprising a small number of graphene layers. They found that the effects of temperature and

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pressure could offset each other to improve hydrogen storage capacity.

Despite the reported improvements in hydrogen storage capacity, the total amount of hydrogen stored in the previously studied carbon nanostructures is unsatisfactory. To enhance hydrogen storage capacity, carbon-based nanostructures comprising both nanotubes and graphene sheets were proposed. However, experimental fabrication of the nanostructure materials and validation of their storage capacities has proved challenging. As a result, different simulation methods have been used for studying the problems of hydrogen storage capacity [9–13]. For example, Dimitrakakis et al. [9] designed a nanostructure that combined CNTs and graphene sheets to form a three-dimensional (3D) configuration and used Monte Carlo simulations to demonstrate that it had an enhanced hydrogen storage capacity. Jiang et al. [11] studied the storage of hydrogen in a 3D pillared graphene bubble system under various environments using molecular dynamics (MD). They showed that the hydrogen storage capacity of the pillared graphene bubble structure could be maximized by increasing the pressure and the graphene interlayer spacing and by decreasing the temperature. In addition, the incorporation of nitrogen atoms and transition metals CNT can enhance the ability of hydrogen storage. Mananghaya [12,13] studied the behavior of hydrogen adsorption of nitrogen-doped CNTs functionalized with transition metals using the density-functional theory method.

To the best of our knowledge, there are few studies examining the mechanical properties of carbon nanostructures following hydrogen adsorption; however, it is important to understand whether the nanostructures in use are strong or weak under operational conditions. In this study, the nanoindentation method is used to analyze the mechanical behaviors of graphene sheets pillared with CNT linkers following the adsorption of hydrogen.

Simulation method

The 3D pillared nanostructure used in this study was the same as that described in the previous study [14]. In the nanostructure, four CNT pillars occupy the empty space between two graphene sheets and are symmetric with respect to the center of the sheets. The two graphene sheets have dimensions of 4.5 nm (length) × 4.5 nm (width). To support the nanoindentation load, the lower graphene sheet was assumed to be fixed. The length of each CNT was 2.3 nm. The distance between two CNTs was set to 3.4 nm in both x and y directions. Periodic boundary conditions were applied to all three dimensions. The hydrogen molecules that initially had a face-centered cubic (fcc) structure were placed above, below, and between the pillared graphene sheets. The hydrogen molecules were treated as single spherical molecules to simplify the model. Fig. 1 shows a snapshot of the hydrogen storage MD simulation.

The system used was a closed chamber in a steady thermal state to permit effective diffusion of the gas molecules and then to simulate the adsorption of hydrogen. In the simulation, the C–C bonds of 3D pillared graphene were described using the Tersoff–Brenner many-body potential [15]. Before adsorption simulations, all hydrogen molecules underwent an MD equilibrium run of 100 ps to achieve energy relaxation and uniform distribution in the system. The van der Waals interactions of C/H_2 and H_2/H_2 were described by the Lennard–Jones potential [16]. A cut-off radius of 0.4 nm was used to evaluate the number of hydrogen molecules adsorbed onto the graphene layers and the CNTs.

To study the mechanical properties of the nanostructure after adsorption of hydrogen, a nanoindentation simulation was performed. The van der Waals interactions between the indenter and the 3D pillared graphene were described by the

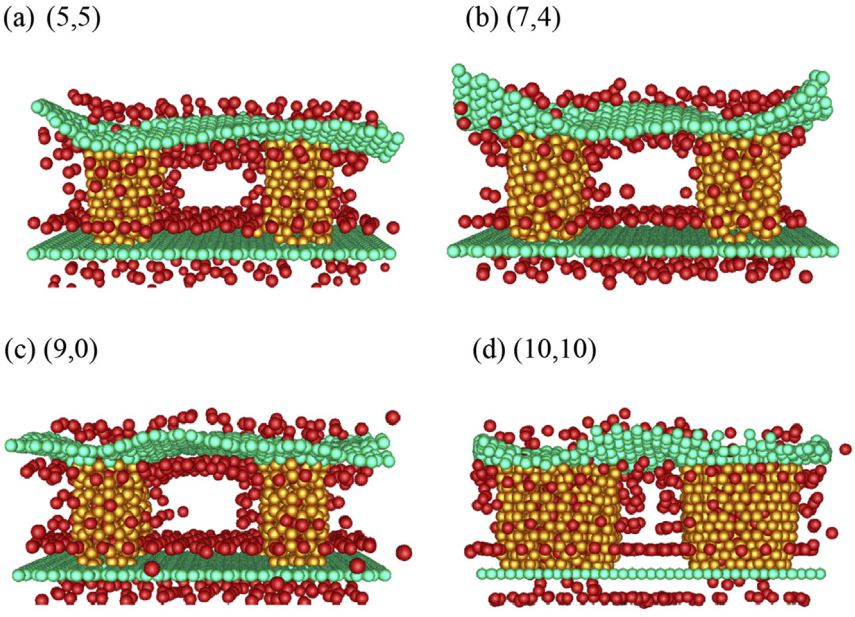

Fig. 1 – A snap of storage hydrogen simulation for a three-dimensional pillared nanostructure with different carbon nanotubes of (a) (5,5), (b) (7,4), (c) (9,0), and (d) (10,10).