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Molecular dynamic simulation of high-quality hydrogen storage in pillared bilayer graphene bubble structure

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ABSTRACT

The storage of molecular hydrogen in a novel 3D carbon structure – pillared graphene bubble system under various environments is calculated using molecular dynamics (MD) method. The graphene-based structures are designed with different sizes of semi-ellipsoidal graphene bubbles. The effects of pressure, temperature, and graphene interlayer spacing are systematically investigated in the isothermal–isobaric (NPT) ensemble. Meanwhile, the internal pressures of molecular hydrogen in bubbles under various environments are also estimated. Results show that the hydrogen storage capacity of the pillared graphene bubble structures can be maximized by decreasing the temperature and increasing the pressure and the graphene interlayer spacing. The MD simulations demonstrate that the maximum gravimetric and volumetric H_2 densities inside the developed system are 13.7 wt% and 121.6 kg/m^3, respectively. Impressively, the maximum gravimetric and volumetric H_2 densities of the developed system are also calculated – 21.3 wt% and 210.3 kg/m^3, respectively, when the outer surface adsorption are taken into consideration. These values satisfy the requirements for mobile applications set by the U.S. Department of Energy (DOE).

1. Introduction

As a clean and renewable energy source, hydrogen has been touted as an immense potential candidate for replacing fossil fuels [1–4]. A 5.5 wt% target was also set by the DOE for reversible hydrogen storage systems to be met by 2017 [5]. However, it has not been available for practical use, because of several obstacles that are needed to be overcome. One of the major difficulties is to store hydrogen safely with high enough gravimetric and volumetric densities [6]. Many methods (e.g., gaseous, liquid and solid-state storage) to store hydrogen have been investigated [6–9]. However, they cannot be popularized because of high cost, loss or safety, etc. Thus, many types of light nanoporous materials, especially carbon-based materials [e.g., carbon nanotubes (CNTs), graphite, and graphene, etc.] which give rise to a new class of hydrogen storage materials through physical adsorption of hydrogen molecules, have been widely studied as media for reversible hydrogen storage because of their mechanical properties and high surface area, etc. [10–14]. In this context, a new type of graphene-based material known as graphene bubble structure has been proposed as potential medium for hydrogen storage [15,16].

Nano-scale graphene bubbles can be obtained when multiple graphene are subjected to the irradiation of energetic protons or hydrogen atoms [15,17]. In this process, the hexagonal rings of graphene net first expand when the hydrogen atoms move close to the graphene plane and then shrink when the hydrogen atoms penetrate into graphene sheets [18]. The hydrogen atoms which penetrate into graphene sheets combine to form hydrogen molecules, and molecules cannot escape from the graphene net because of their large sizes. Then, the interactions between H_2 and carbon atoms can transmit a pressure that pushes up the carbon atoms, resulting in the formation of bubbles on the graphene sheet [15]. The proposed hydrogen storage in graphene bubble systems has been experimentally proven, in which atomic hydrogen intercalates through the graphene sheet and is molecularly stored [15–19]. Typically, these graphene bubbles can keep stable over periods of several months. However, to the best of our knowledge, there is a lack of theoretical survey concerning hydrogen storage property of the graphene bubble structures in scientific literature. This study aims to systematically and theoretically

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investigate the property of graphene bubble structures in the context of hydrogen storage.

In this paper, we perform systematic MD simulations of pillared graphene bubble structures to analyze their functions as media for hydrogen storage. However, we are most interested in the hydrogen molecules which are captured inside the bubble models because of the stability. During the simulations, we just consider the conditions of hydrogen molecules stored between graphene sheets regardless of the hydrogen adsorbed on the outer surface of graphene (This condition will be discussed briefly at the end of the article.). Hydrogen molecules are directly implanted into the graphene bubbles. The properties of hydrogen storage inside the pillared graphene bubble structures are analyzed using MD simulations in different thermodynamic conditions.

The remainder of this letter is organized as follows: In Section 2, we describe the construction process of bubble models and the computational methods of the MD simulations employed in the procedure. Section 3 is devoted on the analyses of the effects of pressure, temperature, and graphene interlayer spacing on the hydrogen storage properties of the pillared graphene bubble systems. Our conclusions are presented in Section 4.

2. Computational details

Graphene bubbles exhibited different shapes and sizes [20,21]; only small and semi-ellipsoidal bubbles were selected in this paper. Two 3D semi-ellipsoidal graphene bubbles were constructed using Materials Studio (MS) with the guide of experiments [15,22]. During this process, we first selected two carbon nanotubes (CNTs) with chiral index of (59,59) and (74,74), respectively. Then the CNTs with chiral index of (59–2n, 59–2n) and (74–20, 74–2n) (n = 1, 2, 3...) were selected, and linked with (59,59) and (74,74), respectively. Fig. 1(a) and (b) showed the connection method of CNTs. Finally, the bubbles were respectively denoted as α and β. The semi-major (b)/semi-minor radii (a) of the bubbles were 4/3 and 5/4 nm, respectively. The bubble area S [πb^2] and volume V [$(2/3)\pi a^2 b$)] for α were 5.02×10^{-13} cm^2 and 7.54×10^{-20} cm^3 respectively; S and V for β were 7.85×10^{-13} cm^2 and 1.69×10^{-19} cm^3, respectively. The pillared graphene bubble systems for the MD simulations were reduced to their building block [i.e., one semi-ellipsoidal graphene bubble, bilayer graphene sheets (lattice vectors: 60×60 and 70×70 for α and β, respectively), and four CNTs] because of computational efficiency. At the onset, four cylindrical holes were created near the corner of the graphene sheets. The diameter of the holes were chosen carefully to fit the armchair (6,6) CNTs. Subsequently, a large cylindrical hole was created at the middle of the upper graphene sheet. The diameter of the hole was selected to fit the bubble (α or β). Fig. 1(c) and (d) showed the schematic of the 3D pillared graphene bubble system. In the nanostructure, CNT pillars occupied the empty space between two graphene sheets. To facilitate the design, the intertube distances of CNT are set to 9 nm and 11 nm for α and β, respectively.

To determine the maximum number of hydrogen molecules that could be stored inside the bubbles, geometry optimization of graphene bubble structures were performed. In this process, we used the force field of condensed-phased optimized molecular potential for atomistic simulation studies (COMPASS) in the Forcite code of MS software [23,24]. The parameters of COMPASS are obtained using high precision quantum mechanical (QM) calculations. The smart algorithm was used during the geometry optimization process. This algorithm was a cascade of the steepest descent, ABNR, and quasi-Newton methods. The convergence thresholds for energy, force, and displacement were 1×10^{-4} kcal mol^{-1}, 0.005 kcal mol^{-1} Å^{-1}, and 5×10^{-5} Å, respectively. Then the samples of the configuration model were implemented in the MD simulation package. Periodic boundary conditions were applied in all three dimensions. These MD simulations were performed in the isothermal–isobaric (NPT) ensemble using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code [25]. The reactive force field (ReaxFF) potential was adapted to describe the interactions between hydrogen molecules and carbon atoms, among carbon atoms, and among hydrogen molecules [26]. The time step for all of the simulations was fixed at 0.1 fs. Each simulation ran for 200,000 equilibration steps, and the average properties of the ensemble were determined over the next 800,000 time steps. The system coordinates were collected every 100 fs. The full-precision trajectory was then recorded, and the results were analyzed. Visualization of the entire process was performed using Visual Molecular Dynamic (VMD) [27].

3. Results and discussion

The pressure, temperature, and graphene interlayer spacing significantly control the gas storage in graphene-based materials. These variables should be carefully controlled to interpret the observed hydrogen storage property of a system. In this section, the effects of pressure, temperature, and graphene interlayer spacing on the hydrogen storage inside pillared graphene bubble

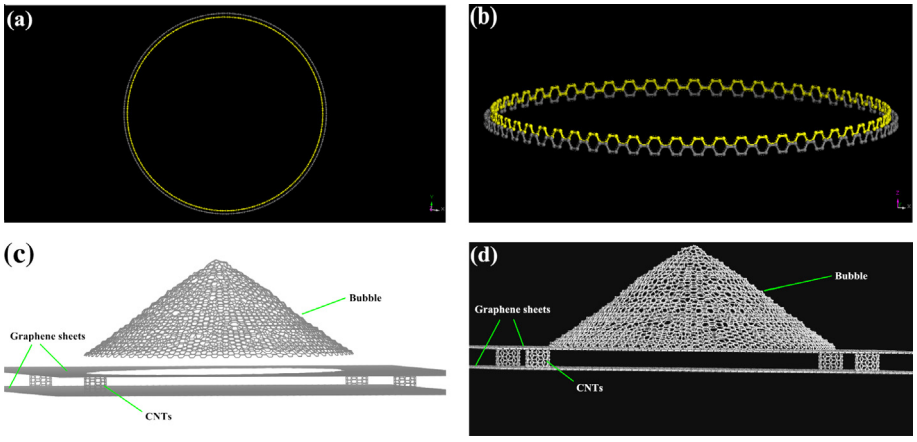

Fig. 1. (a) Vertical view of the connection of CNTs; (b) lateral view of the connection of CNTs. (c) Graphene bubble, graphene sheets, and (6,6) CNTs ready to form a building block. (d) Schematic of the 3D pillared graphene bubble structure which is the initial structure optimized by MD simulations.