Nanopores in carbon nitride nanotubes: Reversible hydrogen storage sites

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Experimental and theoretical approaches are used to determine hydrogen storage mechanisms in nanopores of multiwalled carbon nitride nanotubes (MWCNNTs). First, the authors produce ~0.6 nm pores on the stems of MWCNNTs by plasma-enhanced chemical vapor deposition. Next, thermal desorption spectra were measured and obtained two different peaks. This is explained by hydrogen desorption barriers of 0.36–0.50 eV attributed to two different types of ~0.6 nm pores. Moreover, H₂ adsorption between complete interlayers is found to be endothermic by 1.27 eV. In this respect, open channels and ~0.6 nm pores on MWCNNTs are considered to provide the route for reversible hydrogen storage.

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Hydrogen is an attractive fuel alternative to conventional hydrocarbon fuels because water is the only product when hydrogen burns with oxygen in a fuel cell. On the other hand, one of the main issues for hydrogen economy is the development of a suitable hydrogen storage material that is small, light, and safe. In addition, achieving at least the weight percent of 6.5 wt % is the goal of the U.S. Department of Energy. Because of these requirements, early in the development of hydrogen storage materials various carbon materials were investigated. This is because carbon materials can give many different types of structures, which provide a variety of hydrogen storage sites. For example, the carbon nanotubes (CNTs) having high surface-to-volume ratios were suggested as ideal structures for fast kinetics because of their reversible characteristics during hydrogenation and dehydrogenation.

Despite these advantages, recent studies have shown that the hydrogen stored on a pristine CNT is less than 0.01 wt % at 1 bar condition and room temperature. Moreover, the recent experiment by Lawrence and Xu confirmed that only 0.6 wt % hydrogen at room temperature was adsorbed on the CNT bundle at the high pressure condition of 100 bars. Also our recent study showed that liquefaction of H₂ molecules on the CNT bundle still occurs at the low temperature condition. Our experiments also demonstrate that versatile 6 Å pores could be created on the stems of the multiwalled carbon nitride nanotubes with the uniform distribution, as shown in Fig. 1.

Carbon nitride nanotubes were synthesized using a microwave plasma-enhanced CVD (PECVD). First, a 7-nm-thick Co layer was deposited on a SiO₂/Si substrate via rf sputtering with 100 W rf power. The thickness of SiO₂ on the Si wafer was 500 nm. Then, the substrate was moved...
to the PECVD chamber and the chamber was evacuated to about 0.1 Torr. Next, the substrate was heated to 720 °C in a vacuum by a halogen lamp. After that, the N₂ gas was flowed into the chamber and the substrate was treated by the N₂ plasma created using a microwave power of 750 W for 1 min. Then, 15 SCCM (SCCM denotes cubic centimeter per minute at STP) of CH₄ was introduced at 850 °C, either with N₂ only or with N₂ and H₂ gases simultaneously, and the microwave power was increased to 800 W. Different flow rates of N₂, H₂, and O₂ gases were used in each experiment. The growth time was 20 min. The morphology and the structure of the as-grown samples were analyzed via high-resolution transmission electron microscopy (HRTEM) (FE-TEM F20, Phillips). The pore distribution of the grown nanotubes was analyzed as received from the isotherm of the N₂ adsorption on the samples (Autosorb-3B, Quantachrome). Also for direct observation of nanopores created on the stems of the nanotubes, Ni nanoparticles were dispersed on their stems by the method described in the previous work. In addition, the gas chromatograph equipped with the thermal conductivity detection method and the selected capillary column (Carboxen 1006PLOT) are used to observe the hydrogen desorption property.

Figure 1(a) shows the HRTEM image of a carbon nitride nanotube where the disconnected graphene layers (in a circle) represent nanopores, while Fig. 1(b) compares the pore size distribution of the as-grown nanotubes with respect to different flow rates of N₂, H₂, and O₂ gases. The ~6 Å pores are shown on all the grown nanotubes. The volume of ~6 Å pores increased for the samples grown with an increased nitrogen flowing rate, with the minimum volume observed for those nanotubes grown at 30 SCCM of hydrogen, 55 SCCM of nitrogen, and 15 SCCM of methane. In addition, the peak around 16 Å disappeared after an inclusion of 30 SCCM of H₂ during growth. On the other hand, nanotubes grown with 4 SCCM of oxygen had the largest volume of ~6 Å pores, which was about three times larger than that of nanotubes grown with 30 SCCM of H₂, 55 SCCM of nitrogen, and 15 SCCM of CH₄. Figure 1(c) shows that Ni nanoparticles can be uniformly dispersed, implying that nanopores were uniformly created on our synthesized nanotubes.

To determine the origin of the different volumes of nanopores, x-ray photon spectroscopy (XPS) analyses were performed. We confirmed that our samples were carbon nitride nanotubes from the N 1s signal of the XPS spectrum of the as-grown sample, as shown in Fig. 2. The N 1s XPS spectra were divided by three Lorentz fits: (a) 398.2 eV is the tetrahedral nitrogen phase (N₁) bonded to an sp³-hybridized carbon, (b) 401.3 eV is the trigonal nitrogen phase (N₂) bonded to an sp³-coordinated carbon, and (c) 404.8 eV is the molecular N₂, where the binding energy of 404.8 eV is lower than original binding energy of free N₂ gas of 409.9 eV because of the screening effect between N₁ and H₂. The molecular N₂ was attributed to the trapped N₂ gas in the holes between the nodes in the CN₄ nanotubes. The ratio of peak intensities of the N₁ or N₂ (I₁/I₂) was examined. The relative peak intensity, 0.378, for tetrahedral nitrogen atoms bonded to an sp³-hybridized carbon (I₁/I₂) of CN₄ nanotubes grown with only N₂ and CH₄ is stronger than the 0.306 for nanotubes grown with N₂, H₂, and CH₄. In addition, the molecular wave function is based on the Monkhorst-Pack

FIG. 2. (Color online) N 1s XPS spectra of the carbon nitride nanotubes grown with (a) 15 SCCM of CH₄ and 85 SCCM of N₂; (b) 15 SCCM of CH₄, 55 SCCM of N₂, and 30 SCCM of H₂; and (c) 15 SCCM of CH₄, 81 SCCM of N₂, and 4 SCCM of O₂.
FIG. 3. (Color online) (a) Top and side views of penetration H\textsubscript{2} through N-doped nanopores and (b) the potential energy surface of hydrogen ensnared in the nanopores of multiwalled carbon nitride and carbon nanotubes, where the values in parentheses represent the energies on micropores with only carbon atoms on their edges, where \textit{a} is the adsorption site for H\textsubscript{2} on the exterior wall, \textit{b} is the transition state site for penetration of H\textsubscript{2} through the pore, and \textit{c} is the adsorption site for H\textsubscript{2} ensnared between the neighboring pores. (c) The H\textsubscript{2} thermal desorption spectra obtained from the nanotubes with \textasciitilde 40 nm diameters. Gray, blue, and yellow colors represent C, N, and H atoms, respectively.

We use a plane-wave basis that is truncated to include plane waves having kinetic energies of less than 240 eV. There are four configuration for H\textsubscript{2} on Fig. 3(a): (1) free H\textsubscript{2}, (2) H\textsubscript{2} physissorption on the exterior wall denoted as “\textit{a}” in Fig. 3(a), (3) H\textsubscript{2} penetration through the nanopore denoted as “\textit{b}” in Fig. 3(a), and (4) H\textsubscript{2} physissorption between the two nanopores denoted as “\textit{c}” in Fig. 3(a). The physissorption energy of a hydrogen molecule on the outside of nanopores in a doubled-walled carbon nitride nanotube was \textasciitilde 0.12 eV [see Fig. 3(b)], which is different from the \textasciitilde 0.07 eV of a double-walled carbon nanotube. The distance between the center of the adsorbing hydrogen molecule and the nanotube surface was 2 Å. In addition, the activation barrier for hydrogen penetration through the nanopore from the outside to the inside of the nanotube at \textit{b} in Figs. 3(a) and 3(b) was 0.31 eV. This barrier is found to be much lower than that for the single-wall carbon nanotube (SWNT). Indeed, Ma et al.\textsuperscript{11} estimated that hydrogen molecules need at least \textasciitilde 16.5 eV to pass through a hexagon ring of SWNT. Also the penetration barrier of 0.31 eV is lower than the barrier of 0.47 eV for H\textsubscript{2} penetration through \textasciitilde 0.6 nm pores in a multiwalled carbon nanotube. Hydrogen molecules adsorbed between two nanopores are more stable than the free hydrogen molecules by 0.17 eV, which is compared to the 0.10 eV on a pure MWCNT. Consequently, 0.36–0.50 eV [see Fig. 3(b)] are required to discharge the hydrogen molecules adsorbed between the walls of carbon nitride nanotubes, which appears to be consistent with our experimental hydrogen thermal desorption spectra, as obtained in Fig. 3(c). In this respect, it is considered that \textasciitilde 0.6 nm size pores created on the stems of carbon nitride nanotubes may consist of two different types: the first case is that their carbon atoms on the pore edges are fully replaced by nitrogen atoms while in the other case they just include carbon atoms. In addition, hydrogen ensnared between interlayers with complete benzene ring units (that is with no pore) is found to be unstable due to its having endothermic adsorption energy of 1.27 eV, implying that many interlayers existing inside MWCNNTs could reduce hydrogen storage capacity compared to the double-walled nanotube structures. In this respect, versatile 0.6 nm pores on the stems of double-walled carbon nitride nanotubes are here proposed to be ideal structures for reversible hydrogen storage. For example, the \textasciitilde 0.6 nm nanopore sites constructed by one benzene ring unit missing can be used to store hydrogen. In addition open channels with two benzene rings missing, connecting directly the outside with the inside of the double-walled nanotubes, could be used to store hydrogen inside the wall of the nanotube. The storage method through open channels is capable of giving the increasing hydrogen storage capacities larger than 7 wt % hydrogen as the pressures increase to the moderate values, attributed to many free spaces made by bamboolike structures of carbon nitride nanotubes [see Fig. 1(a)].

In conclusion, hydrogen ensnared in about 6 Å sized nanopores of a multiwalled carbon nitride nanotubes are found to be capable of being released at two different temperature ranges as they have the desorption barriers of 0.36 and 0.50 eV, but hydrogen insertion into the complete interlayer space of a multiwalled carbon nitride nanotube is determined to be endothermic by 1.27 eV. Consequently, these results imply that versatile open channels and \textasciitilde 0.6 nm pores created on MWCNNTs could provide the proper route to reversible hydrogen storage media usable for practical applications.

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