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Hydrogen storage and desorption properties of Ni-dispersed carbon nanotubes

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We report that the H_2 storage method using Ni-mediated CNTs is a viable candidate for fuel cell applications. It is demonstrated that a single Ni coated on the carbon nanotubes' (CNT) surfaces can store up to 5 H_2. In this respect, at high Ni-coverage, Ni-dispersed single-walled CNTs are considered to be capable of releasing ~10 wt. % H_2 at around room temperature. Moreover, the H_2 desorption barrier of 0.26 eV/H_2, corresponding to the desorption temperature of 328 K, is ideal for fuel cell applications. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2189587]

Hydrogen fuel, which can be produced from renewable energy sources, contains much larger chemical energy per mass (142 MJ kg^{-1}) (Refs. 1 and 2) than any hydrocarbon fuel, thus making a hydrogen fuel cell an attractive alternative to solve the present energy and environmental problems resulting from the use of petroleum fuels. The current challenge is how to develop small and lightweight hydrogen storage materials that release 6.5 wt. % (Refs. 1 and 2) or more hydrogen at around room temperature. That development is crucial for practical hydrogen fuel cell applications. Here we report that the Ni nanoparticles-dispersed CNTs could act as new routes to reversible high hydrogen storage and act as catalyst materials for many practical applications.

A hydrogen fuel cell car must store at least 4 kg of hydrogen to cover the range of a gasoline-powered car. On the other hand, to store this hydrogen at room temperature and atmospheric pressure requires such a large volume, corresponding to a balloon with a 4.5 m diameter, that it is hardly practical for a small vehicle. To reduce this problem, one could consider using liquid hydrogen for hydrogen storage since it is relatively safe and has a relatively high mass density (70.8 kg m^{-3}). However, to liquefy hydrogen is an expensive process due to the low condensation temperature (−252 °C at 1 bar) of hydrogen. An additional problem is that heat transfer through modern available containers can result in a loss of up to 40% of the energy content in hydrogen.[3] In this respect there is currently much interest in storing hydrogen in advanced carbons.

Since the first experimental report of Dillon *et al.*[4] on hydrogen storage in carbon nanotubes (CNTs), many experimental and theoretical studies on the hydrogen uptake capacity in various CNT structures have been reported.[5–7] The nanotubes, having high surface-to-volume ratios, are ideal for fast kinetics because of their reversible characteristics during hydrogenation and dehydrogenation. However, recent studies[7,8] have shown that the hydrogen storage capacity on a pristine CNT is less than 0.01 wt. % at room temperature. In this respect, to use pristine CNTs as hydrogen storage media could be impractical for applications due to the expensive cryogenic process for hydrogen adsorption (80–150 K at 1 bar) on the CNT surfaces. The recent experiment by Lawrence and Xu[9] also showed that only 0.6 wt. % hydrogen was adsorbed on the CNT bundle at 294 K and 10 MPa. Moreover, our recent study[10] showed that liquefaction of H_2 molecules on the CNT bundle still occurs at the very low temperature range of ~80 K, even under high pressure conditions larger than 2 MPa. Consequently, the hydrogen storage method using a pristine CNT is not considered as a viable technique for applications.

On the other hand, the theoretical study by Yildirim *et al.*[11] showed that a single Ti atom decorated on a single-walled (8, 0) CNT could store up to 4 H_2 molecules in temperatures up to room temperature, where the exchange-correlation functional parameterized by Perdew, Burke, and Ernzerhof[12] was used for the theory. Furthermore, our experiment for the hydrogen desorption spectra of Ni-coated multiwalled (MW) CNTs (Ref. 13) also showed that a significant amount of hydrogen (~3 wt. % H_2) could be released around room temperature. In this respect, the hydrogen adsorption process facilitated by metal nanoparticles could be suggested as an effective reversible hydrogen storage method.

Here, we demonstrate hydrogen storage and desorption mechanisms of a Ni-dispersed CNT based on density functional theory (DFT) methods[14,15] and experimental methods. We use the KMLYP (Ref. 16) and B3LYP (Ref. 17) methods to determine the electronic wave functions with a split basis set of 6-311+G(d,p) (Ref. 18) basis sets on Ni and H atoms, and the 6-31G valence double-zeta[18] basis sets for C atoms. The B3LYP is shown to accurately predict geometries and thermochemical data compared to generalized gradient approximation (GGA) and local density approximation (LDA), while the KMLYP has been proven to be more accurate in predicting transition state barriers and rate equations than other DFT methods. In this respect, geometries and thermochemical data reported hereafter are based mostly on results from the B3LYP calculations, except the rate equation for a chemisoprtion of H_2 on a metal where the KMLYP is used. The bonding nature of hydrogen with Ni dispersed on the surface of the CNT shows the presence of both strong covalent and physical forces in the bonding. Also, the energies include thermal enthalpy corrections determined at fully optimized geometries. For experiments, detailed conditions are explained in our previous paper.[13] In brief, the MWCNTs were synthesized with microwave plasma enhanced CVD.

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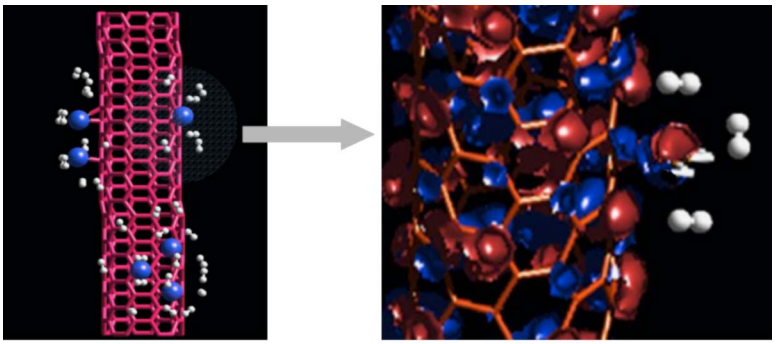

(a) (b)

FIG. 1. (Color online) (a) H_2 molecules adsorbed around Ni dispersed on the surface of a carbon nanotube. White and light blue colors are for H and Ni atoms, respectively, while the pink colors are for carbons. (b) View for molecular orbitals for 5 H_2 molecules adsorbed on the CNT.

First, the cobalt layers, with a thickness of 50 nm, were deposited on a *p*-type Si-substrate by rf magnetron sputtering at 100 W rf power. Prior to the growth of CNTs in microwave PECVD, hydrogen was introduced and plasma treatment was conducted at 1100 W microwave power for 90 s. The plasma treated cobalt seeds were used as catalytic seeds for the growth of MWCNTs. A mixture of H_2 (89.9%, vol %), CH_4 (0.1%), and O_2 (10%) was used as the gas source. The microwave power and working pressure during the growth of CNTs were 700 W and 30 Torr, respectively. The growth temperature was maintained at 750 °C using halogen lamp heating. The obtained MWCNTs had the diameters of ~30 nm. Then, MWCNTs was impregnated with a Ni nitrate acetone solutions. After immersion, the black sample was dried at 60 °C and subsequently heat-treated in H_2 gas flow. Hydrogen evolved from Ni-dispersed MWCNTs was also probed with the gas chromatograph. The temperature scanning range and the rate was set at 280–673 K and 1.5–4.5 K/min, respectively.

We determined that the pristine Ni atom has a negative value of −0.02 eV/H_2 for the change of heat in hydrogen adsorption by one hydrogen molecule. It is also found that the KMLYP activation barrier for this dissociative adsorption on a pristine Ni is 1.11 eV/H_2. Thus, using the computed partition functions for the reactants and the transition state, the reaction rate k of the canonical rate equation[19] at the KMLYP level of theory is obtained as

$$k = \Gamma(T)\frac{k_B T}{h}\frac{Q_{TS}}{Q_A Q_B}\exp\left(-\frac{\Delta E_0}{k_B T}\right), \tag{1}$$

where $\Gamma(T)$ is the thermal tunneling coefficient,[20] Q_{TS} is the partition function for the transition state, Q_A and Q_B are the partition functions for the reactants A and B, respectively, and ΔE_0 is the barrier height. The resulting temperature dependence of the dissociative H_2 adsorption on a Ni atom is given by $k = 1.44 \times 10^{11} \exp(-1.11\ \text{eV}/RT)$ ($R = 0.09$ eV K). In addition, according to the van't Hoff equation,

$$\ln P = \frac{\Delta H - T\Delta S}{RT}. \tag{2}$$

The 0.23 eV/H_2 is required as the change of heat in hydrogen adsorption on the CNT at 1 atm and at room temperature.

Figure 1 shows the adsorption by the first H_2 molecule occurs to induce the charge on Ni and is then followed by adsorptions on Ni by the other H_2 molecules with the help of the ionized charge on Ni. We find that one H_2 has a H-H bond length of ~0.83 Å, while others have physical bond characters by having H-H bond lengths of 0.73–0.74 Å. For adsorption of the first H_2, the Ni-C bond distance is elongated to 1.99 Å and the Ni-H bond distance is 1.6 Å. The Mulliken atomic charges for Ni and H atoms are 0.11*e* and 0.05*e*, respectively. Consequently, the (5, 5) CNT-1Ni$-(H_2)1$ system has 1.12 D of the dipole moment. On the other hand, the H_2 binding energy in the (5, 5) CNT-1Ni$-(H_2)_2$ system is determined to be −0.60 eV/H_2, where the H-Ni distance is 1.63 Å. This H-Ni bond length is more elongated than that in the (5, 5) CNT-1Ni$-(H_2)_1$ system. The Ni-C bond is also found to be more elongated to 2.06 Å, while the H-H bond length is shortened to 0.82 Å.

Figure 2 summarizes hydrogen adsorption enthalpies on a Ni-dispersed CNT determined at the B3LYP level of theory. The adsorption enthalpy is calculated by the following equation:

$$\Delta H = H_{tot}(H_2 + \text{Ni-dispersed CNT}) - H_{tot}(\text{Ni-dispersed CNT}) - H_{tot}(H_2), \tag{3}$$

where $H_{tot}(H_2 + \text{Ni-dispersed CNT})$ is the enthalpy calculated through thermal corrections at 298 K for the H_2-adsorped Ni-dispersed CNT, H_{tot}(Ni-dipsersed CNT) is the enthalpy for the Ni-dispersed CNT, and $H_{tot}(H_2)$ is the enthalpy for an optimized H_2 molecule. The exothermic enthalpy change in hydrogen adsorption by five H_2 molecules is −0.26 eV/H_2. This exothermic enthalpy of 0.26 eV/H_2 corresponds to the hydrogen desorption temperature of 328 K, which compares to the experimental peak (340 K), as shown in Fig. 3. On the other hand, H_2 is determined to be thermodynamically unstable upon insertion into the interlayer of a muitiwalled CNT because it has an endothermic enthalpy of 1.08 eV/H_2.

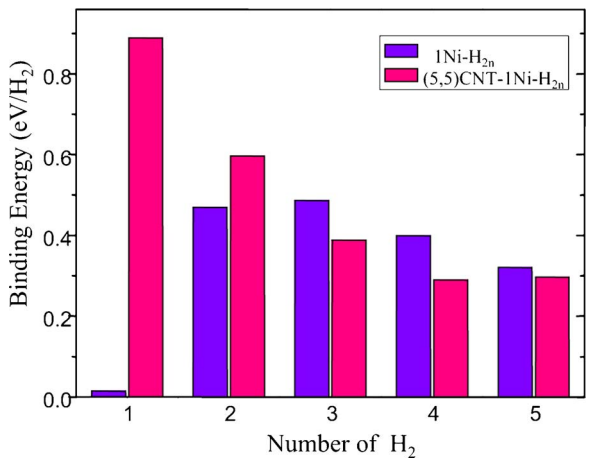

FIG. 2. (Color online) The binding energy for hydrogen adsorption on Ni at room temperature and 1 bar.

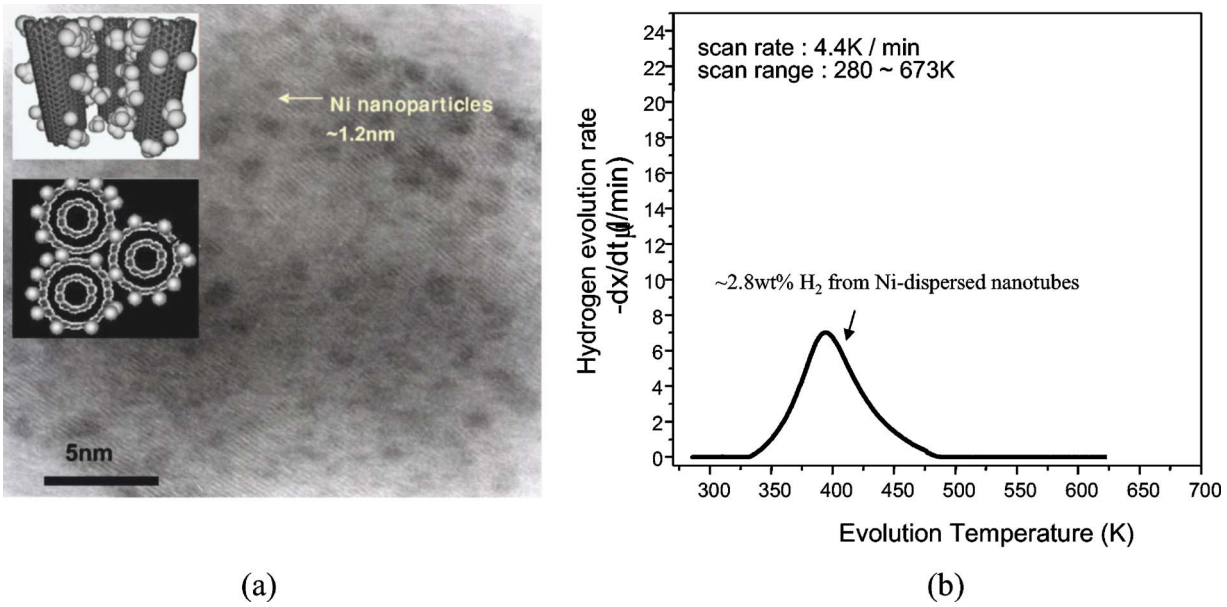

FIG. 3. (Color online) (a) Ni-dispersed multiwalled carbon nanotubes (MWCNTs) where schematic side and top views are also shown, and (b) their thermal desorption spectra of hydrogen.

Also, the change of heat in Ni dispersion, which occurs on the surface of the CNT, is estimated. We find that the most stable site is the bridge site between two neighboring C atoms, and its bonding energy is −0.56 eV/Ni. The Ni-C bond distance is 1.94 Å. However, the bonding energy of −0.06 eV between Ni and the center site of the hexagon are found to be much smaller than those of the bridge site. The Ni-C bond distance is determined to be 2.13 Å. The top site just above the C atom is also found to be less favorable for a Ni atom to be adsorbed than the bridge site. The geometry optimization with the initial positioning of a Ni atom on the top site causes Ni to eventually move to the bridge site. On the other hand, it is found that the binding energy increases to −0.80 eV/Ni when two Ni atoms adsorb on the neighboring bridge sites simultaneously. In addition, our experimental study showed that Ni with ~1 nm could be dispersed on the surfaces of multiwalled (MW) CNTs and ~3 wt. % of hydrogen was evolved between 330 K and 480 K as shown in Fig. 3. Also, the hydrogen desorption activation barrier of 0.32 eV/H_2 was calculated through the Kissinger's method,[21] which is consistent to our theoretical value of 0.26 eV/H_2.

In summary, each Ni dispersed on the surfaces of CNTs was found to store up to five hydrogen molecules with an enthalpy change of 0.26 eV/H_2 in hydrogen adsorption, which is consistent with the 0.32 eV/H_2 from the experiment. The theoretical value for the change of heat in hydrogen adsorption results in a hydrogen desorption peak position of around 328 K. Also our first principles predictions found that hydrogen is energetically unstable upon insertion into the interlayer of multiwalled CNTs. Consequently, the Ni-dispersed single-walled CNT having no interlayer is considered as a novel nanostructure capable solving hydrogen storage problems. In particular, its maximum hydrogen storage capacity of ~10 wt. % at around room temperature is shown to fulfill the United States Department of Energy (DOE) target of 6.5 wt % for hydrogen fuel cell car applications.

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