Hydrogen desorption properties of multiwall carbon nanotubes with closed and open structures

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Hydrogen desorption properties of multiwall carbon nanotubes with closed and open structures

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The multiwall carbon nanotubes (MWNTs) synthesized by microwave plasma enhanced chemical vapor deposition in 0.1% CH_4 (H_2 dilution) reaction gas were shaped in curly structures with the blocked nanoholes and closed caps. On the contrary, the carbon nanotubes with different structures could be obtained in oxygen loaded reaction gas, showing aligned structures with connected holes and open caps. The hydrogen desorption properties of the carbon nanotubes (CNTs) with these closed and open structures were compared by thermal desorption technique. The MWNTs with closed structure desorbed hydrogen at two different temperature ranges such as 290–330 and ~420 K, where the evolved hydrogen amount were ~0.64 and ~0.03 wt %, respectively. In case of aligned and open MWNTs, hydrogen as high as ~1.97 wt % was released at ambient temperature. The hydrogen desorption of MWNTs with open and closed structure at ambient temperature showed the hydrogen desorption activation energies of -16.5 kJ/mol H_2 and -18.5 kJ/mol H_2, respectively. The high temperature hydrogen desorption observed only in CNTs with closed and highly defective structure was high desorption activation energy of -124.4 kJ/mol. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1446208]

The discovery of carbon nanotubes (CNTs) in 1991 by Iijima[1] has stimulated research on a large variety of physical properties of the nanotube. Among the unique physical characteristics of CNTs, the interest in CNTs, and graphite nanofibers for hydrogen storage media is based on the idea that nanostructured environments present in these materials might afford an unusually strong stabilization forces in comparison to more conventional adsorbents. In many experimental results, the excellent hydrogen storage capacities at various temperature and pressure ranges have been reported.[2–6] However, these findings have not been easily reproduced and detailed hydrogen storage sites as well as interaction nature with CNTs are not yet well understood. It has been considered that the inconsistent results may be linked to the difference in structures of CNTs used in experiments. In particular, it has been expected that CNTs with an open end and connected nanohole could store more hydrogen molecules due to high surface area inside nanocavities.

In this report, the multiwall carbon nanotubes (MWNTs) with different structures were adopted to evaluate the hydrogen desorption behavior by the hydrogen thermal desorption apparatus connected to gas chromatograph system. Using the information of hydrogen desorption spectra, the desorption temperature, activation energies for desorption, and storage amount could be measured. The reversibility of the sites was also analyzed by cyclic hydrogen charging and discharging.

MWNTs were synthesized with microwave plasma enhanced chemical vapor deposition (PECVD). First, a cobalt layer with a thickness of 50 nm was deposited on a *p*-type Si substrate by rf magnetron sputtering at 100 W rf power and the pressure was adjusted to 30 mTorr by feeding Ar gas. 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 MWNTs. A mixture of H_2 (99.9%, vol %) and CH_4 (0.1%) was used as the gas source and the different structure of CNT was obtained by the addition of oxygen in the mixed gas (H_2: 89.9%, CH_4: 0.1%, O_2: 10%) as presented in our previous article.[7] 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. No further process was performed to purify the soot or to open the tube end with as-produced samples. To observe the hydrogen storage properties, hydrogen (99.999%) was charged under 4 MPa at 300 K for 5 h in as-produced 0.002 g MWNTs (substrate weight: 2.12 g, CNTs weight: 2 mg), and subsequently cooled to 80 K. The substrate with MWNTs was placed in quartz reactor surrounded by heating element with a programmable power supply. The injection port of gas chromatograph was connected directly to the reactor and high purity Ar (99.999%) of 1 atm was used as carrier gas. Hydrogen evolved from MWNTs was probed with gas chromatograph equipped with the thermal conductivity detection method and the selected capillary column (CARBOXEN 1006PLOT). Temperature scanning range and the rate were set to 273–473 K and 2–5 K/min, respectively. Gas chromatograph separated one gas species and insured that only hydrogen is involved in desorption peak. The reference hydrogen peak enabled the precise calculation of evolved hydrogen amount by integration of peak area. The activation energies for desorption was estimated with the aid of Kissinger's method.[8] Two kinds of MWNTs synthesized by microwave PECVD were evaluated. The first sample grown in CH_4/H_2 plasma was curly shaped

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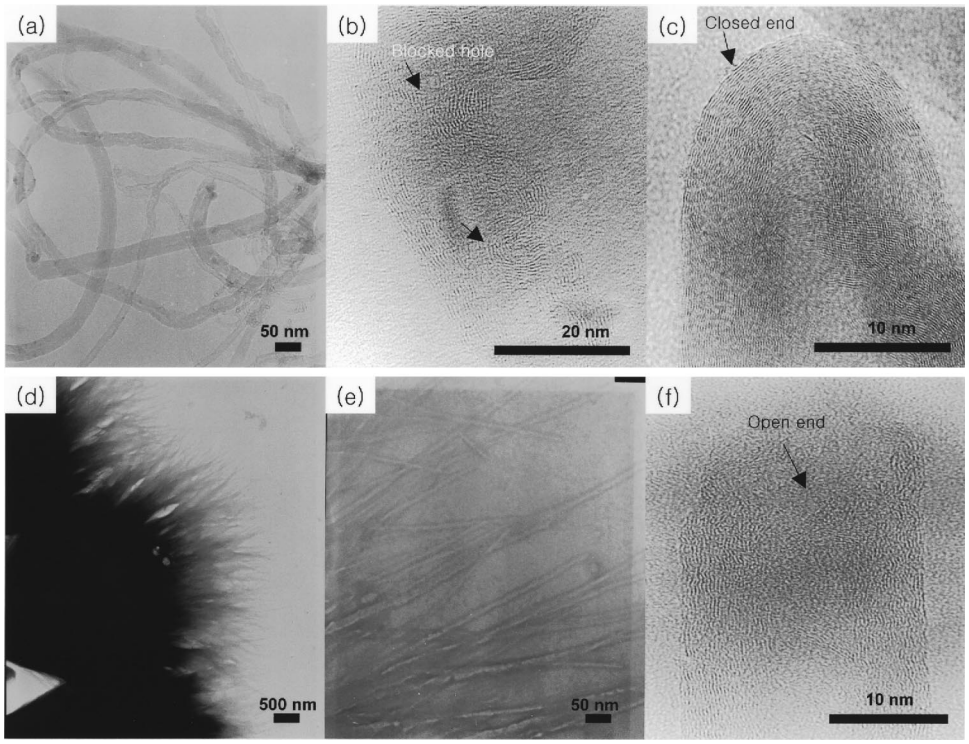

FIG. 1. Transmission electron microscopy images of (a)–(c) the curly and closed MWNTs grown in CH_4 and H_2 plasma by the PECVD method, (d)–(f) the aligned and open MWNTs grown using CH_4, H_2, and O_2 reaction gas. High-resolution transmission electron microscopy images show middle and end parts of tubes.

nanotube. As presented in our previous article, the curly structures are induced by highly defective graphene layers. As shown in Figs. 1(a)–1(c), some parts of nanohole are blocked (indicated as arrows) and most tube ends are capped firmly. The outer diameter was estimated to be from 10 to 30 nm, and the inner diameter was in the range of 5–15 nm. The specific surface area measured by means of the Brunauer–Emmert–Taylor method was ~174 m^2/g. Figure 2(a) shows the hydrogen desorption spectra of these MWNTs. It is observed that first desorption peak around 290–330 K shows a broad spectra with much higher intensity than the second peak around 420 K. In quantitative analysis on the evolved hydrogen, it is observed that ~0.64 wt % hydrogen is released at ambient temperature range and ~0.03 wt % is released near high temperature range. This result implies that the curly MWNTs with closed structure have two distinct hydrogen storage sites. In order to analyze the characteristics of two sites, it is necessary to discriminate the reaction mechanisms of two sites and to calculate the hydrogen desorption activation energies. In general, the hydrogen desorption temperature (T_C) increases with increasing temperature scan rate ($\alpha = 2-5$ K/min), and Kissinger's plot [$\ln(\alpha/T_C^2)$ vs $1/T_C$] enables us to measure the interaction energy between hydrogen molecules and MWNTs.

As shown in Fig. 3(a), the interaction energy at the ambient temperature site is about -18.5 kJ/mol H_2, which is considered to be as low as physical adsorption and somewhat lower value than the estimates on single wall carbon nanotubes reported by Dillon *et al.*[2] Meanwhile, the interaction energy of high temperature site is -124.4 kJ/mol H_2, which is comparable to chemical interaction energy between hydrogen and MWNTs. Considering the activation energy difference, we can guess that the two hydrogen storage sites in MWNTs have different hydrogen storage mechanism.

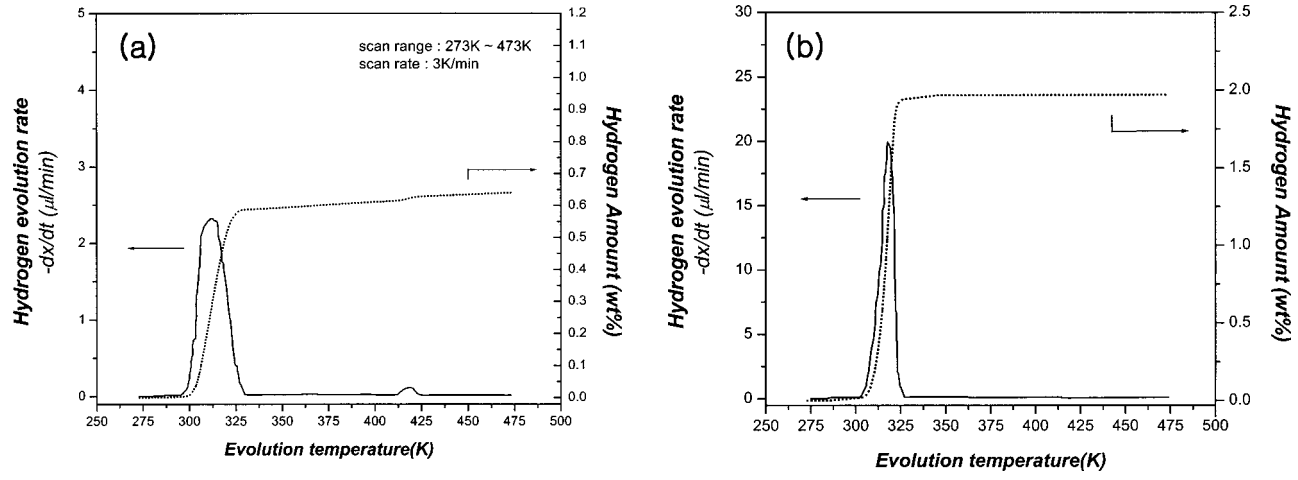

FIG. 2. Hydrogen desorption spectra and the evolved hydrogen amount of (a) MWNTs with closed structure and (b) MWNTs with open structure. The hydrogen amount was quantified by integrating and normalizing desorption peak area with respect to reference peak.

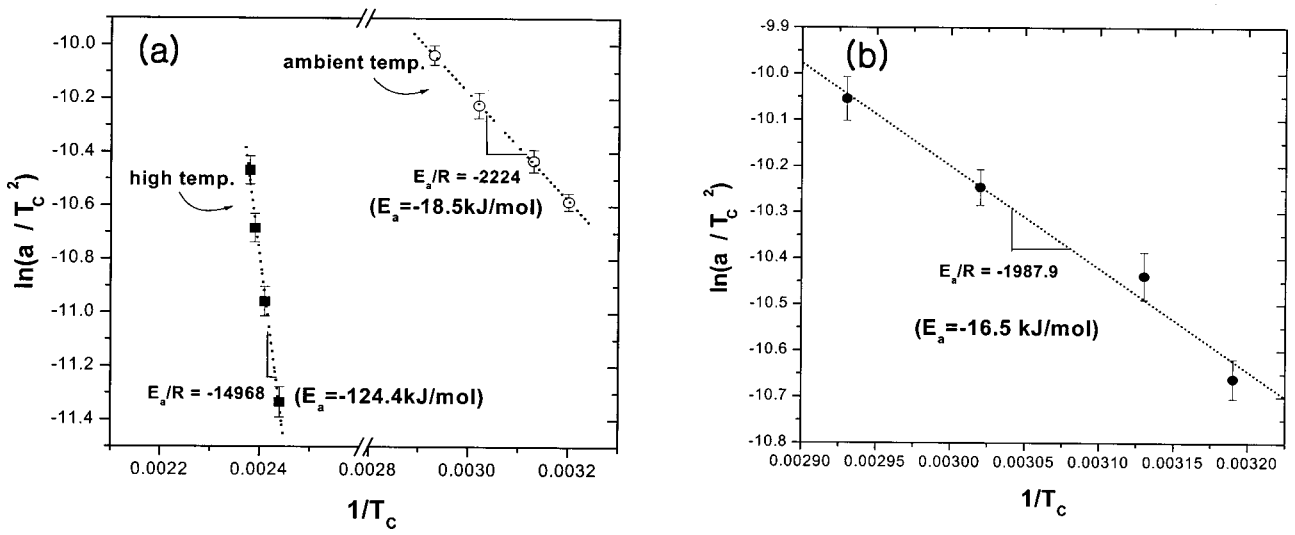

FIG. 3. Hydrogen desorption activation energies of (a) the curly CNTs with closed structure (at ambient temperature and high temperature site) and (b) the aligned CNTs with open structure (at ambient temperature site).

In case of the aligned MWNTs grown using $CH_4/H_2/O_2$ reaction gas, they have less defective structures than curly MWNTs. The nanoholes in MWNTs are connected and most tube ends are in the open state presumably by the oxygen plasma etching effect as shown in Figs. 1(d)–1(f). The outer and inner diameters are about 20 and 8 nm, respectively. The specific surface area of straight shaped MWNTs is measured to be 877 m^2/g and higher specific area is considered to be due to the open caps of these MWNTs. Figure 2(b) shows the desorption behavior of aligned MWNTs with open structure. One desorption peak with high intensity was also observed in ambient temperature range, but the high temperature peak disappeared. The quantitative result shows that the hydrogen amount evolved at the ambient temperature increases up to 1.97 wt %. It is considered that the increased hydrogen storage capacity in aligned MWNTs with open structure is related to the extended hollow holes, where hydrogen gas can be adsorbed at moderate temperature and pressure. The MWNTs used in this experiment does not show the dense alignment and bundle shape, therefore internanotube space (microchannels between the aligned CNTs) is not available hydrogen adsorption site. This result confirms that inner hole of CNTs could be major hydrogen storage site. Figure 3(b) indicates that the hydrogen desorption activation energy is estimated to be -16.5 kJ/mol, which also means the storage site at the ambient temperature range have some bearing with physisorption in nanohole.

In order to investigate the reversibility of these hydrogen sites, the cyclic hydrogen charging and discharging experiments were performed. The ambient temperature site of the curly MWNTs with closed structure is observed at next cycles and the storage amount is maintained. However, the high temperature site disappears at next cycle, indicating an irreversible site. According to Ivanov *et al.*,[9] hydrogen is generally incorporated in highly defective structure during growth stage by hydrocarbon decomposition and defective structure can be compensated by the formation of C–H bonds. The fact that high temperature peak can be observed in curly CNTs with more defective structure and high temperature site shows the characteristic of chemical interaction energy in our results supports the high temperature storage site is related with adsorption in defective structure. In the case of the aligned MWNTs, there is no significant loss in the released hydrogen amount during three cycles. It is concluded that the major hydrogen storage mechanism in the range of ambient temperature is hydrogen physisorption in nanohole of MWNTs and the irreversible chemisorbed hydrogen is attributed to the formation of the C–H bond in defective structure during hydrocarbon decomposition.

A high hydrogen storage capacity at nearly room temperature has been obtained in the aligned and open MWNTs. Even though the curly MWNTs with highly defective structures showed another hydrogen storage site, which was identified as irreversible high temperature site, the overall hydrogen storage capacity was too low to apply the MWNTs in effective storage system. The alignment and straight growth of CNTs are important to maintain the structure for the whole tube with less deformation, as well as high efficiency adsorption due to high surface area. A growth of CNTs with satisfactory morphology of connected hole and open cap is crucial for maximizing the storage capacity at room temperature and moderate pressure.

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