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Atmospheric-pressure plasma treatment to modify hydrogen storage properties of multiwalled carbon nanotubes

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We prepared multiwalled carbon nanotubes by a floating catalyst method using thermal chemical vapor deposition, but then the structures of the nanotubes were modified by the atmospheric-pressure plasma treatment to enable practical applications to hydrogen storage media. As is usually observed in multiwalled carbon nanotubes grown by thermal chemical vapor deposition, the as-grown multiwalled carbon nanotubes showed closed-cap structures and continuous walls that could not provide enough sites for hydrogen storage at ambient conditions. A thermal desorption spectra analysis showed that hydrogen was released at a temperature range of 100–150 K, where the total amount of evolved hydrogen was 4.9 wt %. However, after the atmospheric-pressure plasma treatment performed to open closed caps and create nanopores in multiwalled carbon nanotubes, it was found that the modified structures of the nanotubes released hydrogen not only at a subambient temperature range of 100–150 K, but also at an ambient temperature range of 300–330 K. The amount of released hydrogen was 5.1 wt % and 0.6 wt %, respectively. © 2005 American Institute of Physics. [DOI: 10.1063/1.1957119]

Carbon nanotubes (CNTs) with large surface area and hollow structures have attracted great interest due to their unique structures good for potential applications to hydrogen storage media. Since the first report by Dillon *et al.*¹ on the possibility of the CNT as a potential hydrogen storage material, many researchers^{2–4} have studied mechanisms for hydrogen storage in CNTs. It is commonly agreed that hydrogen storage capacities are interrelated closely with the CNT structures.^{5–9} For example, open-cap multiwalled CNTs (MWCNTs) prepared by plasma-enhanced chemical vapor deposition,¹⁰ short MWCNTs prepared by ball milling,^{11,12} and insufficiently graphitized MWCNTs prepared by an anodic aluminum oxide template¹³ have been shown to have better hydrogen storage capabilities at ambient conditions than conventional MWCNTs. The main reason for these better hydrogen properties is attributed to defective structures, such as nanopores that can also play important roles in store hydrogen. On the other hand, the problem is that plasma-enhanced chemical vapor deposition and anodic aluminum oxide template methods have certain limitations to produce a large amount of dense MWCNTs. In addition, it is also very difficult to precisely control the MWCNT structure by a ball milling process. Consequently, the development of a controllable and scalable method to create nanopores in the CNTs would be essential to enable practical applications of the CNTs to hydrogen storage media. In this letter, we report a new practical method for preparing open caps and nanopores in MWCNTs using atmospheric-pressure plasma treatment.^{14,15} A large amount of MWCNTs can be treated simultaneously by this method without any further processing.

MWCNTs were synthesized by a floating catalyst method that uses a vapor phase mixture of ferrocene

[Fe(C₅H₅)₂] and xylene [C₈H₁₀].^{16,17} A 0.04 g/ml solution of ferrocene in xylene was preheated to about 150 °C and was introduced into the growth zone with 100 sccm Ar and 100 sccm H₂. The growth temperature was set at 800 °C for 10 min and the pressure was maintained at 500 Torr. Then, the obtained MWCNTs on a SiO₂ substrate were etched immediately by the atmospheric-pressure plasma powered by a 3 kV ac field for 15 min. We used a line-shaped plasma capable of etching a large area without stopping, where 2% oxygen was added to He as an etching gas. Next the sample was degassed at 300 °C for 48 h under a vacuum below 10⁻³ Torr, and pure hydrogen (99.999%) was charged under 60 atm at 300 K for 12 h. Then, the sample was placed in a quartz reactor surrounded by the liquid-nitrogen-cooled cryostat and wound by a heating element. After gaseous hydrogen charging, samples were heated from 80 K to 723 K at a rate of 3 K/min. Evolution of the hydrogen at the increased temperatures was measured with the gas chromatograph. The reference hydrogen peak enabled a precise determination of the total amount of evolved hydrogen through integration of the peak area. After gaseous hydrogen charging, samples were heated from 80 K to 723 K at a rate of 3 K/min. Evolution of the hydrogen at the increased temperatures was measured with the gas chromatograph. The morphology of MWCNTs before and after the atmospheric-pressure plasma etching was investigated by scanning electron microscope (SEM) and transmission electron microscope (TEM) characterizations. Plasma etching effects on the crystallinity and the pore size distribution of MWCNTs were also investigated by Raman spectroscopy and nitrogen adsorption at 77 K using the Barrett–Joyner–Halenda equation.¹⁸

SEM and TEM images of MWCNTs prepared by the floating catalyst method are shown in Figs. 1(a)–1(c). As shown in Figs. 1(a) and 1(b), a large amount of MWCNTs in vertical alignments were obtained when a mixture of

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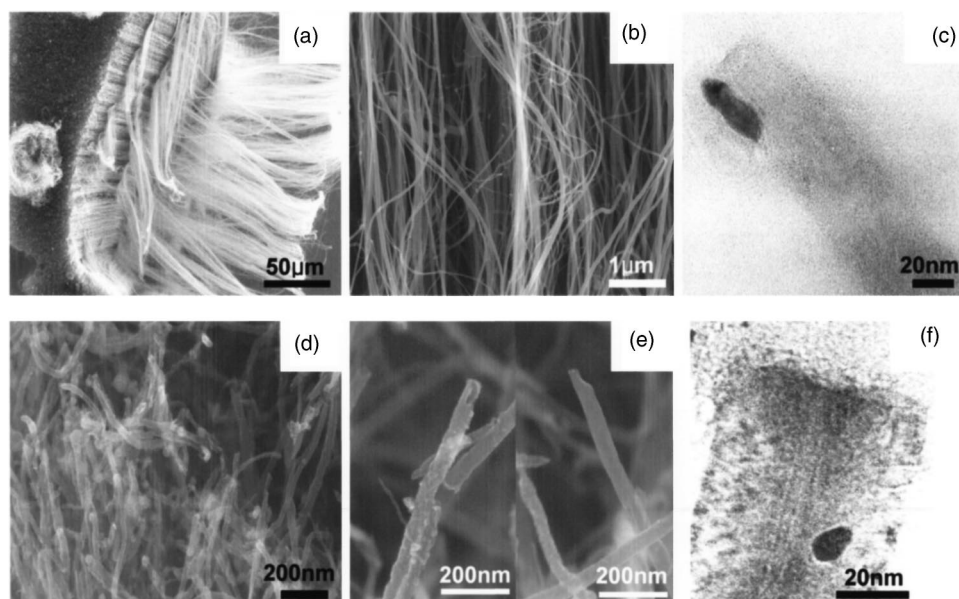


FIG. 1. (a) and (b) SEM images of MWCNTs prepared by a floating catalyst method using ferrocene/xylene. (c) TEM image of the MWCNT tip before atmospheric-pressure plasma treatment; the nanohole is closed with catalysts and graphite layers. (d) and (e) SEM images of MWCNTs after plasma etching, and (f) TEM image of the MWCNT tip after plasma etching; the tip part and the nanotube wall are damaged by plasma

0.04 g/ml ferrocene/xylene was used as a catalyst/carbon source. Their diameters and lengths were measured at 20–50 nm and 200–400 μm , respectively. The specific surface area measured by the Brunauer–Emmert–Taylor method¹⁹ was $\sim 231 \text{ m}^2/\text{g}$. As shown in Fig. 1(c), most of the as-grown MWCNTs have a straight wall and the MWCNT holes are blocked by catalyst and graphite layers. Figures 1(d) and 1(f) show the morphologies of the MWCNTs after atmospheric-pressure plasma treatment for 15 min, where 2% oxygen was added as an etching gas. In Figs. 1(d) and 1(f), the tips of the MWCNTs were removed and nanoholes were observed to be generated without significant destruction to their original structures and alignments. However, when the amount of oxygen was more than 2%, the structure collapsed, and any amount less than 2% is considered to be ineffective for opening the MWCNT holes and creating nanopores.

Figure 2(a) shows Raman spectra used to analyze the crystallinity change of the MWCNTs before and after atmospheric-pressure plasma treatment. Two peaks are detected, one at 1354 cm^{-1} (D band) and one at 1581 cm^{-1} (G band). Before plasma etching, the I_G/I_D ratio is 1.8, but it decreases to 1.2 after the 2% plasma is added. This indicates that the atomic ordering in the MWCNTs is decreased. In addition, carbon atoms etched by the plasma were found to

form amorphous structures around the nanotube wall. Also, after plasma treatment, many defect sites, such as carbon vacancies, were introduced in the etched tip parts and in the nanotube walls. Figure 2(b) shows the size distribution of various pores determined through nitrogen adsorption at 77 K using the Barrett–Joyner–Halenda equation. Compared to the as-grown MWCNTs, those that experienced plasma treatment had more 2–3 nm sized pores, and the greater number of these pores contributes to the opened MWCNT holes. Each result is in good agreement with the previous characterization results by SEM and TEM analyses.

Figure 3(a) shows the hydrogen desorption spectra of MWCNTs before plasma etching. It is observed that hydrogen evolved at only a subambient temperature range of 100–150 K. In the quantitative analysis, about 4.9 wt % hydrogen is determined to be released from this peak. However, as shown in Fig. 3(b), an ambient temperature peak at 300–330 K is also developed after plasma etching. About 5.1 wt % hydrogen is released at a subambient temperature, while about 0.6 wt % hydrogen is released near an ambient temperature. These results imply that an MWCNT after plasma treatment has two different hydrogen adsorption sites, where the peak near an ambient temperature is considered to be developed by plasma treatment.

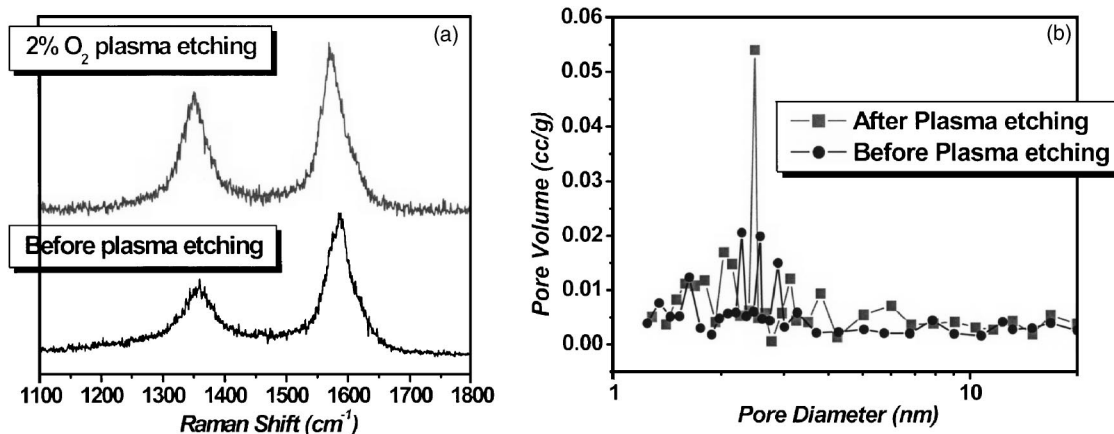


FIG. 2. (a) Raman spectra and (b) pore size distribution before and after atmospheric-pressure plasma treatment

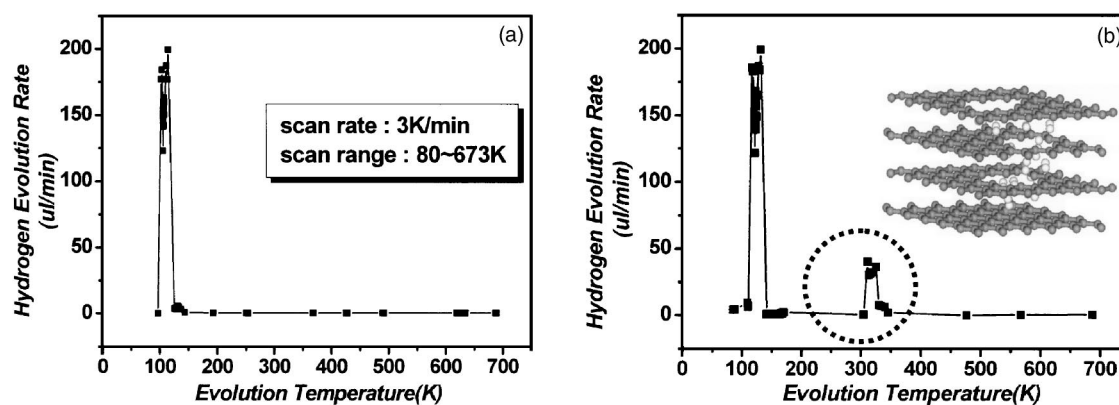


FIG. 3. Hydrogen desorption spectra (a) before and (b) after atmospheric-pressure plasma treatment where molecules shown in the inset describes desorption behaviors near room temperature of hydrogen initially stored in the nanopores. Hydrogen and carbon atoms are in white and gray colors, respectively.

Recently, many papers have reported that a structural modification, especially the creation of nanometer scale size pores in CNTs,^{10–13} was required for higher hydrogen storage capacity at an ambient temperature. From the TEM image shown in Fig. 1(f), it is observed that our MWCNTs were damaged by oxygen radicals during plasma treatment. Compared to the as-grown MWCNTs, the etched MWCNTs have open caps, defective tip edges, and rough nanotube walls. Since our MWCNTs have large open tips with diameters of 2–3 nm [see Fig. 2(b)] to expect capillary condensation, the peak near an ambient temperature was not caused by the desorption of hydrogen stored in the open MWCNT hole. Another possibility is that hydrogen atoms generated through the dissociation of hydrogen molecules adsorb the carbon vacancies in the etched tip edge. If this were true, the hydrogen would have to be very strongly bonded to the dangling carbon atoms, making it very unlikely that the adsorbed hydrogen atoms could have evolved around an ambient temperature. Therefore, hydrogen adsorption on rough surfaces is considered to be the main cause for hydrogen desorption near an ambient temperature. The rough surface, which includes a defective interlayer slit, open-ended cavities, and subnanopores, is generally introduced by insufficient graphitization during MWCNTs growth by a chemical vapor deposition. In our experiment, we used the plasma treatment to intentionally destroy a partial ordering of carbon atoms. This results in nanopores on the walls in the MWCNTs and in imperfect graphite layers, thus providing the routes for hydrogen storage in MWCNTs at an ambient temperature. The cyclic behavior for hydrogen adsorption and desorption was also tested. The amount of hydrogen desorption was maintained in a similar temperature range without significant loss for three cycles, thus implying that defective MWCNT walls with nanopores provide reversible hydrogen storage sites near an ambient temperature. In addition, we performed molecular dynamics simulations to investigate the desorption behavior of hydrogen stored in nanopores at four different temperatures of 200, 250, 300, and 350 K using a reactive force field²⁰ under a canonical ensemble condition, but found that the second peak near room temperature after plasma treatment is attributed to desorption of hydrogen stored in the nanopore [see Fig. 3(b)]. It is also found that hydrogen can be adsorbed with dangling carbon atoms near the nanopore.

In summary, we investigated hydrogen storage properties of MWCNTs before and after atmospheric-pressure plasma treatment. We found that new hydrogen storage sites were developed by plasma treatment, thus showing that an

atmospheric-pressure plasma treatment technique is a scalable and practical method to improve the hydrogen storage properties of MWCNTs. After plasma treatment, the enhanced hydrogen storage capacity was attributed to the newly created nanopore defect sites on the nanotube walls. Consequently, to obtain a higher hydrogen storage amount than that reported here, further study is required for optimizing the sizes and numbers of nanopores by varying plasma conditions such as the gas ratio, sorts, and plasma power.

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- ¹A. C. Dillon, K. M. Johns, T. A. Bekedahl, C. H. Klang, D. S. Bethune, and M. J. Heben, *Nature (London)* **386**, 377 (1997).
- ²P. Chen, X. Wu, J. Lin, and K. L. Tan, *Science* **285**, 91 (1991).
- ³Y. Chen, D. T. Shaw, X. D. Bai, E. G. Wang, C. Lund, W. M. Lu, and D. L. Chung, *Appl. Phys. Lett.* **78**, 2128 (2001).
- ⁴C. Liu, Y. Y. Fan, H. T. Cong, H. M. Cheng, and M. S. Dresselhaus, *Science* **286**, 1127 (1999).
- ⁵Y. Ye, C. C. Ahn, C. Witham, and B. Fultz, *Appl. Phys. Lett.* **74**, 2307 (1999).
- ⁶P. X. Hou, S. T. Xu, Z. Ying, Q. H. Yang, C. Liu, and H. M. Cheng, *Carbon* **41**, 2471 (2003).
- ⁷X. D. Bai, D. Zhong, G. Y. Zhang, X. C. Ma, S. Liu, E. G. Wang, Y. Chen, and D. T. Shaw, *Appl. Phys. Lett.* **79**, 1552 (2001).
- ⁸H. M. Cheng, Q. H. Yang, and C. Liu, *Carbon* **39**, 1447 (2001).
- ⁹M. Shiraiishi, T. Takenobu, A. Yamada, M. Ata, and H. Kataura, *Chem. Phys. Lett.* **358**, 213 (2002).
- ¹⁰H. Lee, Y. S. Kang, S. H. Kim, and J. Y. Lee, *Appl. Phys. Lett.* **80**, 577 (2002).
- ¹¹F. Liu, X. Zhang, J. Cheng, J. Tu, F. Kong, W. Huang, and C. Chen, *Carbon* **41**, 2527 (2003).
- ¹²Y. B. Li, B. Q. Wei, J. Liang, Q. Yu, and D. H. Wu, *Carbon* **37**, 493 (1999).
- ¹³H. Gao, X. B. Wu, J. T. Li, G. T. Wu, J. Y. Lin, K. Wu, and D. S. Xu, *Appl. Phys. Lett.* **83**, 3389 (2003).
- ¹⁴J. Park, I. Henins, H. W. Herrmann, G. S. Selwyn, J. Y. Jeong, R. F. Hicks, D. Shim, and C. S. Chang, *Appl. Phys. Lett.* **76**, 288 (2000).
- ¹⁵C. H. Yi, Y. H. Lee, and G. Y. Yeom, *Surf. Coat. Technol.* **171**, 237 (2003).
- ¹⁶B. Q. Wei, R. Vajtai, Y. Jung, J. Ward, R. Zhang, G. Ramanath, and P. M. Ajayan, *Chem. Mater.* **15**, 1598 (2003).
- ¹⁷Y. J. Jung, B. Q. Wei, R. Vajtai, and P. M. Ajayan, *Nano Lett.* **3**, 561 (2003).
- ¹⁸E. P. Barrett, L. G. Joyner, and J. Halenda, *J. Am. Chem. Soc.* **73**, 373 (1951).
- ¹⁹S. Brunauer, P. H. Emmertt, and E. Teller, *J. Am. Chem. Soc.* **60**, 309 (1938).
- ²⁰A. C. T. van Duin, A. Strachan, S. Stewman, Q. Zhang, X. Xu, and W. A. Goddard III, *J. Phys. Chem. A* **105**, 9396 (2001).