Visible-Light-Induced Water-Splitting in Channels of Carbon Nanotubes

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The visible-light-induced split of water confined in channels of single-walled carbon nanotubes (SWNTs) was experimentally studied. Arc-discharging synthesized SWNTs were used to adsorb water vapor and then were irradiated in a vacuum by using light from a camera flash. It was found that a great amount of hydrogen-rich gases could be repeatedly produced under several rapid flashes of light, occasionally accompanying evident charge emission phenomena. A quantitative method was developed to estimate the relative amount of gas components on the basis of the data acquired with an ion gauge and a quadrupole mass spectrometer. The results indicated that hydrogen occupied about 80 mol % of the photogenerated gases, with other components such as carbon oxides, helium, methane and trace of ethane, and the total gas yield in one flash ($0.1-0.2$ J/cm^2, 8 ms) reached $400-900$ ppm of the mass of the SWNTs. Such a yield could be repeatedly obtained in serial flashings until the adsorbed water was depleted, and then, by sufficiently adsorbing water vapor again, the same phenomena could be reproduced.

Introduction

Nanomaterials generally exhibit diverse and unique properties. Recently it has been reported that by exposure to light from a camera flash, single-walled carbon nanotubes (SWNTs)[1−3] and silicon nanowires[4] can be ignited and reconstructed in air and polyaniline nanofibers can be welded together to form a smooth and continuous film.[5] These surprising phenomena have been ascribed to an unprecedented photothermal effect in nanomaterials, in which the absorbed photons generate heat through nonradiative dissipation and/or photochemical reactions. The heat would be confined within individual nanostructures and difficult to be transferred to the neighboring materials and the environment, so that local hot spots of above 1500 °C in nanostructures under flashing irradiation is expected, although the input energy is only a short-pulsed white light.[1−5] These interesting facts inspired us to think about the possibility of splitting SWNT-confined water under a visible light flash.

Water-containing SWNTs were originally suggested theoretically as a wetting phenomenon by Dujardin and co-workers.[6] Since then, many theoretical studies on the structure and dynamics of water confined in SWNTs by molecular dynamics (MD) simulations have been reported,[7−14] and a few experimental observations have also been carried out to investigate its unique properties.[15] Up to now, although some disagreements about the structure of SWNT−water exist among these papers, it is in high agreement that the existing status of nanotube water is very different from that of the bulk one due to the SWNT confinement. Very recently, Kolesnikov and co-workers[15] studied nanotube water by both neutron scattering and MD simulation and revealed anomalously soft dynamics in it. Either the intramolecular covalent bonds or the intermolecular hydrogen bonds have been verified as considerably different from that of bulk water/ice; especially, the hydrogen bonds among the water chains inside SWNTs are highly softened, so the water molecules have a high mobility in SWNTs. However, the interactions between the entrapped water and the SWNT wall are very strong. The SWNT−water system has been expected to have potential applications in nanofluidic and proton storage devices. In this paper, we will show a new application possibility for such a system.

Now that the nanotube water has a special structure and dynamics different from that of the bulk one and SWNTs have a highly efficient photothermal effect under a flash, one can naturally wonder what would happen when the water-filled SWNTs were irradiated. This question has never been answered until now to our knowledge. Three years ago, for reproduction Ajayan's SWNT ignition experiments,[1] our group occasionally found that by serially exposing SWNT samples in an ultrahigh vacuum (UHV) chamber with the light from a camera flash several times, remarkable hydrogen and other gases could be continually generated. This result has puzzled us for a long time, because there was not any hydrogen source involved in our SWNT sample elaboration, and the adsorption of hydrogen from the ambient air would be very little since hydrogen content in the atmosphere is very low (∼0.5 ppm in volume), and moreover, our UHV chamber containing the SWNT sample had been sufficiently heated under a high temperature. To find a reasonable solution, recently we designed a special experimental procedure, carefully analyzed the flash-released gases by using a quadrupole mass spectrometer (QMS), and managed to obtain some quantitative results. We found that the flash-released gases evidently arose from the split of water encapsulated inside SWNT channels and the chemical reactions between them. Moreover, occasional charge emission phenomena accompanying the gas release have also been observed. We suppose that

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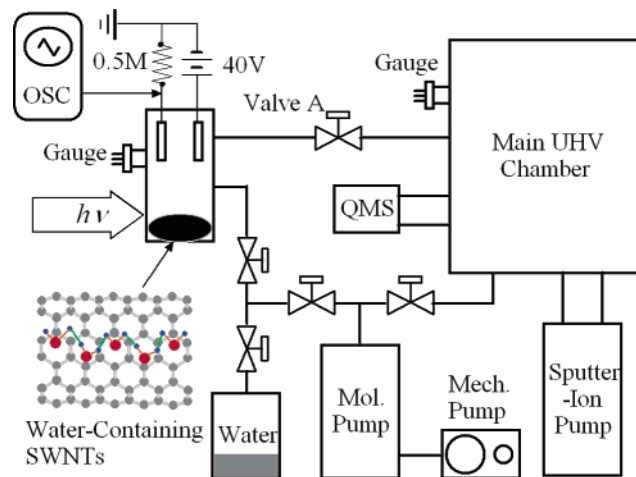‡ College of Chemistry and Molecular Engineering.

Figure 1. Schematic showing the experimental setup. The gas and charge release from water-containing SWNTs under a visible light flash can be detected by using an ionization gauge and a special circuit, respectively. Then the gases can be sampled and analyzed by using a QMS. The insert is a schematic showing a water-containing SWNT.

our research is of significance both in exploration of new hydrogen energy sources and in fundamental research regarding SWNT−water systems.

Experimental Section

Our experimental setup is schematically shown in Figure 1. A glass tube containing ∼10 mg of SWNT raw materials, synthesized by using a direct current (DC) arc-discharge method[16] with Ni−Y particles as the catalyst under a helium pressure of about 500 Pa, was connected through valves to an ultrahigh vacuum (UHV) system and to a vacuum bottle containing distilled water. The sample container (V_s) could be evacuated by using the forestage pumps and the sputter-ion pump through different valves, and its pressure can be measured by using a high-pressure ionization gauge. Two electrodes for charge emission measurement are suspended in the V_s and connected to the ground through 40 V DC batteries and a 0.5 MΩ resistor, respectively. One digital oscilloscope (Tektronix TDS3052) was used to monitor the electrical current passing through the resistor. After sufficient heating (at 180 °C for longer than 24 h) and evacuating, a UHV ($P < 5 \times 10^{-7}$ Pa) was achieved both in the V_s and in the main chamber, to which a homemade quadrupole mass spectrometer (QMS) is attached. Then valve A was closed, and the saturated water vapor (∼3500 Pa) from the water bottle was introduced into the V_s and kept for 1 h. Next, the V_s was heated and evacuated again. Subsequently, by stopping the sputter-ion pump and closing valve A, the two rooms were in a pressure-increasing state separately. When the pressures in the two rooms became quasi-stable, the water-containing SWNT sample was exposed to a photographic flash (0.1−0.2 J/cm², ∼8 ms). The rapid rise of the total pressure in the V_s was recorded. At the same time, the response of the oscilloscope was also monitored. At last, by slightly opening valve A for gas sampling, the gas components were analyzed by using the QMS. When the gas-releasing properties of the sample were obviously degraded, saturated water vapor was introduced into the V_s again, and the same experiments were repeatedly conducted.

For comparison purposes, we also used ∼25 mg of graphite powder (∼20 μm in diameter) containing the same catalyst (Ni−Y particles) as the sample to do the experiments described above.

Quantitative Analysis Methods

After flash irradiation, the total pressure increment in the V_s indicated by the high-pressure ionization gauge, $\Delta P_t(\text{gauge})$, comes from the combination of all of the real partial pressure increments, ΔP_i, as following

$$\Delta P_t(\text{gauge}) = \sum_i \alpha_i \Delta P_i \qquad (1)$$

where α_i is the relative ionization coefficient of the ith gas in the gas mixture ($\alpha_{N_2} = 1$).[17] However, when the gas mixture was sampled for QMS analysis, all components will be reflected in the mass spectra as peaks of ion current increments, ΔI_j. Each peak can be factorized into several gas sources

$$\Delta I_j = SGK \sum_k \alpha_k \beta_k^j \Delta P_k \qquad (2)$$

where S and G are the ionization sensitivity of N_2 and the multiplier gain of the instrument, respectively. K is the sampling factor, k is the index of the gases that contribute ions to the peak at the atomic mass unit (AMU) j, α_k is the relative ionization coefficient of the kth gas, which is assumed to be the same as that in the ionization gauge, and β_k^j is the relative intensity coefficient at AMU j in the cracking patterns of the kth gas.[17] To eliminate the unknown proportionality constants S, G, and K, we divide the concrete formulas as shown in eq 2 for different AMU peaks by that of AMU 2, because the intensity of the flash-released H_2 is stable relative to other gases with increase in the flash times

$$\frac{\Delta I_j}{\Delta I_2} = \frac{\sum_k \alpha_k \beta_k^j \Delta P_k}{\sum_n \alpha_n \beta_n^2 \Delta P_n} \qquad (j \neq 2) \qquad (3)$$

where n is the index of the gases that produce ions at AMU 2. Combining eq 3 with eq 1, one can get a set of linear equations regarding the unknown quantities ΔP_i. The number of the ion current peaks in the mass spectrum is usually more than the number of the gas components, so the equation system is generally overdetermined. (The number of unknown quantities is less than the number of equations.) So, a mean-square method was used to obtain the best-fit solution. After the values of ΔP_i are obtained, the molar amount of each flash-released gas, $\Delta \nu_i$, can be calculated as

$$\Delta \nu_i = \frac{\Delta P_i V_s}{RT} \qquad (4)$$

where $R = 8.314$ J mol⁻¹ K⁻¹ is the gas constant, T is the temperature in Kelvin (taking $T = 300$ K for room temperature), and V_s is the volume (∼200 mL) of the sample container. The molar percentage of the ith gas was defined as

$$\eta_i = \frac{\Delta \nu_i}{\sum_j \Delta \nu_j} \qquad (5)$$

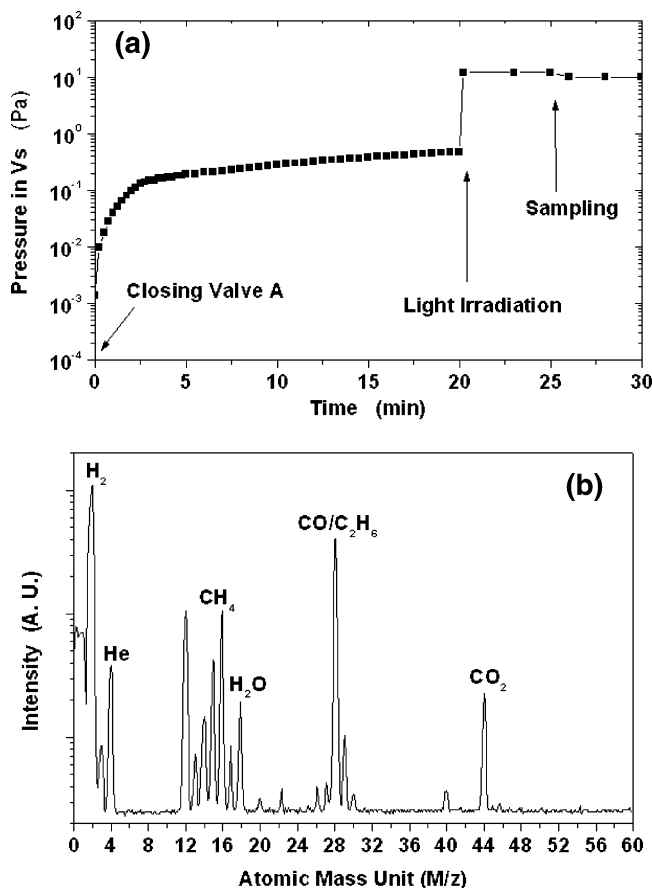The mass yield of gases, defined as the ratio of gas masses to

Figure 2. Typical experimental result of gas release. (a) The total pressure in the V_s evolving with time. A step appears when the sample is irradiated. (b) One mass spectrum of the sampled gases. The base spectrum obtained before sampling has been subtracted from the original data. The main components have been labeled above the corresponding peaks.

the mass of SWNTs, m, can be expressed in ppm

$$\epsilon_i(\text{ppm}) = \frac{\Delta \nu_i M_i}{m} \times 10^6 \qquad (6)$$

where M_i is the molar mass of ith gas.

As for the measurements of charge emissions, we directly monitor the electrical potential difference between the two ends of the 0.5 MΩ resistor by using an oscilloscope and then apply Ohm's law to obtain the current passing through it

$$I\,(\text{nA}) = U/R = 2U \quad (U \text{ in mV}) \qquad (7)$$

At last, the charge quantities can be obtained by using a digital integral method.

Results and Discussion

Figure 2 shows a typical experimental result of gas release. As shown in Figure 2a, the total pressure in the V_s approximately stabilized between 10^{-2} to 10^{-1} Pa several minutes after valve A was closed. Then, when the sample was exposed to a flash, it immediately rose to ~12 Pa, suggesting that a great amount of gases were generated. The mass spectrum of the sampled gases is shown in Figure 2b, noting that the base spectrum obtained before sampling has been subtracted from the original data. One can see that hydrogen is the main component of the flash-generated gases. Besides H_2, other components such as He, CH_4, H_2O, CO, C_2H_6, and CO_2 can also be found, as
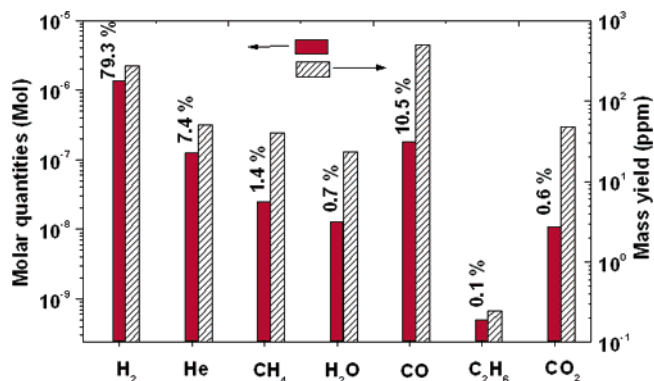

Figure 3. Quantitative estimation of the gas components generated from the water-containing SWNTs in one flash irradiation.
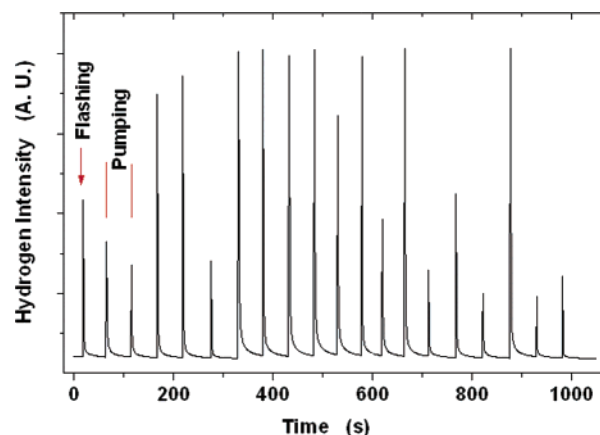

Figure 4. Hydrogen intensity changes with sequent times of flash irradiation, obtained with QMS while the V_s was pumped.

indicated in Figure 2b. The nonlabeled peaks are either attributable to the fragments of these gases or rather insignificant. It should be argued that the presence of N_2 (mainly at AMU 28) in the flash-released gases is nearly impossible. To confirm this, we additionally did a comparison experiment in which dry SWNTs were exposed to dry N_2 instead of H_2O vapor and found that no obvious gas was released under a light flash. We believe that the N_2 adsorbed by the SWNTs in air had been completely desorbed during the heating−pumping process even before the light flash.

The above experimental results were quantitatively calculated, and the result is shown in Figure 3, in which one can see that the production of H_2 in one flash reaches ~1.5 μmol, equaling to ~300 ppm of the mass of SWNTs and to 79.3 mol % of the total flash-generated gases. CO is the second one, occupying about 10.5% (~500 ppm of the mass of SWNTs). All of the other components, He, CH_4, H_2O, CO_2, and C_2H_6, occupy the residual percentage. The total mass yield of all of the gases in one flash reaches about 900 ppm (~0.09%) of the mass of the SWNT sample. Such a yield is considerably high, noting that the time for the gas release is very short (<1 s).

We also found that when the flash times are increased, the total mass yield was in a range of 400−900 ppm, and the relative quantity of each flash-generated gas could change. However, a similar hydrogen yield could last for more than 10 exposures of the sample to the rapid light flash. The spectrum shown in Figure 4 was obtained with the QMS in "single-ion" mode, namely, only H_2^+ ions were detected versus time, by serially irradiating the sample while valve A was open and the sputter-ion pump was working. Each peak corresponds to one hydrogen release in one flash irradiation, and the period between two
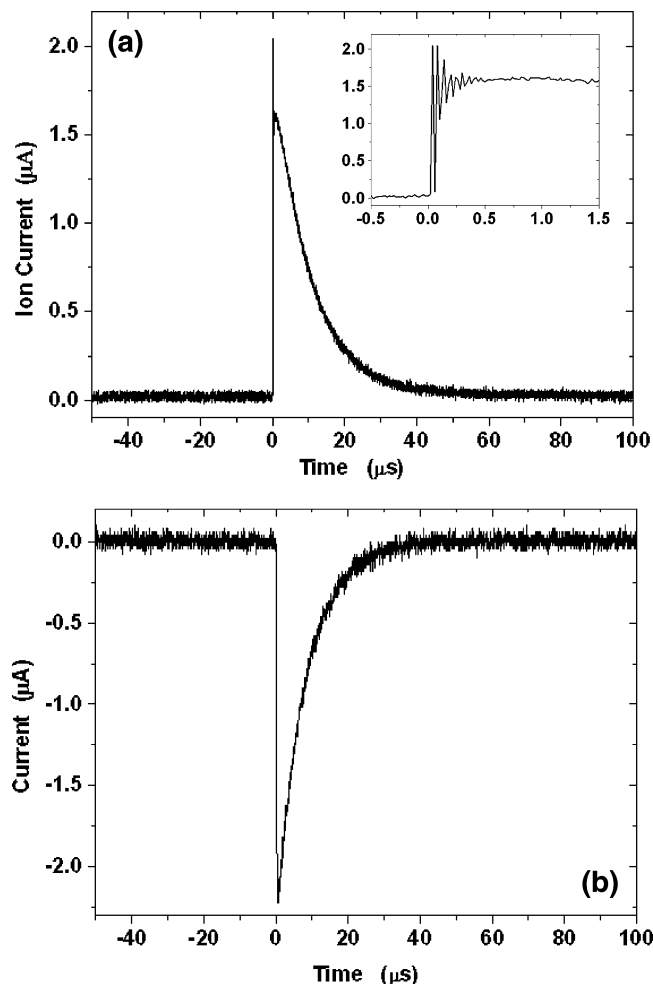
Figure 5. Measurements of charge emission accompanying gas release. (a) A typical result of flash-induced positive current. The insert is an *x*-axial magnification of the measured signal near *t* = 0; the damping oscillation phenomenon is apparent. (b) A typical result of flash-induced negative current.

consecutive peaks corresponds to the pumping time. One can see, during a period of 1000 s, 20 irradiation flashes were carried out, and obvious hydrogen peaks were detected for each time, with a peak intensity difference of a factor of 3−4. If we make an assumption that ∼0.75 μmol of H_2 has been generated on average during each flash irradiation, then during the total period of 1000 s, 15 μmol of H_2 had been released, meaning that the H_2 production rate was 54 μmol/h, which is at least comparable with the data obtained from the photoelectrochemisty (PEC)-based water-splitting method reported by Zou et al.[18] It should be noted that the PEC method requires sophisticated functional (high conversion efficiency and working stability, long lifespan, and low cost, etc.) materials as the photoelectrode, which is the main technical challenge now.[19]

In addition to the gas emission, we also occasionally observed charge emission phenomena. We used the photovoltaic signal of the light of the camera flash as the external trigger of the oscilloscope and monitored the voltage across the 0.5 MΩ resistor. A typical result is shown in Figure 5a. At the very beginning of the flash irradiation, a positive current pulse, 2.2 μA in peak value and 50 μs in bottom width, was generated. The total charge in the pulse can be estimated to be ∼2.6 × 10^{-11} C, corresponding to ∼1.6 × 10^8 singly charged ions. A damping oscillation with a frequency of about 20 MHz appears within the first 0.5 μs, and then the positive current could keep nearly constant for several microseconds before exponentially

decreasing, as shown in the insert of Figure 5a. Also, when the polarity of the DC batteries in the measurement was reversed, the polarity of the current pulse could be accordingly reversed, i.e., negative pulses could be obtained. One such example is given in Figure 5b. The above results suggest that generation of plasma could accompany the gas release when the water-containing SWNTs were illuminated by a visible light flash. Here, we have to emphasize that such current pulses could not be always detected in every flash irradiation. They emerged only occasionally, although gases could be definitely generated once the sample was irradiated by a flash. The reason is not clear to us at the present stage.

More importantly, we also found that when the flash-released gases obviously decreased due to the depletion of nanotube water, i.e., no obvious pressure increase in the sample container could be detected after a flash irradiation and no charge emission could be observed for a long time, the gas generation and charge emission ability could be recovered by inputting water vapor into the sample container again. We repeatedly conducted the above experiments for more than 20 times with the same SWNT sample and found no obvious degradation in gas release and charge emission in the end.

The comparative experiments on a micro-graphite-catalyst sample, in contrast, showed a poor outgassing abilities under the same conditions. For such a sample, we found that the gas-release phenomena appeared only for the first few times of rapid light exposure, and the total gas yield is far lower (<0.01%) than that of the SWNTs, and moreover, no charge emission phenomena have been observed during 20 flash exposures. The components of the released gases mainly included H_2, CO, and CO_2 but no He, H_2O, CH_4, and C_2H_6 have been detected. It means that most water adsorbed on the powder surfaces has been removed during the heating−pumping process, and the few residual water molecules could also be decomposed to form H_2 and carbon oxides through chemical reactions. But some important reactions in the SWNT cases did not occur in this situation.

At last we will give a tentative discussion on the mechanism of the gas release from water-containing SWNTs under a flash. Here, the SWNTs were used both as the carrier of nanowater and as the photocatalyst. Taking the ultra-photothermal effect of nanomaterials[1−5] into account, one could imagine that under an optical flash SWNTs and the confined water absorbed photons, disassociating the water molecules and generating O and H atoms. The local pressure in nanotubes would dramatically increase, so a local explosion would occur in the nanotubes, liberating some C atoms. As a result, H_2 and some C−H and C−O compounds as well as H_2O could be detected. We noted that the molar quantity of oxygen in all of the generated gases was very low compared with that of hydrogen. We think that because atomic O is very active, it could preferentially react with the catalyst particles in the SWNT sample (we indeed found some lumps such as ore in the sufficiently flash-irradiated SWNT sample) and react with the hot filaments of tungsten in our QMS and ionization gauge under high temperature. As for He, although it could be attributed to the synthesis process of SWNTs, it really seems strange to us at the present stage and deserves further investigation. The occasionally observed charge emission phenomena mean that some ionization process, such as thermal ionization and photon ionization, could occur accompanying the gas release under special conditions. Since the first ionization energies for the involved atoms and molecules are between 6.217 eV (for Y) and 24.587 eV (for He),[20] if thermal ionization has occurred, one can infer that the instant

Water-Splitting in SWNTs

J. Phys. Chem. B, Vol. 110, No. 4, 2006 **1575**

local temperature within the channels of the SWNTs should be at least 10^4 K. However, photon ionization seems impossible because visible light does not have high energy. Although the concrete ionization process is not clear at the present stage, this observation makes us believe that some local high-energy spots in the water-containing SWNTs would be generated by exposure to a visible light irradiation. That supports the opinion of thermo-splitting of water confined within the channels of the SWNTs.

Conclusion

In conclusion, on the basis of the unusual photothermal effects of nanomaterials and the special status of the nanotube-confined water, we proposed a simple way to generate hydrogen-rich gases from water-containing SWNTs by only an optical flash. The flash-released gases were quantitatively analyzed by using an ion gauge and a QMS, which shows that H_2 and CO are the main components in the gas mixture. Totally, the mass of the flash-released gases reaches 900 ppm of the mass of the SWNTs. Meanwhile, sometimes we detected charge emissions accompanying the gas release, which deserves further research.

References and Notes

(1) Ajayan, P. M.; Terrones, M.; de la Guardia, A.; Huc, V.; Grobert, N.; Wei, B. Q.; Lezec, H.; Ramanath, G.; Ebbesen, T. W. *Science* **2002**, *296*, 705.

(2) Smits, J.; Wincheski, B.; Namkung, M.; Crooks, R.; Louie, R. *Mater. Sci. Eng., A* **2003**, *358*, 384.

(3) Braidy, N.; Botton, G. A.; Adronov, A. *Nano Lett.* **2002**, *2*, 1277.

(4) Wang, N.; Yao, B. D.; Chan, Y. F.; Zhang, X. Y. *Nano Lett.* **2003**, *3*, 475.

(5) Huang, J.; Kaner, R. B. *Nat. Mater.* **2004**, *3*, 783.

(6) Dujardin, E.; Ebbesen, T. W.; Hiura, H.; Tanigaki, K. *Science* **1994**, *265*, 1850.

(7) Hummer, G.; Rasaiah, J. C.; Noworyta, J. P. *Nature* **2001**, *414*, 188.

(8) Gogotsi, Y.; Libera, J. A.; Yazicioglu, A. G.; Megaridis, C. M. *Appl. Phys. Lett.* **2001**, *79*, 1021.

(9) Koga, K.; Gao, G. T.; Tanaka, H.; Zeng X. C. *Nature* **2001**, *412*, 802.

(10) Mann, D. J.; Halls, M. D. *Phys. Rev. Lett.* **2003**, *90*, 195503.

(11) Mashl, R. J.; Joseph, S.; Aluru, N. R.; Jakobsson, E. *Nano Lett.* **2003**, *3*, 589.

(12) Marti, J.; Gordillo, M. C. *Phys. Rev. B* **2001**, *63*, 165430.

(13) Dellago, C.; Naor, M. M.; Hummer, G. *Phys. Rev. Lett.* **2003**, *90*, 105902.

(14) Wang, J.; Zhu, Y.; Zhou, J.; Lu, X. H. *Phys. Chem. Chem. Phys.* **2004**, *6*, 829.

(15) Kolesnikov, A. I.; Zanotti, J. M.; Loong, C. K.; Thiyagarajan, P.; Moravsky, A. P.; Loutfy, R. O.; Burnham, C. J. *Phys. Rev. Lett.* **2004**, *93*, 035503.

(16) Shi, Z. J.; Lian, Y. F.; Zhou, X. H.; Gu, Z. N.; Zhang, Y. G.; Iijima, S.; Zhou, L. X.; Yue, K. T.; Zhang S. L. *Carbon* **1999**, *37*, 1449.

(17) O'Hanlon, J. F. *A User's Guide to Vacuum Technology*; John Wiley & Sons: New York, 1980; pp 73−383.

(18) Zou, Z.; Ye, J.; Kazuhiro, S. K.; Hironori, A. H. *Nature* **2001**, *414*, 625.

(19) Nowotny, J.; Sorrell, C. C.; Bak, T.; Sheppard, L. R. *Sol. Energy* **2005**, *78*, 593.

(20) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. No. 1, pp 1−872.