

ARTICLES

Surface Area Measurement of Functionalized Single-Walled Carbon Nanotubes

Soma Chakraborty,[†] Jayanta Chattopadhyay,[†] Haiqing Peng,[‡] Zheyi Chen,[‡] Arnab Mukherjee,[†] Rolf S. Arvidson,[‡] Robert H. Hauge,[†] and W. E. Billups^{*,†}

Department of Chemistry and The Richard E. Smalley Institute for Nanoscale Science and Technology, Rice University, Houston, Texas 77251, and Department of Earth Science, Rice University, Houston, Texas 77251

Received: August 5, 2006; In Final Form: September 28, 2006

Single-walled carbon nanotubes have been functionalized and the specific surface areas of the functionalized nanotubes measured. Contrary to expectations, functionalization leads to a decrease in specific surface area compared to that of the unfunctionalized nanotubes. Treatment with a concentrated 1:1 nitric/sulfuric acid mixture followed by high-temperature baking at 1000 °C was found to increase the specific surface area of the nanotubes. For the unfunctionalized SWNTs, this treatment increases the specific surface area (SSA) by 20%. In the case of SWNTs functionalized by *n*-butyl groups the increase in the SSA was nearly 2-fold with the value increasing from 410 (drying at 110 °C) to 770 m²/gm (acid and bake treatment followed by drying at 110 °C). For the ozonized SWNTs, the SSA increases more than 3-fold from 381 (drying at 110 °C) to 1068 m²/gm (acid and bake treatment followed by drying at 110 °C). SEM images indicate that the nanotubes rebundle in the solid state with an average bundle size of 10–30 nm. AFM studies show that the ozonized tubes have been cut to short bundles after ozonolysis. Hydrogen uptake studies carried out on the baked ozonized tubes led to a 3 wt % hydrogen uptake at 77 K and 30 bar.

Introduction

Single-walled carbon nanotubes (SWNTs) have unique one-dimensional characteristics in atomic and electronic structures as well as a strong affinity to bind molecules and ions.^{1–8} These features suggest that SWNTs may be useful for hydrogen storage.^{6,9–14} Hydrogen storage has previously been reported with a sample containing unpurified SWNTs⁶ and various theories have been proposed in this regard.^{15–17} Hydrogen adsorption has also been studied on SWNTs at low temperature (70 K) and it has been reported that hydrogen adsorption is directly proportional to the BET surface area.¹⁸ Other reports describe increased hydrogen absorption for herringbone-like carbon nanofibers resulting from lattice expansion by acid intercalation followed by thermal shock treatment.²³ Our group had reported previously that SWNTs can be reductively coupled to yield debundled functionalized SWNTs.^{19–22} In view of these results we adapted this method of functionalization followed by high-temperature heating to increase the surface area of the SWNTs. In this paper, we report surface area measurements (SSA) for a series of functionalized SWNTs and hydrogen adsorption measurements using samples determined to exhibit the highest specific surface area.

Experimental Section

Materials. The SWNTs were prepared by a gas-phase process with use of carbon monoxide as the feedstock and iron

pentacarbonyl as the catalyst (HiPco process). The crude SWNTs were purified as reported by Chiang et al.²⁴ Lithium (granules, 99%), 1-iodobutane, 1-iodoadamantane, 5-bromovaleric acid, 1-iodododecane, and 3-chloroperoxybenzoic acid (*m*-CPBA) were all purchased from Aldrich. Acids used for exfoliation were purchased from Fischer Scientific and used in concentrated form: sulfuric acid (95–98%) and nitric acid (70%).

Synthesis. The functionalization reactions were carried out as previously reported.^{19–21} A representative example is given herein. The derivatization reaction was carried out in a 100 mL three-necked round-bottom flask fitted with a dry ice condenser and previously flame dried. Under an argon atmosphere, 20 mg (1.6 mmol) of SWNTs was added to the reaction vessel followed by condensation of dry ammonia (60 mL) and addition of small granules of lithium metal (85 mg, 12.0 mmol). The resulting solution was stirred for 30 min in a dry ice–acetone bath and 1-iodobutane (1.18 g, 6.4 mmol) was added slowly. The solution was stirred overnight at room temperature leading to slow evaporation of ammonia. The flask was then cooled in an ice bath and the reaction mixture quenched by slow addition of ethanol (10 mL) and water (20 mL). The product was acidified with 10% HCl and the nanotubes were extracted into hexanes and washed several times with water. The hexane layer was then filtered through a 0.2 μ m PTFE membrane. The precipitate was washed with ethanol as well as chloroform and dried overnight in vacuo at 80 °C.

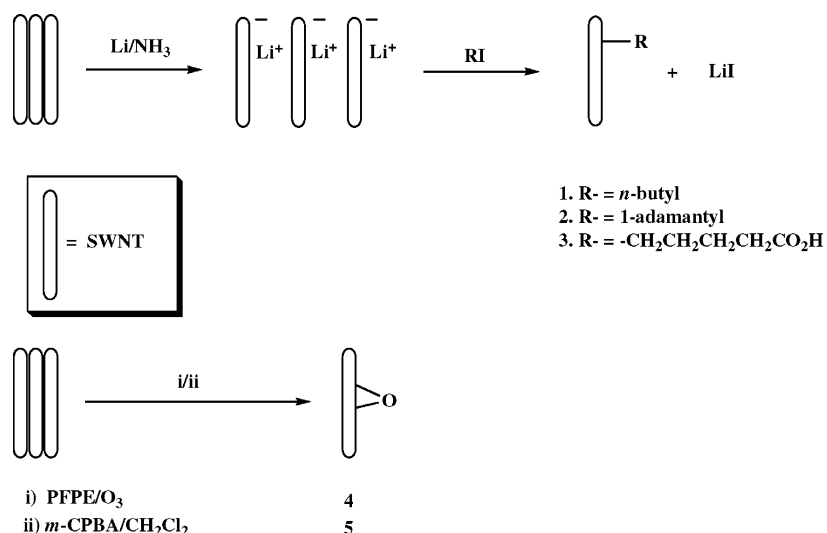
Ozonolysis. Ozonolysis reactions were carried out according to the literature procedure with purified HiPco SWNTs.²⁵ A suspension (concentration of 1 g/L) of 200 mg of purified SWNTs in 200 mL of PFPE (Galden HT-90) was taken in a

* Address correspondence to this author. E-mail: billups@rice.edu. Phone: (713) 348-5694. Fax: (713) 348-6355.

[†] Department of Chemistry and The Richard E. Smalley Institute for Nanoscale Science and Technology.

[‡] Department of Earth Science.

SCHEME 1



250 mL three-necked flask and homogenized thoroughly with a high-shear homogenizer for 30 min. This suspension was sparged with a mixture of 9 wt % ozone (OzoneLab OL80W/FM500 wall mounted line of ozone generators) in oxygen for 1 h. The gas flow was then stopped and the reaction mixture was purged with oxygen for 30 min to remove any residual ozone. The ozonized SWNTs were then extracted with ethanol (immiscible with PFPE) in a separation funnel followed by addition of hexanes and ethyl ether to flock out the SWNTs and remove any residual PFPE. SWNT precipitates were then filtered with 0.2 μ m PTFE membrane and vacuum dried at 90 °C.

Epoxidation of the SWNTs was also carried out following a previously reported²⁶ method with *m*-chloroperoxybenzoic acid (*m*-CPBA). To a 100 mL two-necked round-bottom flask was added *m*-CPBA (1.15 g, 6.6 mmol) and the mixture was dissolved in 60 mL of dichloromethane. After the solid had completely dissolved, purified SWNTs (40 mg, 3.3 mmol) were added and the solution was stirred overnight at room temperature. The reaction mixture was then filtered through a 0.2 μ m PTFE membrane and vacuum dried at 80 °C.

Functionalization of Tubes Cut by Ozonolysis. The basic procedure applied was similar to the one mentioned above for functionalization of purified SWNTs with 1-iodobutane. In this case the ozonized tubes (4) were used as the starting material instead of the purified SWNTs and 1-iodododecane was used instead of 1-iodobutane.

Characterization. The functionalized SWNTs were characterized by Raman spectroscopy, thermogravimetric analyses (TGA), atomic force microscopy (AFM), and scanning electron microscopy (SEM). Raman spectra of solid samples were recorded with a Renishaw 1000 microraman system equipped with 780 nm excitation laser source. Multiple spectra (3–5) were obtained, normalized to the G band, and averaged to give a comprehensive snapshot of the material. Thermogravimetric (TGA) experiments were carried out with a SDT 2960 TA instrument in argon atmosphere. Samples were degassed at 80 °C and then heated for 10 deg/min to 800 °C and held there for 30 min. SEM images were obtained with a JEOL 6500 scanning electron microscope. AFM images were taken of a chloroform solution, spin-coated onto mica, using a Digital Instrument Nanoscope IIIa in tapping mode with a 3045 JYW piezo tube scanner. The tapping frequency was between 270 and 310 kHz. Prior to running the AFM, the ozonized SWNTs were func-

tionalized with *n*-dodecyl groups to render them individually soluble in chloroform. The length measurements were accomplished through image analysis with SIMAGIS software (Smart Imaging Technologies, Houston, TX). Typically, 500–1000 individual SWNTs were counted to obtain meaningful results.

Powder surface areas were obtained by multipoint regression of nitrogen-BET (Brunauer–Emmett–Teller)²⁷ data obtained with a Micromeritics ASAP 2010. Samples were typically dried at 110 °C before BET analyses.

Exfoliation. The primary exfoliation method used in this study was treatment with 1:1 nitric/sulfuric acid mixture followed by baking at 1000 °C for 1 h. SWNTs were mixed with 5 wt % acid mixture and heated to 80 °C for 1 h. The paste was then quickly transferred to a quartz boat and inserted into a quartz tube furnace. The mixture was rapidly heated to 1000 °C for 1 h under flowing argon (0.94 L/min). The sample was subsequently cooled and exposed to air upon transfer to characterization equipment.

Hydrogen Uptake. The hydrogen sorption measurements were carried out at NREL with appropriately designed volumetric hydrogen capacity measurements at liquid nitrogen temperatures.²⁸

Results and Discussion

Single walled carbon nanotubes (SWNTs) have been functionalized by initial lithium reduction in liquid ammonia followed by coupling of the nanotube salts with various halides to yield debundled, functionalized nanotubes (Scheme 1). Nanotubes were also ozonized by conventional ozonolysis methods (Scheme 1).^{25,26} The functionalized tubes were characterized by Raman spectroscopy, TGA-IR, and SEM and AFM microscopy.

Figure 1 shows the typical Raman spectra of purified and functionalized SWNTs 1 and 4. The strong peak at ~ 1590 cm⁻¹ and the peaks at ~ 230 cm⁻¹ correspond to the disorder mode and the radial breathing modes, respectively. The growth of the disorder mode (D-band) for the butylated and ozonized SWNTs (Figure 1b,c) with respect to the purified material (Figure 1a) indicates that covalent sidewall functionalization has taken place during the functionalization reactions.

Further evidence for sidewall functionalization has been obtained by TGA analysis of the degassed, functionalized

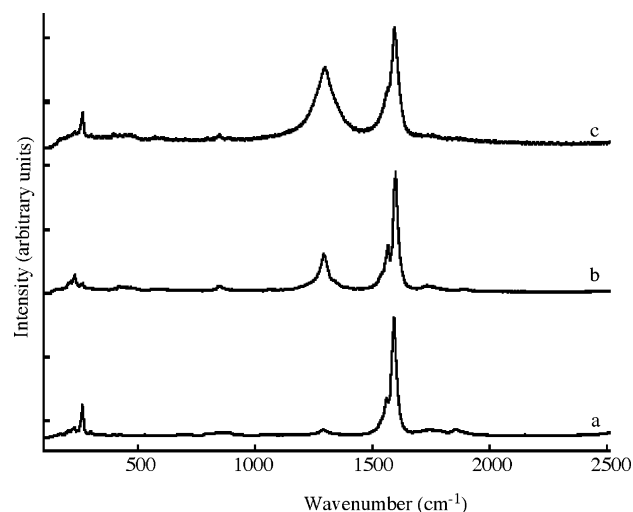


Figure 1. Raman spectra of (a) purified SWNTs, (b) compound **1**, and (c) compound **4**.

TABLE 1: Percentage Weight Loss and Estimated Carbon/Functional Group Ratio from TGA Analyses in the 80–800 °C Range

compd	obsd wt loss (%)	C/functional group ratio
1	15	27:1
2	25	30:1
3	10	74:1
4	23	4:1
5	30	5:1

TABLE 2: Specific Surface Area (SSA) of the Functionalized SWNTs after Drying at 110 °C

compd	SSA (m ² /gm)
purified SWNTs	680
1	410
2	269
3	410
4	381
5	200

samples (**1–5**) in the 80–800 °C range. These results are presented in Table 1 and agree with previously reported values.^{19,25,26}

The SSA of purified SWNTs was 680 m²/gm and is in good agreement with results reported previously for this type of material.^{18,29} Since the addition of functional groups might serve as spacers and force the tubes apart, it was hoped that functionalization would increase the surface area of the SWNTs. However, in each instance it was found that, with respect to the purified SWNTs (Table 2), the specific surface area decreased upon functionalization. Rebundling of the SWNTs with a concomitant decrease in surface area might account, at least in part, for this result.

The functionalized SWNTs were then subjected to a typical acid/bake treatment. The samples were doped by 5 wt % 1:1 nitric/sulfuric acid mixture and then heated at 80 °C for 1 h. The paste was then transferred quickly to a furnace where it was heated at 1000 °C for one additional hour. This intercalation by acid (1:1 nitric/sulfuric acid) followed by high temperature (1000 °C) baking increases the surface area by nearly 20%. The SSA of butylated SWNTs (**1**) increases to 770 m²/g. Under identical conditions the value for ozonized SWNTs **4** increases to 1068 m²/g, a 3-fold increase from the initial value (after drying at 110 °C) of 381 m²/g. Although the ozonized SWNTs **4** undergo an increase in SSA after the acid and bake treatment, the SEM image of the sample shows the nanosized geometry

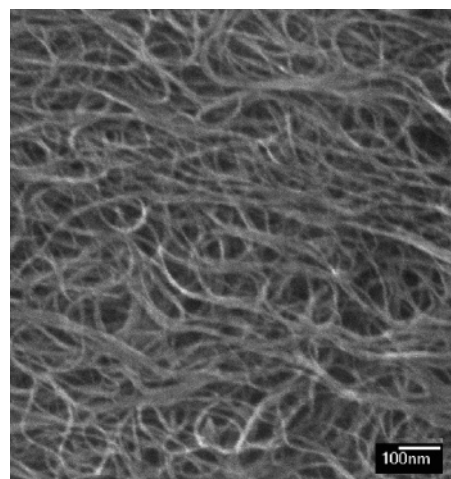


Figure 2. SEM image of ozonized SWNTs (**4**) treated with a 1:1 nitric/sulfuric acid mixture and heated at 1000 °C for 1 h.

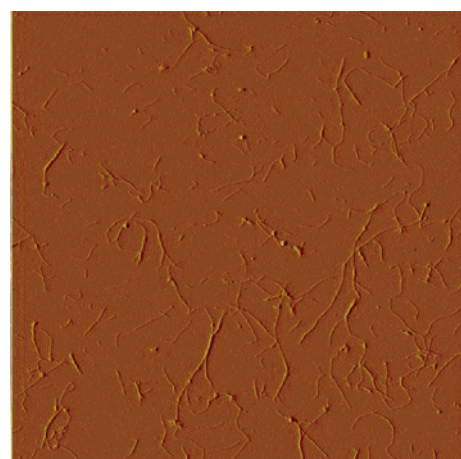


Figure 3. Tapping mode AFM (10 μm × 10 μm) of *n*-dodecylated ozonized SWNTs (see Experimental Section) spin-coated onto mica from chloroform.

with bundles having an average diameter of 10–30 nm (Figure 2). The SEM images of the remaining samples show that the nanotubes are bundled with an average bundle size of 50 nm. The increase in surface area on baking most likely results from the introduction of defects that cannot be detected by SEM. The rebundling of the SWNTs upon functionalization in the solid state most likely prevents a larger increase in the SSA. Curiously, the SSA for the epoxidized SWNTs **5** increases to only 366 m²/g after the acid/bake treatment.

The pristine tubes were cut by ozonolysis then functionalized by dodecyl groups, and length distribution measurements of the soluble dodecylated tubes were determined by AFM microscopy. A typical AFM image of the cut tubes, after functionalization by dodecyl groups, is depicted in Figure 3. The length distribution of the cut tubes is shown in Figure 4. According to AFM measurements, 33% of the cut tubes have an average length of 100 nm and 30% have an average length of 200 nm. Cutting does not enhance the surface area of the pristine tubes but the acid/bake treatment of the functionalized samples most likely introduces defects on the surface leading to an increased surface area.

Hydrogen uptake measurements were carried out with the pretreated ozonized sample (**4**) with a SSA of 1068 m²/g. BET measurements have been an important analytical tool for similar samples that have been studied for hydrogen adsorption.^{30–34} In general, for low-temperature studies the SWNTs that have

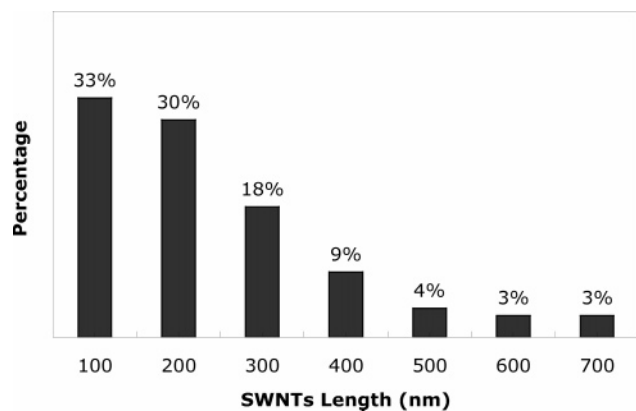


Figure 4. Length distribution histogram of *n*-dodecylated ozonized SWNTs.

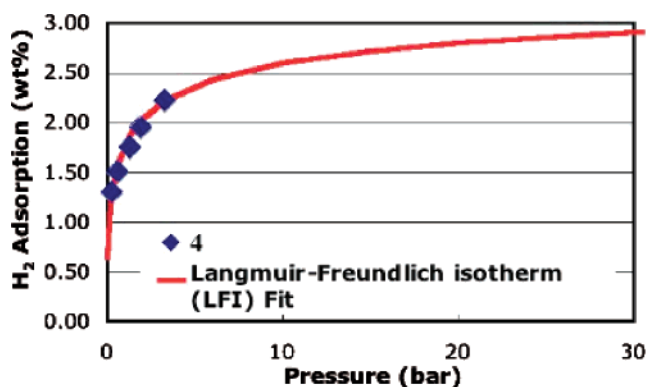


Figure 5. Hydrogen adsorption isotherm at 77 K fitted with a Langmuir–Freundlich isotherm for pretreated ozonized SWNTs 4.

the highest surface area would be expected to exhibit the maximum hydrogen adsorption capacity.¹⁸ The hydrogen uptake of acid/baked ozonized SWNTs 4 is 3 wt % at 77 K and 30 bar (Figure 5). This is nearly 25% greater than a previously reported value (≈ 2.4 wt %) recorded under identical conditions for purified SWNTs.²⁹ It can be concluded that saturation takes place with hydrogen monolayer formation with the hydrogen physically adsorbed onto the SWNT surfaces.

Conclusion

Functionalization leads to a decrease in specific surface area compared to that of the unfunctionalized nanotubes. Treatment with a concentrated 1:1 nitric/sulfuric acid mixture followed by high-temperature baking at 1000 °C was found to increase the specific surface area of both functionalized and unfunctionalized nanotubes. The increased surface area of the ozonized SWNTs led to a 3 wt % hydrogen uptake at 77 K and 30 bar.

Acknowledgment. We thank the Robert A. Welch Foundation (C-0490), the National Science Foundation (CHE-0450085), and DOE (DE-FC3605GO15073) for support of this work. We gratefully acknowledge Drs. L. J. Simpson and M. J. Heben (NREL) for the hydrogen uptake experiments.

References and Notes

- (1) Dresselhaus, M. S.; Dresselhaus, G.; Saito, R. *Phys. Rev. B* **1992**, *45*, 6234.
- (2) Iijima, S. *Nature (London)* **1991**, *354*, 56.
- (3) Iijima, S.; Ichihashi, T.; Ando, Y. *Nature (London)* **1992**, *356*, 776.
- (4) Hamada, N.; Sawada, S.; Oshiyama, A. *Phys. Rev. Lett.* **1992**, *68*, 1579.
- (5) Mintmire, J. W.; Dunlap, B. I.; White, C. T. *Phys. Rev. Lett.* **1992**, *68*, 631.
- (6) Dillon, A. C.; Jones, K. M.; Bekkedahl, T. A.; Kiang, C. H.; Bethune, D. S.; Heben, M. J. *Nature* **1997**, *386*, 377.
- (7) Ajayan, P. M.; Iijima, S. *Nature* **1993**, *361*, 333.
- (8) Fan, X.; Dickey, E. C.; Eklund, P. C.; Williams, K. A.; Grigorian, L.; Buczko, R.; Pantelides, S. T.; Pennycook, S. J. *Phys. Rev. Lett.* **2000**, *84*, 4621.
- (9) Darkim, F. L.; Malbrunot, P.; Tartaglia, G. P. *Int. J. Hydrogen Energy* **2001**, *27*, 193.
- (10) Cheng, H.-M.; Yang, Q.-H.; Liu, C. *Carbon* **2001**, *39*, 1447.
- (11) Ding, R. G.; Finnerty, J. J.; Zhu, Z. H.; Yan, Z. F.; Lu, G. Q. *Encycl. Nanosci. Nanotechnol.* **2004**, *4*, 13.
- (12) Ding, R. G.; Lu, G. Q.; Yan, Z. F.; Wilson, M. A. *J. Nanosci. Nanotechnol.* **2001**, *1*, 7.
- (13) Atkinson, K.; Roth, S.; Hirscher, M.; Grunwald, W. *Fuel Cells Bull.* **2001**, *4*, 9.
- (14) Dillon, A. C.; Heben, M. J. *Appl. Phys. A: Mater. Sci. Process.* **2001**, *72*, 133.
- (15) Maddox, M. W.; Gubbin, K. E. *Langmuir* **1995**, *11*, 2988.
- (16) Darkim, F. L.; Levesque, D. *J. Phys. Chem. B* **2000**, *104*, 6773.
- (17) Rzepka, M.; Lamp, P.; de la Casa-Lillo, M. A. *J. Phys. Chem. B* **1998**, *102*, 10894.
- (18) Ye, Y.; Ahn, C. C.; Witham, C.; Fultz, B.; Liu, J.; Rinzler, A. C.; Colbert, D.; Smith, K. A.; Smalley, R. E. *Appl. Phys. Lett.* **1999**, *74*, 2307.
- (19) Liang, F.; Sadana, A. K.; Peera, A.; Chattopadhyay, J.; Gu, Z.; Hauge, R. H.; Billups, W. E. *Nano Lett.* **2004**, *4*, 1257.
- (20) Liang, F.; Alemany, L. B.; Beach, J. M.; Billups, W. E. *J. Am. Chem. Soc.* **2005**, *127*, 13941.
- (21) Chattopadhyay, J.; Sadana, A. K.; Liang, F.; Beach, J. M.; Xiao, Y.; Hauge, R. H.; Billups, W. E. *Org. Lett.* **2005**, *7*, 4067.
- (22) Liang, F.; Beach, J. M.; Rai, P. K.; Guo, W.; Hauge, R. H.; Pasquali, M.; Smalley, R. E.; Billups, W. E. *Chem. Mater.* **2006**, *18*, 1520.
- (23) Lueking, A. D.; Pan, L.; Narayanan, D. L.; Clifford, C. E. B. *J. Phys. Chem. B* **2005**, *109*, 12710.
- (24) Chiang, I. W.; Brinson, B. E.; Huang, A. Y.; Willis, P. A.; Bronikowski, M. J.; Margrave, J. L.; Smalley, R. E.; Hauge, R. H. *J. Phys. Chem. B* **2001**, *105*, 8297.
- (25) Chen, Z.; Ziegler, K. J.; Shaver, J.; Hauge, R. H.; Smalley, R. E. *J. Phys. Chem. B* **2006**, *110*, 11624.
- (26) Ogrin, D.; Chattopadhyay, J.; Sadana, A. K.; Billups, W. E.; Barron, A. R. *J. Am. Chem. Soc.*, published online Aug 11, 2006, <http://dx.doi.org/10.1021/ja061680u>.
- (27) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.
- (28) Simpson, L. J.; Parilla, P. A.; Blackburn, J. L.; Gennett, T. G.; Gilbert, K. E. H.; Engtrakul, C.; Dillon, A. C.; Heben, M. J. *National Hydrogen Association Conference Proceeding*, Long Beach, CA, March 12–17, 2006.
- (29) Panella, B.; Hirscher, M.; Roth, S. *Carbon* **2005**, *43*, 2209.
- (30) Ahn, C. C.; Ye, Y.; Ratnakumar, B. V.; Witham, C.; Bowman, R. C.; Fultz, B. *Appl. Phys. Lett.* **1998**, *73*, 3378.
- (31) Strobel, R.; Jorissen, L.; Schliermann, T.; Trapp, V.; Schutz, W.; Bohmhammel, K.; Wolf, G.; Garche, J. *J. Power Sources* **1999**, *84*, 221.
- (32) Lueking, A. D.; Yang, R. T.; Rodriguez, N. M.; Baker, R. T. K. *Langmuir* **2004**, *20*, 714.
- (33) Browning, D. J.; Gerrard, M. L.; Lakeman, J. B.; Mellor, I. M.; Mortimer, R. J.; Turpin, M. C. *Nano Lett.* **2002**, *2*, 201.
- (34) Kayiran, S. B.; Lamari, F. D.; Levesque, D. *J. Phys. Chem. B* **2004**, *108*, 15211.