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Water Solubilization of Single-Walled Carbon Nanotubes by Functionalization with Glucosamine

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ABSTRACT

Water solubilization of single-walled carbon nanotubes (SWNTs) has been achieved by functionalizing the SWNT with glucosamine. The grafting of glucosamine to the nanotubes was attained by producing acyl chloride on the carboxylic groups associated with the nanotubes. Subsequently, amide bonds were formed between the glucosamine and the SWNT. This grafting results in solubility of SWNT in water, which ranges from 0.1 to 0.3 mg/mL, depending on temperature.

Introduction. The solubilization of single-walled carbon nanotubes (SWNTs) has been a research goal for the past few years. Having SWNTs in solution opens a large number of possibilities. One of them is to facilitate the purification process.[1−3] If the SWNT are selectively dissolved, they can be separated from the insoluble impurities. Otherwise, having them in solution may help even when the impurities are also soluble. For example, Haddon et al.[4,5] have recently developed a chromatographic method for separating soluble SWNTs from the particulate matter that is also solubilized during the nanotube dissolution process. The other benefit of having SWNTs in solution is that they become manageable to be effectively incorporated in SWNT-reinforced composites, which require high dispersion and alignment. Several approaches have been employed to achieve solubilization as operationally defined by most researchers in the field, i.e., when no precipitation occurs upon prolonged standing. One of the first approaches to achieve solubilization was to shorten the SWNT to 100−300 nm in length by a vigorous acid attack.[6] Although this approach made the SWNT soluble, it eliminated one of the potential advantages of SWNTs, their high aspect ratio (i.e., length/diameter). More recently, the carboxylic acid groups, typically present in purified SWNTs, were employed as anchoring sites for functional groups that made the SWNT soluble in organic solvents.[7] In this method, the carboxylic acid groups were first converted to acyl chlorides, which were then reacted with octadecylamine to form an amide bond that kept a long chain attached to the SWNT.[1] The same acyl chloride-mediated amidation reaction was used by other workers to functionalize carbon nanotubes.[8−10] Recently, the SWNT

functionalization has been achieved by electrochemical reduction of aryl diazonium salts.[11]

The majority of the studies on functionalization of SWNT resulted in solubilization in organic solvents. A much larger range of potential applications would open for water-soluble SWNTs. Certainly, biochemical and biomedical applications would require SWNTs in aqueous media. Two reports of dissolution of SWNTs in water have been recently made. In the method reported by O'Connell et al.,[12] the formation of any chemical bond was avoided by wrapping the SWNT in macromolecules such as poly(vinylpyrrolidone) (PVP) and polystyrene sulfonate (PSS). In the method reported by Sano et al.,[13] the SWNTs were functionalized with monoamine-terminated poly(ethylene oxide) PEO using a preparation method via acyl chloride similar to the one described above.[1,6] In this contribution, we show a very effective method of solubilization of SWNTs in water. We chose an amide-attached molecule of high hydrophilicity to improve water solubility. In this case, we have employed glucosamine, which has both an amine group that can easily form an amide bond with the SWNT and high water solubility.

Experimental Section. The SWNTs employed in this study were purchased from Carbolex (batch CLAP 8256, raw material). They were purified by suspending the as-received nanotubes in a 3 M HNO_3 solution and keeping them for about 10 h in reflux until the evolution of NO_2 vapors subsided. After this treatment, the product was vacuum-filtered, using a Teflon membrane with pore size 0.2 μ (PTFE 0.2 μ). The resulting solid was then thoroughly washed with deionized water until the filter completely lost the yellowish color initially present. The carbon content in this final product was 86 wt %. The analysis of this product by temperature

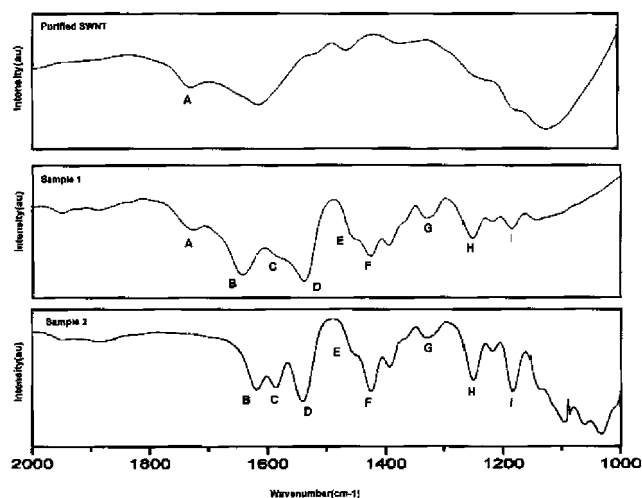* Corresponding author: e-mail: resasco@ou.edu

Figure 1. DRIFTS spectra of SWNT samples after various pretreatments. Upper panel: Purified SWNT after treatment in 3 M HNO$_3$ for 10 h, followed by contact to HCl. Middle panel: Sample 1, glucosamine-grafted SWNT (with a 5:1 ratio). Lower panel: Sample 2, glucosamine-grafted SWNT (with a 15:1 ratio). Band A corresponds to carboxylic groups. Bands B to I correspond to amide bonds (see Table 1).

Table 1: Infrared Absorption Bands Obtained on the Acid Treated-SWNTs and Glucosamide SWNT Solid Samples

	region (cm^{-1})	band assignments
A	1730	carboxylic acid C=O stretching vibration
B	1646	amide C=O stretching vibration
C	1590	amide N−H deformation
D	1540	amide C−N stretching vibration (amide II band)
E−F	1454−1427	amide N−H bending
G	1332	amide C−N stretching
H−I	1257−1187	amide out-of-plane N−H deformation (amide III band)

programmed oxidation (TPO) suggests that most of this carbon is in the same form (i.e., SWNT), which burns in a narrow temperature range centered at around 625 °C. This contrasts with the raw material, which, due to the presence of the metal, burns at lower temperatures and exhibits several oxidation peaks due to different forms of carbon. After filtering, the purified solids were suspended in deionized water, to which an aqueous solution of HCl was added to cause the protonation of the oxidized groups generated during the purification step. It has been previously shown that after this treatment carboxylic groups are left on the SWNT. The ends of SWNT as well as defects on the SWNT walls are more reactive than the cylindrical wall of the nanotube. The presence of pentagons and higher curvatures than on the hexagons of the cylindrical part of the tubes make the opening in those parts of the tubes easier when they are exposed to strong oxidants such as HNO$_3$.[14] Carboxylic groups resulting after oxidizing attacks have been observed in IR spectra by several authors.[15,16] In agreement with these results, the presence of carboxylic groups was clearly evident at this point in our preparation (see Figure 1).

To functionalize the SWNT with glucosamine, we followed a methodology already demonstrated by several authors.[7,17] The first step is to generate the acyl chloride, which is achieved by suspending the purified SWNT in a solution of thionyl chloride (SOCl$_2$) and dimethyl formamide (DMF). The amounts used in this particular example were 20 cm^3 SOCl$_2$ and 1 cm^3 DMF per 0.1 g of SWNT. This suspension was stirred at 65 °C for 24 h. The solid was then separated by filtration and washed with anhydrous tetrahydrofuran (THF). Subsequently, it was vacuum dried at room temperature for 5 min. Finally, the solid was mixed with glucosamine (99% purity from Aldrich) dissolved in anhydrous THF, which was previously distilled and kept in the presence of Na wires to eliminate any traces of water. The

mixture was then refluxed for 48 h and the solid separated by filtration with the same 0.2μ Teflon membrane filter as mentioned above. Finally, it was thoroughly washed with anhydrous THF and vacuum dried overnight. At this moment, the solid exhibited a light gray color that varied with the SWNT-to-glucosamine ratio. In this study, we have prepared mixtures with glucosamine-to-SWNT weight ratios of 5:1 (sample 1) and 15:1 (sample 2). The extent of reaction of the carboxylic groups (via acyl chloride) with the glucosamine was followed by DRIFTS under nitrogen flow, on samples previously exposed to ambient air, as done by other authors.[7] The IR absorption spectra were obtained in the transmission mode on a Bio-Rad 40 spectrophotometer on pressed SWNT pellets mixed with KBr.

To investigate the solubilization of the functionalized SWNTs in water, we obtained solubilization curves following the standard procedure, and to demonstrate the presence of SWNTs in the aqueous solution, we characterized the solution by UV−vis spectroscopy, a method previously used to study SWNTs dissolved in organic solvents.[7]

These measurements were conducted in a Shimadzu UV 2101 PC spectrophotometer, operating in the range 400−800 nm. The glucosamine-grafted SWNTs were further characterized by atomic force microscopy in a commercial AFM scanning probe Nanoscope IIIa (Digital Instruments Inc.) operating in the tapping mode.

Results and Discussion. We have characterized the different functional groups present in the SWNT after the various treatments by DRIFTS spectroscopy. Figure 1 illustrates typical spectra of the SWNT after different treatments. The upper spectrum (purified SWNT) was obtained after the initial acid treatment, i.e., HNO$_3$ followed by HCl. The middle and lower spectra (samples 1 and 2) were obtained after functionalization with glucosamine at two different glucosamine-to-SWNT ratios. Table 1 summarizes the main bands observed in these spectra, together with the corresponding assignment. A clear trend is observed in the spectra as the glucosamine is added to the SWNT. The band corresponding to the carboxylic groups present in the acid-treated SWNT (band A, at 1730 cm^{-1}) is gradually replaced by bands corresponding to amide bonds (bands B to I). It is interesting to note that in sample 1, with a lower glucosamine-to-SWNT ratio, there remains a fraction of unreacted carboxylic groups; but, in sample 2, with a higher glucosamine-to-SWNT ratio, the band corresponding to the

carboxylic groups has completely disappeared, indicating a complete reaction of these groups. The replacement of carboxylic groups by amide bonds indicates that the following reactions take place during the various treatments:
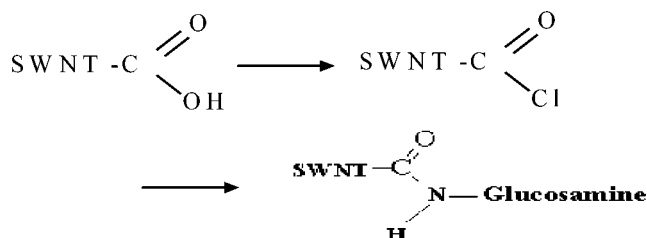
In the high-frequency region, the IR spectrum of the glucosamine-grafted samples, a narrow band at around 3090 cm^{-1} corresponding to the amide N−H bond and a broad band centered at about around 3740 cm^{-1} corresponding to the OH bond of glucosamine were clearly observed. The IR spectra can also be used to determine whether the glucosamine retained its cyclic structure after interaction with the SWNT or the ring opened by breaking the aldehyde-hydroxy group bridge. In fact, the absence of any aldehyde band in the 1740−1720 cm^{-1} region indicates that the rings remained closed after the amide bond was formed.

An interesting observation to discuss is the significant shift in the vibrational frequency of the C=O bond to lower values, observed when the carboxylic acid was replaced by the amide. In the acid state the frequency is 1730 cm^{-1}, while in the amide it is 1646 cm^{-1}. It is well known[18] that the presence of neighboring groups stabilizes the resonance of the double bond, thus decreasing the vibrational frequency of the C−O bond. This stabilization is more effective with the amide than with OH in the carboxylic group. To make the resonance of the double bond possible, in the former, a positive charge is left on the oxygen of the OH, while in the latter the positive charge is left in the nitrogen, which is less electronegative, making this charge more stable as illustrated in the following scheme. This argument would also explain
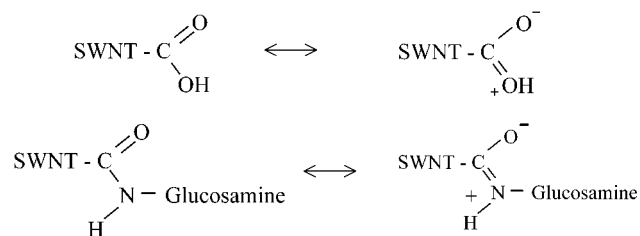
the shift to higher frequencies in the band A of the acid group that remains in the sample after the addition of the lower amount of glucosamine (sample 1). At the same time, the same argument would explain the shift to lower frequencies observed when comparing the position of the band B for samples 1 and 2.

The amide bonds in the glucosamine-grafted SWNTs are very stable and impart solubility in water to SWNTs. Without entering in the discussion whether SWNTs form "true"
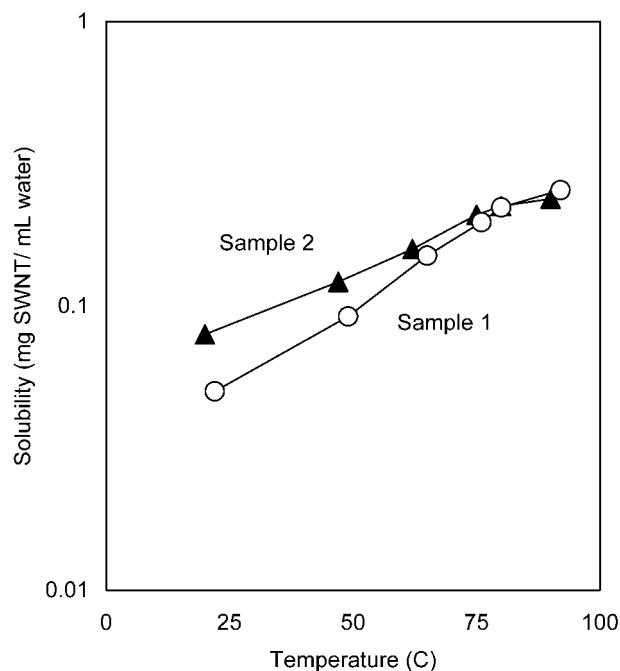

Figure 2. Solubility curves for glucosamine-grafted SWNTs in water. In sample 1 the glucosamine-to-SWNT weight ratio was 5:1 and in sample 2 it was 15:1. Note that the solubility values are of *net* weight of SWNT per unit volume, that is, the weight of the glucosamine has been subtracted.

solutions or colloidal dispersions, one can use the operational definition proposed by Haddon et al.[7] by which a SWNT solution is one that is visually nonscattering and exhibits no precipitation upon prolonged standing. Based on this definition, the glucosamine-treated SWNTs are soluble in water since they have remained translucent and without precipitation for weeks. As the concentration of SWNT was increased, we observed that a solubility limit was eventually reached, and no further solubilization could be attained. We have measured solubility curves as a function of temperature, determining the concentration of glucosamine-treated SWNT at which sedimentation of solids begins at each temperature. Sedimentation of free glucosamine may not affect these measurements since the solubility of glucosamine[19] is a couple of orders of magnitude higher than the values measured here for glucosamine-grafted SWNTs.

Figure 2 shows the net SWNT weight per weight of solution that can be dissolved in water without sedimentation, as a function of temperature. To obtain the net weight, the contribution of glucosamine in the solid was subtracted. It is clear that, as expected, the solubility of SWNT increases with temperature in both cases; however, it is interesting to note that at lower temperatures the solubility increased with the glucosamine-to-SWNT ratio, but the excess glucosamine did not have an effect on solubility at higher temperatures. The range of solubility values is comparable to values reported for functionalized SWNTs in organic solvents.[1]

Interestingly, when the pH of the solution was lowered to 2 at 80 °C by addition of HCl, the SWNTs immediately dropped out of solution. This precipitation is clearly due to the hydrolysis of the amide bond, which is known to occur
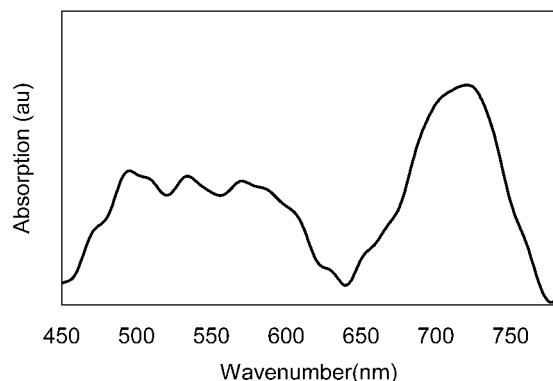
Figure 3. UV−visible absorption spectrum of an aqueous solution containing glucosamine-grafted SWNTs (0.08 mg net SWNT/mL). Shimadzu UV 2101 PC spectrophotometer.
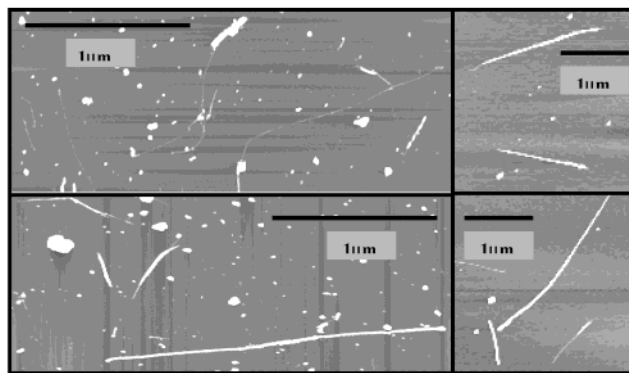

Figure 4. AFM images obtained in the tapping mode on glucosamine-grafted SWNTs (sample 2) deposited on mica. Nanoscope IIIa (Digital Instruments Inc.).

easily under basic or acidic conditions.[20−22] Fu et al.[23] have demonstrated that the amide and/or ester bonds formed during the functionalization can be hydrolyzed in basic or acidic medium. By this defunctionalization method, they effectively recovered the SWNTs from the homogeneous solutions and gave further proof to the formation of amide or ester linkages in the functionalized SWNT. We followed the hydrolysis reaction by monitoring the intensity of the band due to the amide carbonyl group (at 230 nm) by UV−vis spectroscopy. A strong temperature dependence was observed, and it was found that the hydrolysis was much slower at room temperature.

To obtain a direct demonstration of the presence of SWNTs in the aqueous solution and to show that they remain as SWNTs after the pretreatments we characterized the solution by optical absorption spectroscopy, which can be used to detect some of the van Hove singularities present in SWNTs when they have not been significantly disrupted. [24] Both theoretical and experimental studies have demonstrated that for SWNTs, such as those used in this study with average diameter around 1.2−1.3 nm, the band gaps of metallic and semiconducting tubes appear at around 1.7−1.8 eV and 2.1−2.7 eV, respectively.[25−27] Therefore, the optical spectra of these nanotubes should exhibit absorption bands at around 730−690 nm and 590−460 nm. In perfect agreement with these predictions, the spectrum shown in Figure 3 for the glucosamide-SWNTs in water clearly reveals those bands after subtraction of the background. The presence of these bands indicates that the solubilization process has not resulted in destruction of the nanotubes or significant alteration of their structure, but rather kept them in a high state of dispersion.

Another confirmation that the nanotubes conserved their integrity in solution came from the AFM analysis of the glucosamine-grafted SWNTs. After dissolving the SWNT as described above, a small drop of solution was placed on a mica plate and was let dry at room temperature. Figure 4 shows a tapping-mode AFM image of the glucosamide-SWNT. As seen in the AFM images, most of the nanotubes appear in forms of bundles. However, we cannot rule out that a fraction of them may be in the form of individual tubes.[28] We are currently working on the quantification of this fraction by a detailed Raman analysis of aqueous solutions of glucosamine-grafted SWNTs.

References

(1) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95.
(2) Rinzler, A. G.; Liu, J.; Dai, H.; Nikolaev, P.; Huffman, C. B.; Rodriguez-Macias, F. J.; Eklund, P. C.; Smalley, R. E. *Appl. Phys. A* **1998**, *67*, 29.
(3) Hamon, M. A.; Chen, J.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Adv. Mater.* **1999**, *11*, 834.
(4) Niyogi, S.; Hu, H.; Hamon, M. A.; Bhowmik, P.; Zhao, B.; Rozenzhak, S. M.; Chen, J.; Itkis, M. E.; Meier, M. S.; Haddon, R. C. *J. Am. Chem. Soc.* **2001**, *123*, 733.
(5) Zhao, B.; Hu, H.; Niyogi, S.; Itkis, M. E.; Hamon, M. A.; Bhowmik, P.; Meier, M. S.; Haddon, R. C. *J. Am. Chem. Soc.* **2001**, *123*, 11673.
(6) Liu, J.; Rinzler, A. G.; Dai, H.; Hafner, J. H.; Bradley, R. K.; Boul, P. J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; Rodriguez-Macias, F.; Shon, Y.-S.; Lee, T. R.; Colbert, D. T.; Smalley, R. E. *Science* **1998**, *280*, 1253.
(7) Chen, J.; Rao, A. M.; Lyuksyutov, S.; Itkis, M. E.; Hamon, M. A.; Hu, H.; Cohn, R. W.; Eklund, P. C.; Colbert, D. T.; Smalley, R. E.; Haddon, R. C. *J. Phys. Chem. B* **2001**, *105*, 2525.
(8) Jin, Z.; Sun, X.; Xu, G.; Goh, S. H.; Ji, W. *Chem. Phys. Lett.* **2000**, *318*, 505.
(9) Riggs, J. Guo, Z.; Carroll, D. L.; Sun, Y.-P. *J. Am. Chem. Soc.* **2000**, *122*, 5879.
(10) Riggs, J. E.; Walker, D. B.; Carroll, D. L.; Sun, Y.-P. *J. Phys. Chem. B* **2000**, *104*, 7071.
(11) Bahr, J. L.; Yang, J.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 6536.
(12) O'Connell, M. J.; Boul, P.; Ericson, L., M.; Huffman, C.; Wang, Y.; Haroz, E.; Kuper, C.; Tour, J.; Ausman, K. D.; Smalley, R. E. *Chem. Phys. Lett.* **2001**, *342*, 265.
(13) Sano, M.; Kamino, A.; Okamura, J.; Shinkai, S. *Langmuir* **2001**, *17*, 5125.
(14) Mazzoni, M. S. C.; Chacham, H.; Ordejon, P.; Sanchez-Portal, D.; Soler, J. M.; Artacho, E. *Phys. Rev. B* **1999**, *60*, 4, R2208.
(15) Kuznetzova, A.; Mawhinney, D. B.; Yates, J. T., Jr.; Liu, J.; Smalley, R. E. *Chem. Phys. Lett.* **2000**, *321*, 292.
(16) Mawhinney, D. B.; Numenko, V.; Kuznetzova, A.; Yates, J. T., Jr.; Liu, J.; Smalley, R. E. *J. Am. Chem. Soc.* **2000**, *122*, 2383.
(17) Chen, Y.; Haddon, R. C.; Fang, S.; Rao, A. M.; Eklund, P. C.; Lee, W. H.; Dickey, E. C.; Grulke, E. A.; Pendergrass, J. C.; Chavan, A.; Haley, B. E.; Smalley, R. E. *J. Mater. Res.* **1998**, *13*, 2423.

(18) Socrates, G. In *Infrared Characteristic Group Frequencies*; John Wiley & Sons: New York, 1980.

(19) Qian, H.; Li, L.; Xue, H. *Huaxue Shijie* **1994**, *35*, 75.

(20) Yamana, T.; Mizukami, Y.; Tusji, A.; Yasuda, Y.; Masuda, K. *Chem. Pharm. Bull.* **1972**, *20*, 881.

(21) Cremin, D. J.; Hegarty, A. F. *Tetrahedron* **1977**, *33*, 1823.

(22) Kluger, R.; Lam, C. H. *Can. J. Chem.* **1977**, *55*, 640.

(23) Fu, K.; Huang, W.; Lin, Y.; Riddle, L. A.; Carroll, D. L.; Sun, Y−P. *Nano Lett.* **2001**, *1*, 439.

(24) Kim, P.; Odom, T. W.; Huang, J.-L.; Lieber, C. M. *Phys. Rev. Lett.* **1999**, *82*, 1225.

(25) Wildoer, J. W. G.; Venema, L. C.; Rinzler, A. G.; Smalley, R. E.; Dekker, C. *Nature* **1998**, *391*, 59.

(26) Kataura, H.; Kumazawa, Y.; Maniwa, Y.; Umezu, I.; Suzuki, S.; Ohtsuka, Y.; Achiba, Y. *Synthetic Metals* **1999**, *103*, 2555.

(27) Odom, T. W.; Huang, J.-L.; Kim, P.; Lieber, C. M. *Nature* **1998**, *391*, 62.

(28) Bandyopadhyaya, R.; Nativ-Roth, E.; Regev, O.; Yerushalmi-Rozen, R. *Nano Lett.* **2002**, *2*, 25.

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