Modification of Single-Walled Carbon Nanotubes by Hydrothermal Treatment

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Single-walled carbon nanotubes (SWNTs) have been conditioned in water and aqueous acidic solutions at elevated temperatures and pressures; i.e., by hydrothermal treatments (HT). Transmission electron and scanning force microscopies revealed that disentanglement of SWNT bundles, structural changes of amorphous carbon, and complete destruction of the SWNTs with the simultaneous formation of new carbon nanoclusters can be achieved by HT. The introduction of specific surface groups onto SWNTs is investigated by Raman , X-ray, and ultraviolet photoemission spectroscopies. Depending on the type of acid used, chlorine, bromine, or sulfonate could be selectively attached in various densities. With the proper choice of temperature and solvent/agent, HT provides ways to efficiently purify and modify SWNTs in a manageable process.

Introduction

Single-walled carbon nanotubes (SWNTs) have a wide range of potential applications involving composite reinforcement, actuation, field emission, and microelectronics. Almost any of these applications would require an SWNT with special properties and high purity. However, large-scale synthesis routes yield an ill-defined SWNT material containing tubes of varying diameter, length, and internal structure. The current methods for purification, handling, and control of the properties of the SWNTs are still far too crude and inadequate. Often liquid- or gas-phase oxidation is employed for purification, thereby destroying carbon particles smaller than SWNTs. During this treatment, hydroxyl, carbonyl, and carboacidic groups are attached to the tube surface.[1,2] This oxidized material is usually taken as starting material for further chemical modification. In this manner gold,[3] platinum, or ruthenium clusters[4] have been attached to SWNTs. Chen et al. used strongly oxidized SWNTs to render them soluble in organic solvents after the reaction with amines.[5] Generally, the oxidation of SWNTs does not proceed in a selective way and the sites and densities of the reactive groups can hardly be controlled. Furthermore, oxidation alters the properties of the pristine SWNTs,[6–9] which is not tolerable for many applications. Alternative routes such as the fluorination of SWNTs lead to chemically inert products that do not allow any further reactions.[10,11] Recently, attempts to use carbenes as initial reactants have been published.[12]

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(1) Hiura, H.; Ebbesen, T. W.; Tanigaki, K. *Adv. Mater.* **1995,** *7,* 275.
(2) Liu, J.; Rinzler, A. G.; Dai, H. J.; 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.

(3) Burghard, M.; Krstic, V.; Duesberg, G. S.; Philipp, G.; Muster, J.; Roth, S.; Journet, C.; Bernier, P. *Synth. Met.* **1999,** *103,* 2540.
(4) Quintus, M. Thesis, University of Stuttgart, 2002.
(5) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y. S.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998,** *282,* 95.
(6) Lordi, V.; Yao, N.; Wei, J. *Chem. Mater.* **2001,** *13,* 733.
(7) Mawhinney, D. B.; Naumenko, V.; Kuznetsova, A.; Yates, J. T.; Liu, J.; Smalley, R. E. *J. Am. Chem. Soc.* **2000,** *122,* 2383.
(8) Nagasawa, S.; Yudasaka, M.; Hirahara, K.; Ichihashi, T.; Iijima, S. *Chem. Phys. Lett.* **2000,** *328,* 374.
(9) Yao, N.; Lordi, V.; Ma, S. X. C.; Dujardin, E.; Krishnan, A.; Treacy, M. M. J.; Ebbesen, T. W. *J. Mater. Res.* **1998,** *13,* 2432.

Apart from chemical treatments, physical purification methods such as chromatography and filtering have been introduced, which do not affect the properties of the SWNTs.[13] Nevertheless, as initial steps disintegration and dispersion of the pristine material are necessary, which remain difficult and time-consuming procedures. To improve the situation, treatment of SWNTs in water has first been suggested by Tohji et al.[14] In their hydrothermal initiated dynamic extraction (HIDE) experiment the pristine material was boiled for 8 h in water under atmospheric pressure. A certain degree of disentanglement of the raw material was achieved, which facilitated the subsequent purification steps.

In the present work, elevated temperatures and pressures up to the supercritical regime have been employed to modify SWNT raw material. Under hydrothermal conditions graphitic materials undergo structural changes in water;[15] however, in recent studies fullerenes[16] and SWNTs[17] have turned out to be very stable. It is also possible to synthesize large-diameter multiwalled carbon nanotubes from amorphous carbon under hydrothermal conditions.[18] Here we report a comprehensive study on the effects of HT on SWNTs in water, and, more importantly, in acids with different oxidation strengths. The samples have been investigated by transmission electron microscopy (TEM), scanning force microscopy (SFM), Raman spectroscopy, and X-ray and ultraviolet-photoemission spectroscopy (XPS, UPS). As shown in the following, HT can be used to introduce selectively functional groups to the surface of SWNTs and effectively does disintegrate the pristine SWNT material.

Experimental Section

SWNT raw material has been synthesized by the laser ablation method and purchased from Tubes@Rice. The diameter distribution of the SWNTs has a maximum at 1.4 nm.[20] For one HT experiment 10 mg of raw material and 10 mL of water or acid were sealed under vacuum in a 20-mL quartz ampule (acids: 9 M H_2SO_4, 5 M HCl, and 14 M HBr), inserted into an autoclave (Tuttle-type) with CO_2 as filler, and heated to 250 °C or 500 °C. After 24 or 114 h the samples were quenched and the ampules were opened. The ampules may be under pressure and must be handled with care, special precautions must be taken when opening. The various HT conditions are summarized in Table 1. TEM characterization

Table 1. Experimental Conditions of the Various Hydrothermal Treatments of SWNTs

sample	solvent	temperature (°C)	duration (h)
W250	H_2O	250	114
W500	H_2O	500	24
Br250	HBr/H_2O	250	114
Br500	HBr/H_2O	500	24
Cl250	HCl/H_2O	250	114
Cl500	HCl/H_2O	500	24
S250	H_2SO_4/H_2O	250	114
S500	H_2SO_4/H_2O	500	24

was performed in a JEOL 2000 FX with holey carbon grids as substrates. SFM images were recorded with a Digital Instruments Nanoscope III in tapping mode after the samples had been applied onto surface-modified silicon substrates.[19] Raman measurements were performed with a Jobin-Yvon LabRAM system equipped with an optical microscope using a He/Ne laser as excitation source at 632.8 nm. For the XPS and UPS measurements the samples were filtered through polycarbonate membranes, yielding thin, continuous films which were washed vigorously with distilled water. Monochromatized Al Kα radiation ($h\nu$ = 1486.6 eV) and the He II line of a gas discharge lamp ($h\nu$ = 40.8 eV) were used for XPS and UPS measurements, respectively.

Results

All samples, except S500, can be classified as voluminous dispersions of fine black particles after HT. In comparison with the pristine material, the particles had a smaller size and could be wetted more easily. The microscopic investigations showed that in the black soot SWNTs and bundles of SWNTs were still present. In contrast to pristine material the SWNTs were no longer covered with amorphous carbon, as shown in the TEM image in Figure 1. It can be seen that the ropes of SWNTs are free of any coverage with amorphous material. It also becomes apparent that the networks and ropes of the raw material disintegrate during the HT. The SFM image in Figure 2 shows such a disintegrated SWNT rope after a treatment at 250 °C in water. The individual tubes are loosely bound together to a rope. This sort of aggregate is not present in SWNTs raw material, where the ropes appear to be very compact objects.[20] At this point it has to be emphasized that these samples had not been pretreated by ultrasound or oxidative conditioning with HNO_3.
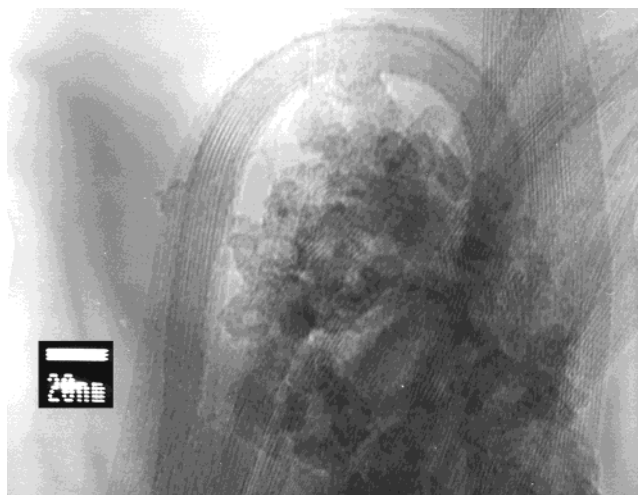
(10) Mickelson, E. T.; Huffman, C. B.; Rinzler, A. G.; Smalley, R. E.; Hauge, R. H.; Margrave, J. L. *Chem. Phys. Lett.* **1998**, *296*, 188.
(11) Hamwi, A.; Alvergnat, H.; Bonnamy, S.; Beguin, F. *Carbon* **1997**, *35*, 723.
(12) Holzinger, M.; Vostrowsky, O.; Hirsch, A.; Hennrich, F.; Kappes, M.; Weiss, R.; Jellen, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 4002.
(13) Dalton, A. B.; Chambers, G.; Byrne, H. J.; Coleman, J. N.; McCarthy, B.; in het Panhuis, M.; Blau, W. J.; Duesberg, G. S.; Roth, S.; Ajayan, P. M.; Maiti, A. *Recent Res. Dev. Phys. Chem.* **2002**, *6*, 327.
(14) Tohji, K.; Takahashi, H.; Shinoda, Y.; Shimizu, N.; Jeyadevan, B.; Matsuoka, I.; Saito, Y.; Kasuya, A.; Ito, S.; Nishina, Y. *J. Phys. Chem. B* **1997**, *101*, 1974.
(15) Gogotsi, Y. G.; Nickel, K. G. *Carbon* **1998**, *36*, 937.
(16) Suchanek, W. L.; Yoshimura, M.; Gogotsi, Y. G. *J. Mater. Res.* **1999**, *14*, 323.
(17) Swamy, S. S.; Calderon-Moreno, J. M.; Yoshimura, M. *J. Mater. Res.* **2002**, *17*, 734.
(18) Gogotsi, Y.; Libera, J. A.; Yoshimura, M. *J. Mater. Res.* **2000**, *15*, 2591.
(19) Muster, J.; Burghard, M.; Roth, S.; Duesberg, G. S.; Hernandez, E.; Rubio, A. *J. Vac. Sci. Technol. B* **1998**, *16*, 2796.
(20) Thess, A.; Lee, R.; Nikolaev, P.; Dai, H. J.; Petit, P.; Robert, J.; Xu, C. H.; Lee, Y. H.; Kim, S. G.; Rinzler, A. G.; Colbert, D. T.; Scuseria, G. E.; Tomanek, D.; Fischer, J. E.; Smalley, R. E. *Science* **1996**, *271*, 483.

Figure 1. TEM image of polished SWNTs after an HT experiment in HCl at 250 °C.
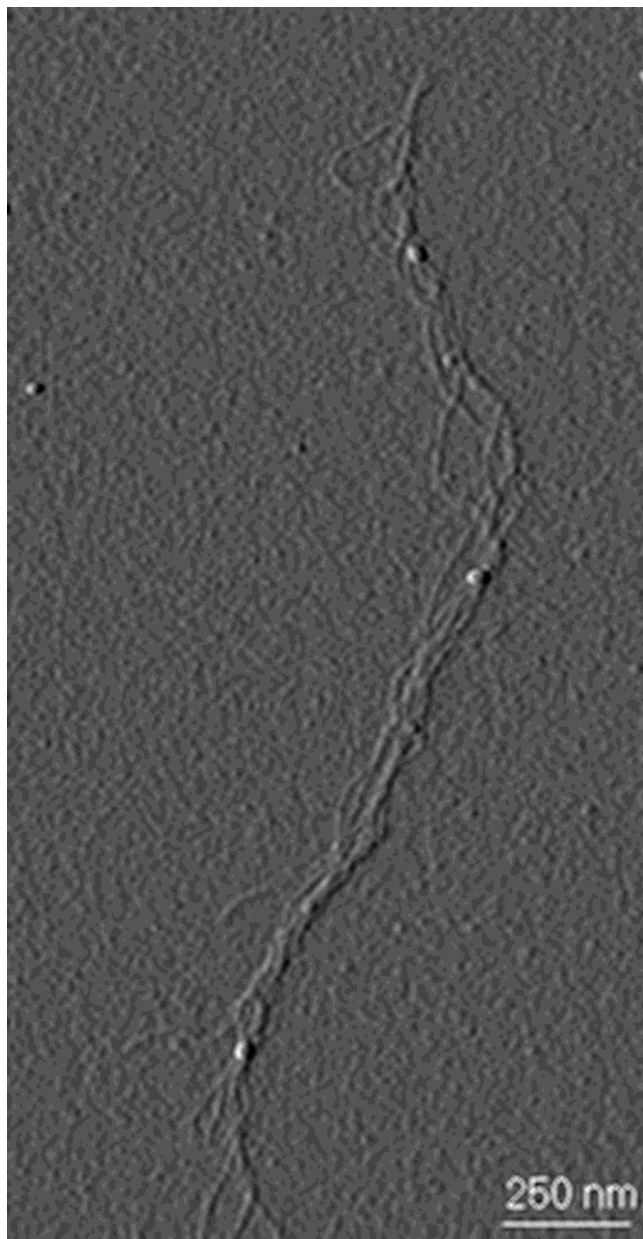
Figure 2. SFM image of a disentangled SWNT rope after hydrothermal treatment in H_2O at 250 °C.

Figure 3. TEM images of (a) chains of onions grown in HT conditions in H_2O at 500 °C, and (b) aggregates of carbon clusters synthesized with HT in sulfuric acid at 500 °C.

All HTs performed at 500 °C yielded new carbon structures. In samples W500, Cl500, and Br500 carbon onionlike structures and chains of these onions as depicted in Figure 3a are found. The TEM investigations of those samples further revealed that the metallic catalyst particles had been removed. In the SWNTs treated in sulfuric acid at 500 °C (S500) a clear solution with a very subtle pink hue was obtained. Directly after opening the quartz ampule the solution was bubbling under atmospheric pressure (outgassing of CO_2). Within a few days, black solid aggregates formed in the solution and fell out. TEM investigations of the sample revealed that the pristine carbon structures, including the SWNTs, had been completely destroyed during this treatment. Small amorphous carbon clusters with average diameter of ≈20 nm are formed from the carbon feedstock besides the complete oxidation to CO_2. The clusters seem to have a tendency toward aggregation, and an agglomerate of these carbon clusters is shown in Figure 3b.
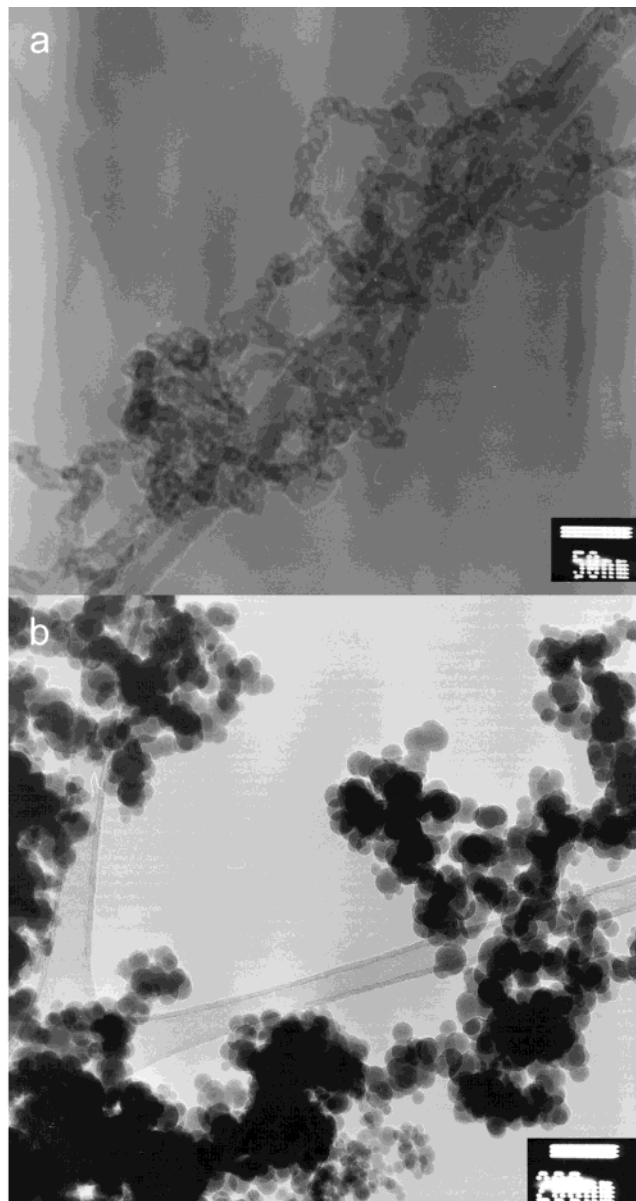
Raman experiments reveal significant changes in the G-line region of the SWNT spectrum. In Figure 4 the Raman spectra of the raw material, W250, and Cl250 recorded with a laser energy of 1.96 eV are presented. The raw sample shows a pronounced asymmetry on the low-frequency side of the graphitic band (G-band) at 1540 cm^{-1} which is attributed to a Breit−Wigner−Fano (BWF) resonance of metallic SWNTs.[21,22] Although the HT samples treated in water also show this feature, the acid-conditioned samples exhibit a substantial decrease of the BWF asymmetry.

Elemental analysis of the pristine and HT samples by XPS yields the following results. Besides carbon, approximately 6 at. % oxygen is detected in the pristine SWNTs, while no signal of the metal catalyst − known

(21) Duesberg, G. S.; Muster, J.; Byrne, H. J.; Roth, S.; Burghard, M. *Appl. Phys. A* **1999**, *69*, 269.
(22) Brown, S. D. M.; Jorio, A.; Corio, P.; Dresselhaus, M. S.; Dresselhaus, G.; Saito, R.; Kneipp, K. *Phys. Rev. B* **2001**, *63*, 5414.
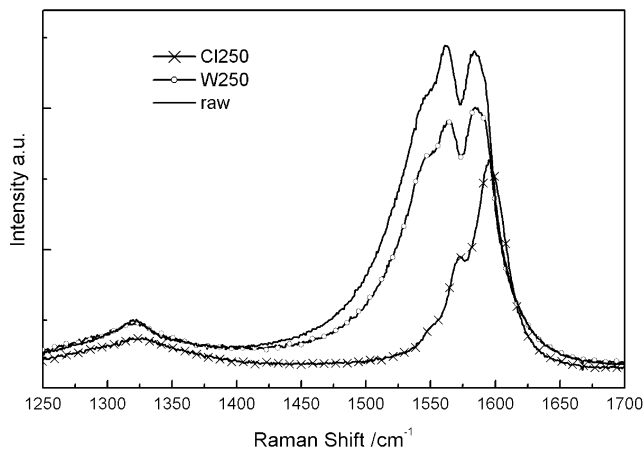
Figure 4. Raman spectra of (a) pristine SWNTs, (b) SWNTs hydrothermally treated in H_2O at 250 °C, and (c) SWNTs hydrothermally treated in HCl at 250 °C.

Figure 5. Br 3d core level spectrum of SWNTs treated in HBr at 500 °C (Br500, top) and Cl 2p core level spectrum of SWNTs treated in HCl at 250 °C (Cl250, bottom).

Figure 6. C 1s loss spectra of highly oriented pyrolithic graphite (HOPG), of pristine SWNTs and SWNTs treated in H_2O at 500 °C (W500).

to be present in the material — is seen.[23] In all HT samples silicon is present in nonnegligible amounts. Sample Cl250 contains 0.6 at. % silicon, and about 4 at. % is present in samples W500, Br500, and HCl500, accompanied with a higher amount of oxygen. The samples heated to 250 °C and 500 °C contain approximately 9 and 17 at. % oxygen, respectively. The oxygen increase, in principle, could be due to silicon-dioxide particles detached from the quartz ampules and adhering to the samples. However, considering the samples have been vigorously rinsed with water after the HT, this is attributed to an increased fraction of oxidized surface C sites; i.e., −C−OH, −C=O, or −COOH groups, which is supported by the analysis of the C 1s spectrum (see below). Interestingly, in both samples treated in water (W250 and W500) traces of the Ni catalyst are present, but in the acid-treated samples no Ni was detected.

The amount of chlorine and bromine in the samples treated with HCl and HBr is consistently around 0.4 at. %. For sample S250 0.8 at. % sulfur is found (no data were obtained for S500 because it was not possible to prepare a substrate for XPS/UPS characterizations of the carbon nanoclusters). The XPS measurements provide clear evidence that the halides are bound to different sites. At least three components are required to obtain a reasonable fit of the Cl 2p core level spectra of sample Cl250 (Figure 5a) and of Cl500 (fit not shown here). Each component consists of the 3/2 and 1/2 level with a spin−orbit splitting of 1.6 eV taken from the literature.[24] The binding energies of the three 3/2 components are 197.3, 198.2, and 200.2 eV. The component at 200.2 eV, which makes up approximately 26% and 35% of the total Cl 2p intensity for the Cl250 and Cl500 samples, respectively, corresponds to chlorine bound to conjugated π-systems in polymers.[24] Similar results are obtained for the brominated SWNTs that show two components at 67.6 and 70.0 eV for the Br 3d 5/2 component (Figure 5b). Again, the high-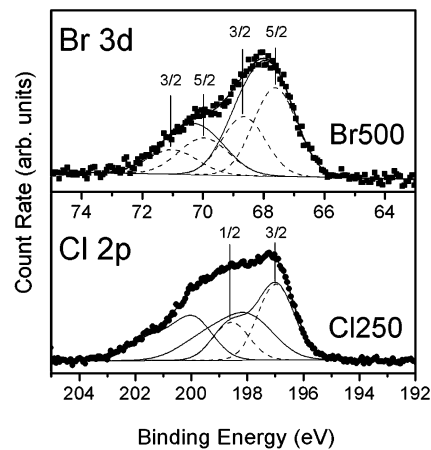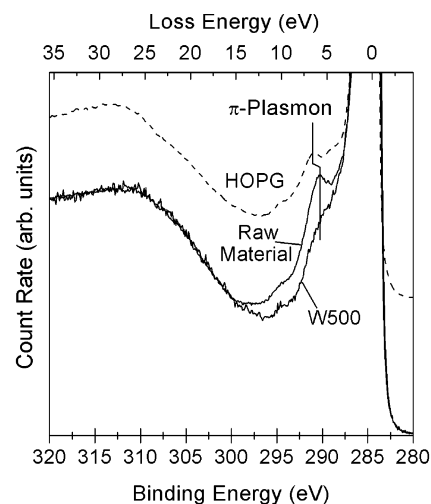energy component arises from the halide coupled to the conjugated π-system. For the sample S250 one component proved sufficient to fit the S 2p core level. On account of its binding energy (168.5 eV for 2p 3/2) it is attributed to HSO_3 groups.

In Figure 6 it can be seen that the structure at the high-binding-energy side of the C 1s core level of the raw material shows a pronounced π-plasmon similar to that observed in highly oriented pyrolytic graphite (HOPG). Acid-treated samples exhibit a weaker π-plasmon than those treated with water and the loss is more pronounced for HT at 500 °C. The strongest loss was found in the S250 sample, however. As demonstrated by the UPS data (Figure 7), the drop in the intensity of the π-plasmon is accompanied by a reduction of the π-electron density-of-states in the energy range between 0 and 3 eV and a slight change of the energy levels between 5 and 10 eV. A detailed report of the UPS/XPS investigations will be published elsewhere.[25]

Discussion

Disintegration, polishing, and chemical functionalization of the pristine SWNTs has been observed after

(23) This is because XPS characterizations are surface sensitive (sampling depth of the photoelectrons is ∼1.0−1.5 nm). The metal clusters are therefore shielded against detection by a shell of amorphous carbon.

(24) Beamson, G.; Briggs, D. *High-Resolution XPS of Organic Polymers*; John Wiley & Sons: Chichester, U.K., 1992.

(25) , Duesberg, G. S.; Downes, P.; Minett, A.; Graupner, R.; Ley, L.; Nicoloso N.; Roth, S. *Synth. Met.*; submitted for publication.
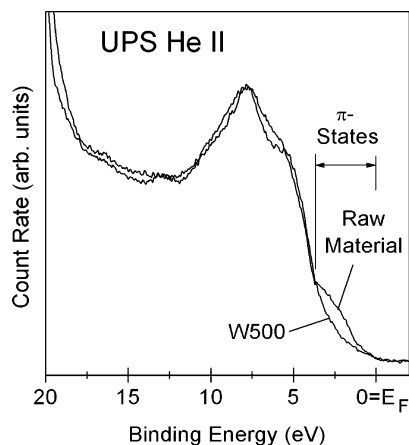
Figure 7. UPS spectra ($h\nu$ = 40.8 eV) of pristine SWNTs and of H_2O-treated SWNTs (T = 500 °C).

HT. A disentanglement of SWNTs has already been reported by Tohji et al.[14] due to the HIDE treatment, where nanotubes are heated to 100 °C at atmospheric pressure. Under hydrothermal conditions the effect is strongly enhanced — notably in acidic solvents/agents — and, hence, the HT method may be generally employed as a highly effective initial purification step of SWNTs. Besides disentanglement, polishing of the pristine material occurs by dissolution and selective reconstruction of amorphous carbon. In accord with the TEM investigations of the samples conditioned at 500 °C, amorphous carbon — less stable than SWNTs and fullerenes under hydrothermal conditions[16,17] — most likely provides the feedstock for the new onion-type carbon structures. A mechanism for the formation of graphitic structures under similar conditions has recently been reported.[26,27] The sulfuric acid acts as a promoter for the formation of new carbon nanostructures at 500 °C, thus the HT method in acids could be used to synthesize novel carbon materials. Concerning SWNT purification, the newly formed onion-like carbon structures may more easily be removed by physical sorting methods (filtering, centrifugation, or chromatography) than amorphous carbon sticking to the nanotubes.

The major advantage of HT lies in its ability to modify the SWNT properties by introducing surface groups in low concentration, i.e., in the functionalization of SWNTs. Qualitatively, the introduction of functionalities is documented by the observed wetting behavior of the SWNTs after the HT. The ease with which they disperse in water indicates that polar functional groups have been introduced onto the tube surface, whereas pristine SWNTs are hydrophobic and do not wet in polar solvents.

Raman spectroscopy provides further evidence that SWNTs have been functionalized. The Raman spectrum of the raw material exhibits a triplet of asymmetric lines with a maximum at approximately 1540 cm^{-1} when excited with laser energies of ≈2 eV. The asymmetry stems from the interaction of phonon excitations with the continuum of electronic excitations characteristic of metallic SWNTs (BWF resonance), and is therefore

commonly attributed to metallic tubes present in the sample.[22] Suppression of the typical BWF line shape in the Raman G band has been assigned to the loss of continuum states due to the introduction of functionalities after oxidation,[13,28] however, it also could be due to the reduction of the size of the bundles of SWNTs.[29]

In accord with the Raman data, the UPS spectra of the functionalized SWNTs exhibit a lower density of π states as shown in Figure 7. Evidently, extended electronic states are transformed into localized states by the chemical modification of the SWNT surface. Similar effects are observed in UPS spectra of multiwall carbon nanotubes upon oxidative treatments, as reported by Ago et al.[30] The decrease in the density of π states is supported by the reduction of the π-plasmon intensity observed in the C 1s loss spectra of the HT samples in comparison with that of the pristine SWNTs as shown in Figure 6.

Interestingly, the samples treated in water still have a strong BWF line in the Raman spectrum, although the wetting behavior and the XPS/UPS results (see also below) indicate substantial oxidation of the tubes. This may be explained by laser-heating of the sample when recording the Raman spectrum. It has been demonstrated that the defects of oxidized tubes easily heal upon heating under formation of CO_2.[28] This leads to a reconstruction of the continuum π-system, and therefore a recovery of the BWF line in the Raman spectra.

Further information about the nature of the bonds of the hetero elements to the SWNTs can be deduced from the XPS core level spectra. For the samples treated with HCl and HBr the Cl 2s and 2p and Br 3s, 3p, and 3d core level peaks were detectable (Figure 5). In all four samples the high binding energy components (200.2 eV for the Cl 2p 3/2 and 70.0 eV for the Br 3d 5/2 line) corresponding to chlorine and bromine bound to conjugated polymers, respectively, add up to ≈0.2 at. %. Hence, approximately 2 out of 1000 carbon atoms of a SWNT are bound to a halide. The fraction is independent of the type of halide and processing temperature and time. This strongly suggests that the density of functionalities is not determined by the reaction conditions but by the defect density (strained sites or dangling bonds) of the pristine tubes. The remaining components of the core level spectra shown in Figure 5a and b might be due to metal-halide salts not completely removed by the purification procedure. However, in this case metal core levels should appear in the XPS spectra as well, but they are not observed. We therefore suggest that Cl and Br are ionically bound to charged sites at the SWNT surface in order to satisfy charge neutrality. Further studies have to be undertaken to clarify this point.

In the samples treated in H_2SO_4 the situation appears to be different. The S 2p core level of sample S250 can be fitted with a single component and the chemical shift corresponds to that observed for sulfonate groups. The concentration of 0.8 at. % sulfur present in the sample is higher compared to the halides. This suggests that

(26) Calderon-Moreno, J. M.; Yoshimura, M. *Mater. Trans.* **2001**, *42*, 1681.
(27) Kraft, T.; Nickel, K. G. *J. Mater. Chem.* **2000**, *10*, 671.

(28) Yu, Z. H.; Brus, L. E. *J. Phys. Chem. A* **2000**, *104*, 10995.
(29) Jiang, C.; Kempa, K.; Zhao, J.; Schlecht, U.; Kolb, U.; Basché, T.; Burghard, M.; Mews, A. *Phys Rev. B.* **2002**, *66*, 161404.
(30) Ago, H.; Kugler, T.; Cacialli, F.; Salaneck, W. R.; Shaffer, M. P.; Windle, A. H.; Friend, R. H. *J. Phys. Chem. B* **1999**, *103*, 8116.

regular π-bonds of the SWNT react in addition to the defect sites. The fact that the SWNTs are completely destroyed when treated at higher temperatures (S500) supports the notion that the graphitic surface of the SWNTs is attacked under the chosen conditions. In this case the amount of sulfonate groups on the tubes surfaces should be adjustable by the reaction time and temperature, a situation which is highly desirable for the controlled modification of the properties of SWNTs and for further chemical modifications.

Conclusions

Hydrothermal treatment, notably in acids, opens new ways to modify chemically pristine SWNTs in a simple and controlled manner. It allows the direct introduction of functionalities such as chlorine, bromine, or sulfonate onto SWNTs which may be used for further selective chemical modification. The combined Raman, UPS, and XPS measurements clearly reveal functionalization of the SWNTs themselves and not of other carbon structures which also might be present in the sample. Prior to the functionalization step, disentanglement and polishing of the raw material takes place. At 500 °C new onionlike structures, or for the treatment in sulfuric acid new nanosized carbon particles, are formed.