CHEMISTRY OF
MATERIALS
Communication

Chem. Mater. **2009,** *21,* 4747–4749 4747
DOI:10.1021/cm902029m

Microwave-Assisted Bromination of Double-Walled Carbon Nanotubes

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Received July 11, 2009
Revised Manuscript Received August 31, 2009

The ability to functionalize carbon nanotubes (CNTs) through controlled structural modifications is an essential prerequisite for application purposes, as it may lead to increased solubility and processability[1−3] as well as opportunities for fine-tuning the physical and chemical properties,[4,5] thereby enabling the exploitation of the mechanical, thermal, and optical properties of CNTs[6] in a wide range of applications in both material[7] and biomedical sciences.[5,8,9] A major challenge in this field, therefore, is to develop a range of reliable and effective functionalization methodologies that allow the construction of CNTs-based macromolecular species of highly versatility and usefulness, to be further modified by coupling them to a variety of organic functionalities and in the mean time do not extensively disrupt the graphitic π-conjugated surface (consequently altering their electronic[10] and thus optical properties[11−13]). In this respect, halogenated CNTs-based materials can represent a useful class of intermediates as they could act as precursors to a number of organometallic species and suitable substrates for metal-catalyzed cross coupling reactions. Halogenation of CNTs has mainly been performed with highly oxidizing F_2 gas,[14−16] with electrochemically generated Cl_2 and Br_2[17] and with I_2 through a modified Hunsdiecker-type reaction.[18] The low-susceptibility of CNTs to weak oxidizing species, such as Br_2, was instead utilized as a means of purification for MWCNTs containing carbon nanoparticles[19] and to the best of our knowledge, no definitive reports about the C−Br bond formation on single- or double-walled CNTs have been reported at time. We thus report the synthesis and characterization of double-walled carbon nanotubes (DWCNTs) functionalized with Br_2 (**Br-DWCNTs**) under microwave-assisted (MiW) conditions,[20−22] to link covalently the Br atoms to DWCNTs with a percentage of functionalization of ca. 5−8 % in weight.

In a typical experiment, 30 mg of DWCNTs (Nanocyl-2100) were mixed with 5 mL of an aqueous solution of Br_2 (35 g·L^{-1}, corresponding to the solubility of Br_2 in H_2O at 20 °C) in a 10 mL glass tube. The tube was then sealed with a Teflon cap and sonicated until the mixture was visually homogeneous, before being irradiated in a MiW oven for 9 min (T = 180 °C). The typical orange color disappeared after completion of the reaction. The **Br-DWCNTs** were then isolated through filtration under reduced pressure (Millipore filter, 0.45 μm) as a black powder and dried. Again, the **Br-DWCNTs** were placed in a tube with 5 mL of aqueous Br_2 in order to perform another reaction cycle. In this way, several reaction cycles were realized, each one increasing the bromine content of **Br-DWCNTs**. After the last cycle, the **Br-DWCNTs** compound was washed with an aq. solution of NaS_2O_3 (~1 M), with pure H_2O (500 mL), rinsed with MeOH (a few mL), and dried under a vacuum to yield about 20 mg of product (~65% w/w). The same functionalization could also be achieved when a Lewis acid catalyst ($FeBr_3$, 0.5% w/w) was added in the presence of an excess of Br_2 (0.5 mL of Br_2 in 4.5 mL of distilled H_2O) under MiW irradiations (180 °C) for 12 h.

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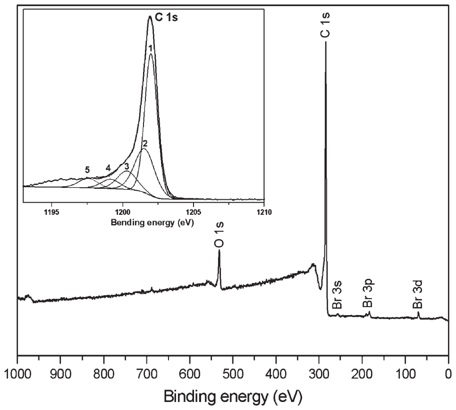

Figure 1. XPS survey spectrum of **Br-DWCNTs**. The C 1s XPS high-resolution spectrum is displayed in the inset.

With the aim to elucidate the chemical composition of the functionalized **Br-DWCNTs** material, XPS was employed as first characterization technique.[23] Figure 1 shows a typical survey spectrum, obtained after seven successive reaction cycles, revealing peaks from C 1s (at 284.7 eV), O 1s (at 532.3 eV), and the Br 3d, 3p, and 3s (at 70, 183.8, and 257.3 eV, respectively), with ~ 0.7 at % of Br and ~ 7.0 at % of O. The spectrum for the pristine DWCNTs (Nanocyl-2100, see Figure S1 in the Supporting Information) instead shows only C and O signals, with the latter displaying a weaker intensity with respect to that observed for **Br-DWCNTs** (2.6 oxygen at %). This slight enhancement of the intensity of the O peak could be attributed to a side nucleophilic-type substitution reaction of H_2O occurring at the C−Br centers.

The high-resolution C 1s core level spectrum (inset in Figure 1) is composed of five different components: (1) a main peak centered at 284.7 eV originated by the photoelectrons emitted from sp^2 carbon atoms with their shape-up structure (at around 291.3 eV); (2) a peak centered at 285.2 eV attributed to the sp^3 carbon atoms; (3) a component localized at 286.3 eV assigned to oxidized carbon atoms in both C−Br and C−O bonds; (4) and (5) two peaks centered at 287.4 and 289.4 eV, most probably generated by photoelectrons emitted from carbon atoms belonging to carbonyl and carboxyl groups, respectively.[23]

The Br 3d spectrum reported in Figure 2 (left) exhibits a single peak localized at 70.8 eV, which can be decomposed on Br 3d 5/2 (70.4 eV) and Br 3d 3/2 (71.5 eV, not shown). Furthermore, in the Br 3p spectrum (Figure 2, right), two characteristic emission peaks at 184.0 (Br 3p 3/2) and 190.6 eV (Br 3p 1/2) could be detected. These binding energy values are consistent with Br atoms covalently bonded to C atoms.[24] Other **DWCNTs**-bromine products could be formed under these reaction conditions, like physically absorbed Br^- and BrO_3^- ions or Br_2-**DWCNTs** charge-transfer complexes (CTC), where the Br_2 molecule act as an electron acceptor. However, the expected binding energies (Br 3p 3/2 = 182.5 ± 0.2 eV and Br 3d 5/2 = 68.5 eV for Br^-, Br 3d 5/2 > 72.6 eV for BrO_3^-, or Br 3p 3/2 = 181.0 ± 0.1 eV and Br 3d 5/2 = 67.4 ± 0.2 eV for CTC), are absent in the spectra.[24] All these observations thus suggest that only covalent C−Br type bonds are present. Further information on the peak positions can be extrapolated using reference compounds, like polymeric brominated hydrocarbons such as polybromostyrene.[25] Its Br-centered binding-energy values of the 3d 5/2 and 3p 3/2 peaks are equal to 70.7 ± 0.2 eV and 184.2 ± 0.2 eV, respectively, and are related to the binding energy of sp^2 carbon atoms at 284.8 ± 0.1 eV. These reference values are very close to those obtained by our investigations. Moreover, the assignation of the binding energy of the Br linked to the carbon is also given at 285.9 eV ± 0.1 eV; in this case, the shift induced by the presence of Br atoms, without considering the O contribution, is in the order of 0.9 eV. In brominated polyisoprenes, taking into account the oxygen component, there is a shift of 1.6 eV for both C−Br and C−O signals. The shift in the energy binding values is close to our experimental values (286.3 eV), supporting our hypothesis that bromohydrin-like species are also formed on the **Br-DWCNTs** surface.[26] The results obtained from XPS were then compared with those obtained from EDX using a scanning electron microscope (SEM, see Figure S3 in the Supporting Information). EDX analysis of both pristine and **Br-DWCNTs** shows signals arising from DWCNTs (carbon and oxygen) and from the catalyst particles (iron and molybdenum). As observed with XPS, **Br-DWCNTs** displayed the presence of brominated species. Moreover, quantitative EDX analysis (see Figure S5 in the Supporting Information) of the **Br-DWCNTs** samples showed 0.72 ± 0.2 at % Br atoms, in close agreement with that reported by XPS investigations.

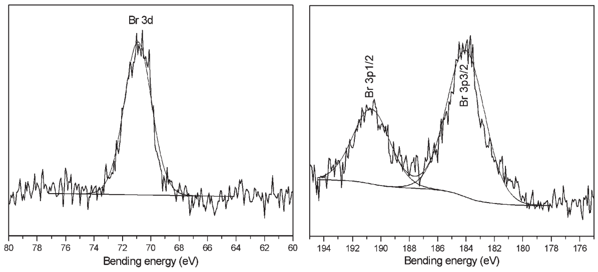

Figure 2. XPS high-resolution spectra (left) the Br 3d and (right) the Br 3p regions for **Br-DWCNTs**.

Raman spectra of both pristine DWCNTs and **Br-DWCNTs** materials were recorded using the 632.8 nm exciting line. The comparison between the Raman spectra of two batches of **Br-DWCNTs**, with functionalization degrees of 0.8 and 1.1 at %, on the basis of XPS results, and the pristine DWCNTs is reported in Figure 3. After spectra normalization, using the G band as a reference, one can observe some characteristic features related to the functionalization of carbon nanotubes. The inset (b) in Figure 3 shows the increase of the D band for the two brominated samples with respect to the pristine one, with

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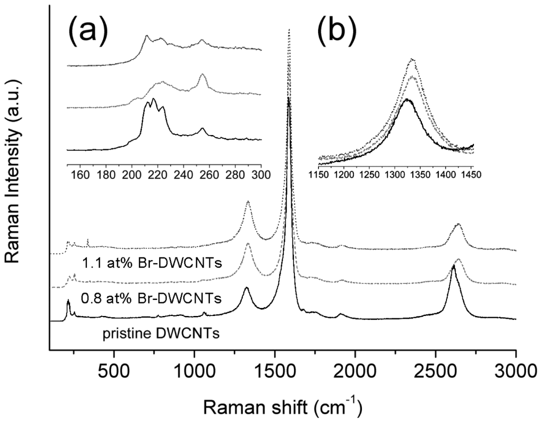

Figure 3. Normalized Raman spectra (λ_{exc} = 632.8 nm) of pristine DWCNTs and **Br-DWCNTs** (0.8 at% (----) and 1.1 at% (····)). In the insets, the magnified RBM region (a) and the D-band region (b).

a higher intensity for the more brominated sample. The D band is related to a double resonance process with the participation of one phonon and one defect state of the sp^2 carbon structure, as one obtains with functionalizing groups.[27] Its increase in intensity shows that more defects, and therefore functional groups, are present for the brominated samples. Other indications of the functionalization comes from the inset (a) in Figure 3, which shows a strong intensity decrease of the RBM bands at about 210 cm^{-1} that can be related to the reaction of the smallest CNTs among the DWCNT external walls,[28] although some intensity variations of bands at higher frequencies (338 and 256 cm^{-1}) suggests some inhomogeneity of the sampled nanotubes. In this part of the spectrum, one also notes the absence of the Br$-$Br band correlated to normal mode stretching of Br_2 at 242 cm^{-1} and of its overtones. This excludes any inner and outer physically adsorption[29] of Br_2 in the **Br-DWCNTs** samples. Many of the features observed Raman spectra support, therefore, the bromine covalent functionalization of the nanotubes.

TGA analysis has been used to evaluate the thermal behavior of the DWCNTs after bromination. Differential thermal plot of 0.8 at % **Br-DWCNTs** in Figure 4 shows a decomposition step between 100 and 425 °C, with a temperature of maximum decomposition (T_{max}) at 304 °C. These temperature values are too high to be associated to the elimination of physically adsorbed Br_2, in agreement with the other analytical results. Furthermore, taking into account the relative high uncertainty of the TGA measurements, the overall weight loss in this temperature range is about 8% w/w, which is in good agreement with the values obtained from the XPS characterizations (Br content of 5.3% w/w). The thermal behavior of **Br-DWCNTs** dramatically differs (see Figure S2 in the Supporting Information) from that of pristine DWCNTs, as the latter shows a pronounced weight loss only at high T (2.1% at 713 °C). The TGA profile very closely resembles that of the iodinated SWNTs reported by Coleman et al.,[18] which showed a similar decomposition range (100$-$400 °C) but a smaller T_{max} value ($\sim$250 °C). The latter observation could be explained considering the lower binding energy of the C$-$I bond with respect to that of C$-$Br, and consequently to the higher decomposition temperature required to remove the Br atoms.

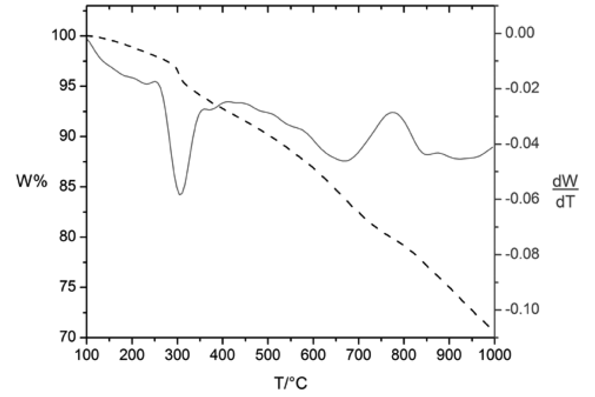

Figure 4. Thermogravimetric plot (-----) and differential thermal plot (——) of **Br-DWCNTs** (4.096 mg) recorded under a N_2 flow (60 mL min^{-1}) with a temperature increase of 10 °C min^{-1}.

To evaluate the presence of structural and morphological changes of DWCNTs after the bromination reaction, scanning and transmission electron microscopies (SEM and TEM, Figures S3, S4 and S6 in the Supporting Information) were carried out. No substantial differences between pristine DWCNTs and **Br-DWCNTs** could be detected, showing that the MiW treatment did not affect the structure of the CNTs frameworks.

In conclusion, in this work we have reported for the first time a bromination reaction between DWCNTs and Br_2, with the presence of the Br atoms around the exo-surface of the DWCNT walls in ca. 5$-$8% in weight. Raman investigations also showed a certain degree of functionalization of the **Br-DWCNTs**, however accounting for a mild alteration of the graphitic π-conjugated surface. Preliminary metal-catalyzed cross-coupling reactions made with **Br-DWCNTs** suggest that these new modified CNTs-based precursor could open new synthetic possibilities for designing novel functionalized CNTs, further expanding the versatility and applications fields of this fascinating allotropic family of carbon.

Acknowledgment. This work was supported by the European Union through the Marie-Curie Initial Training Network "FINELUMEN", grant agreement PITN-GA-2008-215399, the University of Trieste, INSTM, University of Namur, the Belgian National Research Foundation (FRS-FNRS, through Contract 2.4.625.08 F), the "Loterie Nationale", and the Région Wallonne through the "SOLWATT" program (Contract 850551). H.T. thanks the institutional program FUNDP-CERUNA and FRS-FNRS for his postdoctoral fellowships. J.-F.C. is a Research Associate of the FRS-FNRS. We also thank Nanocyl for supplying the Nanocyl-2100 samples.

Supporting Information Available: Experimental details, XPS spectrum (Figure S1), TGA of the pristine **DWCNTs** (Figure S2), SEM and EDX analysis of both pristine and **Br-DWCNTs** samples (0.7 at %) (Figure S3 and S5) and low- (Figure S4) and high- (Figure S6) magnification TEM images (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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