

## Facile Removal of Amorphous Carbon from Carbon Nanotubes by Sonication

Ali Rinaldi, Benjamin Frank, Dang Sheng Su,\*  
Sharifah Bee Abd Hamid, and Robert Schlögl

Department of Inorganic Chemistry,  
Fritz Haber Institute of the Max Planck Society,  
Faradayweg 4-6, D-14195 Berlin, Germany

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Numerous studies on carbon nanotubes (CNTs) for a wide range of applications demonstrate the demand for effective, low-cost, and upscalable purification of this fascinating carbon allotrope. Metal (oxide) particles as the catalyst residues and soot-like amorphous carbon as pyrolysis byproduct are the common impurities present in CNTs produced via catalytic chemical vapor deposition (CCVD). The defect-rich carbon debris has chemical and physical properties different from that of the graphitic CNTs. In particular, it provides a higher reactivity for gasification, that is, combustion or methanation. Thus, in principle, amorphous carbon can be selectively removed from the CNT surface. The presence of amorphous carbon impurities on the CNT surface can have severe consequences for the desired applications, for example, in electrochemistry or catalysis.<sup>1,2</sup> With respect to the interaction of CNTs with other matrices, their specific functionalization is the most common way to get control over the CNT–substrate interaction, for example, for anchoring of nanoparticles, for filling with metal nanoparticles, for the application as a polymer additive, or to enhance the dispersibility in aqueous media for biomedical and environmental applications.<sup>3–5</sup> Thus, accurate synthesis and functionalization strategies are the prerequisite to attach the desired surface groups to the CNTs and not to amorphous carbon.<sup>6</sup> The treatment with HNO<sub>3</sub> of varying concentrations and temperatures is a common method to remove metal (oxide) and carbon impurities from CNTs and to subsequently functionalize the surface. However, the density and type of surface functional groups created

by HNO<sub>3</sub> depend on the graphitic character of the carbon support.<sup>7,8</sup> Thus, to avoid a broad range of different surface functionalities, it is of crucial importance to remove amorphous carbon impurities from CNT samples.

In the present study we investigate the effect of ultrasonic treatment (UST) to remove amorphous carbon from as-received CNTs and from mildly HNO<sub>3</sub>-washed CNTs. In principle, UST provides acoustic streaming and jet pulses in the CNT suspension allowing the loosely attached amorphous carbon to detach and further decompose into organic fragments via pyrolytic and/or oxidative pathways due to the implosion of microbubbles. The starting materials for this study are commercial multiwalled CNTs (Baytubes, Bayer) with a carbon purity of 95 wt % and an average outer diameter of 10 nm. Metal (oxide) particles are encapsulated by graphitic carbon either at the tip or in the hollow channel of the tubes. The physico-chemical characterization of the pristine material has been described elsewhere.<sup>9</sup> High-resolution transmission electron microscopy (HRTEM) shows a broad distribution of defects over the individual CNTs. Some CNTs show a straight texture with well-ordered graphene layers while other CNTs exhibit curved texture as a result of defective graphene layers. The CNT surface is randomly coated with a monolayer up to several layers of amorphous carbon (Supporting Information, Figure S1).

The effect of ultrasonic treatment was investigated for the pristine Baytubes (pCNT) as well as for the oxidized Baytubes (oCNT). For oxidation treatment the pCNT sample was washed with 3 mol L<sup>-1</sup> HNO<sub>3</sub> at ambient temperature for 24 h followed by filtration and rinsing with deionized water. For the UST experiments 1 g of CNT sample was suspended in an aqueous solution of ethanol (10 vol %). A probe-type ultrasonic homogenizer GM2200 (Bandelin) with the sound frequency of 20 kHz and 200 W of maximum power output was used. UST was performed at 10% power in pulse mode with an active interval of 0.5 s. The temperature of the suspension was kept constant at 273 K in an ice bath. The obtained solid was subsequently washed with warm 1 mol L<sup>-1</sup> NaOH followed by Soxhlet extraction with water and acetone for 24 h, respectively. The NaOH washing step was included to improve the dissolution of oxidized amorphous carbon and oxidation debris.<sup>6</sup> Labeling assignments are listed in Table 1. Mild conditions were used during the entire cleaning procedure to minimize structural damage of the CNTs. The pulse mode for UST experiments allows the system to maintain a constant temperature by cooling down after each cavitation cycle.

\*Corresponding author. Fax: +4930 84134405; Tel: +4930 84134464.

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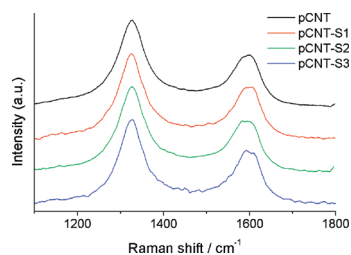
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**Table 1. Physio-Chemical Properties of As-Received, Acid-Washed, and Sonicated Samples**

sample	treatment	$T_{\max}$ , <sup>a</sup> K	$I_D/I_G$ <sup>b</sup>	ash, <sup>a</sup> wt %	CO <sub>2</sub> , <sup>c</sup> mmol g <sup>-1</sup>	CO, <sup>c</sup> mmol g <sup>-1</sup>
pCNT	as-received	795	2.58	4.3	0.051	0.155
pCNT-S1	UST for 1 h	825	2.45	3.54	0.098	0.244
pCNT-S2	UST for 2 h	820	2.4	3.6	0.097	0.246
pCNT-S3	UST for 3 h	825	2.2	0.037	0.097	0.247
oCNT	HNO <sub>3</sub> -NaOH	825	2.47	1.48	0.159	0.256
oCNT-S2	UST for 2 h	875	2.64	1.47	0.121	0.195
oCNT-S3	UST for 3 h	900	2.3	0.77	0.136	0.197

<sup>a</sup> From thermogravimetric analysis (TGA), 5 K min<sup>-1</sup>, 5% O<sub>2</sub> in Ar.

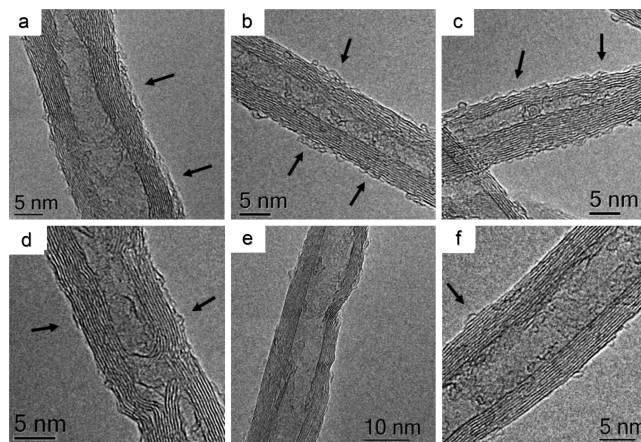
<sup>b</sup> From fitting procedure by Sadezky et al.<sup>10</sup> (Supporting Information, Figure S2 and Table S1). <sup>c</sup> From temperature-programmed desorption (TPD) up to 1123 K.



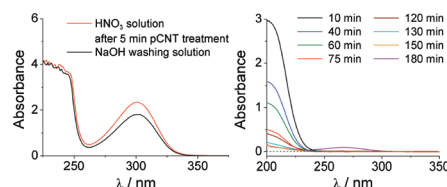
**Figure 1.** Raman spectra of pCNT samples after UST. The spectra are normalized with respect to their D-band intensity.

Oxidation stability and ash content of the samples were determined by TGA performed under 5% O<sub>2</sub> in Ar. After the treatments the oxidation stability increases accompanied by a gradual decrease of the ash content (Table 1). This observation is in agreement with previous works that reported the removal of metal impurities from carbon samples after HNO<sub>3</sub> treatment.<sup>11</sup> Also the mild sonication treatment exhibits the ability to remove metal impurities from the pCNT sample. To our knowledge this effect has not been reported in literature so far. The inorganic impurities observed by EDX (Supporting Information, Figure S3) originate from the catalyst (support) and occasionally from the ultrasonic probe instrument (Ti).

Raman analyses presented in Table 1 and Figure 1 demonstrate the improvement of the graphitic (G) signal after the treatments (lower  $I_D/I_G$ ) which tends to indicate the removal of disordered (D) amorphous carbon. The D-band around 1320 cm<sup>-1</sup> of the sonicated pCNTs is slightly sharper than for the as-received material, and especially after ultrasonic treatment for 3 h, the G-band located at around 1600 cm<sup>-1</sup> appears slightly intensified. Thus, the improvement in the oxidation stability of the treated samples can be attributed to the removal of metal impurities and amorphous carbon. In the context of CNT oxidation, amorphous carbon attached to the basal plane potentially acts as oxidation initiator creating hotspots to induce the CNT combustion. Regarding the mild HNO<sub>3</sub> treatment, the careful HRTEM analysis points out the presence of various structural modifications or damage to the CNT surface (Figures 2a–d). Some of the prismatic



**Figure 2.** HR-TEM images of pCNT (a), oCNT (b–d), pCNT-S1 (e), and pCNT-S2 (f). The arrows highlight the bent/curved prismatic edges and graphene fragments.



**Figure 3.** UV-vis absorption spectra of filtered solutions from HNO<sub>3</sub>-NaOH treatments (a) and from UST depending on the treatment time (b).

edges in the oCNT sample are curved and inclined from the flat basal plane. Single graphene flakes of about 2 nm in diameter attached to the CNT surface are also observed (Figure 2b,d). Oxidation debris is frequently observed on oCNT. The appearance of graphene fragments is a strong indication of the extensive oxidation of the CNT surface. Accordingly, the amount of surface functional groups decomposing as CO and CO<sub>2</sub> doubles after the acid treatment (Table 1 and Supporting Information, Figure S4).

The degradation products from the oxidative treatment are detected in the HNO<sub>3</sub>-NaOH washing solutions by UV-vis and FTIR spectroscopic analyses. UV-vis spectra in Figure 3a show strong and broad absorption from 200–350 nm. This observation is consistent with previous studies on carbon black. Here, the treatment with concentrated HNO<sub>3</sub> resulted in the dissolution of polynuclear aromatic compounds rich in functional groups.<sup>12</sup> Stretching vibrations of aromatic C=C and C=O bonds were detected in the FTIR spectra of HNO<sub>3</sub> and NaOH washing solutions in the present study (Supporting Information, Figure S5). Against that the aliphatic hydrocarbons cannot be detected by FTIR spectroscopy. From the data presented above one can reasonably conclude that the mild HNO<sub>3</sub> treatment oxidatively removes some amorphous carbon and also extensively oxidizes the CNT surface resulting in surface damage and the dissolution of functionalized polyaromatic fragments. The oxidation probably takes place on the existing defects present on the walls and tips of the CNTs.<sup>13</sup>

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In contrast, the ultrasonic treatments avoid rigorous damage to the CNT surface while effectively cleaning from amorphous carbon as verified by HRTEM (Figure 2e,f). The functionalization of the CNTs by UST is moderate as compared to the HNO<sub>3</sub> treatment resulting in a modest increase in the amount of CO and CO<sub>2</sub> from TPD experiments (Table 1 and Supporting Information, Figure S6). The HRTEM analysis indicates that the sonication treatment avoids the opening of the CNT tips (Supporting Information, Figure S7), which is commonly observed after oxidative treatments.<sup>14</sup> UV-vis analyses of the filtrate after different times of sonication reveal absorption in the range of 200–350 nm with much lower intensity at higher wavelengths (Figure 3b). In general the absorption is by far weaker than in the solution of HNO<sub>3</sub> treatment. The intensity decreases with sonication time suggesting the decomposition of the dissolved compounds and/or scattering by carbon particulates in the solution. This is in agreement with almost constant TPD profiles of CO and CO<sub>2</sub> desorption as a function of sonication time indicating that the ultrasonic cleaning via OH radicals as a result of water sonolysis is a rapid process and does not further attack the CNT surface once the attached carbon is removed. TPD experiments were performed with gas-phase analysis by MS and GC in parallel. Slight differences between the *m/e* 28 trace and the actual CO desorption profile for the sonicated samples indicate the presence of further species. Indeed the evolution of methane, ethylene, methanol, ethanol, acetone, and other hydrocarbons with and without functional groups was observed during the TPD of sonicated samples (Supporting Information, Figure S8). The efficiency and nature of such ultrasonic-mediated molecular surface modification can be enhanced and possibly controlled by the type of solvent used for suspension of the CNTs. First experiments using ethanol or THF resulted in a different, however, drastically intensified pattern of hydrocarbons released during TPD (Supporting Information, Figures S9–S10). Against that, the pCNT and oCNT samples show no indication of hydrocarbons released during the course of TPD experiments. Such observations highlight the complex nature of the chemical effect on the CNT samples exerted by the UST. This again supports the argument that oxidation is not the dominant pathway for the purification process. FTIR investigation of the solution after water Soxhlet extraction exhibits the typical bands of C–H and C=O stretching vibrations (Supporting Information, Figure S11). The presence of aromatic groups is not clearly supported by the FTIR spectra obtained. Previous studies on the degradation of polyaromatic hydrocarbons (PAHs) with UST in aqueous solution proposed that the pyrolysis of PAHs occurs inside the microbubbles, which is the dominant pathway to evolve gaseous products such as CO, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub>.<sup>15</sup> Thus, we suggest that the pyrolysis of dissolved amorphous carbon fragments is responsible for the cleaning

effect during ultrasonic treatment. The UST results in the gradual increase of the graphitic character of the CNT sample as demonstrated by the decreasing  $I_D/I_G$  ratio with sonication time (Table 1). This is in agreement with the increase in oxidation stability of the sample and cleaner CNT surface demonstrated in thermal analysis data (Table 1) and HRTEM images (Figure 2e,f), respectively.

In order to strengthen the argument of the efficiency for the removal of amorphous carbon and/or oxidation debris from CNT samples, UST was also performed on the oCNT sample for 2 and 3 h, respectively. These results are consistent with the sonication experiments of pCNT. The sonication treatment of oCNT results in the increase of the oxidative stability derived from the higher combustion temperature  $T_{\max}$  (Table 1). This can be attributed to the gradual decrease of the ash content and the increase of the graphitic character (lower  $I_D/I_G$  value) which is most probably due to the removal of oxidation debris from the oCNT surface. Indeed the TEM investigations of the sonicated samples exhibit less oxidation debris coating on the oCNT surfaces (Supporting Information, Figure S12a–d). However, there is still some surface damage and a certain amount of oxidation debris observed in the sonicated samples. The TPD profiles of sonicated oCNT samples exhibit a decrease in the CO and CO<sub>2</sub> amount released (Supporting Information, Figure S4). This is attributed to the dissolution and decomposition of the functionalized oxidation debris during the UST. We furthermore observe completely different shapes of CO and CO<sub>2</sub> evolution during TPD for the sonicated pCNT and oCNT samples pointing at a substantial restructuring of the CNT surfaces even under applied “mild” HNO<sub>3</sub> treatment conditions. However, the integrity of the CNT samples is still preserved even after HNO<sub>3</sub>-sonication treatments, as shown by similar N<sub>2</sub> adsorption isotherms (Supporting Information, Figure S13). No drastic damage and/or opening of the CNT tip is expected that would otherwise increase the surface area. The removal of the oxidation debris is important to provide a rigid surface for further functionalization and for the chemical and physical interactions with other substrates.

In summary, the effective and nondestructive removal of amorphous carbon and oxidation debris from as-received and HNO<sub>3</sub>–NaOH treated commercial multiwalled CNTs, respectively, has been demonstrated by an easy-to-handle, noncorrosive, eco-friendly, and fast ultrasonic treatment process. This treatment was demonstrated to be competitive with the frequently used HNO<sub>3</sub> washing procedure.

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**Supporting Information Available:** TEM images, Raman spectrum, SEM-EDX, TPD profiles, Experimental Section, FTIR spectra, and N<sub>2</sub> adsorption isotherms (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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