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Imaging of Oxygen-Containing Groups on Walls of Carbon Nanotubes

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Functionalized carbon nanotubes (CNTs) are of great interest in the fields of biomedicine,[1] materials science,[2] synthetic chemistry,[3] electrochemistry,[4] and nanotechnology.[5] Oxygen-containing functional groups on the walls of CNTs are often used as starting points for the covalent attachment of larger inorganic[6] or organic molecules,[3b] nanoparticles,[2b,7] proteins,[1b] and DNA[1a] to nanotubes. The oxygen-containing groups (carboxy, carbonyl, hydroxyl, and lactyl) are typically introduced into carbon nanotubes by treating them with solutions of strong oxidizing mineral acids (e.g., HNO_3) or their mixtures.[1–5] Several methods have been used to shed light on the amount of oxygen-containing groups generated on the walls of CNTs, such as IR spectroscopy,[8a] X-ray photoelectron spectroscopy (XPS),[4f,8c,9] electrochemistry,[9] or Raman spectroscopy.[8] However, these methods provide information only on the amount of the oxygen-containing groups, not on their location on the CNT walls. Since a broad range of nanotechnology applications relies on functionalized CNTs, it is of great importance to be able to image and locate these oxygen-containing groups on the walls of carbon nanotubes to better understand and tailor the properties of functionalized CNTs.

Transmission electron microscopy (TEM) and scanning TEM (STEM) are very powerful methods for the direct imaging and analysis of nanostructures down to the subnanometer range.[10] A combination of TEM and energy-dispersive X-ray spectroscopy (EDX) or electron energy-loss spectroscopy (EELS) enables the collection of chemical and electronic data. However, up to now, the imaging and exact location of oxygen-containing groups on the surface of CNTs has not been achieved. Indeed, the direct imaging of oxygen-containing groups is a very challenging task due to the inherent difficulty in distinguishing low atomic number elements (H, C, O) using EDX and the relatively low sensitivity of EELS towards determination of oxygen.

Very recently Yudasaka and co-workers introduced a method for site identification of carboxyl groups on graphene edges with Pt-ammine complex, imaging these “Pt-stained” graphene sheets by high-resolution TEM.[11] However, in best of our knowledge, there is no report on site identification of oxygen-containing groups on carbon nanotubes.

High-angle annular dark-field STEM (HAADF-STEM) has been recently used for atomic-scale detection of organic molecules tagged with triiodobenzoyl moieties coupled to single-walled carbon nanotubes (SWNTs).[12] In HAADF-STEM micrographs, the imaging intensity is proportional to the square of the atomic number and, consequently, the higher intensities correspond to the heavier elements.

Herein we present for the first time a method for highly precise and high-resolution imaging and location of oxygen-containing groups on the walls of carbon nanotubes. We offer a soft-chemistry approach by means of tagging oxygen-containing groups on the surface of CNTs with Eu^{III} through coordinate covalent bonds. We observe Eu^{III} bonded to oxygen-containing groups by HAADF-STEM, which offers high-contrast and high-resolution imaging of oxygen-containing groups marked with Eu^{III} on the surface of carbon nanotubes.

In detail, multiwalled carbon nanotubes (MWNTs) were first functionalized to give surface oxygen-containing groups at the defect sites of the outer graphene layer of the MWNT by refluxing them in 6 M nitric acid at 80 °C for 24 h.[8b] X-ray photoelectron spectra were collected for both as-received and functionalized MWNTs to confirm functionalization of their surface (Figure S1 in the Supporting Information). Functionalized multiwalled carbon nanotubes (f-MWNTs) that were washed in distilled water and dried were dispersed in water (0.5 $mg\,mL^{-1}$) containing europium nitrate (0.2 mM). Europium nitrate hydrolyzes to europium hydroxide, which after a few hours spontaneously forms coordinate covalent bonds with oxygen-containing groups on the surface of the MWNT (Figure 1).[13] When a control ex-

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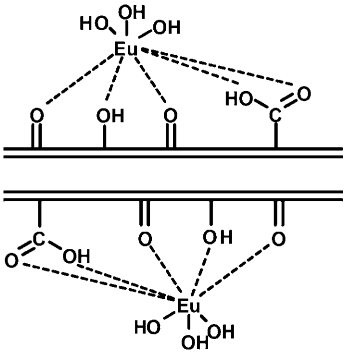

Figure 1. Schematic of tagging of oxygen-containing groups with Eu^{III}.

periment was performed using a nonfunctionalized (vacuum annealed at 1050 °C to remove all oxygen-containing groups) MWNT, no adsorbed Eu^{III} was found on the surface of the MWNT. This is consistent with results of Bonifazi et al. which needed to use Eu^{III} coupled to a phenanthroline molecule to adsorb a phenanthroline-Eu^{III} complex at the surface of the SWNT through π–π interactions.[14]

Europium(III) bonded to oxygen-containing groups on the walls of MWNTs was imaged by HAADF-STEM. Figure 2 A–C shows the distribution of the Eu atoms along the nanotube length. Since dark-field HR-STEM uses high-angle diffracted electrons, it provides a highly sensitive signal dependence on atom mass. It is clearly visible in Figure 2 that oxygen-containing groups to which the Eu^{III} is bonded are irregularly scattered on the surface of the nanotubes and that they form approximately 10 nm wide islands and chainlike structures. This is most likely due to the fact that oxidation of the outer graphene sheet of the MWNT by HNO_3 preferably occurs at defect sites and mechanically stressed regions. Detailed HAADF-STEM observation of one of the Eu^{III} chains shows single bright spot structures (marked by arrows in Figure 2 C) with a diameter of less than 0.9 nm, which represents single Eu atoms and/or their small clusters. Figure 3 demonstrates that there is no Eu^{III} bonded to nonfunctionalized MWNTs after treating them with Eu^{III} using the same procedure as for f-MWNT (control experiment). If we keep in mind that one molecule of europium(III) hydroxide can create up to a maximum of five coordinate covalent bonds with electron donors (oxygen-containing groups), we can conclude that it is possible to image and locate only a few oxygen-containing groups by tagging them with Eu^{III}. TEM/EDX was used to confirm that the bright spots in the HAADF-STEM images correspond to the europium(III). Indeed, the TEM/EDX spectra recorded by point analysis of the high-contrast spots marked by an arrow in Figure 2 A reveal clear Eu Lα and Eu Lβ lines, therefore confirming the composition of these high-contrast spots (Figure 4).

The TEM/EDX elemental mapping was carried out for further confirmation that europium hydroxide was adsorbed on the MWNT, as shown in Figure 5. Elemental distribution

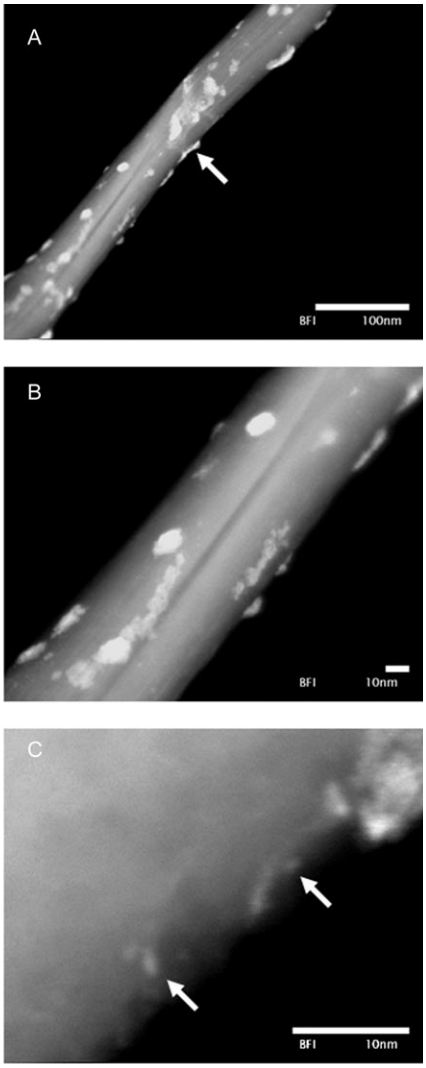

Figure 2. HAADF-STEM images of oxygen-group-functionalized carbon nanotubes marked with Eu^{III} at different magnifications. Image C clearly shows the presence of individual europium atoms (bright dots, marked by arrows).

profiles of europium and oxygen match and show maxima at the same place, corresponding to adsorbed europium hydroxide at the functional groups of the MWNT.

High-resolution TEM (HR-TEM) was employed to study larger spots shown in Figure 2 A,B. Figure 6 shows an HR-TEM image of a europium hydroxide layer adsorbed on the MWNT. It can be seen that the resulting structure of larger spots is actually a multilayer with a spacing of 0.31 nm. This corresponds to the (222) lattice plane of europium(III) oxide.[15] Eu_2O_3 is generated from $Eu(OH)_3$ by evaporation of water molecules owing to prolonged exposure to the high-energy TEM electron beam.

In conclusion, we demonstrated for the first time that it is possible to locate oxygen-containing groups on the walls of carbon nanotubes by marking them with Eu^{III} and observing them by HAADF-STEM. We also demonstrated that oxygen-containing groups are typically scattered over the

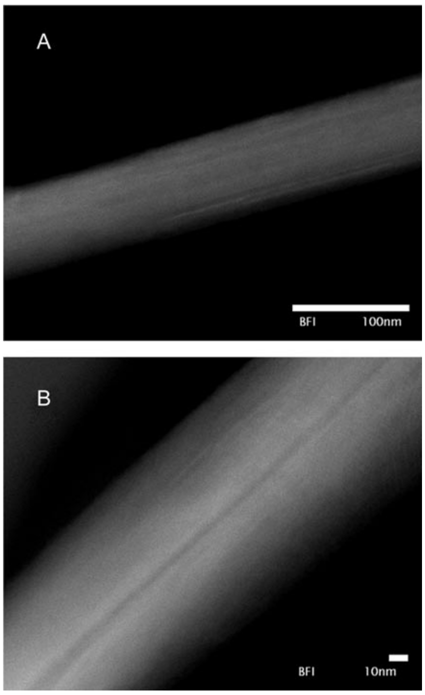

Figure 3. HAADF-STEM images of a nonfunctionalized (annealed) MWNT after treatment with Eu^{III} using the same procedure as for f-MWNT. This control experiment demonstrates that the adsorption of Eu^{III} is oxygen-site specific and that there is no nonspecific adsorption in the framework of experimental conditions used.

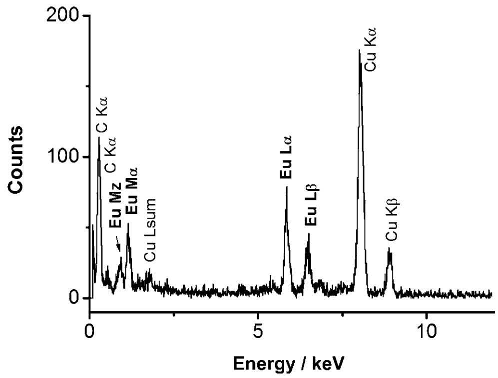

Figure 4. TEM/EDX analysis spectrum of the "bright spots" in the dark-field HR-STEM image marked by an arrow in Figure 2 A.

surface of carbon nanotubes in nanometer-sized islands and several tens of nanometer-long chains. Our method for imaging oxygen-containing groups on the surface of CNTs is simple and sensitive, and it should find applications in many fields of nanotechnology.

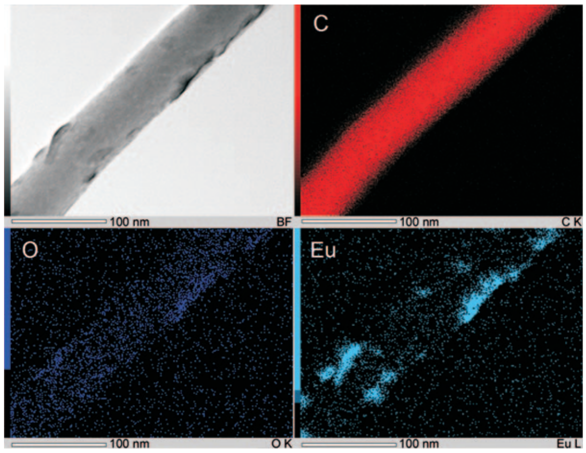

Figure 5. HAADF-STEM/energy-dispersive X-ray spectroscopy elemental mapping of images of oxygen-group-functionalized carbon nanotubes marked with Eu^{III} for C K edge (red), O K edge (dark blue), and Eu L edge (light blue).

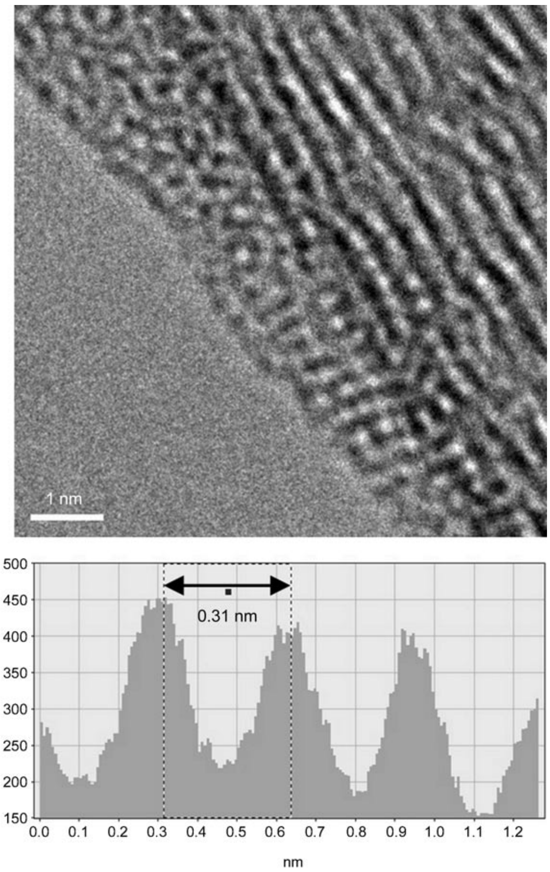

Figure 6. HR-TEM image of a Eu^{III}-tagged MWNT (top), shown with the lattice spacing (bottom).

Experimental Section

Functionalization of CNTs with oxygen-containing groups: Multiwalled carbon nanotubes were functionalized in concentrated nitric acid (6 M) at 80 °C for 24 h.[8b] The acid/MWNT mixture was subsequently washed away with distilled water and centrifuged several times until the aqueous solution reached neutral pH. Subsequently, the oxygen-group-functionalized multiwalled carbon nanotubes were filtered through a 0.2 μm membrane (Nuclepore Track-Etch Membrane, Whatman) and allowed to air dry.

Marking functionalized MWNTs with Eu^{III}: The europium hydroxide marking steps involved dispersion of f-MWNTs in 0.2 mM europium nitrate (concentration of carbon nanotubes of 0.5 mg mL^{-1}; typically 2 mg of f-MWNTs in 4 mL of 0.2 mM europium nitrate) followed by 5 min ultrasonication. This mixture was then stirred by magnetic stirring (at 550 rpm) for 18 h, filtered through a 0.2 μm Nuclepore membrane, thoroughly washed with distilled water, and finally allowed to air dry. Additional information on experimental details and equipment used is presented in the Supporting Information.

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