Electrochemical Functionalization of Individual Single-Wall Carbon Nanotubes

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Abstract. An electrochemical method is applied to attach functional groups to individual single-wall carbon nanotubes. This approach allows both the reductive and oxidative coupling of substituted phenyl groups. Due to polymerization of the reactive species formed at the nanotube/electrolyte interface, coatings with a thickness of up to 20 nm are obtained. The thickness of the deposited layer can be effectively controlled by the magnitude and duration of the potential applied. By choosing appropriate additional substituents in the coupling reagent, the presented method offers the possibility to tune the surface properties of the modified nanotubes over a wide range.

INTRODUCTION

Covalent chemical modification methods for carbon nanotubes developed to date comprise (i) tube oxidation to introduce carboxylic acid groups [1] (in many cases followed by amide linkage formation in order to attach further molecules [2], or nanoparticles [3]), (ii) fluorination [4], (iii) addition of reactive organic species like carbenes [5], nitrenes [6], or phenyl radicals [7], and (iv) 1,3-dipolar cycloaddition of azomethine ylides [8]. All of these methods have been applied exclusively to single-wall carbon nanotube (SWNT) *bulk* material, which consists of a variety of tubes of different chirality and diameter. In addition, such samples, even after the usually employed purification, still contain significant amounts of impurities like amorphous carbon or catalyst particles. In order to gain a better understanding of the chemical reactivity of carbon nanotubes, it is therefore important to investigate the modification of individual tubes. Here we demonstrate that electrochemistry constitutes a powerful approach to couple functional groups to isolated SWNTs. Electrochemistry is especially well suited for that goal since the extent of reaction can be directly controlled by the magnitude and duration of the applied potential. As illustrated in the scheme of Fig. 1, we developed two different coupling schemes, consisting of (**A**) the reductive coupling of an aromatic diazonium salt, and (**B**) the oxidative coupling of an aromatic amino compound. In both cases, first a reactive species is created via charge transfer between the SWNT and an organic molecule at the nanotube/electrolyte solution interface. The reactive radical species then undergoes covalent bonding to the carbon lattice of the tube. While the reductive coupling leads to C-C bond formation, a C-N bond is obtained in the oxidative case. Both coupling types are compatible with a wide range of (additional) substituents attached to the aromatic ring, which could be used as selective binding site for macromolecules or ions. In the present study, we used a 4-nitrobenzenediazonium salt for the coupling under reductive conditions (Fig. 1**A**),

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and either 4-aminobenzylamine (Fig. 1**B**, R = -CH_2-NH_2) or 4-aminobenzoic acid (Fig. 1**B**, R = -COOH) in the oxidative coupling scheme.

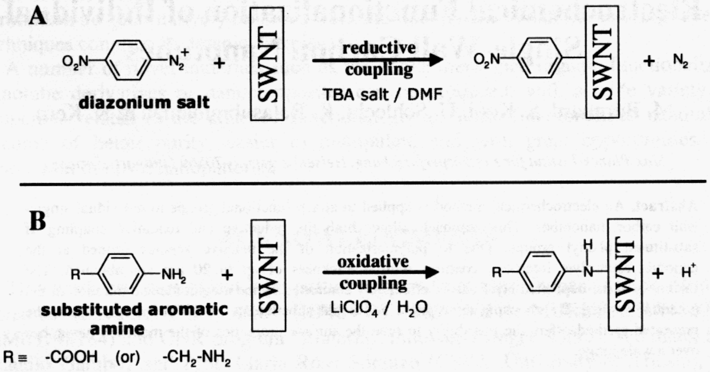

FIGURE 1. Schematic representation of the reductive (**A**) and oxidative (**B**) coupling scheme used to attach substituted phenyl groups to individual SWNTs.

EXPERIMENTAL

SWNTs (arc discharge material purchased from CARBOLEX®, Lexington, KY) were dispersed with the aid of ultrasonication in an aqueous surfactant solution (1 wt % lithium dodecylsulfate), and then purified by centrifugation. The SWNTs were deposited from the purified dispersion on silicon wafers with a 100 nm thick, thermally grown SiO_2 layer by placing a droplet on the substrate, followed by rinsing with pure water after an adsorption time of 30 min. Subsequently, AuPd electrode lines (15 nm thickness on 2 nm of titanium as adhesion layer) were fabricated on top the tubes using e-beam lithography. After lithography, the substrate was cleaned by immersion in dimethylformamide (DMF) for at least two hours at room temperature. This cleaning procedure turned out to be crucial to remove the residues of the e-beam resist (PMMA) form the surface. Electrochemical modification was performed in a home-built miniaturized cell equipped with platinum wires as counter and pseudo-reference electrodes. For potential control, a Solartron 1285 potentiostat was employed. As electrolyte salt, tetrabutylammonium tetrafluoroborate (TBA salt) or lithium perchlorate was used in a concentration of 0.1 M. The concentration of the organic reagents (diazonium salt in DMF, or amine in water) was 1 mM. AFM images were acquired with a Digital Instruments Nanoscope IIIA microscope operated in Tapping Mode, using commercial silicon cantilevers.

RESULTS AND DISCUSSION

Figure 2 displays a representative AFM image of SWNTs after reductive coupling of the aromatic diazonium salt for 60 sec at -1.3V vs. Pt. It is apparent that while the tube parts covered with the AuPd electrode line remained unchanged, the uncovered portions of the tubes are substantially thickened due to the electrochemically deposited layer.

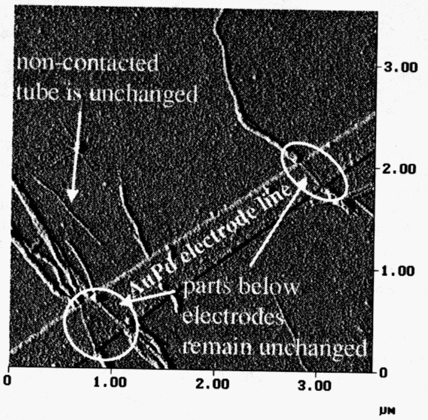

FIGURE 2. AFM image of SWCNTs after reductive coupling of 4-nitrobenzene-diazonium tetrafluoroborate (1 mM in DMF/TBA salt, 60 sec at -1.3V vs. Pt).

Moreover, the nanotubes which make no contact to the electrode remained completely unmodified, testifying that the coating indeed results from the coupling reaction, and not from some type of surface contamination. The average height increase after modification of the tubes in Fig. 1 is 6 nm. This thickness of the coating, which is quite homogeneous along a tube, indicates that more than a mono-molecular layer was deposited. The formation of a thicker coating can be explained by the polymerisation of the radical species created at the electrified SWNT/electrolyte interface. A similar multi-layer growth has been observed in the electrochemical modification of HOPG surfaces [9]. In order to ensure that the observed thickness increase is indeed due to the electrochemically induced layer deposition, we performed a control experiment in which thin (~ 3 nm in height) SWNT bundles, shown in the AFM image of Fig. 3**A**, were first treated under the same conditions as for the electrochemical coupling, however, without an organic reagent in the electrolyte. As apparent from the AFM image in Figure 3**B**, no thickness increase can be detected in this case. This result demonstrates that there is no swelling of the bundle due to an intercalation of solvent and/or ions. Only after the electrochemistry performed on the same bundles in the presence of an amine under oxidative conditions, a coating is observed (AFM image in Figure 3C).

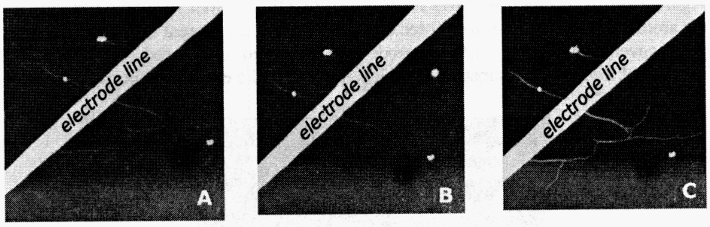

FIGURE 3. Three AFM images acquired during the control experiment performed to exclude that solvent and/or ion intercalation is the origin of the observed thickness increase of the SWNTs. Starting from the unmodified thin SWNT bundles below the electrode line (**A**), a potential of +0.75V vs. Pt was applied for 90 sec in an LiClO$_4$ electrolyte solution without organic reagent. Afterwards, no change in the thickness of the bundles could be observed, as apparent from the AFM image in (**B**). The same bundles were then treated under the same potential conditions in an electrolyte solution containing 4-aminobenzylamine in a concentration of 1 mM. The AFM image in (**C**) clearly reveals that in this case a coating was formed. The height scale is 10 nm in all three images.

Further studies revealed that the thickness of the coating can be controlled by the duration of the applied potential. In case of oxidative coupling of 4-aminobenzylamine, an average height increase of 6, 9, and 12 nm was found after applying a potential of +0.85 V vs. Pt for respectively 30, 60, and 90 sec, as determined from AFM height profiles of tube ensembles (>20 tubes). The tubes are fully covered by a closed layer, provided that coatings thicker than ~6 nm are formed. Coatings with a total thickness of 15-20 nm exhibit a thickness variation of several nanometers. This observation indicates that the attachment of the molecules presumably starts at defects sites, resulting in local deposits that finally become interconnected. Investigations into the first stages of deposition, which could reflect the presence and distribution of those defects, are currently undertaken.

It is difficult to prove the covalent bond formation between the attached molecules and the individual nanotube. Nevertheless, we found evidence of a very strong binding of the molecular layers, reflected in the fact that the coatings could not be dissolved by any type of organic solvent. They are also stable against application of a potential of the same magnitude but of opposite sign as the potential used in the coupling reaction.

SUMMARY

The presented results demonstrate that electrochemistry provides an effective means to attach functional groups to the surface of SWNTs, presumably starting at defect sites. The obtained coatings are stable and open the possibility to tailor the surface properties of the tubes over a wide range, depending on the chemical nature of additional substituents in the organic coupling reagent. The method will be useful for applications that require well-defined surface functionalities on the SWNTs. For example, by attaching appropriate ligand- or receptor-functions nanowires that are compatible with biological entities like (living) cells could be obtained.

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