

Electrochemical Modification of Single Carbon Nanotubes**

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Since the discovery of single-walled carbon nanotubes (SWCNTs),^[1] there has been a continuing interest in exploring their physical and chemical properties, as well as in their possible applications.^[2] Some of these applications, for example as mechanically reinforced composite materials or as tips with tailored chemical sensitivity for scanning microscopy, require appropriate chemical modification of the tubes. Unlike for fullerenes,^[3] techniques for the chemical modification of SWCNTs remain limited. This limitation is largely because of their low reactivity, which is thought to be only slightly higher than that of graphite, because of the curvature of their surfaces.^[4] Typically, chemical modification of SWCNTs has involved vigorous oxidation processes that often lead to damage of the tubes.^[5–8] To avoid the harsh conditions of oxidative treatment, milder and more controllable methods with which to introduce polar groups have been developed, including side-wall fluorination^[9, 10] and electrochemical modification.^[11] However, up to now all of these chemical modification methods were performed only on bulk SWCNT material, not on individual tubes.

Herein we describe a versatile approach to the electrochemical modification of individual carbon nanotubes (small SWCNT bundles), as demonstrated by the attachment of substituted phenyl groups. The electrochemical approach is particularly suitable for the chemical alteration of single-molecular objects, as their electrochemical potential, which determines the extent of reaction, can be directly adjusted by an applied potential. Our results show that functional groups can be controllably attached to appropriately contacted nanotubes, which results in homogeneous molecular coatings of up to several nanometers in thickness. We present two types of coupling reactions, working under oxidative (anodic) or reductive (cathodic) conditions. The corresponding electrochemical reactions are illustrated schematically in Figure 1. In both cases a radical species is produced on the surface of the nanotube, which attacks the carbon lattice to form a covalent bond. When the potential is applied for a suitable length of time, polymerization of the radicals leads to multilayer coating. This situation is similar to the multilayer growth of aryl films observed in the electrochemical modification of highly oriented pyrolytic graphite (HOPG).^[12, 13]

To address individual SWCNTs/small bundles electrically, the purified tubes were first deposited on surface-modified Si/

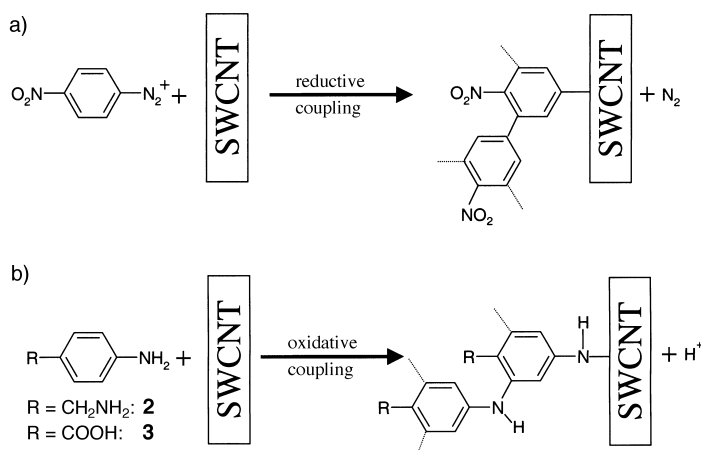


Figure 1. Electrochemical modifications: a) reductive coupling of **1** to SWCNTs, b) oxidative coupling of **2** and **3** to SWCNTs. The dotted lines mark positions of further linkages that could form during the growth of a thicker, polymerized layer of phenyl units on the single-walled carbon nanotube (SWCNT).

SiO₂ substrates, and then contacted with electrodes which had been shaped by electron-beam lithography. Typically, one third of the objects consist of individual SWCNTs, and two thirds are SWCNT bundles with diameters of 3–5 nm. Electrochemical modification was carried out in a home-built miniaturized electrochemical cell, equipped with platinum wires as counter and pseudo-reference electrodes, and with a needle probe to make contact with one of the Au/Pd bonding pads on the Si/SiO₂ substrate. To obtain reproducible deposition conditions, the surface was thoroughly cleaned of any residues from the electron-beam mask prior to applying the potential. Individual SWCNTs and SWCNT small bundles were characterized by atomic force microscopy (AFM) before and after modification. Different degrees of modification could be achieved, depending on the concentration of the coupling species, the duration, and the magnitude of the applied potential.

The cathodic coupling was tested on the reduction of 4-NO₂C₆H₄N₂⁺BF₄⁻ (**1**-BF₄⁻; 1 mM), in DMF and with NBu₄⁺BF₄⁻ as the electrolyte (Figure 1a). In an electrochemical cell, the peak of the irreversible reduction wave of **1**-BF₄⁻, which signifies the formation of the phenyl radical, was observed at a voltage of –1.3 V versus Pt. The same voltage was applied to the deposited SWCNTs for a fixed period of time, typically between 30 s and 2 min, to form a coating thick enough to be detected by AFM. Figure 2a is an AFM image of electrically contacted SWCNTs before the reductive coupling of the 4-nitrophenyl groups. After application of –1.3 V (versus Pt) for 30 s to the left-hand electrode line, only the contacted bundle close to the left margin (marked by the arrow) shows an increase in thickness (Figure 2b). The nanotubes on the right remained unchanged as they were not connected to the current-leading electrode, which demonstrates the selectivity of the method. The height increase of the marked bundle was ~6 nm, determined from the corresponding AFM section profile.

Investigation of the coated tubes by scanning Auger microscopy (10 nm spot diameter of the electron beam)

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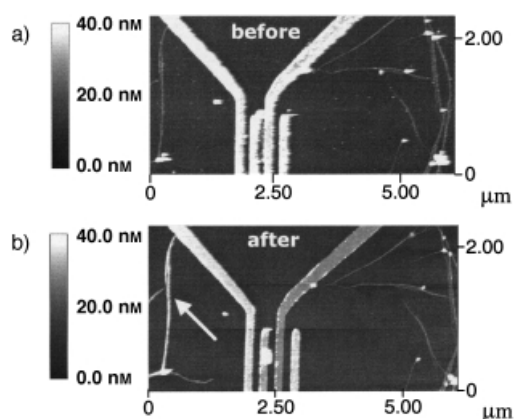


Figure 2. AFM image of SWCNTs before (a) and after (b) reductive coupling with **1**.

revealed an increased nitrogen signal compared to the substrate background. This finding supports the conclusion that the tubes are covered with NO₂-substituted phenyl groups. In control experiments performed under the same conditions but without **1**-BF₄⁻, no coating of the nanotubes was observed.

Anodic coupling to SWCNTs was accomplished with two aromatic amines, 4-aminobenzylamine (**2**), and 4-aminobenzoic acid (**3**; Figure 1b). The functional groups of **2** and **3** allow the linking of further molecules, which may facilitate further tailoring of the surface properties of the nanotubes. Oxidative coupling of the amines was carried out in absolute ethanol with LiClO₄ as the electrolyte salt, and the same control experiments were performed as for the diazonium salt (**1**).

The irreversible oxidation wave of **2**, caused by the formation of the radical cation, was observed at +0.85 V (versus Pt) in the bulk electrochemical cell. Figure 3 shows an

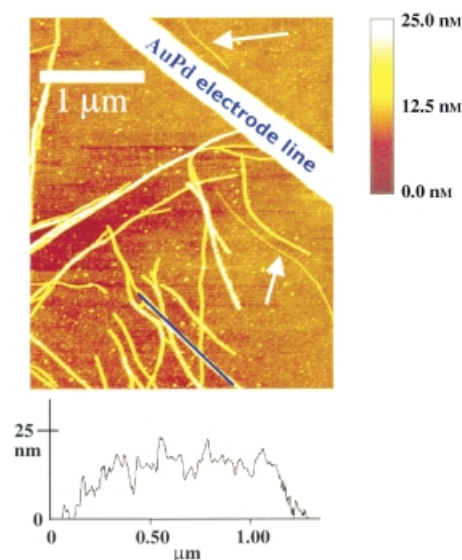


Figure 3. Top: AFM image of SWCNTs after oxidative coupling with **2** (1 mM in LiClO₄/ethanol) by application of +0.85 V vs. Pt for 90 s. The white arrows mark two individual tubes, which remained unmodified as no conducting path to the electrode line exists. Bottom: AFM height profile of one modified SWCNT bundle is shown (along the blue line in the lower half of the image).

AFM image of SWCNTs after oxidative coupling with **2** by application of this potential for 90 s. All of the SWCNTs in contact with the Au/Pd electrode, or with a close connection to other contacted nanotubes, show an increase in thickness as a result of the deposited layer. After application of +0.85 V (versus Pt) for 30, 60, and 90 s, the corresponding change in the average AFM height of the tubes/bundles before and after modification was found to be 6, 9, and 12 nm, respectively. Similar behavior was observed in the coupling of **3** by using the same electrolyte solution, and a potential of +0.90 V (versus Pt; this is the peak potential of the irreversible oxidation wave observed in the bulk electrochemical cell).

The AFM height profile along one of the modified bundles (Figure 3) reveals that, although the bundle is covered with a closed layer of homogeneous material, the thickness of the coating varies by ± 6 nm. The bundle is rougher than before the modification (by ± 1 nm). The formation of a layer of nonuniform thickness has also been reported in the electrochemical modification of other carbon materials. Both the oxidation of amines^[14] and the reduction of aryl diazonium ions^[13, 15–17] have been investigated as a means of modifying the surface of glassy carbon and HOPG. In these systems, Raman microscopy showed that defects act as reactive sites for the formation of covalent bonds to the carbon lattice,^[18] and a similar function is generally ascribed to defects in carbon nanotubes.^[11] We therefore attribute the roughness of the molecular layer to the attachment of radicals and to radical polymerization starting at defects on the tubes, which results in local deposits that grow in size and finally become interconnected.

The presented method is an approach to the adaptation of the surface chemistry of nano-sized charge-transport channels for use in electrical devices. Electrochemical modification may be useful in transforming metallic SWCNTs into semi-conducting tubes, which are of interest for field-effect devices. The attachment of ligand- or receptorlike functionalities offers the potential of producing nanowires that are compatible with biological structural motifs for applications such as the contacting of nerve cells on a solid support.

Experimental Section

SWCNTs were produced by arc discharge and kindly supplied by P. Bernier (GDPC Montpellier, France). The SWCNTs were dispersed in a surfactant solution (sodium dodecyl sulfate, 1 wt %) and purified by centrifugation.^[19] The resulting suspension was placed on a highly doped Si substrate with a 100 nm thick thermally grown SiO₂ layer, after the surface was treated for 2 min in an aqueous solution of 3-(aminopropyl)triethoxysilane. After an adsorption time of 30 min, the substrate surface was dried in a stream of argon and then rinsed in ultra-pure water and dried again. A standard electron-beam lithography (EBL) procedure was used to deposit electrodes on top of the randomly deposited SWCNTs. Finally, a 1 nm titanium adhesion layer and a 15 nm layer of gold–palladium were evaporated onto the surface of the substrate, to form the electrodes. The substrates were cleaned in DMF for 2 h. The electrochemical experiments were carried out in 0.1 M electrolyte solution, and a Solartron 1285 potentiostat was employed to control the applied potential. AFM images were acquired with a Digital Instruments Nanoscope IIIA microscope operated in tapping mode, which used commercial silicon cantilevers.

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Selective Complexation of *N*-Alkylpyridinium Salts: Recognition of NAD⁺ in Water

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N-Alkylpyridinium salts are widely used in nature in coenzyme-mediated redox processes; the oxidized form of nicotinamide adenine dinucleotide (NAD⁺) formally abstracts a hydride ion from other biomolecules and is converted into its reduced form, NADH. Efficient and selective molecular recognition of this important class of compounds by artificial receptor molecules opens up the possibilities of influencing biological redox processes, alteration of the NAD⁺ redox potential,^[1] targeted transport of NAD⁺, attach-

ment of NAD⁺ to artificial enzymes, and many others. In water, the challenge in constructing such a synthetic receptor molecule was to find a way to replace the highly stable solvation shell around this organic cation with attractive, intermolecular, noncovalent receptor–substrate interactions. Salt bridges alone are not sufficient, because of the energetic costs of anion and cation desolvation. Much more appropriate is the cation– π interaction, because only the cation has to be dehydrated prior to complexation and, in water, this interaction is also supported by the hydrophobic effect.^[2] This major noncovalent force has recently been discovered in numerous natural recognition events^[3] and has been intensively studied by several groups.^[4] These groups found that macrocycles containing aromatic units are able to completely desolvate a number of biologically important organic cations, for example, quaternary ammonium ions,^[5] guanidinium ions,^[6] and *N*-alkylpyridinium ions.^[7] Usually, however, these macrocyclic receptors are not very selective towards their substrate topology. To date, for example, such receptors cannot distinguish between ball-shaped or planar structures.

Molecular clips with planar side walls should be much more shape-selective toward flat structures. Porphyrin clips derived from diphenylglycoluril are capable of complexing *N*-alkylpyridinium cations (for example, viologen cations),^[8] but they also bind to electron-rich aromatic compounds such as pyridine, hydroxypyridine, and phenols.^[9] To date, such clips have been only studied in organic solvents.^[8] Recently, a new molecular clip has been introduced that features two face-to-face naphthalene systems, held apart at a maximum distance of 10 Å by a rigid substituted benzene spacer (Figure 1).^[10, 11]

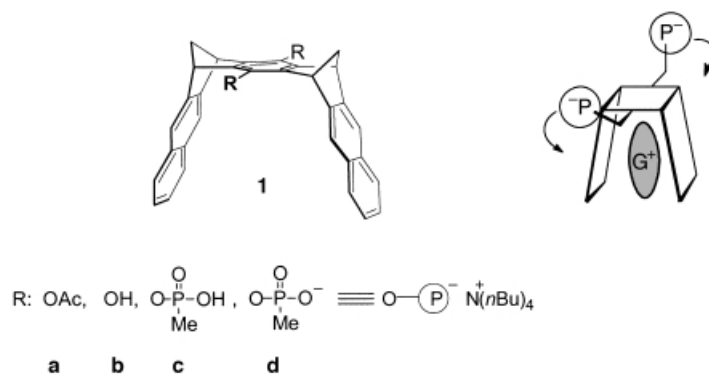


Figure 1. Left: Structures of the molecular clips **1a–d**. Right: Design of the new hybrid receptor system by combination of an electron-rich molecular clip and a bisphosphonate tweezer.

Single-crystal structural analyses of various complexes revealed that the aromatic walls of the clip embrace the substrate molecule tightly, by reducing the distance between the naphthalene tips from about 10 to 8 Å,^[10] as shown in the single-crystal structure of the 1:1 complex between *N*-ethyl-4-carbethoxypyridinium triiodide and the diacetoxy-substituted clip **1a** (Figure 2). Herein, we report the synthesis of the water-soluble molecular clip **1d** and its intriguing receptor properties in aqueous solution.

The synthesis of the clip molecule **1d** began with the reaction of the hydroquinone **1b** with two equivalents of

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 NAD = nicotinamide adenine dinucleotide