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# Asymmetric End-Functionalization of Carbon Nanotubes

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- porous membranes

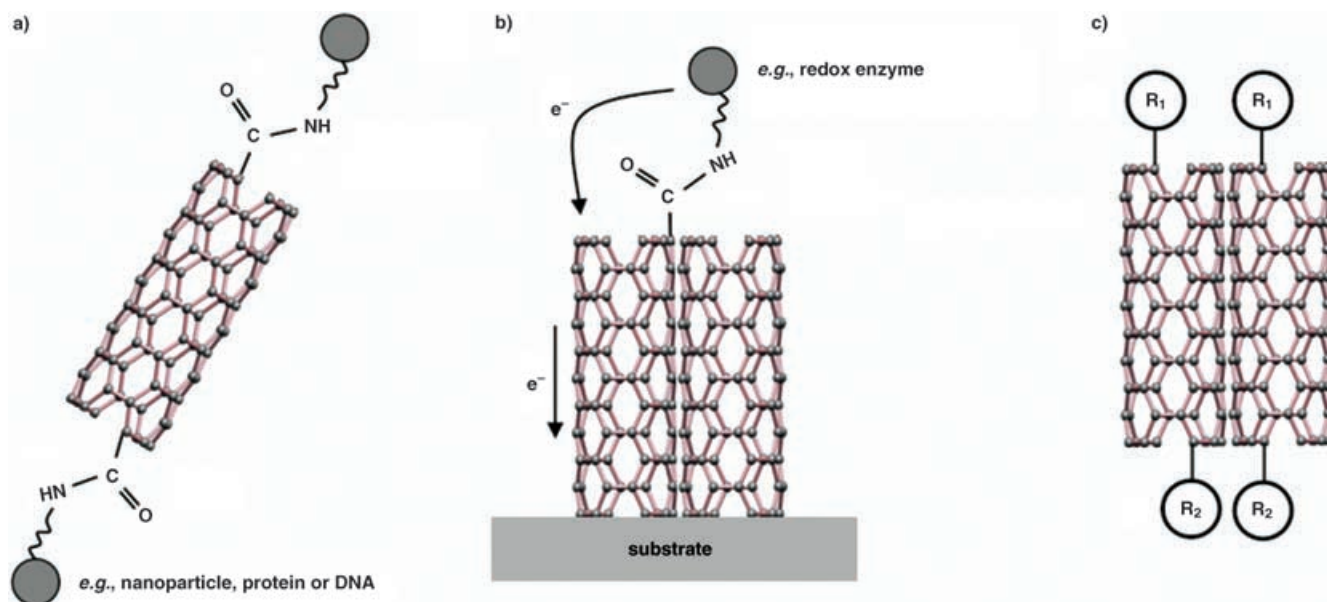
Many micro- or nanostructured objects owe their functionality to asymmetry. For instance, bifunctional molecules bearing two different groups at their ends are essential components of self-assembled monolayers (SAMs) with tailored surface properties. While one of these groups serves to anchor the molecule to the substrate surface, the group at the opposite end is exposed on the SAM surface. SAMs equipped with appropriate surface functional groups have been successfully employed as model biological surfaces useful for biocompatibility tests or cell-adhesion studies. The terminal groups can also be utilized to bind, for example, macromolecules like proteins or DNA, thus opening a wide range of bioanalytic applications. Alternative uses of these groups involve the oriented nucleation of crystals,<sup>[1]</sup> the immobilization of metal complexes for catalytic applications,<sup>[2]</sup> as well as the initiation of the growth of polymers from the SAM surface.<sup>[3]</sup> In addition, structural asymmetry is often of importance in the assembly of macromolecules into larger biological superstructures. One well-documented example is microfilaments, which constitute a major part of the cytoskeleton in (eukaryotic) cells. They are made of G-actin subunits—platelike molecules consisting of two different lobes—which connect to each other such that a polar arrangement with all subunits pointing toward the same filament end is obtained.<sup>[4]</sup> Further to this, with respect to the electrical behavior of molecules, an asymmetric arrangement of an electron donor and an electron acceptor is a prerequisite for the realization of molecular diodes.<sup>[5]</sup> Likewise, in donor-( $\pi$ -conjugated bridge)-acceptor materials, which are important for nonlinear optical applications such as second-harmonic generation (SHG),<sup>[6]</sup> an asymmetric charge distribution is imparted by the donor and acceptor groups located at opposite ends of the  $\pi$ -conjugated pathway. As a final example that shall be considered here, it is

worth mentioning so-called ‘catalytic nanomotors’ formed by metal nanorods consisting of one platinum and one gold segment.<sup>[7]</sup> Upon placing these microscale objects in an aqueous hydrogen peroxide ( $H_2O_2$ ) solution, they start to self-propel, which enables them to explore their environment in a random fashion. The driving force for this autonomous motion<sup>[8]</sup> is the interfacial tension gradient created along the nanorod due to the catalytic decomposition of  $H_2O_2$  at the platinum segment, where the generated oxygen lowers the liquid–vapor interfacial tension.

In view of the above outlined application perspectives, it is not surprising that soon after the emergence of ‘carbon nanotube (CNT) chemistry’, the creation of CNTs with asymmetrically modified ends became highly desired. This task has been approached in a stepwise manner, starting from symmetrically end-functionalized CNTs, through CNTs modified at only one tip, finally to CNTs having different functional groups at their ends, with each of these configurations offering its own specific utility (Figure 1).

In the initial stages, solution-based CNT functionalization methods were developed,<sup>[9]</sup> in most cases involving a strong oxidative treatment that yields (shortened) CNTs bearing similar oxygen-containing functional groups at the sidewall as well as their ends. The tube ends are inherently quite reactive due to their 2D curvature and localized carbon–carbon double bonds, whereas the chemical attack of the less curved sidewalls usually requires the presence of sidewall defects such as Stone–Wales defects.<sup>[10,11]</sup> The carboxyl groups at the open ends of strongly oxidized CNT fragments (‘fullerene-pipes’) have been exploited to link gold nanoparticles through amide coupling (Figure 1a).<sup>[12]</sup> The same type of coupling has also been employed to thiol-derivatize the ends of such fragments, which enables their assembly on gold substrates via Au–S bonds.<sup>[13]</sup> Later, an increased capability to functionalize CNTs in a location-specific manner has become possible. For example, in order to achieve selective end functionalization, single-walled carbon nanotubes (SWCNTs) were cut using a lithographic procedure, and then the exposed tube ends were chemically modified via plasma treatment, while the tube sidewalls remained protected by a resist layer.<sup>[14]</sup>

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**Figure 1.** Schematic illustration of the structure and functionality of the three major types of end-functionalized carbon nanotubes realized so far. These are a) nanotubes bearing identical functions at their ends, b) solid-supported nanotubes modified at their end exposed on the surface, and c) bifunctional nanotubes comprising two different chemical moieties at their opposite ends.

In contrast to CNTs freely floating in a solvent, dense vertically aligned CNT arrays on a solid support expose only one tube end to chemical reactants from the gas or liquid phase. Appropriate methods to functionalize the surface of such arrays include microwave glow-discharge plasma treatment, which allows for subsequent grafting of biopolymers.<sup>[15]</sup> Plasma treatment normally leads to opening of the tube ends, which is manifested in, for example, an increased field-emission efficiency of the tubes.<sup>[16]</sup> Vertically assembled, end-functionalized CNTs are highly versatile platforms for (bio-)electrochemical sensors. In particular, SWCNTs have proven effective as electrical connectors between conducting surfaces and redox enzymes (Figure 1b).<sup>[17]</sup> At present, the efficiency of the CNT-based wires is limited by sidewall defects introduced upon the oxidative shortening of the tubes prior to their assembly on the electrode. Another reflection of the utility of end-functionalized CNTs is their use as chemically sensitive scanning microscopy probes, which are accessible via covalent coupling of molecules containing a specific functional group to the open end of an individual SWCNT attached to an atomic force microscopy (AFM) tip.<sup>[18]</sup> Chemical force microscopy using such tips has tremendous potential for probing the structure and function of biological systems at the nanometer scale.<sup>[19]</sup>

Only very recently, a method has been developed that enables the asymmetric end-functionalization of CNTs. In their elegant approach, Lee et al. modified free-standing films of vertically aligned multi-walled carbon nanotubes (MWCNTs) floating at the air-liquid interface via a chemical reagent added to the liquid phase. To obtain this arrangement, nanotube arrays grown via chemical vapor deposition (CVD) on quartz glass substrates were floated onto an aqueous hydrofluoric acid solution. The films were prevented from dwindling down into the liquid by combining the hydrophobic CNTs with either a hydrophilic solvent or

a lower polarity solvent of high density. Chemical modification was then accomplished by transferring the films onto a solution containing an appropriate agent that can be activated through photo-irradiation with UV light.<sup>[20]</sup> By subsequently placing the film with reverse orientation onto a second modifier solution and performing a second UV irradiation, they finally obtained an array of MWCNTs bearing different chemical moieties at their opposite ends (Figure 1c). The authors were able to prove the asymmetric functionalization via an X-ray photoelectron spectroscopic (XPS) investigation of the two film surfaces. Through ultrasonic dispersion of the modified films, this simple but effective method provides access to individual (or at least small bundles of) bifunctional CNTs. The recent progress in the fabrication of aligned SWCNT arrays makes it likely that this type of tube will also become amenable to the same functionalization method in the near future. It is noteworthy that according to a later, closely related study, the small extent of sidewall modification, which may result from capillarity-induced uptake of the reactive solution, can be avoided by simple impregnation of the CNT array with a protective polymer film.<sup>[21]</sup>

The now-available asymmetrically end-modified CNTs potentially open up a range of intriguing applications. A first possibility is to utilize them for nanoscale biofuel cells. This task, as recently suggested by Katz et al., may be realized by modifying the two tube ends with appropriate oxidative and reductive redox enzymes.<sup>[22]</sup> Secondly, CNTs with two well-differentiated ends are attractive building blocks for self-assembly into larger, more complex systems with molecular-level control. As a very first step in this direction, it has been shown that MWCNTs comprising one hydrophobic and one hydrophilic end self-assemble at the polar/non-polar interface in a two-phase solvent system.<sup>[20]</sup> Furthermore, Chopra et al. succeeded in the selective attachment of

gold nanocrystals to the thiol-modified end of asymmetrical-ly functionalized MWCNTs, while their carboxyl ends remained mostly uncovered.<sup>[21]</sup> Another possible application of the end-attached functional groups involves controlling ion transport through the CNT channels, extending the work of Majumder et al., who used ‘gatekeeper’ molecules at the entrance of MWCNTs to enhance the selectivity of ion transport.<sup>[23]</sup> Moreover, if the asymmetric functionalization scheme is adapted to shorter CNT segments with lengths in the lower nanometer range, photoinduced electron transfer (PET) studies between donors (D) and acceptors (A) attached to the opposite ends of a CNT could be performed, in correspondence with PET investigations on, for example, (D–porphyrin–A) systems.<sup>[24]</sup>

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