Functionalization: Tailoring nanocarbons through attached molecules and particles

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1 Introduction

Since their discovery the applications for carbon nanotubes have kept growing: Transistors, extremely strong fibers or even space elevators. The possibilities seem to be only limited by our fantasy. Functionalizing carbon nanotubes (i.e. introducing additional molecules on their surface or inside them) can help achieving many of these goals by subsequently changing certain properties and thus optimizing the tubes for the desired application. On the following pages the different kinds of functionalization (covalent, non-covalent, including π-π-stacking and polymer wrapping, as well as endohedral functionalization) will be discussed and some applications will be described.

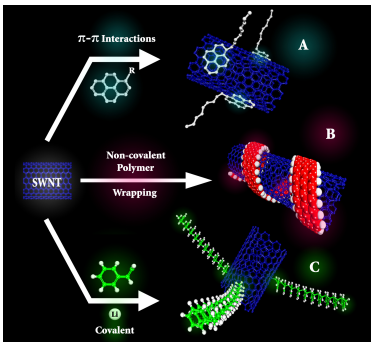

Figure 1: Different forms of functionalizations `http://www.jmtour.com/images/Nanotubes/NanotubeFunctionalizationLiBottomStyreneTop.jpg`

2 Covalent functionalization

Covalent functionalization uses the tubes' chemical reactivity on the outside to introduce functional groups via chemical reactions. The chemical bonds can be

achieved through different methods: **Oxidation and Carboxyl-based coupling** is a quite aggressive method, where defects on the CNT are introduced by heating it in a strongly acid environment. The newly introduced defects then make it possible for carboxyl groups to be formed. These groups are a starting point for further reactions. The desired functional group can now be attached by letting the according substance react with the carboxyl groups. Through the acid treatment the nanotubes will not stay intact, though. Instead nanotube fragments with a length between 100 and 300 nm will be created [1].
Functionalization can also be achieved via **Electro Chemical Modification**: As the name suggests the nanotubes are functionalized by using them as an electrode in a medium. An applied voltage (or current) then starts a redoxreaction. In this process the tube is functionalized.
The last method is **Photochemical functionalization**. Here, an addition reaction is started by exciting the outer valence electrons with light.

2.1 Application

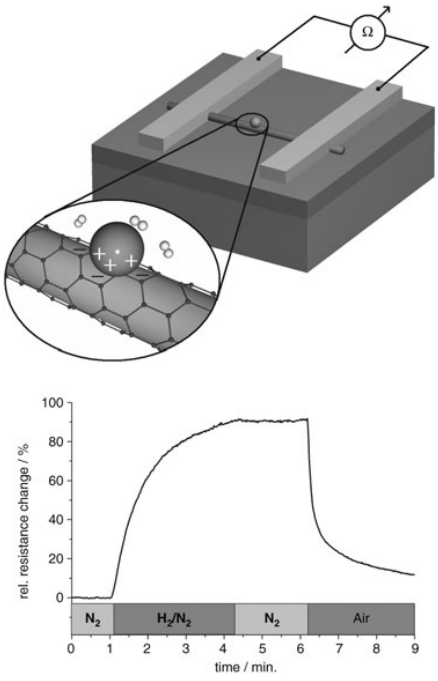

Figure 2: Upper picture: Gas sensor consisting of a semiconducting nanotube covered with Pd. Lower picture: resistance change after exposure to hydrogen. [1]

A gas sensor is an example for covalent functionalization via Electro Chemi-

cal Modification(see fig. 2). The hydrogen sensor in this example is a nanotube transistor whose nanotube was functionalized with Palladium. The Palladium layer is needed to split the incoming H_2 into hydrogen ions. When the hydrogen ions come in contact with the nanotube surface, its charge-carrier concentration is altered which leads to a change in the electrical resistance which can then be measured.

3 Non-covalent bonding

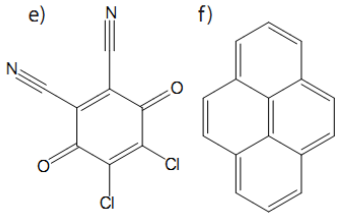

Figure 3: Possible anchors for non-covalent bonding. e)2,3-dichloro-5,6-dicyano-1,4-benzoquinone(DDQ), f)Pyrene [5]

Often one does not want to alter the properties of one's CNTs permanently. In this case covalent bonding is not recommendable. Furthermore in the covalent functionalization process, the carbon framework of the nanotubes is destroyed in order to establish bonds. In order to avoid these issues, non-covalent bonding can be used, where certain molecule groups can be used as an anchor which connects to the nanotube. As an example fig. 3 shows Pyrene and DDQ as possible anchors. The connection is established via $\pi - \pi$-bonding and van-der-Waals bonding.

3.1 Functionalization with switches

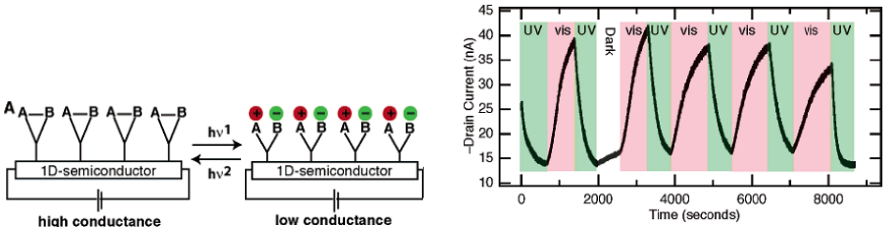

Figure 4: Left: Nanotube functionalized with Spiropyran. Change of conductance after change of the switch by irradiation. Right: Drain current dependent of irradiation [6]

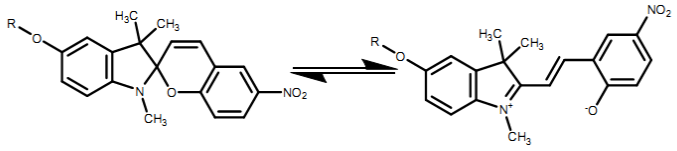

Figure 5: Spiropyran (left) and its isomer Merocyanin (right)[5]

A possible application of non-covalent bonding is functionalization with switches, where a switch molecule is connected to a tube via an anchor molecule group. Switch molecules change its structure when they are exposed to light with a certain frequency. Retinal for example changes from a cis structure to a trans structure, so it kind of "'stretches"' at certain light frequencies. This could be used in a formation, where the switch molecule is connected to a functional group. The switch can then be used to change the distance between nanotube and functional group and thus change the electronic properties of the tube.
Alternatively the functionalization can be realized with switches that change their dipole moment. As an example Spiropyran is shown in fig. 5. Again, the electronic properties of the tube are altered. The group of Xuefeng Guo et al. [6] used Spiropyran to functionalize a semiconducting nanotube. As a result the nanotube changed its resistance, depeding on whether it was exposed to UV light or visible light. In the polarized Merocyanin state the conductance dropped, in the Spiropyran state it was increased.

3.2 Functionalization with antibodies

By functionalizing nanotubes with antibodies that attached to breast cancer cells, the group of Shao and Lu were able to "'mark"' the cancer cells. As the nanotubes showed absorption at wavelengths in the infrared spectrum ($\sim$ 800 nm and $\sim$ 900 nm) it was possible to excite the tubes by an infrared laser and thus destroy the cancer cells. In a further experiment nanotubes were functionalized with non-specific antibodies. In this case no destruction of the cancer cells occurred which shows that only the functionalization with the cancer-specific antibodies can lead to their destruction.

4 Polymer wrapping

Polymer wrapping can also be considered as some kind of non-covalent bonding. However, instead of smaller molecules that are attached by an anchor molecule, polymer wrapping needs long molecule chains that twine around the nanotube. The forces responsible for the attachment are $\pi - \pi$-stacking and van-der-Waals forces [2].

4.1 Chirality enrichment

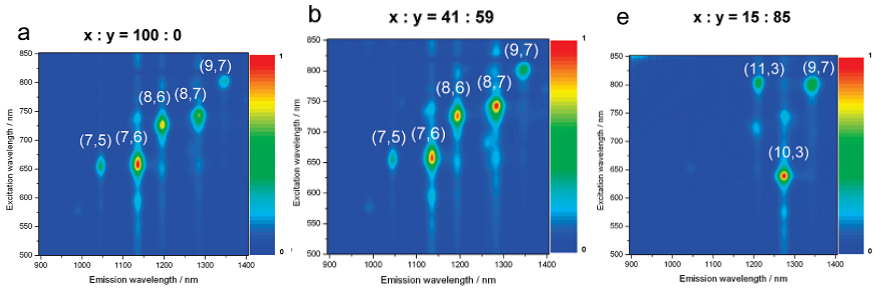

Figure 6: PL pictures of dissolved nanotubes for different ratios of the copolymer parts [3]

By wrapping nanotubes in appropriate polymers, it is possible to increase their solubility. As Ozawa et al. showed [3], depending on the used polymers, nanotubes of certain chiralities will be dissolved preferably. Copolymers (a copolymer is a polymer that consists of two or more different constituents) consisting of a fluorene part and a so called bulky chain part were produced with different ratios of the fluorene and bulky chain parts and used to make the nanotubes soluble. Afterwards the prevalence of dissolved nanotubes with certain chiralities was measured via photoluminescence. As can be seen in fig. 6, at a ratio of (100:0) mainly (7,6) nanotubes were found in solution. At a ratio of (41:59) the intensity of (8,6) and (8,7) chiralities increased and at a ratio of (15:85) mainly nanotubes with chirality (10,3) were found.

5 Endohedral functionalization

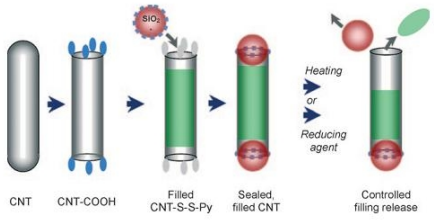

Figure 7: Different steps of the "tube filling" process [4]

Due to a lower reactivity inside the nanotubes it is possible to store reactive chemicals inside them. This concept was used for example by Chen et al. to store a chemical inside MWCNTs and also realize a triggering mechanism that

makes it possible to release the chemical by adding another substance.
In the first step the nanotubes were opened via a heat/oxidation process. In that way the open ends were functionalized with carboxyl groups (compare section 2), which then reacted with S-(2-aminoethylthio)-2-thiopyridine. The newly created functionalized groups at the tube ends could then be used to connect to silica spheres to close the tube and this way store the chemical (flurorescine in this example). Opening was achieved either by heating the nanotubes up to temperatures of about 900° C or by adding dithiothreitol (DTT) to disconnect the silicon spheres from the nanotubes.

6 Summary

As could be seen in this report, there are already several interesting and useful applications for nanotube functionalization. Especially the chirality enrichment may become a very useful tool to specifically select nanotubes with a desired chirality. But also the medical applications that are being researched at the moment seem to deliver promising results which may come to use in the (not so distant) future. The functionalization of nanotube transistors may help developing new electronic devices such as digital cameras, new computer parts or (as explained before) new types of gas sensors. The potential of the Carbon nanotubes has certainly not been fully exploited yet and it will be interesting to see how these ideas will finally find their way into our daily lives.

References

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[2] D. Tasis, N. Tagmatarchis, A. Bianco, and M. Prato. *Chemistry of carbon nanotubes* Chemical Reviews, 106(3):11051136, March 2006.

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