

Editor's Note: On the heels of the European setting of the 203rd ECS meeting, we thought it would be interesting to gather perspectives from some of the speakers at this gathering. Excerpted below are comments from invited speakers in the A2-Nanotechnology Symposium in Paris this past April. PRASHANT KAMAT, a co-organizer of this symposium (which was sponsored by all the Divisions) and the current chairman of the Fullerenes, Nanotubes, and Carbon Nanostructures Division, is thanked for his assistance in coordinating the following submissions.

What Will Nanoscience Contribute in the Next Few Years?

by M. P. Pileni

In the next few years we have to solve several outstanding problems in nanoscience. In this short note, I will try to give my opinion on the perspective in this area.

Stability and Impurity

We all want to make the best nanomaterials, without any impurities, and with the highest stability. These properties are claimed in most papers. The major procedures developed in the last decade to produce nanomaterials are based on soft-chemistry, which may result in impurities in the nanocrystal matrix. This of course could markedly change the physical properties of the materials. This is well demonstrated when we make alloys. As an example we can consider semi-magnetic semiconductors. We know that inclusion of manganese ions in the CdS matrix drastically changes the physical properties of the nanocrystals.¹ In this case the inclusion is controlled but no evidence has been given concerning other inclusions and their roles. Also we need to know the behavior of the produced nanomaterials when they are subjected to external forces. CdSe nanocrystals, considered in our community as having the best crystallinity, size distribution and, probably, composition, are neutral when they are protected from light and positively charged on exposure to ambient light.² This is also valid for the stability of nanocrystals self-organized in 2D and 3D superlattices. We know these nanocrystal organizations induce collective properties,³ which involve various domains such as electronics, high-density magnetic recording media, and transport. Organization of 3D aggregates with long-range order could also be used for photonic crystals. All these properties could be a real advantage for new technologies if the systems are well defined and have very high stability. In fact, we are able to self-organize a large variety of nanocrystals but very few groups mention their stabilities. For example, silver nanocrystals coated with dodecanthiol and deposited on cleaved graphite (HOPG) form monolayers of nanocrystals organized in a compact hexagonal network. This makes it possible to grow "supra" crystals on a mesoscopic scale with long-range order. After a few months the self-organization in 2D superlattices disappears with coalescence of nanocrystals.⁴ This is also observed for 3D "supra" crystals with a progressive loss of the long-range ordering.⁵ Conversely, with lauric acid-coated cobalt nanocrystals, the self-organizations in 2D and 3D are highly stable with formation of "supra" crystals in a FCC structure that is retained for a few months.⁶

Control of Nanocrystal Shapes

From the literature, nanocrystal shapes are not a determining factor in controlling the shape of inorganic materials.⁷ Crystal growth on the nanoscale seems to follow behavior similar to that of the bulk phase⁸ with a marked dependence on pH. The latter is particularly important when some impurities are present in the growth medium because it influences, *e.g.*, the formation either of zwitter-ions or of complex ions, the efficiency of which is greater than that of the initial impurity. These species lead to a decrease in the growth rates of certain crystal faces. Most of the changes are based on the existence of a more or less epitaxial adsorption layer on the crystal. This layer is composed of solvent, impurity, molecules, or salts. Their precise roles are as yet uncertain. The changes are due to the differences between the growth rates of the various crystallographic faces and from this it can be concluded that the template is not the key parameter in the shape control.

From these considerations, we can ask why templates made of surfactants are quite effective in controlling formation of nanospheres whereas rather large exceptions are observed for anisotropic shapes. This is probably due to the fact that colloidal templates are highly dynamic. The energy needed to produce spherical nanocrystals is less than that for producing anisotropic nanocrystals. A general method for controlling nanocrystal shapes through soft chemistry has not yet been found but this does not mean that such a method cannot be discovered. To reach a conclusion we need more data and to compare the fabrication of anisotropic nanocrystals with various types of materials.

Collective Properties

As mentioned, we demonstrated that collective properties are observed when nanocrystals are organized in 2D superlattices.³ Several groups have to apply a magnetic field during the deposition process to get a well-ordered monolayer.⁹ This obviously perturbs the physical properties of cobalt nanocrystals deposited on a substrate. Similarly several mesoscopic features of nanocrystals are obtained by applying a magnetic field during the deposition process inducing change in the structure morphology of the nanocrystal arrangements. To determine the collective properties due to the mesoscopic structures the arrangements have to be produced without any external forces. This comment is also valid for the collective optical and transport properties. ■

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Chemical Modification of Carbon Nanotubes From Single Molecule Chemistry to Single-Electron Transistors

by Marko Burghard and Klaus Kern

Controlled chemical modification of carbon nanotubes is required for applications that are based on the specific interaction of nanotubes with other molecules.

These applications include chemical sensors in the gas or liquid phase, mechanically reinforced composite materials, atomic force microscopy tips of tailored chemical sensitivity, as well as electrical contacting of biological systems like nerve cells. The chemistry of carbon nanotubes, however, is far less developed than the chemistry of their small counterparts, the fullerenes. Up to now chemical modifications were performed only on bulk nanotube material, and hardly allow control over the functionalization degree.

Electrochemical modification of individual carbon nanotubes—We were able to demonstrate that individual single-wall carbon nanotubes (SWCNTs) can be controllably modified via an approach that combines nanolithography and electrochemistry. In this way it is possible to separately study the effect of chemical modification on the electronic properties of both metallic and semiconducting SWCNTs. Moreover, electrochemical functionalization is well-suited to alter the nanotubes since the extent of reaction can be directly controlled via the magnitude and duration of the applied potential.

Two different coupling schemes were established for SWCNTs, working under either reductive or oxidative conditions. In the reductive coupling, schematically presented under Fig. 1a, electron transfer takes place from the SWCNT to an aromatic diazonium salt in the electrolyte solution. As a result, a phenyl radical is created that can form a covalent bond to the carbon lattice of the tube, presumably at a defect site. In the case of oxidative coupling, shown in Fig. 1b, a radical cation is pro-

duced as reactive agent at the SWCNT surface. The oxidative coupling reaction especially offers the possibility to functionalize the carbon nanotubes with acidic ($R = -COOH$) or basic ($R = -CH_2-NH_2$) groups attached to the benzene ring. These functional groups could be used for further attachment of functional building blocks, for example nanowires or nanocrystals, and therefore provide access to more complex device architectures.

As a representative example, the AFM image in Fig. 2 depicts individual SWCNTs (and small bundles with a diameter in the range of 3-5 nm) after oxidative coupling of 4-amino-benzylamine ($R = -CH_2-NH_2$ in Fig. 1). The two SWCNTs marked by arrows remained unchanged since they are not electrically connected to the electrode line. In contrast, the other, contacted objects show a thickness increase of ~10 nm, which is attributed to the formation of a layer consisting of polymerised phenyl radicals. Thinner layers can be deposited by shorter application of the potential, however, the coating is then much harder to detect by AFM. It was found that the thickness of the coating correlates well with the time for which the fixed potential is applied.

Room temperature single-electron transistor (SET) by local chemical modification of SWCNTs—Individual SWCNTs, due to their small diameter of 1-2 nm, appear as suitable components of devices that operate on the basis of single-electron tunnelling. In this context single-electron transistors are of special interest, e.g. for application as current standard. Normally single-electron tunnelling can be observed in individual SWCNTs only at low temperatures since the electrode distance is typically ~100 nm, which is still accessible by conventional e-beam lithography. The fabrication of SWCNT-based SETs that operate at

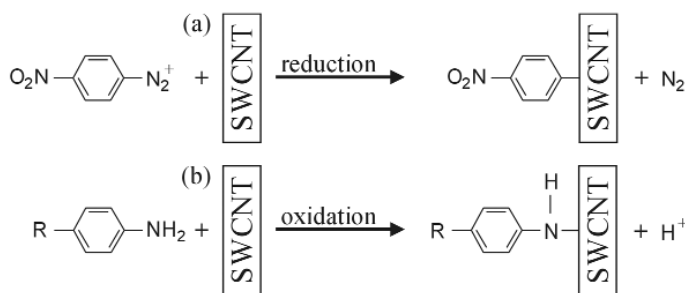


Fig. 1. Electrochemical modification of carbon nanotubes based on reductive (a) or oxidative (b) coupling of substituted phenyl groups.

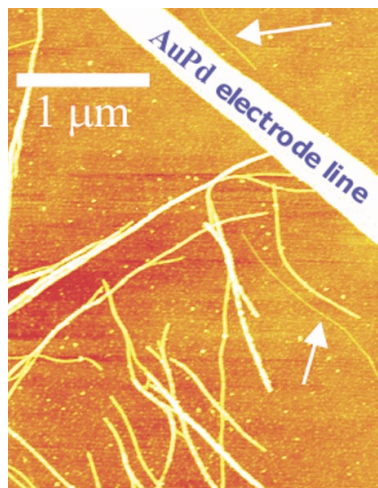


Fig. 2. Single walled carbon nanotubes, contacted by an AuPd electrode, after oxidative coupling of a substituted aromatic amine.

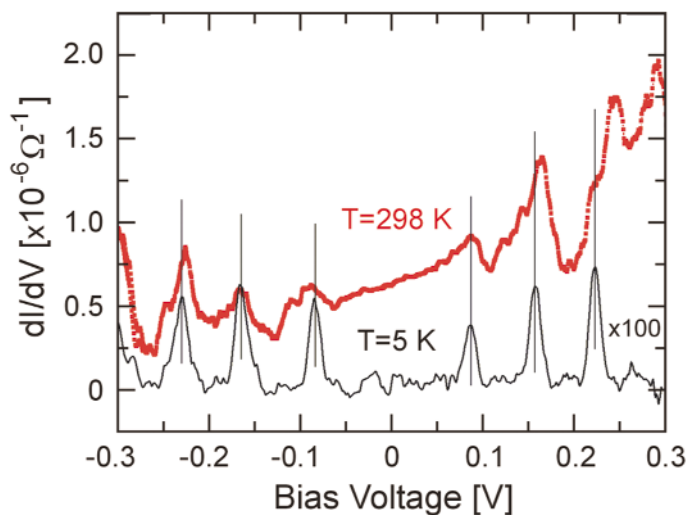


FIG. 3. Differential conductance of the locally modified carbon nanotube at 5 K (black curve) and room temperature (red curve). The red curve is vertically shifted for clarity.

higher temperature therefore requires to define an ultra-small island within the tube. Such an island or quantum dot has been realized by creating a chemically modified section of 10 nm length within a thin SWCNT bundle by a short O₂ plasma treatment.

The SWCNT device, which comprises the modified region as quantum dot and the unaltered bundle parts as electrical leads, clearly shows single-electron tunnelling features at liquid helium temperature, as revealed by the differential conductance peaks in Fig. 3

(black curve). These peaks are likely to reflect both Coulomb charging and the discrete energy levels due to electron confinement in the axial direction. Due to the small dot size ($\sim 2 \times 2 \times 10 \text{ nm}^3$), the differential conductance peaks are still observable at room temperature (red curve in Fig. 3). Moreover, since the device revealed conductance oscillations as a function of an applied gate voltage at 298 K, it functions as room temperature SET. Although the nature of the chemical modification brought about by the plasma treatment and the origin of the two tunnelling barriers required for decoupling the dot from the rest of the bundle are not yet clarified, it is expected that better defined modification of the SWCNTs (for example via electrochemical coupling of chemical groups) will allow to fabricate devices of high stability and tailored transport characteristics. ■

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