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Nanotube Synthesis

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Growth of Single-Walled Carbon Nanotubes without a Metal Catalyst—A Surprising Discovery**

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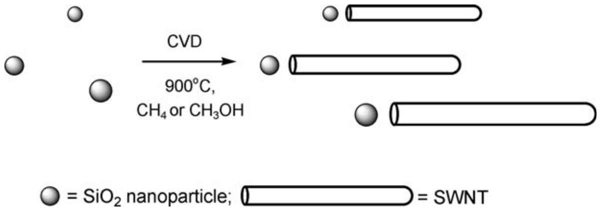
Carbon nanotubes[1–3] are characterized by outstanding and unprecedented electronic and mechanical properties. Single-walled carbon nanotubes (SWNTs), in particular, are very attractive materials with a series of potential applications as sources for electron field emission[4,5] and scanning probe microscopy,[6,7] in nanoelectronic devices,[8–11] and as components of electrochemical energy storage systems.[12,13] They represent the ultimate carbon fiber, with the highest thermal conductivity[14] and the highest tensile strength of any material;[15] SWNTs have Young's moduli of around 1 TPa and are thus up to 100 times stronger than steel. In contrast to the synthesis of multiwalled carbon nanotubes (MWNTs), however, the inexpensive mass production of SWNTs in multikilogram quantities is still an elusive goal.

The techniques for the productions of SWNTs can be classified roughly into three main categories:[16,17] a) laser ablation, b) arc discharge, and c) chemical vapor deposition (CVD). Whereas methods a and b use graphite as the starting material, the CVD techniques are based on small precursor molecules such as methane, acetylene, alcohols, and carbon monoxide. Common to all of these techniques is the use of transition-metal catalysts, typically elements of the iron (Fe, Co, Ni, and their alloys). It was believed that the application of these carbide-forming metals is indispensable for the growth of SWNTs. However, these metal catalysts have a major drawback for both the characterization of the SWNTs as well as their application; namely, it is difficult if not impossible to remove them completely after the tube production. Owing to the chemical, redox, and magnetic properties of the metal nanoparticles, interference with the corresponding tube properties cannot be avoided. Moreover, the performance of SWNT-based materials as catalyst supports as well as in applications in molecular electronics, biology, and medicine is obscured by the presence of metal particle impurities. In many cases the catalyst particles are covered by a carbon shell, which imposes additional problems for the non-destructive purification of the SWNTs such as by treatment with non-oxidizing acids. In

Very recently, two research groups have independently discovered methods for the production of SWNTs, which do not require the use of iron-group catalysts.[18,19] As a consequence, the field of carbon nanotube research has made significant advances. These developments were stimulated by the fact that in the past three years substantial efforts have been invested in replacing the iron-group catalysts with other metal nanoparticles such as Au, Cu, Pd, Rh, Mg, Mn, Cr, Sn, and Al as well as semiconductor nanoparticles like Si, Ge, and SiC and Fe_3C. All of these systems have been demonstrated to be active for SWNT growth, although they were originally considered to be inactive based on the traditional thinking for SWNT formation. As a consequence, new questions concerning the growth mechanism have been posed.

Ren and Cheng et al.[18] could now show that in a CVD procedure, in which a SiO_2 film 30 nm thick deposited onto a Si or Si/SiO_2 (1 μm thick thermally grown SiO_2 layer) wafer served as substrate, the formation of dense and uniform SWNT networks was observed after a flow of CH_4 and H_2 at 900 °C was applied. Interestingly, almost no impurities were found by AFM, SEM, and HRTEM measurements. AFM experiments on the deposited SiO_2 film further indicated that SiO_2 nanoparticles with an average size of 1.9 nm formed after H_2 treatment at 900 °C. The authors suggest that the presence of these SiO_2 nanoparticles is crucial for the catalytic activity of these substrates (Scheme 1). In another experiment the same researchers found that it is possible to promote a patterned growth of SWNTs on a Si/SiO_2 wafer at any desired position by scratching the wafer with a sharp tip. After CVD growth SWNTs were found only in the scratched areas of the



Scheme 1. Formation of SWNTs catalyzed by SiO_2 nanoparticles.

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substrate. The authors explain these findings with the scratching-induced formation of SiO_2 nanoparticles.

Along the same lines, Huang and co-workers have discovered that after they had scratched a 1 μm thick SiO_2 layer with a diamond blade without putting any additional catalyst on the surface, SWNTs were formed around the edges of the scratched areas during a subsequent CVD process.[19] These findings also indicate that SiO_2 nanoparticles can serve as catalytically active nucleation points for the SWNT growth (Scheme 1). The existence of SiO_2 nanoparticles was demonstrated by AFM measurements. Since most of the formed SWNTs have a diameter distribution in the range between 0.8 and 1.4 nm, it was suggested that only SiO_2 nanoparticles with an appropriate size (<2 nm) catalyze the growth of SWNTs. To exclude any effects that could be due to the diamond blade, an alternative method for the generation of SiO_2 nanoparticles was developed. Both Si wafers and quartz plates were treated with an aqueous solution of HF; when the samples were heated to 1000°C in air, evaporation of the water droplets on the surface resulted in circular traces of SiO_2 nanoparticles, which in turn served as nucleation sites for the growth of SWNTs in a subsequent CVD experiment.

The obvious question related to both contributions refers to the mechanism responsible for the observed SWNT formation in the absence of common transition-metal catalysts. One might speculate that SiC is formed in situ as an effective catalyst.[19] However, careful XPS measurements on the wafer did not provide evidence for the presence of SiC. Only SiO_2 was found on the substrate, which suggests that the SiO_2 nanoparticles themselves act as the catalytically active species. This is very surprising, since unlike metals of the iron family, conventional SiO_2 is neither able to dissolve carbon nor does catalyze the decomposition of hydrocarbons. Huang et al. propose that the melting point of the small SiO_2 nanoparticles (<2 nm) is lower than the growth temperature of the nanotubes.[19] They suggest that the high mobility of the Si and O atoms in the molten SiO_2 might cause the intermediate formation of holes or defects, strongly enhancing the catalytic capacity to decompose hydrocarbons. They further suggest that the highly curved structure of the nanoparticles can act as template for the formation of a graphitic SWNT end cap, which then can undergo a further one-dimensional growth (Scheme 1).

If this would be indeed the case, then it may be possible to produce SWNTs with a very narrow diameter distribution. The authors also point out that any material of a suitable size may be an effective catalyst for SWNT formation. They refer to unpublished work in which have demonstrated that nanosized SiO_2 prepared by a sol–gel process and some other oxides including Al_2O_3, TiO_2, and all lanthanide oxides except promethium oxide also act as catalysts for SWNT growth.

The two contributions[18,19] discussed in this Highlight represent a major breakthrough in the synthesis of SWNTs, since a) metal-free production methods were introduced leading to clean SWNTs, whose properties are not obscured by the metal catalyst impurities, b) new aspects of the SWNT growth mechanism are brought up, and c) the "scratching–growth approach" does not require complex patterning processes and could form the basis for a precise and straightforward method for the engineering of SWNT-based devices by using, for example, a very tiny Si AFM tip to "write" a pattern onto a Si/SiO_2 wafer. These investigations also show that surprises can happen even in areas thought to be well understood. The ultimate goal in carbon nanotube production is to find a catalytic system that would allow for the growth of tubes of a single helicity. If (and when!) this goal is reached, the field of molecular electronics will be revolutionized.

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