Introduction and aims

Since their discovery in 1991 by Iijima, carbon nanotubes have attracted great attention because of their unique mechanical and electric properties arising from their special atomic and electron structure. Various potential applications involving carbon nanotubes including catalysts support, energy storage, hydrogen storage, reinforced materials, nanoeletric devices, field emission, etc. have been proposed. In order to use these applications on an industrial scale it is important to carry out their large scale and selective synthesis and seems to be expedient to modify them chemically and/or mechanically. Different techniques such as laser ablation, arc discharge are known to produce carbon nanotubes. Besides these techniques the catalytic chemical vapor deposition (CCVD) of hydrocarbons seems to be the best way to upscale the production. To achieve this aim further optimization is needed.

The chemical and mechanical modification of carbon nanotubes has come to the frontline in the recent years as proved by the increasing number of papers in this topic. The importance of this research lies for example in the application of carbon nanotubes in composites as reinforcing material. By controlling the length of the nanotubes by mechanical methods and attaching suitable functional groups onto the outermost surface of them we can promote better dispersity of the tubes in the polymer matrix giving higher mechanical stability to the composite materials.

In the Department of Applied and Environmental Chemistry (University of Szeged) research on carbon nanotubes is going on since 1995. The following objectives were set for me when I joined to this research team:

1. optimization of the synthesis and purification of multiwall carbon nanotubes,
2. mechanical breaking (ball milling) of carbon nanotubes,
3. chemical functionalization of carbon nanotubes and producing junctions,
4. modification of carbon nanotubes using a mechano-chemical way,
5. further applications of the modified carbon nanotubes such as catalysts supports and reinforcing materials.

Experimental

The multiwall carbon nanotubes (MWNTs) were prepared by catalytic chemical vapor deposition (CCVD) of acetylene in a horizontal quartz reactor placed into a furnace set to 973

K. The Co-Fe/$Al(OH)_3$ catalyst was prepared by impregnation method. The MWNTs were purified in two steps. In order to dissolve the support and the metal particles NaOH and cc. HCl solution were used. The quality and the quantity of the purified nanotubes were examined by transmission electron microscopy (TEM). We determined the average outer and inner diameter of the tubes. The number of the walls was also calculated.

For the chemical functionalization amine group containing compounds were used and the process was monitored by infrared spectroscopy (IR). Different shapes of junctions were produced by a multi step functionalization method between the individual nanotubes (oxidation with a strong acidic mixture, reaction with $SOCl_2$, reaction with diamines or triamines). The junctions were analyzed by scanning tunneling microscopy (STM) and TEM.

The mechanical modification of carbon nanotubes was carried out in ball mill. After 100 hours of breaking the tubes were characterized by TEM.

The mechano-chemical functionalization of the nanotubes was performed in a ball mill under reactive atmospheres (Cl_2, CO, CH_3SH, $COCl_2$, NH_3). The ball milled samples were analyzed by X-ray photoelectron spectroscopy (XPS), TEM and STM. The specific surface area of the modified tubes was measured (BET) and their pore size distribution was determined as well.

Besides the chemical way another method was utilized to produce carbon nanotube junctions. Purified nanotubes were impregnated by different transition metal salts (Co, Fe, Mo and their mixture) and a new generation of nanotubes was grown on the surface of the parents in a second CCVD procedure.

Nanotubes modified by several different methods were homogenized in the mixture of epoxy monomer, hardener and accelerator (Tabb 812) and polymerized at 333 K to form epoxy/nanotube composites. Preliminary investigations were carried out in each case to determine the electric conductivity of the composites. The hardness and the Young modulus were also calculated using nanoindentation measurements.

Carbon nanotubes were applied as catalysts support. Pt/nanotubes catalysts were produced and their catalytic activity was investigated in the dehydrogenation reaction of 2-propanol using *in situ* gas chromatography (GC) and the results were compared to other carbon supports (active carbon, graphite).

Results

1. Multiwall carbon nanotubes (MWNTs) were prepared by catalytic decomposition of acetylene over Co-Fe/$Al(OH)_3$ catalyst with 2.5–2.5 w% Co and Fe content. The reaction conditions were as follows: reaction temperature – 973 K, reaction time – 60 minutes, gas flow rates – 300 cm^3/min N_2 and 30 cm^3/min C_2H_2. Under these conditions the carbon yield, calculated by using the initial weight of the catalysts as base, was over 105 w%. Transmission electron microscopy investigations proved that this carbon material contains multiwall carbon nanotubes and the amount of amorphous carbon was negligible. By TEM we determined the outer (4.6–14.4 nm) and inner (1.3–7.9 nm) diameter distribution of the purified material, and the number of carbon layers (8–27) in the tubes was calculated as well.

2. We studied the possibility of chemical functionalization of nanotubes. In the first method nanotubes were reacted with ethyl acetoacetate followed by amidation reaction with ethylenediamine. The existence of the different functional groups was proved by infrared spectroscopy (IR). We described another procedure for functionalization of MWNTs with amine-containing materials. Besides functionalization, this procedure provides a viable method to connect individual tubes to each other and form junctions between them. The method consists of 3 steps. During the first one (treatment of the tubes with cc. HNO_3/H_2SO_4), carboxylic groups are generated on the surface of nanotubes. These carboxylic groups can be converted into carbonyl chloride functional groups simply by reaction with $SOCl_2$. The resulting material is very reactive toward amines, diamines (propylenediamine) or triamines (melamine). The resulting $–C(O)NH(CH_2)_nNH_2$ groups thus formed play the role of the coupling agent between the tubes. Depending on the number of amine groups (2, 3) it was possible to produce double and triple junctions as well. It was proved by STM investigations that the tubes are not only lying on each other but there are strong chemical interactions between them. In order to prevent steric inhibition due to the difference between the sizes of the linking molecule and the diameter of the tubes, it was advisable to use relatively large molecules such as modified oligonucleotids.

3. We proved that ball milling is a very efficient way of breaking carbon nanotubes. It was found that after 100 hour grinding the length of the tubes decreased from several

micrometers to 200–300 nm, although the final material contained high-density particles. Thus, further purification seemed to be necessary. We performed a purification protocol using $KMnO_4$ followed by treatment with concentrated HCl to disintegrate the particles and form well-separated carbon nanotubes. This substance could be homogenized easily in liquid phase, which may be a significant asset in the preparation of polymer/nanotube composites.

4. A simple mechano-chemical functionalization of carbon nanotubes was performed applying the ball milling technique in specific atmospheres (CO, Cl_2, CH_3SH, NH_3, and $COCl_2$) allowed the introduction of functional groups like carboxylic, carbonyl, chlorine, thiol, amine, amide etc. onto the outermost surface of nanotubes of rather uniform size. This way we achieved the mechanical grinding and the chemical functionalization of the tubes in one step. The resulting functional groups were characterized using IR spectroscopy and X-ray photoelectron spectroscopy. It was proved by STM measurements that the functional groups were not well dispersed on the surface, but they were located as islands of 0.3 nm size.

5. In order to prepare junctions between the nanotubes a new method was elaborated. In this method the nanotubes functioned as support of transition metal particles in a second CCVD process when new carbon nanotubes grew from the parent sample. Depending on the reaction conditions different kinds of junctions were built with various shapes.

6. We produced epoxy/nanotube composite materials using variously treated carbon nanotubes. It was observed that the hardness and the Young modulus of the final materials are strongly depended on the quality of the tubes. Mixing 1 w% purified nanotubes without further modification in the polymer the hardness and the Young modulus increased with 45 % and 19 % respectively, compared to the parent epoxy matrix.

7. Preliminary catalytic investigations were carried out using platinum catalysts supported on various carbonaceous materials (graphite, activated carbon, nanotubes with original length, ball-milled nanotubes). We studied the dehydrogenation of 2-propanol in a pulse micro reactor connected to a gas chromatograph. Comparing the

different catalysts, the two nanotube-containing materials proved to be the most efficient.

Conclusions

As a result of our research, good conditions were found to the large-scale and selective production of carbon nanotubes. Hereafter these good quality nanotubes could be functionalized easily by mechanical, chemical and mechano-chemical way, which may be important to their further applications.

Besides the production, the purification and the functionalization of the carbon nanotubes, we have taken steps to prove that after these kinds of modifications the nanotubes can be used as catalyst support and reinforcing agent in composites utilizing their unique properties.

Publications

Papers related to the thesis

1. **Mechanical and chemical breaking of multiwalled carbon nanotubes**
K. Niesz, A. Siska, I. Vesselényi, K. Hernádi, D. Méhn, G. Galbács, Z. Kónya, I. Kiricsi, *Catalysis Today* **76**, 3-10 (2002)
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9. **Mechano-chemical functionalization of carbon nanotubes**
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11. **STM investigation of carbon nanotubes completely covered with functional groups**
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12. **Synthesis Procedures for Production of Carbon Nanotube Junctions**
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13. **Synthesis Procedures for Junction Production of Carbon Nanotubes**
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1. **Functional groups generated by mechanical and chemical breaking of multiwalled carbon nanotubes**
1st NANOCOMP meeting, Kirchberg, 05-06/03/2001, lecture

2. **Ball-milling induced functionalization of carbon nanotubes**
2nd NANOCOMP meeting, Zaragoza, 10-12/09/2001, lecture

3. **Functionalization of nanotubes and further applications**
3rd NANOCOMP meeting, Namur, 27/02-01/03/2002, lecture

4. **Functionalization of multiwall carbon nanotubes**
4th NANOCOMP meeting, Nice, 09-11/10/2002, lecture

5. **Chemical linkage of individual nanotubes**
5th NANOCOMP meeting, Szeged, 05-07/03/2003, lecture

6. **Large Scale Synthesis of Carbon Nanotubes and Their Composite Materials**
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7. **Synthesis Procedures for Production of Carbon Nanotube Junctions**
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11. **Modification of multiwalled carbon nanotubes by different breaking processes**
I. Vesselényi, A. Siska, D. Méhn, K. Niesz, Z. Kónya, J. B.Nagy, I. Kiricsi, 13th European Conference on Chemical Vapor Deposition, Athens, 26-31/08/2001, poster

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14. **STM investigation of carbon nanotubes completely covered with functional groups**
A. A. Koós, Z. E. Horváth, Z. Osváth, L. Tapasztó, K. Niesz, Z. Kónya, I. Kiricsi, N. Grobert, M. Rühle, L. P. Biró, SPIE-Microtechnologies for the New Millenium, Maspalomas, 19-21/05/2003, poster

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16. **Single and multi junctions from carbon**
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1. **Production of carbon nanotubes on different metal supported catalysts**
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2. **Modifying the acidic properties of PtZSM-5 and PtY zeolites by appropriately varying reduction methods**
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Chemistry with carbon nanotubes

Ph.D. Thesis

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