Synthesis and manipulation of carbon nanotubes

J W Seo\textsuperscript{1,3}, E Couteau\textsuperscript{1}, P Umek\textsuperscript{1}, K Hernadi\textsuperscript{1,2}, P Marcoux\textsuperscript{1}, B Lukić\textsuperscript{1}, Cs Mikó\textsuperscript{1}, M Milas\textsuperscript{1}, R Gaál\textsuperscript{1} and L Forró\textsuperscript{1}

\textsuperscript{1} Institute of Physics of Complex Matter IPMC, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland
\textsuperscript{2} University of Szeged, Department of Applied and Environmental Chemistry, 6720 Szeged, Rerrich B tér 1, Hungary
E-mail: jinwon.seo@epfl.ch

\textit{New Journal of Physics} 5 (2003) 120.1–120.22 (http://www.njp.org/)
Received 7 July 2003
Published 30 September 2003

Abstract. This paper reviews recent results in the field of carbon nanotube (CNT) research obtained at our institute at EPFL. We show in particular that CNTs can be synthesized by the catalytic vapour deposition (CVD) technique with high efficiency and purity. Furthermore, we present recent examples of advances in the large-scale production of CNTs as well as in the chemical and mechanical manipulation of CNTs. The chemical manipulation involves covalent and non-covalent sidewall functionalization of single-wall CNTs and preparation of inorganic coatings on CVD-grown nanotubes for the realization of fibres and CNT-reinforced composites. Mechanical manipulation aims at the application of CNTs as tips for scanning probe microscopy.

\textsuperscript{3} Author to whom any correspondence should be addressed.
1. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima [1], CNTs have been in the focus of materials research as a result of their unique electronic and mechanical properties in combination with their chemical stability [2, 3]. Promising applications of CNTs include electronic devices [4], field emitters [5] and mechanical strengthening [6]. Among the different methods of CNT synthesis [7], i.e. electric arc-discharge [8], laser ablation [9] and catalytic vapour deposition (CVD) [10]–[13], the catalytic method seems to be the most promising, in particular in terms of large-scale industrial applications, due to the relative ease with which it is possible to upscale both the preparation and the purification methods [14, 15].

This paper is intended to highlight recent advances in molecular technology involving CNTs, particularly related to CNT growth, manipulation and progress in some applications.

2. Experimental details: characterization of CNTs

Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) have been carried out to characterize all samples. The latter was performed in nitrogen atmosphere or in air (Derivatograph-Q, MOM), in particular to monitor the weight loss of the catalysts at the temperature of CVD, the thermal stability of purified samples and to determine the amount of functional moieties covalently attached to sidewalls of the CNTs. TEM and SEM have been used to characterize the CNT samples, in particular to verify the yield, the wall structure and the purity of the samples. The TEM sample preparation involved grinding the synthesized material mechanically and gluing the ground powder on a Cu TEM grid. For the TEM studies, Philips CM20 and CM300 microscopes have been used for conventional and high-resolution mode operation at 200 and 300 kV, respectively. Both microscopes are equipped with an energy-dispersive x-ray (EDX) detector for chemical analysis, and the latter also provides electron-energy loss spectroscopy (EELS) by means of a Gatan image filter (GIF 6000). SEM micrographs were taken using a Philips XL 30 FEG. The mechanical properties...
of plain and Mg-coated multi-walled CNTs (MWCNTs) were measured by means of atomic force microscopy (AFM) (Autoprobe CP Park Scientific Instruments). For the measurement, the CNTs were dispersed in ethanol by sonication for about 5 min. A droplet of the suspension was placed on a polished alumina-ultrafiltration membrane (Whatman Anodisc) with nominal pore diameter of 200 nm. AFM images were taken in contact mode (operating in air) by varying the load. For the AFM tip, Si3N4 cantilevers with force constant of 0.01–0.1 N m⁻¹ were used.

3. CVD synthesis of CNTs

3.1. CVD synthesis using CaCO₃ catalyst support

Catalytic decomposition of carbon-containing compounds is considered to be an appropriate method for the synthesis of CNTs in large quantities [16]. Numerous catalyst materials as well as carbon sources have been tried out [17]–[20]; many promising results have been published underlining good selectivity, flexibility and technical simplicity [21, 22]. The choice of the catalyst support has been found to be critical for scalable CVD as well [23]–[26]. In particular, recent results based on silicagel- or zeolite-supported catalysts [23]–[25] have shown that porous materials are excellent supports in catalytic nanotube production.

Very recently, we have shown that MWCNTs can be produced with high selectivity and purity using CaCO₃ as catalyst support [27]. Since both metallic particles and catalyst support can be removed in diluted acids, purification is performed in one step. Hence, multi-step purification processes and strong oxidants have been avoided and, consequently, CNTs with high purity and less damage of graphitic walls have been obtained. Details about our MWCNT synthesis procedure were reported elsewhere [27]. To summarize, MWCNTs were synthesized by catalytic decomposition of acetylene at 720°C in a fixed-bed flow reactor. As catalysts, monometallic Co(II), Fe(II) and Fe(III) salts were applied as well as the bimetallic combination Fe(II), Co(II) and Fe(III), Co(II) salts, all supported by CaCO₃. The total concentration of catalysts was about 5 w%. Approximately 50 mg of the prepared supported catalysts was placed in a quartz boat which was inserted in a quartz tube under nitrogen flow. Our standard fixed-bed flow reactor contains a reaction quartz tube and a quartz boat of 18 and 12 mm diameter, respectively; the length of the heated area measures 200 mm.

Recent results based on silicagel- or zeolite-supported catalysts made evident that porous materials are excellent supports in catalytic CNT production [24, 25]. However, porous supports tend to accumulate huge amount of amorphous carbon during the synthesis. With respect to the reaction conditions (especially the temperature) during the catalytic CNT synthesis by CVD, acetylene is decomposed in either homogeneous or catalytic reaction. In the case of porous support, catalyst particles on outer surfaces proved to be rather selective for CNT formation whereas the inner centres produce amorphous carbon. By using CaCO₃ as catalyst support, we can overcome all these difficulties of catalytic CNT production. CaCO₃ is a non-porous material where the formation of amorphous carbon is suppressed during the nanotube growth, and therefore selective formation of CNTs is promoted. Figure 1 shows low-magnification (a) and high-resolution (b) TEM micrographs of MWCNTs grown over Fe(III), Co(II)/CaCO₃. The catalyst particles and support material, which show dark contrast in the image, are thickly covered with CNTs. In addition, no amorphous carbon or carbonaceous particles can be seen. The high-resolution TEM image presented in figure 1(b) clearly reveals well-graphitized walls of MWCNT and indicates that no amorphous carbon attaches on the outer surface of the tubules.
Figure 1. Low magnification and high-resolution TEM micrographs of CNTs grown over Fe(III), Co(II)/CaCO₃ before (a), (b) and after purification (c), (d). Most of the dark spots in the purified sample (see (c)) are due to nanotube endings aligned parallel to the electron beam. In the high-resolution image, no amorphous carbon layer is visible on the outer surface of the nanotube before and after purification.

Recently, MgO has been reported to be effective for the growth of high-quality single-walled CNTs (SWCNTs) [11, 26, 28] and MWCNTs [29, 30]. Currently CaCO₃ represents an appropriate alternative to MgO with respect to the CNT yield, selectivity and purity. Our purification method using 30 wt% HNO₃ is as mild as that reported for MgO [26] or milder, when compared with treatments in boiling conc. HCl [29], in conc. HCl [31] or in 65 wt% HNO₃ [32]. An advantage of using CaCO₃ as catalyst support is the decomposition of CaCO₃ into CaO and CO₂ at the reaction temperature. Hence, after MWCNT synthesis the main by-product is CaO, which is soluble in diluted acids, and only half of the applied amount of support remains to be removed after synthesis, which simplifies the purification procedure significantly. Typically, 100 mg catalyst resulted in approximately 70 mg of purified MWCNTs, and the total yield is about 700 mg of purified MWCNTs per day.

3.2. Large-scale synthesis of MWCNTs

The capacity and the scalability of fixed-bed reactors are limited. Therefore, we elaborated a continuous production method based on a rotary-tube furnace. The oven has an 80 mm diameter
Figure 2. View of the rotary-tube oven used for large-scale synthesis of CVD nanotubes. Two reservoirs are located at the ends of the tube, one containing the catalyst (right-hand side) and the other collecting the product (left-hand side). The inset shows the raw product of MWCNT after one day of production in the reaction tube with 80 mm diameter. From primary results we obtained high-quality and pure MWCNTs with a yield of 100 g day$^{-1}$ (after purification) by this method.

rotating quartz tube with a heating area of 750 mm length. Figure 2 shows a photograph of the installed apparatus. It is equipped with two reservoirs, one containing the catalyst and the other collecting the product. The catalyst is introduced into the reaction tube by gentle motor-driven shaking of the feeder. The rotation of the reaction tube and its inclination are manually set. The latter determines the speed of the catalyst passing through the heated zone, where the decomposition of acetylene takes place. All other processes such as heating, cooling and gas switching are automatically controlled. Finally, the product is collected at the lower end of the reaction tube.

MWCNTs were synthesized by the catalytic decomposition of acetylene at 750 $^\circ$C over Fe(III), Co(II) catalysts supported by CaCO$_3$. The catalysts were prepared as described above, in the same way as for the fixed-bed flow reactor [27]. Typically, using our new rotary-tube oven, mass production of purified CNTs on the scale of 100 g day$^{-1}$ can be performed. The effect of rotation speed, inclination, particle size of initial catalyst support and other parameters still need to be optimized.

3.3. Purification of CNTs

Highly purified CNTs are in general required for sophisticated measurements and practical applications. Purification mainly involves the separation and removal of catalyst particles, support material and amorphous carbon from CNTs. Since these materials mostly have to be
Figure 3. EDX spectra of purified and unpurified samples clearly indicate the significant reduction of the Fe and Co signals. The strong Cu peaks originate from the Cu grid used as TEM supporting grid.

removed independently by different chemicals, the purification of catalytically prepared CNTs can become a multi-step procedure [33] and one risks additional contamination and/or structural damage of the CNTs at each step. In particular, a large amount of undesirable carbonaceous by-products (amorphous carbon, nanoparticles, fullerenes, etc) can be present when CNTs are produced by the electric arc-discharge method. Several methods to purify the soot have been reported. For instance, polyhedral particles can be removed by different oxidants but these oxidation treatments also destroy the overwhelming part of the sample and the end caps [34]–[36]. A non-destructive method has been carried out in a colloidal suspension of nanoparticles stabilized with surfactants, followed by centrifugation and filtration [37, 38]. Separation methods based on chromatography gives CNTs with high purity but they are nevertheless not suitable for purification of large amounts [39]–[41].

We have developed two different approaches for purification of CNTs. For MWCNTs produced by CVD using CaCO3 support, catalyst and support can be removed by sonication in nitric acid (30 wt% HNO3) [27]. To be precise, the purification involves sonication for about 30 min, filtering, washing with de-ionized water and finally drying at 120°C overnight. Hence, it is a one-step chemical treatment, simple and harmless to the CNT structure, and therefore, in particular, promising for large-scale and low-cost production of CNTs for industrial applications. Figure 1 shows CNTs before and after purification; the number of catalytic particles, which can be seen as dark spots in figure 1(a), is considerably reduced compared to figure 1(c). Representative EDX spectra taken from both samples (figure 3) also confirm a dramatic reduction of Fe and Co signals. Since CaCO3 has no pores, no additional residual can be trapped during and after the acidic purification step. As can be seen in figure 1(d), the purification step neither damaged the CNT structure nor generated additional contaminants. Hence, CNTs with high yield, high purity and less damage to graphitic walls can be obtained.

Our second approach applies to SWCNTs. The main obstacle in the purification of SWCNTs is related to catalytic particles embedded in a capsule of several graphene sheets (figure 4(a)). These particles with their graphitic shells cannot be easily separated by dispersion since they
strongly adhere to bundles and since their chemical stability is higher than that of SWCNTs. An efficient purification method was elaborated based on a mixing of the SWCNT suspension with inorganic nanoparticles (mainly ZrO$_2$) in an ultrasonic bath [42]. We use the energy of elastic impact between encapsulated catalysts and small hard inorganic particles during sonication to eject the metal kernels and trap them by a strong magnet (figures 5(a) and (b)). With a subsequent chemical treatment, where also the inorganic nanoparticles will be chemically removed, a high purity SWCNT material is obtained (figure 4(b)). This process is simple and does not require intricate equipments and enables the production of SWCNTs free of magnetic impurities as our highly sensitive electron spin resonance measurement has proven [42].
4. Manipulation of CNTs

At present, CNTs are available in a quality and quantity which makes their industrial application possible and practical. Currently, applications that take advantage of the extremely high elastic modulus and tensile strength of CNTs [43] are attractive and promising. For instance, CNTs are ideal candidates for scanning probe microscope (SPM) tips or can be incorporated as reinforcement elements in composite materials. Another interesting approach is to assemble CNTs in a macroscopical fibre. Very recently, Dalton et al [44] have shown that 100 m-long CNT composite fibres can be produced, which can be woven into textiles.

The main obstacles to overcome in the research of CNT-based composite materials are (i) the wettability of the CNT surface [45], (ii) the load transfer from the matrix to the nanotubes [46] and (iii) the ability to disperse CNTs homogeneously into the matrix [38, 47]. One possible way to achieve these requirements is chemical functionalization; the interaction between nanotubes and the matrix can be significantly improved when chemically functionalized CNTs are employed instead of pristine CNTs.

In our group we search for practical applications and for modification of CNTs. The following section will summarize our research along these efforts.

4.1. CNTs mounted on SPM tips

Due to the outstanding mechanical properties combined with nanometre sharpness, CNTs represent ideal candidates as tips for SPM, e.g. for AFM, and scanning tunnelling microscopy. Nanotubes have a small tip radius and a high aspect ratio, which is essential for the investigation of surfaces with strongly pronounced topographic features such as trenches or undercuts. Currently, there are two approaches to make CNT tips for SPM: the one method involves a direct growth of CNTs on the tip by CVD [48] whereas by the other method CNTs are attached one-by-one in a SEM or TEM [49, 50]. In our institute we have developed a nanomanipulator for a TEM which has mechanical and piezo-induced stage for the control of the movement inside the manipulator. Details can be found in [50]. Using this manipulator we have succeeded in mounting MWCNTs on AFM tips; several examples are shown in figure 6.

Figure 6. The SPM probe was coated with approximately 100 nm of indium which serves as a conductive ‘glue’ to hold the nanotube. (a) SEM and (b) TEM images of tips with attached MWCNTs.
Our recent study [51] has shown that MWCNTs grown by CVD have inferior mechanical properties than those grown by the arc-discharge method. A large proportion of the CVD-grown tubes reveal well-formed caps but the graphitization of the walls is poor. The tip shapes are also more rounded and the tip radius is higher when compared to arc-discharge tube tips [51]. In general, the CVD process occurs at low temperature in the range of 720–900 °C, whereas the arc-discharge involves plasma reaching 3000 °C [7]. At low temperatures, where the catalytic process takes place, the mobility of the carbon atoms is low and defects are more likely to form. In the arc-discharge process, growth is assumed to stem from equilibrium structures. Nevertheless, CNTs grown by the CVD process are attractive because they can be grown directly on a substrate, tailored precisely for the application one has in mind. Although attractive, CVD-grown MWCNTs typically contain structural disorder [51, 52] and lead to a strong decrease of the Young’s modulus [53, 54]. Indeed, we have observed that CVD-grown MWCNTs attached to a probe are also more fragile than arc-discharge MWCNTs.

Apart from these mechanical considerations, the quality of the probe also depends on the morphological and crystallographic properties of the tube and its tip, especially at the nanometre scale. Furthermore, the length of the CNT determines the maximum force that can be applied from the probe to the sample before buckling of the CNT occurs. Hence, a reliable and reproducible method for the production of SPM probes made out of CNT is needed which can control the length and the quality of the CNT. Although the \textit{in situ} deposition of CVD-grown tubes on SPM probes seems to be technologically easier, by now the quality of these CNT tips might be insufficient. The mounting of arc-discharge tips one-by-one using a manipulator is time consuming but gives customer-specified, well-defined SPM probes made out of CNTs. As we previously reported, when AFM images taken using a commercial PSI Ultralever probe and a MWCNT-attached tip are compared, the one obtained using a MWCNT shows clearly better resolution. Moreover, using the CNT, we are able to penetrate into the substrate more than twice as deep as in the case of the PSI Ultralever [50].

4.2. CNTs with inorganic coating

Due to their tremendous mechanical properties [43, 55] CNTs represent a promising candidate to substitute the carbon fibres as reinforcing elements in composites. To date, a large variety of possible composite materials using SWCNTs and MWCNTs combined either with different polymers [56]–[58] or with inorganic compounds has been prepared (e.g. [46]). Composites with inorganic metal matrix reinforced with CNTs are expected to have unique mechanical properties [54, 59]. Using CNTs as reinforcing additive, either in metal- or polymer-based composites, the most critical issues are the wettability of the CNT surface and the load transfer from the matrix to the nanotubes. Both aspects are mainly determined by effective interaction between CNT surface and precursors. Indeed, several references on processing of CNT-based composites have pointed out the importance of good interfacial bonding, unfortunately without specifying in detail what determines the interaction [60]–[63]. Nevertheless, an increase of the interfacial bonding strength has been observed in composites when heat-treated CNTs were used [62, 63] indicating that purity of the CNT surface plays an important role for interfacial interaction. MWCNTs, synthesized and purified by the procedure described above (see sections 3.1 and 3.3), provide an excellent starting material for composite formation, since the CNT surface is free of amorphous carbon.

Very recently, we succeeded in producing MWCNTs with a homogeneous coverage of various inorganic materials, such as alumina, silica and titania [64, 65]. For the composite
formation, purified MWCNTs were used ‘raw’ or modified by surfactant (sodium dodecyl sulfate, SDS). The impregnation was carried out with and without solvent (isopropanol) for both types of MWCNTs. To be precise, the former impregnation involved MWCNTs dispersed in isopropanol via sonication, whereas the latter used MWCNTs directly suspended in liquid or melted compounds under nitrogen. In our experiment, organometallic and inorganic compounds were implemented: as aluminium sources, two compounds, namely aluminium trichloride (AlCl$_3$·6H$_2$O) and aluminium isopropoxide (Al(OiPr)$_3$) were applied, whereas tetraethyl orthosilicate (Si(OEt)$_4$); and tetraethyl orthotitanate (Ti(OEt)$_4$) were used for silica and titania coatings. Very recently, we also studied magnesium sources, such as magnesium ethoxide (Mg(OEt)$_2$) and MgCl$_2$. In order to avoid confusion, representative experimental results are summarized in table 1.

Impregnation based on organometallic sources revealed CNTs and inorganic nanoparticles mostly separated, when SDS-treated MWCNTs were used as starting material [65]. This observation indicates that no strong interaction between MWCNTs and the coverage material can be obtained. In contrast, the direct impregnation method using purified ‘raw’ MWCNTs resulted in homogeneous coverage of CNTs. Surprisingly, the use of isopropanol plays rather a repressive role on the adherence of inorganic materials to CNTs for both cases. We assume that the interaction between the CNT surface and isopropanol is much stronger than that of the coating material resulting in segregation of the inorganic material. In the case of the Ti(OEt)$_4$ source, the impregnation is additionally affected by the limited solubility of Ti(OEt)$_4$ in isopropanol; consequently, segregation of inorganic particles occurs. The results obtained using different inorganic sources are just the opposite: the best coating was obtained when SDS-treated nanotubes were applied for impregnation. For an ionic compound like AlCl$_3$ or MgCl$_2$, raw MWCNTs do not provide an ideal surface for cohesive binding and an adsorbed layer of surfactant can yield a better interaction via their ionic groups.

Figure 7 shows representative TEM images of the composites obtained by using organometallic and inorganic Mg sources (Mg(OEt)$_2$ and MgCl$_2$). As can be seen in figure 7(a), a separated phase of magnesia predominates when plain MWCNTs are impregnated by using Mg(OEt)$_2$ sources with isopropanol. From our experience with Al(OiPr)$_3$, Si(OEt)$_4$ and Ti(OEt)$_4$ [65], we know that the best coating can be obtained when the impregnation is performed without isopropanol. For this process, we tried to melt the Mg(OEt)$_2$ compound, which was not possible below 200°C, thus our effort has not been successful so far. When the MgCl$_2$ source is applied, a thick layer of amorphous magnesia is obtained over SDS-treated MWCNTs (see figure 7(c)), whereas the use of plain MWCNTs results in a few tubes showing slight coverage, as can be observed in figure 7(b).

In order to improve the mechanical properties of MWCNTs, impregnation with Mg has been performed. Homogeneous coverage of Mg was obtained on plain MWCNTs when the impregnation was carried out in an identical way to that described above using organometallic and inorganic sources. Figure 8(a) shows a representative TEM image of a plain MWCNT after coating with Mg. The coating is about 2 nm thick and the MWCNT is homogeneously covered. The EDX taken from the coated MWCNTs clearly confirms the presence of Mg as coating material (figure 8(b)).

The mechanical properties of plain and Mg-coated MWCNTs were measured by means of an AFM using the method described by Salvetat et al [55]. Young’s modulus was estimated by elastic deformation of a CNT with an AFM tip and by recording vertical deflection as a function.
| Organometallic sources | Al(OiPr)$_3$ | Si(OEt)$_4$ | Ti(OEt)$_4$ | Mg(OEt)$_2$ |
|------------------------|--------------|-------------|-------------|-------------|
| Plain MWCNTs            | With solvent | Rudiment coverage, alumina clusters | Almost no coverage, separate phase of SiO$_2$ | Rather homogeneous coverage with few segregated particles | No coverage, segregated inorganic particles |
|                        | With solvent | Homogeneous coating, accompanied by needle-like crystals | Homogeneous coverage, some separate segregations | Coating with irregular thickness, some separate segregations | |
| Soap-treated MWCNTs     | With solvent | Preferentially thin, irregular coverage | Thin, irregular coverage, non crystalline SiO$_2$ particles | Thin, irregular coating together with segregated crystals | |
|                        | With solvent | Separated alumina crystals | Irregular coating | No coverage, only segregated particles | |

| Inorganic sources | AlCl$_3$ | MgCl$_2$ |
|-------------------|----------|----------|
| Plain MWCNTs      | With solvent | No nanocrystals, but thin, not continuous coverage | No nanocrystals, almost no coverage |
| Soap-treated MWCNTs | With solvent | MWCNTs covered with a thick homogeneous layer of amorphous alumina | MWCNTs covered with a thick, rough, inhomogeneous deposit of an amorphous film |
Figure 7. TEM images of MWCNTs after impregnation (a) with organometallic Mg(OEt)$_2$ and (b), (c) inorganic MgCl$_2$ compounds. (a), (b) The use of isopropanol during impregnation is unfavourable for both types of sources when plain MWCNTs are used. (c) A thick amorphous layer of magnesia was obtained when SDS-treated MWCNTs were impregnated with MgCl$_2$ using isopropanol.

Figure 8. (a) TEM micrograph of a MWCNT with Mg coating. White arrows indicate the homogeneous coating of Mg with a thickness of 2 nm. (b) The EDX spectrum reveals a significant peak of Mg. Cu peaks are due to the TEM grid used as sample supporting grid; the Ti peak is an artefact of our EDX set-up. No significant peak of O K$\alpha$ at 0.523 keV is visible.
Figure 9. AFM image of a Mg-coated MWCNT suspended over an alumina membrane in contact mode. A small section of the nanotube lies over a hole, whereas the major part of the nanotube is in contact with the membrane surface. Image size is 1 µm × 1 µm.

of applied force. For the measurement, MWCNTs were dispersed in ethanol by sonication and a droplet of the suspension was placed on a polished alumina membrane. As can be seen in figure 9, CNTs occasionally lie over a hole for a short section of the entire length, with the major part of the CNT still in contact with the membrane surface. The parameters, such as the MWCNT diameter \( D \), suspended length \( L \) and vertical deflection in the middle \( \delta \), were deduced directly from an AFM image. Deflection versus applied force \( \delta(F) \) is illustrated in figure 10. Using simple beam mechanics, Young’s modulus \( E \) is estimated from the following formula:

\[
\delta = \frac{(F L^3)}{(E \alpha I)}
\]  

(1)

where \( \alpha = 192 \) for a clamped beam, and \( I = \pi (D^4 - D_i^4)/64 \), \( D_i \) being inner diameter which was neglected in the calculation. Since \( E \) is inversely proportional to \( F/\delta \), \( E \) can be directly estimated from \( \delta(F) \) in figure 10. More details about the determination of Young’s modulus by this method can be found in [54, 55].

We assume that the CNTs are rigidly clamped through the adhesion of tubes with long lengths in contact with the membrane, since the CNTs are not lifted off during loading in the applied force range up to 11 nN. Measurements are carried out with coated and pure MWCNTs. Since the experimental error in determining the suspended length is estimated to be around 15%, \( E \) can be measured with about 50% precision. \( D \) was determined from the MWCNT height and has an error of 8% on average. The average value for four coated MWCNTs with diameters between 16 and 19 nm yields a Young’s modulus of about 12 ± 6 GPa. Purified MWCNTs, the same as used for coating, show a larger dispersion of Young’s modulus, from 10 to 70 GPa; those values are in agreement with the results (values from 10 up to 50 GPa) previously reported by Salvetat et al [53] for CVD-grown MWCNTs.

New Journal of Physics 5 (2003) 120.1–120.22 (http://www.njp.org/)
Figure 10. Deflection versus applied force for a Mg-coated MWCNT. The suspended length was 225 ± 34 nm and the diameter of the tube was 16.1 ± 0.6 nm. For forces up to 5.5 nN, response in deflection was linear. The red line is a linear regression fit of experimental data, and its inverse value \( F/\delta \) is used to calculate Young’s modulus in equation (1).

Mg has a Young’s modulus about 45 GPa. Hence, the coverage with Mg did not enhance the Young modulus of the composite; at first sight it rather seems to lower the modulus. On the other hand, a coated MWCNT has to be considered as a complex coaxial structure composed of a MWCNT with a diameter \( D_{\text{MWCNT}} \) and with a Mg layer of thickness \( d \sim 2 \text{ nm} \). Consequently, the total diameter used for modulus estimation has to be written as

\[
D = D_{\text{MWCNT}} + 2d.
\]

With \( D_{\text{MWCNT}} > d \), when we assume that the Mg layer is much softer than a pure MWCNT, the measured force–deflection curve will mainly reflect the stiffness of the MWCNT tube, without any noticeable contribution of the coverage layer. In this case, the tube diameter has to be corrected with respect to equation (2), which will give a higher \( E \) value since Young’s modulus is inversely proportional to the tube diameter. Indeed, when we subtract the thickness of the coating, we obtain an average modulus of 34 GPa, which is in agreement with values measured for CVD-grown MWCNTs.

In contrast, when we assume that the coating has a higher \( E \) value than the MWCNT core, the calculation is more complicated; since \( D_{\text{MWCNT}} > d \), we also have to take the MWCNT core into account. Moreover, the determination of the load transfer in the CNT composite is very complex; more detailed studies are needed. A valuable and complementary measurement might be made by Raman spectroscopy [46]; load transfer in CNT epoxy composites was studied by monitoring the shift of the second-order Raman peak.

Our preliminary results on the Young’s modulus make a clear conclusion very difficult. Nevertheless, the fact, that we obtain an \( E \) value comparable to pristine MWCNTs by including the correction of the tube diameter, rather suggests that the Young’s modulus of the coverage is lower than that of the MWCNT. Possible explanations for a relatively low Young’s modulus of the Mg coating (compared to 45 GPa in Mg) are that

(i) the coating is not complete or is damaged during sonication,

\[\text{New Journal of Physics} \ 5 \ (2003) \ 120.1-120.22 \ (http://www.njp.org/)\]
(ii) a 2 nm thin layer of amorphous Mg has a lower Young’s modulus than that known for the bulk value, or

(iii) the coating has a different chemical composition leading to a decrease of the Young’s modulus.

So far from EDX analysis we have only detected Mg. Knowing that EDX is not sensitive to light elements such as hydrogen, we cannot yet exclude oxide or hydroxide and more detailed analysis (e.g. XPS) has to be performed. So far, EELS measurement has proved to be tricky due to trembling and drift of the CNT caused by focusing of the electron beam. However, we believe that homogeneous coating of CNTs produces composites with the mechanical strength of CNTs and with an improved adhesion and shearing behaviour compared to CNTs. For the future, composite materials based on coated MWCNTs will have to be prepared on the macroscopic scale, and the macroscopic load transfer has to be determined and correlated with the load transfer applicable on the nanometre scale. Research on inorganic CNT-based composites is still in the early stages, but our results are very encouraging for the future.

4.3. Assembling macroscopic fibres from CNTs

One of the most promising applications in the research of CNT-based composites is their assembly into long macroscopic fibres. For the preparation of macroscopic fibres we use techniques similar to those described by Gommans et al [66]. To summarize briefly, purified CNTs were dispersed either in solvent, such as DMF (dimethylformamide), or in solution of the polymer PmPV (poly(m-phenylenevinylene-co-2,5-diocetyloxy-p-phenylenevinylene)) in toluene. From a suspension containing about 1 wt% of CNTs, ordered ropes were slowly pulled out by means of a carbon fibre mounted on a motor driven translation stage. Figure 11 shows a schematic illustration of our apparatus.

Figure 11. Schematic illustration of the set-up used for pulling out macroscopic fibres of CNTs.
Very recently we found that the use of the solution of PmPV in toluene instead of the solvent DMF improved the pulling procedure of CNT fibres. PmPV is a polymer well known for the high dispersability of CNTs in organic solvents [67] and therefore has been frequently used in the synthesis of polymer–CNT composites. Applied to fibre assembly, the pulling procedure is more stable. In general, the assembly of MWCNTs into fibres is rather difficult since MWCNTs are not as straight as SWCNTs and they contain a high density of structural defects. Using DMF, only SWCNT fibres could be successfully pulled together whereas using PmPV fibres consisting of MWCNTs could also be obtained. SEM micrographs of assembled fibres composed of SWCNT and MWCNT bundles are presented in figure 12. Typically we achieve a diameter of about 10 µm and a length up to 10 cm using the technique described above. As can be seen in the SEM images (figure 12), the ropes consist of CNT bundles which are well aligned along the fibre axis.

The mechanical strength of these fibres is not as high as expected, which is due to weak interaction between the individual nanotubes and bundles within the fibre [68]. CNTs can easily slide along their axis leading to lower shear modules. Very recently, we have shown that electron irradiation can create cross-links between individual tubes inside a CNT bundle and results in a considerable increase of Young’s modulus [69]. We have also observed that the conductivity of a CNT rope significantly changes with electron irradiation [70].

**Figure 12.** SEM micrographs of typical ropes made from solution of (a) SWCNTs and PmPV in toluene, (b) SWCNTs in DMF and (c) MWCNTs and PmPV in toluene.
In the field of production of macroscopic fibres, our current goal is to improve the mechanical properties through cross-linking between adjacent nanotubes. This implies a chemical modification of nanotubes either before the production of fibres, or during the pulling of fibres from the solution, or after drying them. We started to investigate the latter possibility, through electron irradiation. Currently we are exploring alternative ways, either by modifying the composition of the solution from which fibres are pulled out, or by functionalizing the sidewalls of the nanotubes.

4.4. Covalent functionalization of CNTs

Considerable effort has been devoted to the chemical modification of CNTs [71, 72], which would not only assist in composite preparation [73] but also open new prospects in aligning and forming molecular devices [74] as well as generating nanoscale architectures [75]. First attempts at functionalization of CNTs were limited to a few reactions of oxidation with different oxidants [76]–[78], which resulted in the opening and shortening of nanotubes. After so-called ‘acidic treatment’, carboxylic groups are found on the open edges and also on places where five- or seven-membered rings existed before oxidation [78]. With further functionalization of carboxylic groups, the dispersability of CNTs in different solvents was considerably improved [76, 79, 80], but in order to achieve effective incorporation of modified CNTs into the polymer matrix, the functional moieties have to be more uniformly attached to the sidewalls of the CNTs. So far several derivatization approaches on the sidewalls of SWCNTs have been successful, such as hydrogenation via Birch reduction [81], fluorination [82], 1,3-dipolar cycloaddition of azomethine ylides [83], ozonization [84, 85], and electrochemical reduction of aryl diazonium salts [86, 87]. Addition of radicals generated in situ from diazonium salts also yielded functionalized SWCNTs [88].

Research into covalent sidewall functionalization of SWCNTs in our group proceeds mainly in the direction of functionalizing SWCNTs with carbon radicals. The chemical reactivity of CNTs is assumed to be slightly higher than that of graphite, which is considered as chemically inert. The small difference in their chemical reactivity is due to the curvature of the graphene sheets [89]. Although inert, graphite can be derivatized without destroying its layer structure. Beside the ionic intercalated compounds, only fluorinated and oxidized derivatives can be produced [90]. Derivatization of graphite was also successful with aryl radicals generated electrochemically [91]. Recently a new approach for functionalization of SWCNTs with carbon radicals was reported [92]. The approach is very promising for large-scale functionalization of SWCNTs since the reaction is performed without any solvent.

Carbon radicals are highly reactive species and can be in general generated in three different ways: photo-chemically, thermally and in oxidation–reduction reactions. As the precursor compound, from which we thermally generated radicals, organic peroxides were used (scheme 1). These organic peroxides thermally decompose to carbon radicals and CO₂. This is an advantage for the large-scale functionalization of SWCNTs because the only by-product is CO₂. Once the reaction is finished there is no need for extra separation of either side products or non-reacted species from the reaction mixture.

The reaction products were characterized with several techniques such as TGA, UV–visible spectroscopy, Raman scattering, TEM and SEM. While the UV–visible spectra confirmed the covalent modification of SWCNTs [84, 87, 88] (figure 13), the TGA data gave the amount of
Figure 13. UV–visible spectra of pristine SWCNTs and SWCNTs after reaction with dibenzoyl peroxide (DBP). Spectra were measured in dimethylformamide between 400 and 900 nm. The spectrum of functionalized nanotubes shows a complete loss of the van Hove singularities which indicates covalent modification of SWCNTs.

Scheme 1.

functional moieties covalently attached to the sidewalls of the SWCNTs. In the case of SWCNT material functionalized with alkyl groups (R=CH$_3$(CH$_2$)$_{10}$) where the lauroyl peroxide was added in $\approx$0.3 equiv mol$^{-1}$ of carbon, the weight per cent of alkyl groups found was 2.9% with respect to the mass of the whole material analysed. Dibenzoyl peroxide (R=Ph) was added in higher quantities ($\approx$0.6 equiv mol$^{-1}$ of carbon) and the weight per cent of phenyl groups covalently attached to SWCNTs was also higher (6.1%) [93].

In general, the functionalization of SWCNTs by radical addition is a relatively simple but efficient technique for attaching alkyl or aryl groups on the sidewalls of SWCNTs. Therefore, it is currently one of the most promising functionalization techniques. Moreover, functionalization
with alkyl or aryl chains allows additional insertion of different functional groups onto these chains. Hence, this approach will enable adjustable modification of the chemical properties of SWCNTs with respect to their applications.

5. Conclusions

CNTs are currently under consideration for a variety of applications. We have demonstrated here that MWCNTs grown by the CVD process provide high yield and purity. With our current expertise in synthesis, catalysis and purification, we are able to obtain about 100 g MWCNTs per day after purification using our large-scale production oven. The progress in CNT synthesis provides novel approaches for promising applications. The realization of CNT-based composites, where CNTs are homogeneously coated with a thin layer of inorganic material or assembled into macroscopic fibres, opens the door for the production of nanoscale materials with novel electronic and mechanical properties in macroscopic use. CNT functionalization allows us to tune their chemical reactivity and to obtain cross-links between CNTs and CNT bundles. However, for SPM tips, CVD-grown CNTs are not ideal candidates due to their defective structure and rounded tip shape. The mounting of arc-discharge MWCNTs on SPM cantilevers is time-consuming but gives well-defined CNT probes with excellent performance.

From both the macroscopic (fibres and composites) and microscopic (SPM probes, functionalization) points of view, CNTs offer a wide variety of promising applications, which are the focus of our current research.

Acknowledgments

The authors thank the European Commission (RTN Program, NANOCOMP network, RTN 1-1999-00013), Swiss NCCR ‘Nanoscale Science’ and the Swiss National TopNano21 program 5933.1 for the financing of this investigation. We are also grateful to Centre Interdisciplinaire de Microscopie Electronique (CIME) at EPFL for access to electron microscopes as well as for technical support. Contributions of R Foschia, A Kis, A Kulik, L Thienv-Nga are gratefully acknowledged. We are also grateful to M Cadek for the PmPV sample.

References

[1] Iijima S 1991 Nature 56 354
[2] Saito R, Dresselhaus G and Dresselhaus M S 1998 Physical Properties of Carbon Nanotubes (Singapore: World Scientific)
[3] Harris P J F 1999 Carbon Nanotubes and Related Structures: New Materials for the Twenty-First Century (Cambridge: Cambridge University Press)
[4] Fuhrer M S, Nygård J, Shih L, Forero M, Yoon Y-G, Mazzoni M S C, Choi H J, Ihm J, Louie S G, Zettl A and McEuen P L 2002 Science 288 494
[5] Lee Y-H, Jang Y-T, Kim D-H, Ahn J-H and Ju B-K 2001 Adv. Mater. 13 479
[6] Yu M-F, Files B-S, Arepalli S and Ruoff R S 2000 Phys. Rev. Lett. 84 5552
[7] Journet C and Bernier P 1998 Appl. Phys. A 67 1
[8] Journet C, Maser W K, Bernier P, Loiseau A, Lamy de la Chapelle M, Lefrant S, Deniard P, Lee R and Fischer J E 1997 Nature 388 756
[9] Thess A, Lee R, Nikolaev P, Dai H, Petö P, Robert J, Xu C, Hee Lee Y, Gon Kim S, Rinzler A G, Colbert D T, Scuseria G E, Tománek D, Fischer J E and Smalley R E 1996 Science 273 483

New Journal of Physics 5 (2003) 120.1–120.22 (http://www.njp.org/)
[10] Hernadi K, Fonseca A, Nagy J B, Siska A and Kiricsi I 2000 Appl. Cat. A 199 245
[11] Colomer J-F, Stephan S, Lefrant S, Van Tendeloo G, Willems I, Kónya Z, Fonseca A, Laurent Ch and Nagy J B 2000 Chem. Phys. Lett. 317 83
[12] Bacsa R R, Laurent Ch, Peigney A, Bacsa W S, Vaugien Th and Rouset A 2000 Chem. Phys. Lett. 323 566
[13] Li W Z, Xie S S, Qian L X, Chang B H, Zou B S, Zhou W Y, Zhao R A and Wang G 1996 Science 274 1701
[14] Varadan V K and Xie J 2002 Smart Mater. Struct. 11 728
[15] Lee C J, Lyu S C, Kim H-W, Park C-Y and Yang C-W 2002 Chem. Phys. Lett. 359 109
[16] Chen B, Parker G, Han J, Meyyappan M and Cassell A M 2002 Chem. Mater. 14 1891
[17] Dai H, Rinzler A G, Nikolaev P, Thess A, Colbert D T and Smalley R T 1996 Chem. Phys. Lett. 260 471
[18] Kong J, Cassell A M and Dai H 1998 Chem. Phys. Lett. 292 567
[19] Nikolaev P, Bronikowski M J, Bradley M K, Rohmund F, Colbert D T, Smith K A and Smalley R E 1999 Chem. Phys. Lett. 313 91
[20] Murayama S, Koijima R, Miyauchi Y, Chiashi S and Kohno M 2002 Chem. Phys. Lett. 360 229
[21] Cassell A, Delzeit L, Nguyen C, Stevens R, Han J and Meyyappan M 2001 J. Physique IV 11 401
[22] Bonard J M, Kurt R and Klinke C 2001 Chem. Phys. Lett. 343 21
[23] Ivanov V, Nagy J B, Lambin P, Lucas A, Zhang X B, Zhang X F, Bernaerts D, Van Tendeloo G, Amelincx S and Van Landuyt J 1994 Chem. Phys. Lett. 233 329
[24] Hernadi K, Fonseca A, Piedigrosso P, Delvaux M, Nagy J B, Bernaerts D and Riga J 1997 Cat. Lett. 48 229
[25] Hernadi K, Fonseca A, Nagy J B, Bernaerts D, Fudala A and Lucas A A 1996 Zeolites 17 416
[26] Li Q W, Yan H, Cheng Y, Zhang J and Liu Z 2002 Carbon 40 965
[27] Willems I, Konya Z, Fonseca A and Nagy J B 2000 Appl. Cat. A 229 229
[28] Yan H, Li Q, Zhang J and Liu Z 2002 Carbon 40 2693
[29] Tang S, Zhong Z, Xiong Z, Sun L, Liu L, Lin J, Shen Z X and Tan X L 2001 Chem. Phys. Lett. 350 19
[30] Hou P X, Yan H, Cheng Y, Zhang J and Liu Z F 2002 J. Mater. Chem. 12 1179
[31] Moon C Y, Kim Y S, Lee E C, Jin Y G and Chang K J 2002 Phys. Rev. B 65 155401
[32] Steckel J A, Jordan K D and Avouris P 2002 J. Phys. Chem. A 106 2572
[33] Mews A, Jiang C Y, Schuessler T, Philipp G, Fan Y and Burghard M 2001 Isr. J. Chem. 41 15
[34] Coleman J N, O’Brien D F, McCarthy B, Barklie R C and Blau W J 2001 Monatsh. Chem. 132 53
[35] Bonard J M, Stora T, Salvetat J P, Maier F, Stockli T, Duschi C, Forró L, de Heer W A and Chatelain A 1997 Adv. Mater. 9 827
[36] Edelmann F T 1999 Angew. Chem., Int. Ed Engl. 38 1381
[37] Duesberg G S, Blau W, Byrne H J, Muster J, Burghard M and Roth S 1999 Synth. Met. 103 2484
[38] Niyogi S, Hu H, Hamon M A, Bhowmik P, Zhao B, Rozenzhak S M, Chen J, Itkis M E, Meier M S and Haddon R C 2001 J. Am. Chem. Soc. 123 733
[39] Thiên-Nga L, Hernadi K, Ljubović E, Garaj S and Forró L 2002 Nano Lett. 2 1349
[40] Wong W E, Sheehan P E and Lieber C M 1997 Science 277 1971
[41] Dalton A B, Collins S, Muñoz E, Razal J M, Ebron V H, Ferraris J P, Coleman J N, Kim B G and Baughman R H 2003 Nature 423 703
[42] Li S, Li H, Wang X, Song Y, Liu Y, Jiang L and Zhu D 2002 J. Phys. Chem. B 106 9274
[43] Schadler L S, Giannaris S C and Ajayan P M 1998 Appl. Phys. Lett. 73 3842
[44] Bahr J L, Mickelson E T, Bronikowski M J, Smalley R E and Tour J M 2001 J. Chem. Soc., Chem. Commun. 193
[45] Hafner J H, Cheung C L and Lieber C M 1999 Nature 398 762
[46] Nishihima H, Kamo S, Nakayama Y, Hohmura K I, Yoshimura S H and Takeyasu K 1999 Appl. Phys. Lett. 74 4061
[86] Kooi S E, Schlecht U, Burghard M and Kern K 2002 Angew. Chem., Int. Edn Engl. 41 1353
[87] Bahr J L, Yang J, Kosnykin D V, Bronikowski M J, Smalley R E and Tour J M 2001 J. Am. Chem. Soc. 123 6536
[88] Bahr J L and Tour J M 2001 Chem. Mater. 13 3823
[89] Aihara J 1994 J. Phys. Chem. 98 9773
[90] Holliday A K, Hughes G and Walker S M 1973 Comprehensive Inorganic Chemistry vol 1, ed J C Bailar, H J Emeleus, R Nyholm and A F Trotman-Dickenson (Oxford: Pergamon) chapter 13
[91] Kariuki J K and McDermott M T 1999 Langmuir 15 6534
[92] Dyke C A and Tour J M 2003 J. Am. Chem. Soc. 125 1156
[93] Umek P, Seo J W, Hernadi K, Mrzel A, Pechy P, Mihailovic D D and Forró L 2003 Chem. Mater. submitted