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SiO$_2$-coated carbon nanotubes: theory and experiment

A novel route is reported for the processing of nanocomposites consisting of multi-walled carbon nanotubes (MWNT) embedded in amorphous SiO$_2$. SiO$_2$ is used for the sintered composite matrix and SiO$_x$ either for the unsintered or for the interface region with the MWNT. The material has been characterized by high-resolution transmission electron microscopy, high-resolution electron energy loss spectroscopy and thermal gravimetric analysis. Based on our observations, theoretical simulations were performed which were based on tight binding calculations. Models are proposed which acount for a stable SiO$_x$/tube interface.

Keywords: Carbon nanotubes; SiO$_2$; SiO$_x$; Nanocomposites

SiO$_2$-beschichtete Kohlenstoff-Nanoröhrchen: Theorie und Experiment

Es wird ein neues Verfahren zur Herstellung von Nanoverbunden auf der Basis von mehrwandigen Kohlenstoff-Nanoröhrchen (MWNT) vorgestellt, die in amorphem SiO$_2$ eingebettetet sind. Die Untersuchungen der Verbundwerkstoffe erfolgte mit hochauflösender Transmissionselektronenmikroskopie, hochauflösender Elektronenenenergieverlust-spektroskopie und thermogravimetrischer Analyse. Die Ergebnisse der Untersuchungen liegen theoretischen Modellen nahe, die auf der Dichtefunktionaltheorie basierenden Tight binding-Rechnungen beruhen. Experimentelle und theoretische Daten sprechen für die Ausbildung stabiler SiO$_x$/MWNT-Grenzflächen über Si−C−Brücken.

1 Introduction

Carbon nanotubes (CNTs) are excellent components for mechanically strong composites [1, 2] and conducting polymers [3] due to their fascinating mechanical and electronic properties. In this paper investigations on processing structural composites are presented for the case when the multi-walled carbon nanotubes (MWNT) are embedded in a ceramic matrix. The properties of the interface between the CNTs and the surrouding matrix dictates the properties of the composite applied as a structural material [4]. However, the surface of MWNTs of large diameter (outer diameter > 20 nm), which exhibit large Young's moduli of ca. 1–1.3 TPa [5,6], is similar to graphite, and chemically "inert". It is expected that the bonding between the "flat" surface of the MWNTs and any ceramic should be very weak. Therefore, chemical treatments are required which modify the surface of the MWNTs so that an efficient tube-matrix interaction is established. Unfortunately, these treatments can also result in an extreme degradation of the tubes and a decrease in the Young's modulus, which then result in a significantly lower tensile strength of the composites [7].

It is, therefore, much desirable to create stable nanotube coatings, which do not alter *significantly* the tube surface. The coated nanotubes are expected to exhibit enhanced mechanical properties which should be similar to an uncoated MWNT but definitively enhanced compared with *heavily degraded* nanotubes. An advantage of the coated MWNTs would be that the oxidation resistance of the MWNT is strongly improved, since SiO$_2$ is oxidation resistant and forms a barrier for oxidation diffusion. Therefore, the synthesis of MWNT/SiO$_2$ model composites and their detailed study of their MWNT/SiO$_2$ interface is crucial and of great interest.

Recent work addressed the formation of irregular metal oxide coatings on MWNTs using *single-step* chemical routes at low (ca. 200 °C) [8, 9] and high temperatures (> 500 °C) [8, 10]. A novel synthesis method is described which generates *bulk* nanocomposites consisting of SiO$_2$-coated MWNTs embedded within a SiO$_2$ matrix. The materials were prepared by combining a sonogel technique [11, 12] with a sintering process at high temperatures. In this paper results are presented on the experimental work including high-resolution transmission electron microscopy (HRTEM) studies, high-resolution electron enegery loss spectroscopy (HREELS) investigations and simulations on the stability of such interfaces were performed on the basis of density functional based tight binding approximations [13].

2 Experimental studies

2.1 Synthesis of the composite

The MWNT/SiO$_2$ bulk composite was produced as follows: a mixture of 250 mg MWNTs (generated by the arc discharge [14]) with 5 g H$_2$O (pH = 2 adjusted with HCl) and 10 g tetraethoxysilane (TEOS, molar ratio $n_{H_2O}/n_{TEOS} = 6$;

total carbon content in the composite: 7.7 wt.%) was sonicated using an ultrasonic probe for 5 min (SonoPlus with tip KE76, Bandelin, power: 40 %), in order to achieve a good dispersion of the MWNTs in the solution. Subsequently, gelation occurred in an ultrasonic bath (Bandelin Sonorex RK 100H) within 12 h. For aging, the resulting composite gel was immersed in a solution of 10^{-2} mol NaOH for 96 h and subsequently dried at room temperature for 24 h. Then, the composite gel was milled (mortar and pestel), and compressed uniaxially at 500 MPa (Sack & Kiesselbach, Germany). Finally, the pellet was sintered at 1150 °C for 15 h in 300 mbar Ar atmosphere.

2.2 Characterisation of the composite

Transmission electron microscopy (TEM) specimens were prepared from the bulk composite by dimpling and ion milling (Gatan PIPS Model 591 at 3.8 kV). Conventional TEM investigations were performed using a JEOL 2000 FX operating at 200 kV. HRTEM studies were carried out using a JEOL 4000 EX operating at 400 kV, and HREELS using a GATAN DigiPEELS 766 attached to a dedicated STEM VG HB 501UX operating at 100 kV. Line scans were recorded by stepping the electron beam along a line perpendicular to the tube axis. The distance of the steps was adjusted to 2 nm. The electron energy loss spectrum

(EELS) was recorded for each step. Thermogravimetric analysis was performed using a Netzsch STA 409C in air up to a temperature of 1220 °C.

2.3 Calculations

Density functional calculations based on a tight binding approximation were carried out on a single-walled carbon nanotube covered by an individual layer of SiO_x in order to understand the interaction of the MWNTs and the SiO_x coating and the stabiliy of SiO_x-coated MWNTs. The density functional based tight binding method has been described elsewhere [13]. Seifert et al. demonstrated the applicability of this method to SiC and SiO systems [15, 16].

3 Results and discussion

3.1 Microstructural studies of the composite

Fig. 1a depicts a TEM micrograph of a small section of the composite exhibiting a typical feature of this material. The diffraction contrast reveals a coating around a MWNT. Elemental distribution profiles derived from the EELS line scan analysis across such a structure are shown in Fig. 1b. The profiles of Si and O correlate to one another and show maxima on both sides of the tubular structure, correspond-
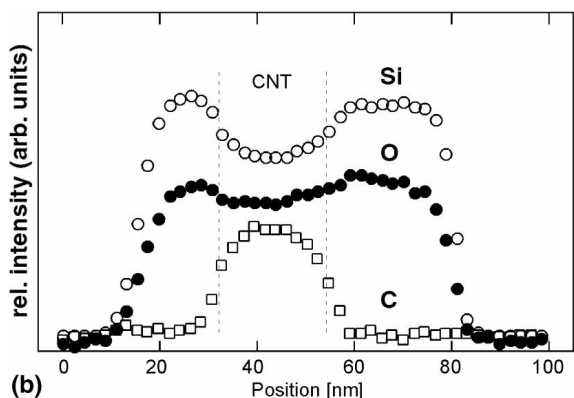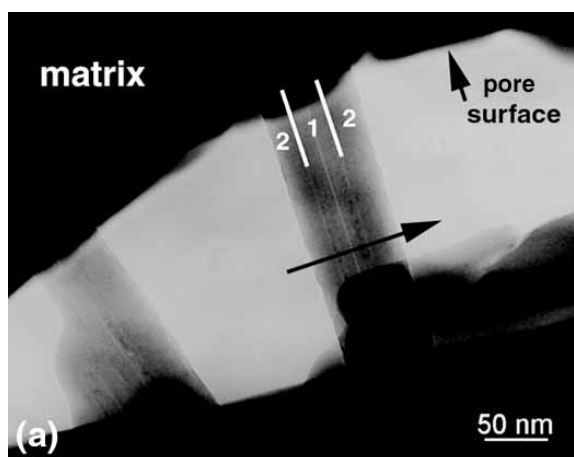

Fig. 1. (a) TEM micrograph of a typical MWNT (1) coated with SiO₂ (2) bridging a crack or pore in the CNT/SiO₂-bulk composite. (b) EELS line scan [black arrow in (a)] analysis of a similar structure from for the Si–L, C–K and O–K ionisation edges, indicates that the tubular composite consists of a CNT wrapped by a 20–30 nm thick SiO₂ coating.
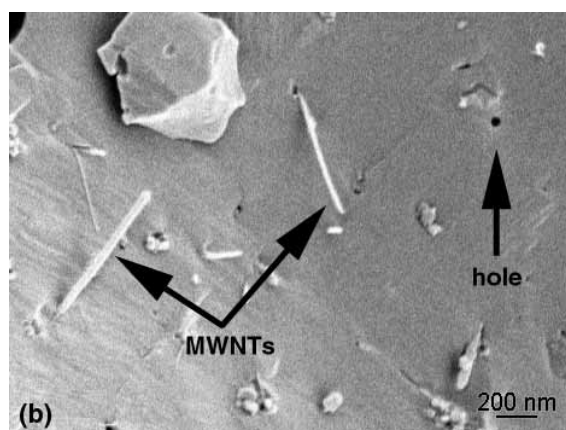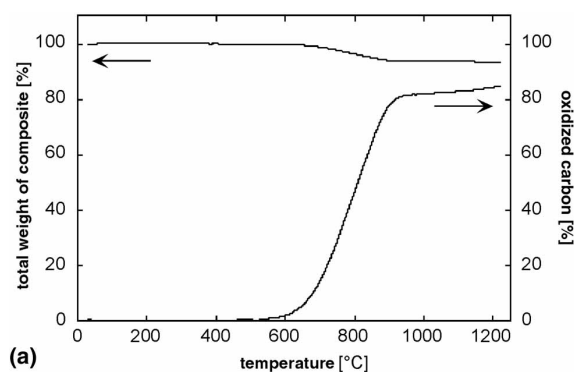

Fig. 2. (a) Thermogravimetric analysis plot for the MWNT/SiO₂ composite: The upper curve represents the total weight, whereas the other plot represents the carbon-loss relative to the total C content exhibiting saturation at ca. 84 %. (b) Scanning electron microscopy image of a cracked surface of the MWNT/SiO₂ composite after the thermogravimetric analysis (carried out up to 1200 °C) of this particular sample. It is noteworthy that the coated tubes have survived oxidation, a fact that is commensurate with the thermogravimetric analysis curve.

ing to a SiO$_2$ coating. The C profile of the MWNT dominates the centre of the profile (dashed line). The coating thickness derived from this intensity profile is ca. 20 – 30 nm.

The thermogravimetric analysis was performed on four different pieces of the same composite sample. The upper curve in Fig. 2a depicts the average weight loss (of the four pieces measured) as a function of temperature. During heating, only oxidation of carbon can occur at applied temperatures, from that the total loss of carbon was calculated of the composite, as shown in the lower part of Fig. 2. After a high weight loss at *ca.* 800 °C the curve reaches a saturation at about 84 %. This implies that 16 % of the carbon remains unoxidised up to the maximum temperature of 1200 °C. Figure 2b shows a scanning electron microscopy image of a cracked composite surface after thermogravimetric analysis. Unoxidised CNTs still exist and the diameter of the latter MWNT remained constant. These studies demonstrate that coated nanotubes are extremely resistant to oxidation. It is important to note, that the MWNTs remain intact after heating in air up to 1220 °C, provided the carbon tubes are completely embedded in the SiO$_2$ matrix.

A cracked SiO$_x$-coating on CNT, (only observed once in our studies) is depicted in Fig 3a. The broken segments of the SiO$_2$ matrix are shifted apart by ca. 40 nm and held together by the CNT. A magnification of the cracked region (Fig. 3b) reveals an undamaged inner MWNT consisting of 15 concentric carbon cylinders. However, higher magnification of the cracked region at the interface of the tube and the coating (Fig. 2b) reveals 5 – 8 heavily damaged outer graphene layers. This suggests that the outer nanotube shells (strongly bonded to the SiO$_2$ matrix) broke apart along the fault of the SiO$_2$-coating, and slipped off together with the coating. Therefore, we believe that there is a strong bond in the C/SiO$_x$-interface due to the carbothermal reduction. The sliding took place between the unreacted inner MWNT and the strongly bonded C–SiO$_x$ shell (Fig. 2b).

3.2 Calculated structures

The coating of a (20,20) carbon nanotube with a cylinder constructed of SiO$_4$ tetrahedra was studied (Fig. 3). Various systems involving the formation of different SiO$_x$ ($x = 3/2$, 2, 5/2) coatings were tested. These include: (i) Si–C interactions; (ii) Si–O–C bonds, and (iii) non-bonding interactions between the carbon tube and the oxide layer. The 'initial-guess' tubules were fully relaxed with respect to the atomic positions using conjugate gradient techniques. Dangling bonds on the oxygen atoms were saturated with hydrogen, and periodic boundary conditions were applied along the tube direction.
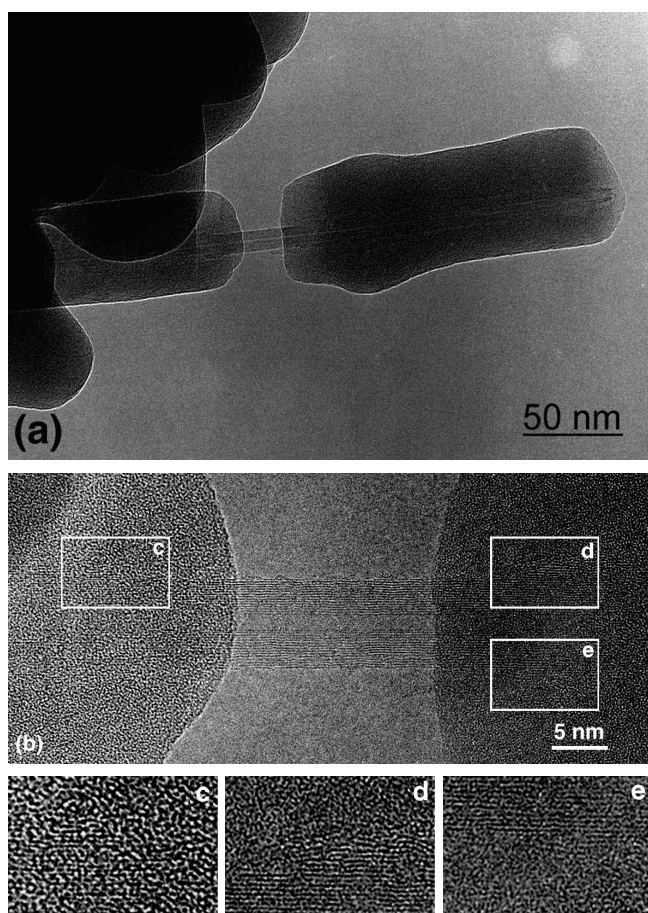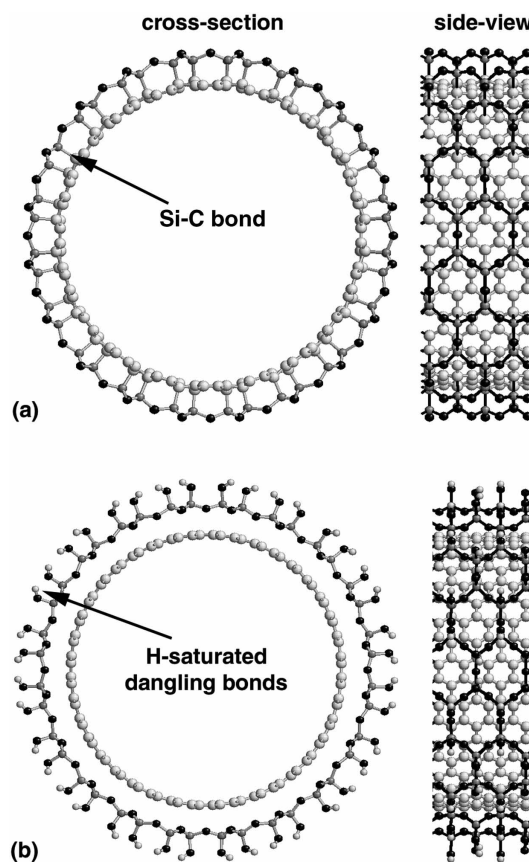

Fig. 3. (a) SiO$_x$-coated tube produced at 1150 °C, which is broken (unusual in our samples). The inner cylinder is composed of a MWNT with 15 undamaged cylinders. (b) Magnification of the crack region exhibits broken graphene sheets [regions c, d and e] on the surface of the MWNT within the SiO$_x$ matrix. (c), (d), and (e) are close-ups of the marked regions in (b).

Fig. 4. Molecular models of (20,20) carbon tubules covered by (a) a cylindrical SiO$_x$ layer ($x = 5/2$) bonded to the carbon tubule via Si–C bridges. (b) A tubular SiO$_x$ layer ($x = 3/2$) without bonding towards the carbon tubule. Here dangling bonds are saturated by H. The O atoms are drawn black. Note the six membered SiO$_4$ rings on side views.

The structure shown in Fig. 4a represents the relaxed arrangement for a stable $C-SiO_x$ ($x = 5/2$) composite nanotube having covalent bonds at the interface. This coating exhibits six-membered SiO_4 rings within the SiO_x layer (Fig. 4a), and $Si-C$ bonds appear to be the only stable intertubular connections. It is noteworthy that bonding using $Si-O-C$ bridges does not lead to a stable structure for either the SiO_x layer (when $x = 2$) or the CNT (not shown here) [17].

In addition, (20,20) CNT coated with a SiO_x monolayer ($x = 5/2$) was considered, which exhibits no bonding interaction between the SiO_x layer and the carbon tube (Fig. 4b). Interestingly, an individual SiO_x cylinder without a carbon nanotube in the core is unstable. It tends to collapse because the low average coordination number ($K < 3$) results in an insufficient stiffness for the tubular structure. However, this is stable when formed around a (20, 20) CNT. Therefore, the inner carbon tubule stabilises the external constraint of the SiO_x cylinder.

The formation of $Si-C$ bonds between the inner and outer tube (Fig. 4a) leads to a partial rehybridization of the carbon atoms ($sp^2 \rightarrow sp^3$). The structure of this particular $SiO_{x\text{-}}$ layer does not lead to any bonding frustration of carbon atoms (e.g., no dangling bonds appear). In this case, localized benzene-like 6π-electron systems are separated by the sp^3 carbon atoms, contrary to a delocalized graphene-like π-electron system. It is important to note that structures exhibiting SiC bonds, as shown in Fig. 4a, would be unstable for narrow carbon nanotubes, possessing a larger curvature. For example, a stable SiO_x coating on a (10, 10) carbon nanotube was not formed.

4 Conclusions

For the first time, it was possible to characterize the MWNT/matrix interface in an inorganic composite. The composites were fabricated using novel sol-gel techniques in conjunction with pressure methods and thermal annealing. These SiO_2/MWNT materials have proved to be oxidation resistant at temperatures $< 1220\,°C$. The results give new insights into MWNT/matrix interactions, which is vital for producing MWNT-reinforced composites. Based on theoretical modelling of uniform SiO_x coatings, we have proposed that SiO_x can be deposited on MWNTs: (i) by establishing covalent bonds between Si and C, or (ii) without links between the SiO_x shell and the MWNT outer shell. Thus, it should be possible to observe these two types of stable coatings at the SiO_x MWNT interface, in which the outermost region of the SiO_x coating may well consist of amorphous material (see top in Fig. 3b). We envisage that coated carbon nanotubes with monolayers of different materials will open up a new area of nanotechnology research.

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