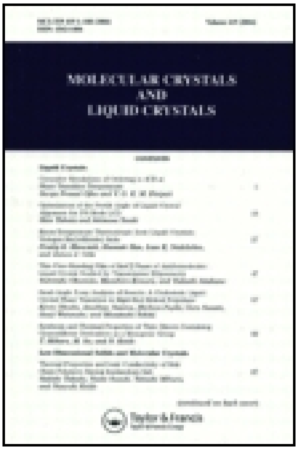

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Three Types of Behaviour of Multiwall Carbon Nanotubes in Reactions with Intercalating Agents

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Three Types of Behaviour of Multiwall Carbon Nanotubes in Reactions with Intercalating Agents

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Interaction between multiwall nanotubes and intercalating agents (K or $FeCl_3$) was studied using seven different nanotube materials. SEM, TEM, X-ray diffraction, Raman spectroscopy and other techniques were employed to study the reaction products. It was found that the reaction way is determined by nanotube structural type and that nanotubes may exhibit three types of reaction behaviour: intershell intercalation; no-reaction; and intercalation-assisted break-up.

Keywords: carbon nanotubes; intercalation; electron microscopy

INTRODUCTION

Since the discovery of carbon nanotubes by S.Iijima in 1991[1] substantial progress has been achieved in understanding of nanotube formation, structure and properties. In particular, there is now common understanding that multiwall carbon nanotubes (MWNT) may exist in a variety of structural types such as concentric (Russian doll), scroll, etc. Though the dependence of chemical reactivity on MWNT structural type ought to be essential there have been no works on comparison of chemical properties of different nanotubes except our earlier work[2,3] on comparison of two different MWNT.

It is commonly accepted that there are two main types of intratube shell arrangement: concentric or Russian doll and scroll. There was also a "pâpier-maché" model discussed[4] - it proposed that nanotubes were composed of pieces of graphitic sheets stuck together. It was however claimed by Ebbesen [5] that this model is not consistent with some more recent experimental data.

Analysis of literature experimental results shows that different types of chemical reactivity may be manifested by MWNT of different origin. In particular, most interesting observations were done by Zhou et al.[4] (alkali metals successfully intercalated into arc-discharge origin MWNT but the reaction was accompanied with irreversible tubular structure destruction), Méténier et al.[6] (ferric chloride or potassium reversibly intercalated into catalytically grown MWNT) and A.Bougrine et al.[7] (no-reaction behaviour in intercalation attempt of K on arc-discharge origin MWNT). Also in our earlier works[2,3,8] reversible intercalation of $FeCl_3$ or K metal was reported into arc-discharge origin MWNT.

In the present work seven different nanotube materials were tested in reactions with $FeCl_3$ or K metal with the purpose to find a correlation between MWNT structural type and chemical reactivity.

EXPERIMENTAL

Seven nanotube materials of different origin were studied. All the samples were purified from non-nanotube carbons and catalysts (if any) and contained, as SEM showed, carbon nanotubes as a predominant component. TEM was used to find on-top views of nanotubes and determine their structural type. It was found that three samples (two of He and one of H_2 arc-discharge origin) comprised scroll nanotubes and the other four (two of cobalt-catalysed acetylene pyrolysis and two of benzene CVD origin) comprised Russian doll nanotubes.

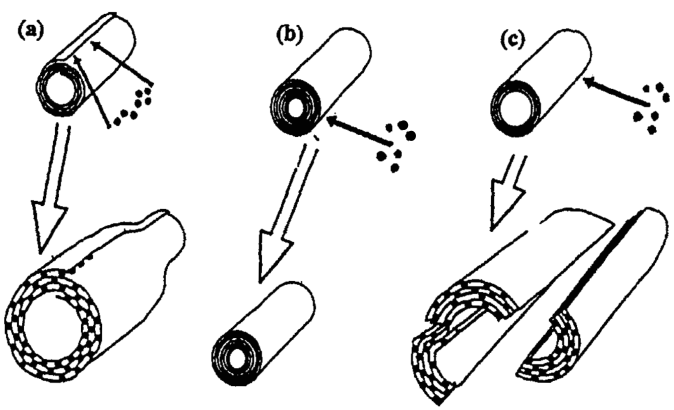

FIGURE 1. Schematic representation of three types of MWNT behaviour in reaction with intercalating agents: (a) intershell intercalation; (b) no-reaction; (c) intercalation-assisted break-up.

Intercalation reaction test was carried out in two-bulb evacuated sealed glass tubes where MWNT sample was put into one section and intercalating agent – into another section. Details of the technique are described elsewhere[8] and generally reproduce the conventional two-bulb technique for graphite intercalation compounds (GIC) synthesis[9]. The reaction time was established 1 day at 280°C for $FeCl_3$ and 300°C for K. Also experiments with some other metal chlorides were done. In those cases the tube was filled with Cl_2 gas before sealing. All the manipulations with samples were done in a glove box under atmosphere of purified Ar gas.

SEM, TEM, Raman spectroscopy, X-ray diffraction and galvanomagnetic measurements were used to study the synthesis results.

RESULTS AND DISCUSSION

As a result of testing different nanotubes in intercalation reaction we found that three types of behaviour may be manifested by MWNT depending on the nanotube structural type. Schematically those three types are shown in Fig. 1.

Intershell Intercalation

The first type is reversible intercalation and it is exhibited by scroll nanotubes which constituted our arc-discharge origin sampes. The nanotubes undergo significant changes after reaction though the samples preserve their dark colour. Significant weight uptake and huge visible swelling of the samples were observed. Intercalant unrolls the nanotube and intercalates into the helicoidal intershell space as shown in Fig. 1a. XRD and TEM measurements showed that MWNT outer diameter increased because of the intershell space expansion to the value close to that in corresponding GIC. The tube swells and takes a shape of a beadline consisting of intercalated "beads" and non-intercalated "necks" – see typical SEM and TEM images in Fig. 2. The synthesis results are summarized in Table 1.

The nanotube intercalation compounds (NTIC) resemble GIC in many aspects though galvanomagnetic properties are quite different. In particular, no substantial increase in a nanotube bundle conductance was usually detected after intercalation (bundles are microscopic fibrous pieces which constitute cathode deposit rods in arc-discharge technique[10]). Magnetoresistance measurements of intercalated nanotubes with the magnetic field applied perpendicular to the axis of pristine and intercalated nanotube bundle samples revealed several noteworthy features. All the nanotube samples exhibit magnetoresistance fluctuations about an underlying trend, the amplitude being greatest in the case of the pristine sample and least in the $FeCl_3$-intercalated sample. When plotted as magneto-conductance, the amplitude of the fluctuations exhibited by the pristine sample is in good agreement with that of the universal conductance fluctuations[8, 11].

TABLE 1. Nanotube intercalation compounds

Intercalate	Synthesis Temperature	Weight Uptake (%)	Formula	Intershell spacing (Å)
K	300°C	18-33	$C_{9-18}K$	5.3
$FeCl_3$	280°C	190-260	$C_{5-7}FeCl_3$	9.5
$ZnCl_2$	400°C	60-66	$C_{18}ZnCl_2$	9.43
$CdCl_2$	400°C	110-140	$C_{12}CdCl_2$	9.51
YCl_3	800°C	65-80	$C_{24}YCl_3$	9.8
$AlCl_3$	280°C	65-90	$C_{12-17}AlCl_3$	-

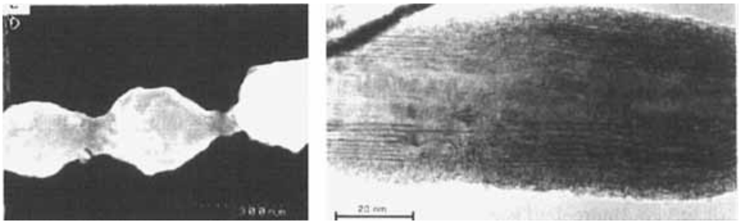

FIGURE 2. SEM (left) and TEM (right) micrographs of scroll MWNT after $FeCl_3$ intercalation. There are areas with different spacing in the TEM image due to partial de-intercalation which occured while moving samples into a TEM chamber. The outer amorphous layer in the image corresponds to $FeCl_3$ released in the course of partial de-intercalation.

Another difference between NTIC and GIC is observed in Raman spectra. All pristine nanotubes in our experiments showed a prominent band at 1580 cm^{-1} which is usually assigned to an in-plane graphitic E_{2g} symmetry mode vibration which is observed at 1582 cm^{-1} in single crystal graphite[12]. $FeCl_3$-intercalated scroll nanotubes displayed a substantial (down to 1570 cm^{-1}) undershift of the frequency of this band which witnesses a certain softening of lattice modes and may be associated with unrolling the scroll (see Fig.1a) and easing the lattice strain. One should note here that $FeCl_3$ intercalation into graphite leads to upshift of E_{2g} frequency due to charge transfer.

No-reaction behaviour

The second type (see Fig. 1b) is no-reaction behaviour and it is exhibited by robust thick-walled (core diameter is less than one third of the outer diameter) Russian doll nanotubes which constituted our samples of CVD-produced nanotube films. Typical wall thickness of such nanotubes was 140 Å (40 shells) and core diameter 70 Å. Individual robust tubes were also observed in the samples of arc-discharge and pyrolysis origin though A.Bougrine et al.[7] reported He arc-discharge cathode deposits consisting mostly from such nanotubes. No visual nor microscopic nor Raman spectral changes have been registered after intercalation test on thick-walled Russian doll nanotubes.

Intercalation-assisted break-up

The third type is intercalation-assisted break-up of nanotubes and it is schematically shown in Fig. 1c. We observed it with thin-walled Russian doll nanotubes from cobalt-catalysed acetylene pyrolysis products. Typical wall thickness of such nanotubes was 11 Å (4 shells) and core diameter 50 Å. $FeCl_3$ intercalation leads to break-up into amorphous mass of intercalated graphite nanoflakes. SEM and TEM images of the reaction product are shown in Fig. 3. It can be seen in Fig. 3 that several surviving nanotubes still exist after intercalation test.

In case of K intercalation the break-up is not so complete i.e. some remnants of nanotubes or their big fragments stay but get numerous shell cracks and displacements in the same way as Zhou et al.[4] observed in their 1994 alkali metal-nanotube experiments. X-ray diffraction and Raman spectroscopy of the reaction product resemble closely the data of corresponding GIC. In particular, upshift of the frequency of E_{2g} band (up to 1600 cm^{-1}) was observed after $FeCl_3$ intercalation-assisted break up.

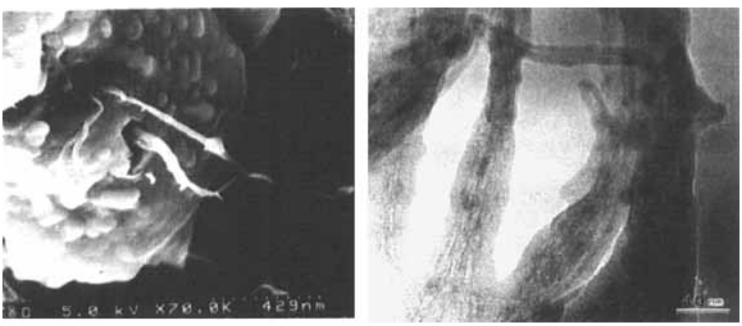

FIGURE 3. SEM (left) and TEM (right) micrographs of thin-walled Russian doll MWNT after $FeCl_3$ intercalation. Nanotube destruction and general amorphization can be seen.

CONCLUSIONS

Multiwall carbon nanotubes may exhibit three types of behaviour in reactions with intercalating agents: intershell intercalation; no-reaction; and intercalation-assisted break-up. The reaction way is determined by nanotube structural type: scrolls, thick-walled Russian dolls and thin-walled Russian dolls undergo intershell intercalation, no-reaction, and intercalation-assisted break-up, respectively.

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