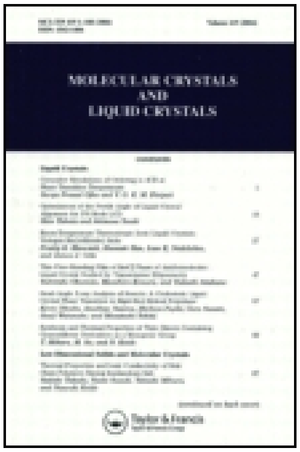

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Successful Intercalation into Multiwall Carbon Nanotubes without Breaking Tubular Structure

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Though the presence of nanotubes in a carbon sample may be clearly detected by electron microscopy, yet it has been difficult to determine if the nanotubes in question belong to a Russian doll or scroll type. This work shows how a chemical reaction with ferric chloride or with potassium metal reveals the differences between the two types of intratube shell arrangement. Scroll nanotubes are intercalated by alien molecules which penetrate from the side of the scroll and fill the intershell spaces. The corresponding intershell spaces expansion was directly observed in this work by TEM. Russian doll nanotubes do not enter the reaction and stay intact. The reaction with scroll nanotubes is accompanied with a remarkable tube swelling which is easily observed by scanning electron microscopy. The presence of intercalated nanotubes may also be detected by X-ray diffraction and Raman spectroscopy.

Keywords: carbon; nanotubes; intercalation; electron microscopy

INTRODUCTION

One cannot underestimate the importance of intercalation reaction for the chemistry of carbon. Hundreds of graphite intercalation compounds (GIC) discovered by the moment demonstrate how one can alter electronic properties of a host lattice by introducing a certain amount of intercalating agent into the spaces between graphene sheets.

So it is only natural that since the discovery of carbon nanotubes the idea of doping them has been very attractive[1-6]. The reason is that this kind of doping (by intercalation of donor or acceptor species in the spaces between carbon shells) could allow the control of the electronic properties of nanotubes in the same way as this is accomplished in GICs[7]. Intercalation into carbon nanotubes was first reported by Zhou et al[1] though until recently it had remained uncertain whether the intercalation was possible without breaking the tubular structure. Only very recently we demonstrated that potassium metal and ferric chloride may intercalateinto scroll carbon nanotubes[6]. It suggested the idea that if one brings different nanotubes into contact with the same reagent in the same experimental environment one may see the differences revealed by the intercalation reaction (see model in Fig. 1).

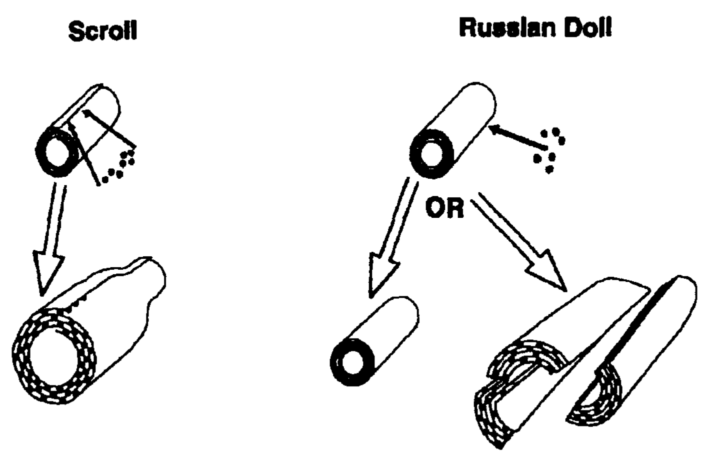

FIGURE 1 Schematic representation of nanotubes interaction with intercalating agents. Left part illustrates intercalation into a scroll nanotube; intershell spaces expand due to unrolling the scroll. Right part shows that a Russian doll nanotube must either stay intact (due to no possibility of intershell spaces expansion) or the intercalation inevitably breaks the tubular structure.

It is commonly accepted that there are two main types of intratube shell arrangement: closed or Russian doll and scroll. There was also a "pâpier-maché" model discussed[1]: it was proposed that nanotubes were composed of pieces of graphitic sheets stuck together. The problem with this model is that it is not consistent with some more recent experimental observations[8].

The purpose of this work was to show how intercalation reaction reveals differences between the two types of intratube shell arrangement and to make direct observation of after-intercalation intershell spacing expansion by TEM.

EXPERIMENTAL

We performed experiments with three different carbon nanotube materials: (A) oriented nanotubes of arc-discharge origin "buckybundles"[9]; (B) nanotube films grown by Ni-catalysed chemical vapour deposition (CVD)[10] and (C) nanotube films grown by Fe-catalysed CVD[10]. Further in the text we will refer to those nanotubes as to A-, B- and C-, respectively. The defectlessness of nanotubes in the pristine materials was preliminary confirmed by TEM. It was also confirmed by TEM (end-on view of a nanotube) that A-nanotubes belong to a scroll type[9].

Intercalation was carried out in two-section glass tubes. Nanotubes were placed in one section, intercalating agent (non-aqueous ferric chloride or distilled potassium metal) into another. The glass tube was evacuated, sealed and then placed into a furnace. All manipulations with intercalated samples were performed in a glove box under atmosphere of purified argon.

RESULTS AND DISCUSSION

The A-nanotubes underwent significant changes after 1 day of reaction with potassium metal at 300°C or 3 hours of reaction with $FeCl_3$ at 280°C. The samples preserved their dark colour and microscopic fibrous structure after the reaction. Significant weight uptake and substantial visible swelling of the samples were observed. The weight uptake varied between 15-33% after the reaction with K, and 110-260% after the reaction with $FeCl_3$.

Scanning electron microscopy (SEM) studies showed that A-nanotubes had dramatically changed their appearance after intercalation. Fig. 2 demonstrates how straight nanotubes of the pristine material swell after intercalation. The swollen sections alternate non-intercalated "necks" forming a characteristic "bead-line " pattern.

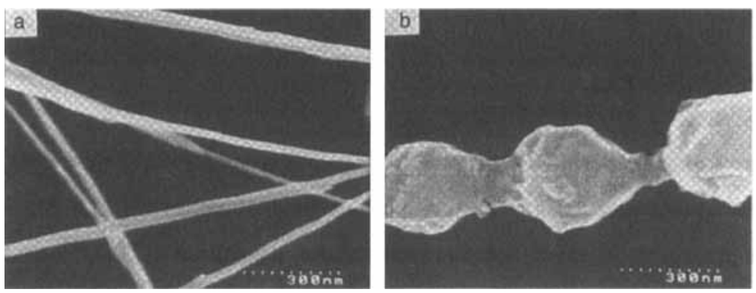

FIGURE 2 Scanning electron micrographs of A-nanotubes: (a) pristine; (b) $FeCl_3$-intercalated.

Fig. 3 shows TEM pictures of A-nanotubes before and after intercalation. One can see the expansion of intershell spaces d_i (from 0.34 nm up to 0.93 nm in case of $FeCl_3$ and up to 0,52 nm in case of K). The d_i expansion seems the greatest at the center of Fig. 2b and decreases in the directions of the edges.

The d_i expansion was also measured by X-ray diffraction (XRD) in our earlier work[6] - see Table 1. The new after-intercalation diffractograms closely match those of corresponding GICs[7]. Thus the XRD provides another proof for the assertion that intercalation occurs within the nanotube body.

Raman spectra of all pristine nanotubes showed a prominent band at 1580 cm^{-1}. This is usually assigned to an in-plane graphitic E_{2g} symmetry mode vibration which is observed at 1582 cm^{-1} in single crystal graphite[7]. A-nanotubes after $FeCl_3$ intercalation displayed a substantial undershift of the frequency of this band (see Table 1) which witnesses a certain softening of lattice modes and may be associated with unrolling the scroll (see Fig.1) 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.

Thus it has been demonstrated how intercalation into scroll multiwall nanotubes results in the expansion of intershell spaces which in turn leads to swelling of the tubes. The "necks" at the swollen tubes may be assigned to non-intercalated sections. The rather regular sequence of the "necks" can not be explained in the limits of this work; it may be connected with the formation of non-intercalable fragments during the nanotube growth.

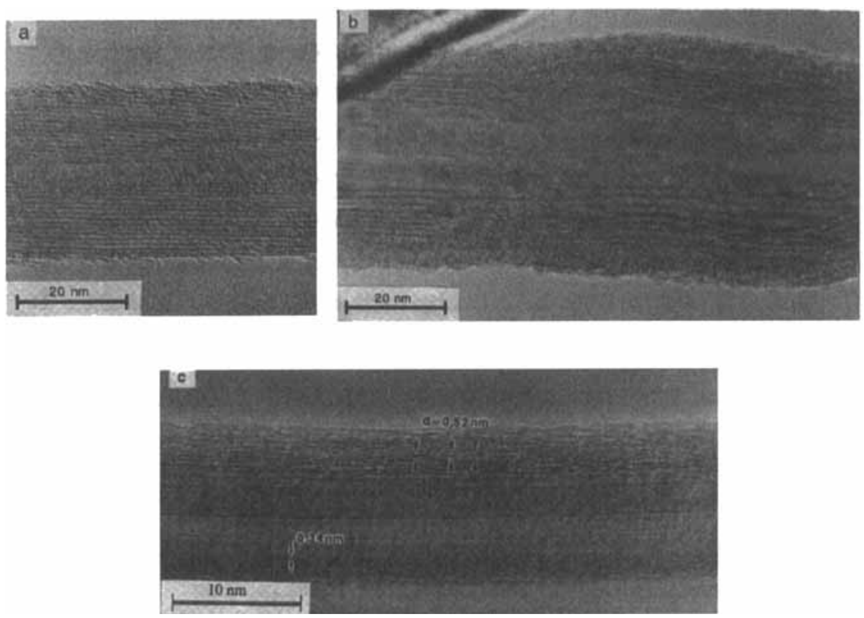

FIGURE 3 TEM images of A-nanotubes: (a) pristine; (b) $FeCl_3$-intercalated; (c) K-intercalated. There are areas with different spacingin (b) and (c) images due to partial de-intercalation which occured while moving samples into a TEM chamber. The outer amorphous layer in the image (b) corresponds to $FeCl_3$ released in the course of partial de-intercalation.

TABLE 1 Comparative characterization of different nanotubes before and after the reaction with ferric chloride

	Raman spectra: E_{2g} band (cm^{-1})	TEM: d_i (nm)	SEM appearance	XRD d_i (nm)
A-tubes: before	1580	0.34	Uniform thickness	0.342
after	1570	0.93	Bead-line pattern	0.95
B-tubes: before	1580	0.34	Uniform thickness	
after	1580	0.34	The same	
C-tubes: before	1580	0.34	Uniform thickness	
after	1580	0.34	The same	

B- and C-nanotubes however did not enter the reaction even after a 3 day experiment. No swelling was observed at SEM pictures after intercalation. Corresponding micrographs are not shown here due to lack of space in this publication. TEM, too, indicated that B- and C-nanotubes did not change after the experiment. Raman spectra showed no shifts, either (see Table 1).

Clear tube edges at TEM images of B- and C-nanotubes had already suggested us that those nanotubes were of Russian doll type. The test by intercalation attempt has shown that reactivity in intercalation reaction may become an instrument for distinguishing Russian doll and scroll nanotubes.

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