Dissolution of poly(vinyl alcohol)-modified carbon nanotubes in a buffer solution

ZHANG Fa-ming[1, 2]， CHANG Jiang[1]， BURKEL Eberhard[2]

(1. *Shanghai Institute of Ceramics，Chinese Academy of Sciences，Shanghai　200050，China*；

2. *Institute of Physics，University of Rostock，August Bebel Str. 55，Rostock 18055，Germany*)

Abstract： Multiwalled carbon nanotubes(MWCNTs) were modified with a water-soluble poly(vinyl alcohol)(PVA) polymer(MWCNTs-PVA). The dissolution of the MWCNTs-PVA in Tris-HCl buffer solution was carried out in a shaking water bath by a soaking method. The microstructural changes of the MWCNTs-PVA during soaking was investigated using Fourier transform-infrared spectroscopy，differential scanning calorimetry，transmission electron microscopy，and X-ray diffraction. It is found that part of the MWCNTs-PVA was dissociated into amorphous carbonaceous debris，but most of tubular structures were retained after 21 d of soaking. The dissolution process revealed that the C—C bonds of the MWCNTs-PVA were broken-down with the generation of carbonaceous debris and residual carbon nanotube layers，and the latter can be further dissociated into amorphous carbonaceous debris. A possible dissolution mechanism of the MWCNTs-PVA in the buffer solution was proposed and discussed. The surface modified MWCNTs have many defects and open C—C bonds on the surfaces of the CNTs. The dissolution of the PVA in the buffer solution leads to a release of carbon atoms on the outer surface of the MWCNTs. It results in a further rupture of the C—C bonds and destroys the tubular structure .

Keywords： Carbon nanotubes；Surface modification；Dissolution；Structural stability；Biomedical applications

CLC number： TB 332　　　　**Document code**： A

1　Introduction

Since their discovery，carbon nanotubes(CNTs) have attracted great attention because of their unique tubular structure and excellent properties. In recent years，a great deal of research efforts have been made on the exploration of the application of CNTs，both single-walled (SWCNTs) and multiwalled carbon nanotubes(MWCNTs)，in biomedical and biological fields as nerve cell stimuli，diabetes sensors，cancer therapy，drug delivery carrier，or bone scaffolds materials etc[1-3]. Nevertheless，the CNTs have yet to cross many technological hurdles in order to realize their potential as the preferred materials for bioapplications. The insolubility of CNTs in aqueous media has been a major technical barrier. The advance in methods to chemically modify and functionalize CNTs with water-soluble polymers has now made it possible to solubilize CNTs in water，thus opening the way for their easy manipulation and processing in physiological environments[4-6]. The soluble CNTs or disper-

sible CNTs implied that the surface modification of CNTs with water-soluble polymers provided hydrophilic surfaces with a high enough zeta potential to be colloidally stable. Most of the researches are focused on the synthesis of the aqueous-soluble CNTs and the functionalization chemistry of CNTs to enhance their solubility and processability[7-10]. However，the possible dissolution mechanism of the water-soluble polymers modified CNTs are scarcely reported.

Our interests in the aqueous-soluble CNTs are on the dissolution process and mechanism of the surface-modified CNTs. Many water-soluble polymers have been modified on the surface of CNTs[11-14]. Poly(vinyl alcohol)(PVA) is a type of water-soluble and biocompatible polymer. The PVA/CNTs composites and coatings have been studied by a number of researchers[15-17]. Binding polymers to the CNTs can be fulfilled by the "grafting to" or "grafting from" approaches. In this study，the MWCNTs were functionalized with "grafting to" approach using a direct reac-

tion of PVA polymer with carboxylic acid (—COOH) groups on the MWCNTs based on the procedures of Zhao et al[14] and Lin et al[15]. Furthermore，Tris-HCl buffer solution was used as a soaking media to study the dissolution process of MWCNTs，which is widely used as a biomimetic solution for degradability investigation of inorganic biomaterials. The modified MWCNTs were soaked in the Tris-HCl buffer solution for different days. The microstructure transition of the modified MWCNTs during the dissolution process was investigated using Fourier transform-infrared spectroscopy （FT-IR），differential scanning calorimeter （DSC），transmission electron microscopy （TEM），and X-ray diffraction （XRD） techniques.

2   Materials and Methods

2.1   Materials

The MWCNTs were obtained from Shenzhen Nanotech Port，Ltd.（Shenzhen China），which were produced by catalytic chemical vapour deposition，in which CH_4 or C_2H_2 was converted into CNTs at $1\,000\,℃$ in the presence of Ni and La catalysts. The purity of the pristine MWCNTs was claimed above 95% by the producer with the presence of some Ni catalysts and La impurities.

2.2   Surface modification method

Pure MWCNTs were first refluxed in a $2.6\,mol/L$ nitric acid（HNO_3）at $120\,℃$ for 24 h to increase their purity and modify their surface to —COOH groups （Fig. 1）. Upon filtration with $0.22\,\mu m$ membrane to remove the liquid phase，the remaining MWCNTs-COOH solids were washed repeatedly with deionized water until neutral pH and then dried under vacuum. The resulting carboxylated CNTs were mixed and reacted with 2.0% （mass fraction）PVA solution by ultrasonic shaking for 60 min and stirring at temperature of $140\,℃$ for 72 h. The PVA is a biocompatible，water-soluble synthetic polymer with chemical formula of （C_2H_4O）$_n$. The reaction between carboxylic acid and PVA is an esterification reaction（Fig. 1）. To remove the liquid phase by vacuum filtration with $0.22\,\mu m$ membrane，the remaining MWCNTs-PVA black solids were washed and dried under vacuum.

2.3   Dissolution test

The dissolution of the MWCNTs was studied in a Tris-HCl buffer solution. The Tris-HCl solution was prepared by dissolving tris-hydroxymethyl aminomethane（analytical reagent grade）in deionized water and buffering to pH 7.25 ± 0.1 at $30\,℃$ with $0.1\,mol/L$ HCL. The MWCNTs were dispersed in the Tris-HCl
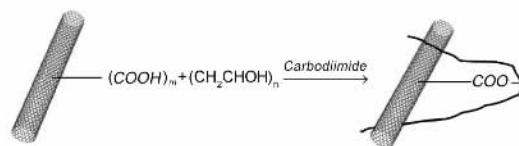

Fig. 1   Schematic illustration of surface modification of PVA onto MWCNTs

solution at a concentration of $0.1\,mg/mL$. The suspensions in polystyrene bottles were shaken in a water bath at $37.0\,℃$ with frequency of $50\,Hz$. The samples were soaked for 3，7，14，21，and 30 d without updating soaking solutions. At each time point，one group of these samples was taken out and the Tris-HCl/ MWCNTs suspension was filtrated to obtain MWCNTs solids. The filtrated MWCNTs were rinsed with deionized water and dried under vacuum.

2.4   Microstructure analysis

The surface-modified MWCNTs obtained were subjected to FT-IR，DSC，TEM，high-resolution TEM（HRTEM），and XRD analysis. The FT-IR analysis was preformed on FT-IR（Nexus Thermo Nicolet instruments，Wisconsin，USA）. The DSC was operated on LABSYS TG-DSC system（Setaram Instrumentation，Caluire，France）. The TEM and HRTEM observations were undertaken with a JEOL JEM-2010 operating at accelerated voltage of $200\,keV$. The XRD analysis was conducted on a Rigaku D/max 2550 V（Rigaku Industrial Corporation，Tokyo，Japan）.

3   Results and discussion

3.1   Characterization of the surface-modified MWCNTs

Fig. 2a shows the FT-IR results of the surface-modified MWCNTs and the PVA polymer. The samples of MWCNTs-COOH and MWCNTs-PVA both show absorption bands at 3 430，2 922，1 390，and $1\,635\,cm^{-1}$. The intense absorption band at $3430\,cm^{-1}$ corresponds to the OH^- stretching vibration of carboxylic acid. The band at $2\,922\,cm^{-1}$ belongs to the C—H stretching and the band at $1390\,cm^{-1}$ belongs to the H bonds. The strong absorption band at $1\,635\,cm^{-1}$ in the MWCNTs-COOH sample is assigned to the carbonyl vibration band corresponding to the carboxylic acid（COOH）stretching，which is very weak in the sample of MWCNTs-PVA. The band at $1\,740\,cm^{-1}$ in MWCNTs-COOH is the stretching of C=O groups and the band at $1058\,cm^{-1}$ is correlated with the C—O vibration. The FT-IR spectrum of the PVA polymer shows absorption bands

centred at $3\,248$，$2\,906$，$1\,711$，$1\,560$，$1\,324$，$1\,151$，$1\,087$，and $800\ cm^{-1}$，which are due to the O—H stretching，C—H，O—H bending，and C—C bonding[18]. The MWCNTs-PVA sample also exhibits bands at 800，1151，and $1560\ cm^{-1}$ indicating the existence of PVA polymer on the MWCNTs. It can be noticed from the spectra of the MWCNTs-PVA that the band at $1\,058\ cm^{-1}$ in MWCNTs-COOH shifted to $1\,076\ cm^{-1}$，indicating the formation of an esterified product. Bond length is shortened resulting in the shift of band peak to a higher wave number after esterification. There is a new absorbance band at $1\,022\ cm^{-1}$ in the MWCNTs-PVA sample. It is attri-

buted to the interfacial covalent reaction between the CNTs-COOH and PVA[19]. Fig. 2b shows the DSC thermal analysis of the modified MWCNTs and the PVA polymer. The samples of MWCNTs-PVA and PVA both show the endothermic peaks in the range of 200-400 ℃ as indicated by circles. These endothermic peaks are ascribed to the pyrolysis and carbonation of the PVA polymer during heating. However，the DSC result of the MWCNTs-COOH sample has no such peaks in such range. On the basis of the above results，it is confirmed that the PVA polymer has been covalently modified onto the MWCNTs successfully.
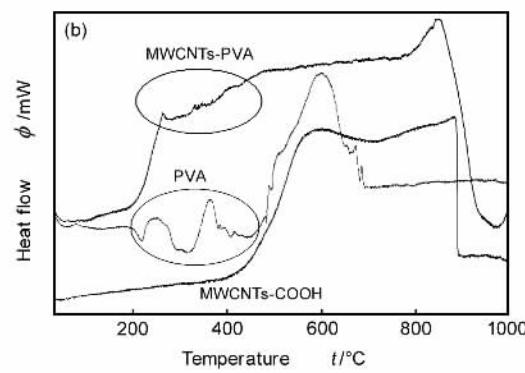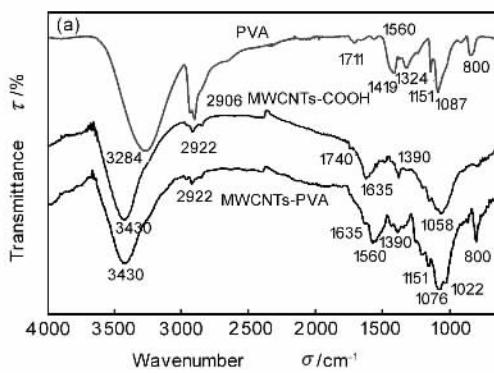

Fig. 2　FT-IR spectra（a）and DSC thermal analysis（b）of MWCNTs-COOH，MWCNTs-PVA and PVA exhibiting a covalent loading of the PVA onto the MWCNTs

Fig. 3 shows the TEM micrographs of the MWCNTs-COOH and MWCNTs-PVA samples. The acid-treated MWCNTs-COOH sample is well dispersed with outer diameter of 20-30 nm，and no catalysts and other carbon impurities are detected by the TEM that equipped with energy dispersive X-ray spectroscopy（EDX）（Fig. 3a）. Some open-tipped MWCNTs are found in the micrograph（Fig. 3a）. It is known that

the hot concentrated nitric acid could attack and break the structure of MWCNTs effectively. The hot，oxidizing nitric acid treatment has lead to the open tips and has broken down some C—C bonds on the walls of MWCNTs. The MWCNTs-PVA sample in Fig. 3b shows that there are many agglomerates in the CNTs，some polymer can be observed on the background.
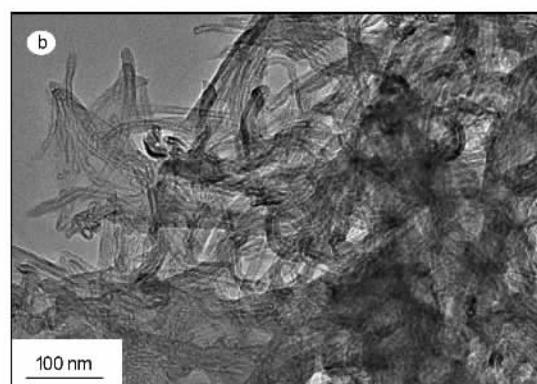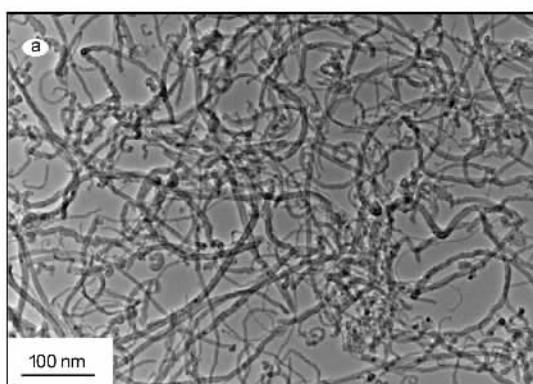

Fig. 3　TEM micrographs of the samples of MWCNTs-COOH（a）and MWCNTs-PVA（b）

3.2 Dissolution process

The samples of MWCNTs，MWCNTs-COOH，and MWCNTs-PVA were soaked in the shaking Tris-HCl buffer solution for different days. However，after 3-30 d of soaking，there were no microstructure and morphology variations in the sample of MWCNTs and MWCNTs-COOH. In the MWCNTs-PVA sample，there was no morphology change observed after 3 d of soaking，but morphology variation was found after 7 d of soaking. The TEM micrographs of MWCNTs for 7 d of soaking at different magnifications are shown in Fig. 4（a，b）. Some polymer and open-tipped MWC-NTs are found in the micrographs，but most of the MWCNTs are intact. The open-tipped MWCNTs are indicated by arrows in the micrograph. Fig. 4（c，d）shows the 21 d soaked MWCNTs-PVA sample at different magnifications. It is noticed that some MWC-NTs are dissociated；however，most of the MWCNTs retained their tubular structure of CNTs from the high magnification image（Fig. 4d）. The sample of 30 d soaked MWCNTs shows the similar results with the 21 d soaked MWCNTs.
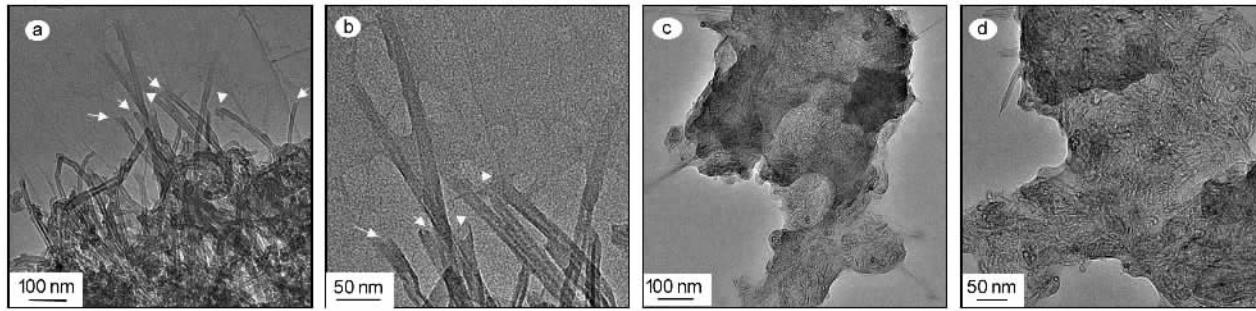

Fig. 4　TEM micrographs of the MWCNTs-PVA after soaking in a Tris-HCl buffer solution for 7（a，b）and 21 d（c，d）at different magnifications exhibiting the dissolution of some MWCNTs

In order to capture the dissolution process of the MWCNTs-PVA，HRTEM was used to analyze the 21 d soaked MWCNTs-PVA. In the 21 d soaked MWCNTs-PVA，it is found that some MWCNTs are in the beginning of dissolution. As shown in Fig. 5a，the C—C bonds in the MWCNTs are further broken-down on their wall and tip as indicated by circles. It is noticed that some MWCNTs are in the intermediate process of the dissolution. Some MWCNTs dissociated from the open carbon bonds with some residual CNT layers and carbonaceous debris left（Fig. 5b）. The residual CNT layers are tangled together，and the carbonaceous debris with disordered carbon atoms are observed in the micrograph as indicated by circles（Fig. 5b）. The dissolution process of these residual CNT layers is shown in Fig. 5c. The dissociated CNT layers are noted with circles. It is also found that some MWCNTs are in the final stage of the dissolution；most of the residual CNT layers are dissociated with a generation of several layers of carbonaceous debris（Fig. 5d）. The lattice spacing between neighboring planes of one small piece of residual MWCNT layers is about 0. 34 nm. The MWCNTs have been dissociated into dispersible amorphous carbonaceous debris. It is a fact that part of MWCNTs transited into amorphous carbonaceous debris，most of the MWC-NTs still retained their tubular structure and tangled together as shown in the low-magnification TEM images（Fig. 4 c，d）.
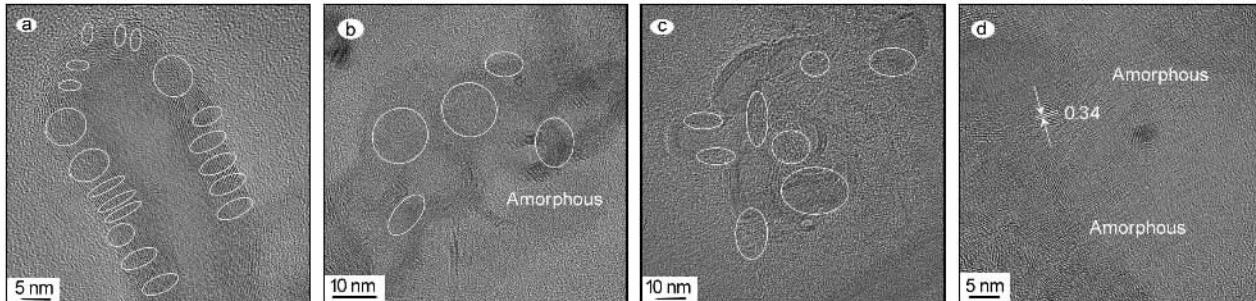

Fig. 5　HRTEM micrographs showing the dissolution process of the MWCNTs-PVA：（a）further broken-down of C-C bonds in the wall and tip of MWCNT，（b）MWCNTs dissolution with generation of residual CNT layers and carbonaceous debris，（c）dissolution of the residual CNT layers，（d）final amorphous carbonaceous debris

Fig. 6 shows the XRD patterns of the MWCNTs-PVA and the dissolved MWCNTs. The MWCNTs-PVA shows a sharp peak of（002）plane with d-spacing of 0. 343 nm at 25. 86（2θ）. After soaking for 21 d，the main peak becomes broadened and the background shows hump and noise indicating the formation of amorphous carbon. The existence of the（002）peak in the dissolved MWCNTs indicates that part of the MWCNTs were preserved in the sample. But its peak has shifted a little to 26. 18（2θ），and the d-spacing has changed to 0. 339 nm. The（002）*d*-spacing of the graphite-2H phase is 0. 337 nm at 2θ of 26. 38（PDF#41-1487）. The shifting of the（002）plane of MWCNTs to the direction of graphite-2H indicates that some graphite layers are formed during the dissolution process. The peak at 23. 12（2θ）with *d*-spacing of 0. 386 nm is identified as griseofulvin polyethylene glycol with structural formula $[(C_2H_4O_2)_n]1$-x$(C_{17}H_{17}ClO_6)_x$（PDF#52-2283）. The formation of this complex polymer may be ascribed to the reaction among the Cl^- ions and the released C atoms in the Tris-HCl buffer solution with the dissolved PVA. After filtration and drying，the complex polymer is precipitated in the sample. The height of peaks of 23. 12 and 26. 18 in the dissolved MWCNTs indicates that part of the MWCNTs is dissociated already. Consequently，the XRD results in Fig. 6 confirmed the formation of amorphous carbonaceous debris. Part of the PVA-modified MWCNTs is dissociated into amorphous carbonaceous debris and most of them are intact. A MWCNT is a tube made of multilayer graphite rolled up into a hollow cylinder. After dissolution in the buffer solution，some MWCNTs dissociated into pieces of graphite-2H layers and subsequently transited into amorphous carbonaceous debris.

Fig. 6   XRD patterns of the MWCNTs-PVA and dissolved MWCNTs
exhibiting amorphous carbon formation

3. 3   Dissolution mechanism

The MWCNTs are generally sp^2 carbon hybrid，which is very biopersistent and difficult to be dissociated. However，we found that the MWCNTs modified with soluble polymer PVA could partly dissociated into amorphous carbonaceous debris in this study. The degradation of the inorganic bioceramics with good crystallization is mainly driven by dissolution，and the dissolution always happens easily on the boundary of the micropores[20]. Generally，weight loss and ions release were measured to analyze the dissolution process. The amorphous carbon and the CNTs are both allotrope of the carbon element. It is a process of phase transformation that the PVA-modified MWCNT transited into amorphous carbon after soaking. The carbon ion release cannot be measured by the usually used inductively coupled plasma-atomic emission spectroscopy. The measurement of the weight loss of MWCNTs after soaking is also infeasible due to the loss of CNTs through filters. Therefore，in this study，the TEM and HRTEM are used to observe the microstructure variation of the MWCNTs during soaking in the buffer solution. XRD method is used to analyze the phase compositions of the dissolution product.

The TEM，HRTEM，and XRD results confirmed that part of the PVA-modified MWCNTs transited into amorphous carbonaceous debris，and most of the MWCNTs retained tubular structure after dissolution. The carbonaceous debris is one of the carbon allotropes and a well-known precursor for carbon that is usually amorphous and easily dispersible in the aqueous media. In the comparison study，it is found that the MWCNTs and MWCNTs-COOH did not dissociate over time. The hot nitric acid has lead to the open tip and broken down of some C—C bonds in the MWCNTs. It is noted in Fig. 4（c，d）that the dissociation of the MWCNTs generally happened in the agglomerates of the MWCNTs-PVA. And complex polymer of $[(C_2H_4O_2)_n]1$-x$(C_{17}H_{17}ClO_6)_x$ was formed after the dissociation. It is indicated that the PVA polymer may play the key role for the MWCNTs-PVA dissociation into amorphous carbonaceous debris. The dissociation may happen easily on the polymer binding sites of the MWCNTs-COOH with more open C—C defects，which have high free energy and can be easily modified with PVA polymer. The PVA polymer was dissolved，and the outer tube wall and open carbon bonds generated several carbonaceous debris.

On the basis of the above-mentioned analysis，a possible model for explaining the phenomenon of the part dissociation of MWCNTs-PVA into amorphous carbonaceous debris during the dissolution process is
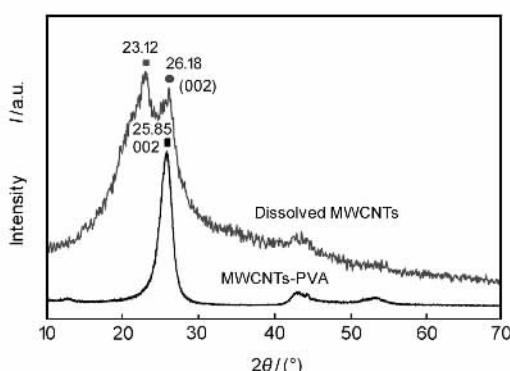
proposed in Fig. 7. The HNO_3 oxidizing treatment on the MWCNTs resulted in many open C—C bonds defects and COOH groups on the surfaces of CNTs. Then, the MWCNTs-COOH was grafted with PVA polymer by ultrasonic shaking and stirring reaction (Fig. 7a). With soaking in the shaking buffer solution, the PVA polymer dissolved first. The dissolution of the PVA on the walls of the MWCNTs leads to release of carbon atoms on the outer surface and open C—C bonds of MWCNTs. It results in a further breakage of the C—C bonds and tubular structure destruction (Fig. 7b). Then, the tubular structure and nanotube tips collapsed with the MWCNTs dissociation. Many residual MWCNT layers and amorphous carbonaceous debris are left in the solution. With continues soaking in the buffer solution, the residual CNT layers are also dissociated into amorphous carbonaceous debris in the solution finally (Fig. 7c). This possible mechanism proposed in this article will be further verified and modified in the future researches.
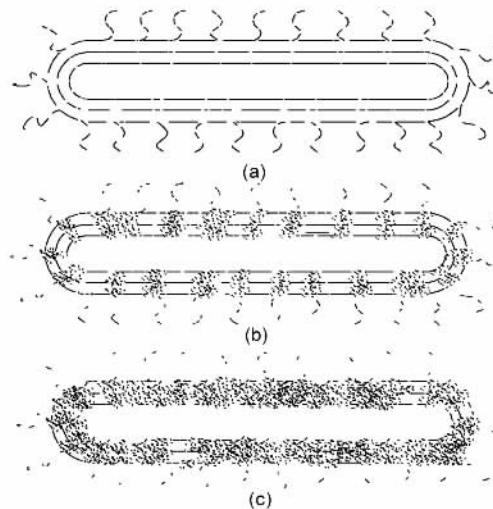

Fig. 7　Schematic illustration of dissolution mechanism of MWCNTs-PVA: (a) MWCNTs-COOH were modified with PVA polymer, (b) dissolution of PVA lead to release of carbon atoms on open C—C bonds of MWCNTs resulting further broken-down of C—C bonds and residual CNT layers, (c) residual CNT layers were dissolved into amorphous carbonaceous debris

There is a surprising finding that the MWCNTs surface modified with water-soluble PVA polymer could partly dissociate into amorphous carbonaceous debris at 37 ℃ in a pH neutral salt solution over relatively short time. Chen et al[21] have found that full-length SWCNTs can be solubilized in common organic solvents by noncovalent functionalization of the carboxylic acid groups present in the purified SWCNTs. The majority of the SWCNTs ropes were exfoliated into small ropes (2-5 nm in diameter) and individual nanotubes with lengths of several micrometers during the dissolution process. Zeng et al[22] have found that biodegradable poly (e-caprolactone) grafted onto MWCNTs can be completely enzymatically degraded within 4 d in a phosphate buffer solution in the presence of pseudomonas lipase, but the CNTs retained their tube like morphologies. In this study, it is first found that the MWCNTs surface modified with water-soluble PVA polymer could be partly dissociated into amorphous carbonaceous debris with most of MWCNTs retained in the Tris-HCl buffer solution. Nowadays, the MWCNTs are applied to biofields. This finding is important for promoting the potential applications of the MWCNTs in biological and biomedical fields.

4　Conclusions

MWCNTs were surface modified with COOH groups and then grafted with PVA polymer by " grafting to" approach. After 21 d of soaking, it is found that part of the MWCNTs-PVA was dissociated into amorphous carbonaceous debris and most of tubular structures were retained in the buffer solution. The dissolution process revealed that C—C bonds of the MWCNTs-PVA were broken down in the beginning, and then the MWCNTs were dissociated with generation of carbonaceous debris and residual CNT layers, these residual CNT layers were further dissociated into amorphous carbonaceous debris in the end. The PVA polymer on the surface of MWCNTs may play the key role for the dissolution process. This finding is important for promoting the potential applications of the MWCNTs in biological and biomedical fields.

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聚乙烯醇修饰的碳纳米管在缓冲溶液中的溶解过程

张法明[1,2]，　常　江[1]，　伯克尔 伊博哈德[2]

（1. 中国科学院 上海硅酸盐研究所，上海　200050；
2. 罗斯托克大学物理系，奥古斯特白拜尔特街 55 号，罗斯托克 18055，德国）

摘　要：　采用水溶性的聚乙烯醇修饰多壁碳纳米管表面,研究了聚乙烯醇修饰的碳纳米管在水浴摇床 Tris-HCl 缓冲溶液中的溶解过程。通过红外光谱,差示扫描量热仪,透射电镜及 X 光衍射的方法对聚乙烯醇修饰的碳纳米管在溶解过程中的显微结构变化进行了研究。结果表明:浸泡 21 d 后,聚乙烯醇修饰的碳纳米管部分溶解于缓冲溶液,形成无定形碳碎片;但大部分碳纳米管没有溶解,仍然保持管状结构。揭示出聚乙烯醇修饰的碳纳米管的溶解过程为:碳—碳键在浸泡过程中发生断裂,碳纳米管的部分溶解产生了无定形碳碎片与残留纳米管层片,残留纳米管层片进一步溶解最终成为无定形碳。提出与讨论了聚乙烯醇修饰的碳纳米管在 Tris-HCl 缓冲溶液中可能的溶解机理是:修饰后的碳纳米管表面具有很多缺陷和断裂的碳键,在缓冲溶液中聚乙烯醇的溶解导致嫁接位置的碳管壁的碳原子的释放,最终导致其管状结构的破坏。

关键词：　碳纳米管；表面修饰；溶解；结构稳定性；生物医学应用