CHEMICAL FUNCTIONALIZATION OF INNER WALLS OF CARBON NANOTUBES WITH LONG-CHAIN ALIPHATIC AMINES

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ABSTRACT

Synthesis of carbon nanotubes (CNTs) using porous anodic alumina membrane (PA) as template and the chemical functionalization of their inner walls is presented. The CNT were prepared by catalyst-free process using the pyrolysis of liquid aerosol of toluene: ethanol (1:1 v/v). The surface modification of the inner surface walls of CNT was performed using the gas phase synthesis by aliphatic amines (1,8-diaminooctane, DO). SEM, TEM and XPS analysis confirmed the morphology of prepared CNT inside of PA pores and their successful functionalization by amino groups. The presence and growth of interesting carbon nanoparticle inside CNT was observed during amination process. We hypothesized their origin as nanodiamonds formed as a result of the heat treatment in the presence of air that support etching mechanism and defects formation which acts as a diamond growth sites.

INTRODUCTION

The growth of carbon nanotubes (CNTs) inside porous substrates (templates) is considered as a promising strategy with respect to many applications such as cold field-emission (FE) cathodes, flat-panel displays (Quy et al., 2006, Lee et al., 2001) and microwave amplifiers (Tsakalakos et al., 2003). This approach based on the use of nanoporous alumina (PA) as a template with defined pore dimensions, was particularly attractive for fabrication of CNT arrays with controllable and defined nanotube dimensions (Kyotani et al., 1995, Altalhi et al., 2010, Orikasa et al., 2006, Sakintuna and Yurum, 2005). The length and diameter of the PA template can be easily controlled and therefore CNT with tailorable dimensions and properties can be fabricated. (Sakintuna and Yurum, 2005). Depending on the synthesis conditions, CNTs can be open on both ends, as well as closed on one end. The alumina template membrane can then be dissolved liberating carbon nanotubes which are attractive for biomedical applications as nanocapsules for targeting drug delivery (Orikasa et al., 2006).

It is well known that CNTs can be modified with molecules of different structure by forming stable covalent bonds or supramolecular assemblies based on noncovalent interactions (Veloso et al., 2006, Li et al., 2008, Hu et al., 2008). The development of chemical modification methodologies makes possible the use of CNTs for drug, protein, gene and vaccine drug delivery.
systems (Bianco and Prato, 2003, Gao et al., 2006, Kam et al., 2005, Pantarotto et al., 2004, Wallace et al., 2009). Functionalized CNTs could link to a wide variety of active molecules, including peptides, proteins, nucleic acids and other therapeutic agents, and can be charged with biologically active moieties, which can then be delivered to the cell nucleus. The most important feature in the chemistry of CNTs is the possibility of introducing of targeting molecules, contrast agents, drugs, or reporter molecules at the same time onto the same tube, that widen horizons in the development of new nanocarriers, specially for anticancer treatment (Wu et al., 2010). However the most of these studies were performed for modification of external surface of free CNTs and the modification of the inner CNT surface is considered as more difficult, but important for membrane and drug delivery applications.

A new gas-phase CNT functionalization strategy which is solvent-free functionalization, simple in implementation and attractive for “green” chemistry of nanomaterials, was recently proposed by this group for chemical modification of MWNTs and SWNTs with different functional groups (Basiuk Golovataya-Dzhymbieeva et al., 2011, Basiuk et al., 2005). In order to perform direct and one-step gas amination of MWNTs, the reactivity of structural (presumably pentagonal) defects at the closed ends and sidewalls of the pristine nanotubes was explored (Basiuk et al., 2004, Basiuk et al., 2005, Basiuk Golovataya-Dzhymbieeva et al., 2011). The procedure requires thermal treatment only, with no need to use an organic solvent medium, since increasing the temperature not only evaporates and activates the amine, but also helps to remove the unreacted amine physisorbed to nanotube surface. In this work, we employed this technique via “green” approach for gas-phase functionalization of CNTs prepared in PA template with the aim to achieve their covalent bonding of the inner walls. We explored functionalization using several amine molecules including (octadecylamine, 1,8-diaminoctane, polyethylene glycol diamine and polyethylenimine) and in this paper results with 1,8-diaminoctane (DO) is only presented.

The fabrication and modification process is presented in scheme (Figure 1)

Fig. 1: Schematic of fabrication CNT/PA composites membrane by CVD growth of carbon nanotubes inside of porous alumina oxide pores followed by gas phase modification of their inner surface using 1,8-diaminoctane (DO).
EXPERIMENTAL DETAILS

Preparation of CNT/PA composite and their functionalization

A high purity (99.997%) aluminium foil supplied from Alfa Aesar (USA) was used as the substrate material. The amine compound 1,8-diaminooctane (NH₂(CH₂)₈NH₂) from Sigma, Aldrich and Fluka, were employed. Porous alumina template was prepared by anodization of Al foil using oxalic acid (0.3 M) electrolyte as previously described (Losic et al 2010). The CNTs were fabricated on the pores of the PA template by the custom designed aerosol-assisted chemical vapor deposition (CVD) system as described in our previous work (Altalhi et al., 2010). In a typical experiment, the PA template was placed at the central high-temperature zone of the quartz tube (42.75 mm in diameter, 1000 mm long) and the carbon precursor source were introduced into the reaction tube as ultra-fine particle aerosols by utilising a particle generator with argon as carrier gas (flow rate 1L/min). During the temperature rising period, the inert gas of argon was keep pushing into the furnace to make sure there's no air, especially oxygen in the reaction system. After the temperature reached, the particle generator was switched on to allow to start growth of CNT structures inside PA pores. The reaction time for CNT growth was varied from 15 minutes to 1 hours. When growth process is completed the tube furnace is slowly cooled to room temperature (cooling time is approximately 24 hours).

The amine (DO) was placed together with CNTs composite in a proportion 2:1 (w/w) inside Pyrex ampoules, which were pumped out to ca. 10⁻²–10⁻¹ Torr and sealed. The ampoules were placed into a cylindrical furnace to carry out the solvent-free amination. The gas-phase functionalization with DO, which are volatile at temperatures above 150 °C in vacuum, was performed as described elsewhere (Basiuk et al., 2011). After cooling down, the ampoules with DO were opened, heated at 130 °C and simultaneously pumped out for 2 h to eliminate the excess of amine.

Structural and chemical characterization

The structural characterization of prepared PA and CNT/PA composites was performed by scanning electron microscopy (SEM) using XL30ESEM (Philips) and transmission electron microscopy (TEM) by utilising CM 200 TEM (Philips). Before inserting sample grids into the microscope, the samples were sonicated in ethanol, then dropped in the copper grids and dried at room temperature. X-ray photoelectron spectroscopy, XPS (Kratos AXIS Ultra-DLD spectrometer) was used to identify the molecular moieties attached onto the CNT by surface analysis.

RESULT AND DISCUSSION

Morphology and Structure

According to SEM imaging, the morphology structure of both unmodified CNTs-PA and DO-CNTs-PA shows no structural difference (Fig. 2 a-b and 2c-d). The SEM images shows the formation of CNTs structures inside the PA pores and their external diameter and length matched respectively to the PA pore diameters and thickness. We should note that PA with different pore diameters and length can be fabricated under different anodization conditions and hence the dimensions of CNT can be precisely controlled with specific pore diameter. Figure 2a and b
show low and high resolution image of the unmodified CNTs-PA imbedded inside the PA membrane after fracturing the composite structure. While the Fig.2 c-d shows low and high resolution of liberated DO-CNTs from the PA (inset image) and DO-CNTs imbedded inside the PA DO-CNTs/PA composite respectively. Surprisingly the appearance of some cluster particles and thin transparent layer on the top surface of DO-CNTs/PA see the red arrows Figure 2c-d.

In agreement with the SEM images a unique feature of the functionalized CNTs was observed by the TEM high resolution. The tubular structure of the functionalized CNTs is still at the same shape in comparison to the pristine CNTs (0-CNTs) Fig. 3a-d. However, high resolution TEM images for the functionalized tubes showed number of nanoparticles inside CNTs (Fig 3 d). We believe these carbon structures are diamond amorphous carbon nanoparticles formed on CNT defects during amination process. It has been known that the sidewalls of the CNTs are composed of benzene rings which are difficult to chemically react and almost to be inert especially in respect to amines compounds. Usually, what is involve in the reactions with the amines is the five-membered rings which is categorized as defects and reactive spots that is to be targeted for chemical reactions (Ajayan, 1999, Basiuk et al., 2004). However, as pointed out
from many groups and our previous work (Altalhi et al., 2010, Orikasa et al., 2006) the CNTs grown in PA template without of catalyst have a lower crystallinity structure and also rough surface induces many defects on CNTs this structure. We propose, these defects may influence the activity of the CNTs sidewalls to be anchoring sites for the activated amine molecules.

Further analysis was conducted to explore the chemical structure and importantly provide evidences that the inner graphitic layers surfaces of CNTs are functionalized with amine. To verify the differences between inner and outer CNT surface and confirm that the outside CNT were unaffected, we carried out the analysis of amine-functionalized nanotubes composite DO-CNTs/PA and also (liberated from PA) by means of X-ray photoelectron spectroscopy.

Fig. 3: Low and high resolution TEM images of (a-b), 0-CNTs and (c-d) DO-CNTs.

**X-ray photoelectron spectroscopy analysis**

In general an XPS spectrum reveals the surface structure with 5 nm depth and it is difficult to obtain information of the inner surface of CNT deeply inside PA template. However, the elemental composition and the surface chemistry of the inners surface of the nanotubes is assumed to be analogous to the upper layer of the CNTs/PA composite as pointed out by other group (Yang et al., 2005b, Yang et al., 2005a). The comparative XPS survey spectra from CNT exposed with the inner surface and external surface (after liberation) is presented in Figure 4, to proof that the inner surface of the nanotubes (DO-CNTs) was functionalized with the amine group. The XPS spectrum of the upper layer of the DO-CNTs/PA composite (equal to the inner surface of the CNT) compared to the outer surface of the liberated tubes from the PA membrane (DO-CNT) showed considerable difference regarding presence of nitrogen peak (4% N vs 0 % N)
Further comparison was carried out by examination of the C1s peak of the unmodified 0-CNTs (pristine), DO-CNTs/PA(inner surface) and DO-CNTs liberated from the PA template (outer surface) (Fig. 5 a-b). The C1s spectra (at 284.5± 0.3 eV) of the DO-CNTs liberated from the PA membrane and the pristine 0-CNTs without amine treatment (Fig. 5b) shows presence of graphitic carbon (sp2), with no difference in shape which confirmed to no presence of amino groups (Xu et al., 2010, Pinault et al., 2005). In case of DO-CNTs/PA (inner surface) the C1s peak is considerably broader (Fig. 5a) showing high energy shoulder over 285-289eV, (Robertson, 2002, Liu et al., 2010). These results verify that the outer surface of the both CNTs (liberated from 0-CNTs/PA and from DO-CNT/PA) is unaffected during the amination treatment.
High resolution XPS analysis from C1s and N1s peaks were further performed for the DO-CNTs and the unmodified CNTs (0-CNTs) and summarized in Fig. 6a-c. Following, to previous reports it is expected to see the amine compounds present in several chemical states, including: the free amine (NH$_2$) form, protonated or quaternary state (NH$_3^+$) and carbamate from the reaction with oxygen-containing functional groups or even H$_2$O and CO$_2$ (Sharma et al., 2004, Haimov et al., 2004, Pompeo and Resasco, 2002). The deconvolution of N1s for DO-CNTs (Fig. 6c) shows two peaks at 400.1 and 402.6 eV, corresponding to the quaternary form —NH$_3^+$ and —NH$_2$ free, respectively (Haimov et al., 2004, Sharma et al., 2004). The —NH$_3^+$ peak was 89.08% of the total N1s peak area. This combined with the broaden shape of the C1s line and the presence of two strong peaks at 285.20eV (26.45 %) and 287.10 eV (6.38 %) corresponding to the single carbon atom bonded to the nitrogen in the amine group and to the amide (carbamate form) respectively (Ishpal et al., 2010, Ramanathan et al., 2005). The appearance of the amide groups were combined with the both the presence of high percentage of oxygen atoms on the XPS spectrum Fig. 4a (12 %) and the carboxylic acid group COOH at 288eV (6 %) (Stobinski et al., 2010, Ishpal et al., 2010, Beuvelot et al., 2010). As expected, the N1s peaks were not observed in the pristine carbon nanotubes (0-CNTs) (Fig. 6a).

Fig. 6: a) High resolution C 1s from unmodified 0-CNTs, and b-c) N1s and C1s of amino modified CNTs (DO-CNTs/PA).

XPS data indicates a high percentage of sp$^3$ formation (higher binding shoulder detected at larger than 284.5± 0.3 eV) as seen in the in Fig. 6c accompanied with a high level of sp$^2$ declining compared to the 0-CNTs Fig. 6a. This result corresponds to both the SEM and TEM images (Fig 2 and 3), for observed diamond like carbon particles inside the tubes and on the top of the PA.
We hypothesize that the process of formation these structures can then follow with two different paths, depending on the time heating and conditions treatment during the amination process of CNTs. Under the functionalization conditions, the nanotubes begin to be attacked by either the highly reactive intermediates of the amines compounds (which is not stable above 150 ºC) and by the oxygen atoms during the heating process in the opened environment. This leads to form defective sites inside the inner surface of the nanotube wall, which provides suitable sites for the nucleation of carbon nanodiamond. The second is etching mechanism of the graphitic structure of the carbon atoms (double C=C bond, sp² carbon) which is in agreement with several studies (Zhang et al., 2005, Li et al., 1993, Ruffieux et al., 2002) demonstrated that graphite can be converted to the diamond structure depend mainly on the purity and integrity of the graphite structure. The etching sp² structure of the graphite makes the transformation easier since these defects will play a role as suitable sites for nucleation of diamond crystallites (Ruffieux et al., 2002, Raty et al., 2003, Mehandru et al., 1992). Our current studies are in process to explain proposed mechanism and composition of formed carbon nanoparticles.

CONCLUSION

In this paper the functionalization of the inner surface of CNT array grown inside PA template is reported for the first time. The selective inner surface functionalization of the CNTs was successfully demonstrated using gas phase and solvent-free modification process leaving the outer surface of CNT unaffected, which is confirmed by XPS. The advantage of gas phase approach is reduction of the contaminants in the nanotubes structure (e.g., chemical reagents or solvents) which makes these CNTs with double surface chemistry particularly promising material for targeting drug delivery applications. The formation of carbon nanostructures in various forms such as carbon thin film and nanodiamond particles confirmed by SEM and TEM are interesting and unexpected outcomes, which will be explored in future with more details.

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