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Oxidative functionalization of carbon nanotubes in atmospheric pressure filamentary dielectric barrier discharge (APDBD)

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Abstract

The surface compositional and any structural changes that occur on carbon nanotubes using air–atmospheric pressure dielectric barrier discharge (APDBD) for functionalization are investigated employing Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA), X-ray diffraction (XRD), and neutron diffraction techniques. Atmospheric pressure plasmas (APP) are suggested to be particularly suitable for functionalization of aligned nanotubes, where wet chemical manipulation could damage or even destroy the highly desirable vertical alignment. In this work a detailed experimental study elucidating the effects of APDBD plasma treatment parameters (e.g. power density, discharge composition, inter-electrode gap and treatment time) on the electronic structure, physical, and chemical behaviour of carbon nanotubes has been conducted. In an atmospheric air we find an optimal oxidative functionalization of CNTs in our DBD system within few seconds (<5 s) at a discharge power of $\sim$0.5 kW. This investigation may find useful application as functionalization technique for CNT engineered devices and sensors.

Keywords: Carbon nanotubes; Oxidation; Raman spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction

1. Introduction

Carbon nanotubes [1] are 3-D nanometric hexagonal arrays of graphitic carbon atoms folded so as to form single-walled and multi-walled tubular structures. In the latter, smaller diameter tubes are nested within similar tubes of larger diameter. Within the nanotubular structures, the carbon atoms form locally pseudo-graphitic lattices which self-wrap into seamless cylinders of microns length. The lattice vector parameters can be used to define the various types of nanotube conformation as armchair (n,n), or zig-zag $(n,0)$ or chiral $(n,m \neq n)$ where values of n and m determine the chirality (twist) of the nanotube which in turn determines the nanotube properties. These properties are also affected by the tube diameter. The armchair form has been predicted from calculations [2] to be metallic due to their bands crossing the Fermi level. The other nanotubes (chiral and/or zigzag) are thus either metallic or semiconductive (with $E_{\text{gap}} \sim 0.5$ eV and $E_{\text{gap}} \alpha 1/d_{\text{t}}$) depending on the indices $(n-m)/3$ being an integer or fraction, respectively.

The current interest in the science and applications of carbon nanotubes arises from their unique structure and the associated properties. Obviously, the later can be tailored by doping and/or post-synthesis treatments depending on the application envisaged.

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Carbon nanotubes grown on either plain or nanometric lithographically/focused ion beam (FIB) patterned surfaces (aligned nanotubes) usually have some impurities present including amorphous carbon and/or metal catalyst (serving as seed on substrates used for nanotube growth). Thus, vigorous reagents such as H_2SO_4 are usually used to removed these impurities and at same time to functionalise the CNT. However, in these circumstances the essential nanotube structure and/or their alignment can be damaged [3]. An alternative to the use of these strong chemicals is the use of APDBD techniques which offer, arguably, marked advantages over wet chemical techniques. In recent years, non-equilibrium dielectric barrier discharges running at atmospheric pressure have been developed as effective means for the surface modification of materials. Clearly, effective APDBD processing (at atmospheric pressure) of solid surfaces also offers advantages compared to vacuum-based plasma and as well as over wet chemical methods. In practice, using APDBD methods, the need for relatively expensive vacuum system and components are avoided. Moreover, high processing speed, and even the continuous processing of large area substrates become possible, thus meeting likely industrial production requirements. Obviously, the more usual exposure to reactive solutions, solvents and the like is avoided and handling is minimised. While APDBD has been successfully used to surface-modify various polymeric materials there appear to be no reports on the use of this technology for the treatment of nanotubes.

In this work we examine APDBD as an alternative route to the functionalization of CNTs and address the primary DBD processing parameters involved. XRD and neutron diffraction, TGA, Raman, and XPS techniques were used for the material characterisation.

2. Experimental details

2.1. CNT preparation

The multi-wall carbon nanotubes (MWCNTs) were prepared by CVD. Acetylene was used as the carbon source with Fe and Ni as catalyst. The reaction temperature was 700–800 °C. The as-deposited MWCNTs were rinsed with HCl, distilled water and dried. MWCNT suspensions were prepared by dispersing 10 mg of CNT material in 10 ml of *N*,*N*-dimethylformamide (DMF), or methanol with the aid of ultrasonic agitation for 1–2 h. The films used for DBD processing were prepared by depositing CNT suspensions on Au/Si substrates by a drop-dry technique (i.e. the suspension was dropped onto the substrates and the DMF allowed to evaporate).

2.2. DBD systems for CNT functionalization

The DBD reactor system (ARCOTEC VB-A4, GmbH, Germany) running in a 'volume discharge' configuration employs a self-tuning high voltage supply (3–20 kV) with an output frequency of 25–50 kHz and is provided with a variable speed moving platen lower electrode (silicon rubber or aluminium) and an upper set of three selectable electrodes (respectively, metal covered by a ceramic sleeve or stainless steel wire) has an external power setting knob for output power choices. A Tektronix TDS-5032S digital oscilloscope (with integrated functional software) is provided along with a high impedance high voltage probe for monitoring the electrical characteristics of the discharge assembly. The a.c. high voltage provided has peak-to-peak values in the 3–20 kV range. The applied voltage with a resistor connected in series yields the current generated, and if the resistor is replaced with a capacitor, then the voltage across the series capacitor is proportional to the charge stored on the electrode. The voltage versus the charge plots (Lissajous figures) displayed on the oscilloscope yields the energy deposited during the DBD cycle. The DBD energy dissipation depends mainly on the applied voltage (adjustable) and demonstrably varies little with any reasonable changes in the inter-electrode gap. The discharge takes the form of a myriad of randomly located micro-filaments which switch on and off on nanosecond time scales such that while significant energy is dissipated the gas in the electrode gap remains cold. At the high voltage inputs used (~10–20 kV range) an inter-electrode gap of 1–2 mm is appropriate (with the power supply and electrodes used here 2.2 mm is the practical upper limit for production of uniform discharge over the sample between the electrodes) the resultant energy surface density was in the order of 10^2–20^2 μJ/cm^2. The DBD discharge 'dose' (D) in J/cm^2 is given by this relation [4]:

$$D\ (\mathrm{J/cm^2}) = IV\cos\phi 2N/lS \tag{1}$$

where I = current, V = voltage, ϕ = phase shift, $2N$ = cycle (number of passes to and fro through the electrode gap), l = electrode length (cm) and S = speed of moving platen/lower electrode (cm/s).

2.3. X-ray diffraction (XRD) and neutron diffraction

Bruker D8 X-ray diffractometer (Cu Kα 1.54 Å, tube I = 40 mA, V = 40 kV) was used for powder XRD, at a scanning rate of 0.02°/s in the 2θ range of 10–80°. X-ray photon of 1.5 Å wavelength has energy of ~8.2 keV, is very penetrating and could lead to molecular degradation, but the energy of a neutron of the same wavelength (1.5 Å) is only 36.4 meV. The interaction of neutron with matter is weak and its absorption by most material is very small, thus it is equally very penetrating, but non-