

Effect of oxygen rf-plasma on electronic properties of CNTs

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Abstract

Multi-wall carbon nanotubes (CNTs) were modified by an oxygen radio frequency plasma treatment, the appropriate duration of which was determined from post-treatment high-resolution transmission electron microscopy (HRTEM) images. A comparison of HRTEM results from gold-decorated pristine and plasma treated CNTs showed that the plasma treatment improves the uniformity of the distribution of surface defects. X-ray photoelectron spectroscopy confirms that oxygen atoms attach to the surface of CNTs. Changes in the C 1s photoemission signal point towards a loss of delocalization of valence electrons, confirmed by the modifications of valence band spectra, and consistent with currently accepted theory.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The impulse to the study of carbon nanotubes (CNTs) goes back to the work of Iijima [1] in 1991. Since then CNTs have attracted considerable interest due to their unique physical properties associated with their crystallinity and structure (they are molecules in the circumference direction while they are almost infinite crystals in the direction along their axis). Their electronic properties range from semiconducting to metallic depending on their chiral angle and diameter [2]. Although one might imagine that the electronic properties of CNTs can be ‘easily’ tailored by controlling their chiral angle and/or diameter, such modulation has not yet been achieved. To date, conventional synthesis methods provide CNTs with mixed chirality, not separable by current technology. Not only is chirality control lacking, and hence precise control on the electronic properties, but also a mixture of both metallic and semiconducting tubes are synthesized simultaneously. While it is possible to ‘burn out’ the metallic tubes leaving only semiconducting, this approach has limited application [3]. One approach to tackle this drawback is to tailor the physical and chemical properties by post-growth treatments such as grafting molecules to the tube sidewall. By grafting species to the

sidewall, the electrical and/or mechanical properties can be modified [4, 5]. Consequently, understanding the effect of post-treatments on the CNT electronic structure is essential in terms of exploiting the full potential of CNTs for developing new technologies.

Typically, functionalization of CNTs is accomplished by immersing in appropriate chemical solutions or exposing them to vapours at high temperatures. Alternatively chemical radicals can be added to tubes using a cold plasma treatment [6, 7]. Functionalization by plasma treatment has the advantage of being non-polluting and providing a wide range of different functional groups depending on the plasma parameters such as gas source, applied power, pressure and treatment time.

In this work, we investigate the impact on the electronic structure of CNTs upon using an oxygen plasma to graft oxygen containing surface groups. In order to perform our study, the density of states (DOS) of pristine and oxygen rf-plasma functionalized CNT-layers were investigated by photoelectron spectroscopy. Both x-ray and ultraviolet photoelectron spectroscopy were used. Defects were labelled by evaporating gold atoms onto the CNT-surface [8] and quantitative analysis was performed by high-resolution transmission electron microscopy (HRTEM).

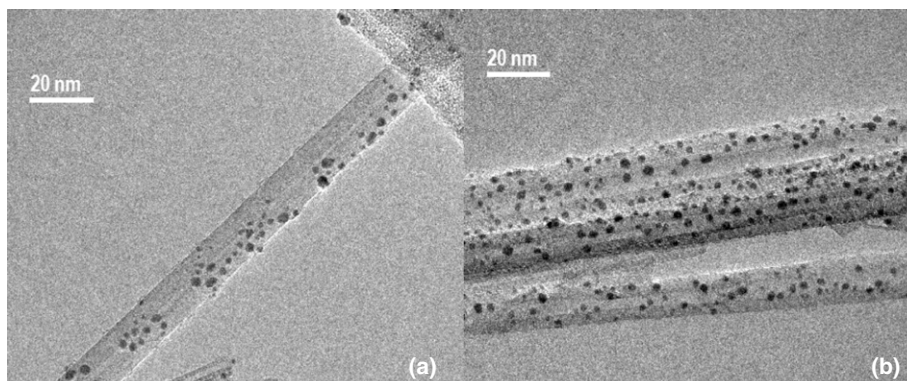


Figure 1. CNTs decorated with gold clusters. (a) pristine CNTs and (b) oxygen rf-plasma functionalized.

2. Experiment

Samples were prepared using commercial MWCNT powder synthesized via catalytic chemical vapor deposition (CCVD) [9]. (The MWNTs are characterized by an average inner diameter of 5 nm and an average outer diameter of 15 nm, corresponding to 14–15 concentric layers. The average length is ca 20 μm .) The functionalization was performed in a homemade chamber using inductive coupled plasma at an rf frequency of 13.56 MHz [7]. Samples for XPS, UPS and TEM were treated simultaneously: for the XPS and UPS analysis, the MWCNT powder was supported on a copper conductive tape suitable for ultra-high vacuum; the thickness and the homogeneity of the obtained ‘CNT-layers’ were checked to assure the absence of interference from the tape. For TEM analysis the CNT powder was dispersed in ethanol, and the solution was dropped onto a honeycomb carbon film supported by a copper grid. The samples were treated on their support in order to avoid dispersion inside the plasma chamber and post-treatment contamination. Once the sample was placed inside the plasma glow discharge, the treatment was performed at a gas pressure of 0.1 Torr, using 15 W. Two treatment times were investigated: 5 and 30 s.

The XPS measurements were performed with a system (HP 5950A) equipped with a hemispherical electron energy analyzer. The photon source was a monochromatized Al K α line ($h\nu = 1486.6$ eV). The nominal resolution of the system (source + analyzer) was 0.7 eV.

UPS measurements were performed at FLIPPER II beamline-Hasylab (Hamburg) using a photon energy of 55 eV. The overall resolution of the system (source plus analyser) was 0.2 eV [10]. The zero of the binding energy was calibrated for the Fermi edge of the evaporated Au thin film.

High-resolution electron microscopy (HRTEM) was performed using a JEOL 4000EX microscope at 400 kV. In order to reduce potential knock-on radiation damage caused by the 400 keV electron beam, the electron dose was significantly decreased such that during the entire electron-beam exposure no changes in the nanotubes were observed.

3. Results and discussion

HRTEM images recorded on pristine MWCNTs (figure 1) show that the gold clusters are elongated, aligned along the

axis of the nanotube and poorly dispersed. The elongated shape of the gold nanoparticles suggests that the gold atoms are mobile and have higher mobility along the axis of the CNTs. The nature of the gold–CNT interaction was reported to be of the Van der Waals type [11]. It is this weak interaction and high diffusion rates that lead to few nucleation sites for gold growth and large particle formation on the nanotubes observed in figure 1(a). Conversely, TEM images recorded on gold-decorated plasma treated MWCNTs show that the gold clusters are much more uniformly dispersed than on pristine nanotubes (figure 1(b)). The improved dispersion suggests that plasma treatment induces the formation of cluster nucleation sites. It has been shown that for a metal that weakly interacts with the CNT surface (as in the case of gold), its dispersion can be used to monitor the presence of active sites such as morphological defects as well as their uniformity [8]; defect sites are more reactive than the CNT-surface lattice and hence act as active sites for gold cluster nucleation, as verified for metal coating on the basal plane of graphite [12, 13]. From these results, it can be deduced that the exposure of the MWCNTs to the oxygen plasma treatment created well-dispersed active sites at the CNT surface.

Figure 2 shows a HRTEM image recorded on CNTs that were treated for 35 s and then decorated with gold. It can be seen that the interaction of oxygen active species with the CNT surface resulted in the removal of several walls due to chemical etching for plasma treatments longer than 30 s. The dispersion of the gold clusters does not follow the new morphology of the sample. Based on these results, the treatment times were limited to those shorter than 30 s in order to avoid damage at the CNT surface.

XPS analyses were performed in order to evaluate the chemical change at the CNT surface associated with the plasma treatment. Figure 3 shows the XPS survey spectra of the nanotubes recorded before and after treatment. The peak at 284.3 eV, observed on all the spectra, is generated by photoelectrons emitted from the C 1s core level. On the XPS spectrum recorded after oxygen plasma treatment, a peak near 535 eV can be observed. This peak is generated by photoelectrons emitted from the O 1s core level. The atomic concentration of oxygen atoms grafted at the CNT surface increased for increasing treatment times: for 5 s it was found to be 10.4%, increasing to 12.4% for 30 s of treatment.

Identifying the chemical modification produced by plasma treatment at the surface of nanotubes is straightforward when

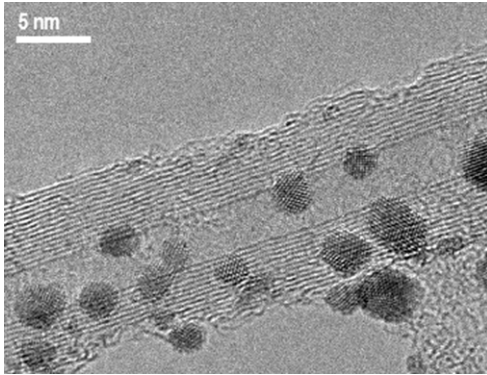


Figure 2. Oxygen rf-plasma treated CNT decorated with gold clusters. The figure shows the removal of several CNT walls induced by the oxygen treatment.

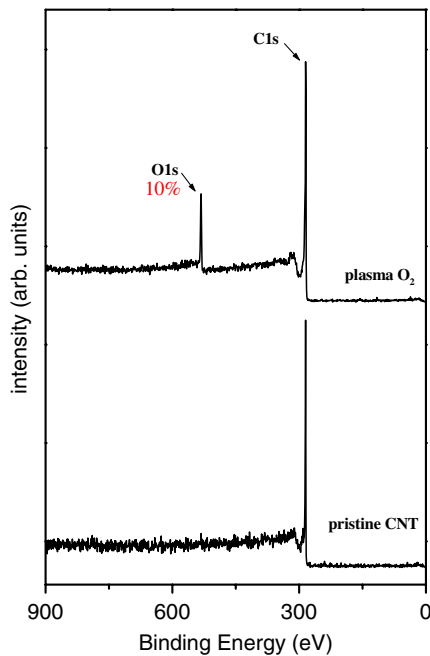


Figure 3. XPS survey spectra. (a) Pristine CNTs and (b) oxygen plasma treated CNTs.

the C 1s core level spectrum is analysed. Figure 4 presents the C 1s spectra recorded before and after oxygen plasma treatment. Photoelectrons emitted from carbon atoms in the 'graphite-like' walls generate the main feature of these spectra at a binding energy of 284.3 eV (peak A), i.e. 0.3 eV lower than the value for photoelectrons emitted from graphite samples [13]. This shift was associated with the weakening of C–C bonding caused by the redistribution of the electron density with respect to graphene resulting from the curvature of the sheets [13]. The chemical modification produced by the oxygen plasma treatment can be identified by a broad structure peaking at 287.5 eV (peak B). Theoretical modelling reports that oxygen plasma treatment induces the grafting of C=O and C–O–C functional groups at the CNT surface as a result of O₂ dissociation on vacancies created during the plasma treatment [14]. Based on reports [7] the broad structure at 287.5 eV can be attributed to photoelectrons emitted from carbon atoms arising from hydroxyl (~286.2 eV), carbonyl or

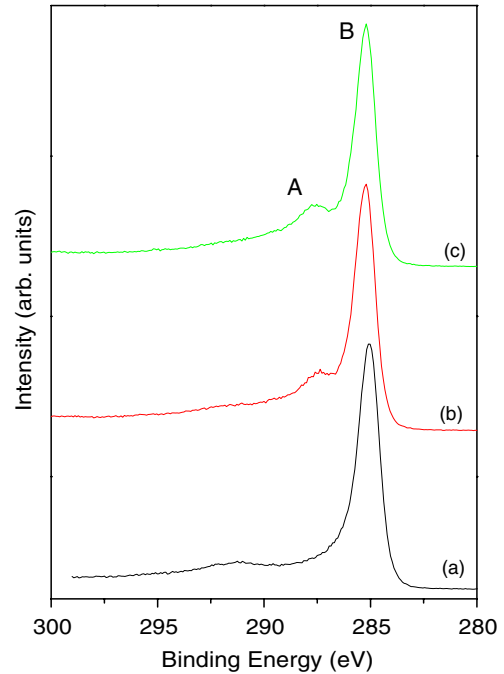


Figure 4. XPS C 1s core spectra recorded on (a) pristine, (b) 5 s plasma treated and (c) 30 s plasma treated CNTs. Photoelectrons emitted from carbon atoms in the 'graphite-like' walls generated at 284.3 eV (peak A). The chemical modification produced by the oxygen plasma is identified by the broad structure peaking at 287.5 eV (peak B).

ether (~287.2 eV) and carboxyl or ester (~288.9 eV) groups. Consequently, it can be assumed that the oxygen plasma treatment effectively induces the grafting of oxygen species to the otherwise chemically inactive surface of the MWCNTs.

The broad structure centred at 291.0 eV, observed in the C 1s spectrum recorded on pristine CNTs, is characteristic of sp² carbon systems such as graphite, which is assigned to the so-called π plasmon, reflecting the collective excitation of the π electrons. Similar loss features are not observed in the spectra recorded from the plasma treated CNTs. The energy position of the π plasmon loss peak is known to be related to the delocalization of 2p- π electrons; for a higher plasmon energy, larger electron delocalization is expected; conversely, a smaller plasmon energy is related to electronic localization. Therefore, the absence of the loss structure at energies higher than 291.0 eV for plasma treated CNTs suggests increased electron localization.

Figure 5 presents UPS spectra recorded on MWCNTs before and after oxygen plasma treatment. The valence band structure of the pristine CNTs is essentially the same as for graphite [13]. The characteristic features for the threefold coordination of the C atoms is the 2p- π band near 3.5 eV, the 2p- σ states near 5.5 and 8.0 eV and the mixed 2s-2p hybridized states at 13.6 eV. The curvature of graphene sheets reduce the p- π electron density for CNTs, thus the related features on the valence band spectrum are less pronounced than for graphite. On the contrary, due to σ - π hybridization resulting from the formation of tubes structures, the intensity near 11.5 eV binding energy, attributed to p- σ contribution, is more pronounced in the case of MWCNTs [13]. The features near 19 and 14 eV were associated with oxygen molecules that

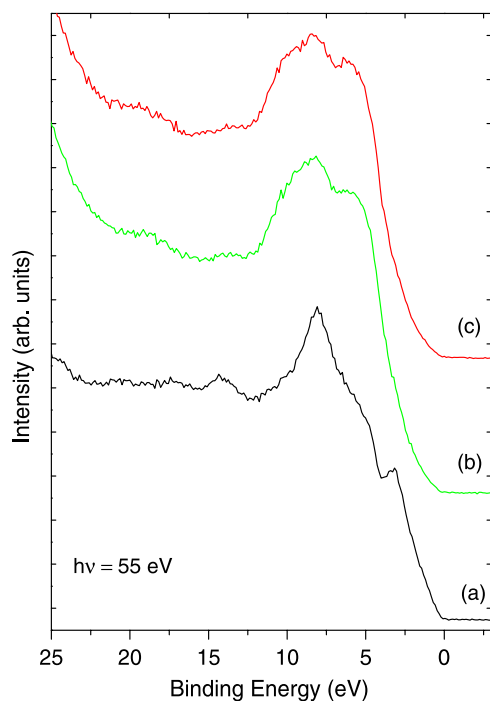


Figure 5. UPS valence band spectra recorded on (a) pristine, (b) 5 s plasma treated and (c) 30 s plasma treated CNTs.

are physisorbed on the walls and at the edge of the MWCNTs [15]. The UPS spectra recorded on the functionalized samples show that the exposure of the MWCNTs to the oxygen plasma considerably changes the DOS. After the plasma treatment, there is no residual DOS at E_F and the structure associated with the π -derived DOS in the energy range between 0 and 3 eV is significantly reduced in the spectrum recorded on the sample functionalized for 5 s and cannot be observed for samples functionalized for 30 s. These results suggest that extended electronic states are transformed into localized states due to the grafting of oxygen radicals at the CNT surface, supporting the interpretation that the functionalization increased the electron localization obtained by XPS.

Reported theoretical studies on disorder-induced electron localization in metallic CNTs have shown that disorder induced by chemical functionalization causes electron localization in metallic CNTs with the localization length ξ being inversely proportional to the disorder concentration, at the lower concentration limit. In 1D and 2D systems, the electronic wavefunctions are exponentially localized for any non-zero disorder concentration [16]. However, in nanometre scale samples, the localization length ξ may exceed the size of the sample; in this case the samples will then remain conducting. On the contrary, if the localization length ξ is shorter than the sample, the conductance will decrease exponentially with the sample length. Thus from the results discussed above it can be suggested that oxygen plasma

functionalization can be used to tailor the conductance regime of MWCNTs by modifying the quantity of oxygen atoms grafted at the CNT surface, i.e. the density of active sites (i.e. localized states).

4. Conclusion

In conclusion, HRTEM shows that gold clusters are much more uniformly dispersed on oxygen rf-plasma treated MWCNTs compared with pristine nanotubes. The improved dispersion suggests that the plasma treatment induces the formation of defects that act as reactive sites for gold cluster nucleation. Photoelectron spectroscopy shows that the plasma treatment of CNTs effectively grafts oxygen atoms at the CNT surface. The existence of metallic nanotubes was confirmed from the characteristic DOS at near the Fermi level. The grafting of oxygen atoms at the CNT surface was found to reduce the DOS at E_F suggesting a method to tailor the CNT electronic structure.

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