

IMAGING AND SPECTROSCOPY OF MULTIWALLED CARBON NANOTUBES DURING OXIDATION: DEFECTS AND OXYGEN BONDING

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ESCA MICROSCOPY
and
SPECTROMICROSCOPY

The Carbon NanoTubes (CNTs) with their particular tubular structure of honeycomb carbon network are excellent candidates for many potential applications in electronics, composite materials, catalysis etc. Functionalization of CNTs modifies significantly their properties, e.g. converting them from hydrophilic to hydrophobic, in particular changing their chemical activity and selectivity. Processing the CNTs in oxidising environments has already been used for purification, tailoring their length [1] and homogenizing the mixture of metallic/semiconducting CNTs by converting the metallic ones into semiconducting [2]. The atomistic picture of oxidation is complicated involving several consecutive or parallel elementary processes, such as formation of particular O bonds to graphene network and gasification with formation of CO_2 and CO volatile products. (For atomistic picture of oxidation at the initial stages see the highlight by O. Bariş Malcıoğlu *et al.* on page 114.) Both the presence of defects in the CNT graphene cage and the defects created in the oxidation process play important roles in formation of different oxygen functional groups on the CNT surface and facilitate the gasification.

Using the Scanning PhotoElectron Microscopes at the ESCA Microscopy and Spectromicroscopy beamlines of Elettra, we explored the morphology of a multi-walled CNTs array and obtained spectroscopic information from small areas of individual CNTs. The interpretation of photoemission spectra in terms of relative abundance of various functional groups enabled us to correlate the presence of particular functional groups to the morphological state of the CNT array.

The CNT forest arrays were exposed to atomic oxygen, supplied from a radiofrequency plasma source. We observed strong tempera-

ture dependence of the morphology evolution of the CNT array, as displayed in Figure 1. At room temperature (300 K) only minor changes in the images are visible up to the oxygen doses of 2×10^{18} atoms cm^{-2} equivalent to 30 hours (h): maximum exposure time used in our experiments. At 500K the CNTs visibly bend and shorten already at doses of $\sim 10^{17}$ atoms cm^{-2} and undergo almost complete extinction due to gasification after 8×10^{17} atoms cm^{-2} dose. At both reaction temperatures the formation of different oxygen functional groups was detected. The O 1s spectra corresponding to different oxidation conditions are shown in Figure 2. In the beginning of the oxidation process three main types of oxygen functional groups are present: epoxy (green), ether (red) and carbonyl (blue). The appearance of a second carbonyl component is attributed to the carbonyl in different configurations in the advanced oxidation stages. As the exposure increases the components related to carbonyl (O atom bonded to a single C atom) prevail. They become unique in the O 1s spectra of the arrays when the significant morphology changes of CNT array are evidenced. Our results correlate the morphology changes of CNTs, a natural consequence of increasing density and size of the vacancy defects, with type and abundance of characteristic oxygen functional groups. Since the ether-bonding configuration can be realized only in a few atom vacancy defects the carbonyl becomes dominant when the multi-atom vacancy defects are formed and prevail [3].

In summary the most important finding is that the type and abundance of the formed oxygenated functional groups is controlled by the presence and size of the vacancy defects in the graphene layers of the CNTs. On one hand this introduces an uncertainty

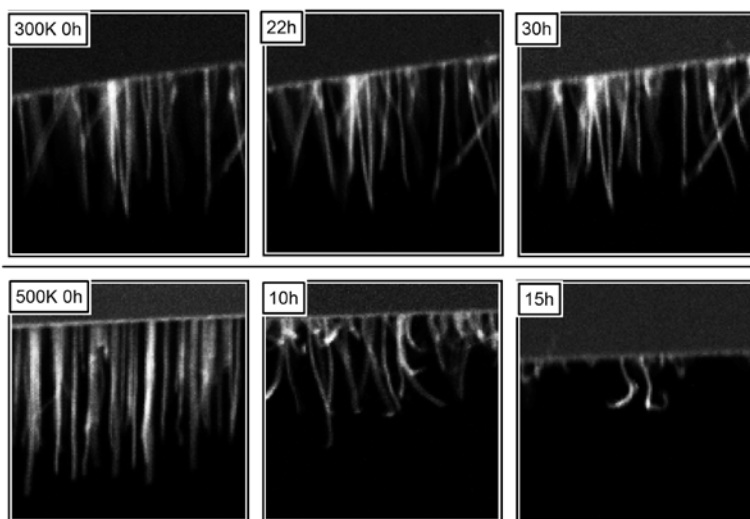


Figure 1. The evolution of CNT array morphology at 300K and 500K at various oxygen doses. The oxygen flux $9 \times 10^{14} \text{ cm}^{-2} \text{ min}^{-1}$. Image size is $12.8 \times 12.8 \text{ }\mu\text{m}^2$.

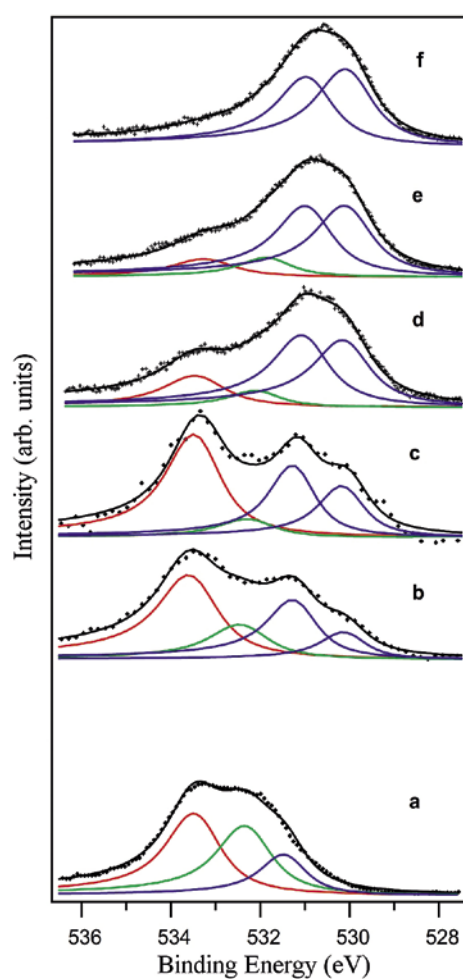


Figure 2. O 1s spectra after oxidation at 20°C : defective HOPG (a) 4×10^{14} and (b) $1.4 \times 10^{16} \text{ atoms cm}^{-2}$; CNTs (c) 1.4×10^{16} and (d) $5.4 \times 10^{17} \text{ atoms cm}^{-2}$ O 1s spectra oxidation of CNTs 200°C (e) 2.7×10^{17} and (f) 5.4×10^{17} . The components related to the O functional groups are drawn in red (ether), epoxy (green) and carbonyl (blue). The picture is reproduction from the work published [3].

when analogous procedures are employed for functionalization of CNTs with undefined density and type of defects, on the other hand it prompts an approach for tailoring the CNTs via controlled introduction of defects, which favor the formation of a preferred functional group.

References

- [1] T.W. Ebbesen, P.M. Ajayan, H. Hiura, K. Tanigaki, *Nature* **367**, 519 (1994).
- [2] J.B. Cui, R. Sordan, M. Burghard, K. Kern, *Appl. Phys. Lett.* **81**, 3260 (2002).
- [3] A. Barinov, L. Gregoratti, P. Dudin, S. La Rosa, M. Kiskinova, *Adv. Mat.* **21**, 1916 (2009).