

## Electronic structure of Pd nanoparticles on carbon nanotubes

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### Abstract

The effect of the oxygen plasma treatment on the electronic states of multi-wall carbon nanotubes (MWCNTs) is analyzed by X-ray photoemission measurements (XPS) and UPS, both using synchrotron radiation. It is found that the plasma treatment effectively grafts oxygen at the CNT-surface. Thereafter, the interaction between evaporated Pd and pristine or oxygen plasma-treated MWCNTs is investigated. Pd is found to nucleate at defective sites, whether initially present or introduced by oxygen plasma treatment. The plasma treatment induced a uniform dispersion of Pd clusters at the CNT-surface. The absence of additional features in the Pd 3d and C 1s core levels spectra testifies that no Pd–C bond is formed. The shift of the Pd 3d core level towards high-binding energy for the smallest clusters is attributed to the Coulomb energy of the charged final state.  
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### 1. Introduction

More than a decade after their first observation, CNTs are still at the center of the scientific community interest due to their unique properties; they are molecules around their circumference while they are almost infinite crystals along their axis. The well-defined tubular crystalline structure composed by rolled graphene sheets with a diameter of nanometer size and their length up to a few microns is a perfect playing ground for hosting new scientific concepts with the potential for several promising technological applications (Saito et al., 1998).

However, the non-reactive nature of the CNT-surface prevents their optimal integration in complex assemblies (Ciraci et al., 2004). Consequently, an important step for achieving true technological applications is the integration of CNTs with other materials, ranging from inorganic compounds and polymer coating to biomolecules. In order to achieve efficient integration, it is necessary to activate the CNT-surface, which shows an inherently low chemical reactivity (Kuchib-

hatla et al., 2007). One promising approach to tackle this problem is to tailor chemical properties of the CNT-surface by post-growth treatments such as by grafting molecules or suitable nanostructures to the sidewall of the CNTs (Bittencourt et al., 2007; Ciraci et al., 2004; Ruelle et al., 2007; Zhu and Xaxiras, 2006). Reports on the post-treatment potentiality are given by theoretical studies which predict that by grafting metal clusters at the CNTs surface their reactivity towards a specific gas increases (Ionescu et al., 2006). In addition, nanostructured materials composed by CNTs decorated with metal nanoparticles such as Pt or Ru or bimetallic Pd/Rh nanoparticles are reported to display good catalytic behavior (Larciprete et al., 2006).

Among the metals used to decorate CNTs, Pd appears to be particularly important since besides the catalytic behavior found for Pd decorated CNTs, Pd is considered the most promising metal to achieve transparent contacts; ballistic transmission of electrons was reported for the Pd–CNT contact (Javey et al., 2003). The interaction between CNTs and metal contacts and the resulting electronic structure are crucial for the performance of CNT devices (Javey et al., 2003). Experimental studies showed that the metal used as an electrode and the variation in nanotube diameter are the two main parameters

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responsible for the performance of CNFET (Chen et al., 2005), with the best performance achieved by combining Pd contacts with CNTs of diameter larger than 1.4 nm. In these experimental studies, the details of the interface geometry are believed to affect the nature of the contact.

The understanding of the interaction between Pd atoms and CNT-surface is a key issue in the design and optimization of practical applications. In the present study of the Pd–CNT interaction, pristine and oxygen plasma-treated multi-wall carbon nanotubes (MWCNTs) with different amounts of Pd evaporated onto their surface were analyzed by high-resolution transmission electron microscopy (HRTEM) and photoemission spectroscopy (PES) techniques.

## 2. Experimental

X-ray photoemission measurements (XPS) were performed at beamline BW2 of HASYLAB using a photon energy of 3300 eV (Drube et al., 1995). The Au  $4f_{7/2}$  peak at 84.0 eV, recorded on a reference sample was used for calibration of the binding energy scale. In order to track small photon energy drifts during the measurements, reference spectra were measured before and after each core level and valence band datasets recorded on all the samples.

The oxygen plasma treatment was performed by using inductively coupled RF-plasma (13.56 MHz) (Felten et al., 2005). After placing the CNT powder inside the plasma glow discharge, the treatment was performed at an oxygen pressure of 0.1 Torr, applying 15 W for 60 s. The samples were prepared using commercially available MWCNTs powder ([www.nano-cyl.com](http://www.nano-cyl.com)). For the photoemission analysis, the MWCNT powder was supported on a UHV-compatible conductive carbon adhesive tape. For the TEM analysis, carbon nanotubes were sonically dispersed and a drop of the solution deposited on 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 contaminations.

For the XPS and TEM analysis samples were prepared by depositing different amounts of Pd onto pristine and plasma-

treated MWCNTs using e-beam evaporation from a high-purity Pd rod (nominally evaporated amounts of 0.3, 1.0, 2.0, 5.0, 10 and 20 Å). Sample transfer from the preparation to the XPS analysis chamber was carried out under UHV conditions, the residual pressure in the analysis chamber was  $2 \times 10^{-10}$  mbar. A quartz microbalance was used to calibrate the metal evaporation rate *in situ* prior to the deposition onto the CNT samples used for transmission electron microscopy and photoemission analysis. By mounting samples of pristine and plasma-treated CNTs onto the same holder, they were simultaneously exposed during the metal evaporation ensuring the same amount of Pd on each pair of samples.

High-resolution transmission electron microscopy was performed using a JEOL 3000F microscope at 300 kV.

## 3. Results and discussion

Fig. 1 shows the result of evaporation of 10 Å of Pd onto pristine and oxygen plasma functionalized CNTs; the formation of nanoparticles can be observed for both cases. The influence of the oxygen plasma treatment of the CNT-surface on the formation of the Pd “overlayer” is clear in Fig. 2 that shows high-resolution images recorded on samples prepared with different amounts of Pd (2, 5 and 10 Å) evaporated onto pristine and oxygen plasma functionalized CNTs. Compared to the evaporation on pristine CNTs (Fig. 2a–c) the nanoparticles formed at the plasma-treated CNT-surface are more uniformly dispersed (Fig. 2d–f). During the onset of the evaporation poorly dispersed nanoparticles are formed at the pristine CNT-surface (Fig. 2a). At the graphite surface, transition-metal atoms were found to be mobile and to form clusters as the cohesive energy of these metals is much larger than the adsorption enthalpy, the nucleation centers are defects (chemical or structural) at the surface (Kuhrt and Harsdorff, 1991). Considering the reported similarities between the graphite and the CNT-surfaces, it can be assumed that Pd atoms are mobile and diffuse at the CNT-surface until they find a nucleation center. Consequently, the cluster dispersion will depend on the dispersion of the defects at the CNT-surface.

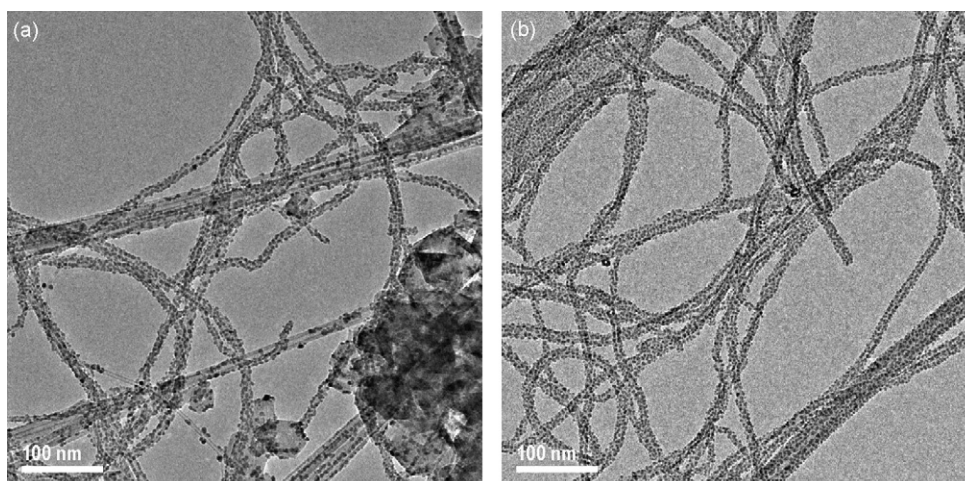


Fig. 1. HRTEM image of Pd on (a) MWCNTs and (b) oxygen plasma-treated MWCNTs. Thermal evaporation of 10 Å (nominal deposition).

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