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NO2 and CO interaction with plasma treated Au-decorated MWCNTs: Detection pathways

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Abstract

The detection mechanisms of gas sensors based on oxygen plasma functionalised multi wall carbon nanotubes (MWCNTs) and rf plasma-treated nanotubes decorated with gold nanoclusters are experimentally and theoretically investigated. Results from X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM) analysis are discussed. It is found that NO_2 detection involves the interaction with oxygenated vacancies and/ or Au nanoclusters present on the nanotube walls, while CO detection is significantly enhanced by the interaction with Au nanoclusters anchored at the nanotube sidewalls. These differences in detection pathways open the possibility for fabricating selective MWCNT sensors.

Keywords: Carbon nanotubes; gas sensors.

1. Introduction

Since the discovery of carbon nanotubes by Iijima 1991, pristine CNTs are rather inert. But thanks to their unique physico-chemical properties [1], carbon nanotubes and especially on gas sensors area are becoming very attractive sensor nano-materials for the next-generation of the innovative gas nano-sensors.

Recently different methods for increasing their surface reactivity to gases detection such as CNT surface functionalisation and CNT surface decoration either with noble metal nanoclusters [2,3] and/or metal oxide nanoparticles have been used. In [4] we studied the effect of an oxygen plasma functionalisation on the gas sensing properties of MWCNTs. In particular, oxygenated vacancies (carbonyl, carboxyl groups) play a role for enhancing the sensitivity towards NO_2. Additionally, such vacancies act as nucleation sites for the growth of Au nanoclusters [fig.3] evenly distributed onto the nanotube sidewalls as revealed by XPS [fig.1], TEM and Density Functional Theory (DFT) calculations.

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2. Material preparation and characterization

Carbon nanotubes were obtained from Nanocyl S.A. They were synthesized by chemical vapor deposition. The MWCNT powder had purity higher than 95%. Nanotubes were up to 50 micro-meters in length and their outer and inner diameters ranged from 3 to 15 nm and 3 to 7 nm, respectively.

Carbon nanotubes were functionalized by inductively coupled plasma at a RF frequency of 13.56 MHz in the presence of oxygen. Treated nanotubes were decorated with gold nanoclusters by thermal evaporation.

TEM and XPS analysis were carried out in order to analyze the structure and chemical composition of the sensing materials. Fig.1 shows the XPS analysis of oxygen functionalized MWCNTs and Au decorated MWCNTs which affirms the existence the oxygenated groups into the walls of carbon nanotubes, TEM analysis confirm also the attachment of gold nanoparticles to the nanotubes' walls. Fig.2a

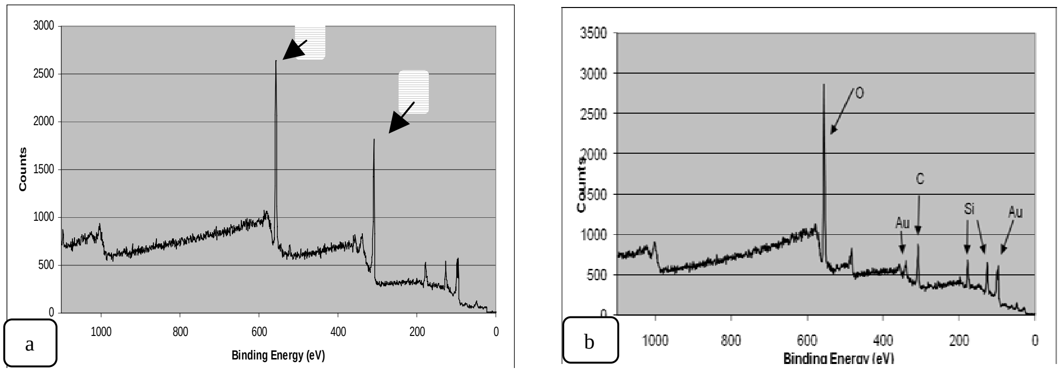

Fig. 1: XPS analysis of: (a) oxygen functionalized MWCNTs; (b) Au decorated oxygen fictionalized MWCNTs.

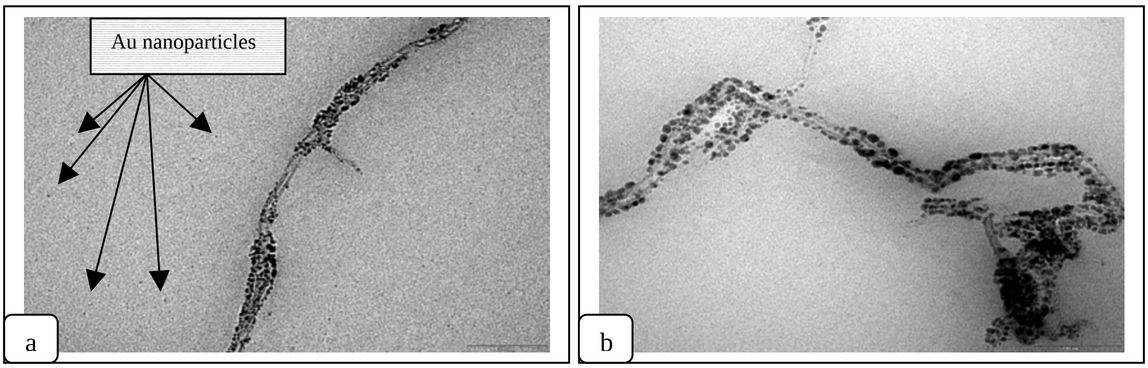

Fig. 2. (a) Direct drop coating of metal decorated MWCNTs; (b) drop coating of untreated MWCNTs and then functionalize them and decorated them.

3. Sensor fabrication and characterization

3.1 Sensor fabrication

Two sensor preparation methods were employed. The first one consisted of drop coating plasma treated and Au-decorated MWCNTs onto micromachined sensor substrates while in the second one, the sensor substrate was drop-coated with un-treated nanotubes and then underwent plasma treatment and Au decoration.

3.2 Sensor characterisation

The sensors based on un-treated MWCNT, oxygen plasma treated MWCNT and Au-decorated oxygen plasma treated MWCNT deposited by two methods were inserted in the measurement circuit. Their response to NO_2 (100 ppb to 1 ppm), CO (2 to 20 ppm), were obtained at operating temperatures of R.T. and 150ºC. To assess the reproducibility of results, each measurement was replicated 4 times and sensors from different fabrication batches were tested.

4. Results and discussion

From TEM images:

- We confirm that functionalizing CNTs in oxygen plasma creates an active sites (carbonyl and carboxylic groups) that help to have a good dispersion homogeneity of gold nanoparticles onto the nanotubes' walls (fig.3).

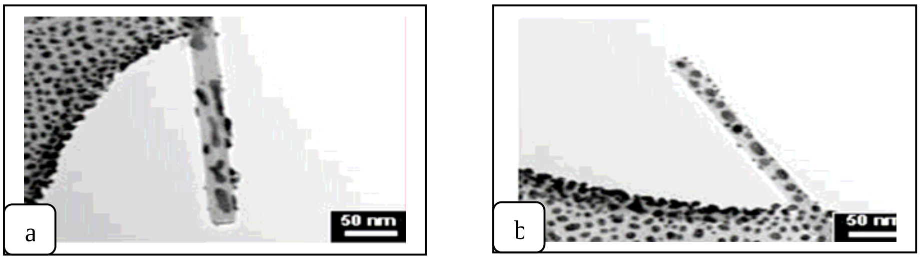

Fig. 3. (a) Au decorated pristine MWCNTs; (b) Au decorated oxygen functionalized MWCNTs

- By the inverse drop coating method, we avoid the removal of Au nanoparticles from the nanotubes' walls after the thermal treatment. (fig.2b). As it is known that Au nanoparticles have weak interaction energy with carbon nanotubes, the thermal treatment break the interaction between metal and nanotubes which induce the gold nanoparticles to leave the carbon nanotube sidewalls.

Un-treated MWCNTs have a weak responsiveness to the gases tested. While oxygen plasma treated MWCNT sensors are significantly more sensitive to NO_2 than to CO, Au-decorated MWCNT sensors show increased CO and reduced NO_2 sensitivity. This is because NO_2 interacts both with oxygenated vacancies or Au nanoclusters present in the walls of plasma treated MWCNTs and CO preferentially interacts with Au nanoclusters. Such clusters are anchored on oxygenated vacancies and, therefore, Au-decorated nanotubes show a significantly reduced number of such vacancies.

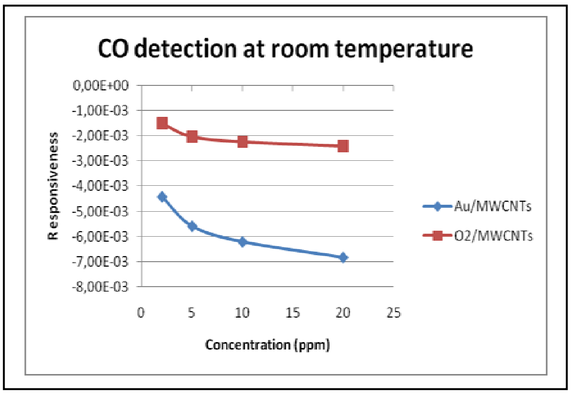

Fig.4. Average responsiveness (Responsiveness is defined as: S=(Rgas-Rair)/ Rair) of Au/CNTs and O2/CNTs sensors for the detection of CO at room temperature. (Inverse drop coating)

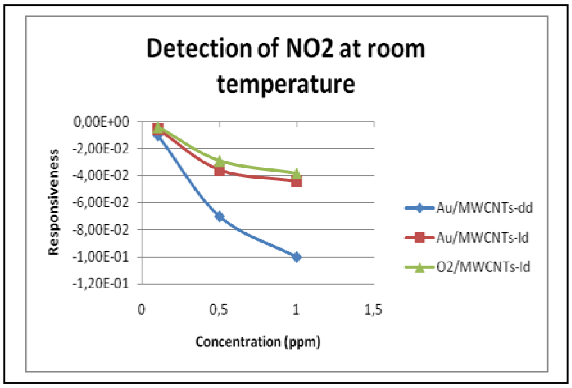

Fig.5: Average responsiveness of NO2 at room temperature.

Acknowledgements

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References

1. M. S. Dresselhaus, G. Dresselhaus, and P. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, San Diego, CA 1996.
2. R. Leghrib, et al., Integrated microarrays of metal decorated carbon nanotubes gas sensors, Proceedings of Eurosensors XXII, Dresden, Germany (2008) 1511-1514
3. E.H. Espinosa, et al., Thin Solid Films, 515 (2007) 8322-8327
4. R. Ionescu et al., Sensors Actuators B, 113 (2006) 36-46