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# RF sputtering as a tool for plasma treating and metal decoration

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**Abstract**

Multiwalled carbon nanotubes were functionalized and decorated with metal or bi-metallic nanoparticles by employing an RF sputtering machine. First, CNTs were functionalized in oxygen + argon plasma and then decorated with Au, Pt or Au/Pt. The size and density of the metal nanoparticles on the nanotube surface could be controlled by the process parameters such as power and deposition time. Structure morphology and chemical composition of the different hybrid materials were characterized by means of TEM and EDX. EDX reveals the presence of oxygen species grafted to CNTs functionalized in oxygen + argon plasma and TEM shows that the average diameter of nanoparticles is 2 nm. Particle size and distribution remain stable upon thermal treatment. The gas sensing properties of these materials have been studied.



*Keywords:RF sputtering, Metal decorated CNTs, Metal nanoparticles, gas sensors, Room temperature.*

## 1. Introduction

Since the discovery of CNTs, the scientific community presents a huge interest on their special properties which allow for their implementation in a wide range of applications. To date, a lot of challenge was devoted to improve some pristine CNTs characteristics which limit their use in many areas such as optics, electro-mechanics or chemistry because of their non-appropriate compatibility [1-3].

Their important surface to volume ratio and their use at room temperature make from CNTs very promising candidate for gas sensing application. Recent works are focusing on functionalizing the CNTs

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sidewall with highly reactive groups or decorate their surface by metal nanoclusters which let to achieve more chemically reactive CNT surface. Another critical point is how to choose carefully adequate parameters for their functionalization and metal decoration. These attempts open new ways for producing performed CNTs based gas sensors.

The performance of metal decorated carbon nanotube (CNT) based gas sensors strongly depends on the size of metal nanoparticles and their stability on CNT surface. The smaller are the nanoparticles the higher their reactivity is [4] and sensors show increased sensitivity. However, a high reactivity of metal nanoparticles coupled to their weak interaction with the surface of CNTs can cause migration and coalescence. This results eventually in the occurrence of huge metal islands [5], which is not recommended for gas sensor applications, because this induces response drift and low sensitivity.

## 2. Experimental setup and Results

In the present work, we introduce a method based on RF sputtering to achieve a highly stable grafting of metal nanoparticles of small diameter to CNT sidewalls. At first, as-grown CNTs, provided from Nanocyl S.L and produced by CVD, were diluted in dimethylformamide (DMF), and then the solution agitated in ultra-sonic bath at room temperature. After that, the sample was kept several minutes out of the bath to let precipitate the agglomerated CNTs which permit the use of the part of solution that contain the isolated CNTs. This later was airbrushed over alumina substrate (figure.1).
The as deposited MWCNts on alumina substrate were put inside the sputtering chamber (Sputtering ATC Orion 8-HV-AJA International machine) and functionalized in an RF oxygen + argon plasma (figure.2). The objective was to clean CNTs from amorphous carbon and to create reactive sites (i.e. oxygenated vacancies) in which metal nanoparticles can nucleate. Treated CNTs were decorated with Au, Pt, and Pt/Au. Treatment and metal decoration parameters were varied in order to study their effect on the percentage of oxygen grafted to nanotubes and also on the size, distribution and quantity of metal nanoparticles attached to CNTs. Samples were analyzed by TEM and EDX.

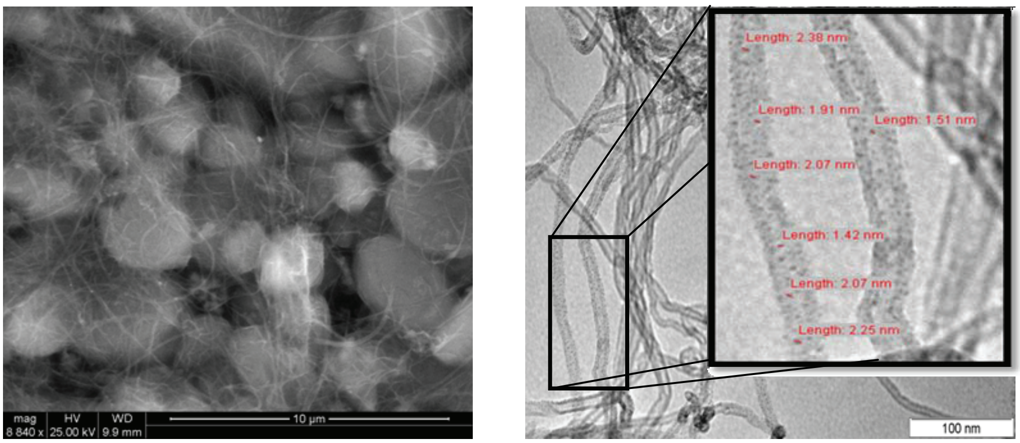


Figure 1: a) SEM image of as deposited MWCNTs on alumina substrate, and b) TEM image of Au decorated oxygen plasma functionalized MWCNTs

Figure 1a shows a very thin and homogeneous layer of MWCNTs on alumina substrate. The deposition of thin layer allows a good and homogeneous fictionalization and metal decoration. From figure 1b, we can see well dispersed metal nanoparticles with a very small diameter in the range of 1.5 to 2.5 nm. The presence of oxygen species was confirmed by EDX analysis (see figure.3b). In our previous work, we saw that when heating the sensors at elevated temperature, gold nanoparticles tended to agglomerate and form very big metal islands. Herein, decorated samples underwent thermal treatment at 100, 150 and 250 ºC during 2 h. Metal nanoparticles were stable and only a slight increase in size was detectable at 250ºC (see figure.3a).

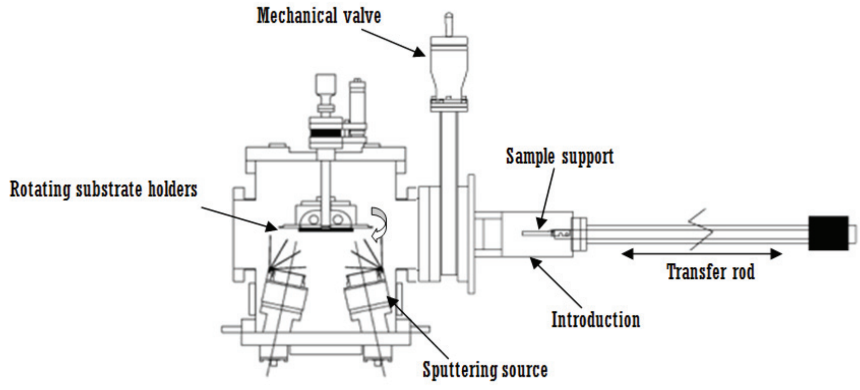


Figure 2: Schema of the sputtering chamber

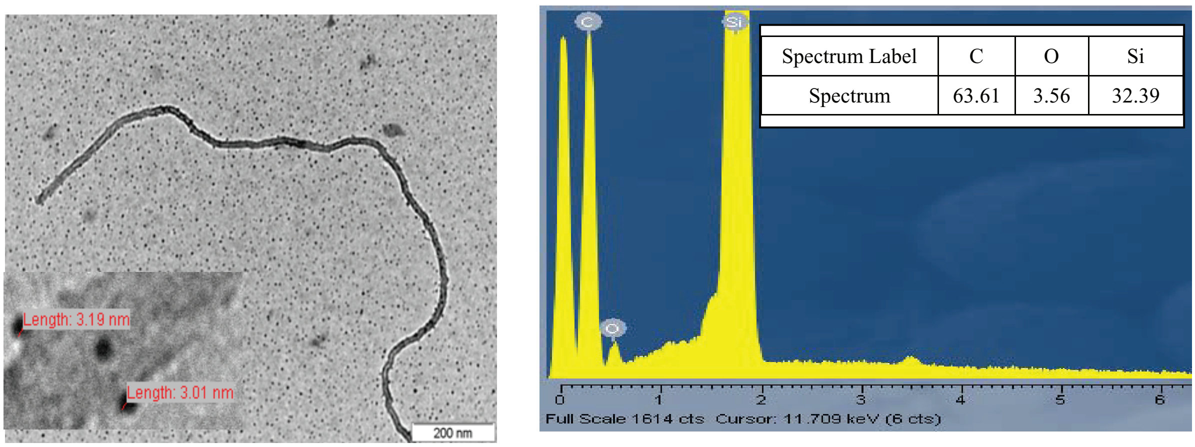


Figure 3: a) Metal nanoparticles size after thermal treatment at 250 ºC during 2 h., b) EDX analysis and the atomic percentage of oxygen functionalized MWCNTs

The sensors, which employed alumina substrates, were packaged and then introduced in the test chamber. The sensing properties of different hybrid materials (oxygen functionalized MWCNTs, Au, Pt , or Pt/Au decorated oxygen functionalized MWCNTs) were subject to the test towards different concentration of different gases at room temperature in dry and humid ambient.

Figure 4 shows the results obtained when sensors were exposed to $NO_2$ at room temperature.

The sensors were heated during the cleaning step at 150 ºC in order to quickly recover their baseline. From the same figure, we can conclude that sensors have a very good recovery of their baseline.

A full characterization with other gases (CO, $NH_3$, $H_2S$) and humidity will be shown at the Conference. This method enables a reliable and reproducible surface treatment of CNTs in a wide range of substrates including MEMS.

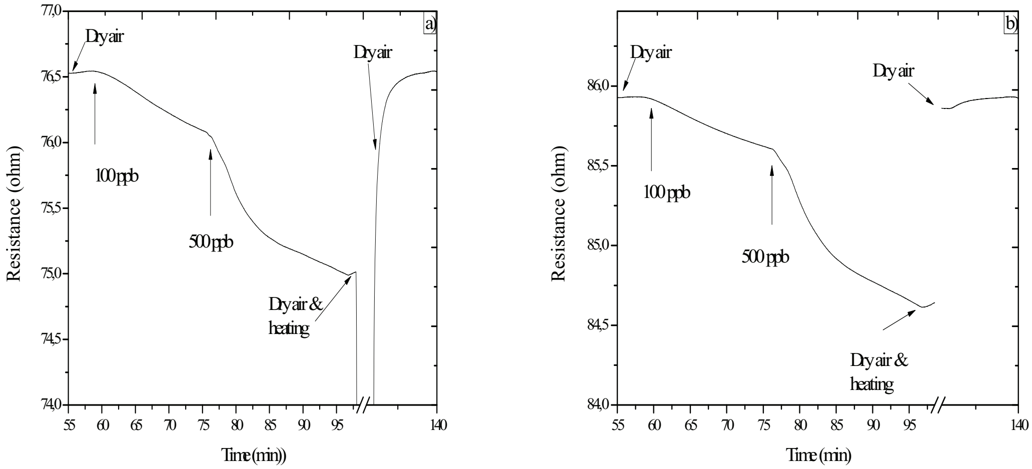


Figure 4: Response towards $NO_2$ at room temperature of gas sensors based on: a) Pt/Au oxygen functionalized MWCNTs, b) Au-oxygen functionalized MWCNTs. The sensor is heated at 150ºC for speeding up baseline recover.

## 3. Conclusion

Using RF sputtering deposition method, very small and stable metal nanoclusters were deposited onto MWCNTs. The test of these hybrid materials towards different gases at room temperature reveals that Pt/Au/MWCNTs based sensor show higher response than Pt/MWCNTs or Au/MWCNTs based sensors. These new results are very promising for getting more sensitive and selective gas sensors

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