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Ultrapure Organically Modified Gold Nanoparticles for Breath Analysis

T.G. Welearegay[1,2], O.E. Gualdrón[3], A.L. Jaimes[3], J.M. Cáceres[3], G. Pugliese[1,3], U. Cindemir[2,4], C.M. Durán[3], L. Österlund[2,4], R. Ionescu[1,5*]

[1]*MiNoS, Universitat Rovira i Virgili, Av. Paisos Catalans 26, 43007 Tarragona, Spain*
[2]*Molecular Fingerprint Sweden AB, Eksatravagen 130, 75655 Uppsala, Sweden*
[3]*GISM, Universidad de Pamplona, Pamplona Km 1 Vía Bucaramanga, 543050 Norte de Santander, Colombia*
[4]*The Ångström Laboratory, Department of Solid State Physics, Uppsala University, 75121 Uppsala, Sweden*
[5]*Faculty of Engineering, Universidad Autónoma del Caribe, Barranquilla, Colombia*

Abstract

In this study we present a new technological approach for the fabrication of ultrapure organically modified gold nanoparticles (AuNPs) for chemical sensing applied to exhaled breath analysis. To achieve a high purity level of the sensing films, we combined Advanced Gas Deposition (AGD) technique to deposit ultrapure monodispersed AuNPs, and dip coating process for functionalization of the AuNPs with thiolated organic ligands. Morphology and surface analysis revealed the deposition of ultrapure isolated AuNPs after the first processing step, and a network of nanoparticle–ligand nanoassemblies after the second processing step. Gas sensing measurements were performed with exhaled breath samples collected from a group of smokers, a group of non-smokers, and ambient air. Sensors responses towards these samples demonstrated characteristic responses for each study group. PCA analysis further revealed samples classification in three distinct characteristic clusters, which indicates the suitability of the molecularly modified AuNPs presented in this communication for breath analysis applications.

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Keywords: Monolayer capped AuNPs; Advanced Gas Deposition; Breath analysis

1. Introduction

The search for non-invasive diagnostic methods and diseases monitoring on the basis of volatile organic compounds (VOCs) detected in exhaled breath has led to the development of sensors arrays sensitive to low VOCs concentrations. In this regard, molecularly modified gold nanoparticles have proven excellent potential for detecting very low VOCs concentrations in biofluid samples [1]. The conventional fabrication method of these nanomaterials

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is based on wet-chemistry processes, which can leave traces of impurities and residual compounds in the sensing film [2]. In order to counteract this negative effect, we propose in this study an innovative methodology that employs the Advanced Gas Deposition technique to fabricate ultrapure, size-controlled, dispersed AuNPs in the first processing step, followed by AuNPs functionalization with thiolated organic ligands in the second processing step. A chemical sensors array based on monolayer-capped AuNPs fabricated employing this innovative technique was tested for exhaled breath analysis.

2. Experimental

2.1. AuNPs fabrication and functionalization

AuNPs were deposited on sensing devices fabricated on one side polished p-type <100> Si substrates (13 mm x 8 mm) with two parallel Au electrodes, 15 µm gapped, patterned on top by rf-sputtering. Nanoparticles growth and deposition was achieved employing the AGD equipment (ULVAC, Japan) configured in a two-chambers set-up for ultrapure AuNPs generation and deposition [3] – see **Fig.** 1. A piece of pure gold metal (99.99% purity) was placed on a carbon crucible inside the lower evaporation chamber, and a copper induction coil surrounding the crucible provided the heating necessary to melt the gold metal piece. The sensing substrates were mounted onto a movable stage in the upper deposition chamber. The two chambers of AGD were connected via a narrow transfer pipe (3 mm inner diameter), positioned in the vapor zone where melted gold atoms are evaporated.

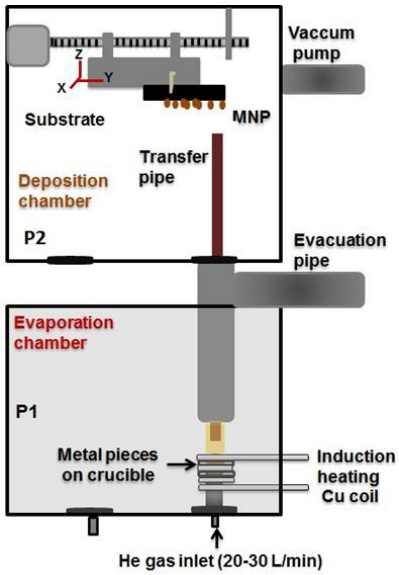

Fig. 1. Advanced Gas Deposition (AGD) technique adapted for AuNPs fabrication and deposition.

High purity He gas with a laminar flow rate of 20 L/min introduced underneath the heated gold piece, with upward direction, transported the Au atoms through the transfer pipe from the evaporation chamber to the deposition chamber. Because of the pressure difference between the two AGD chambers (0.88 mbar and 90 mbar in the upper and lower chamber, respectively), the Au atoms were propelled at high speed and got deposited onto the sensing substrates when impinging into them. Induction heating power, pressure in AGD chambers, speed of the movable stage and number of deposition cycles were optimized to obtain ultrapure monodispersed and crystalline AuNPs.

Next, the as-deposited AuNPs films were coated with various thiolated molecular ligands (4-methoxy-α-toluenethiol, methyl-3-mercaptopropionate, and 1-decanethiol) by dip coating the substrates in a solution containing 100–200 µL ligand dissolved in 20 ml ethanol for one hour, followed by drying at 50 °C for one hour for evaporating the solvent.

3. Results and discussion

3.1. Films characterization

The morphology and elemental structure of the films were examined by Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS). These analysis confirmed the deposition of ultrapure randomly dispersed individual AuNPs, which were roughly cubic and had pure single crystalline structure. **Fig**. 2a shows a monolayer of AuNPs dispersed onto the electrodes area of a sensing device, while **Fig**. 2b displays a network of nanoparticles–ligand nanoassemblies got after AuNPs functionalization. The crystallite size of the as-deposited films, calculated using Scherrer's formula, was ~ 10 nm, in agreement with the mean crystallite size distribution shown in **Fig**. 2c.

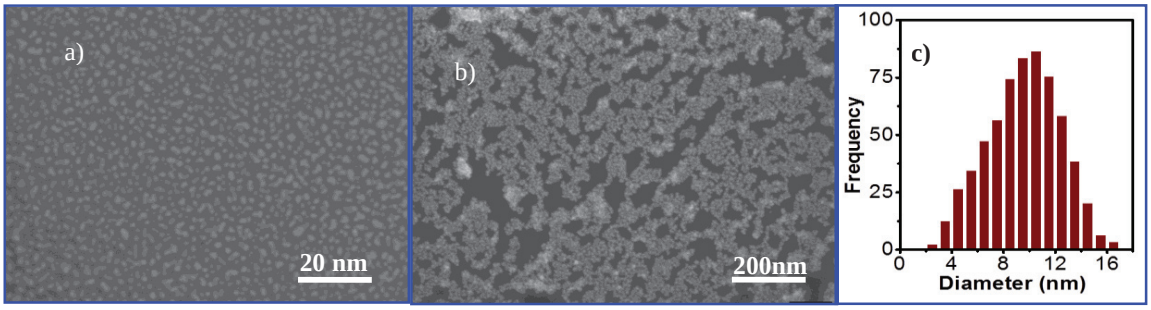

Fig. 2. SEM images of; a) dispersed AuNPs; b) AuNPs functionalized with 4-methoxy- α-toluenethiol; c) AuNPs crystallite size distribution

XPS measurements of the AuNPs films exhibited typical Au4f core level peaks at 88 and 84.5 eV, consistent with elemental Au (**Fig**. 3a), and weak intensity S2p peak at 162.5 eV that depicts the covalent binding of thiols to AuNPs surface in the case of the monolayer-capped AuNPs films (**Fig**. 3b). The small shift of 0.5 eV in $Au4f_{7/2}$ and the relatively strong intensity S2p peak at 168 eV suggest that the organic ligands were strongly bound to AuNPs surface through the thiol group.

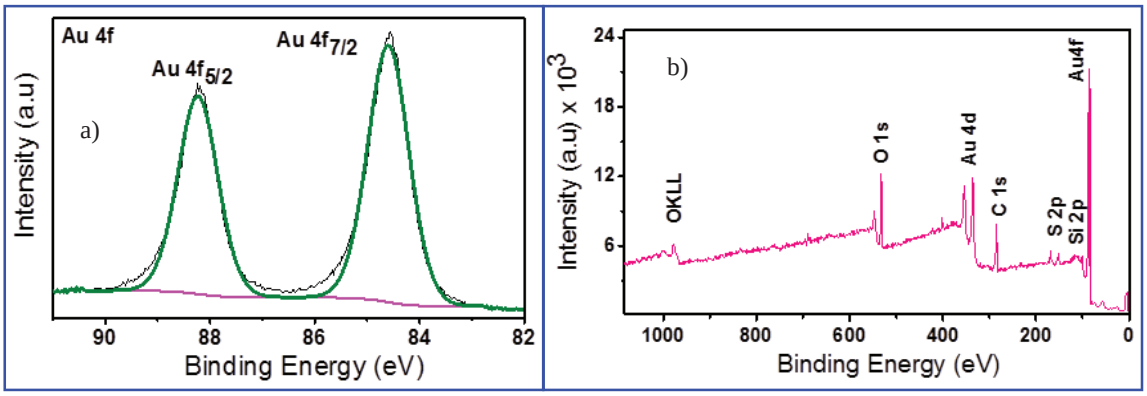

Fig. 3. XPS spectra of: a) Au4f core level splitting; b) AuNPs capped with 4-methoxy- α-toluenethiol.

3.2. Exhaled breath samples analysis

The responses of the sensors were analyzed upon exposure to exhaled breath samples of a group of 5 smoker and 5 nonsmoker volunteers, and to ambient air samples collected in the same place of the experiments. For performing the sensing tests, the sensors were placed inside a Teflon test chamber (26 cm^3 inner volume). Each measurement comprised the following cycles: (i) 5 min under steady state baseline conditions; (ii) 5 min exposure to the analyzed

sample under steady state conditions; (iii) 5 min under continuous synthetic dry air flow used for cleaning the sensors surface and purging the test chamber. The samples were acquired employing the BioVOC^{TM} sampling system and immediately introduced to the sensors chamber. 5V constant voltage was alternately applied for intervals of 10 sec to each sensor during operation, and the current through the sensors was recorded for further analysis.

The sensors responded to the exhaled breath samples of both smoker and non-smoker volunteers, displaying different characteristic responses towards each study group and a good recovery after samples evacuation, as it is remarked from the investigation of **Fig**. 4a. In this kind of sensing films, the AuNPs act as electrical conductors, while the molecular component of the nanoassembly provides the sensing surface that interacts with the VOCs from the sample analyzed. The smaller increase in sensor's response towards the smokers breath samples compared with the non-smokers breath samples could be related to the lower concentration of VOCs adsorbed.

Fig. 4b shows the results of the Principal Component Analysis (PCA) performed with the overall responses of four sensors (1 sensor with 4-methoxy-α-toluenethiol ligand – $R_{baseline}$≈190kΩ; 1 sensor with methyl-3-mercaptopropionate ligand – $R_{baseline}$≈100kΩ; and 2 sensors with 1-decanethiol ligand – $R_{aseline}$≈11MΩ and ≈450kΩ), which demonstrates excellent discrimination between smokers, non-smokers, and ambient air.

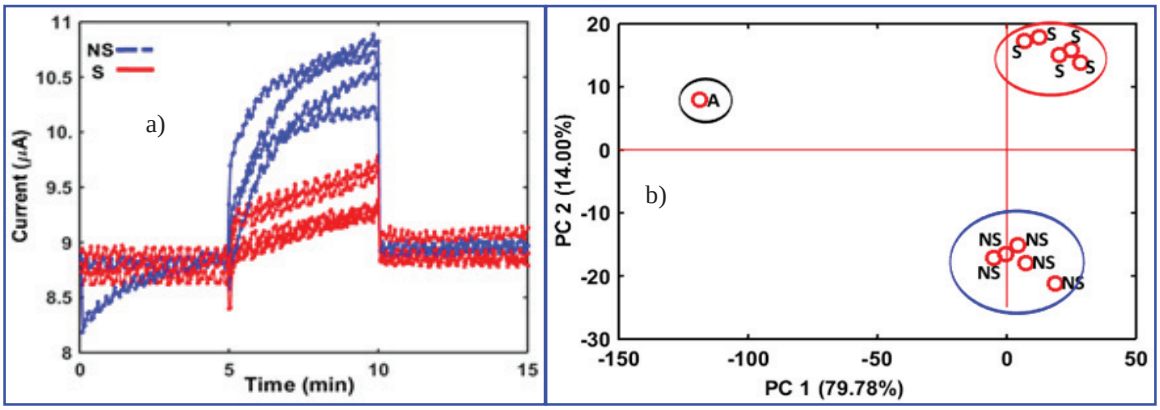

Fig.4. a) Responses of the 4-methoxy-α-toluenethiol capped AuNPs sensor to the exhaled breath of the 5 smokers and 5 non-smokers volunteers; b) PCA plot showing excellent discrimination of exhaled breath samples of smokers, non-smokers, and ambient air.

4. Conclusion

A new technological approach that combines the advanced gas deposition technique for the fabrication of ultrapure monodispersed AuNPs and single step functionalization of the AuNPs with thiolated organic ligands, was demonstrated for gas sensing applications in the present study. The morphological and surface analysis of the sensing films demonstrated a high purity level. Sensors responses towards ambient air and exhaled breath samples of smokers and non-smokers showed characteristic responses for each study group. PCA analysis revealed the excellent discrimination potential between different samples achieved by the sensors array, which suggests the suitability of the developed sensors for breath analysis applications.

Acknowledgements

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