ROBUST ELECTROACTIVE SUBSTRATES BASED ON GOLD-NANOPARTICLE ARRAYS ELECTRODEPOSITED ON INDIUM TIN OXIDE FOR REPRODUCIBLE SURFACE ENHANCED RAMAN SPECTROSCOPY

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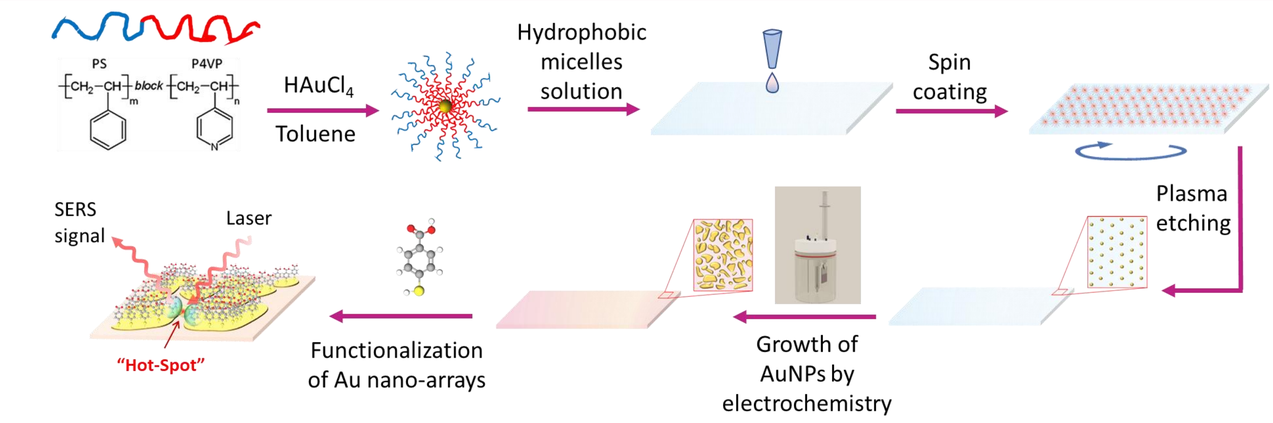
INTRODUCTION

Surface Enhanced Raman Spectroscopy (SERS) is a powerful technique by which Raman signals are amplified by several orders of magnitude, providing chemical information from the unique vibrational fingerprint of each molecule adsorbed on a rough metal surface. All these characteristics have made SERS to be a versatile technique and increasingly used in different fields such as material science, biology, biomedicine, forensic science among others. Nevertheless, is still challenging to obtain reproducible SERS measurements when working with solid substrates. To overcome these limitations, we have developed a substrate for reproducible SERS measurements by a simple two steps procedure. The first step involves deposition of gold nanoparticles (AuNPs) on a conductive and transparent indium-tin oxide (ITO) glass substrate by block-copolymer micellar lithography (BCML), obtaining a quasi-hexagonal array of nanoparticles homogeneously distributed on the substrate. In a second step, AuNPs are enlarged by electrodeposition of gold, under the application of a chemical pulse. In this way, particles become bigger and in consequence, smaller interparticle distances that favors the creation of hot-spots, responsible for the Raman signal enhancement. These electroactive substrates, besides being an improved SERS tool, can be used to study electroactive molecules, opening up new opportunities for better understanding electrochemical reaction mechanisms in biochemistry, simultaneously allowing the in-situ monitoring.

PREPARATION OF SUBSTRATES BY BCML AND ELECTROCHEMISTRY



Preparation of substrates involves two simple steps:

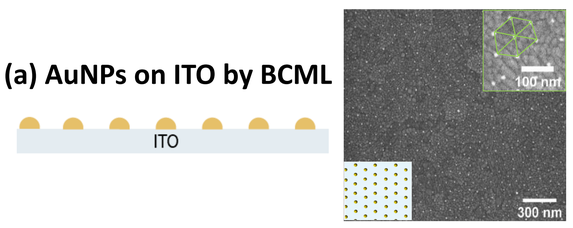
- Block copolymer micellar lithography on ITO glass substrate, corresponding to the first fourth steps in the scheme, ending with a quasihexagonal distribution of AuNPs on the ITO substrate.
- A second step involves electrodeposition of gold on top of the AuNPs by the application of an electrochemical pulse.

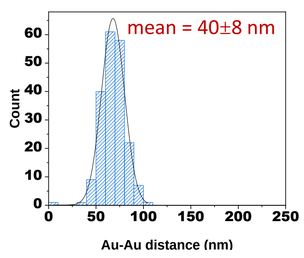
The developed substrate is then functionalized with a 1mM solution of ethanol, with the molecule of interest, through the thiol-gold interaction, for 24h.

CHARACTERIZATION OF SUBSTRATES

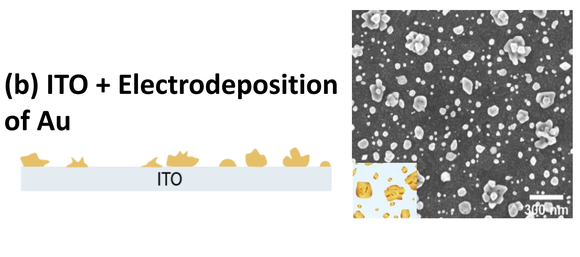
1 INTERPARTICLE DISTANCES: Scanning Electron Microscopy

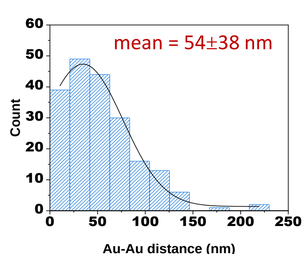
(a) AuNPs on ITO by BCML



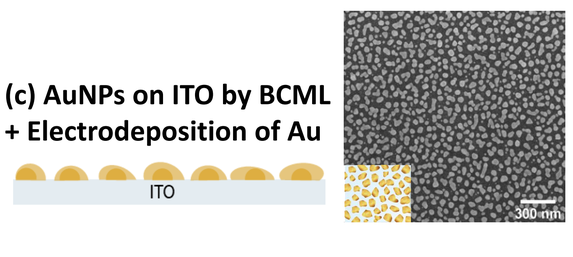


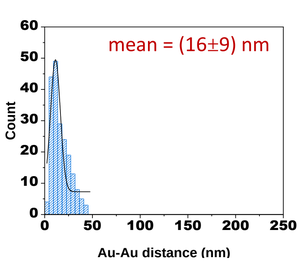
(b) ITO + Electrodeposition of Au





(c) AuNPs on ITO by BCML + Electrodeposition of Au





Schematic representation of the gold particles on top of the ITO substrate, with three different strategies.

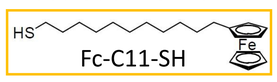
The middle column represent SEM images, where particle size and distribution can be observed.

Histograms, on the right, represent the interparticle distance between gold particles.

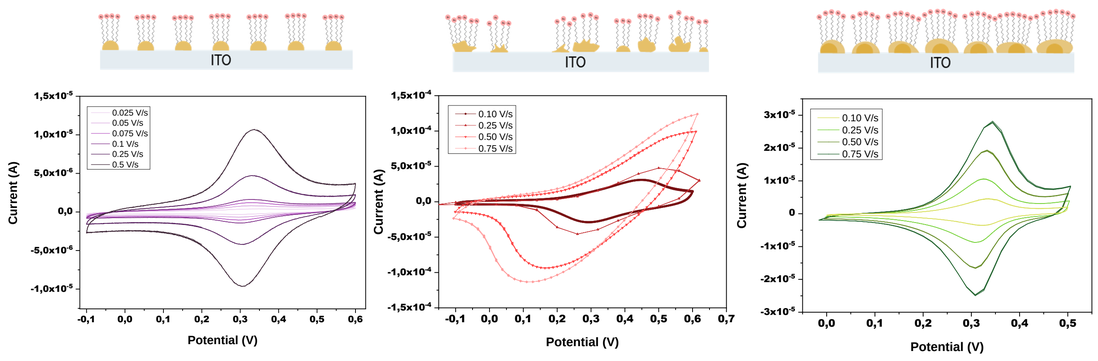
The substrate that we have developed, in the last row, shows an homogeneous distribution of gold particles together with smaller distances, which will be one of the reasons of SERS enhancement intensity.

2 ELECTROACTIVE CHARACTERIZATION: Cyclic Voltammetry

Electroactive marker



(a) AuNPs on ITO by BCML | **(b) ITO + Electrodeposition of Au** | **(c) AuNPs on ITO by BCML + Electrodeposition of Au**

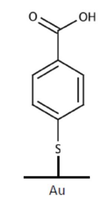


These experiments were carried out with an electroactive model molecule, to study the conductivity of the substrate after the electrodeposition step. Cyclic voltammetry curves demonstrate that the substrates we have developed (c) keep their conductivity and can be used to study electroactive molecules that switch between two states.

Linear dependency of current vs scan rate have been observed demonstrating that molecules are covalently anchored to the gold and are stable with increasing scan rate, except for substrate (b) that cyclic voltammogram shifts indicating that molecules are detaching from gold, and are not stable.

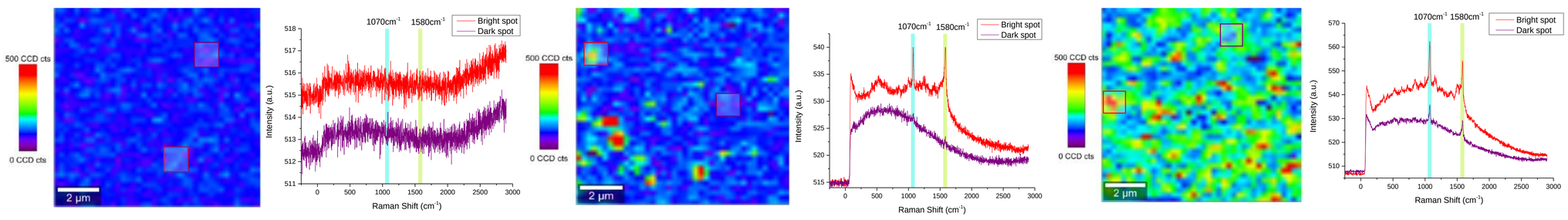
SURFACE ENHANCED RAMAN SPECTROSCOPY (SERS)

Raman Tag



4-MBA molecule

(a) AuNPs on ITO by BCML | **(b) ITO + Electrodeposition of Au** | **(c) AuNPs on ITO by BCML + Electrodeposition of Au**



Raman maps and spectra from the highlighted areas of each substrate, functionalized with the 4-MBA molecule and using a 633nm laser. The results show that the designed conductive substrate (c) presents hot-spots homogeneous distributed along the whole surface, a perfect tool to trigger electrochemical surface reactions. This opens up new opportunities for a better understanding of the electrochemical reaction mechanisms in biochemistry, simultaneously allowing the in-situ monitoring.

SIMPLE
LOW COST
CONDUCTIVE
REPRODUCIBLE
HOMOGENEOUS

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