



Surface enhanced Raman scattering improvement of gold triangular nanoprisms by a gold reflective underlayer for chemical sensing

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ABSTRACT

We report on an improvement way of the SERS signal of Au triangular nanoprisms for a highly sensitive detection of chemical molecules. This improvement is obtained by a simple addition of a gold reflective layer under Au nanoprisms. Using the same Au triangular nanoprisms obtained by nanosphere lithography, we studied experimentally the thickness effect of this gold underlayer on the SERS intensity of the triangular nanoprisms. We demonstrated that this SERS intensity increased with the thickness of the gold reflective underlayer, and this is due to the increment of the Au underlayer reflectivity. Thus, we showed that the metallic reflective underlayer has an important key for SERS enhancement. Indeed, enhancement factors of 10^8 were found for the most important thickness of the gold underlayer.

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1. Introduction

Since these last years, the fabrication of Surface Enhanced Raman Scattering (SERS) substrates having high enhancement factors (EF) is one of the most important works in this domain. Indeed, the SERS sensitivity is strongly dependent on the optical properties of the SERS active surface (electromagnetic field [1]). Thus, a critical point of SERS is to finely control the surface properties and the nanostructure geometries in order to achieve high, stable and reproducible enhancement factors [2,3]. Several lithographic techniques, which allow to tune the size, shape, and the organization of nanostructures, exist to fabricate the SERS substrates like X-ray Interference Lithography (XIL) [4], Nanoimprint Lithography (NIL) [5–7], NanoSphere Lithography (NSL) [8–13], Deep UV lithography [14], and Electron Beam Lithography (EBL) [15–19]. In addition, structures with metallic multilayers can improve SERS signal such as a three-layer SERS substrate consisting of an Ag film over Ag-clad colloidal Au submonolayer developed by Mulvaney et al. [20]. This SERS substrate has reached an EF of 7×10^4 . Other groups have studied Au nanostructures on Au or Ag underlayer

and they demonstrated larger EFs than those obtained in the absence of metallic underlayer [17,19,21]. Pérez-Mayen et al. have also showed SERS substrates based on star-like gold nanoparticles, which are deposited on silicon substrates or gold underlayer coated on silicon substrates, where the highest EFs (up to 10^{12}) are obtained with the presence of the gold underlayer [22]. However, the explanation of these higher EFs in presence of metallic underlayer is not very well-understood, and the thickness effect of this metallic underlayer was little studied at our knowledge. In this paper, we present a simple way to improve the SERS signal of gold triangular nanoprisms, which consists of a gold reflective underlayer under the gold nanoprisms. The thickness effect of this gold underlayer on the sensitivity of Au triangular nanoprism SERS substrates is investigated. To do that, we used the NSL technique to realize gold triangular nanoprisms, because NSL is a simple, low cost and versatile fabrication tool. Then, we used gold underlayers with 3 different thicknesses.

2. Experimental details

2.1. SERS substrate fabrication

The fabrication process of Au triangular nanoprisms on gold underlayer is as follows: (i) cleaning of the glass substrate, (ii) deposit of titanium and gold layers under vacuum, (iii) deposit

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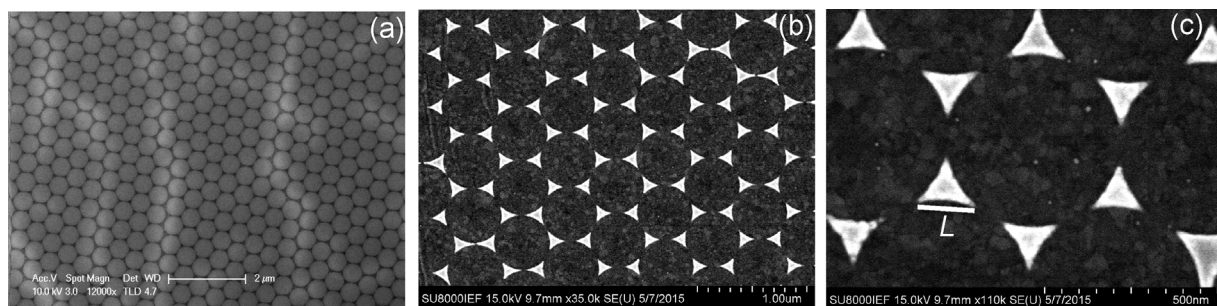


Fig. 1. SEM images: (a) polystyrene beads (diameter = 500 nm) deposited on gold underlayer (film), (b) Au triangular nanoprisms obtained by NSL associated to a lift-off process, and (c) zoom of triangular nanoprisms: $L \sim 150$ nm.

of colloidal beads of polystyrene on the gold underlayer, (iv) second Au layer deposition by evaporation under vacuum, (vi) lift-off process.

Firstly, the following protocol: ethanol, acetone, and Piranha solution ((3:1) $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ 30%), is used to clean the glass substrates. Then, a 2 nm titanium layer, which is used as adhesion layer, and a gold underlayer (film) are evaporated by Electron Beam Evaporation (EBE). Three underlayer thicknesses (T_{ul}) were studied 30 nm, 50 nm and 100 nm. Then, the aqueous colloidal bead suspensions (bead diameter of 500 nm, purchased from Polysciences GmbH) were further diluted in a mixture of ethanol and deionised water and drop coated. Then, these colloidal beads were spread over the gold underlayer and left until the solvent was completely evaporated [23] (Fig. 1(a)). The substrates were placed in a position inclined of $\sim 10^\circ$ to further facilitate the large scale formation of close packed single layer periodic particle arrays, through attractive capillary forces and convective transport during solvent evaporation. Next, a second gold layer of 60 nm is deposited by EBE, and triangular nanoprisms were obtained after a lift-off process in acetone. On Fig. 1(b) and (c), SEM images of Au triangular nanoprisms obtained by NSL are displayed. These nanoprisms exhibit good definition with an average length L of 150 nm. The samples reveal also good uniformity of 0.2 mm^2 . These parameters are very important for industrial applications of SERS.

2.2. Thiophenol functionalization on SERS substrates

Thiophenol molecules are used in order to study the effect of the underlayer thickness on the sensitivity of these SERS substrates. The functionalization protocol is divided into four steps: (i) preparation of a 0.1 mM solution of thiophenol in ethanol, (ii) dipping the sample in the solution during 2 h, (iii) washing thoroughly with pure ethanol, (iv) drying with nitrogen. On the other hand, the thiophenol concentration used for the Raman experiments in solution is 1 M.

2.3. Optical characterization

An XploRA spectrophotometer from Horiba Scientific is used for the Raman measurements. The acquisition time was fixed to 30 s. Two excitation wavelengths ($\lambda_{exc} = 660 \text{ nm}$ and $\lambda_{exc} = 785 \text{ nm}$) were used for all experiments with a power of 2.7 mW and 3.5 mW, respectively. The laser was focused on the substrate using a microscope objective ($\times 100$, N.A. = 0.9). The same objective was used to collect the Raman signal from the SERS substrates in a backscattering configuration. This spectrophotometer has a spectral resolution under 4 cm^{-1} . In addition, for classical Raman measurements in solution, a macro-objective with a focal length of 40 mm (N.A. = 0.18) and the 660 nm and 785 nm wavelengths were also used. All obtained spectra have been normalized by the acquisition time and the laser power so they can be compared. In

addition, the same spectrophotometer is used for the extinction spectrum in order to determinate the surface plasmon resonance of gold nanoprisms.

3. Results and discussion

Firstly, the surface plasmon resonance of gold triangular nanoprisms was measured, and we found a plasmon resonance at $\lambda_{plasmon} = 812 \text{ nm}$ (see Fig. 2). Then, Au nanoprisms were functionalized with the thiophenol molecules following the protocol described in Section 2.2, and were characterized by SERS measurements. Fig. 3 represents the SERS spectra of Au triangular nanoprisms obtained for three different thicknesses of the gold underlayer at two excitation wavelengths: (a) $\lambda_{exc} = 660 \text{ nm}$ and (b) $\lambda_{exc} = 785 \text{ nm}$. Thus, characteristic Raman shifts of thiophenol molecules [24] are well-observed. Fig. 4(a) displays the reflectivity of Au underlayer versus the excitation wavelength, which is obtained by numerical simulations using the Rigorous Coupled-Wave Analysis (RCWA) method. In these RCWA simulations, the incident light is normal to the gold surface, similar to our experimental SERS measurements. Fig. 4(b) represents the SERS intensity as function of the reflectivity for two characteristic Raman shifts.

Previously, we have studied and compared gold nanostructures with and without gold underlayer in order to observe the effect of this metallic underlayer. A same behavior for these two distinct geometries (nanodiscs and nanolines) was found, which is an enhancement of the SERS signal with the presence of the gold underlayer [25]. For our nanoprisms, we think that an identical behavior is observed as previously demonstrated with two different geometries. On Fig. 3, the effect of the underlayer thickness

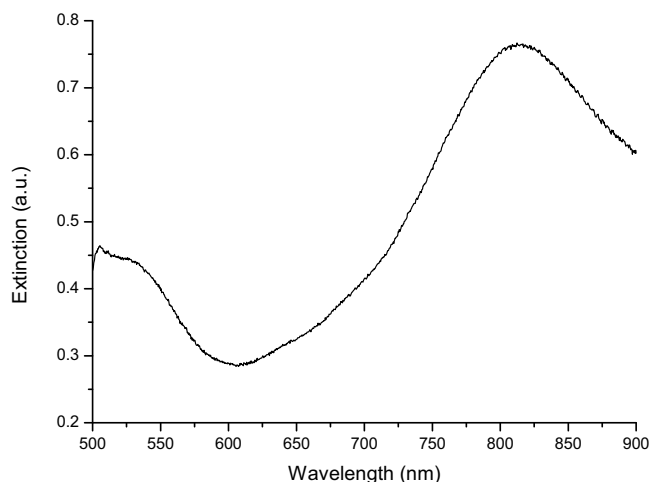


Fig. 2. Extinction spectrum of gold nanoprisms with the following dimensions: $L \sim 150$ nm and a height of 60 nm, and $\lambda_{plasmon} = 812 \text{ nm}$.

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