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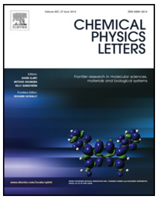

# Bare and protected sputtered-noble-metal films for surface-enhanced Raman spectroscopy

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ABSTRACT

Sputtered silver and gold films with different surface morphologies have been prepared and coated with a benzenethiol self-assembled monolayer. Rough noble metal films showed strong Raman features assigned to adsorbed benzenethiol molecules upon irradiation over a wide energy range in the visible spectrum, which disclosed the occurrence of a significant surface-enhanced Raman scattering with maximal enhancement factors as high as $6 \times 10^6$. In addition, the adsorption of ethanethiol onto silver surfaces hinders their corrosion over days while preserving mostly intact enhancement properties of naked silver. This study may be applied to develop stable and efficient metalized probes for tip-enhanced Raman spectroscopy.

## 1. Introduction

Surface-enhanced Raman spectroscopy (SERS) has become established as an extremely sensitive technique for chemical analysis in various disciplines, such as art [1], chemical warfare [2], biology [3] and biomedicine [4]. For instance, it has been recently used for detection of DNA hybridization and discrimination of mutations [5], the imaging of cancer cells and their photothermal therapy [6]. The originality of SERS resides in the use of noble metal nanostructures with distinct optical properties and SERS-efficiencies depending on their size, shape and dielectric surrounding medium [7], allowing for the detection of a vast range of organic and inorganic species. The enhancement of the Raman signal derives from an electromagnetic mechanism, mainly due to the excitation of localized surface plasmon resonances (LSPRs) associated with the metal nanostructures, and chemical mechanisms involving molecular resonances, metal-molecule charge transfers or non-resonant phenomena [8].

Noble metal nanostructures are usually produced using top-down or chemical synthetic strategies. Silver (Ag) and gold (Au) colloidal nanoparticles (NPs) are commonly synthesized as SERS-active nanostructures with well-controlled morphologies by means of the citrate reduction or the polyol process, where a chemical agent reduces the dissolved $Ag^+$ ($Au^+$) ions to Ag (Au) atoms, which grow into small clusters and finally nanostructures [7]. Polymers or surfactants are employed to stabilize these NPs in solution, but these protective wrapping prevent any chemical enhancement of the Raman signal. The top-down approach consists in the use of lithographic methods, such as the electron beam lithography [9], to manufacture nanostructured platforms but it is generally time-consuming, costly and the resolution is often limited to ~50 nm. Alternatively, physical deposition techniques such as thermal evaporation [10], pulsed laser deposition [11] and sputtering [12] have been proposed to prepare SERS-active nanostructured metal substrates.

Hereafter, we describe the morphology and plasmonic properties of cheap sputtered Ag and Au metal SERS platforms for molecular detection. In particular, the SER enhancement factor (EF) of these metalized substrates will be quantified using benzenethiol (BT) molecules adsorbed on their surface as probes. A strategy to limit the corrosion of Ag films will be also discussed.

## 2. Experimental

### 2.1. Sample preparation

Thin (~170 μm) borosilicate glass coverslips were selected as substrates. Prior to any metallization, every glass slide was carefully cleaned following a three-step procedure involving successive 5 min sonication (Fisherbrand FB11201, 37 kHz, 100% of the maximal power) in acetone (≥99.9% purity, Sigma–Aldrich), absolute

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ethanol (99.9% purity, Sigma–Aldrich) and Milli-Q water. Clean glass coverslips were coated with a 10 nm-mass-thickness silver (Ag) or gold (Au) layer by means of a sputtering system (Q300TD, Quorum Technologies) equipped with two quartz microbalances and a flat rotation stage. Rough Ag-coated samples (**S1**, **S3**, **S5** and **S6**) were prepared using a 20 mA current under $10^{-2}$ mbar Ar atmosphere (99.999% purity), with a stage rotation speed at 70% of the maximal value allowed. Rough Au-coated samples (**S2** and **S4**) were produced on a still rotation stage using a 10 mA current under $10^{-1}$ mbar Ar atmosphere. Smooth silver-coated (50 mA, $3.10^{-3}$ mbar Ar, 100% of the maximal stage rotation speed) and gold-coated (20 mA, $5.10^{-3}$ mbar Ar, 100% of the maximal stage rotation speed) samples were also prepared in order to serve as reference. Samples **S3** and **S4** were immersed during 18 h in a 5 mM ethanolic BT solution (98% purity, Fluka) to allow for their specific functionalization and the formation of a self-assembled monolayer (SAM) of BT. Similarly, samples **S5** and **S6** were immersed during 18 h in a 5 mM ethanolic solution of ethanethiol ET (97% purity, Aldrich) to create a molecular carpet onto the Ag surface. Samples **S3**–**S6** were subsequently rinsed with ethanol (99.9% purity, Sigma-Aldrich) to remove the excess BT (or ET) and dried in air. Finally, 20 $\mu$L of a $10^{-4}$ M ethanolic solution of Brilliant Cresyl Blue (BCB, Fluka) was spin-coated onto **S6** following a four step procedure composed of a 1-min sedimentation, a 30 s rotation with 400 rounds $\text{min}^{-1}$ speed, a 30 s rotation with 800 rounds $\text{min}^{-1}$ speed and a 30 s rotation with 1600 rounds $\text{min}^{-1}$ speed. The rotating acceleration was always set to 400 rounds $\text{min}^{-1}$ $\text{s}^{-1}$.

### 2.2. *Experimental setups*

Atomic force microscopy (AFM) was undertaken in tapping mode using a Bioscope II (Bruker) AFM instrument endowed with a commercial highly-doped silicon tip (Nanosensors PPP-NCST). Visible-infrared microabsorption measurements were carried out over the 430–950 nm spectral range using a tailor-made experimental setup already described elsewhere [13]. Raman measurements were performed in backscattering geometry using a commercial LabRAM HR 800 (Horiba scientific) confocal Raman spectrometer, equipped with motorized xyz stages, a 600 grooves/mm grating, a 50× short-working-distance objective with a numerical aperture (NA) of 0.75. Irradiation wavelengths (752.0, 647.0, 568.2, 514.5, 488.0 and 457.9 nm) corresponded to the emission lines of $\text{Ar}^+$ and $\text{Kr}^+$ lasers. In order to avoid sample damage, the laser power was set between 7 and 150 $\mu$W depending on the excitation wavelength. A DuoScan™ system composed of two galvanometric mirrors could be additionally activated to realize a micrometric (5 $\mu$m × 5 $\mu$m) laser scanning and hamper thermally induced sample degradation or metal annealing.

## 3. Results and discussion

Figure 1 shows typical topographic tapping mode AFM images of sputtered rough Ag (**S1**) and Au (**S2**) substrates. It reveals the presence of oblate spheroidal NPs homogeneously dispersed on the borosilicate glass surface. For **S1** (Fig. 1A), the mean size of Ag NPs is estimated to be $\sim$40 nm × 40 nm × 10 nm, with 5–15 nm high particles. This film corresponds to a monolayer of Ag NPs, with a few additional NPs on top of them. For **S2** (Fig. 1B), the size of Au NPs is $\sim$23 nm × 23 nm × 4 nm, with 2–6 nm high protrusions. This observation suggests the presence of a bilayer of small Au NPs. Therefore, almost all Ag NPs are in direct contact with the borosilicate glass coverslip while many Au NPs are sitting on their underlying counterparts and immersed in air as sole dielectric medium.

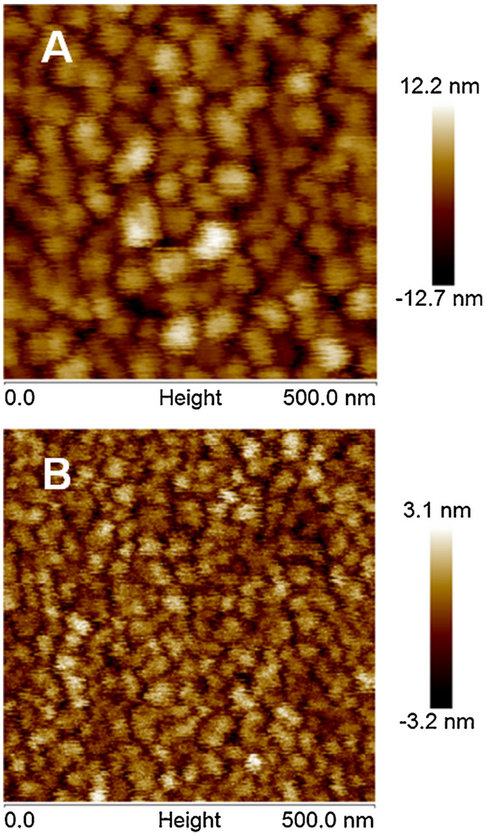

**Figure 1.** Typical topographic tapping mode AFM image of a 500 nm × 500 nm region in **S1** (A) and **S2** (B).

**S1** and **S2** metal films with distinct surface morphologies can be typified by their absorbance property in the visible-near-infrared spectral range (Fig. 2). They exhibit broad absorption bands centred at $\sim$565 and $\sim$725 nm, respectively, and covering nearly the whole visible spectrum. These strong absorptions are related to the nanostructuration of the metal films, which are able to sustain LSPRs in this energy range. The absorption band at $\lambda_{\text{max}} \approx 565$ nm for **S1** is congruent with the expected value for a 10 nm Ag island monolayer deposited on $\text{SiO}_2$, since $\lambda_{\text{max}}$ has been found to redshift from 444 to 506 nm upon increasing the sputtered Ag film mass thickness from 0.6 to 5.7 nm [14]. Similarly, the absorption band at $\lambda_{\text{max}} \approx 725$ nm for **S2** matches well the value expected for Au films sputtered on glass substrates, considering the size of Au NPs in **S2** [12]. Note that the wavelength-dependent contribution of bulk gold and silver absorptions [15], assessed upon measuring the absorption of smooth reference Ag and Au metal films, was subtracted from the raw data in order to emphasize the plasmonic absorption in our 10 nm-thick films.

The absorption spectrum of the Ag film **S3** covered by a BT SAM is also plotted in Figure 2A. The adsorption of BT causes a redshift by $\sim$65 nm of the maximum of the LSPR ($\lambda_{\text{max}} \approx 630$ nm) with respect to the case of a bare Ag film like **S1**. As the strongest SERS enhancements are expected when the excitation wavelength is higher in energy than the spectral maximum of the LSPR extinction spectrum [2], Raman experiments were performed on **S3** under light irradiation in the visible spectral range, at 457.9, 488.0, 514.5 and 568.2 nm (Fig. 3A). The intense Raman peaks that can be discerned are assigned to BT vibration modes, such as the C—S stretching vibrations at 418 and 694 $\text{cm}^{-1}$ ($\nu_{7a}$ and $\nu_{6a}$), ring vibrations involving C—C stretches and C—H deformations at 999, 1023, 1074 and 1111 $\text{cm}^{-1}$ ($\nu_{12}$, $\nu_{18a}$, $\nu_1$ and $\nu_{6a}+\nu_{7a}$) and C=C stretching vibrations at 1574 and 1586 $\text{cm}^{-1}$ ($\nu_{8a}$ and $\nu_{8b}$) [16]. The S—H stretching vibration at $\sim$2550 $\text{cm}^{-1}$ cannot be distinguished, which indicates the absence of free BT molecules at the metal surface. The cleavage