

Supplementary Information:

Highly Crystalline ZnO film Decorated with Gold Nanospheres for PIERS Chemical Sensing

Grégory Barbillon,^{*a} Thomas Noblet^b and Christophe Humbert^b

^a EPF-Ecole d'Ingénieurs, 3 bis rue Lakanal, 92330 Sceaux, France.

^b Université Paris-Saclay, CNRS, Institut de Chimie Physique, UMR 8000, 91405 Orsay, France.

* Corresponding author's email: gregory.barbillon@epf.fr

Fabrication of PIERS substrates

- ZnO films were grown on *c*-plane sapphire (*c*-Al₂O₃) substrates by pulsed laser deposition from a 99.9995% pure sintered ZnO target using a KrF excimer laser. After deposition, an annealing at 600°C in O₂ was carried out.
- Gold nanoparticles were synthesized according to the Turkevich method where 1 mL of 8.5×10⁻⁴ M trisodium citrate (Na₃C₆H₅O₇) was added to a boiling aqueous (Millipore water, resistivity = 18 MOhm cm) solution of 20 mL HAuCl₄ (2.5×10⁻⁴ M) under vigorous agitation during 30 minutes (all chemicals were purchased from Sigma-Aldrich). The average nanoparticle diameter is 30 nm.
- 30 µL of AuNP solution was deposited on the ZnO film, and air dried.

Irradiation of PIERS substrates with UV light

The UV-irradiation was made with a short wave UV quartz pencil lamp (Edmund Optics, 254 nm, 4.89 eV, nominal output of 4.5 mW/cm²). The irradiation was carried out at 2.4 cm above the sample.

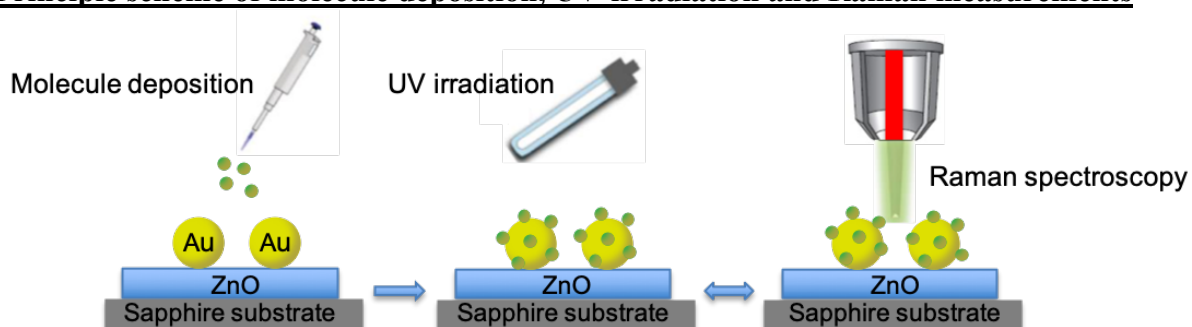
Structural and optical characterizations

- For the structural characterization of PIERS substrates, X-ray diffraction (XRD) measurements were performed with a Siemens D5000 XRD system in reflection mode with a quartz monochromator (Cu Kα₁ = 1.54056 Å).
- For all the extinction spectra of ZnO films and PIERS substrates, a Cary-5000 spectrophotometer (Agilent) in transmission configuration was used.
- For all the Raman spectra with PIERS substrates, a Labram spectrophotometer (Horiba Scientific) was used with a spectral resolution of 1 cm⁻¹. The excitation wavelength of 633 nm was employed with a power of 1 mW. The acquisition time was fixed to 5s. The laser was focused on the substrate using a microscope objective (×100, N.A. = 0.9), and the Raman signal was collected by the same objective in a backscattering configuration.

Functionalization of PIERS substrates with thiophenol molecules

The thiophenol solution was prepared by dissolving thiophenol powder in ethanol to a concentration of 1 mM. Then, the solution was diluted with ethanol to 1 µM. Then, 30 µL of thiophenol was deposited on the PIERS substrate and allowed to air dry.

Principle scheme of molecule deposition, UV-irradiation and Raman measurements



Probing procedure for evaluation of the reproducibility

Relative standard deviations (RSDs) for Raman intensity were obtained on basis of Raman spectra recorded for 10 different positions on the PIERS substrate where have been deposited the gold nanoparticles. For each position on the substrate, the sample is irradiated with the UV lamp (located at 2.4 cm above sample) followed by Raman measurement during which the UV lamp is switched off (see above the principle scheme). We repeated this for each step of 5 min up to 30 min. During all these Raman measurements, the positions of the sample and the UV lamp were fixed, and during UV-irradiation, the laser source for Raman measurements ($\lambda = 633$ nm) is stopped by a shutter.

SEM picture with a higher magnification of the ZnO/AuNPs substrate

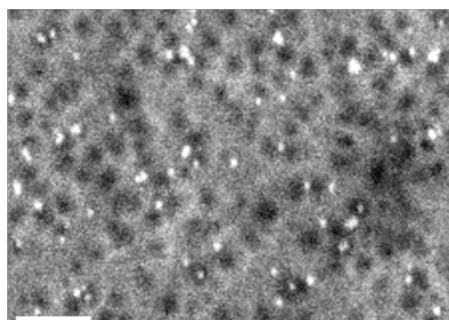


Figure S11 : SEM picture of the porous ZnO film with gold nanoparticles (scale bar = 250 nm) where we observed AuNPs on the top of the ZnO film and also in the pores of this latter (« black zones »). The AuNPs are in contact with the ZnO film.

Optical characterization by extinction spectroscopy of gold nanospheres

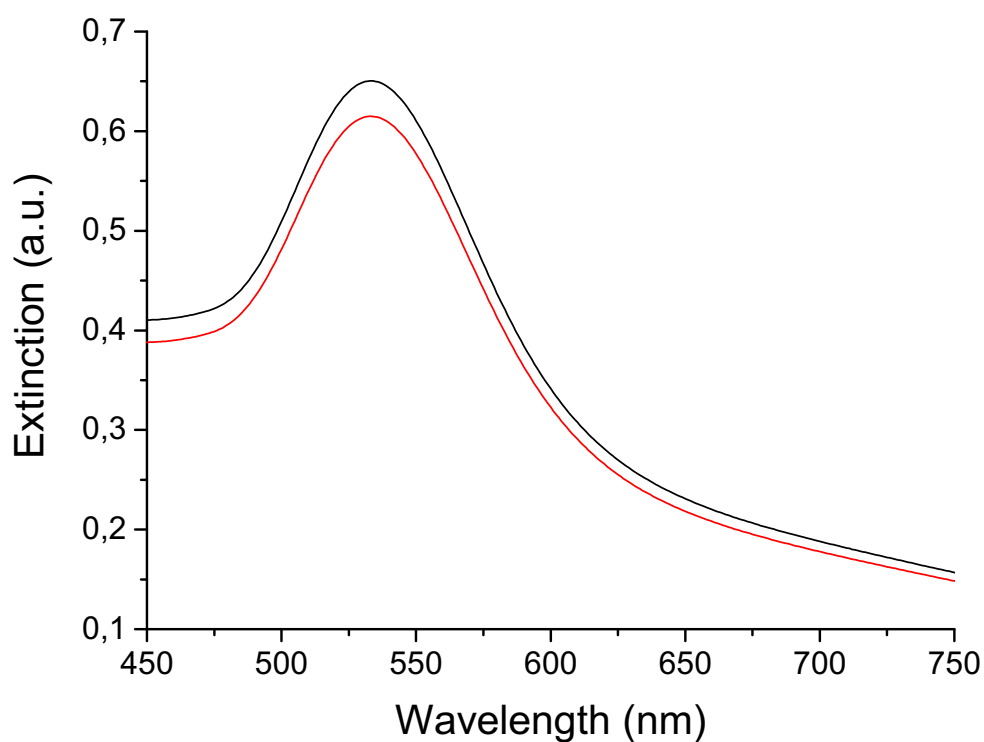


Figure SI2 : Extinction spectra of AuNPs (diameter = 30 nm) in solution before (in red) and after UV-irradiation of 30 min (in black).

Raman characterization for the AuNPs on sapphire substrate with thiophenol molecules (without ZnO film)

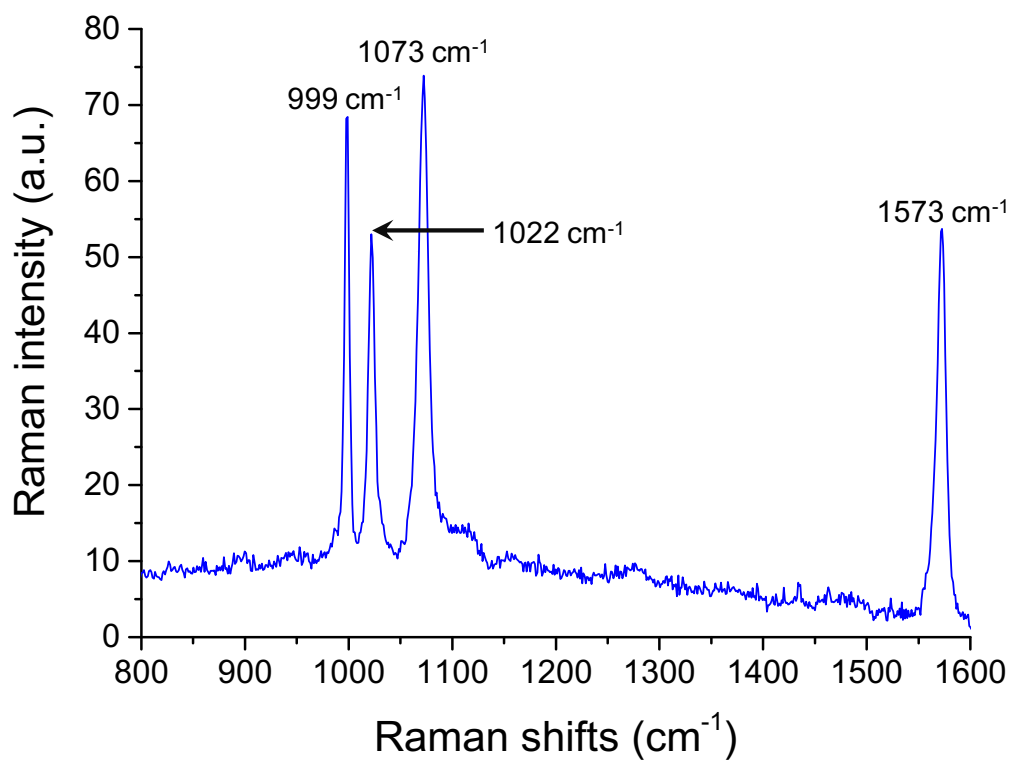


Figure SI3 : SERS spectrum of AuNPs + thiophenol on sapphire substrate (without ZnO film).

Raman characterization for the ZnO film with thiophenol molecules (without AuNPs)

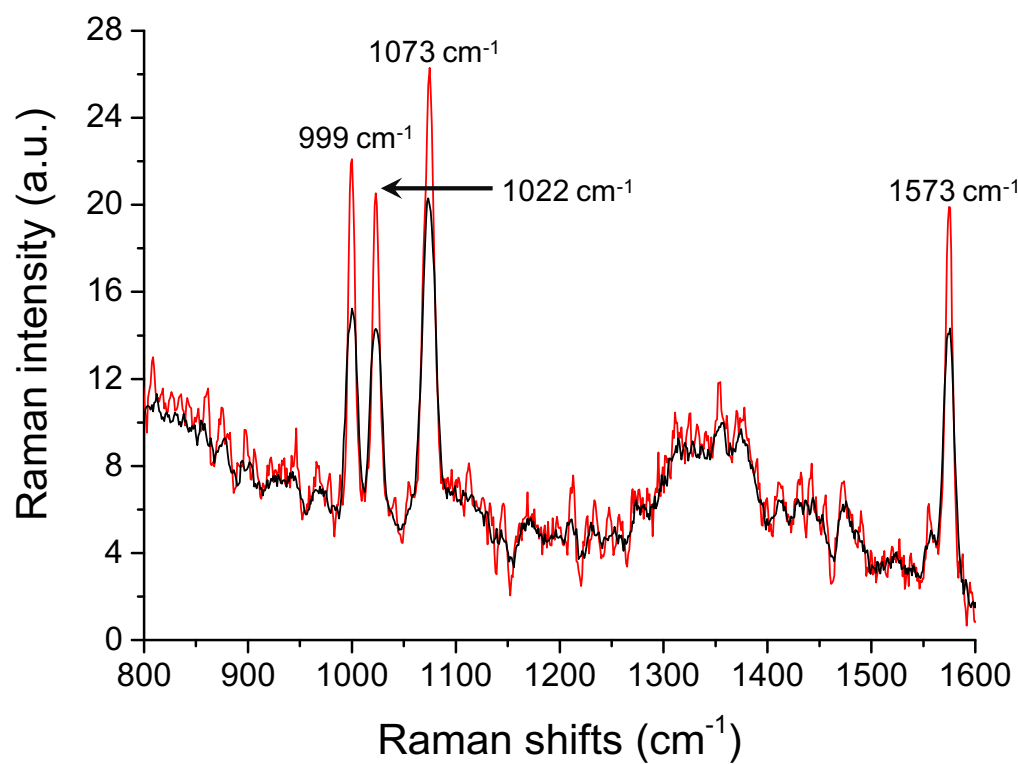


Figure SI4 : SERS spectra of ZnO film + thiophenol (without AuNPs) before (in black) and after UV-irradiation of 30 min (in red).