

## Ag-modified Au nanocavity SERS substrates: Supplementary Information

Emiliano Cortés<sup>1</sup>, Nicolás G. Tognalli<sup>2</sup>, Alejandro Fainstein<sup>2</sup>, María E. Vela<sup>1</sup>, and Roberto C. Salvarezza<sup>1,†</sup>

<sup>1</sup>*Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA),  
Universidad Nacional de La Plata - CONICET, Sucursal 4 Casilla de Correo 16 (1900) La Plata, Argentina and*

<sup>2</sup>*Centro Atómico Bariloche and Instituto Balseiro,  
Comisión Nacional de Energía Atómica,  
8400 S. C. de Bariloche, Río Negro, Argentina*

### STRIPPING/DEPOSITION OF ULTRATHIN AG FILMS ON AU CAVITIES

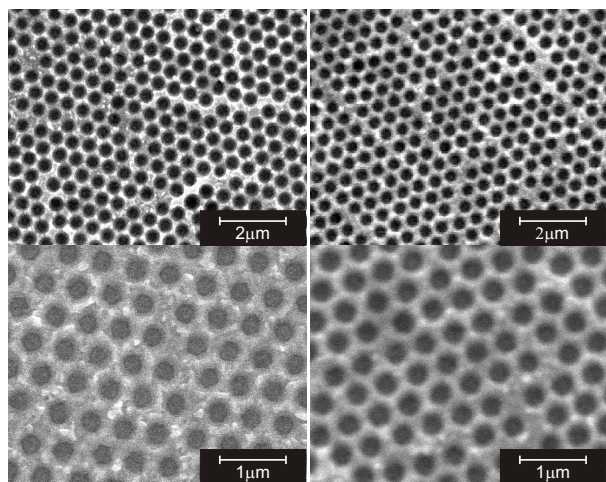


FIG. 1: SEM images of gold nanocavity arrays before (left side) and after (right side) 10 deposition/stripping Ag cycles.

We have tested that stripping/deposition cycles do not result in substrate damage by using SEM and voltammetric data. In Fig. 1 we show that the patterned substrate remains unaltered after the stripping and deposition procedure, without any evidence of structural changes. On the other hand, voltammetry is also a sensitive method to evaluate changes in real surface area and also in the preferred orientation of Au substrates. [1, 2] Figure 2 shows that the voltammetric features related to the Au double layer and the oxide/reduction AuO monolayer remain unchanged after the Ag stripping/deposition cycles. These results agree with our previous observations about the stripping of Ag from Au substrates in 40 nm sized cavities where no significant changes can

be observed. [3]

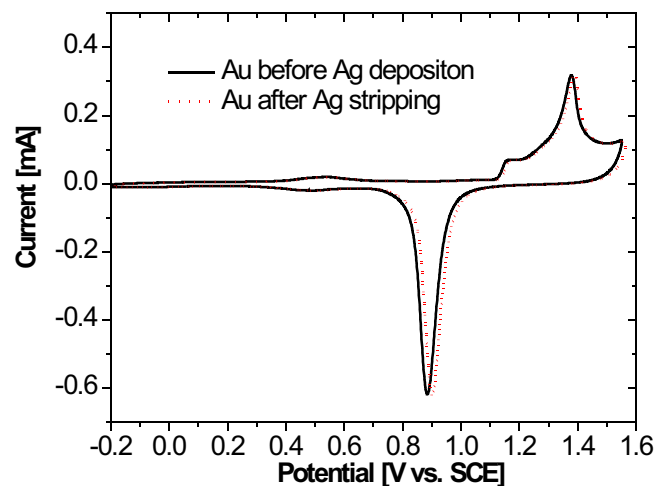


FIG. 2: Cyclic voltammograms at  $v = 0.1$  V/s of gold nanocavity substrates in 0.5 M  $\text{H}_2\text{SO}_4$  before (black) and after (dotted red line) deposition and stripping of 100 MLs of silver. The same substrate has been modified and stripped three times with silver before taking the data shown in this figure.

[†] e-mail: robsalva@inifta.unlp.edu.ar

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[2] Angerstein-Kozłowska, H.; Conway, B. E.; Hamelin, A.; Stoicoviciu, L., *Journal of Electroanalytical Chemistry* **1987**, 228, (1-2), 429-453.

[3] P.C. Dos Santos Claro, M. Fonticelli, G. Bentez, O. Azaróni, P.L. Schilardi, N.B. Luque, E. Leiva y R.C. Salvarezza, *Nanotechnology*, **2006**, 17, 3428-3435.