# Ag@TiO$_2$ nanogranular films by gas phase synthesis as hybrid SERS platforms

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# Supporting Information

SI 1: Short times stability of nanogranular Ag@TiO$_2$

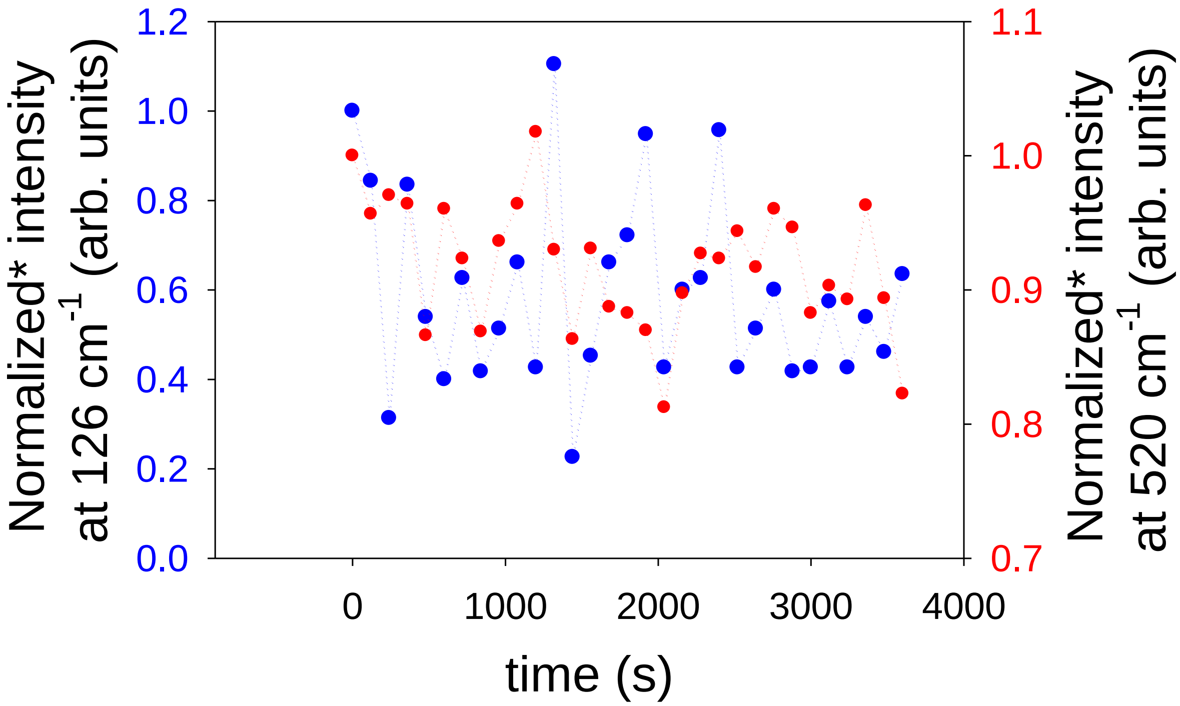

**Fig. SI1:** Intensity of the Ag@TiO$_2$ band at 126 cm$^{-1}$ (left axis, in blue) and intensity of the silicon main band at 520 cm$^{-1}$ (right axis, in red) as function of time.

In order to test the Ag@TiO$_2$ nanogranular film stability under a laser beam we have tested them under multiple measurements in the same spot region. **Fig. SI1** reports 30 measurements sent every 120s. The spectra have been all obtained using the same experimental conditions (Laser Power 5%, Acquisition time 30s, the sample used was 60 nm thick).

Even the Ag@TiO$_2$ signal oscillates between 0.2 and 1.2, the signal of the Silicon substrate underneath is really stable (between 0.8 and 1) in line with classic plasmonic SERS substrate (doi:10.3390/nano7060142). This also indicates a regular thickness of the nanogranular film.

[*: the normalization has been done on the first measurement done at time zero.]

## SI 2: Long Time stability nanogranular Ag@$TiO_2$ in sensing Methylene Blue

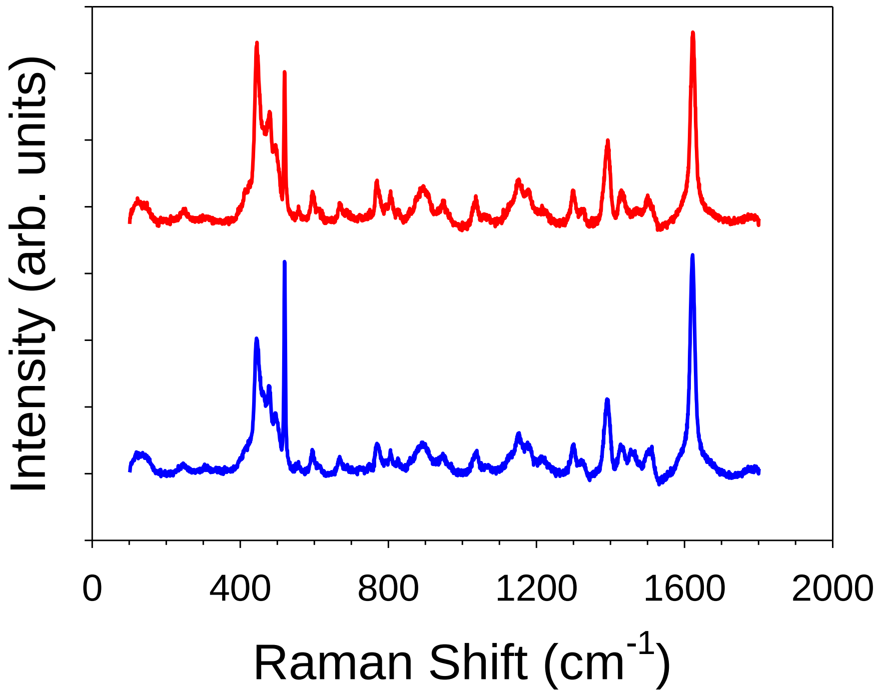

**Fig. SI2:** Raman Spectra of Ag@$TiO_2$ samples with a thickness of 60nm; sensing Methylene Blue $10^{-5}$ M after drying of 10 µl droplet of an aqueous solution directly after the fabrication (in blue) and after 3 months of sample storage at room conditions (in red).
The spectra have been obtained using the same experimental conditions (Laser Power 5%, Acquisition time 30s, same methylene blue $10^{-5}$ M aqueous solution).

| | Intensity (arb. Units) |
|---|---|
| As deposited | 15500 ± 3700 |
| After 3 months | 14900 ± 4200 |

**Table SI1:** Averaged Intensity of the Methylene Blue band at 1621 cm$^{-1}$ for the Ag@$TiO_2$ 60nm sample right after the deposition and after 3 months.

Both **Fig. SI2** and **Table SI1** present a comparison between the Raman enhancement results for the sample measured right after the deposition and a sample produced in the same deposition batch but after 2 months of storage in room conditions (T = 20°C; P = 1atm; not directly exposed to air and sun light).
**Fig. SI2** compares two selected Raman spectra. It is possible to appreciate that the main features (of the Ag@$TiO_2$ substrate, the Silicon underneath and the MB) are not modified by the time and by the storage. In **Table SI2** is reported the averaged intensity (of 20 different spectra) of the measurements done. There is a little decrement in the averaged value and a very little increment of the error, but this variation stays inside the experimental vaiations.

## SI 3: Main text Fig.3, complete data serie

The following graph shows all the data serie regarding Fig 3 in the main test, where, for clariry, we have reported just the reference spectrum on Si (blue) and the 120nm Ag@$TiO_2$ sample.

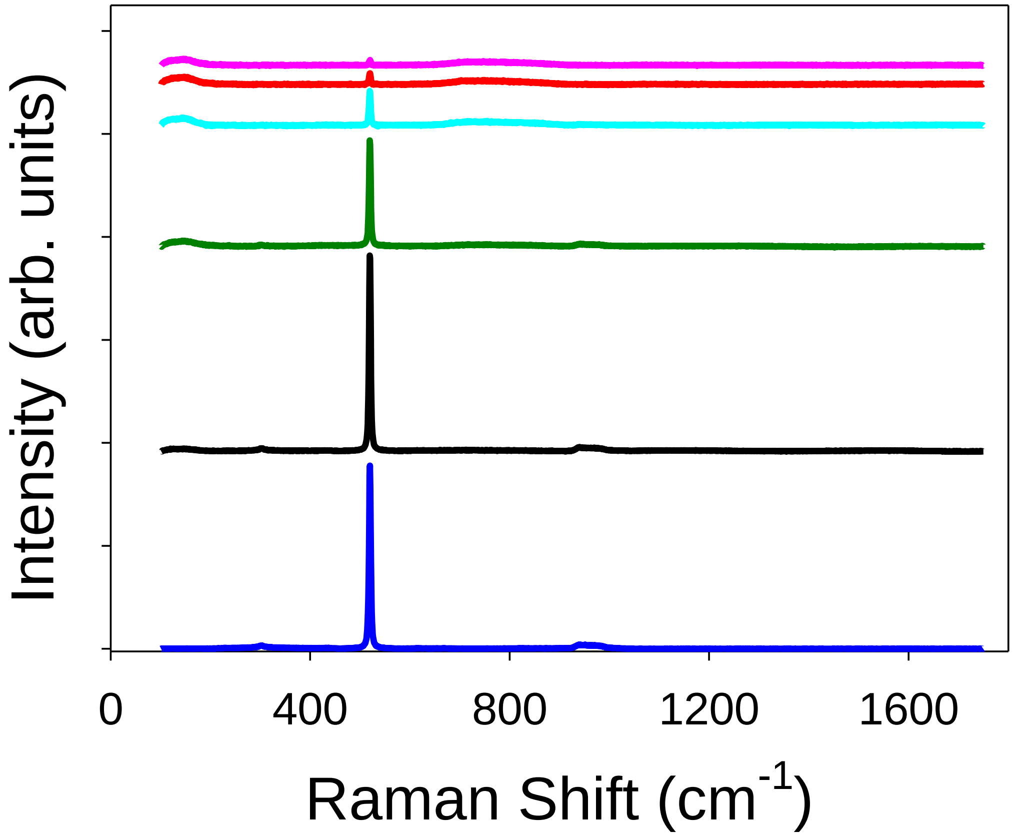

**Fig. SI3:** Raman Spectra of Ag@$TiO_2$ samples with a thickness of 30nm (black), 60nm (green), 90nm (light blue), 120nm (red), 150nm (purple) in comparison with a Si reference. All the spectra have been obtained under the same experimental conditions: Laser Power 5%, Acquisition time 30s.

SI 4: UV-vis

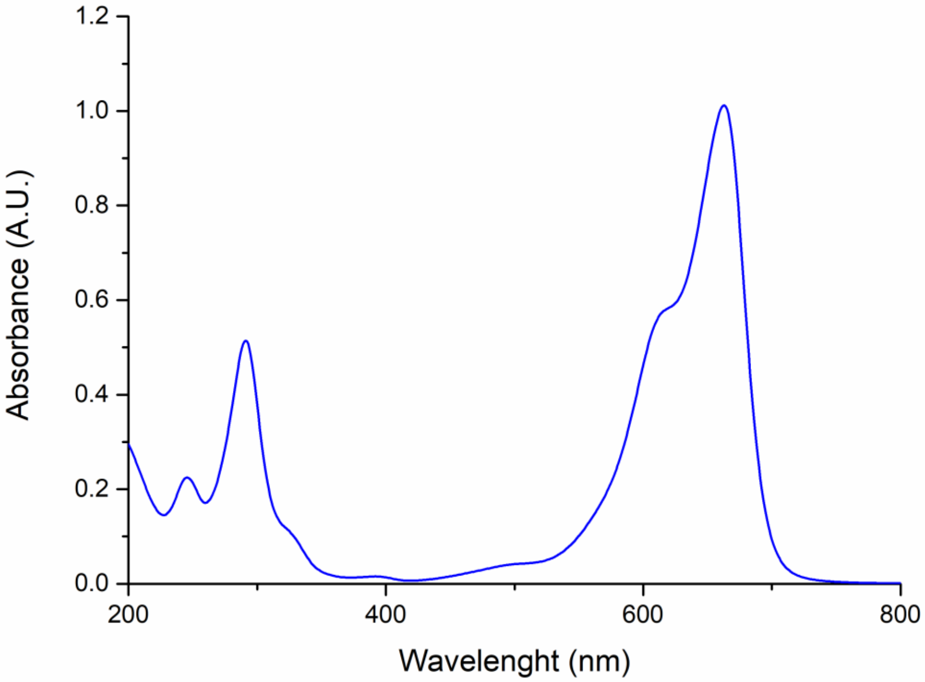

**Fig. SI4:** Absorbance spectrum of a 20 μM aqueous solution of Methylene Blue.

## SI 5: Enhancement Factor Calculations

This SI section shows the details of our calculations for obtainting a value of 1.6 $10^6$ of analytical enhancement factor. By considering our Ref [35] indicated in the main text (E. C. Le Ru, E. Blackie, M. Meyer and P. G. Etchegoin, J. Phys. Chem. C, 2007, 37, 13794-13803) the analytical enhancement factor may be calculated as follow:

$$AEF = \frac{I_{SERS}/c_{SERS}}{I_{RS}/c_{RS}}$$

Where $c_{RS}$ is analyte solution for non-SERS conditions with concentration which produces a Raman signal $I_{RS}$ and $c_{SERS}$ and $I_{SERS}$ are the same under SERS experimental conditions.
And the author indicates that in this case the spectra must be "*Under identical experimental conditions (laser wavelength, laser power, microscope objective or lenses, spectrometer, etc.), and for the same preparation conditions, the same analyte on a SERS substrate, with possibly different concentration ($c_{SERS}$), now gives a SERS signal $I_{SERS}$.* "

By inserting our results presented in the main text in the above mentioned formula, we get:

$$AEF = \frac{I_{SERS}/c_{SERS}}{I_{RS}/c_{RS}} = \frac{23000cps/10^{-9}M}{170cps/10^{-5}\,M} = 1.3\ \cdot\ 10^6$$