Supporting Information

Self-Organized Nanogratings for Large-Area Surface Plasmon Polariton Excitation and Surface-Enhanced Raman Spectroscopy Sensing

Matteo Barelli[1], Maria Caterina Giordano[1], Pietro Giuseppe Gucciardi[2], Francesco Buatier de Mongeot[1,*]

[1] Dipartimento di Fisica, Università di Genova, Via Dodecaneso 33, I-16146 Genova, Italy

[2] CNR IPCF Istituto per i Processi Chimico-Fisici, viale F. Stagno D'Alcontres 37, I-98156 Messina, Italy

* *To whom correspondence may be addressed:* buatier@fisica.unige.it

Fig. S1a shows the 2D self-correlation function of the self-organized glass nanograting AFM topography presented in Fig. 1a of the main manuscript, computed by means of Gwyddion software. The grating average periodicity λ is calculated by measuring the real space distance between the maximum and the secondary neighboring peaks in the 2D self-correlation line profile of Fig. S1b.

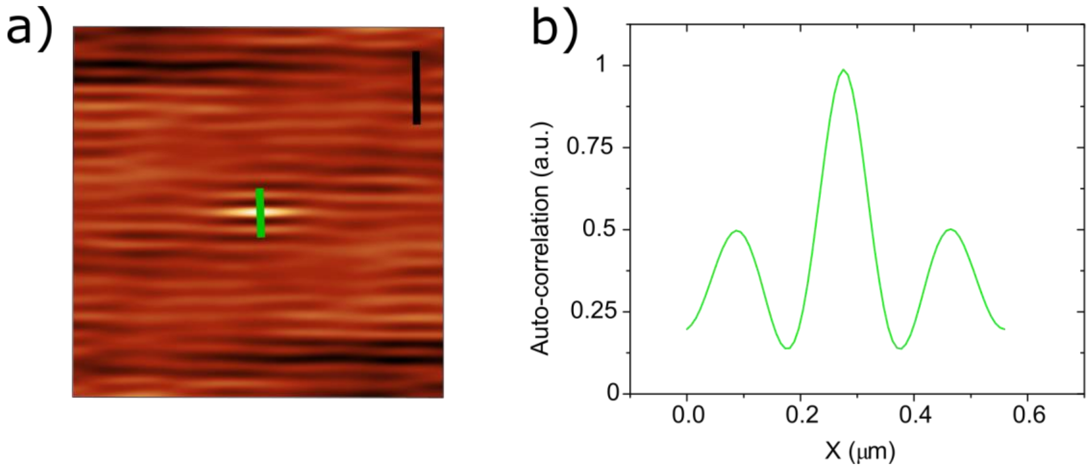
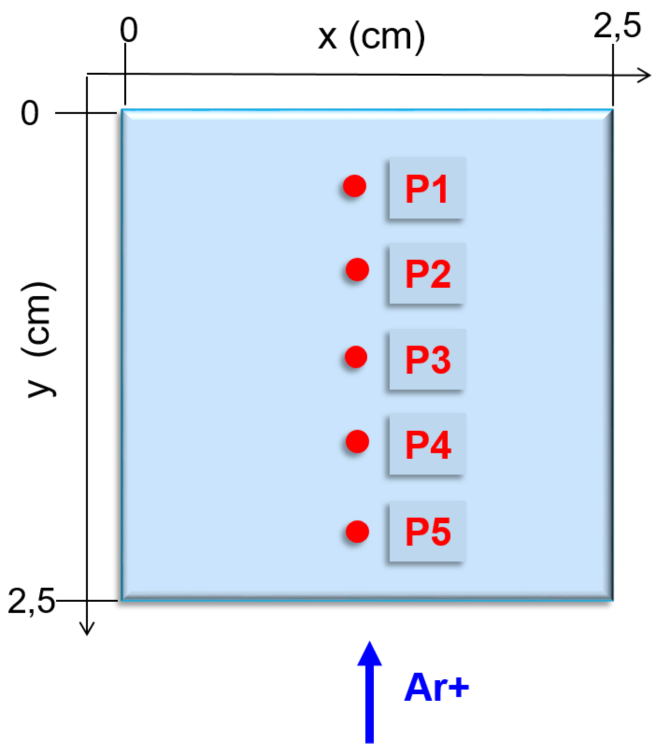


Figure S1 *– a) Self-correlation of the AFM topography shown in Fig. 1a of the main manuscript. The black scale bar corresponds to 800 nm. b) Self-correlation line profile corresponding to the green line in panel a).*

Fig. S2 shows the linear grating periodicity gradient as a function of sample position along the incident ion beam direction due to our engineered self-organized Ion Beam Sputtering fabrication process. The grating periodicity λ is measured by means of AMF microscopy through the 2D self-correlation of topographies as previously described.



Position (P)	Grating periodicity λ (nm)
P1 (x;y=12,5;5)	183 ± 3
P2 (x;y=12,5;10)	194 ± 3
P3 (x;y=12,5;15)	203 ± 3
P4 (x;y=12,5;20)	211 ± 3
P5 (x;y=12,5;25)	223 ± 3

Figure S2 *– A sketch of the sample: red dots indicate the coordinates of different AFM measurements, while the blue arrows indicate the incoming Argon ion beam direction (left panel). The corresponding measured grating periodicity λ is reported in the table (right panel).*

In Fig. SI 3 we demonstrate the long-range morphological properties of the self-organized Au/glass nano-rippled grating, thought the analysis of a large area 2D auto-correlation extracted from AFM topography measurements (Fig. S3a). Remarkably, in the self-correlation line profile of Fig. S3c (corresponding to the green line in Fig. S3b), which has been measured by moving more than 10 μm away from the origin of the auto-correlation map, the modulations at the characteristic period around 200 nm persist well visible. This ensures that the grating morphological coherence can spatially match the incoming photons transverse coherence length in our experimental conditions, as required for SPP coupling to occur.

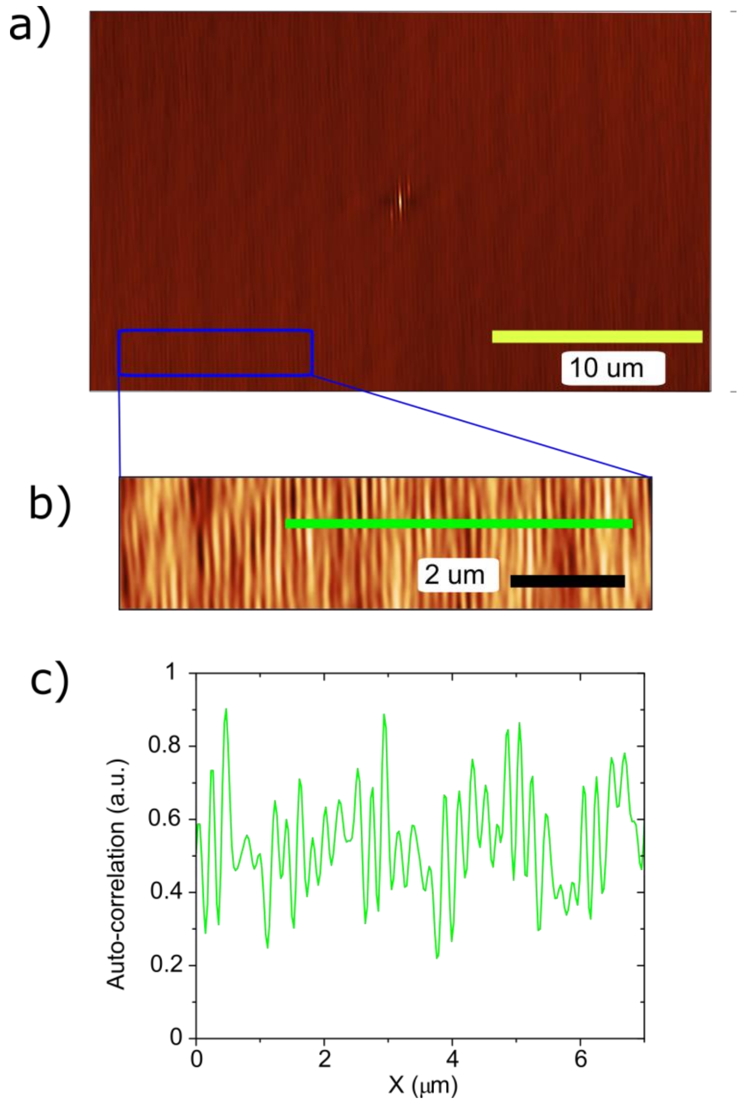


Figure S3 *–a) 2D auto-correlation of a AFM topography acquired on the Au/glass self-organized nanograting. b) Detail of panel a) highlighting a region several microns away from the central 2D auto-correlation maximum. c) Auto-correlation line profile corresponding to the green line in panel b).*

In Fig. S4 we show how the transmission properties of the nanowires (black lines) closely mimic those of a continuous gold film (colored lines) when the excitation polarization is parallel to their long axis, as expected. Here we use the model developed by Pascoe [1] to calculate the transmission of a gold film embedded between two dielectric layers (air and glass). As in the experiment, we assume a plane wave coming from the glass substrate side, at normal incidence. The refractive index of gold is taken from the data of Olmon et al. [2] for an evaporated film. The peak in the transmission at 530 nm is related to the behavior of the imaginary part of the refractive index of gold at the onset of the interband transitions, and it is not related with plasmon resonances.

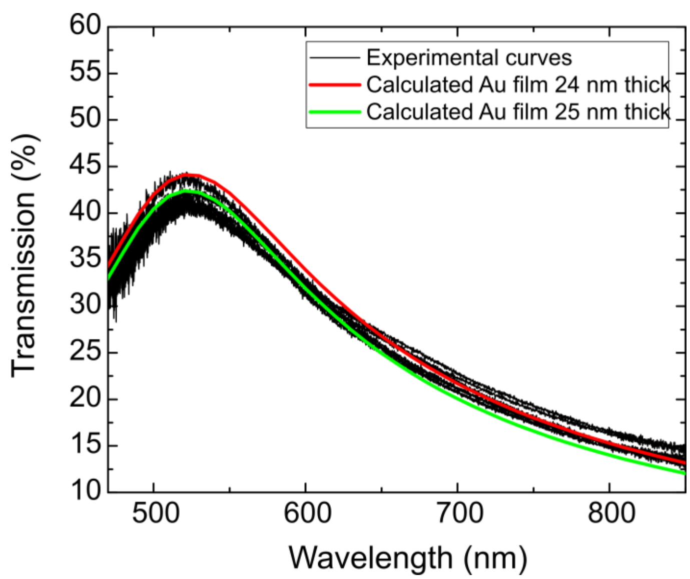


Figure S4: (*black lines) Transmission spectra acquired on the nanowires with polarization parallel to the long axis. Spectra are acquired on different points. (colored lines) transmission of a continuous gold film with thickness 24 (red) and 25 nm (green).*

In Fig. S5a we plot the SERS co-localized transmission measurements for the different grating periodicities considered in Fig. 5 of the main manuscript. The measurements are normalized to the spectrum of a bare flat glass. Extinction is computed from transmission as 1-T and plotted in

Fig. S5b after optical background is subtracted to isolate the plasmonic spectral fingerprint. Spectra are normalized to the most intense peak (yellow curve). The normalized plasmonic extinction values gain reported in Fig. 5e,f are extracted in correspondence of the pump laser frequencies, 638 and 785 nm respectively.

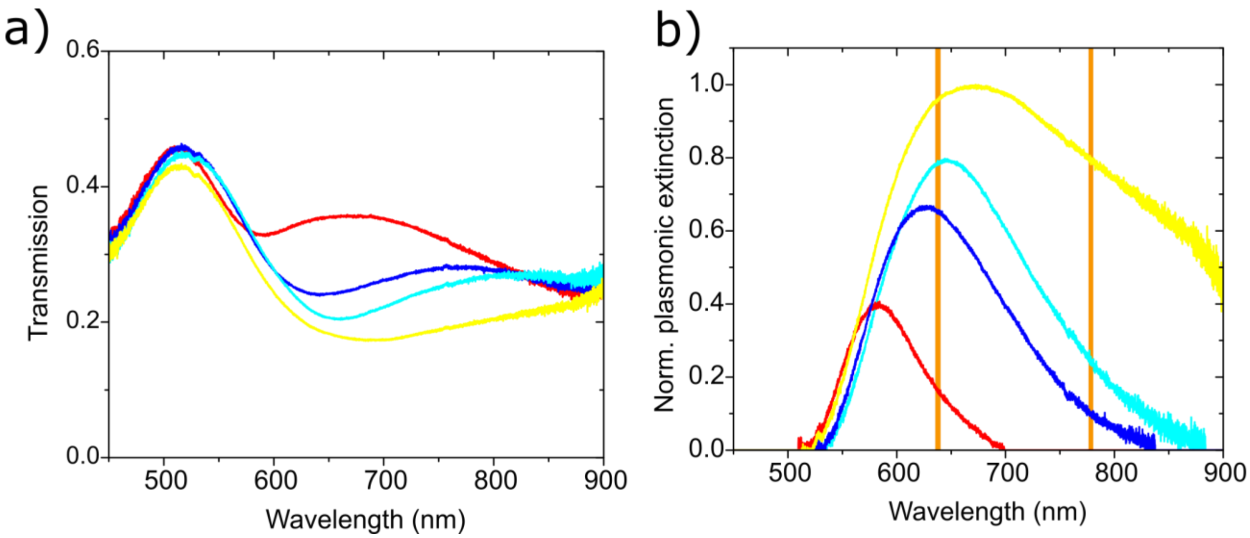


Figure S5 *– a) Transmission spectra colocalized with SERS measurements acquired at different sample coordinates corresponding to the following grating periodicities: 171 nm (red curve), 198 nm (blue curve), 211 nm (cyan curve), 226 nm (yellow curve). b) Extinction is computed from the transmission spectra of panel a) and the optical background is subtracted from the curves. Data is then normalized to the most intense peak. The two orange lines correspond to the wavelengths of the two pump lasers, 638 and 785 nm respectively.*

References

[1] Pascoe, K.J. Reflectivity and Transmissivity through Layered, Lossy Media: A User-Friendly Approach. https://pdfs.semanticscholar.org/6336/69e495b7b5d8309bc59cff5db041f8d799bc.pdf

[2] Olmon, R. L.; Slovick, B.; Johnson, T. W.; Shelton, D.; Oh, S. H.; Boreman, G. D. and Raschke M. B. Optical dielectric function of gold. Phys. Rev. B 86, 235147 (2012).