Extending Nanoscale Patterning with Multipolar Surface Plasmon Resonances

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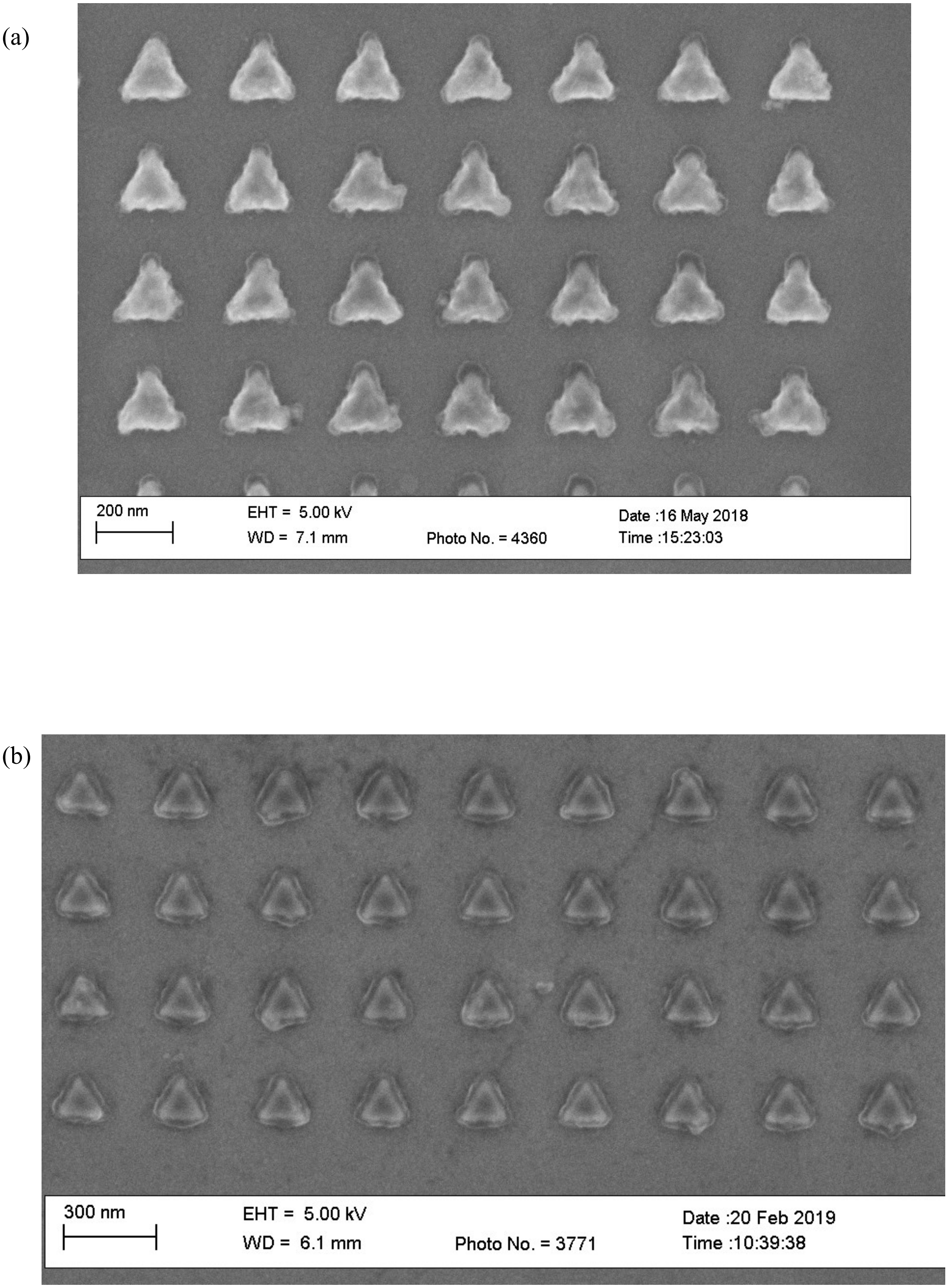
Figure SI1


(a)
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EHT = 5.00 kV
WD = 7.1 mm
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(b)
300 nm
EHT = 5.00 kV
WD = 6.1 mm
Photo No. = 3771
Date :20 Feb 2019
Time :10:39:38

Fig SI 1: (a) SEM image of a regular array of gold triangles (170 nm side length, height 50 nm, and grating constant 340 nm), after immersion in an aqueous solution of diazonium salt (3 mM) and optical exposure at 785 nm; (b) SEM image of a regular array of gold triangles (170 nm side length, height 50 nm, and grating constant 340 nm), after immersion in an aqueous solution of diazonium salt (3 mM) and optical exposure at 633 nm

Figure SI2:

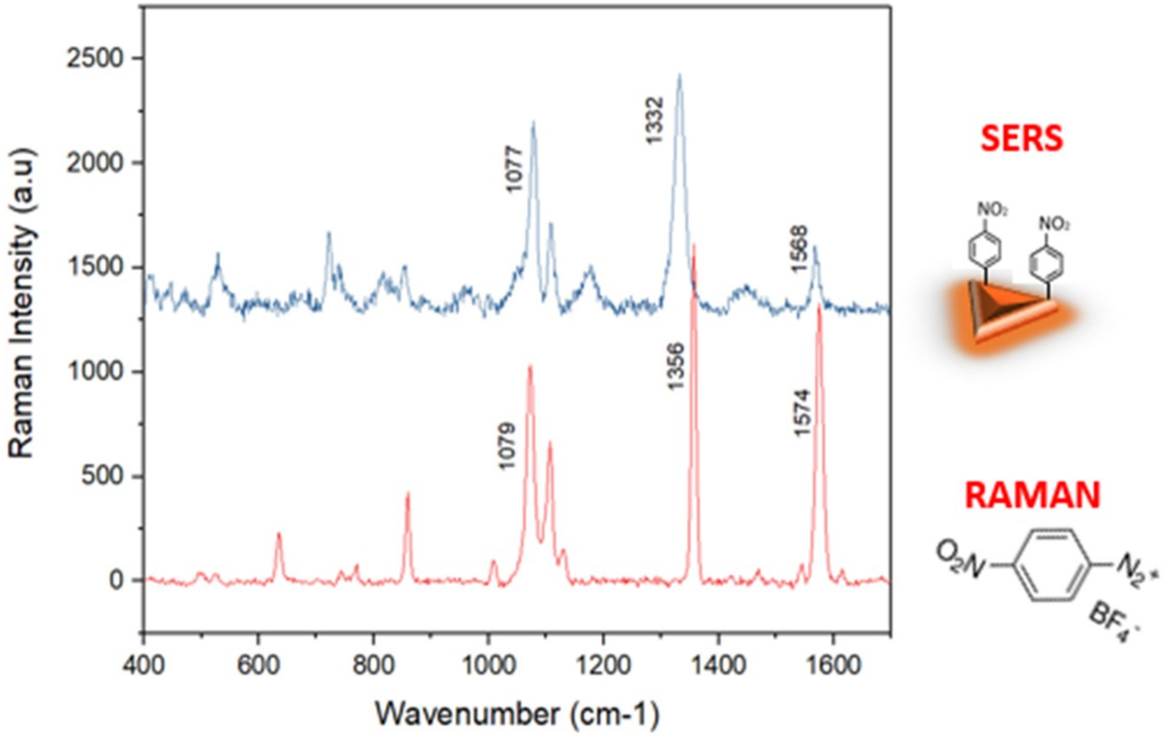


Fig. SI 2a The Raman and SERS experiments were carried out by using a Jobin-Yvon LABRAM HR 800 Raman micro spectrometer. The incident sources are a He–Ne laser (632.8 nm), and a laser diode (785 nm) focused on the sample, through a microscope equipped with a 100× objective (Olympus, NA #0.8). The Raman spectrum, displayed in Fig. SI1 (spectrum below), shows the signature of a powder of 4NBDT molecules, with the appearance of three main Raman bands in the range 500–2000 cm^{-1}. The most characteristic bands are related to the CH in-plane bending for mono- and para-substituted benzenes (coupled with the ring-N stretching mode) at around 1080 cm^{-1}, the symmetric NO_2 stretching at 1356 cm^{-1}, and the aromatic ring deformations at 1574 cm^{-1} (C==C stretching). The SERS spectrum (above), recorded after plasmon-induced grafting, looked very similar to those obtained with the powder, apart from small deviations in wavenumbers. We thus conclude that the organic layer is attributed to an aryl film derived from 4NBDT molecules.

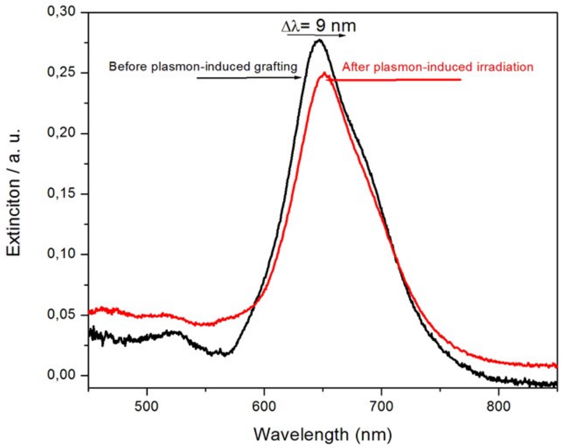
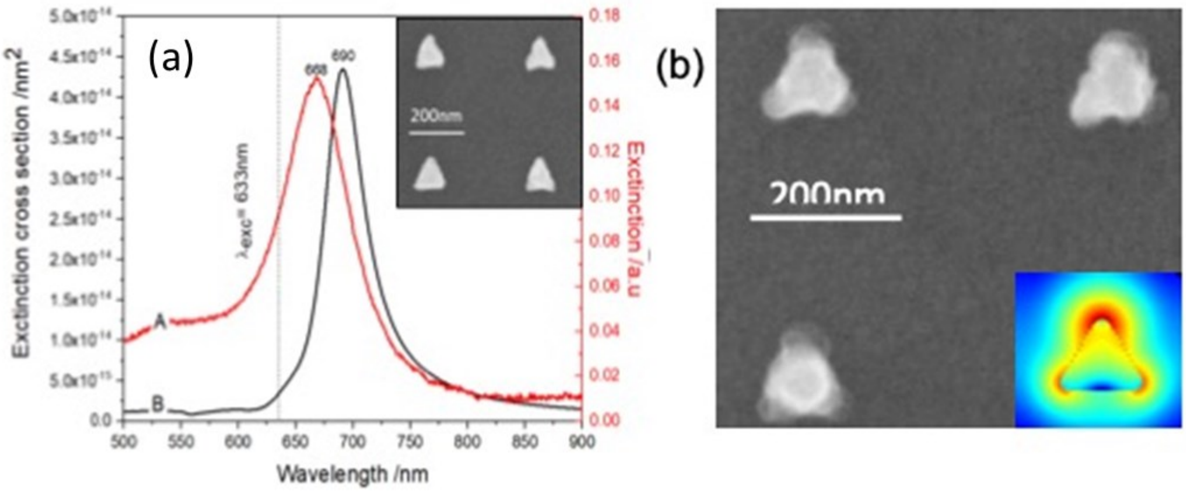


Fig. SI2 b: Extinction spectra of a regular array gold triangles (lateral size 100 nm, height 50 nm): (black) before irradiation; (red) after irradiation at 633 nm (close the dipolar mode) in presence of 4-nitrobenzenediazonium tetrafluoroborate.

Figure SI3



(a) (in red) Experimental extinction spectrum of equilateral triangles, with edge lengths of 90 nm, a thickness of 50 nm, and an inter-particle distance of 400 nm (center to center). The spectrum is recorded in water; (in black) Calculated extinction cross section of a target, with the same geometrical parameters, by the FDTD method. In inset: SEM image of the gold nanotriangles over a glass substrate covered by a thin layer of ITO; (b) SEM images of the triangles, after immersion in an aqueous solution of diazonium salt (3 mM) and optical exposure at 633 nm for a polarization along the Y axis. In inset: mapping of the intensity of the electric field, calculated by the FDTD method, for an incident light at 690 nm, and a polarization along the Y axis.

In addition, the illumination off LSP excitation didn't result in any aryl film grafting spatially resolved, evidencing the plasmon-induced mechanism in the process.

The Au structures were also irradiated in the UV region, in order to investigate the capability to generate electrons through inter-band transitions. However, we could not observe any spatially resolved grafting on the triangles. Although the UV excitation of the diazonium salts in water was reported to lead to aryl, those formed near the gold surface can attach to it, but without any selective spatial locations [1, 2, 3].

References

- [1] M Busson, A Berisha, C Combellas, F Kanoufi, J Pinson, Chemical Communications 47 (47), 12631-12633;
- [2] J. Canning, K. McCrudden, H. Maskill and B. Sexton, J. Chem. Soc., Perkin Trans., 1999, 2735–2740;
- [3] A. Mesnage, X. Lefèvre, P. Jégou, G. Deniau and S. Palacin, Langmuir, 2012, 28, 11767–11778.