Supplementary Material (ESI) for Chemical Communications

Supporting Information

Using plasmon heating of gold nanoparticles to generate local SER(R)S-active TiO_2 spots (on colloidal crystals)

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S1. Experimental details

The colloidal crystals were prepared as follows. Monodisperse PS nanospheres (diameters: 150±6 and 420 ± 10 nm) suspended in milliQ water (10% wt) were assembled as multilayered colloidal crystals on microscope glass slides either by sedimentation or by crystallization under capillary forces. [1] The glass substrates were previously UV-cleaned for 5 minutes to remove organic contaminants from the surface.

The 50 nm-thick TiO_2 layer was deposited in a Savannah 100 ALD flow reactor (Cambridge Nanotech Inc., MA), using TDMAT (tetrakis-dimethyl-amido titanium, Aldrich, Germany) as titanium source and water as oxygen source. The deposition temperature and pressure were respectively 90°C and 0.5 Torr. TDMAT (99.999%) and H_2O were evaporated from stainless steel reservoirs held respectively at 80°C and at room temperature, and led into the reactor through solenoid valves. Nitrogen was used as a precursor carrier and purge gas. The processing cycle consisted of a TDMAT pulse of 0.1 s, a 5 s purge pulse of N_2, a 0.1 s pulse of water vapour and 5 s pulse of N_2. The deposition rate was 0.0667 nm per cycle.

The gold nanoparticles were synthesized by the Turkevich's method [2] from $HAuCl_4$ and trisodium citrate (Sigma-Aldrich). Few microliters of Au NPs suspension were dropped onto the surface of the colloidal crystals. Upon drying, the Au NPs decorated the PS/TiO_2 surface forming microscopic aggregates which can be easily detected by optical inspection. The surface density of AuNPs aggregates depended on the concentration of the initial Au NPs suspension.

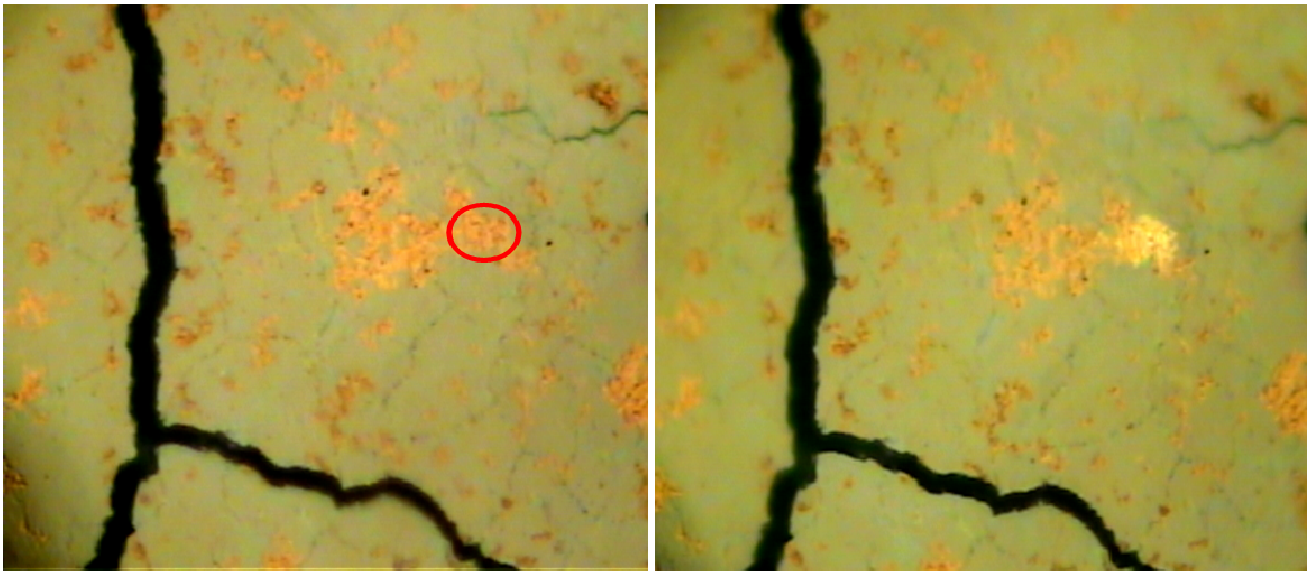
To generate anatase spots the colloidal substrates were set upon the motorized x-y stage (resolution: 0.1 μm, scanning range: 100x100 mm) of a high resolution Raman microscope (Horiba/Jobin-Yvon). The spots were obtained by focussing a He-Ne (λ=632.8 nm) laser through 100x (NA: 0.9) objective with different dwell time (*see* the text for further details) on some of the Au NPs aggregates. The power of the unfiltered laser radiation incident on the sample was about 4.5 mW. Raman spectra were acquired

using optical filters that allowed to attenuate the power of the laser to about 0.5 and 0.05 mW. The photocatalytic degradation experiment was performed by placing a drop of an aqueous solution containing 1pmol of methylene blue (MB, $C_{16}H_{18}N_3SCl$) onto an anatase spot which was visualized by an optical microscope. The adsorption of the MB on the anatase surface was checked by Raman spectroscopy (*see* the text for details). The photodegradation was carried out by irradiating the sample with a Philips UV lamp, that emits from 340-410 nm, with a peak maximum at 365 nm. The distance between the lamp and the sample was 1 cm. The sample was directly UV irradiated without moving the Raman stage, to ensure that all the Raman spectra were acquired on the same zone.

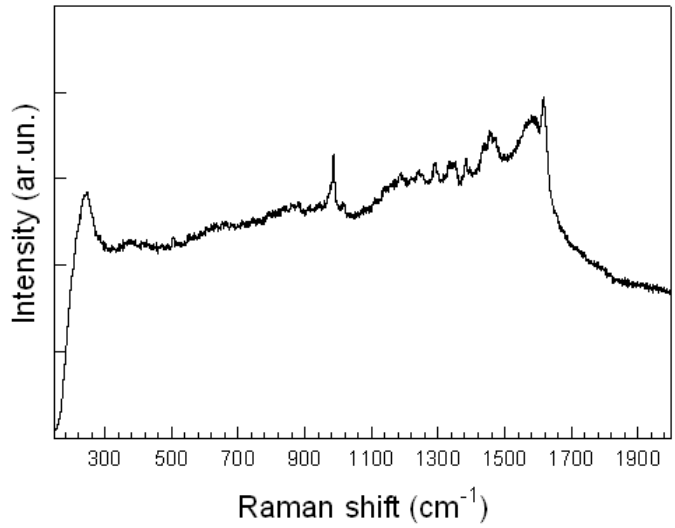
REFERENCES

[1] P. Jiang, J. F. Bertone, K. S. Hwang and V. L. Colvin, *Chem. Mater*., 1999, **11**, 2132; I. Alessandri, E. Bontempi, P. Bergese and L. E. Depero, in *Encyclopedia of Nanoscience and Nanotechnology 2nd edition,* H. S. Nalwa (editor), APS, in press.

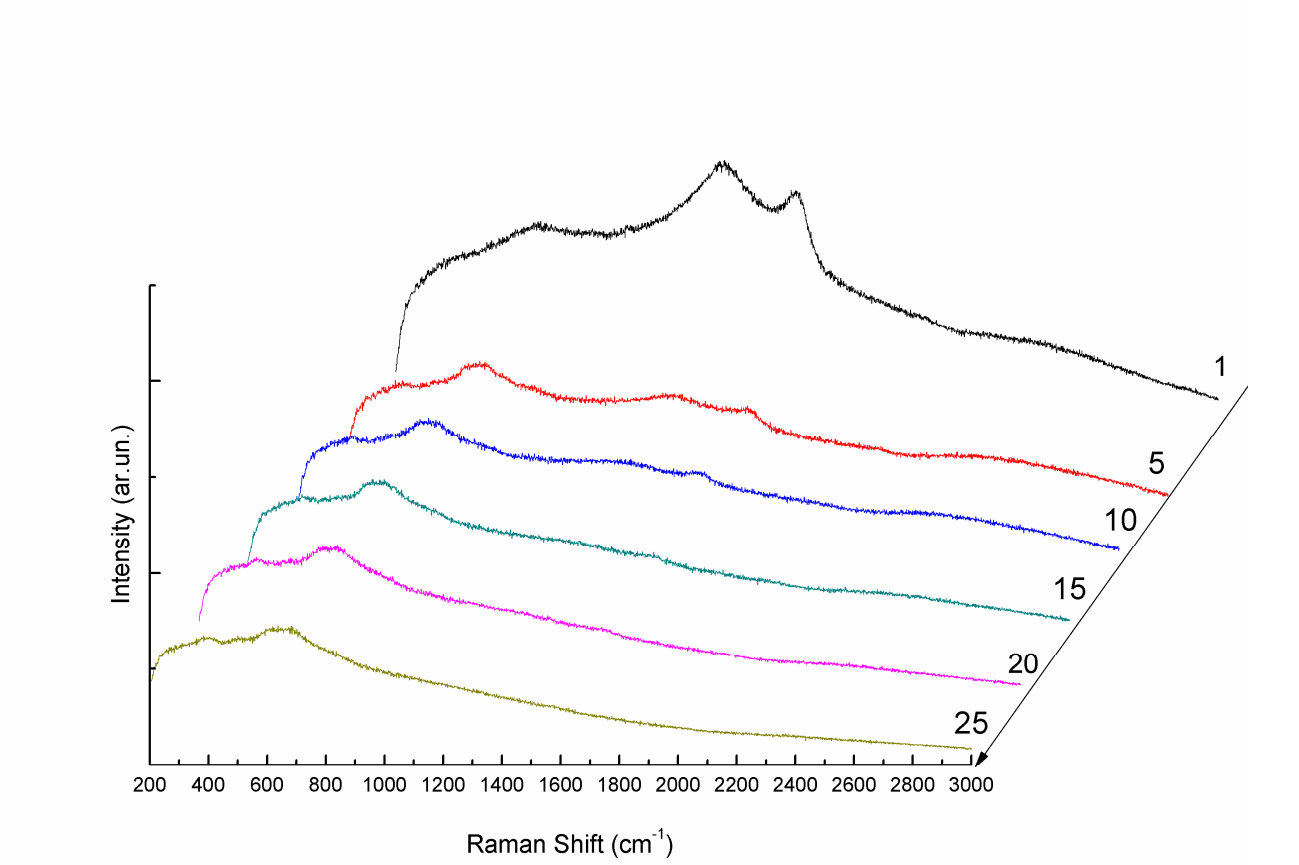
[2] J. Turkevich, P. C. Stevenson and J. Hillier, *Discuss. Faraday Soc.*, 1951, **11** 55.



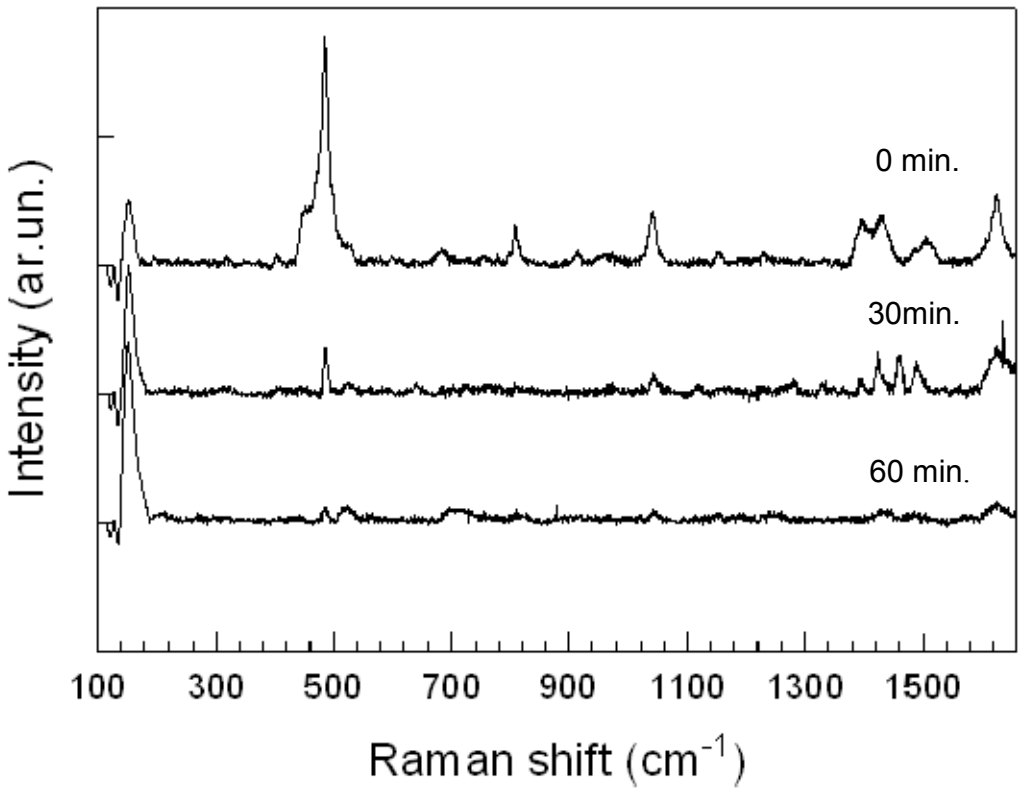
S2. Example of highly concentrated citrate-stabilized Au NPs dispersed onto PS/a-TiO_2 before (left side) and after (right side) laser irradiation. The irradiated region is indicated by a red circle.



S3. MicroRaman spectrum of citrate-stabilized Au NPs before laser irradiation. The spectrum was acquired using an optical filter that decreased to 0.5 mW the power of the laser on the sample.



S4. MicroRaman spectra showing the process of crystallization of anatase after 25 laser scans. Each scan was acquired for 1 second.



S5. MicroRaman analysis (after background subtraction) of MB degradation as a function of UV irradiation time. See the text for further details.