

Supporting Information

A novel method for *in-situ* synthesis of SERS-active gold nanostars on polydimethylsiloxane film

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Experimental section:

Materials

Gold (III) chloride trihydrate, sodium citrate tribasic dehydrate, hydroxylammonium chloride, 4-mercaptobenzoic acid, thiabendazole, ethanol and *N,N*-dimethylformamide were purchased from Sigma-Aldrich and used without any further purifications. Silicone elastomer and silicone elastomer curing agent (Sylgard® 184 silicone elastomer kit) were purchased from Dow Corning Corporation.

Sample preparation

4-MBA: The molecules of 4-MBA were absorbed on the AuNSs/PDMS surface by incubating the substrates with a solution of 4-MBA 0.2 mM in ethanol for 3 h. Afterwards the surface was rinsed with Ethanol and dried with N₂ gas.

Thiabendazole on apple skin: The apple was first washed with an aqueous solution of commercial vinegar to remove contaminations and eventual pesticide traces. Afterwards a piece of apple skin was immersed in an aqueous solution of thiabendazole (10⁻⁵ M) overnight; the skin was then dried by N₂ gas. Since thiabendazole has low solubility in water, the stock solution (10⁻³ M) was prepared in *N,N*-dimethylformamide and then diluted in milli-Q water.

SERS apparatus

SERS measurements were conducted using an inverted optical microscope (TiU, Nikon) equipped with a piezoelectric stage. Continuous wave 633/785 nm laser light was reflected by a dichroic mirror (Z633RDC, Chroma / Di02-R785, Semrock) and was then focused to the sample by an objective lens (PlanApo x60, N.A. 0.95, Nikon). Raman scattering light from the sample was collected by the same objective and was guided to the spectrograph (iHR320, Horiba) equipped with a cooled-charge coupled device (CCD) (Newton 920P, Andor), before passing through a confocal pinhole and longpass filters (HQ645LP / HQ800LP (x 2), Chroma).

Supporting Figures

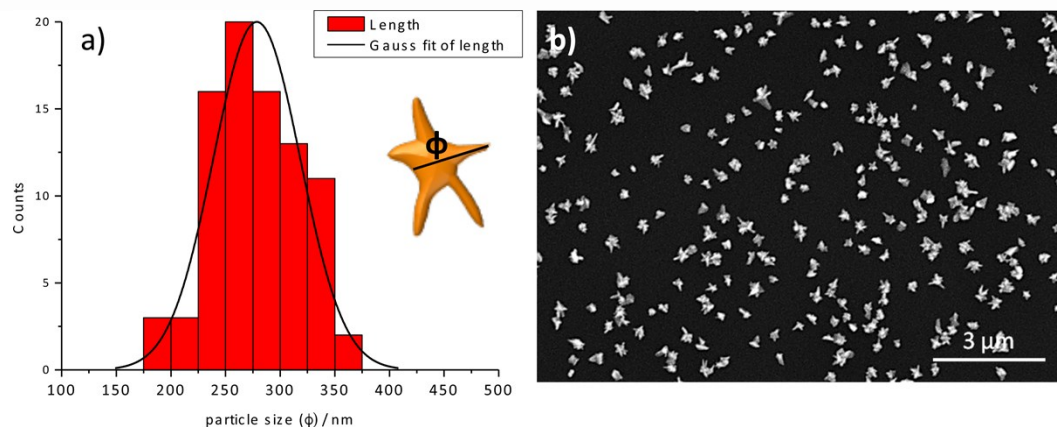


Figure S1. Particle Size distribution histogram (a) and related SEM image (b) of AuNSs on PDMS surface (reaction time: 120 s). The mean particle size is 275 nm, estimated by fitting the histogram with Gaussian function (black curve).

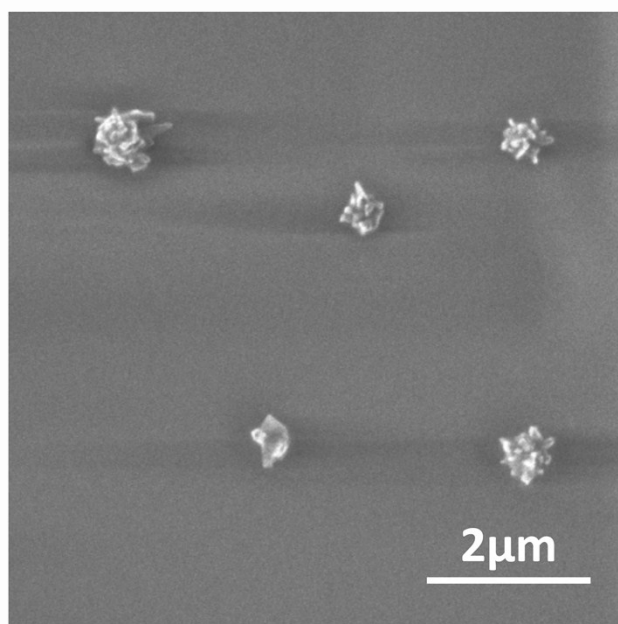


Figure S2. SEM image of gold nanostructures obtained after 120 s reaction time, on a 2-week old PDMS slide.

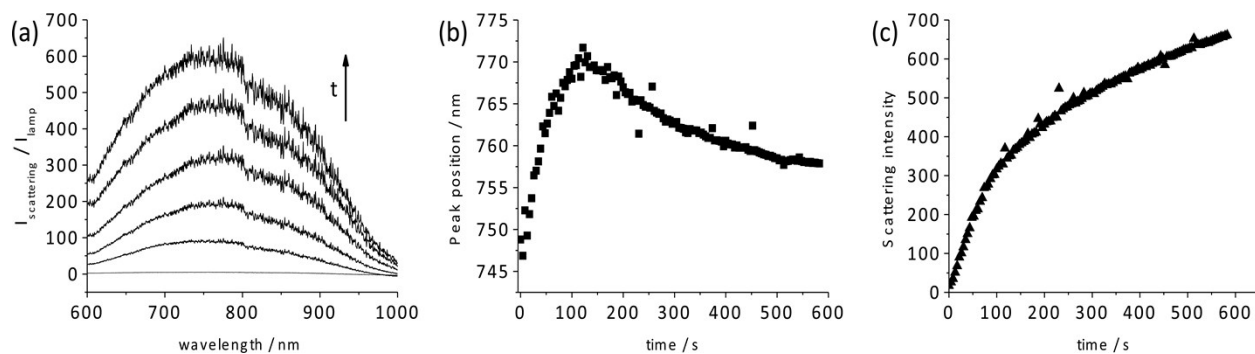


Figure S3. Dark-field spectra collected during the synthesis of gold nanostars on PDMS film at different reaction times (0, 30, 60, 120, 300 and 600 s) (a). Peak position shift (b) and related scattering intensity trend (c) during the reaction (0-600 s).

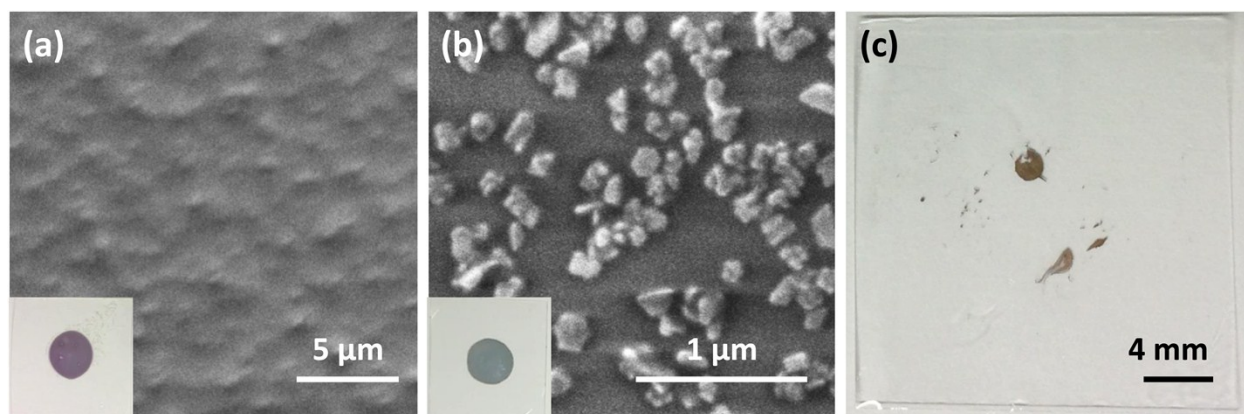


Figure S4. (a-b) SEM images of PDMS/gold NPs composites (120 s reaction time), prepared with different ratio of curing agent and PDMS monomer (η): 1 (a) and 0.05 (b). Insets show the photographs of the samples, respectively. (c) Photograph of PDMS/gold NPs obtained with $\eta = 0.01$.

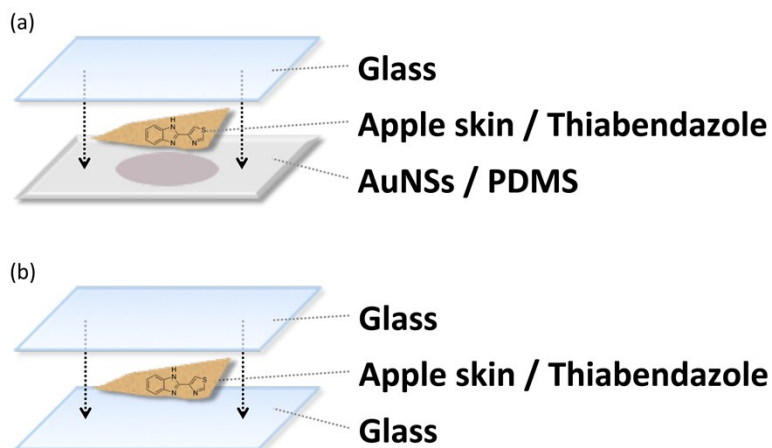


Figure S5. Schematics of the sample configuration employed in SERS measurements of apple skin/thiabendazole on AuNSs/PDMS film (a) and in Raman measurements of apple skin/thiabendazole on glass (b).

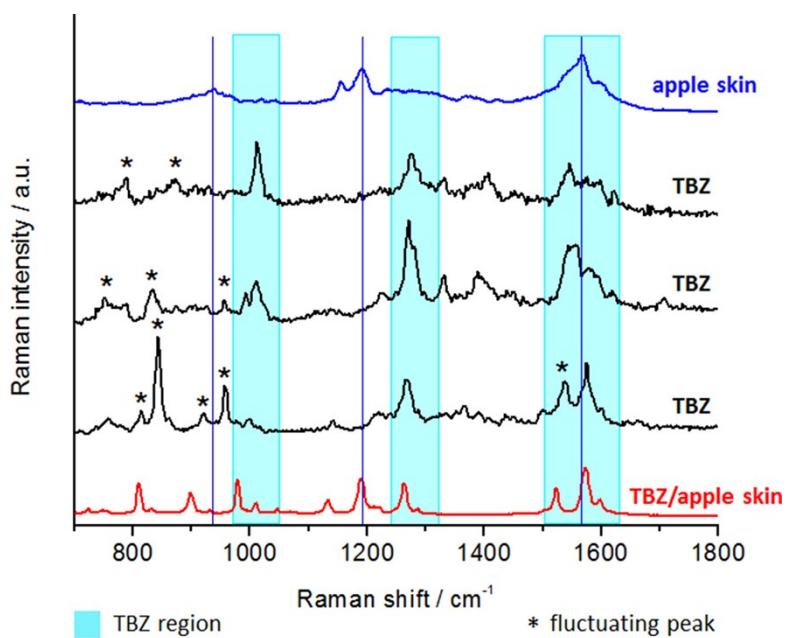


Figure S6. SERS spectrum collected on AuNSs/PDMS composites of: Thiabendazole (TBZ) adsorbed on the apple skin (10^{-5} M) (red line); TBZ adsorbed on AuNSs/PDMS (10^{-4} M) (black line); apple skin (blue line).

Thiabendazole SERS spectrum: peak assignment

Raman peaks at 978 and 1009 cm^{-1} may be assigned to C-S stretching mode and C-H bending mode, respectively. The strong band at 1264 cm^{-1} is assigned to the ring stretching mode. Finally, the high Raman intensity at 1573 cm^{-1} is associated to a vibrational complex of ring stretching mode and C=N stretching mode. A less intense peak contributing to the C=N stretching mode appears at 1597 cm^{-1} .^{S1}

References:

- S1. M.S. Kim, M.K. Kim, C.J. Lee, Y.M. Jung and M.S. Lee, *Bull. Korean Chem. Soc.*, 2009, **30**, 2930-2934.