Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information

Robust raspberry-like metallo-dielectric nanoclusters of critical sizes as SERS substrates

A. Le Beulze,[a] S. Gomez-Graña,[a] H. Gehan,[a] S. Mornet,[a] S. Ravaine,[b] M. Correa-Duarte,[c] L. Guerrini,[d] R.A. Alvarez-Puebla,[d,e] E. Duguet,[a*] E. Pertreux,[f] A. Crut,[f] P. Maioli,[f] F. Vallée,[f] N. Del Fatti,[f] O. Ersen[g], M. Treguer-Delapierre[a*]

[a] *CNRS, Univ. Bordeaux, ICMCB, UPR 9048, 33600 Pessac, France. treguer@icmcb-bordeaux.cnrs.fr; duguet@icmcb-bordeaux.cnrs.fr*

[b] *CNRS, Univ. Bordeaux, CRPP, UPR 8641, 33600 Pessac, France.*

[c] *Departamento de Química Física, Biomedical Research Center (CINBIO), and Institute of Biomedical Resaerch of Ourense-Pontevedra-Vigo (IBI), Universidade de Vigo, Vigo, Spain.*

[d] *Universitat Rovira i Virgili. C/ Marcellí Domingo s/n, 43007 Tarragona, Spain.*

[e] *ICREA. Passeig Lluís Companys 23, 08010 Barcelona, Spain.*

[f] *FemtoNanoOptics group, Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622 Villeurbanne, France*

[g] *Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504 CNRS, Université de Strasbourg, 23 rue du Loess, 67034 Strasbourg Cedex 2, France.*

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Table S1 Physico-chemical features of the negatively-charged silver and gold nanoparticles prepared.

Batch	Diameter of the used seeds (nm)	Diameter of the as-obtained nanoparticles (nm)	Concentration of the as-obtained particles (L^{-1}) *	λ_{max} (nm)
AgNP26	-	26 ± 5	$8.0\ 10^{16}$	404
AuNP10	-	10 ± 1	$1.9\ 10^{16}$	520
AuNP20	10 ± 1	20 ± 3	$1.8\ 10^{15}$	518
AuNP30	20 ± 3	33 ± 6	$1.2\ 10^{14}$	522
AuNP40	33 ± 6	40 ± 9	$1.2\ 10^{14}$	525
AuNP50	33 ± 6	50 ± 8	$3.1\ 10^{13}$	530

* as determined by ICP-OES on samples after washing stages

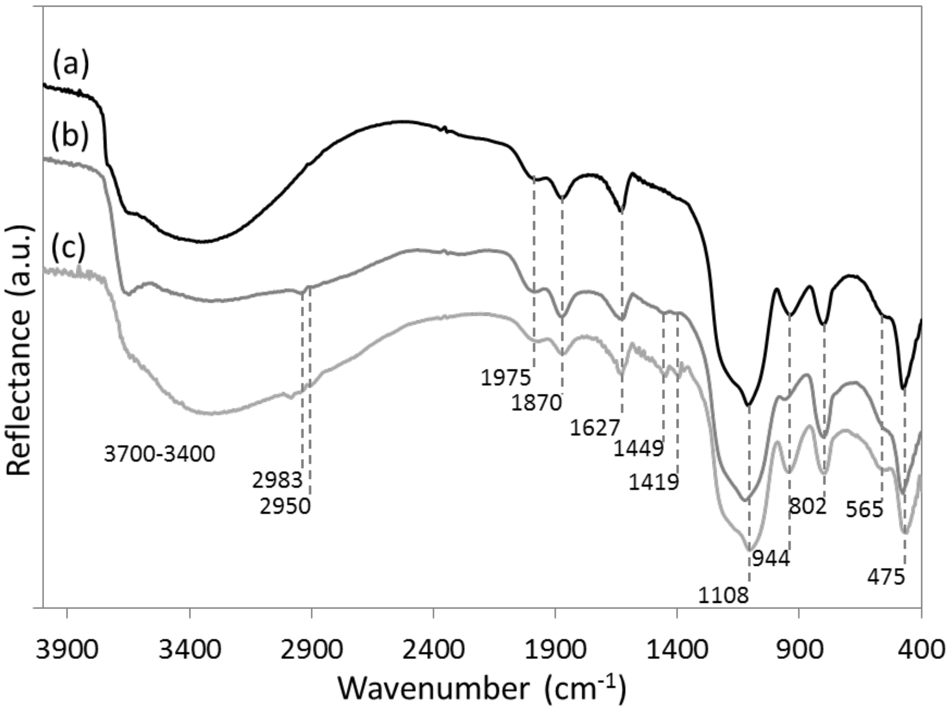

Fig. S1: DRIFT spectra of 89-nm silica nanoparticles (a) before and (b) after modification with EDPS. A sample of silica with a smaller diameter (50 nm) was specifically prepared and surface modified with EDPS in order to exalt the surface bands by increasing the surface to volume ratio. Its comparative DRIFT spectrum is spectrum (c).

ν (cm^{-1})	Intensity	Assignment	89-nm silica particles		50-nm silica particles
			pristine	**EDPS-modified**	**EDPS-modified**
3700-3400	s	ν(OH)	x	x	x
2983	m	ν_{asym}(CH_x)		x	x
2950	m	ν(NCH_x)		x	x
1975	shoulder	typical silica overtone	x	x	x
1870	w	typical silica overtone	x	x	x
1627	w	δ(H_2O) enclosed water	x	x	x
1449	w	δ(NCH)		x	x
1419	w	δ(CN^+)		x	x
1108	s	ν_{asym}(Si-O-Si)	x	x	x
944	s	ν_{sym}(Si-O-Si)	x	x	x
802	s	δ(Si-O-Si)	x	x	x
565	m	cyclic (Si-O-Si)	x	x	x
475	s	ρ(Si-O-Si)	x	x	x

Table S2: Summary table of the observed vibration bands on pristine and EDPS-modified silica nanoparticles. A sample of silica with a smaller diameter (50 nm) was specifically prepared and surface modified with EDPS in order to exalt the surface bands by increasing the surface to volume ratio. Abbreviations: s, strong; m, medium; w, weak intensity; ν_{sym}, symmetric stretching; ν_{asym}, asymmetric stretching; δ, bending; ρ, rocking vibrations.

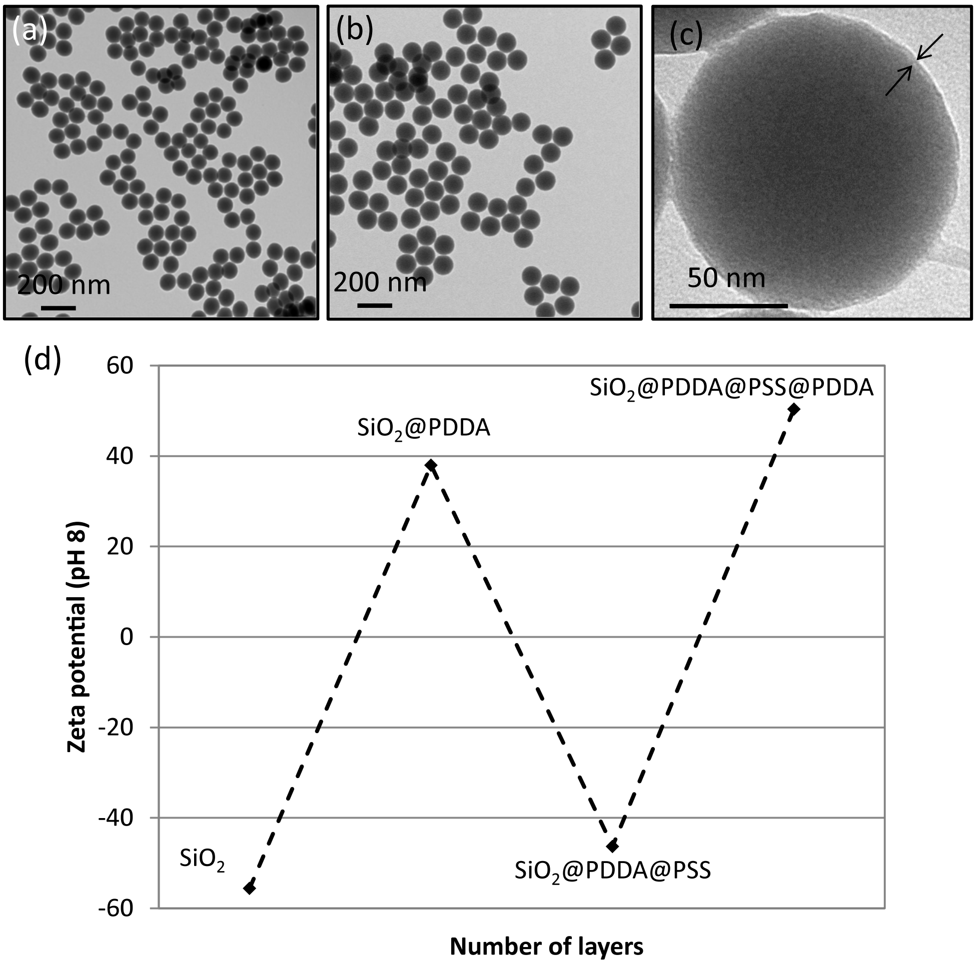

Fig. S2: TEM images of (a) 89-nm and (b) 106-nm silica nanoparticles after the adsorption of PDDA/PSS/PDDA multilayer. (c) Magnified view of a single 89-nm silica nanoparticle, where both arrows delineate the polyelectrolyte multilayer. (d) ζ-potential values of the PDDA/PSS/PDDA coated silica nanoparticles as a function of the number of layers deposited at pH 8.

Informations concerning the calculation of the SERS enhancement factor

The SERS enhancement factor was calculated according to the following formula [1]:

$$\mathbf{EF} = \frac{\mathbf{I_{SERS} / N_{Surf}}}{\mathbf{I_{Raman} / N_{Vol}}}$$

where N_{Vol} is the average number of molecules in the scattering volume, V, for the normal Raman measurement, and N_{Surf} is the average number of adsorbed molecules in the same scattering volume for the SERS measurement. As normal Raman and SERS intensities (I_{Raman} and I_{SERS}) we selected the height of the band at ca. 999 cm^{-1}. Both Raman and SERS measurements were performed under the same experimental set-up (i.e. identical scattering volume).

The metallic surface available for a single SiO_2@AgNP26 clusters (silica core of 106 nm diameter and ca. 60 satellites of 26 nm diameter) is ca. 127×10^3 nm^2/cluster. On the other hand, for SiO_2@AuNP30 assemblies (silica core of 106 nm diameter and ca. 25 satellites of 30 nm diameter) the estimated gold surface available is of ca. 71×10^3 nm^2/cluster. The cluster concentration in the samples was kept constant to ca. 6×10^{13} cluster/L. Thus, the corresponding metallic area available for SiO_2@AgNP26 and SiO_2@AuNP30 suspensions are ca. 7.6×10^{17} and 4.3×10^{17} nm^2/L, respectively.

The density of self-assembled monolayer of TP on a flat Au surface is 4.7 molecules/nm^2.[2]. Thus, we can use this value to estimate the maximum number of TP molecules that can be attached to each cluster, which correspond to ca. 35×10^{17} molecules/L for SiO_2@AgNP26 solution and ca. 20×10^{17} molecules/L for SiO_2@AuNP30 solution (i.e. 5.8×10^{-6} M and 3.4×10^{-6} M, respectively). For SERS studies, 10 µL of a 0.1 mM ethanolic solution of thiophenol (TP) were added to 1 mL of colloidal dispersion, corresponding to a final concentration of 1×10^{-6} M. Therefore, for both SiO_2@AgNP26 and SiO_2@AuNP30 suspensions, an equal submonolayer amount of TP was used to label the metallic surfaces. Assuming a 100% adsorption efficiency of TP onto gold and silver, we can consequently estimate N_{Surf} equals to 1 millimole of TP per 1 L of clusters.

By direct comparison of the SERS spectra to the normal Raman spectra of a TP 98% solution (9.74 M), we can then calculate the EFs at different excitation wavelengths. The values are reported in Fig. 10d.

References

(1) Aroca, R., *Surface-enhanced Vibrational Spectroscopy*. **2006**: John Wiley & Sons, Chichester.

(2) Kang, H., et al., *Two-dimensional ordering of benzenethiol self-assembled monolayers guided by displacement of cyclohexanethiols on Au(111).* Chemical Communications, **2008**, *41*, 5197