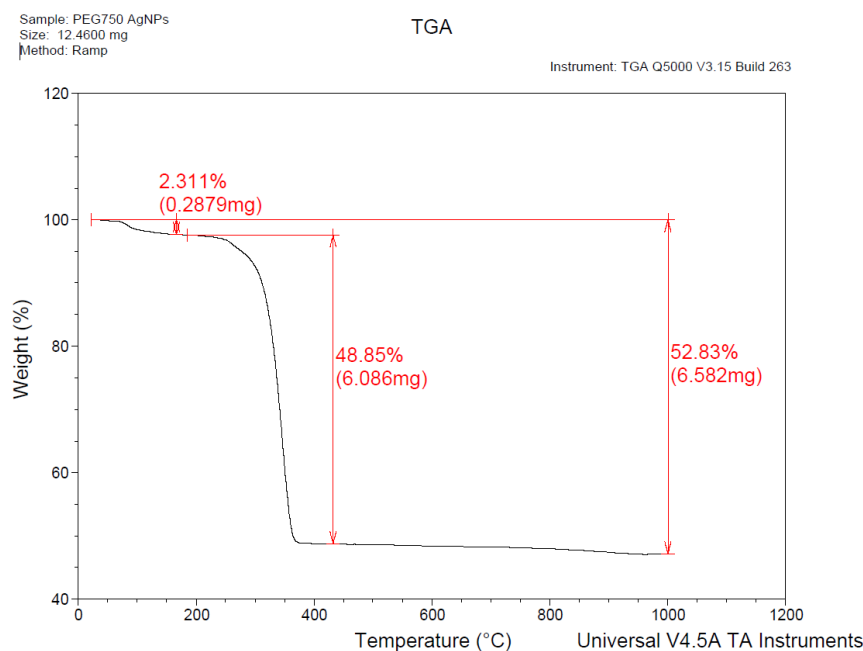


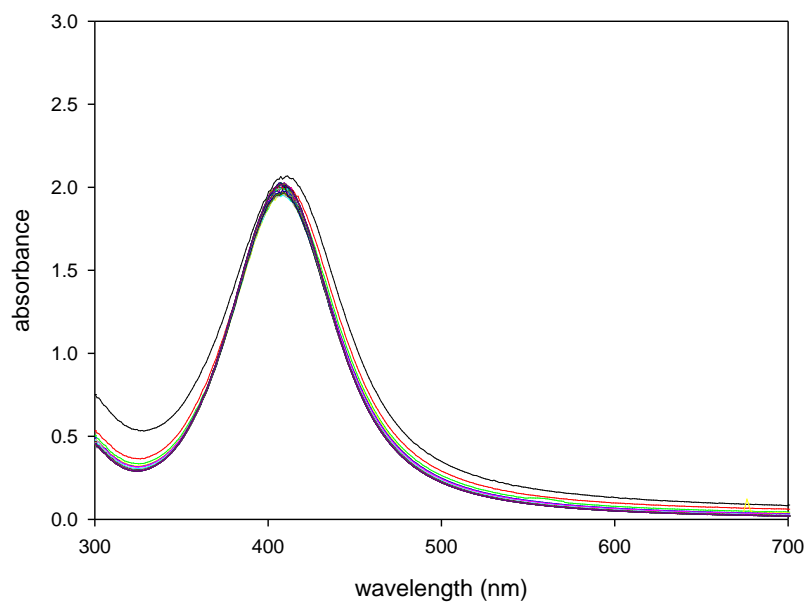
Piersandro Pallavicini, Luca Preti, Maria L. Protopapa, Daniela Carbone, Laura Capodiecì,
Yuri A. Diaz Fernandez, Chiara Milanese, Angelo Taglietti, and Lavinia Doveri
**Nanoparticle-imprinted silica gel for the size-selective capture of silver ultrafine
nanoparticles from water**

Figure S1. TGA (thermogravimetric analysis) on Ag-ufNP (8 nm) coated with HS-PEG₇₅₀.



Mass loss at $T < 200$ °C is adsorbed water; mass loss at 320 °C is HS-PEG (mw 750). The remaining mass % ($100 - 2.311 - 48.85 = 47.17$). From this data, from Ag atomic weight and density, and considering spherical Ag particles of 8 nm (as determined by TEM), the average number of HS-PEG₇₅₀ molecules per nanoparticle is calculated.

Figure S2. Stability of sol-gel mixtures.



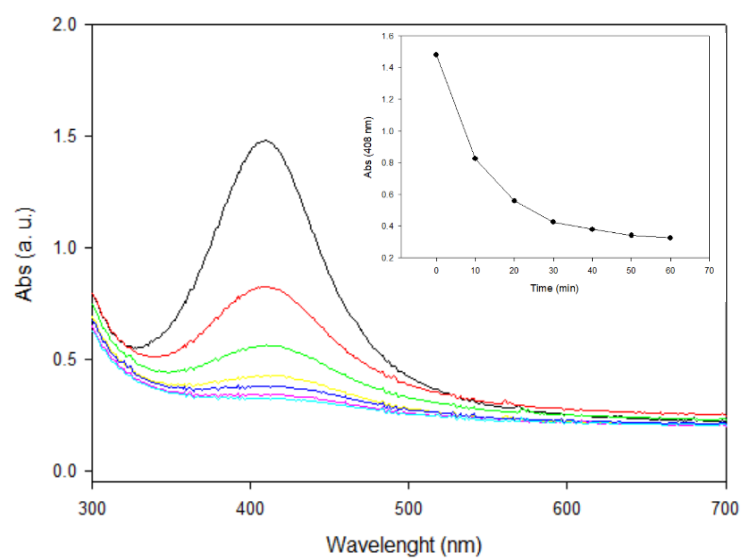
Absorption spectra of a gelating solution in basic conditions (DMF included), containing Ag-ufNP (8 nm; Ag 5.8×10^{-4} M, spectra recorded at 10 min intervals for 3 hours

Figure S3. Photos of silica gel monoliths containing Ag-ufNP at different total Ag concentrations in the starting solution.

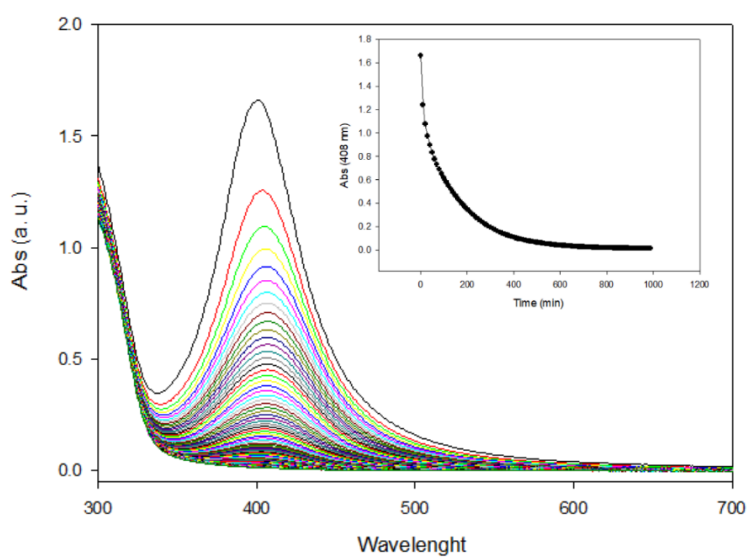


Ag tot. (mol/L)	$5.8 \cdot 10^{-5}$	$4.66 \cdot 10^{-4}$	$9.3 \cdot 10^{-3}$
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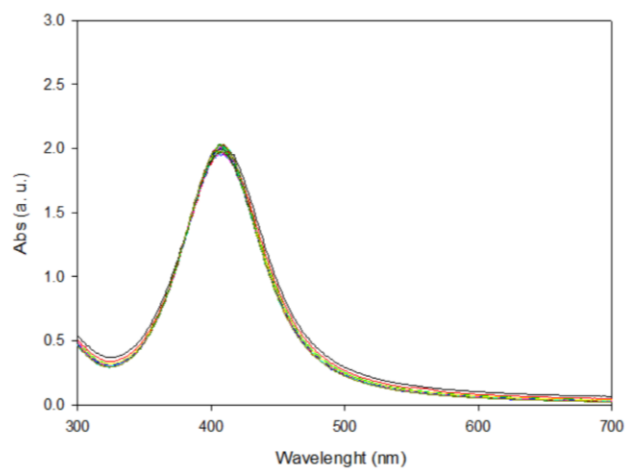
Figure S4. oxidation of **Ag@SiO₂-8** monoliths.



A: absorption spectra on a **Ag@SiO₂-8** monolith dipped in 0.5 M cysteine, exposed to air (spectra recorded at 10 min intervals). Inset: Abs on absorption maximum vs time



B: same, in 0.5 M $\text{Fe}(\text{NO}_3)_3$



C: control (spectra on a **Ag@SiO₂-8** monolith dipped in bidistilled water)

Figure S5. XRD on **Au@SiO₂-115** and **void@SiO₂-115** powders from grinded monoliths.

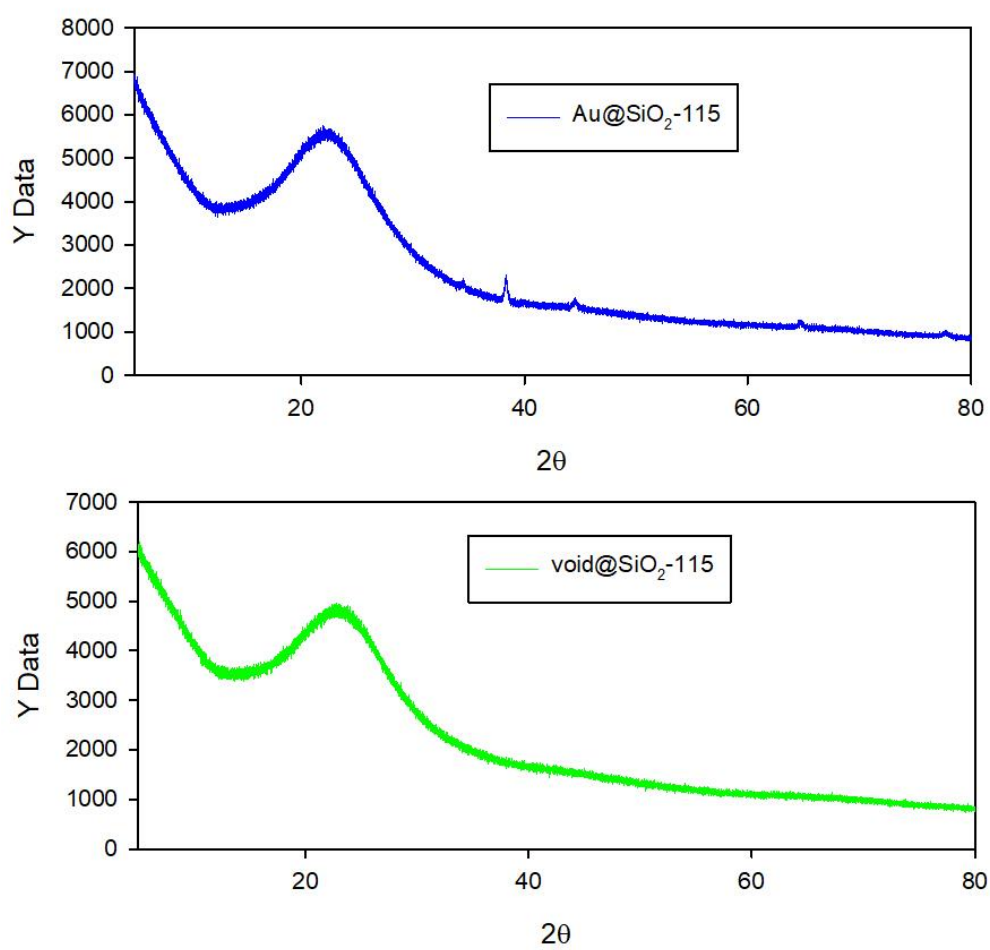
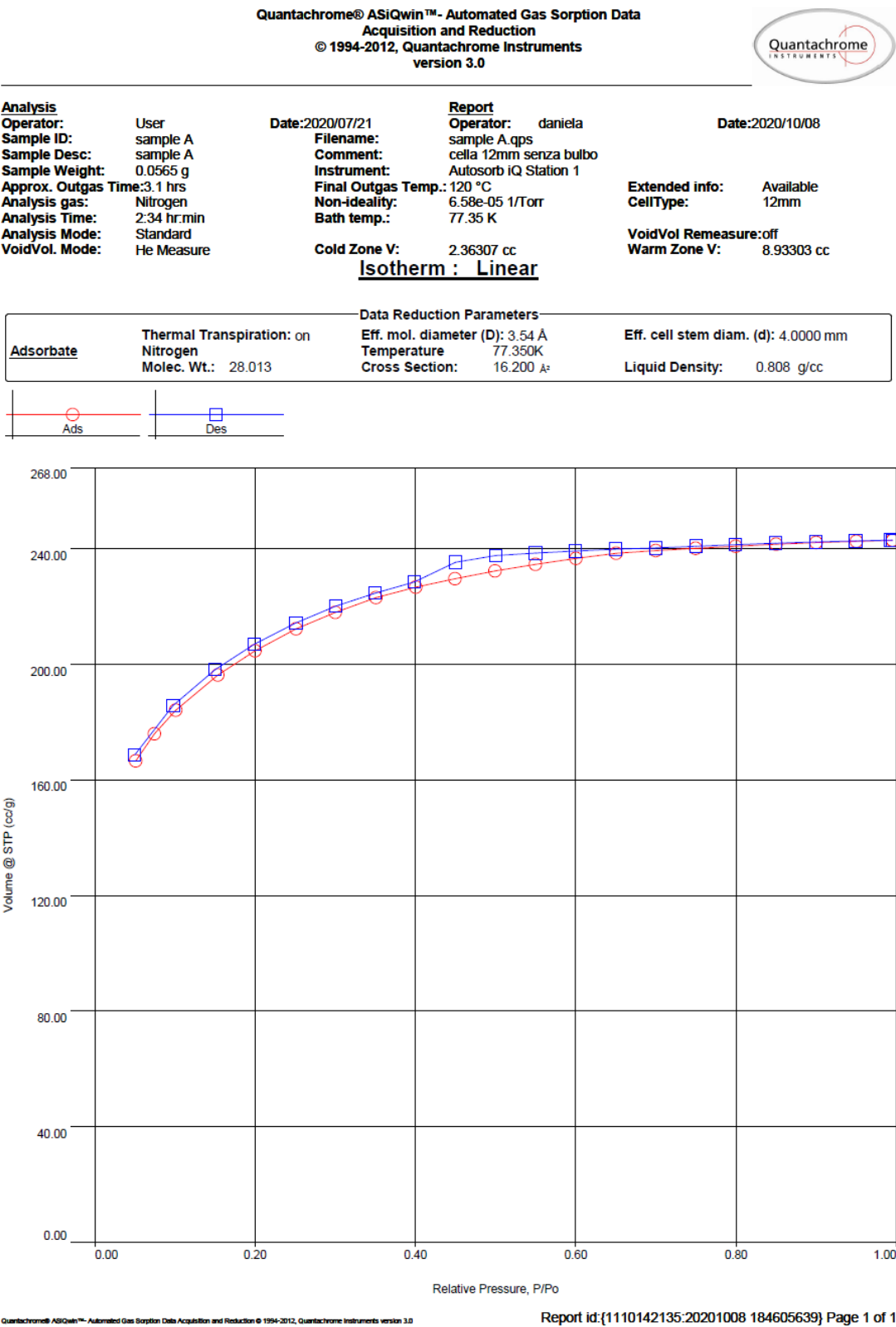


Figure S6. Surface area analysis.



A – Adsorption and desorption isotherms for Ag@SiO₂-8



Analysis

Operator: User
Sample ID: sample B1
Sample Desc: silice+ AgNps+cisteamina
Sample Weight: 0.0561 g
Approx. Outgas Time: 3.1 hrs
Analysis gas: Nitrogen
Analysis Time: 2:36 hr:min
Analysis Mode: Standard
VoidVol. Mode: He Measure

Date: 2020/07/16

Filename: sample B1.qps
Comment: cella 12mm senza bulbo
Instrument: Autosorb iQ Station 1
Final Outgas Temp.: 120 °C
Non-ideality: 6.58e-05 1/Torr
Bath temp.: 77.35 K

Cold Zone V: 2.18258 cc

Report

Operator: daniela
Sample B1.qps
cella 12mm senza bulbo
Autosorb iQ Station 1
Final Outgas Temp.: 120 °C
Non-ideality: 6.58e-05 1/Torr
Bath temp.: 77.35 K

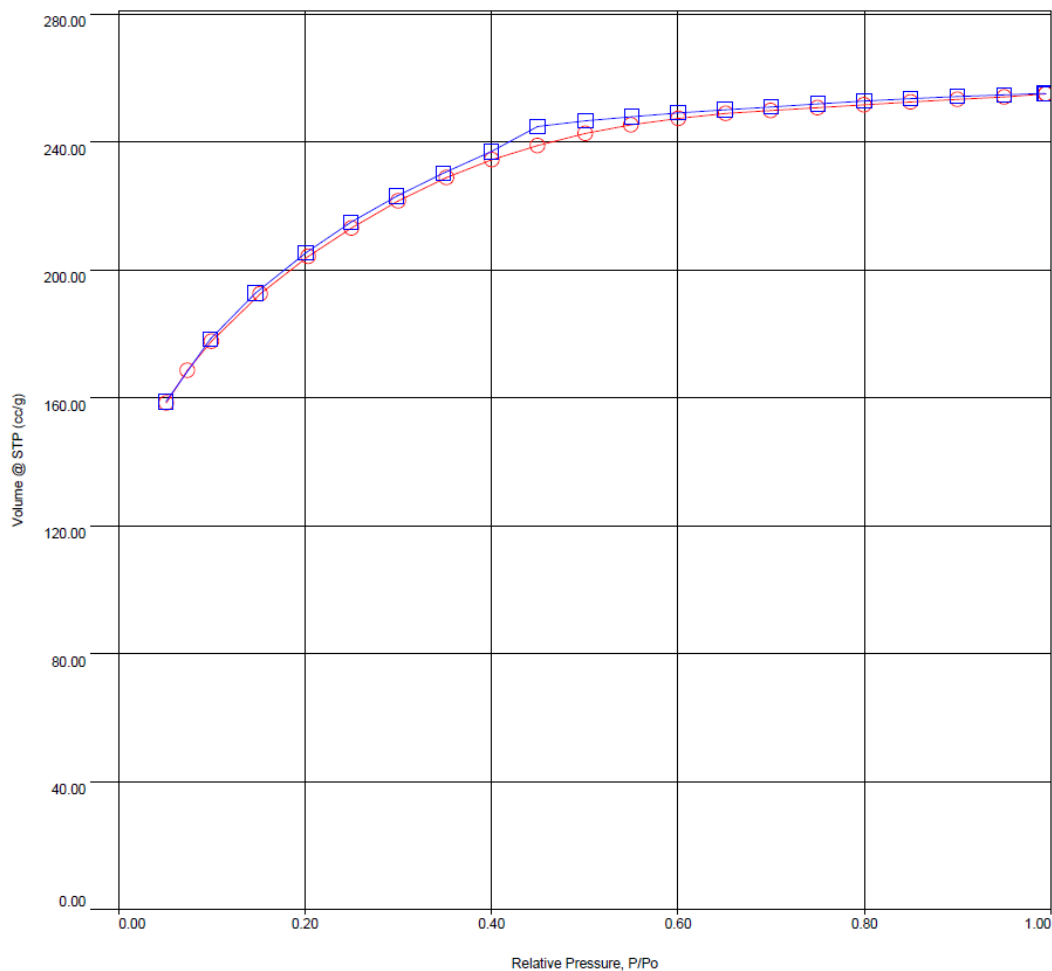
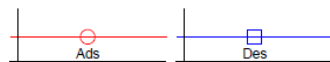
Date: 2020/10/19

Extended info: Available
CellType: 12mm

VoidVol Remeasure: off
Warm Zone V: 9.09856 cc

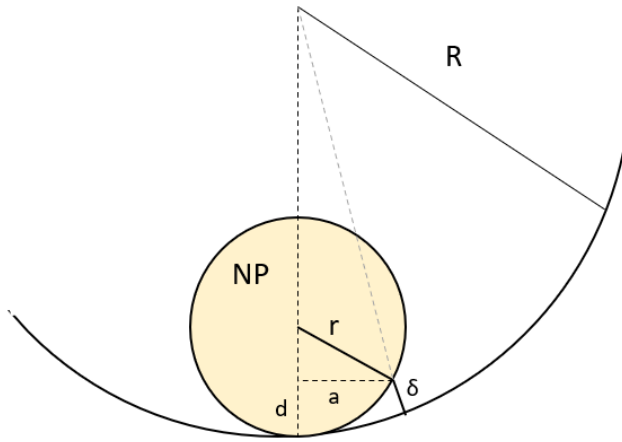
Isotherm : Linear

Adsorbate	Thermal Transpiration: on		Data Reduction Parameters	
	Nitrogen	Molec. Wt.: 28.013	Eff. mol. diameter (D): 3.54 Å Temperature 77.350K Cross Section: 16.200 Å²	Eff. cell stem diam. (d): 4.0000 mm Liquid Density: 0.808 g/cc



B – Adsorption and desorption isotherms for void@SiO₂-8

Figure S7. Geometrical model for size selectivity.



A: geometrical features for a spherical NP (r radius) interacting with a spherical cavity (R radius of curvature)

When a spherical NP interacts with a curved surface, such as the inner surface of a cavity, it is possible to calculate the fraction of the particle surface interacting with the curved cavity. In this case, the fraction of interacting NP surface will depend on the ratio between the particle size (r) and the radius of curvature of the cavity (R), leading to a relative increase of the particle-cavity interactions as this ratio increases (see Figure SM7B). In fact, within a curved cavity, we can expect a larger fraction of the NP surface to be close enough to the solid material, compared to a flat surface of the same material. This effect can be modelled using simple geometrical considerations (Figure SM7A), leading to the conclusion that the interactions will be stronger when the particle size and the radius of curvature of the cavity are similar.

$$\text{Triangle 1: } (R - \delta)^2 = a^2 + (R - d)^2$$

$$\text{riangle 2: } r^2 = a^2 + (r - d)^2$$

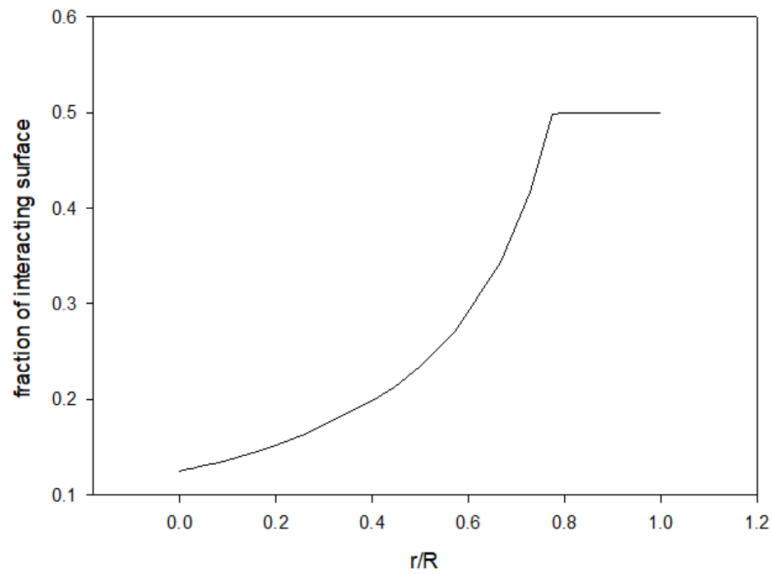
$$(R - \delta)^2 - r^2 = (R - d)^2 - (r - d)^2$$

$$(R - \delta)^2 - r^2 = (R + r - 2d)(R - r)$$

$$d = -\frac{(R - \delta)^2 - r^2}{2(R - r)} + \frac{1}{2}(R + r) \quad \text{With } R \neq r$$

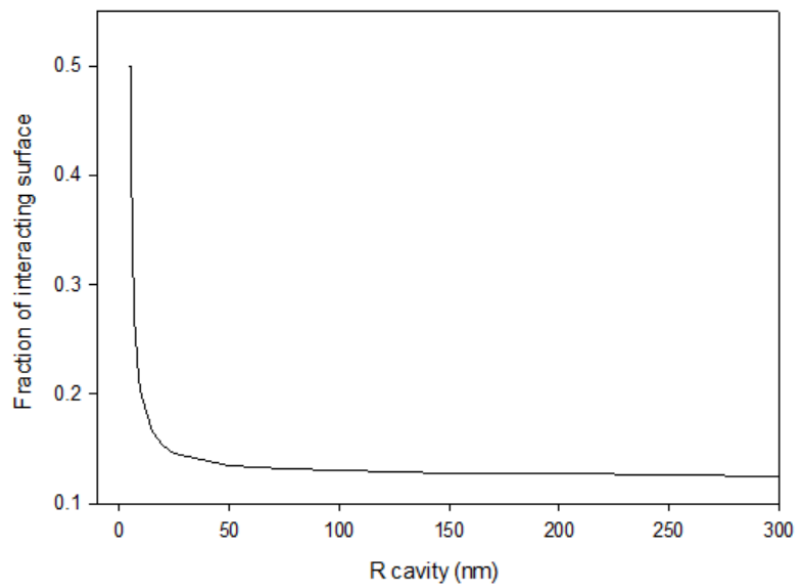
$$d = \frac{1}{2}[(R + r) - \frac{(R - \delta)^2 - r^2}{(R - r)}]$$

This simple geometrical model can explain the selectivity of the silica materials decorated with cavities, in the reuptake process of AgNPs.



B: increasing of interacting surface as the reaching of the R value.

It is important to note that within this model we have assumed that cavities are half-hemispheres, to allow for the NP to enter (i.e. when the size of the NP is close to the cavity radius, the NP can only enter the cavities that have been cut through at least by half). For this reason, the limiting value of the NP surface fraction is 0.5 when NP and cavity sizes become equal. This assumption is not limiting the overall interpretation of the results and become irrelevant for cavities much larger than the NP size.



C: fraction of interacting surface VS the cavity size.