SUPPLEMENTARY INFORMATION

Polydopamine coated flat glass surfaces for nanoplastics uptake and Raman based detection: a case study with polystyrene

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Table S1: characteristic Raman peaks of polystyrene. [1,2]

Peak position cm^{-1}	Assignment
621	Ring deformation
795	Out of plane C-H deformation
1001	Ring breathing
1031	In plane C-H deformation
1155	In plane N-H bend, in plane xanthene ring breathing
1450	CH_2 scissoring
1583	C=C stretching
1602	Ring-skeletal stretching

Table S2: characteristic Raman peaks of Rhodamine 6G. [3,4]

Peak position cm^{-1}	Assignment
613	Xanthene ring deformation (in plane C-C-C bend)
775	Out of plane C-H bend and in plane xanthene ring deformation
1124	Weak band due to the in-plane C-H bend
1184	In plane xanthene ring deformation, in plane C-H and N-H bending
1312	In plane xanthene ring breathing, in plane N-H bend
1364	Xanthene ring stretching (C-C stretching), in plane C-H bending
1512	Xanthene ring stretching (C-C stretching), C-H stretching, C-H bend and N-H bending
1577	In plane N-H bend, xanthene ring stretching (C-C stretching)
1651	Xanthene ring stretching (C-C stretching), in plane C-H bending

Table S3: surface zeta potential (SZP) values of glass@PDA substrates at different pH values.

pH values	Average SZP (mV)
3.1	18 ± 2
3.7	10 ± 1
4.6	-6 ± 2
5.0	-13 ± 2
6.0	-32 ± 3
7.0	-35 ± 4

Reported SZP values are averaged from two distinct set of measurements on two different glass@PDA substrates.

Figure S1: a) Uv-Visible spectrum of glass@PDA substrate (red line) in comparison with Uv-Visible spectrum of clean glass cover slips (black line). b) Enlargement of glass (black line) and glass@PDA substrate (red line).

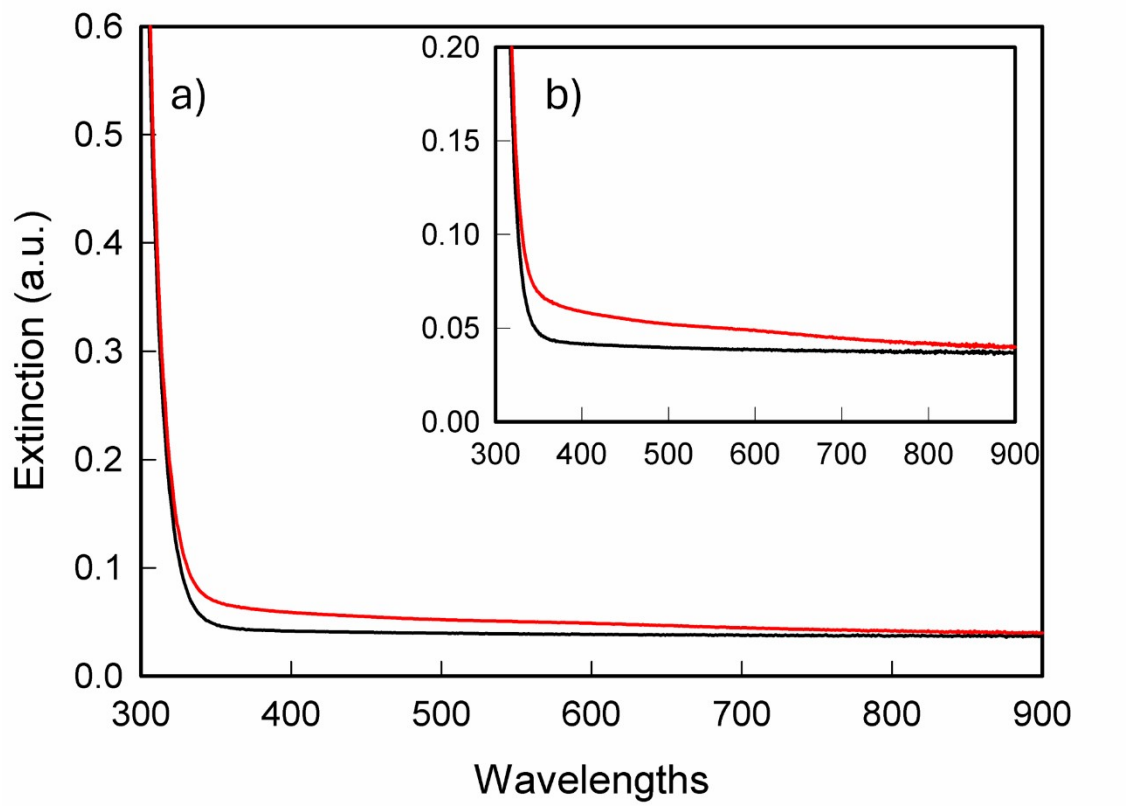


Figure S2: representative SEM images of glass@PDA samples after different immersion time in 10-ppm suspension of 100nm PS-NPs, respectively after 1h a), 2h 30 minutes b), 4h c) and 24h d). e) Number of PS-NPs per unit area extrapolated from SEM images as a function of immersion time.

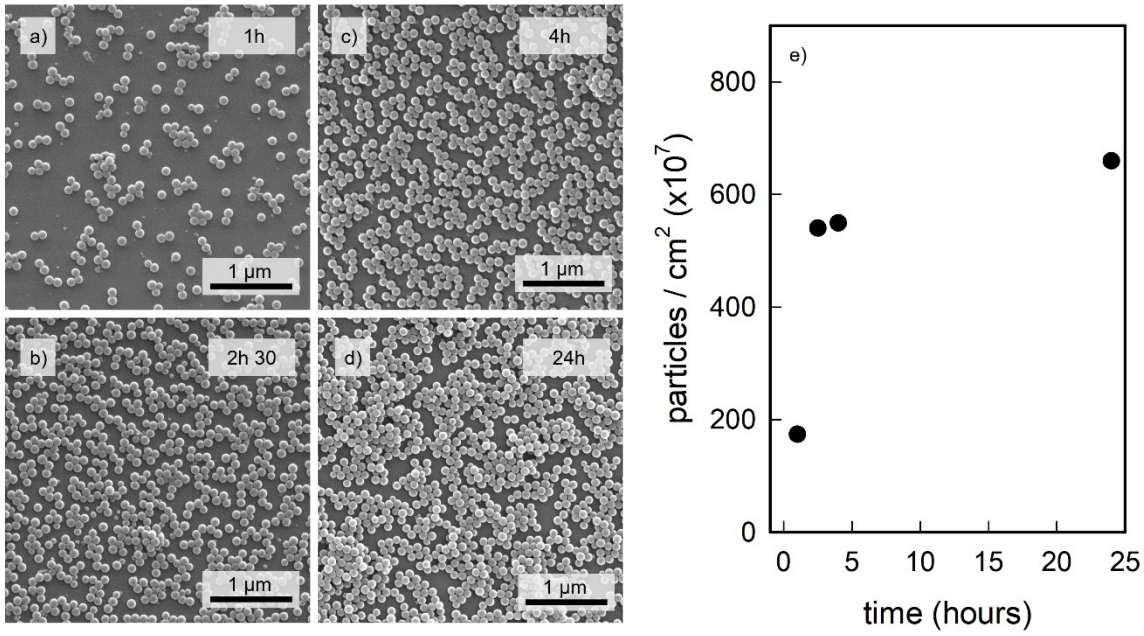


Figure S3: representative SEM images of glass@PDA samples immersed in 60 mL water suspension of 15 nm diameter plane PS-NPs at pH 3 (10 ppm concentration).

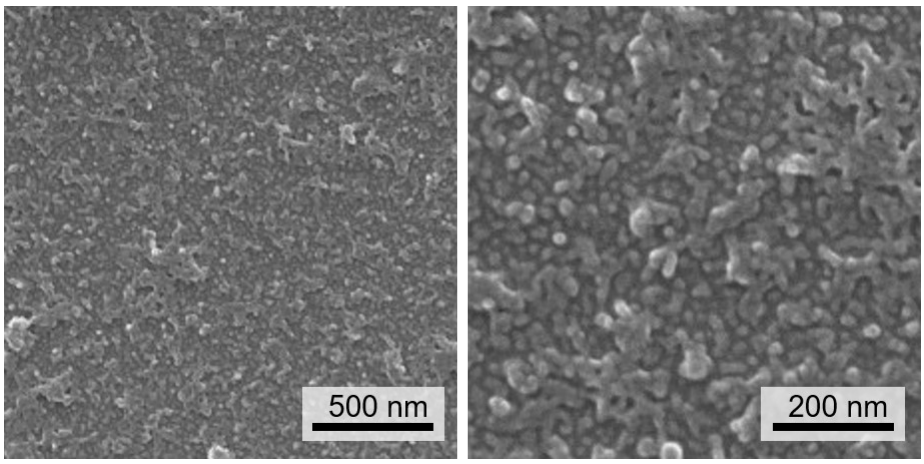


Figure S4: SEM images, acquired without Pt sputtering, of Silicon@PDA samples immersed in 60 mL water suspension of 15 nm diameter plane PS-NPs at pH 3 (2.5 ppm concentration).

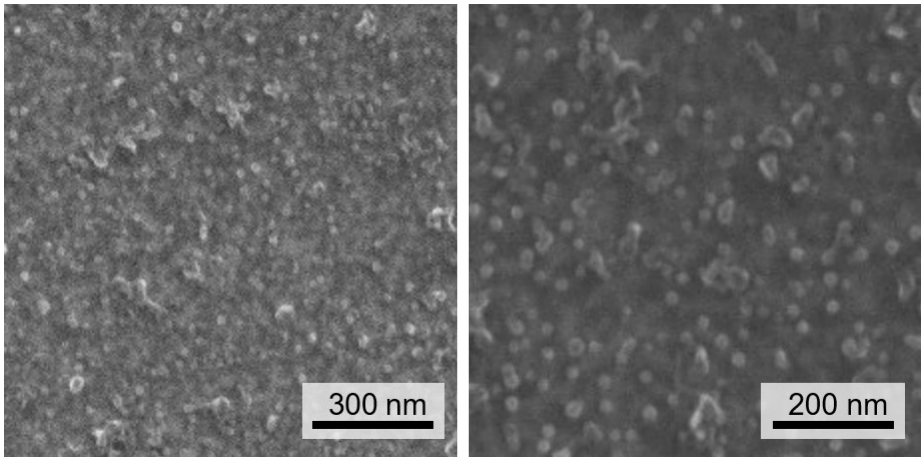


Figure S5: SEM images acquired on control experiments performed on bare glass substrates after the immersion respectively in a) 100-ppm water suspension of 1 μm PS-NPS and b) in a 10-ppm water suspension of 100 nm PS-NPs.

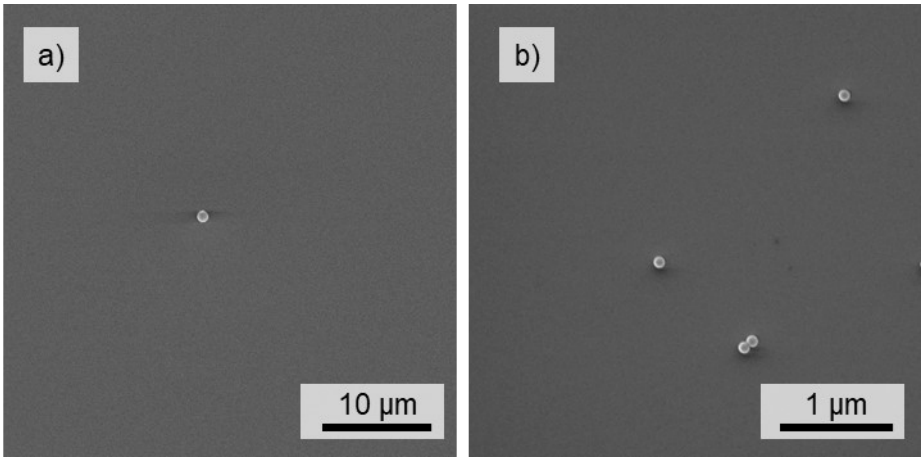


Figure S6: Raman spectra obtained on glass@PDA substrates after the immersion in a) tap water and b) river water (Roggia Vernavola, Vernavola park, Pavia) spiked with a 10-ppm suspension of 1 μm PS-NPs

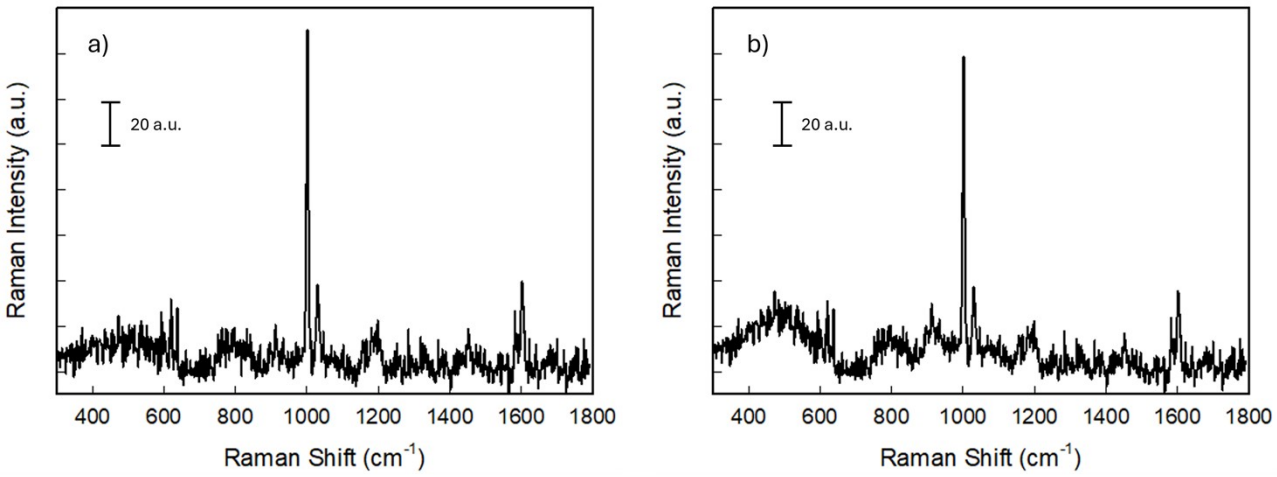


Figure S7: comparison between a) Raman spectrum of 100-ppm preconcentrated 1 µm PS-NPs on glass@PDA substrate and b) Raman spectrum of 100-ppm suspension of 1 µm PS-NPs as control experiment.

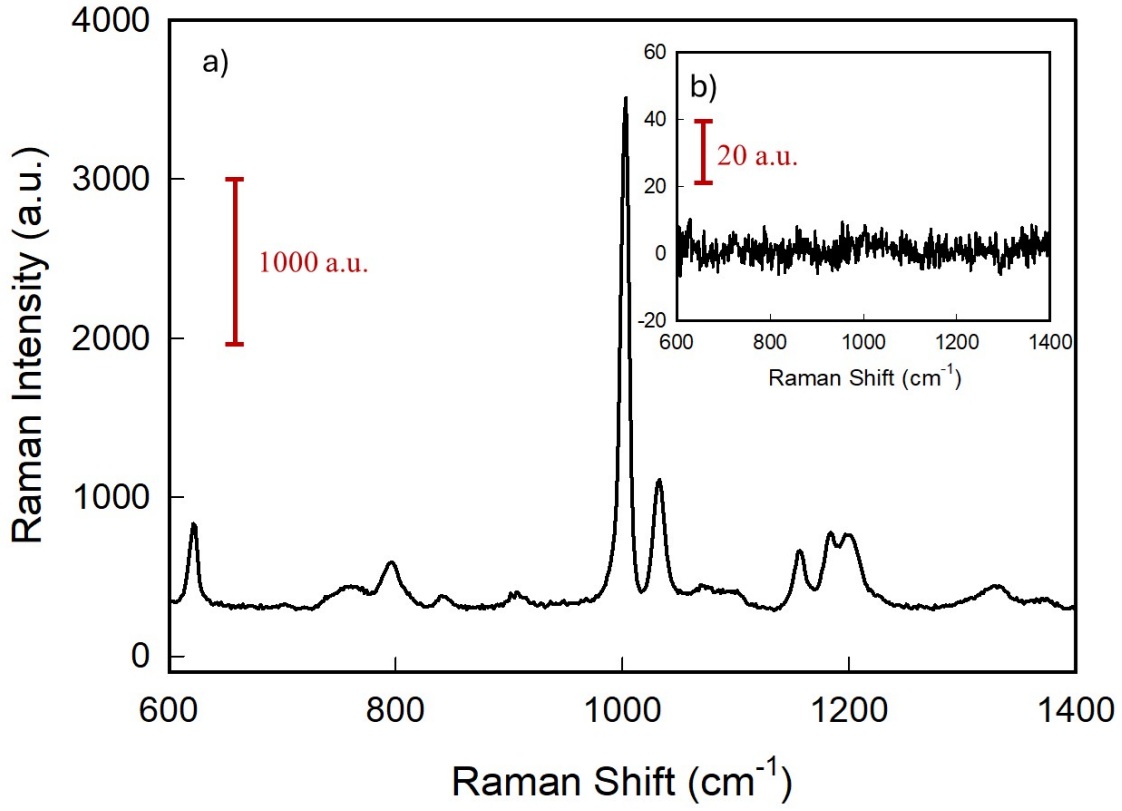


Figure S8: comparison between a) Raman spectrum of 10-ppm preconcentrated 100 nm PS-NPs on glass@PDA substrate and b) Raman spectra of 10-ppm suspension of 100 nm PS-NPs as control experiment.

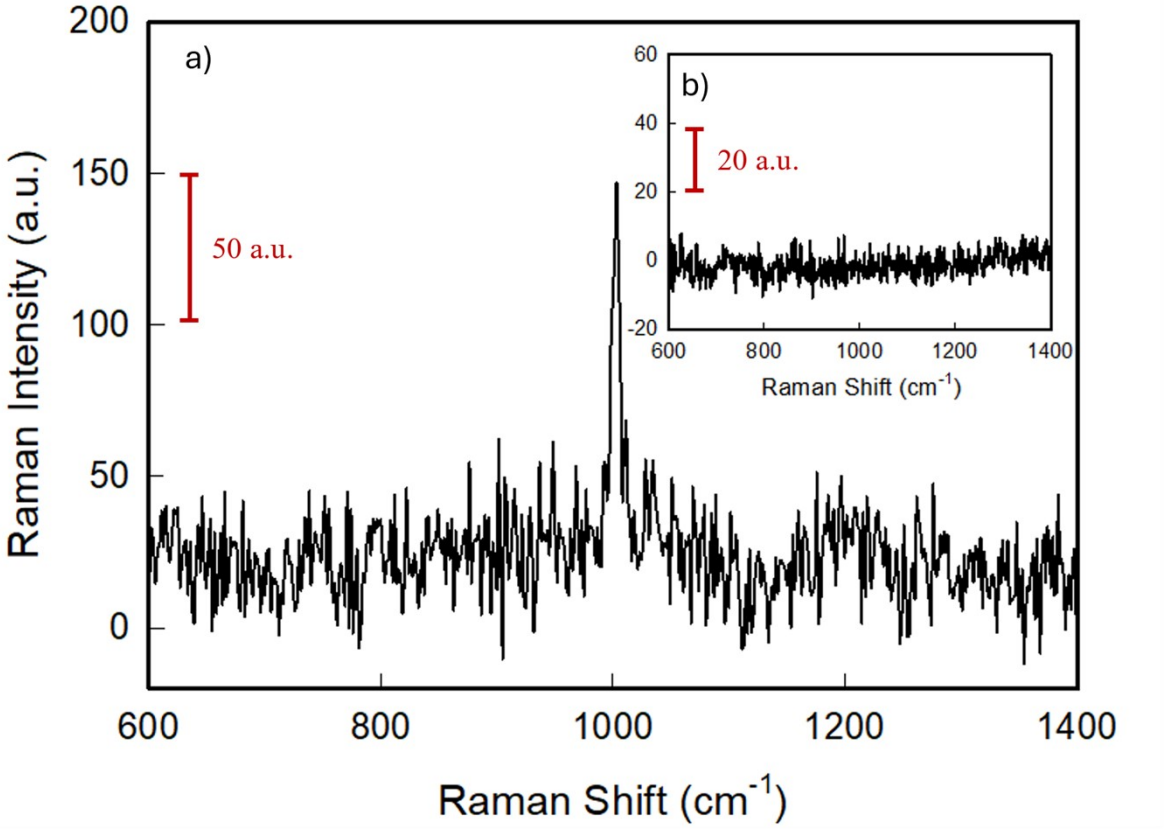


Figure S9: Average Raman spectrum obtained on glass@PDA samples after immersion in 60 mL water suspensions of 100 nm diameter PS-NR_3^+-NPs at pH 6.

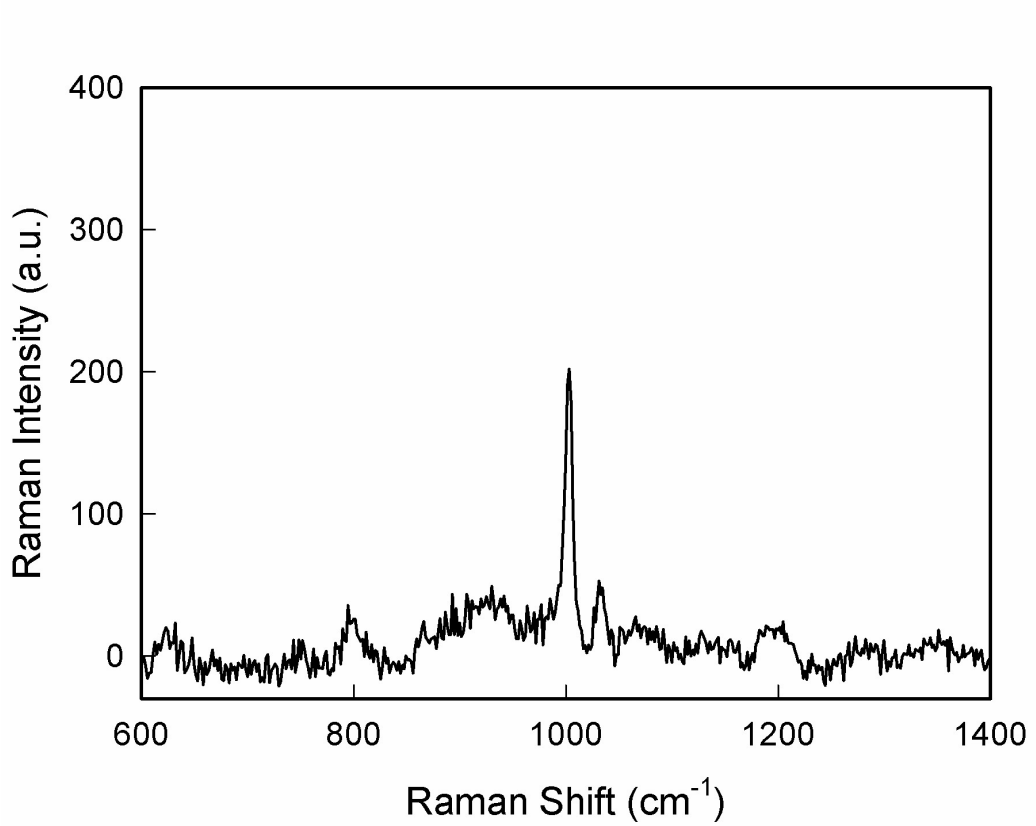


Figure S10: Raman spectra obtained on glass@PDA substrates after the immersion in a 10-ppm suspension of 100 nm PS-NPs for 1h, 2h and 30 minutes, 4h and 24 h.

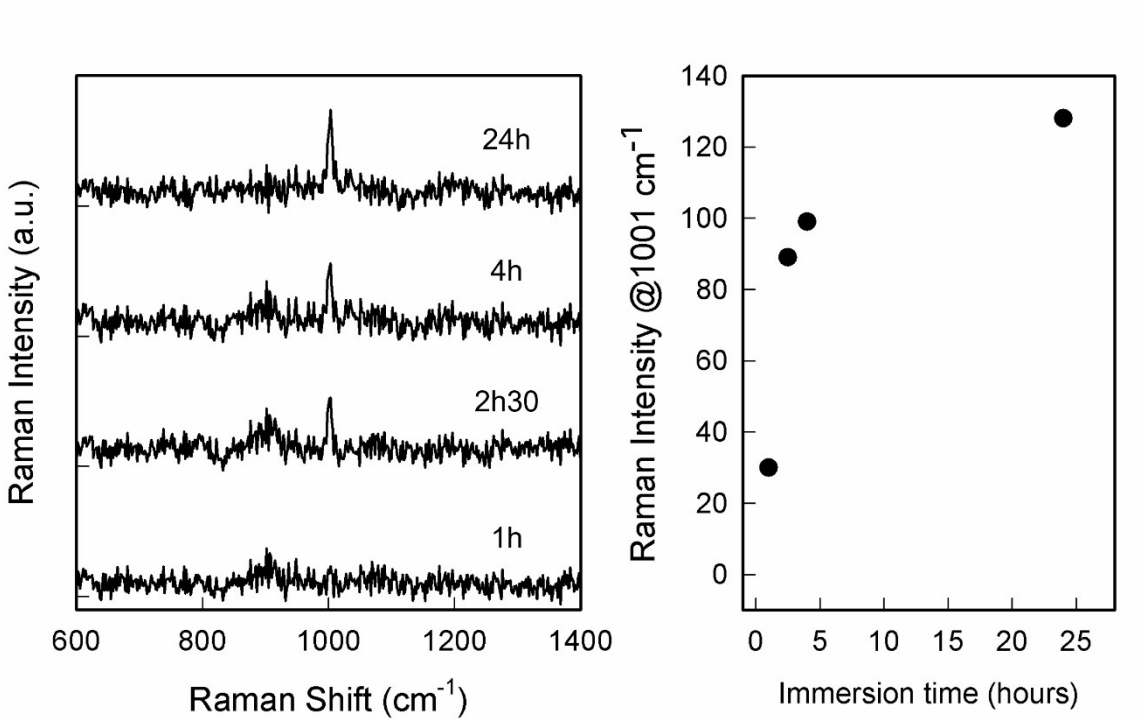


Figure S11: representative SEM images of glass@PDA samples immersed in 60 mL of 10 ppm water suspension of: a) PMMA-NPs at pH 3 and b) PMMA-NPs at pH 6

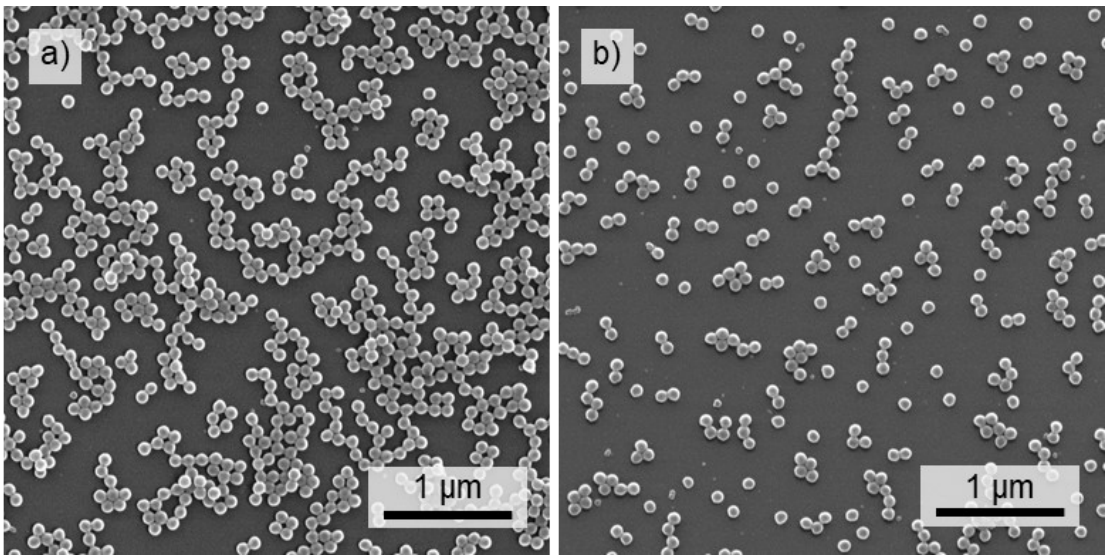


Figure S12: Representative TEM images of GNS nanoparticles.

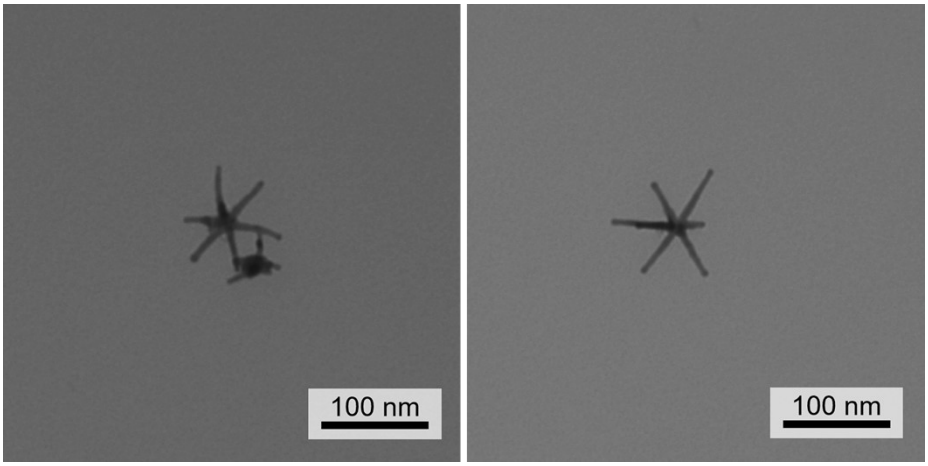


Figure S13: UV-vis-NIR spectrum of colloidal GNS nanoparticles showing the characteristic longitudinal LSPR of one single branch of the nanostars centred at around 900 nm.

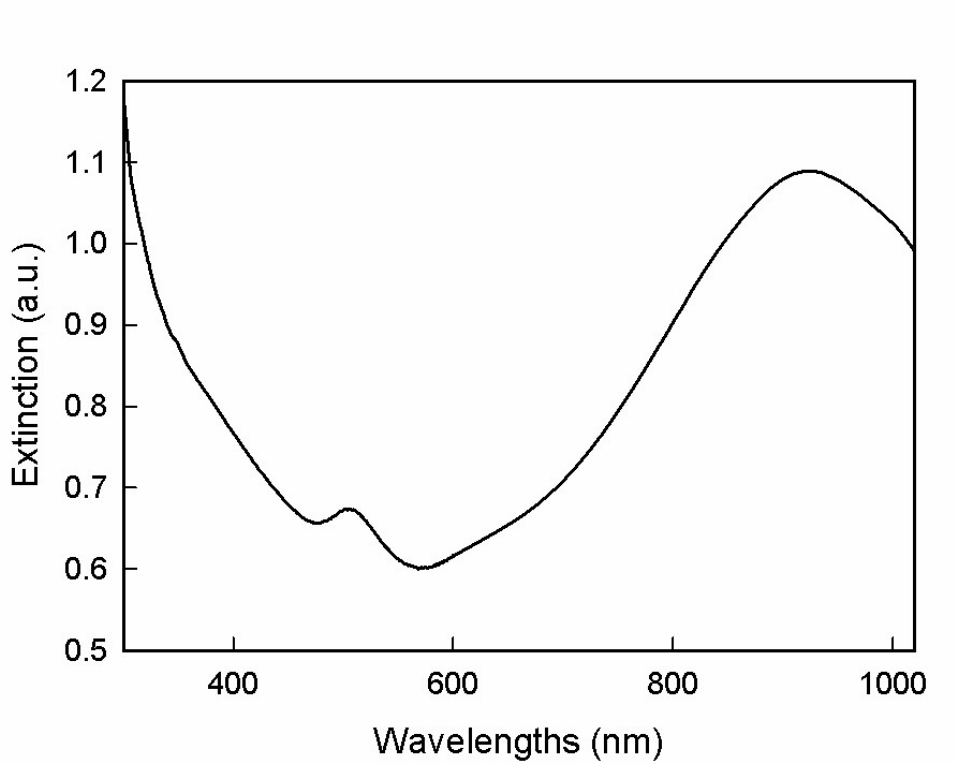


Figure S14: representative SEM images of a typical glass@PDA@GNS substrate.

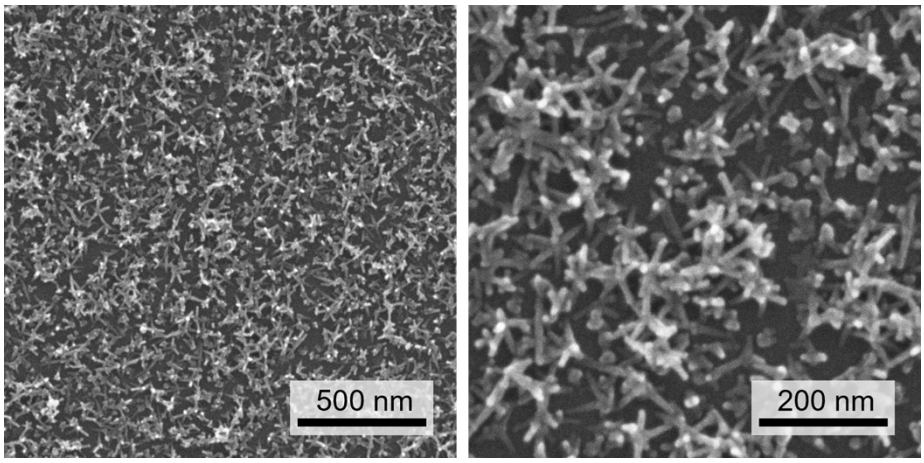
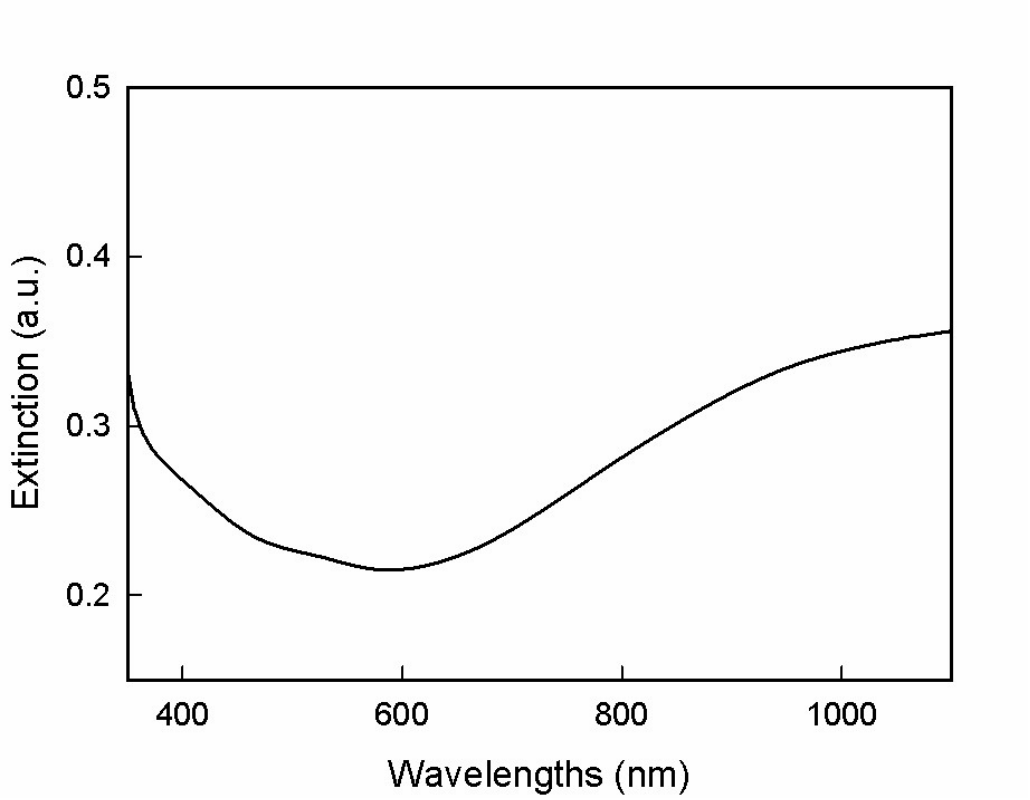


Figure S15: UV-vis-NIR spectrum of glass@PDA@GNS substrate.



S16: EF calculation

The operative formula employed for the estimation of the EF is the following:

$$EF = \frac{I_{SERS}\ C_{Raman}\ H_{SERS}}{I_{Raman} C_{SERS} H_{Raman}} \quad (1)$$

where I_{SERS} and I_{Raman} are the integrated intensity of the 610 cm^{-1} R6G mode, C_{Raman} and C_{SERS} are the molar concentrations of R6G solutions, namely 10^{-3} M and 10^{-5} M, respectively, while H_{Raman} is the Raman height, equal to 20 μm, as estimated from a previous work[5] and H_{SERS} the SERS one, considered equal to the distance beyond which the SERS signal drops to zero (estimated it to be about 10 nm).[6]

The formula employed for the calculation of the EF was derived from the general formula[7]:

$$EF = \frac{I_{SERS}\ N_{Raman}}{I_{Raman}\ N_{SERS}} \quad (2)$$

Where N_{Raman} and N_{SERS} are the average number of molecules in the scattering volume in Raman and SERS experiments, respectively.

Although, since in this work we were able to use the same scattering volume for Raman and SERS experiments, we thus operatively used the equation (1) to obtain an estimation of the EF since the only parameter changing was the height of the scattering volume (as previously described).

Figure S17: comparison between the SERS spectrum of 10^{-5} M R6G solution with the respective Raman spectrum obtained with a 10^{-3} M solution of R6G.

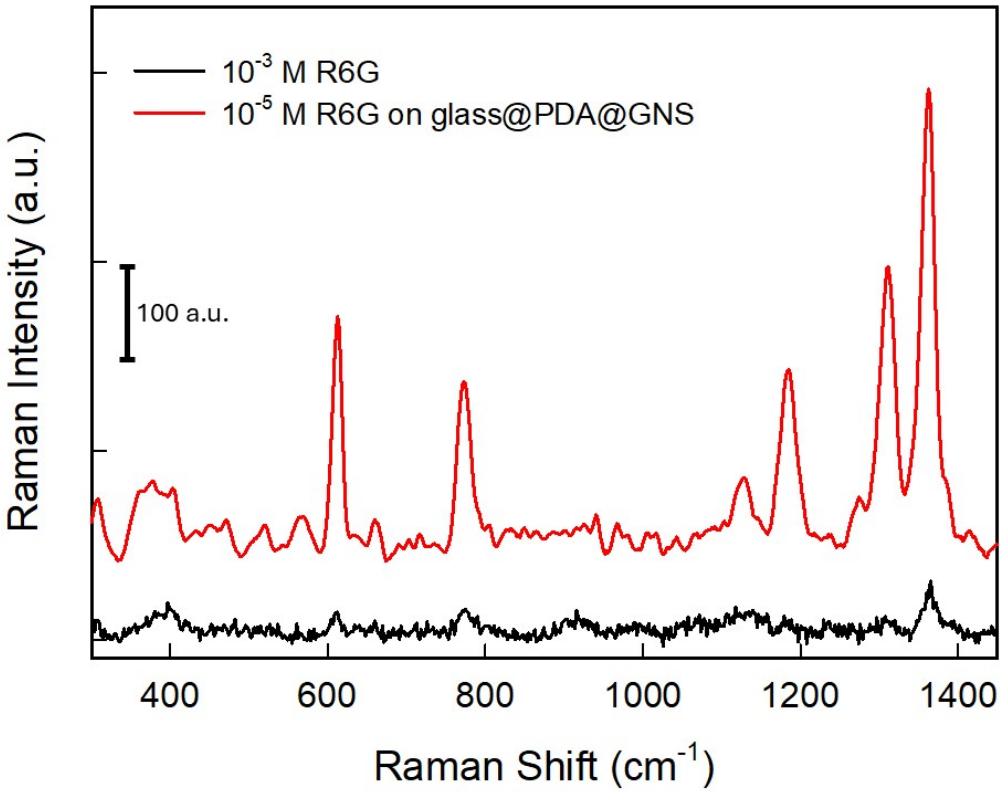


Figure S18: SERS spectra of 10^{-5} M R6G solution. a) spectra collected on ten different spots on the same glass@PDA@GNS substrates; b) average spectrum of R6G obtained by sampling three different glass@PDA@GNS substrates.

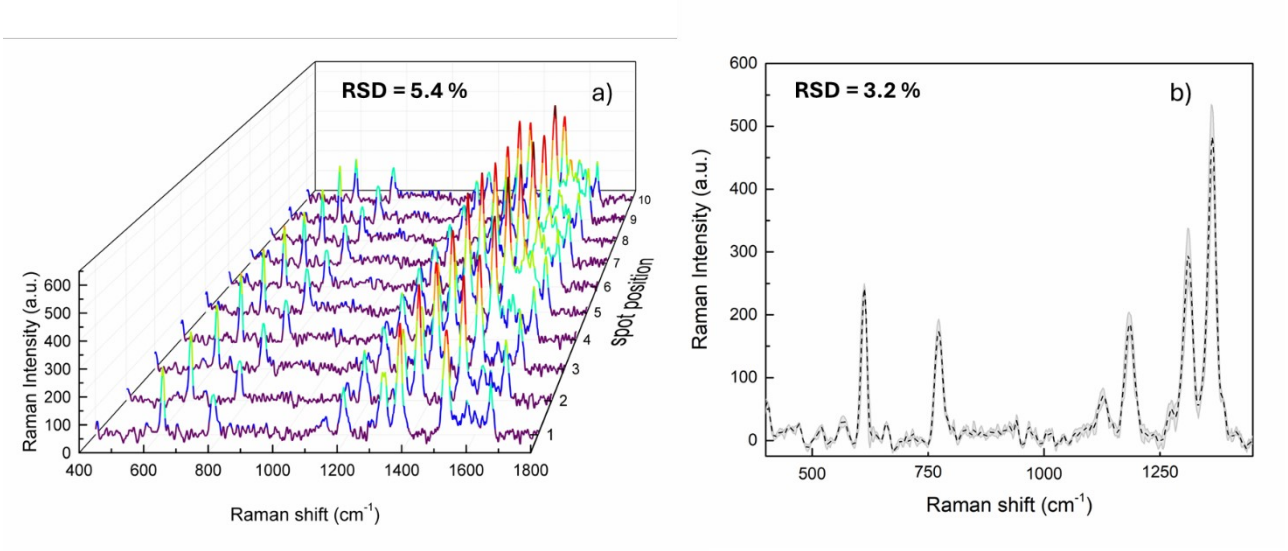


Figure S19: UV-vis-NIR spectrum of glass@PDA@GNS substrate just after its preparation (black solid line) and after 25 days (red dashed line).

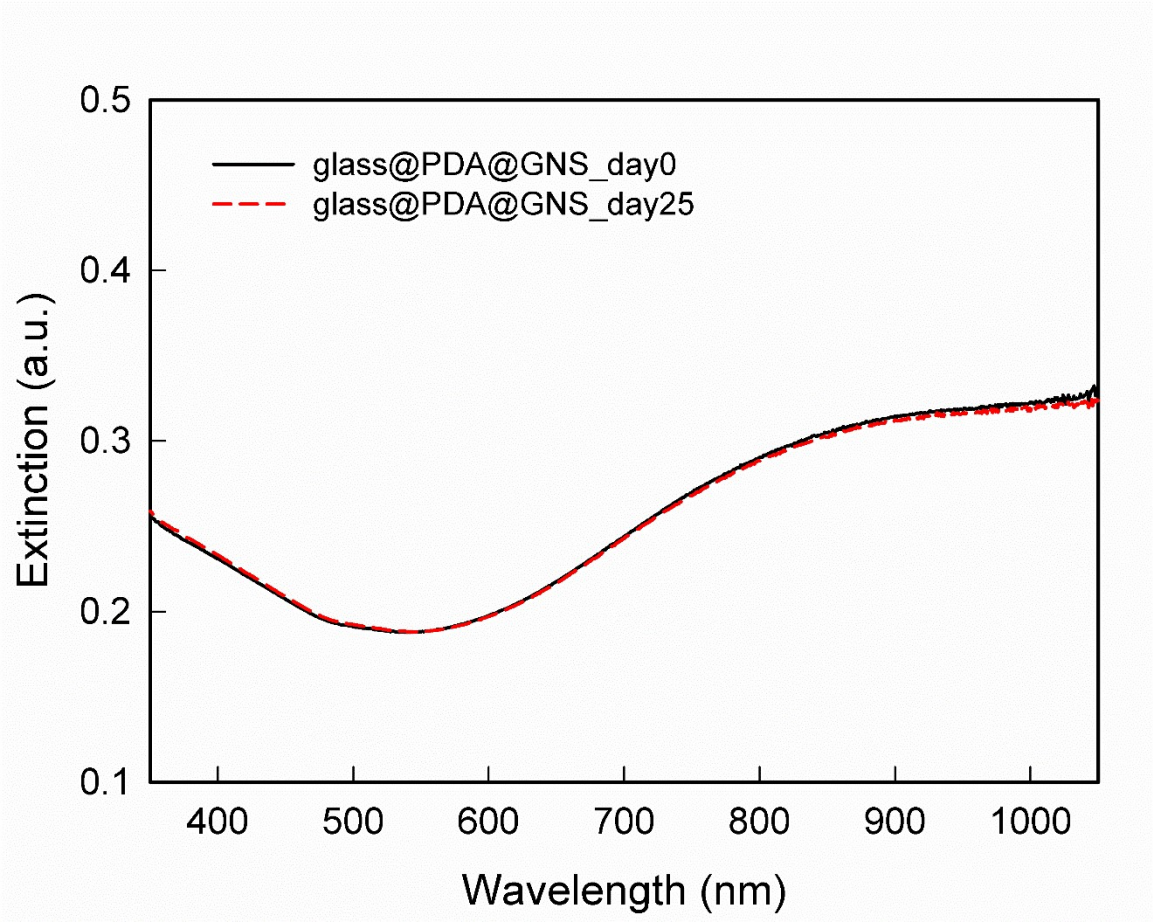


Figure S20: representative SEM images of a glass@PDA@GNS substrate after the immersion in a 10-ppm 15 nm PS-NPs suspension. Red circles highlight the presence of the small PS-NPs both in the gaps between GNS nanoparticles and directly on top of them.

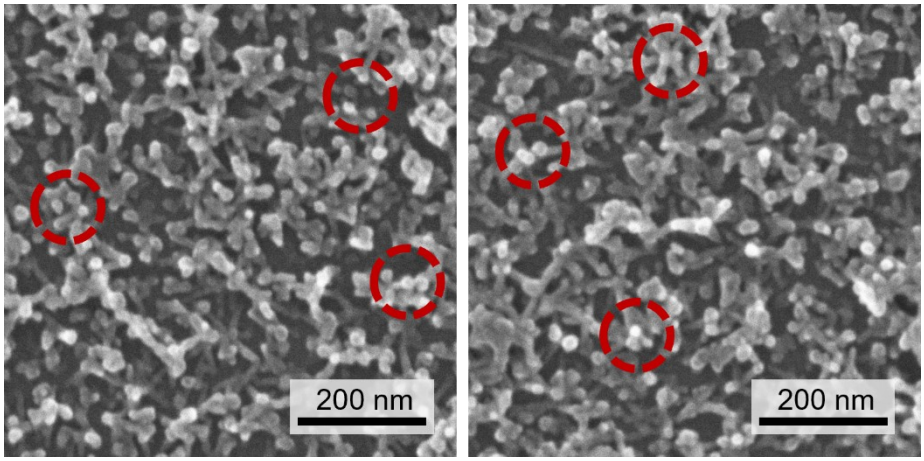
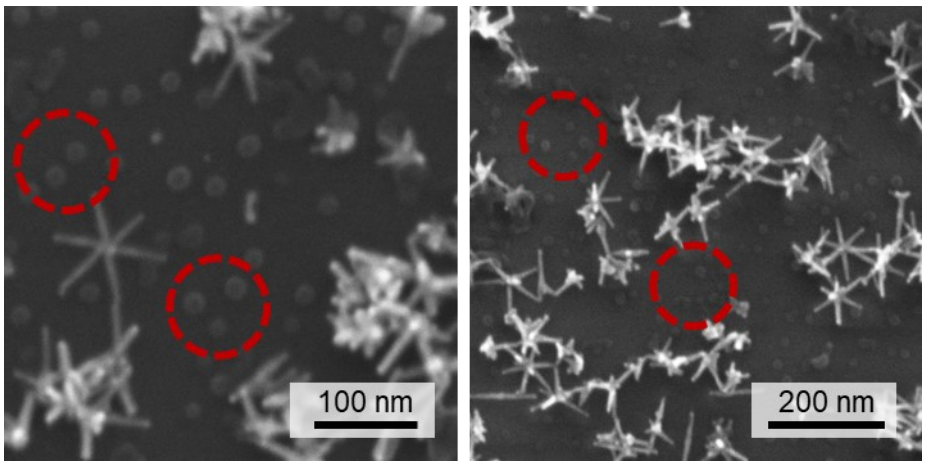


Figure S21: representative SEM images of a glass@PDA@GNS substrate after the immersion in a 10-ppm 15 nm PS-NPs suspension. Red circles highlight the presence of the small PS-NPs in the gaps between GNS nanostars.



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