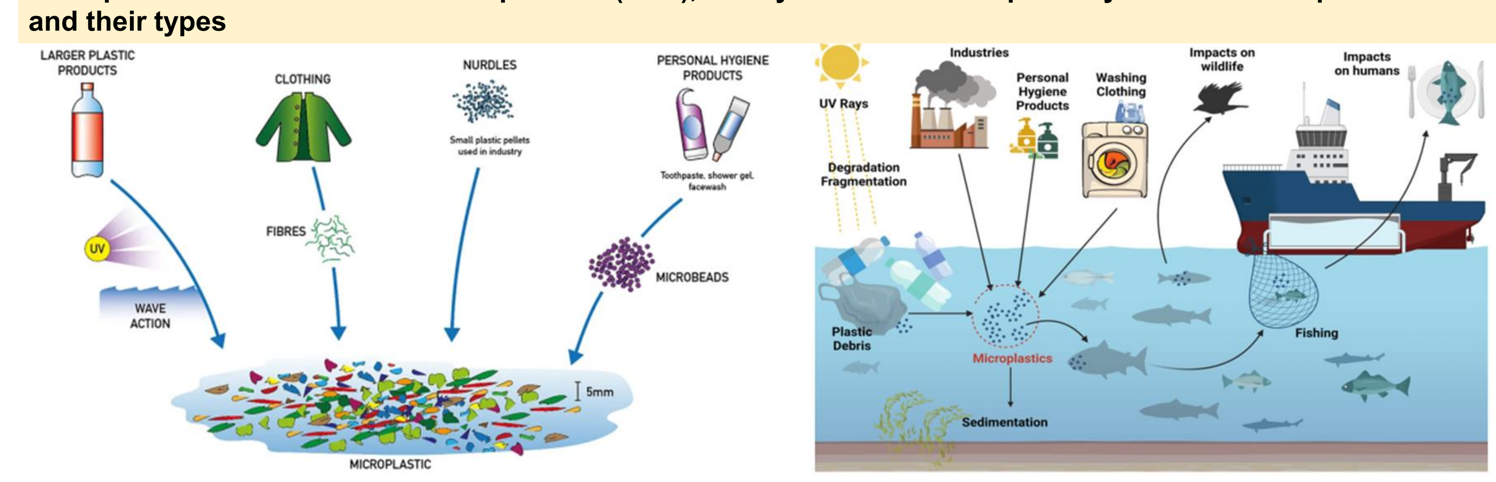
Raman and SERS performances of PDA-coated silver and gold nano-objects for emerging pollutants monitoring

P. Galinetto[1], A. Taglietti[2], S. Schiavi[2], O. Prakash[1], M. Patrini[1], G. Pellegrini[1]
[1] Physics Dept. "A. Volta" - University of Pavia
[2] Chemistry Dept. (InLab) - University of Pavia

Abstract

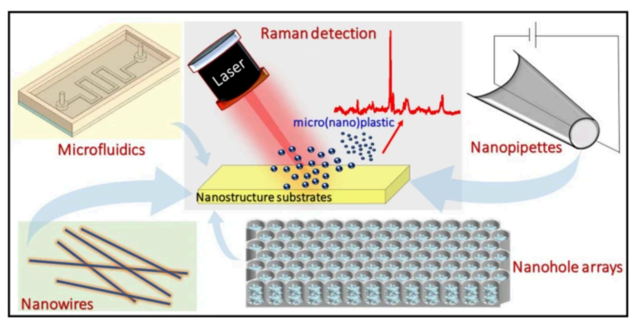
Pollution caused by nanoplastics presents great challenges for researchers because of the lack of sensitivity of traditional analytical methods, with Raman and surface-enhanced Raman spectroscopy (SERS) becoming strategic for their detection. The main drawbacks lie in the poor signals of traditional Raman spectroscopy, requiring high concentrations of analytes, and the non-homogeneous distribution often limiting reliable detection when exploiting SERS on dried samples. Herein, we propose a simple strategy based on a coating layer of polydopamine (PDA) on simple glass substrates to exploit the adhesive properties of the biopolymer for the grafting and thus evenly pre-concentration of polystyrene nanoplastics (PS-NPs), further analysed using Raman and SERS. An in-depth analysis on the role of pH in PDA adhesive properties demonstrates the importance of electrostatic interactions toward different kinds of PS-NPs, presenting different *Z*-potential values. Moreover, PS-NPs of different sizes were analysed, ranging from 1 µm down to 15 nm. Raman detection of 100 nm and 1 µm PS-NPs was achieved, demonstrating that the PDA coating layer enables NPs pre-concentration and their subsequent detection by Raman spectroscopy. The versatility of the PDA substrate was also proven by grafting gold nanostars, creating a SERS substrate capable of detecting PS-NPs down to 15 nm.

Example of main sources of microplastics (MPs), life cycle of MPs and pathways of human exposure to MPs and their types



Raman spectroscopy

Raman spectroscopy is a premier, non-destructive technique for identifying and monitoring microplastics, particularly for particles smaller than 150 microns and down to 1 microns. It provides precise chemical composition, polymer type, and size distribution, making it highly effective for analyzing microplastics in water, soil, and biological samples. (Journal of Nanostructure in Chemistry Volume 12, pages 865–888, (2022))



Key Aspects of Raman for Microplastics Analysis:

Small Particle Detection: Highly sensitive to microplastics and crucial for analyzing small particles that can be ingested.

Non-Destructive & Chemical Identification: Identifies specific polymer types (e.g., Polyethylene, Polypropylene, PVC) and differentiates them from environmental contaminants or fillers.

Automation: Modern Raman microscopy allows for automated mapping and counting of particles, improving efficiency in environmental monitoring.

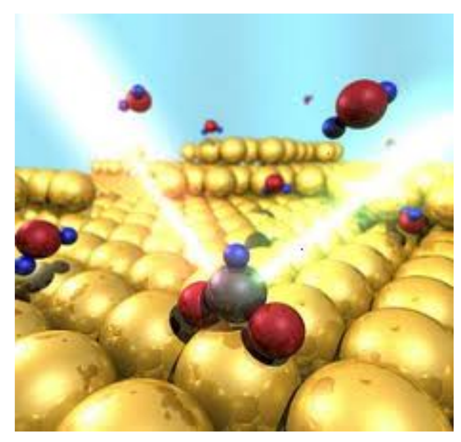
Applications: Employed to identify microplastics in diverse media, including marine environments, wastewater, and food sources.

Limitations: Weak effect. The technique can be time-consuming, and fluorescence from additives or environmental organic matter can sometimes interfere with the signals.

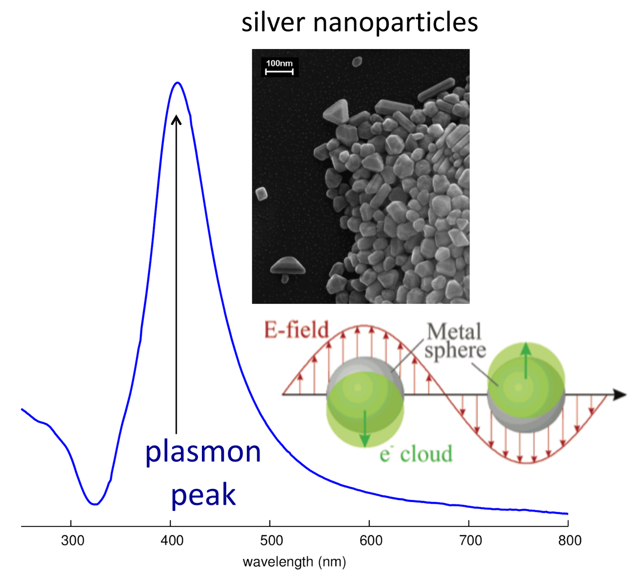
How can weaknesses be improved?

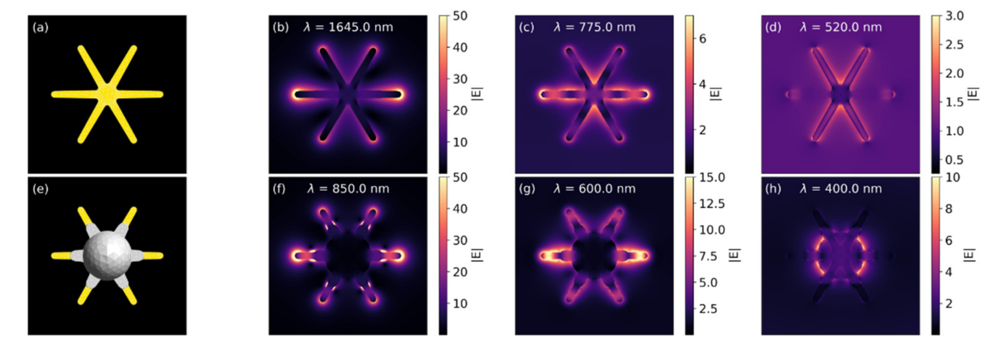
SERS (Surface Enhanced Raman Scattering)

strong (> 10^6) enhancement of the Raman signal for molecules deposited on nanostructured metals



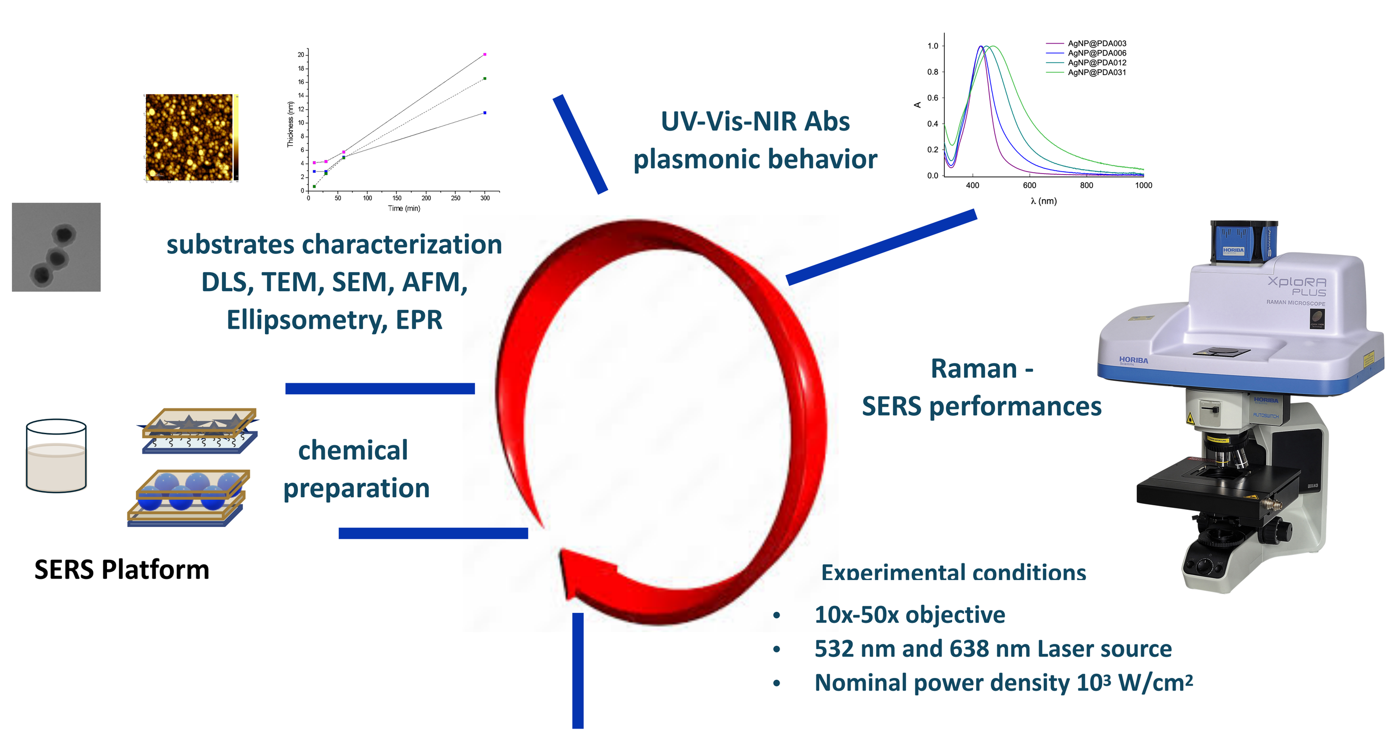
due to plasmon resonance the molecule at the surface feels very strong local fields



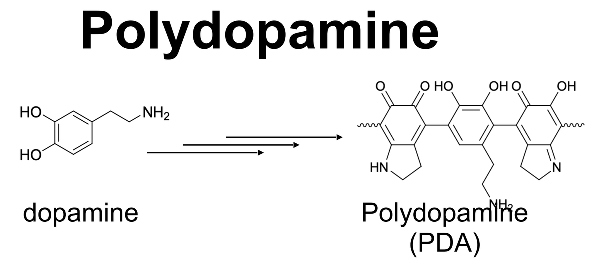


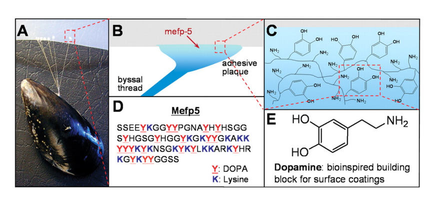
Theoretical modelling can be performed in order to understand the local field behaviour. The boundary element method is used to model the experimental systems. As an example here we report the results for a six-branched gold nanostar surrounded by a silver shell of increasing thickness and immersed in water. This modelling leads to a better comprehension of the experimental SERS results, with a better insight ointo the nature and type of the field enhancement mechanisms.

Methods and experimental



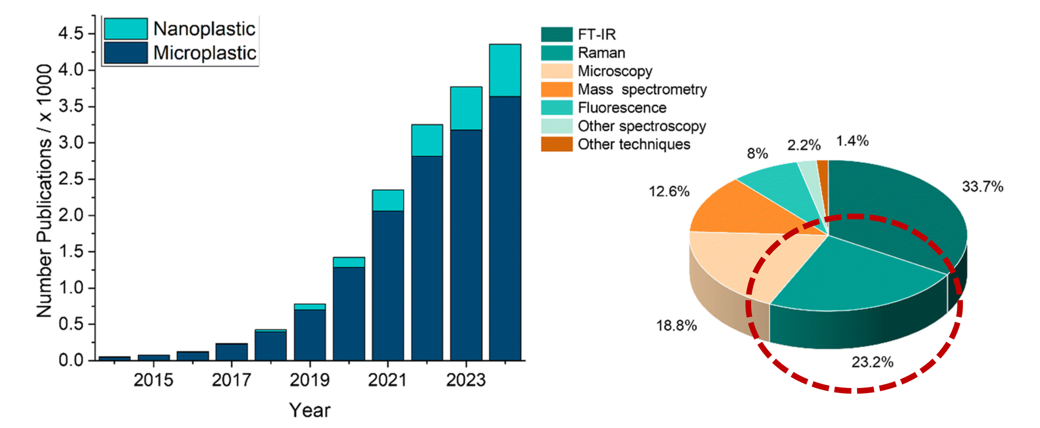
Polydopamine





Lee H., Dellatore S. M., Miller W. M., Messersmith, P.B. *Science*, **2007**, *318*(5849), 426-430

Can we leverage PDA surface chemistry as preconcentrating tool for water pollutants?



Santos A. et al., *Environ. Sci.: Nano*, **2025**,*12*, 3442-3467

Cost-effectiveness | Versatility | Easy coating capability | Adhesive properties

Raman weaknesses

- Long sample pre-treatment
- Difficult Raman detection of plastics debris < 1 µm

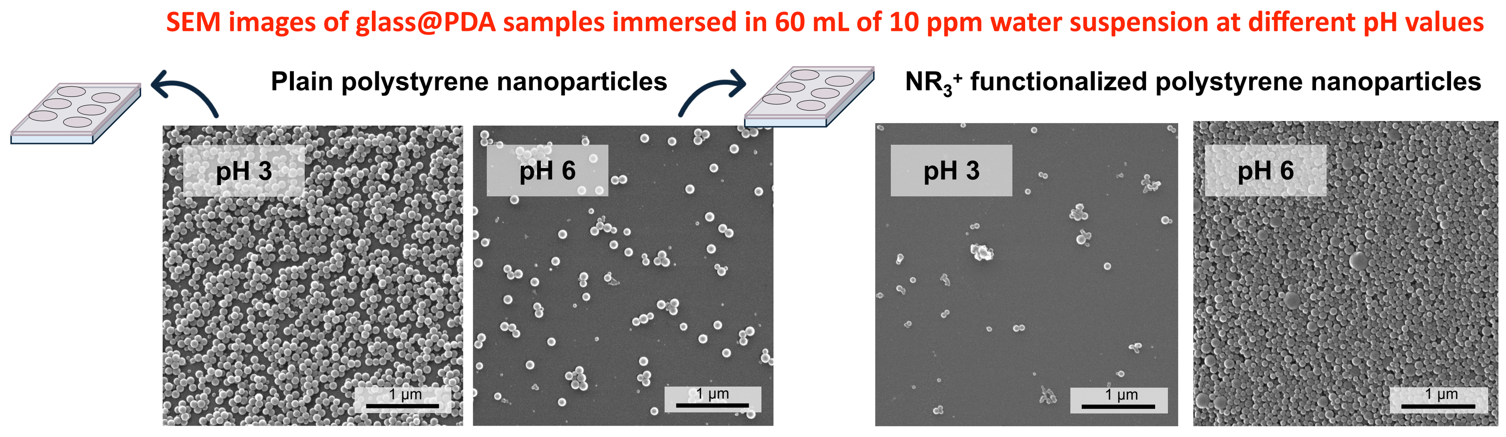
SERS (Surface Enhanced Raman Scattering)

Results

Tester: Polystyrene nanoplastics (PS-NPs)

1 Test with different charged nanoplastics (Ø 100 nm)

SEM images of glass@PDA samples immersed in 60 mL of 10 ppm water suspension at different pH values



Negative ζ-potential of PS-NPs

pH3: electrostatic **attraction** between PDA and PS-NPs

pH6: electrostatic **repulsion** between PDA and PS-NPs

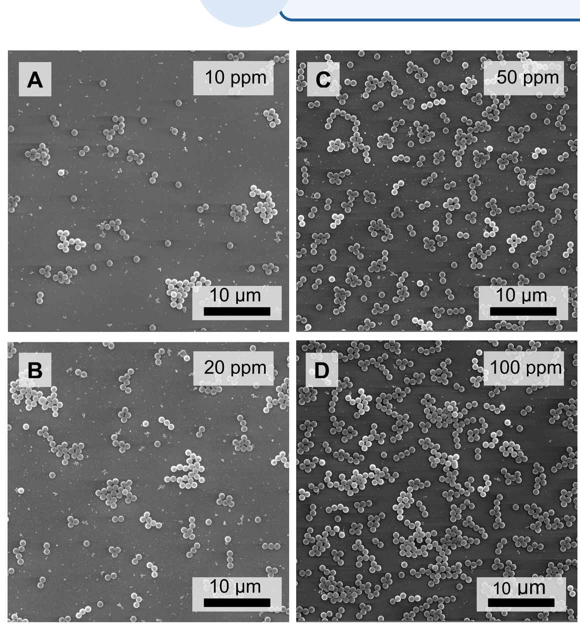
Positive ζ -potential of PS-NPs

pH3: electrostatic **attraction** between PDA and PS-NPs

pH6: electrostatic **repulsion** between PDA and PS-NPs

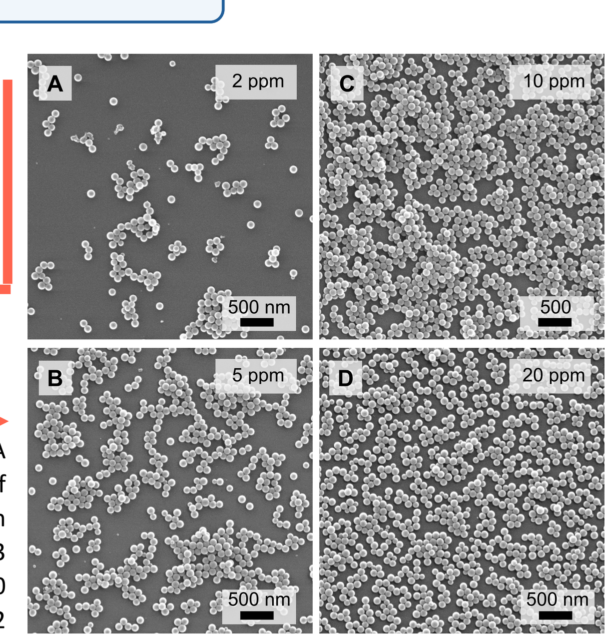
2 Raman detection of pre-concentrated PS-NPs

1 µm PS plastics

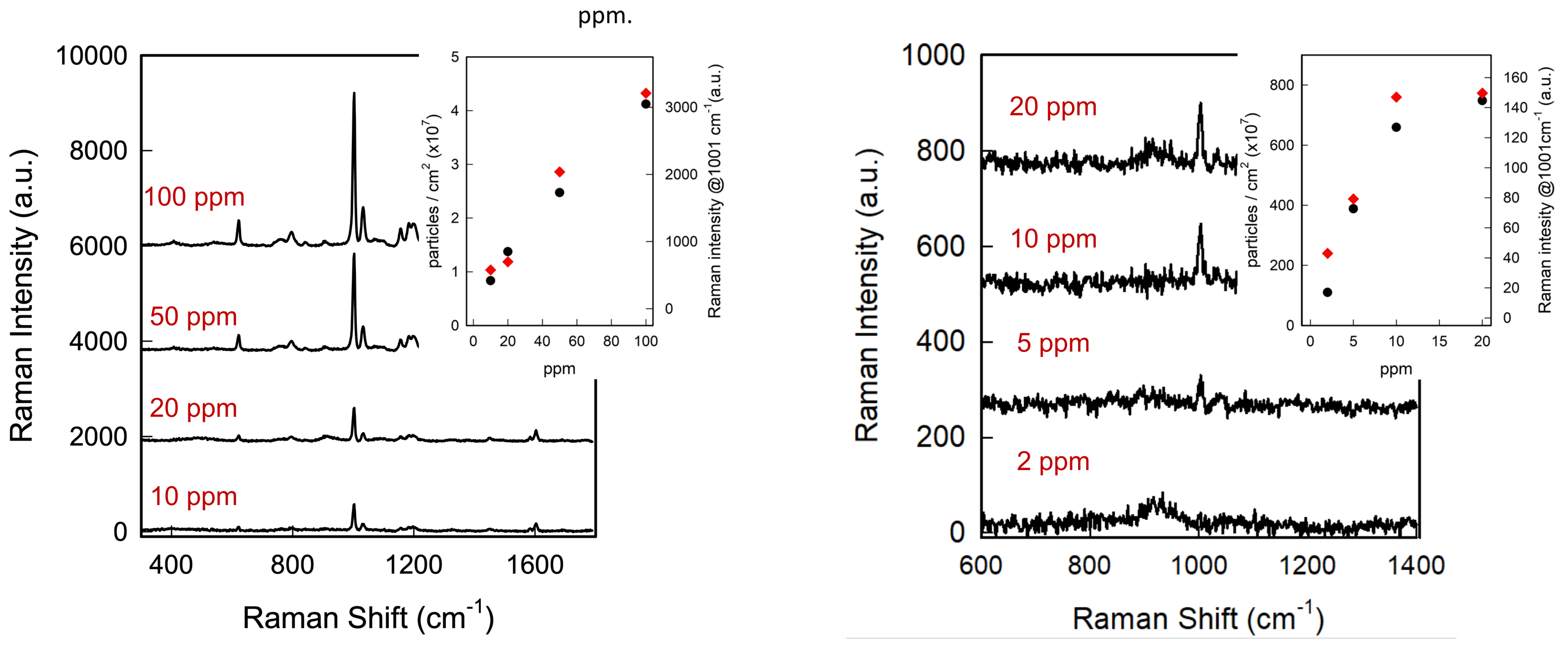


SEM images of glass@PDA samples immersed in 60 mL water suspension of 1 µm diameter plain PS-NPs at pH 3 at concen- trations (a) 10 ppm; (b) 20 ppm; (c) 50 ppm; (d) 100 ppm

100 nm PS plastics



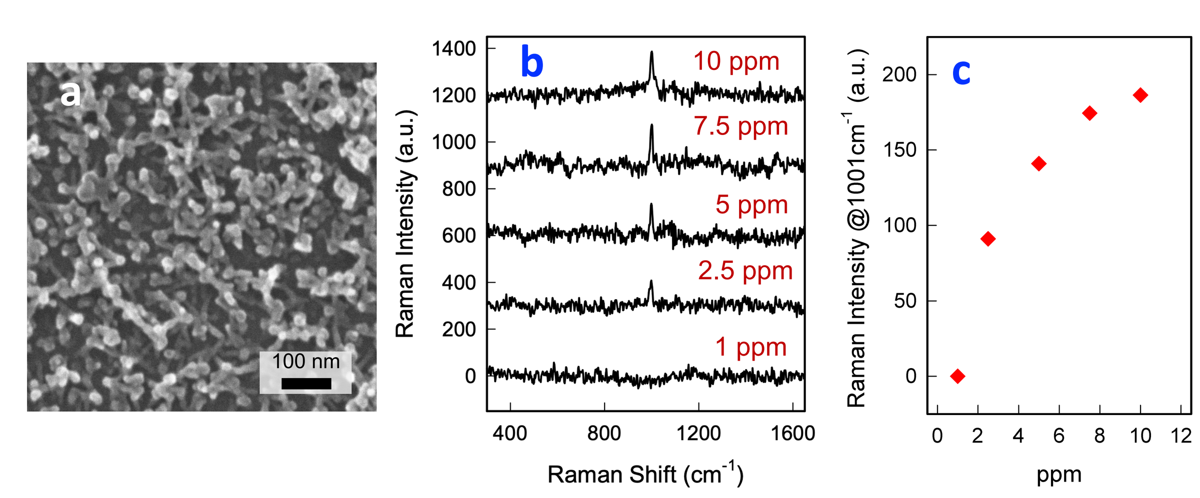
SEM images of glass@PDA samples immersed in 60 mL of aqueous suspensions of 100 nm diameter plain PS-NPs at pH 3 with concentrations of (a) 20 ppm; (b) 10 ppm; (c) 5 ppm; (d) 2 ppm.



Average Raman spectra obtained on glass@PDA samples after immersion in 60 mL water suspensions of 1 µm (left) and 100 nm (right) diameter plain PS-NPs at pH 3 at concentrations ranging between 2 ppm and 100 ppm with the intensity plot of 1001 cm−1 peak as a function of concentration (red diamonds) superimposed on the number of PS particles per unit area obtained from SEM images, as a function of PS-NPs concentration in suspension (black circles)

3 Detection of smaller nanoplastics (Ø 15 nm)

SERS-based detection of 15 nm PS-NPs



SEM images (a), average SERS spectra (b) obtained on glass@PDA@GNS samples after immersion in 60 mL water suspensions of 15 nm PS-NPs at pH 3 between 1 and 10 ppm; intensity of 1001 cm−1 peak as a function of concentration of 15 nm PS-NPs (c).

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By employing this simple strategy, we successfully achieved the Raman-based detection of PS-NPs of 1 µm and 100 nm size. Additionally, the versatility of the PDA substrate was exploited to immobilize gold nanostars (GNS), producing a SERS-active platform capable of detecting PS-NPs as small as 15 nm at concentrations down to the ppm level. It must be stressed that, even in the latter case, the proposed methodology relies on quite simple substrate preparation. This was accomplished by grafting colloidal GNS onto glass@PDA, once again exploiting the favourable interactions enabled by the bio- polymer, which were also harnessed for the further preconcentration of 15 nm PS-NPs. The Raman- and SERS-based methods proposed so far, even though capable of successfully detecting NPs from aqueous suspensions even at very low concentrations, usually involve complex preparation of the sensing substrate and/or rely on poorly reproducible detection strategies, such as nanoparticle aggregation or dry dropping of NPs suspension. We thus believe that this simple approach will provide valuable insights for the development of reliable Raman- and SERS-based methods for the detection of NPs.

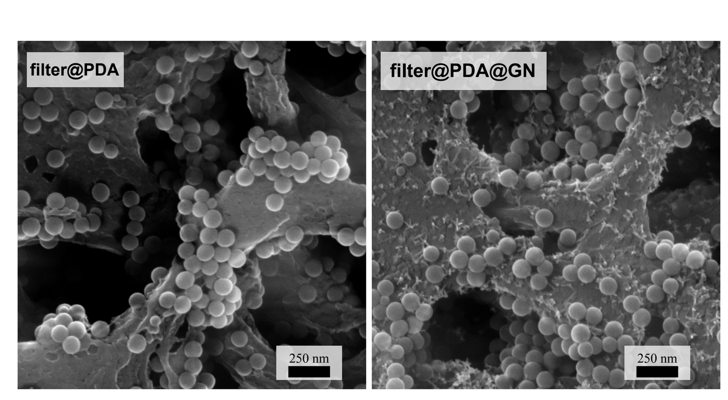
Conclusions and perspectives

Disclaimer!

Proof of concept
bi-dimensional substrate

What's next?

PDA-coated **3D substrate** for SERS-based size independent nanoplastics detection



PS-NPs Ø 100 nm