EFSA Scientific Colloquium N°25

European Food Safety Authority

May 6th, 2021

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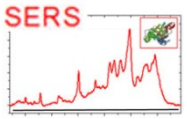

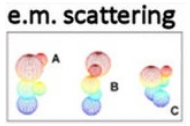

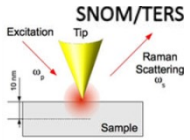

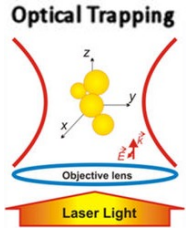

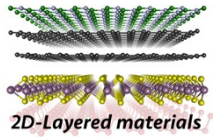

Optical trapping and Raman spectroscopy of micro- and nano- plastics

Pietro G. Gucciardi

CNR – Istituto Processi Chimico-Fisici

Viale F. Stagno D'Alcontres 35, 98158 Messina

Email: gucciardi@ipcf.cnr.it

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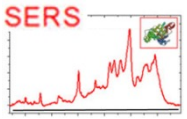
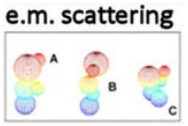
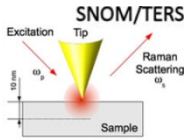
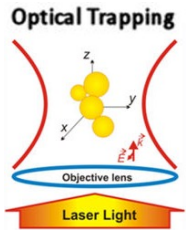
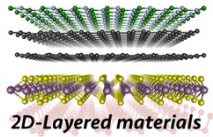










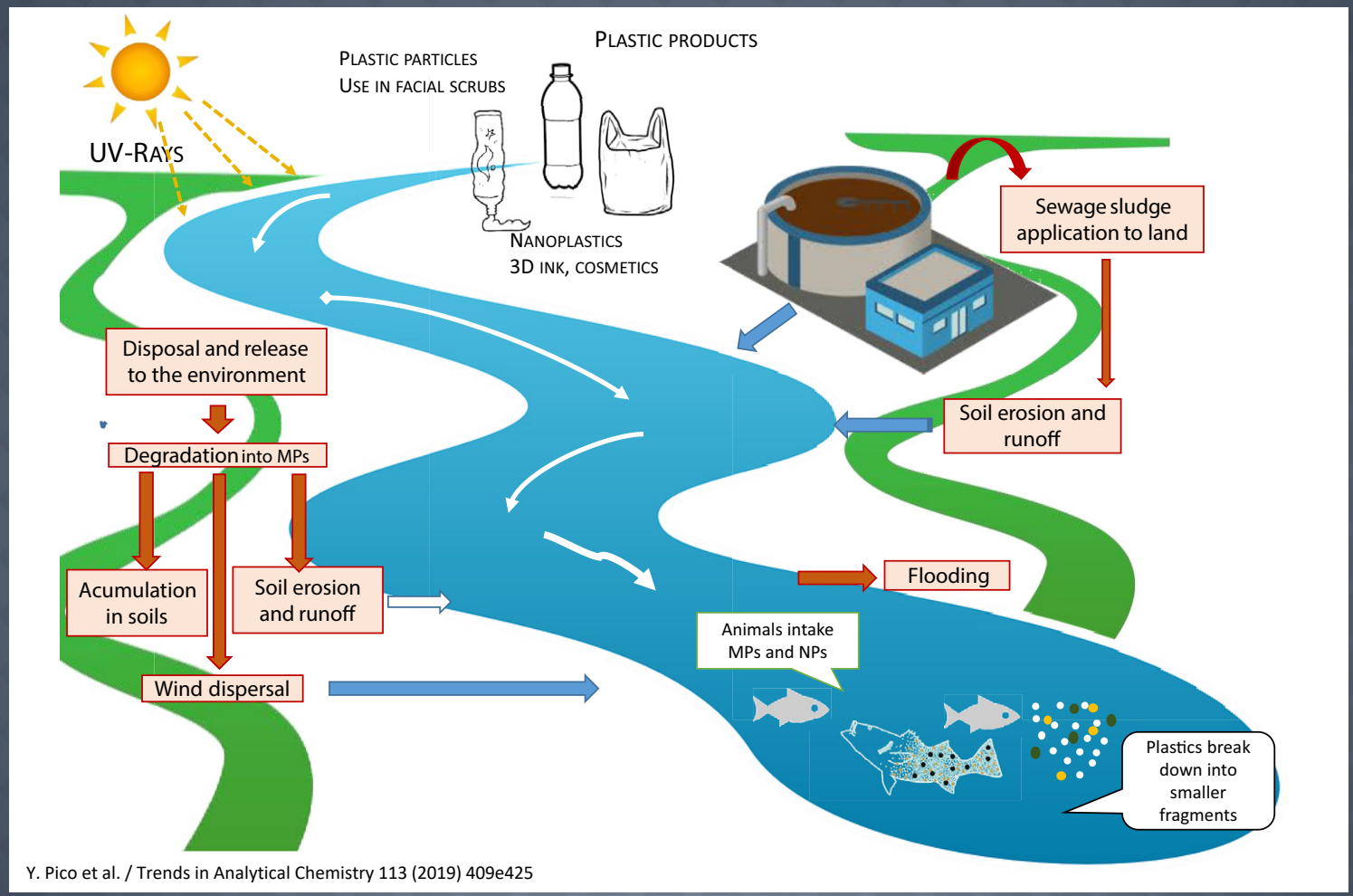
Overview

- Analytical tools for nanoplastics analysis: technological gaps
- Optical trapping and Raman spectroscopy can help bridging the gap
- Analysis of model and environmental plastic particles
- Conclusions & outlook

Source, transport, and fate of MPs and NPs.

Between 5 and 13 million tons of plastic debris are released into freshwater per year through domestic/industrial discharges and sewage plants. Among this, an indetermined fraction is NANO.

- Primary sources: Waterborne paints, adhesives, cosmetics, 3D printers
- Secondary sources: Photo/Thermal oxidation yields fragmentation of micro- into nano- plastics



Y. Pico et al. / Trends in Analytical Chemistry 113 (2019) 409e425

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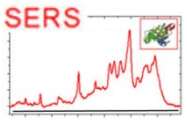

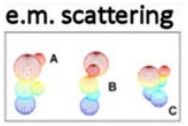

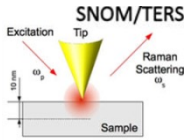

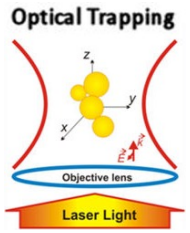

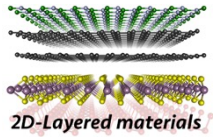

Small Micro- and Nano- plastics in food

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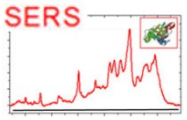
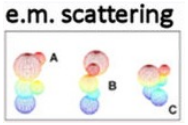
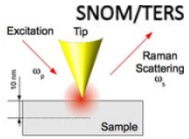
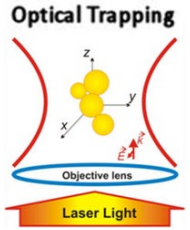
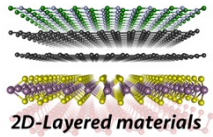










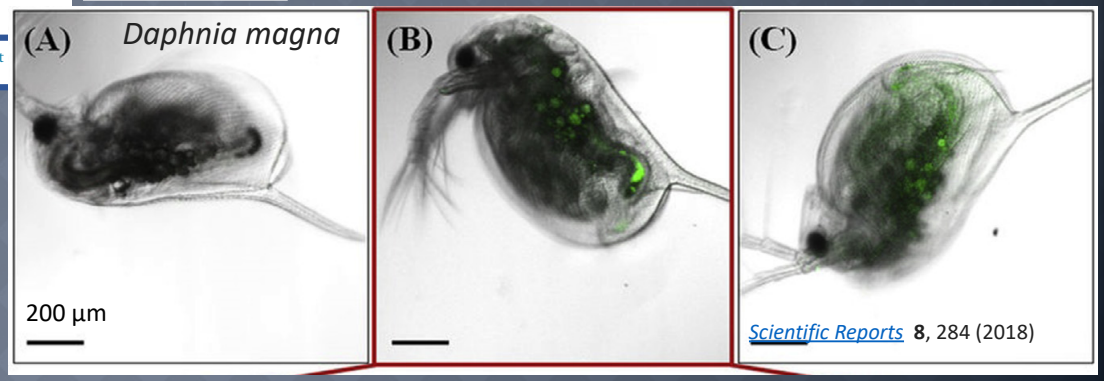
Environmental Pollution 268 (2021) 115811

Table 1
A summary of recent worldwide studies that reported microplastics from commercial drinking products for human consumption.

Country	Source	Sample container	Microplastics (average items L^{-1})	Shape	Size	Color	Polymer types	References
Bottled drinking water								
Germany	Bottled (mineral water)	NR	1	Fiber	NR	NR	Cellulose	Wiesheu et al. (2016)
Germany	Bottled (mineral water); Commercial store	Single use PET Reusable PET Glass	2649 ± 2857 4889 ± 5432 6292 ± 10,521	NR	>5 μm	NR	PET in plastic bottles, PE and styrene butadiene copolymer in glass	Oβmann et al. (2018)
Germany	Bottled (mineral water)	Single use Returnable Glass Beverage	14 ± 14 118 ± 88 50 ± 52 11 ± 8	Fragments	5, 10 and < 20 μm	NR	PET, PP, PE	Schymanski et al. (2018)
Global	Bottled (mineral water)	Single use PET	315	Fragments, fibers and films	NR	NR	PP, Nylon (50% samples analyzed)	Mason et al. (2018)
Italy	Bottled (mineral water)	Single use PET capped with HDPE	148 ± 253	NR	0.5–40 μm	NR	PET, HDPE	Winkler et al. (2019)
Italy	Mineral still and sparkling	Single use PET 10 brands	5.42×10^{7} $\pm 1.95 \times 10^{7}$	NR	NR		NR	Zuccarello et al. (2019)
Thailand	Bottled (sparkling and still water)	Single use PET Returnable glass	140 ± 19 52 ± 4	Fibers and fragments	6.5-> 50	Blue, reddish brown, bluish green, transparent, black.	PET, PE, PP, PA and PVC	Kankanige and Babel (2020)
U.K.	Bottled water	Single use plastic bottle	NR	Fibers and fragments	NR	NR	NR	Stanton et al. (2019)
Beer								
Germany	NR	NR	Fibers: 2-79 Fragments: 12-109 Granules: 2-66	Fibers, fragments and granules	NR	Transparent, blue, black and green	NR	Liebezeit and Liebezeit 2014
Germany	NR	Glass bottle	Fibers: 16 ± 15 Fragments: 21 ± 16 Granules: 27 ± 18	Fibers, fragments and granules	NR	NR	NR	Lachenmeier et al. (2015)
Germany	Pilsener beer	NR	10–19	Fibers	1–5000 μm	NR	PE, Cellulose, PS, PET and PE-PS	Wiesheu et (2016)

Not exposed

Exposed to nanosized (60nm) fluorescent PS spheres



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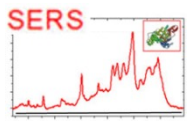
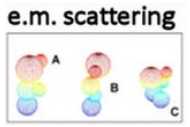
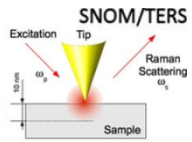
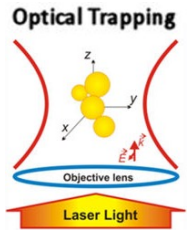
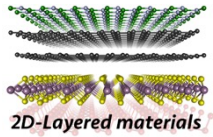




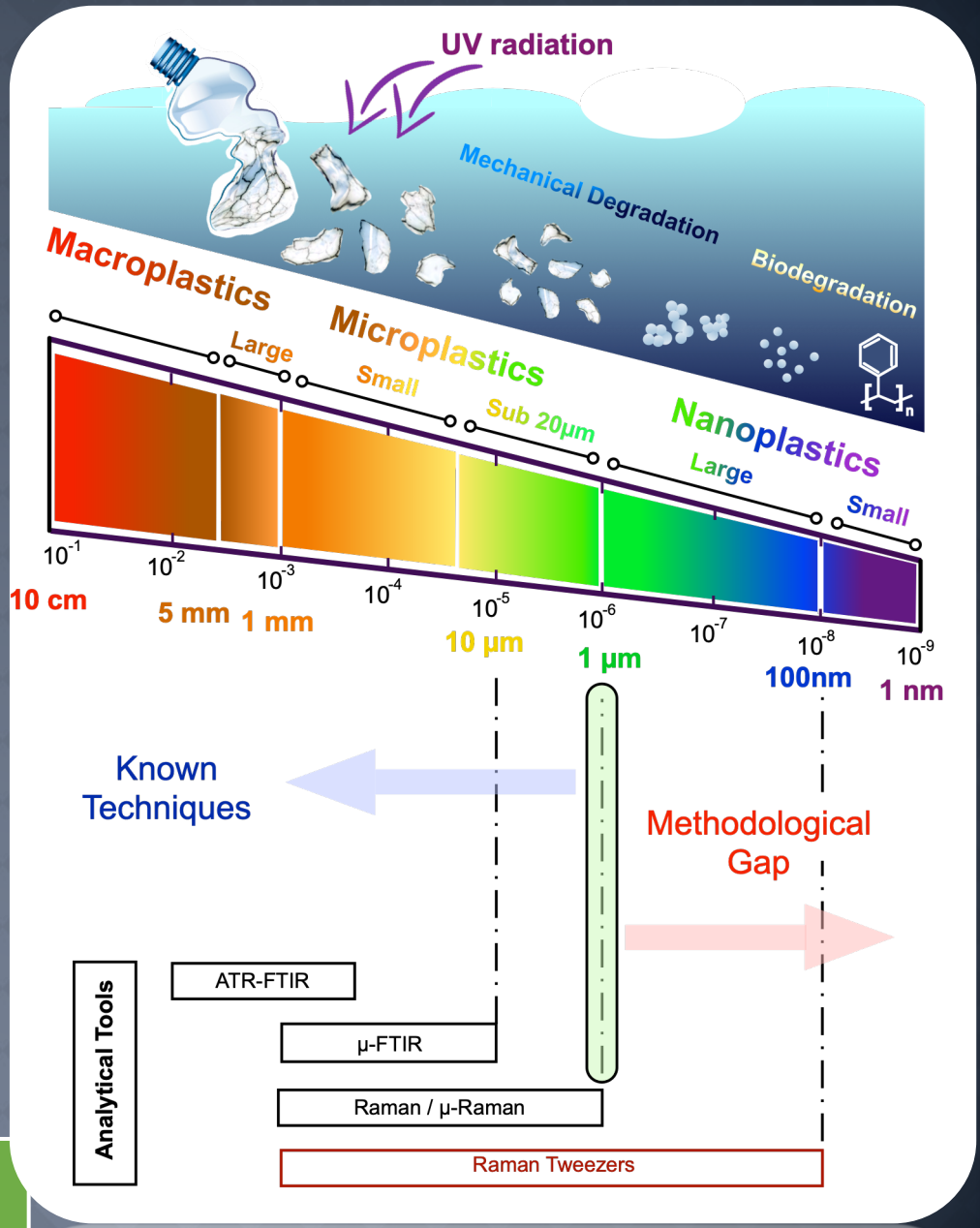






Analytical tools and size limits

- Particle size analysis: **OK**
  - Dynamic Light Scattering,
  - NP-Tracking
  - Microscopy
  - SEM/TEM/EDX
  - AFM
- Chemical analysis: **Gap**
  - FT-IR spectroscopy
  - Raman spectroscopy
  - Py-GC-MS



- NanoPlastics < 1 µm
- Small micro– and nano- plastics analysis … in liquid

Raman spectroscopy

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SERS

e.m. scattering

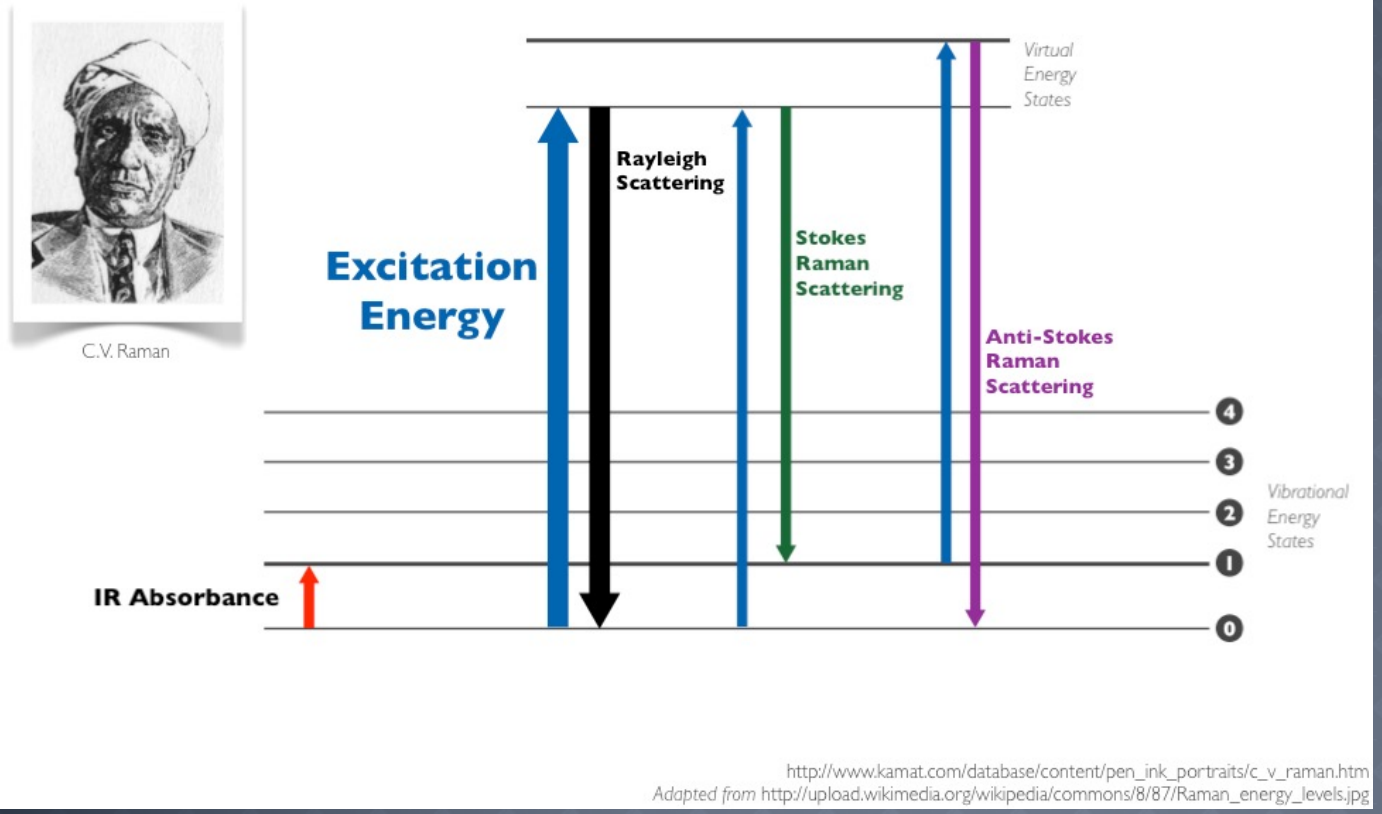
SNOM/TERS

Optical Trapping

2D-Layered materials

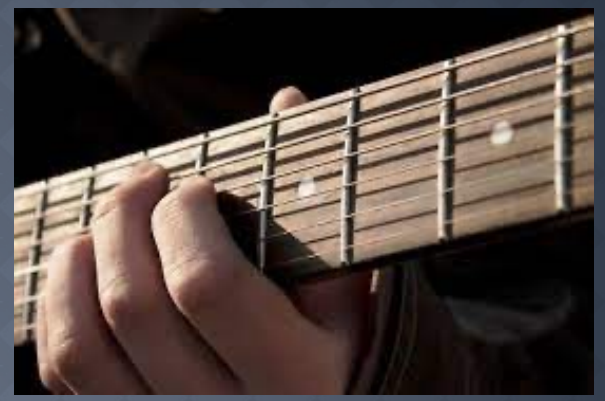
Vibrational spectroscopy using visible/NIR laser light

Symmetric stretching | Anti-symmetric stretching | Twisting | Scissoring



http://www.kamat.com/database/content/pen_ink_portraits/c_v_raman.htm
Adapted from http://upload.wikimedia.org/wikipedia/commons/8/87/Raman_energy_levels.jpg

Detect «the sound» of molecules



- Applications: materials recognition, structure and electronic properties
- Specific fueatures: Imaging capabilities, Non invasive, works in water

MicroRaman spectroscopy

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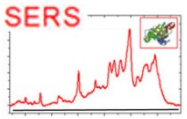
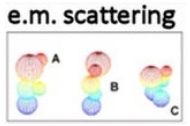
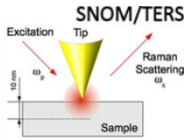
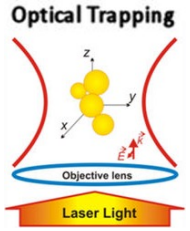
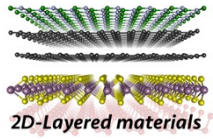


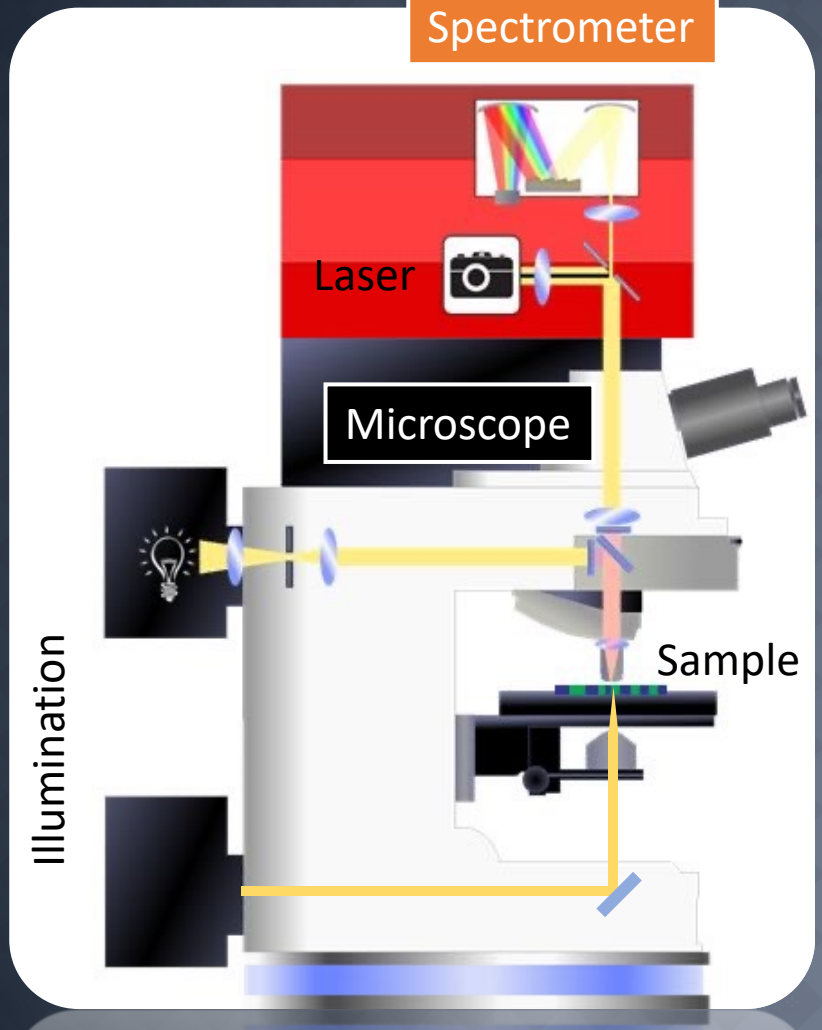




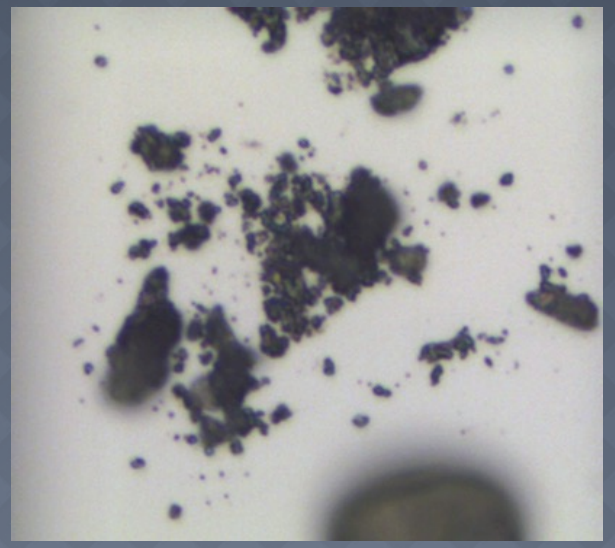




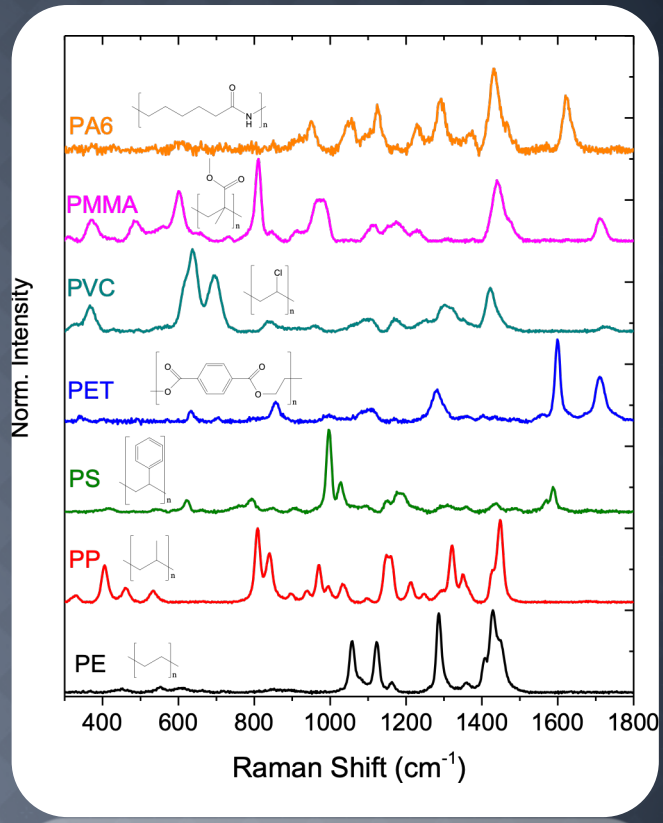
Spectrometer



Optical image of dried microplastics



Raman spectra: what is made of what



- Raman works well:
  - on dried samples
  - liquids
  - molecular solutions
  - Precipitated samples in liquid environment

Criticalities of Raman for µPlastics analysis

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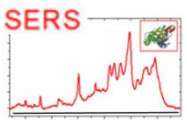
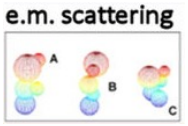
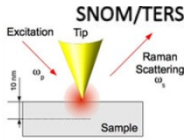
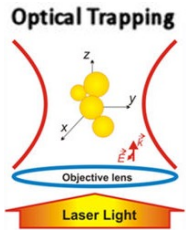
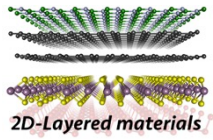


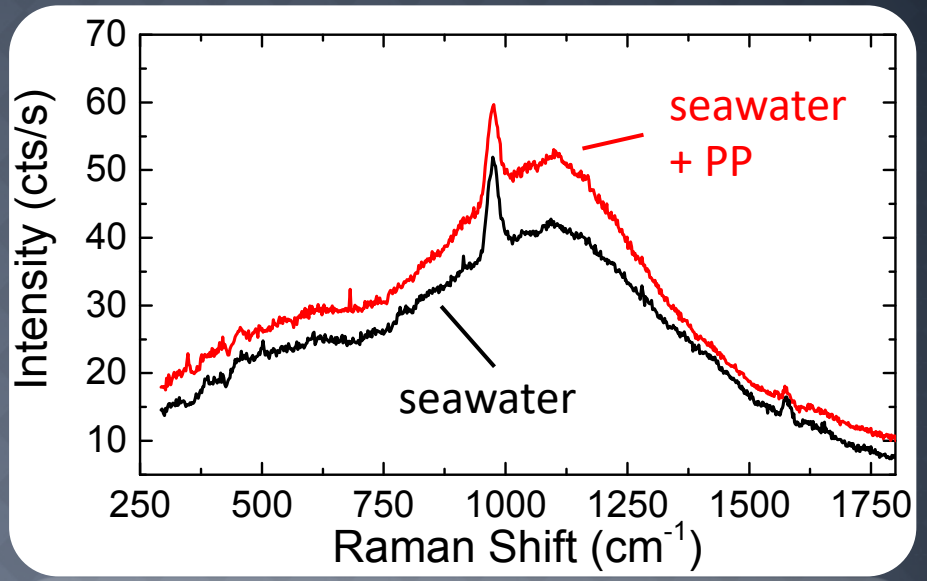


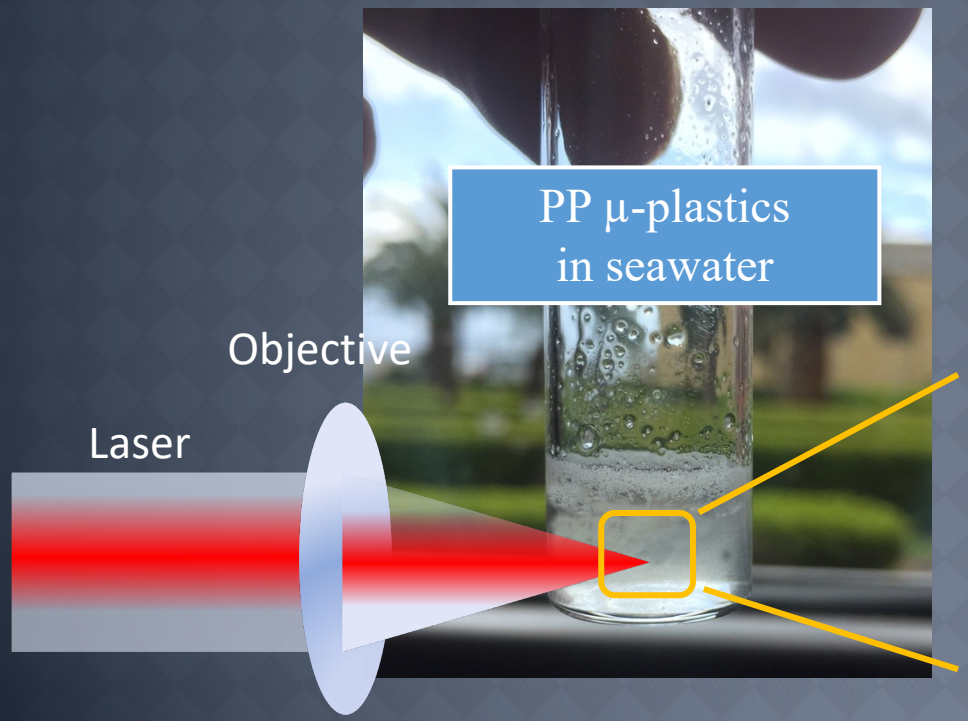


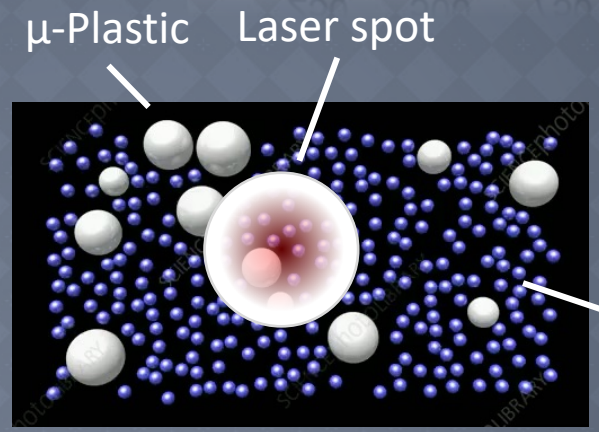




Dispersions of sparse particles are hard to analyzed because of limited interrogation time







https://www.sciencephoto.com/media/611608/view/brownian-motion-animation

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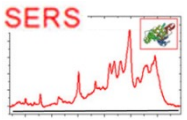
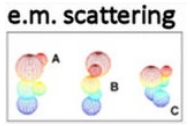
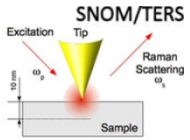
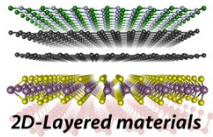
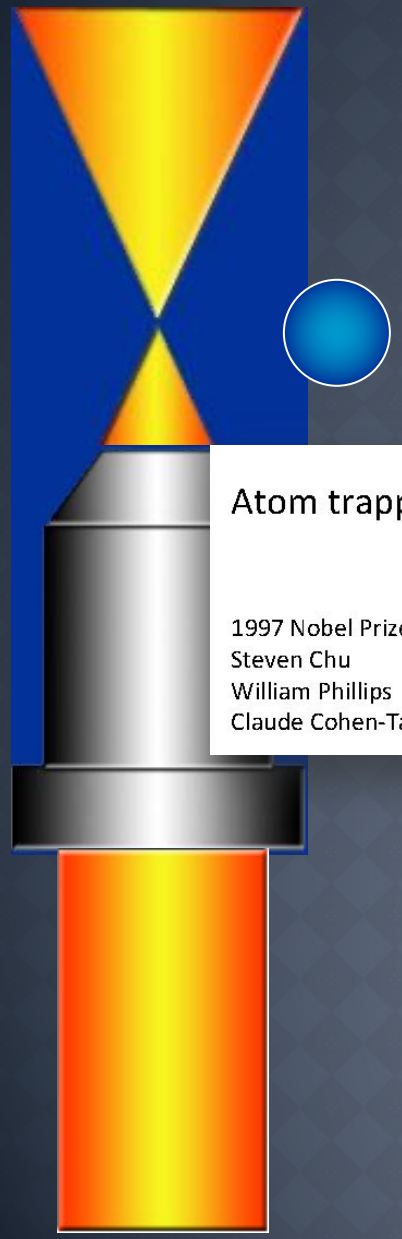










nature nanotechnology

REVIEW ARTICLE

PUBLISHED ONLINE: 7 NOVEMBER 2013 | DOI: 10.1038/NNANO.2013.208

Optical trapping and manipulation of nanostructures

Onofrio M. Maragò[1]*, Philip H. Jones[2], Pietro G. Gucciardi[1], Giovanni Volpe[3] and Andrea C. Ferrari[4]*

Atom trapping

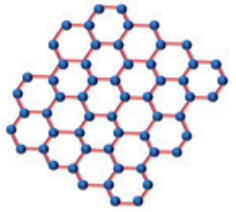
Nanotweezers

Optical tweezers

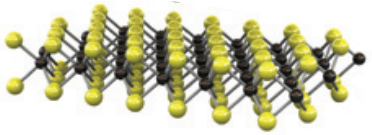
Atom trapping

1997 Nobel Prize in Physics:
Steven Chu
William Phillips
Claude Cohen-Tannoudji

Nanowires and nanotubes

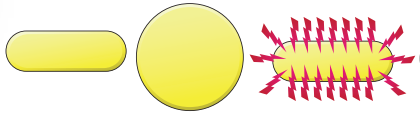


Graphene



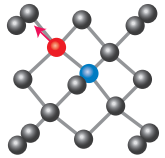
Layered materials

Molecules

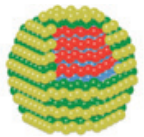


Plasmonic nanoparticles

Atoms

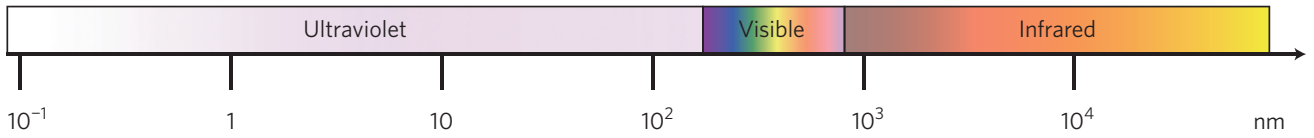


NV centres



Quantum dots

Synthetic colloids



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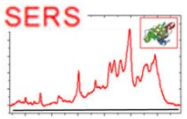

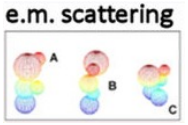

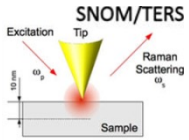

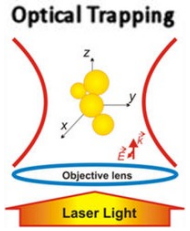

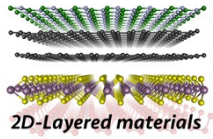

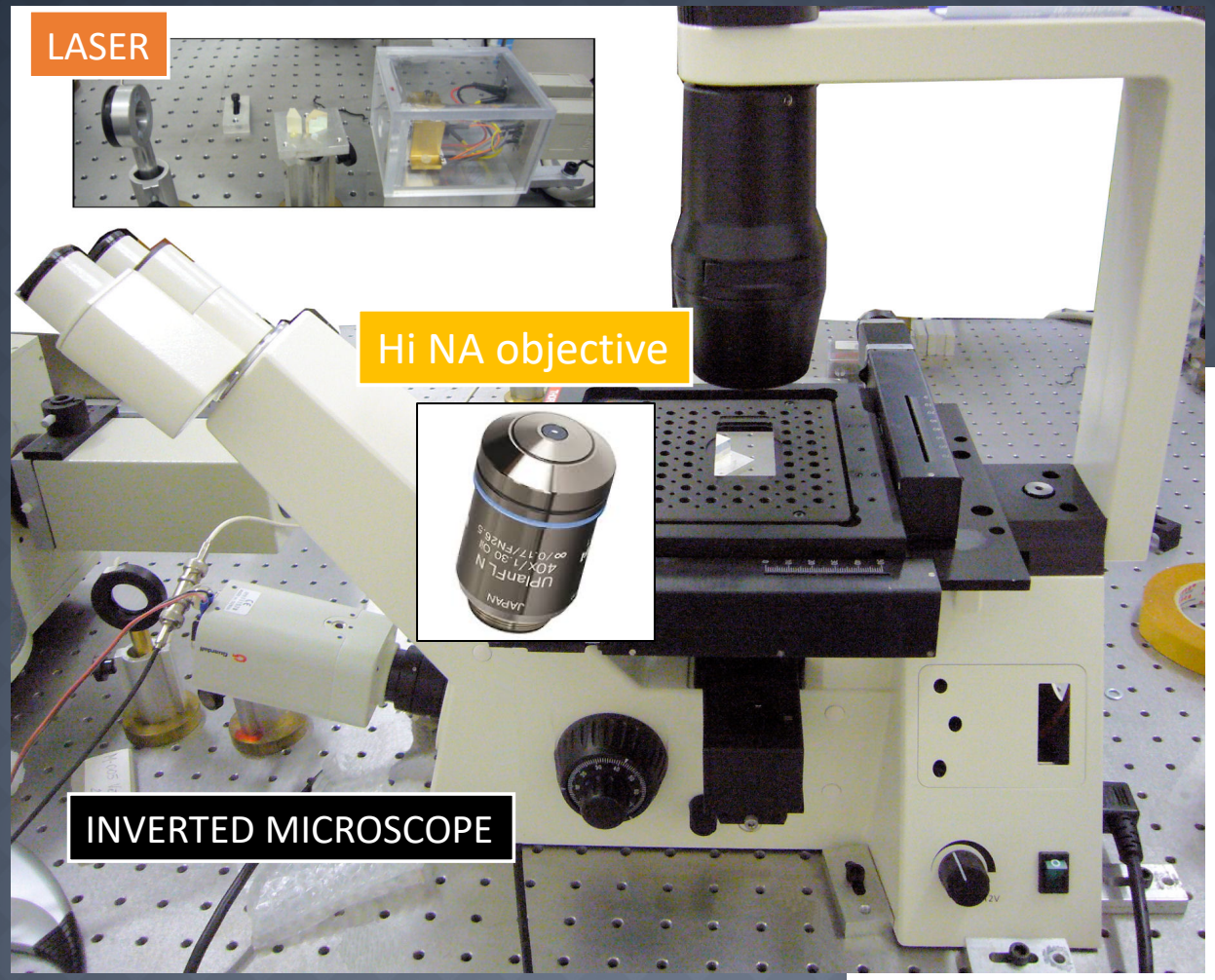

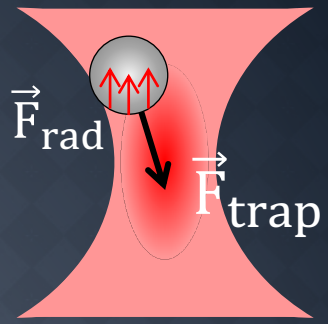

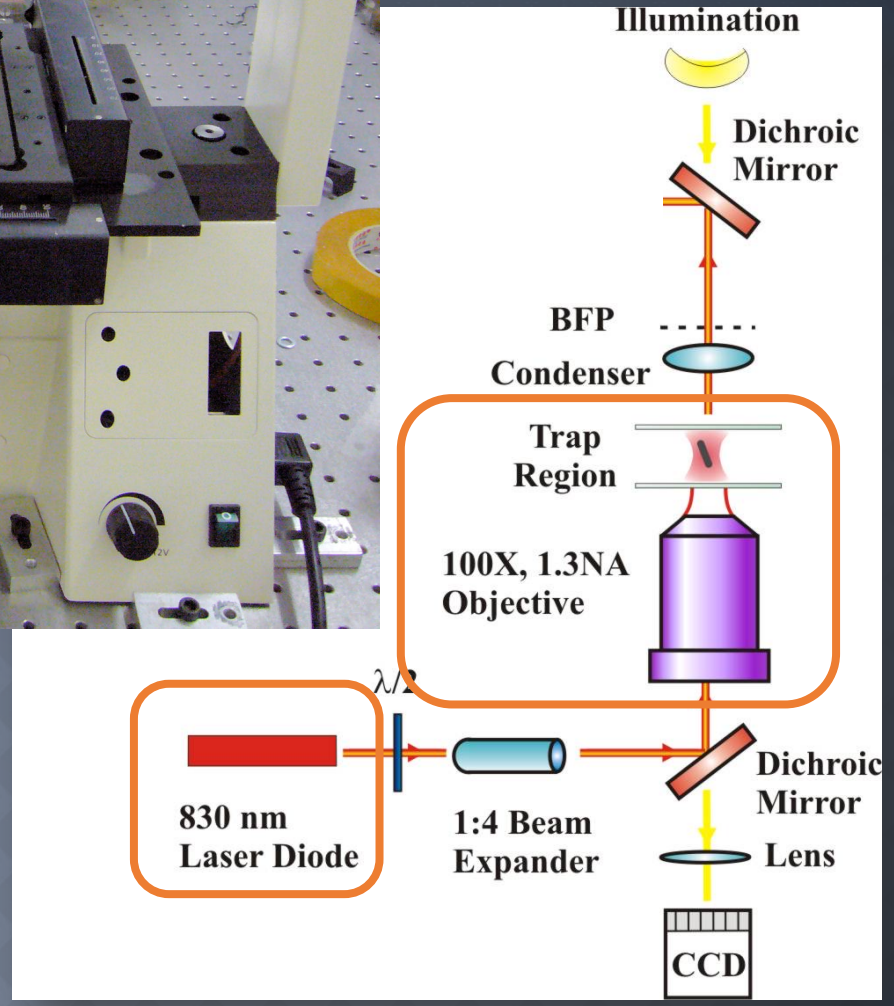

Optical Tweezers

Optical Forces

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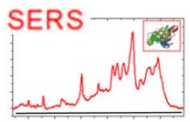
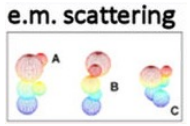
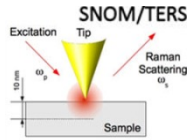
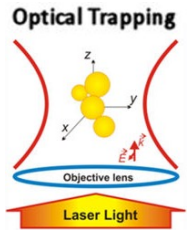
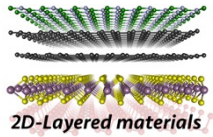
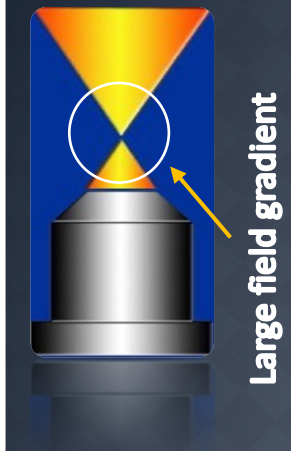












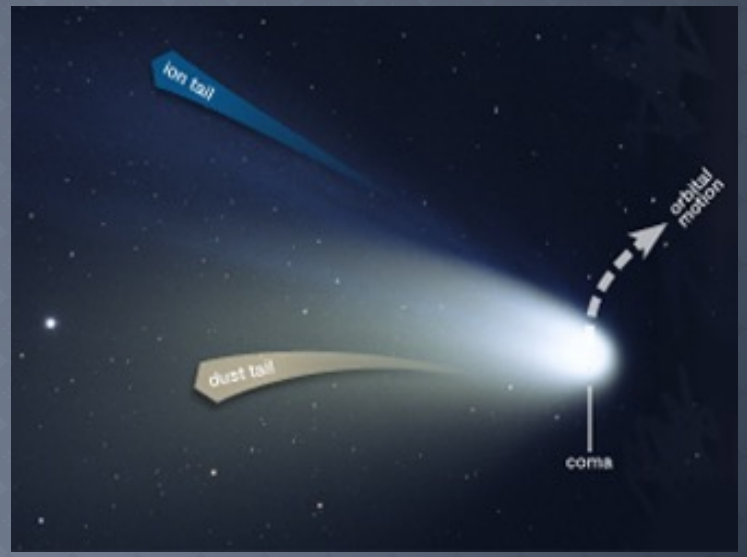
$$\langle \vec{F} \rangle = \underbrace{\frac{1}{2c\varepsilon_0 n_m}\mathrm{Re}(\alpha_p)\vec{\nabla}I(r,z)}_{\text{Intensity gradient}} + \underbrace{\frac{n_m}{c}\sigma_{\text{ext}}\, I(r,z)\hat{z}}_{\text{Radiation pressure}} + \underbrace{\frac{c\varepsilon_0}{4\omega i}\sigma_{\text{ext}}\vec{\nabla}\times\vec{E}\times\vec{E}^*}_{\text{Polarization gradient}}$$

Attractive Force, responsible for optical trapping

Non-conservative Forces: repulsive

Optical Trapping of carbon nanotubes

Radiation pressure on comet star



Optical Tweezers + Raman = Raman Tweezers

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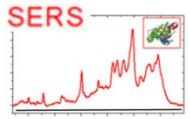
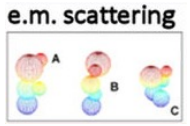
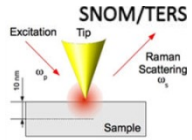
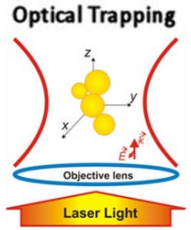
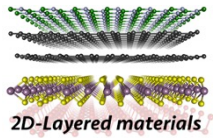


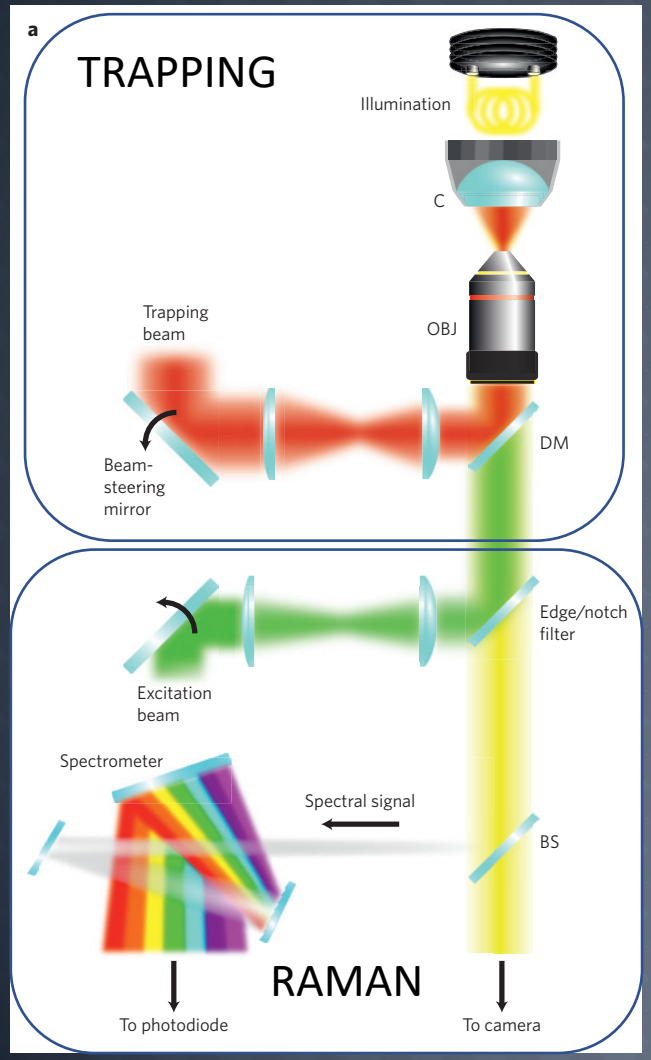




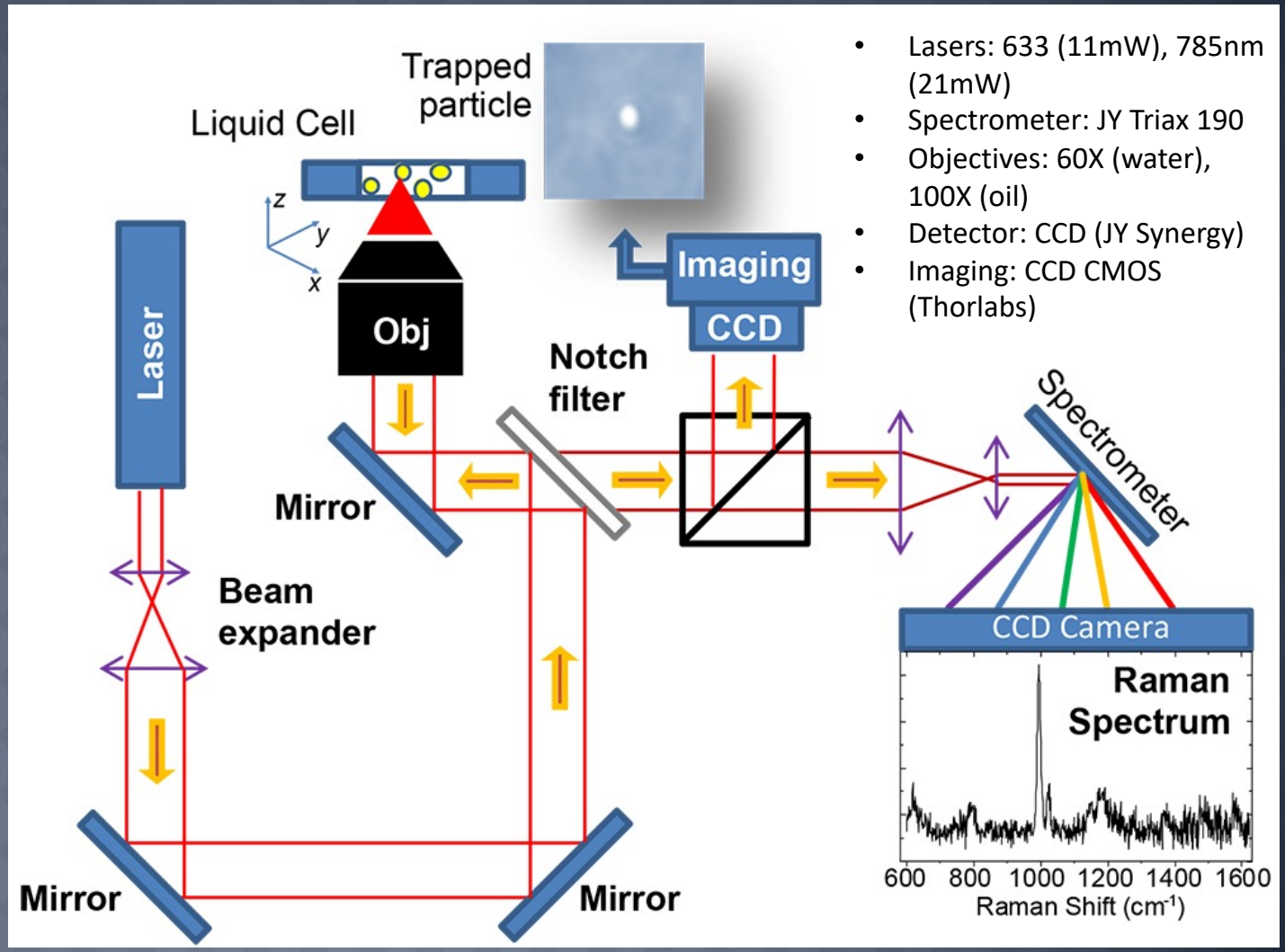




2 BEAMS RAMAN TWEEZERS



SINGLE BEAM RAMAN TWEEZERS



- Lasers: 633 (11mW), 785nm (21mW)
- Spectrometer: JY Triax 190
- Objectives: 60X (water), 100X (oil)
- Detector: CCD (JY Synergy)
- Imaging: CCD CMOS (Thorlabs)

Marago et al. Nat Nanotechnol 2013;

Bernatova et al., JPCC 2019, 123, 9; Gillibert et al. Environ. Sci. Technol. 2019, 53, 15, 9003

Photo of the setup

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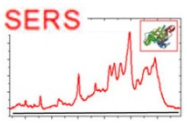
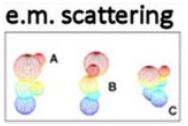
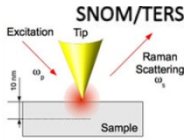
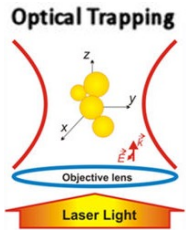
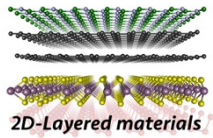






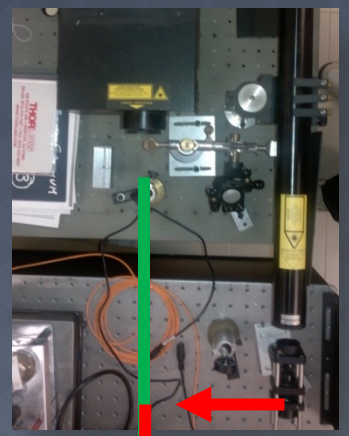




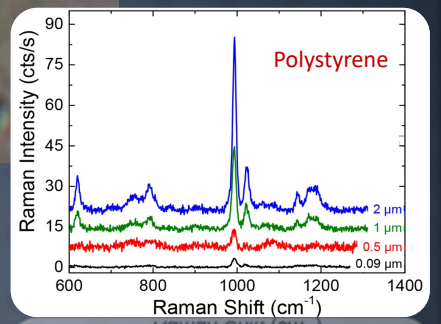
Laser Sources

Sample compartment

Ar++ laser

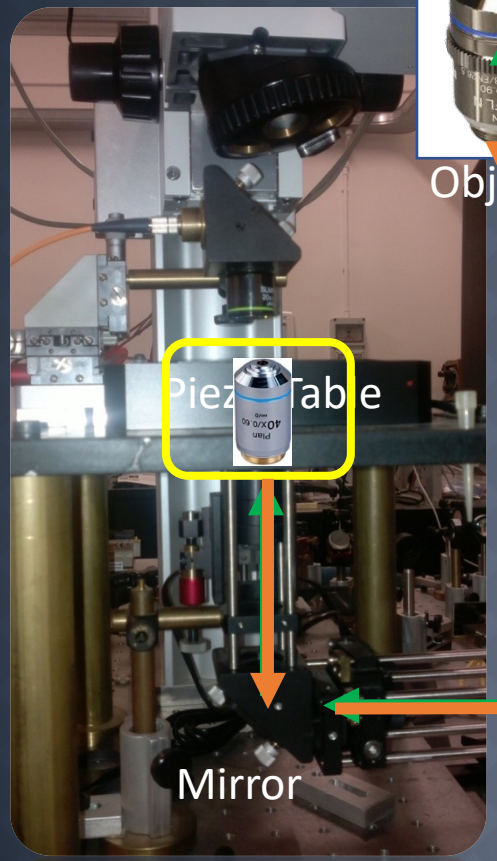


HeNe laser
Diode Laser



Illumination

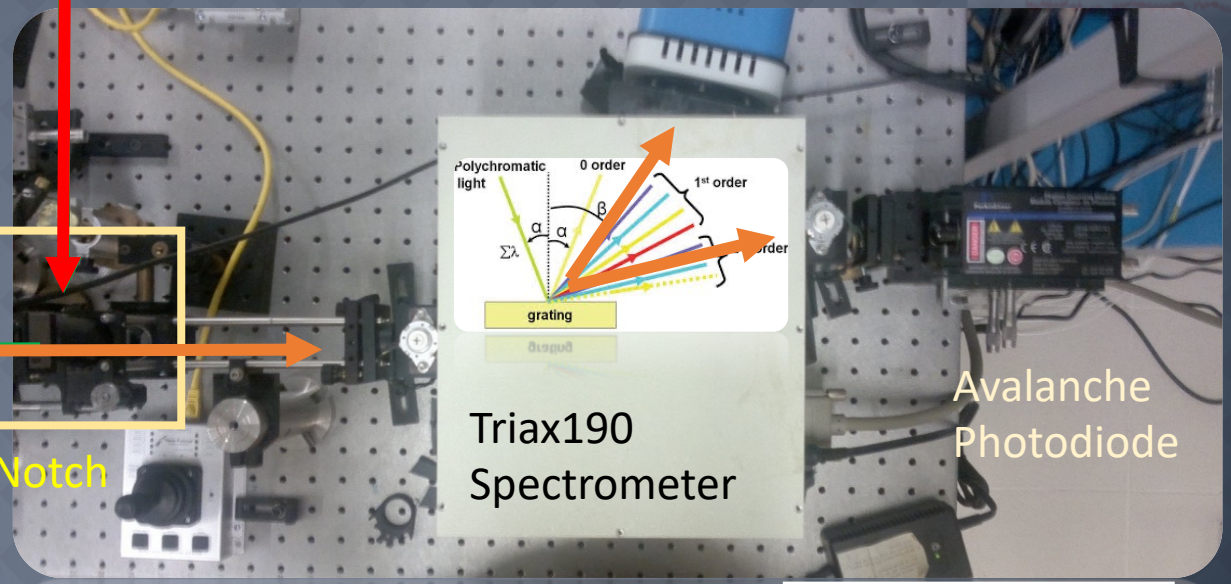
Objective



Piezo Table

Mirror

CCD camera



Edge/Notch
Filter

Optical Tweezers

Spectroscopy

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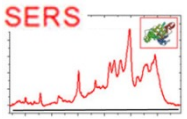
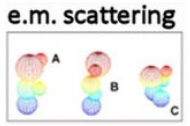
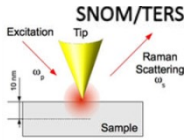
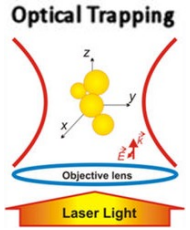
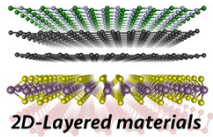










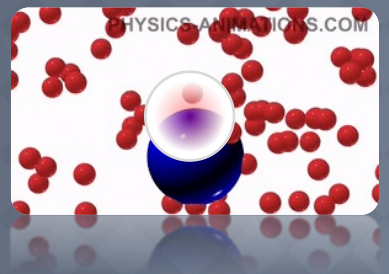
Can we trap micro and nanoplastics ?

Microplastics

Microplastics (d > 1 μm) in water are always trapped
n_{plast} (~1.5) > n_{H2O} (1.33)

Nanoplastics

Brownian fluctuations can drive the particle out of the trap



The optical potential must overcome the Brownian energy

Existence of a threshold power

$$P_{\mathrm{thr}} > \frac{1.12\, c\, k_{\mathrm{B}}\, T\, \lambda^2 \left(n_{\mathrm{p}}^2 + 2n_{\mathrm{m}}^2\right)}{a^3 N A^2\, n_{\mathrm{m}} \left(n_{\mathrm{p}}^2 - n_{\mathrm{m}}^2\right)}$$

100 nm PS
@ 633nm

$P > P_{\mathrm{thr}} \sim 15$ mW

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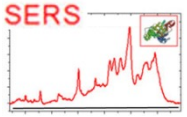
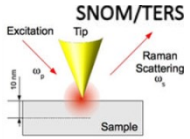
SERS

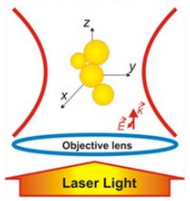


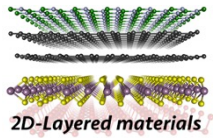
e.m. scattering

SNOM/TERS



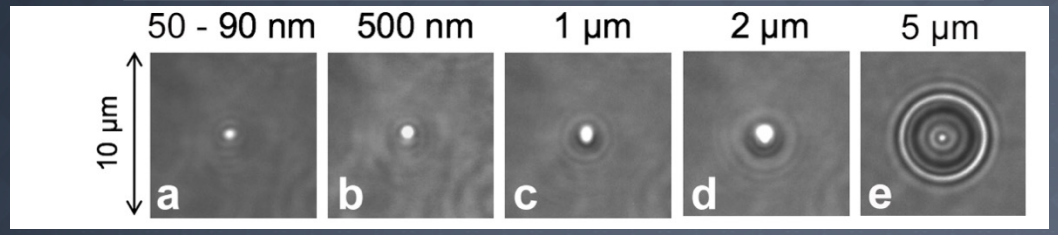
Optical Trapping

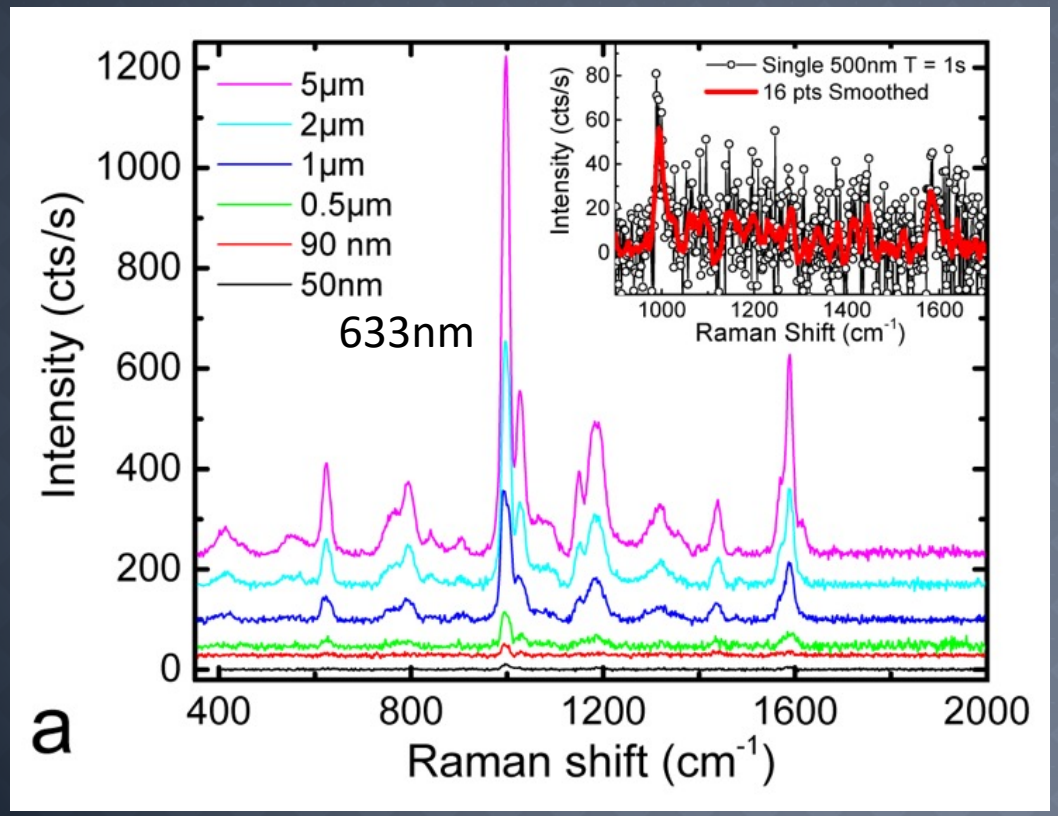




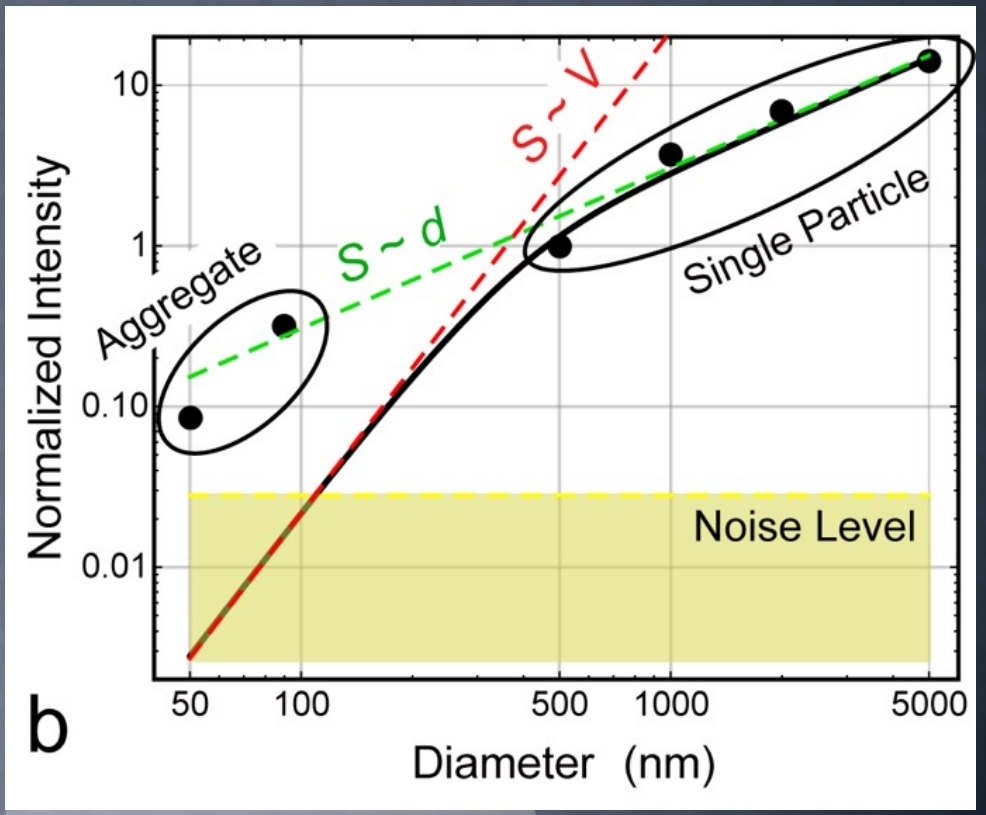
PS particles in distilled water

Identification of 500nm PS particle in 0.5s





Once the particle is trapped we can «Raman» it



Gillibert et al. Environ. Sci. Technol. 2019, 53, 15, 9003

Single particle detection

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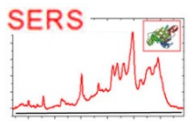
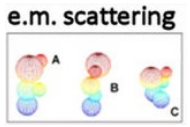
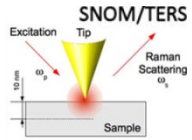
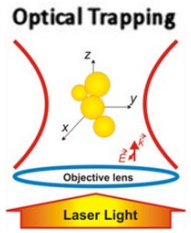
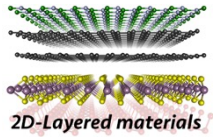


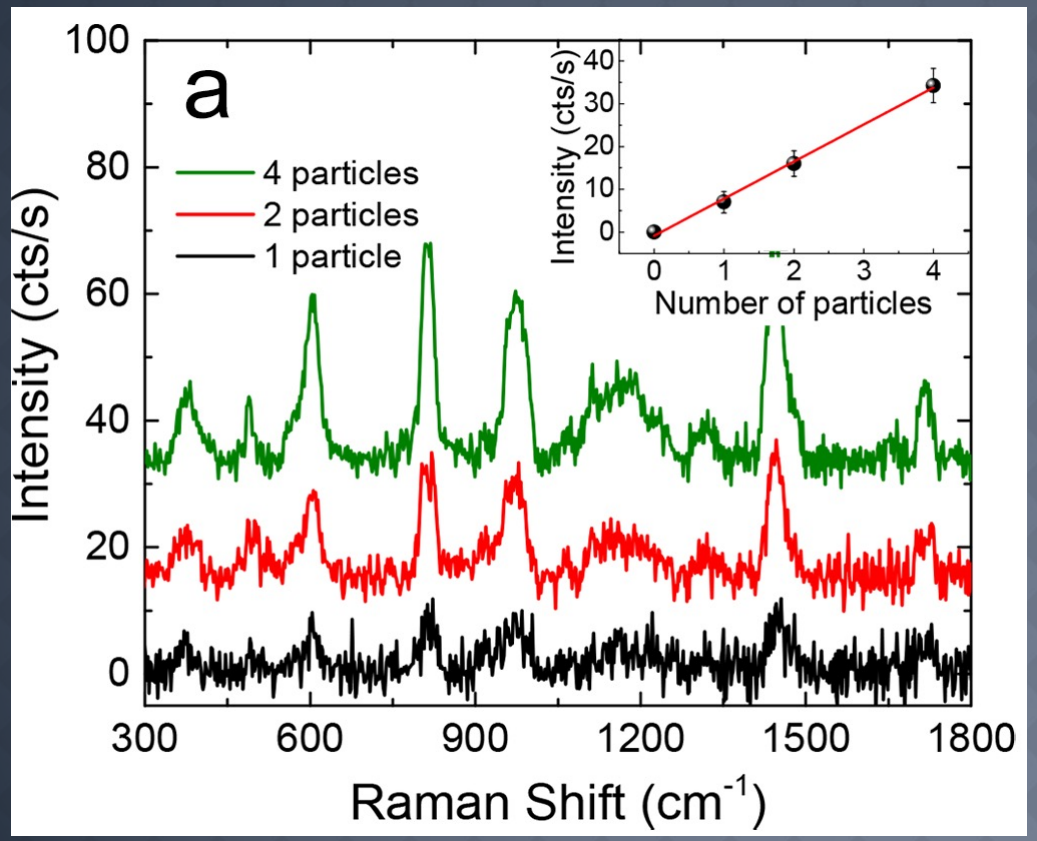




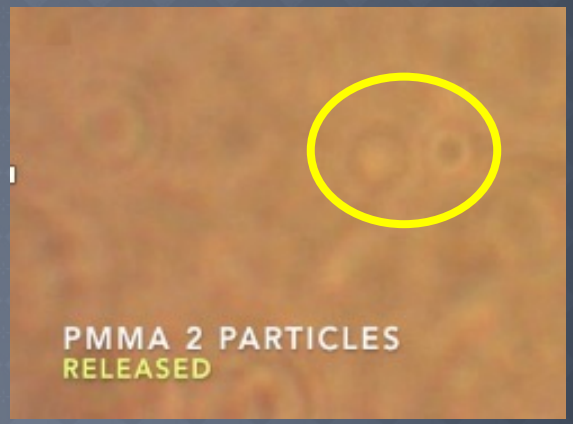




Raman of PMMA 300 nm beads



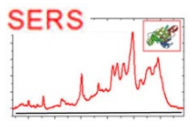
OPTICAL IMAGING OF TRAPPING PROCESS

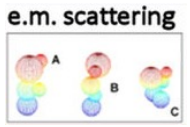


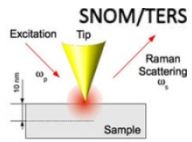
Single particle analysis is demonstrated down to 300nm

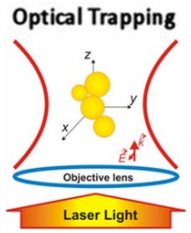
Raman Tweezers analysis of different microplastics

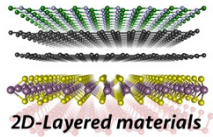
NanoSoftLab





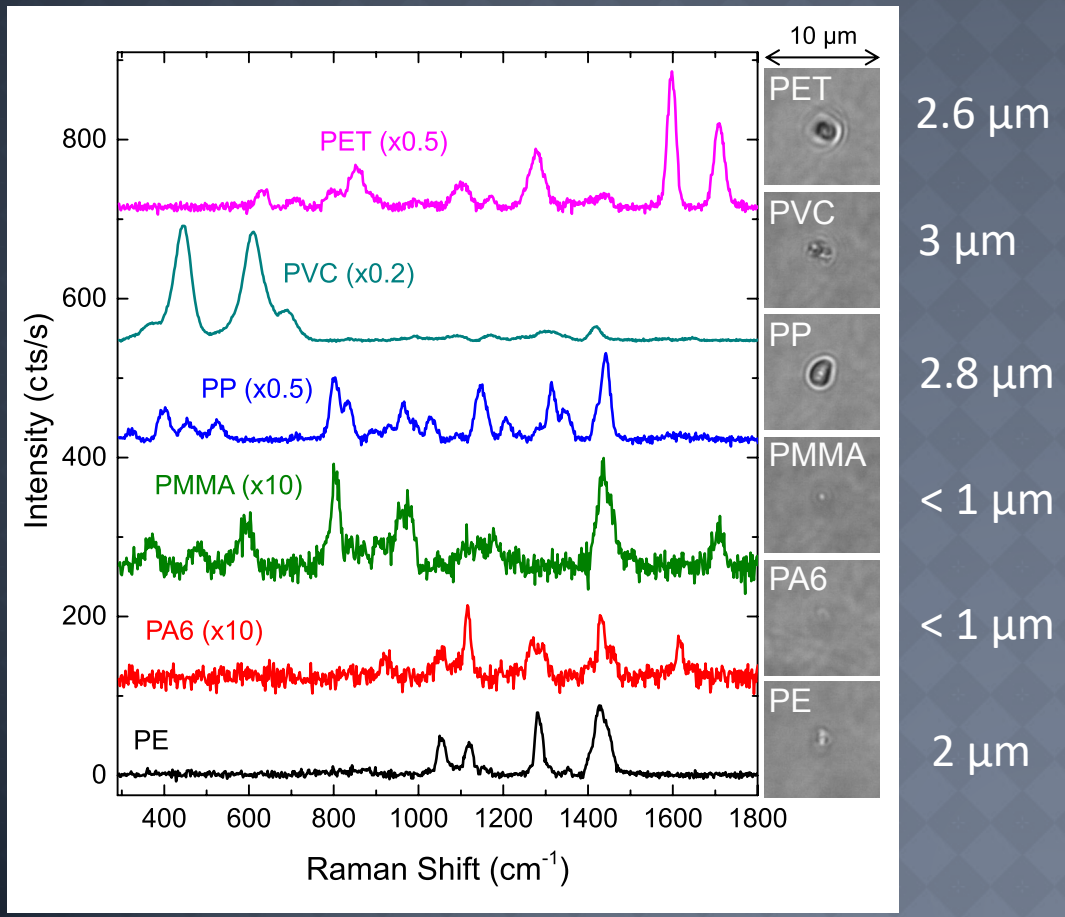




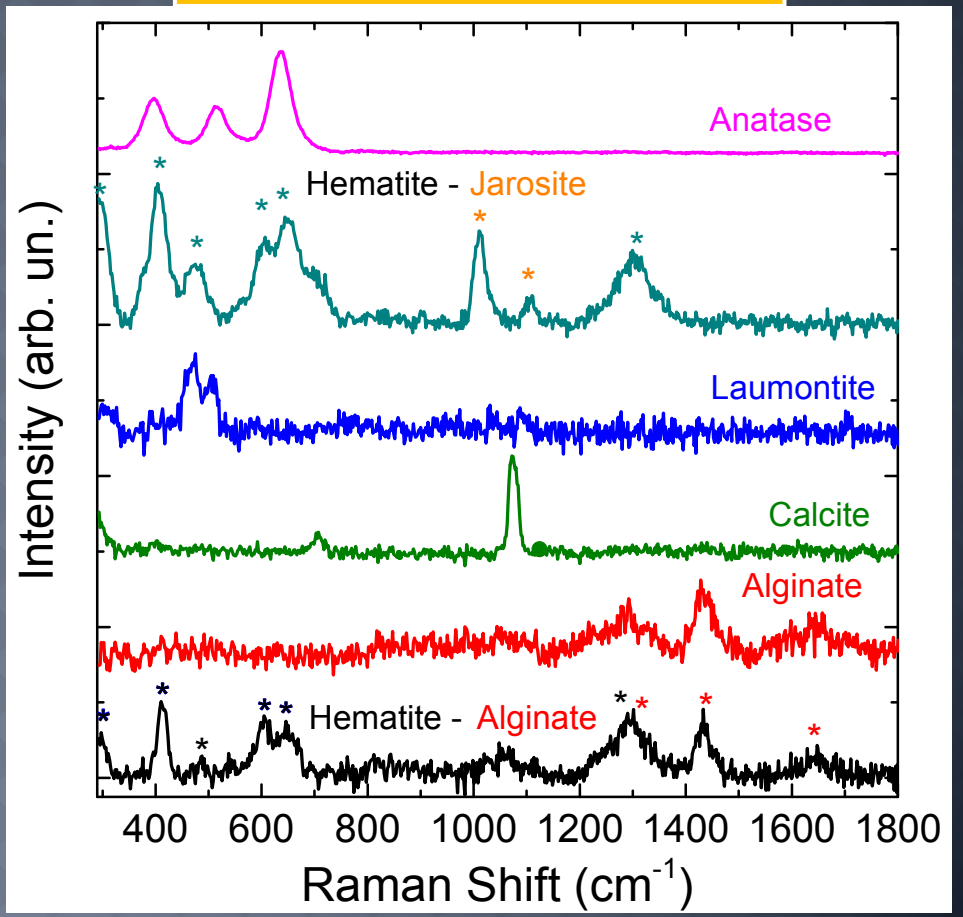


Nanoplastics produced by stone-grinding in seawater

Microplastics and Nanoplastics



Micro-sediments in seawater



Optical trapping and analysis of fibers in PP particles dispersd in seawater

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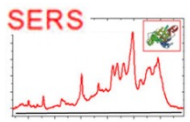
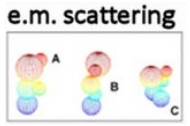
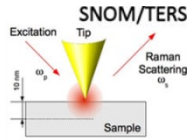
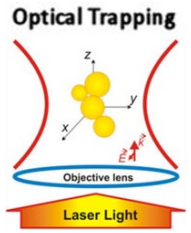
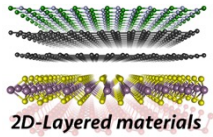


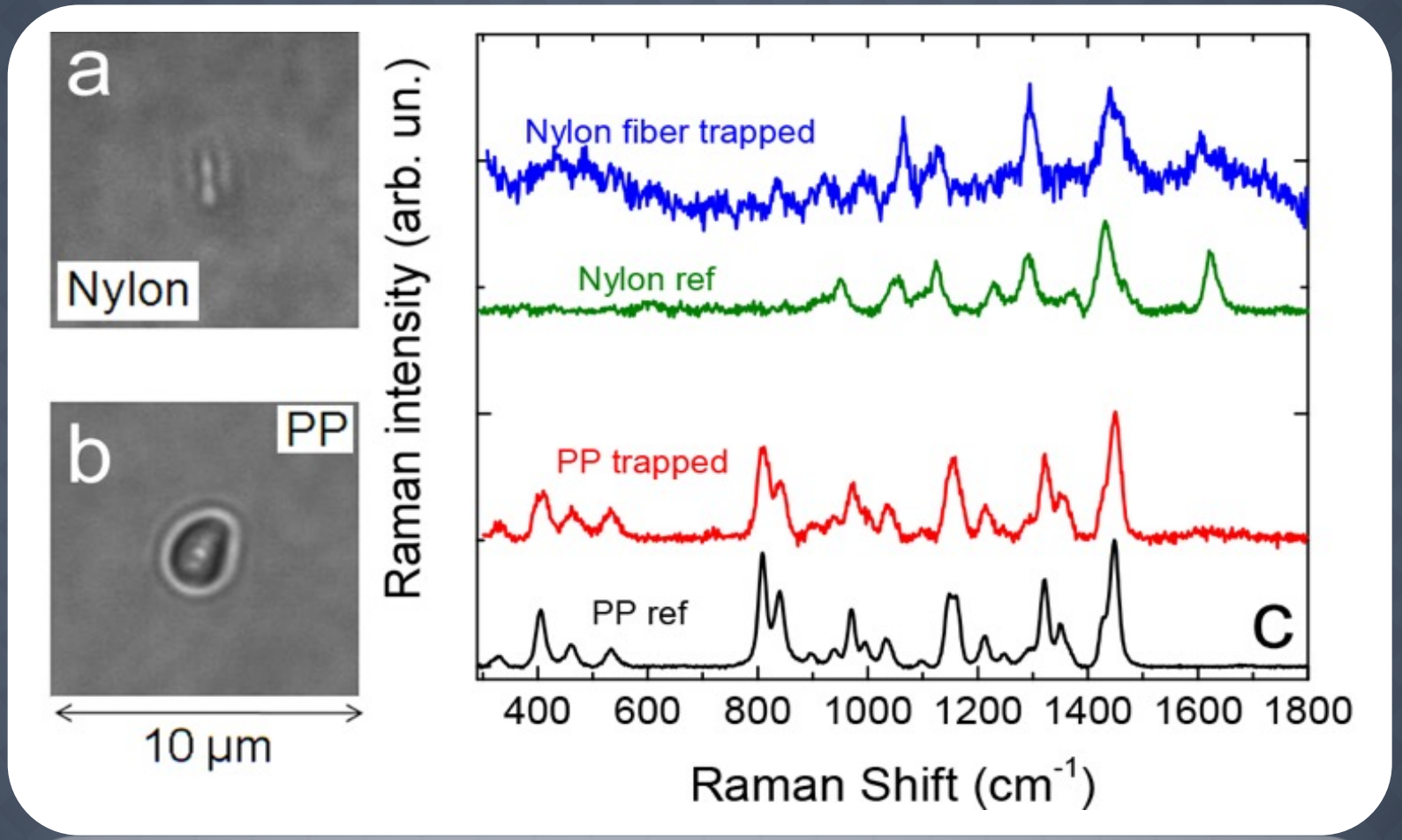








Textile fibres could have been accidentally mixed to the PP during fabrication, or maybe the fibre was already present in the seawater sample



Environmental sample 1: a weathered polyethylene bottle cap

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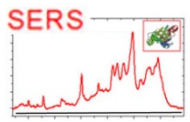
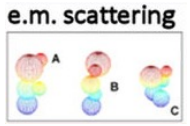
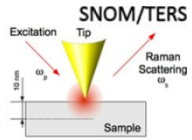
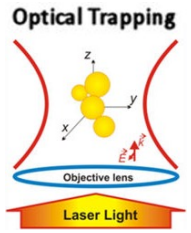
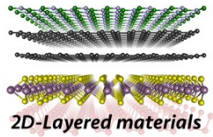


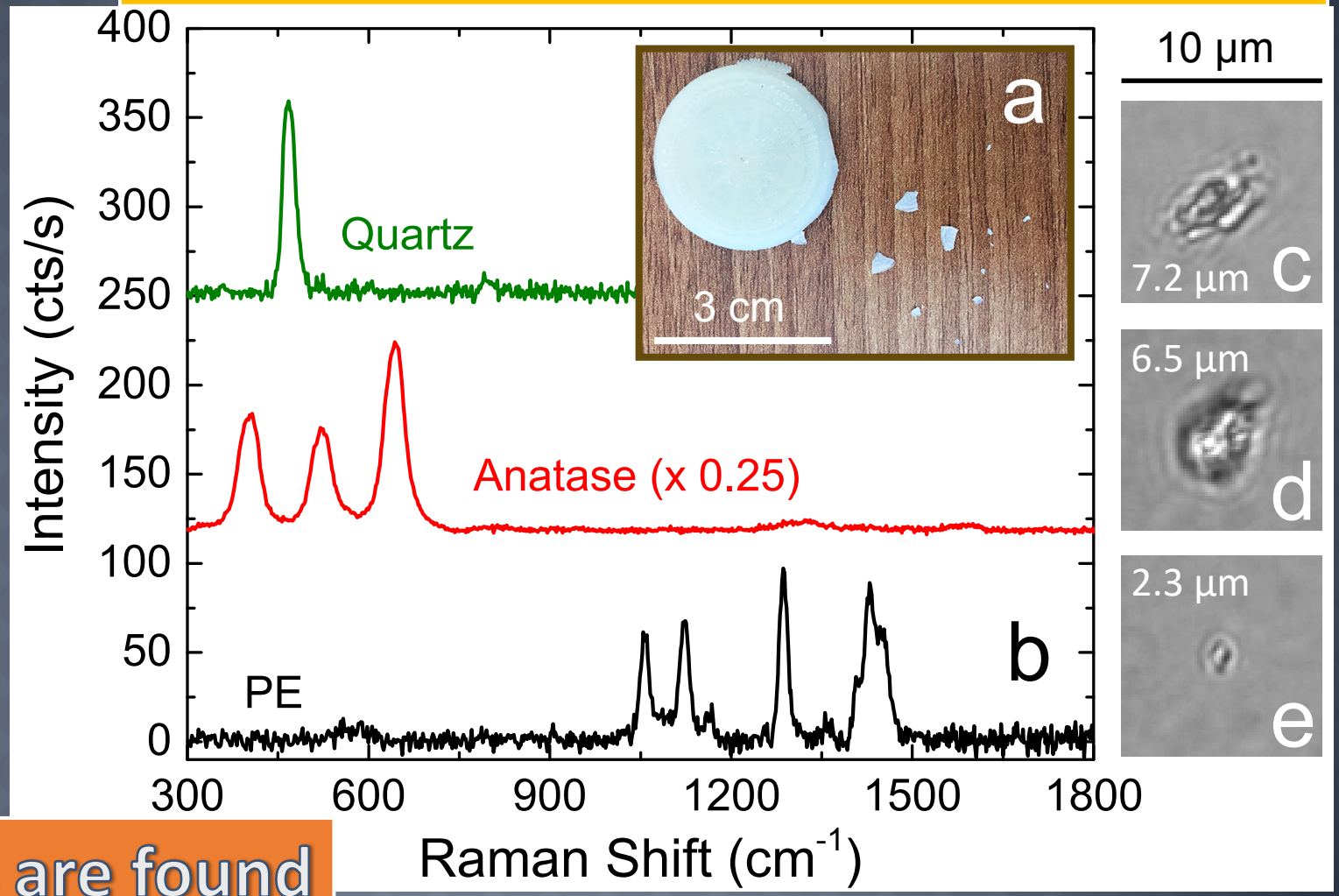








Naturally aged PE bottle cap fragmented under mechanical pressure



Microplastics are found

Environmental sample 2: a weathered polypropylene paint bucket

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SERS

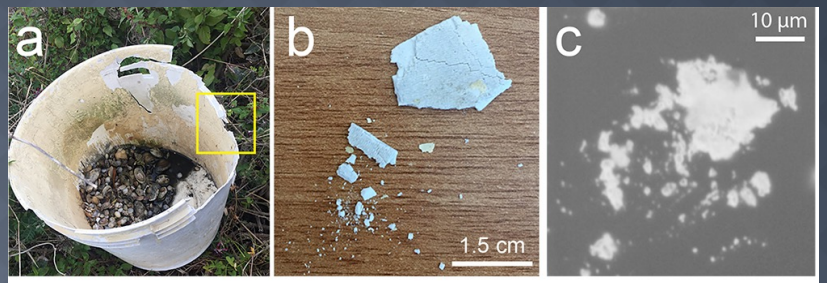
e.m. scattering

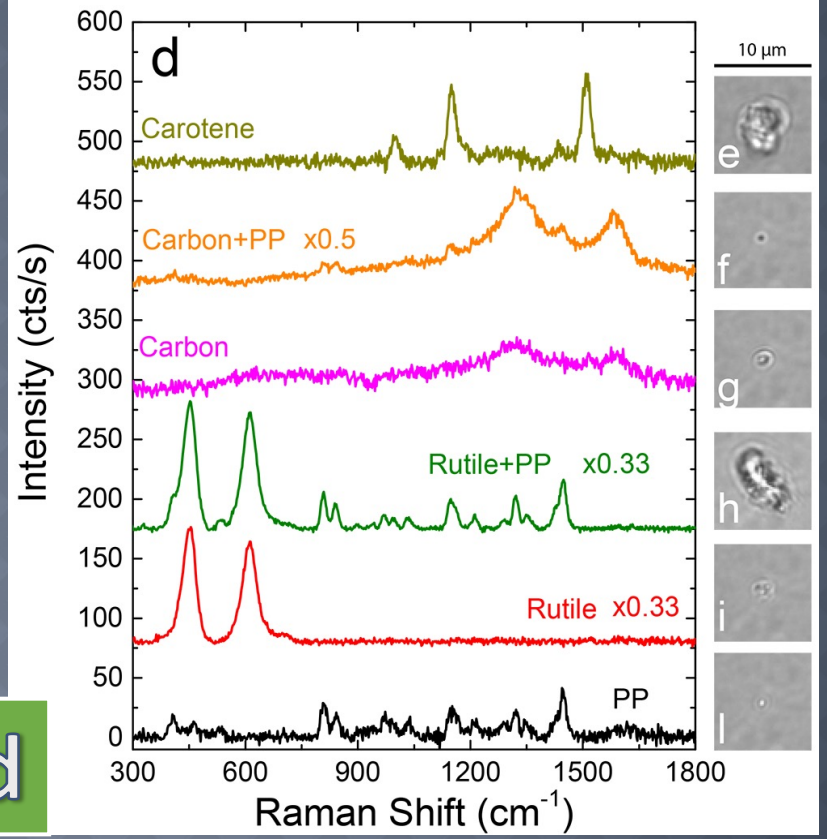
SNOM/TERS

Optical Trapping

2D-Layered materials

Naturally aged PP paint bucket from Lakes of Ganzirri, fragmented under mechanical pressure in seawater





Nanoplastics are observed

CONSIGLIO NAZIONALE DELLE RICERCHE

IPCF ISTITUTO PROCESSI CHIMICO-FISICI

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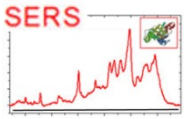

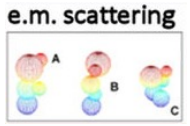

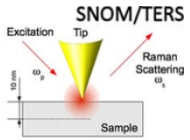

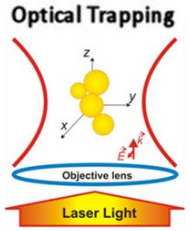

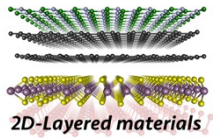

Conclusions

- 3D trapping and Raman detection of PE, PP, PET, … microplastics in seawater and distinction from sediments
- Single particle sensitivity proved down to 300nm
- Detection of aggregates 50nm particles (few tens)
- Observation of nanoplastics in weathered environmental samples mechanically broken

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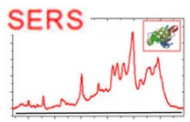

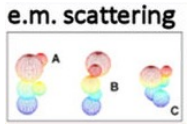

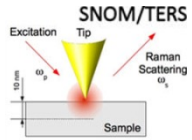

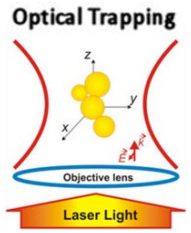

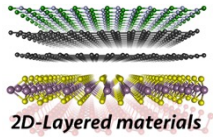

Extraction

Trapping & Analysis

Concentration

Raman Tweezers can play a role

People & Funding

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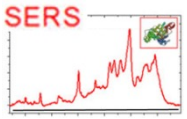

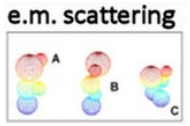

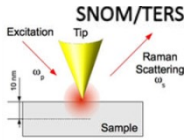

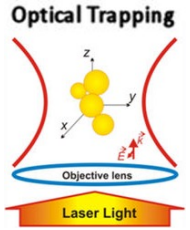

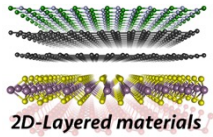

CNR-IPCF: R. Gillibert (now @IIT-Rome), A. Magazzù, D. Bronte-Ciriza, A. Foti, MG Donato, O. M. Maragò

IFREMER - Brest: Q. Desoules, M. Tardivel, F. Colas (now @Safran Aerotechnics)

UniMans - IMMM: G. Balakrishnan, M. Lamy de La Chapelle, F. Lagarde

Uni-Gothenburg: A. Callegari, G. Volpe

MERLIN - MICROPLASTIQUES

ASI-INAF n. 2018-16-HH.0

MSCA ITN (ETN) project “Active Matter”

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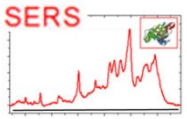

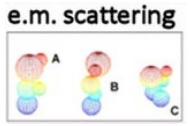

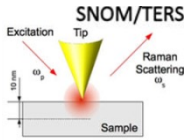

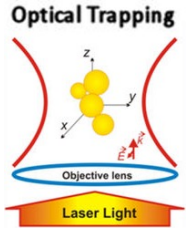

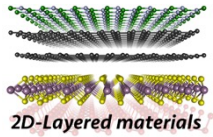

Thank you

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