

Synthesis and characterization of whispering gallery modes microresonators synthesized by in-situ lasing dye encapsulation during microwave-assisted styrene polymerization



José González Rivera

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Consiglio Nazionale delle Ricerche

Area della Ricerca di Pisa



Outline

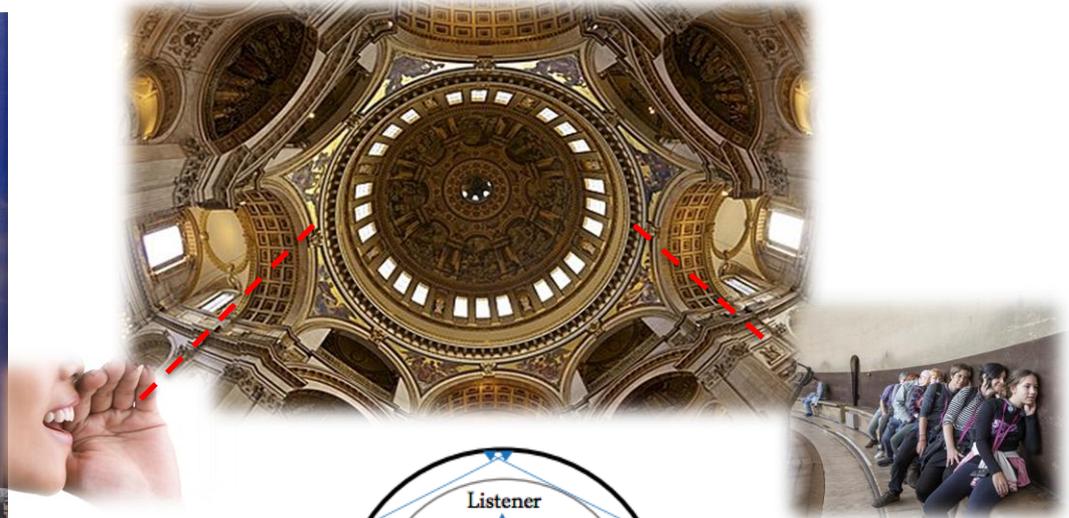
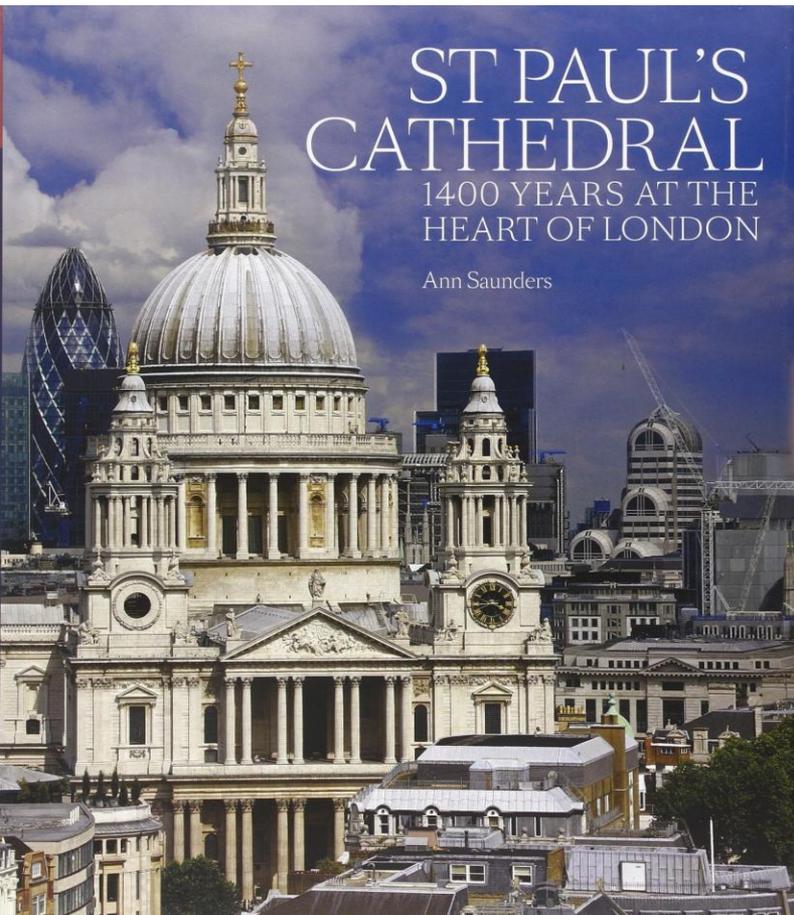
- **Whispering Gallery modes microresonators**
- **Polymer based microresonators**
- **MW assisted polymerization approach**
- **Evaluation of PS microspheres as WGM`s microresonators**
- **Conclusions**

Whispering Gallery modes



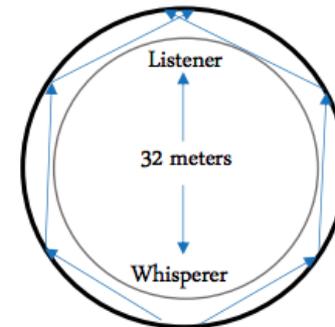
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the origins of such a weird name...



Whisperer

Listeners



A person just whispering close to the wall can be heard all the way along the gallery, around 30 m to the other side, due to the sound reflections along the circular wall

L. Rayleigh, "The problem of the Whispering Gallery", Philosophical Magazine 20, 1001-1004 (1910)

Confining the light:

optical microresonators

- Not only the sound but also the light can act as whispering gallery waves.
- Light can be confined inside a circular dielectric materials
- Applications as outstanding optical sensors due to their highly sensitive, label-free, rapid, selective and multiplexed detection capabilities

➤ WGMs microresonators are based on:

- **Resonance modes and Total internal reflection (TIR)**

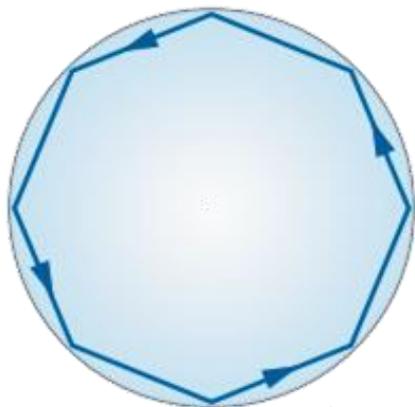
Light is trapped and propagates in phase along the inner surface of the resonator causing a constructive interference. The spectral positions and linewidths of the peaks not only depend on the microresonator shape but also on the surrounding environment.

➤ TIR occurs in WGM resonators only when $\theta > \theta_c$ where θ_c is the critical angle

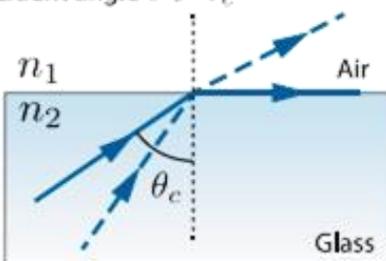
➤ A crucial parameter of WGMs resonators is the so-called **Q factor**,

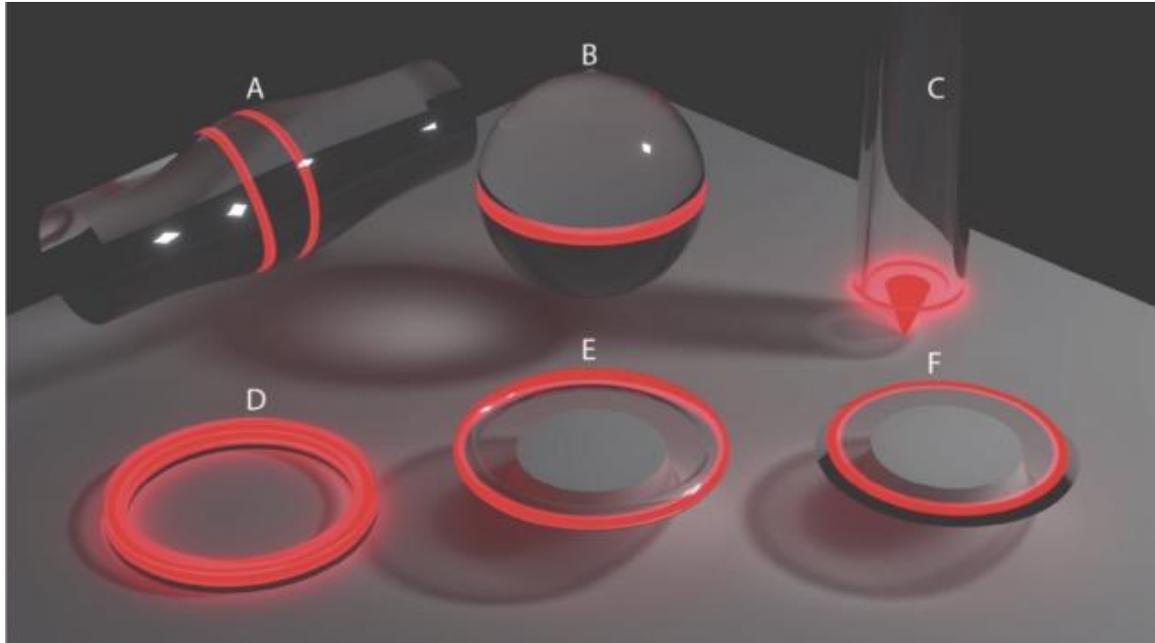
(average photon lifetime in the resonator, that means how many round trips a photon can undergo within the resonator before being lost either by absorption or scattering)

Optical whispering gallery



total internal reflection for incident angle $\theta > \theta_c$





microspheres, microrings or microdisks, microtoroids, microbottles and microcylinders

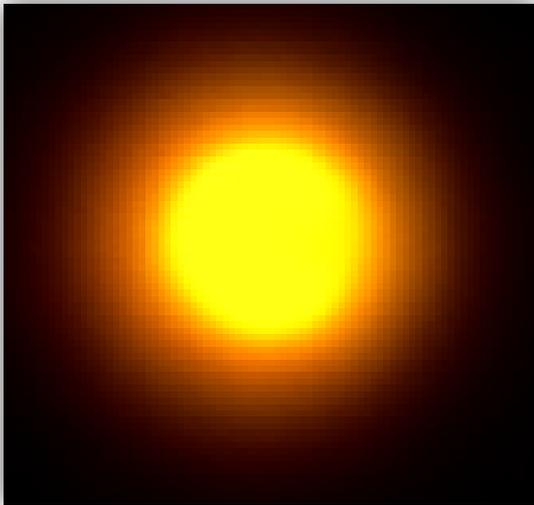
The detection limit and the sensitivity in WGM sensing are dependent on the Q-factor of the resonator. The higher the Q-factor, the smaller the resonant shifts

- Selection parameters:
- Fabrication approach
- Composition and integration on sensing devices
- Cost

In WGM, the fabrication of a spherical resonator is focused on achieving **perfect sphere** in order to ensure all angles of incidence are the same so that the ray can be optimally trapped.

The spherical shape is the simple and easy geometry to be fabricated.

Exceptionally high Q-factors of up to $Q \approx 10^{10}$ that can be achieved



- Different materials can be used (polymers, metallic oxide, etc)
- The shell protect the encapsulate lasing material promoting long stability and robust performance
- Chemical functionalization of the surface of microspheres is routinely performed

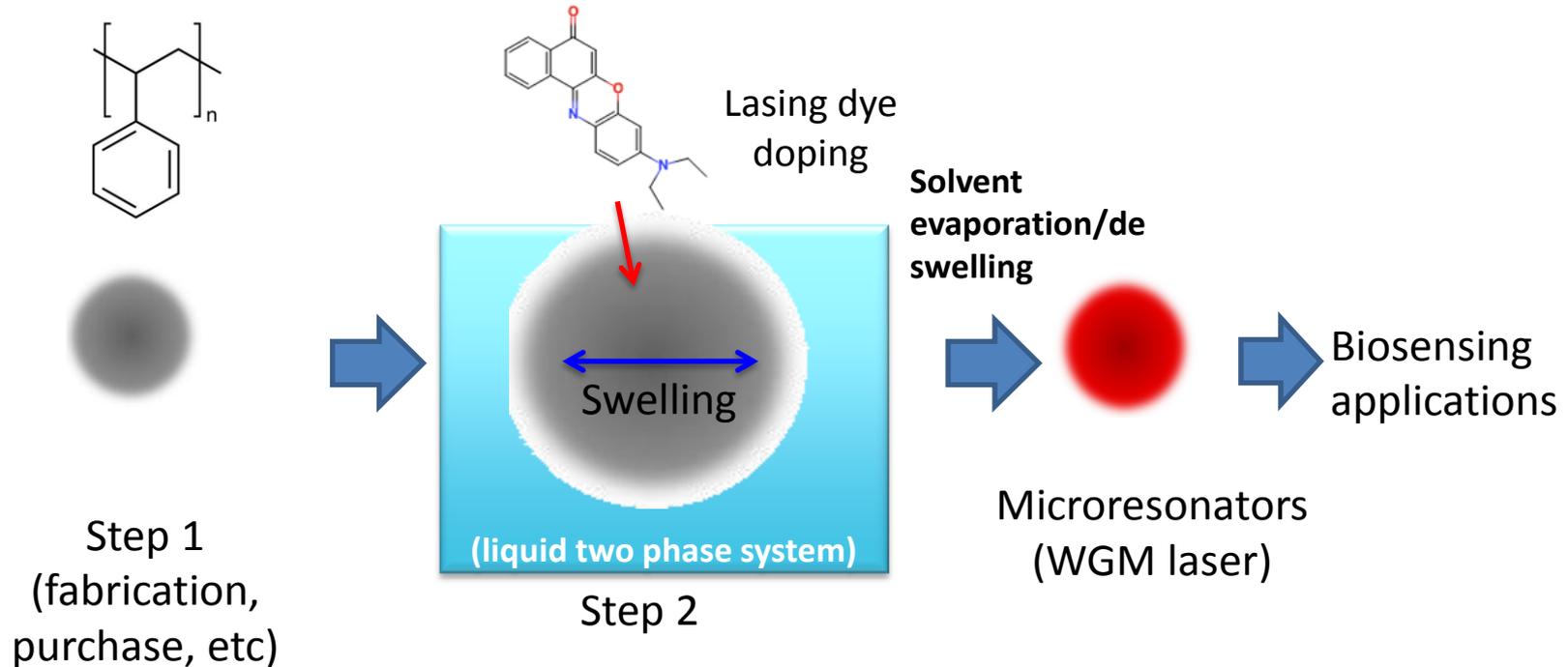
Polymer based whispering gallery mode laser



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(dye doped polystyrene microspheres)

A.Francois et al (2015) Applied Phys. Lett. 106, 031104



Nile red doped microsphere ($d=10 \mu\text{m}$) (the smallest ever tested)

The refractive index sensitivity is inversely proportional to the resonator dimension

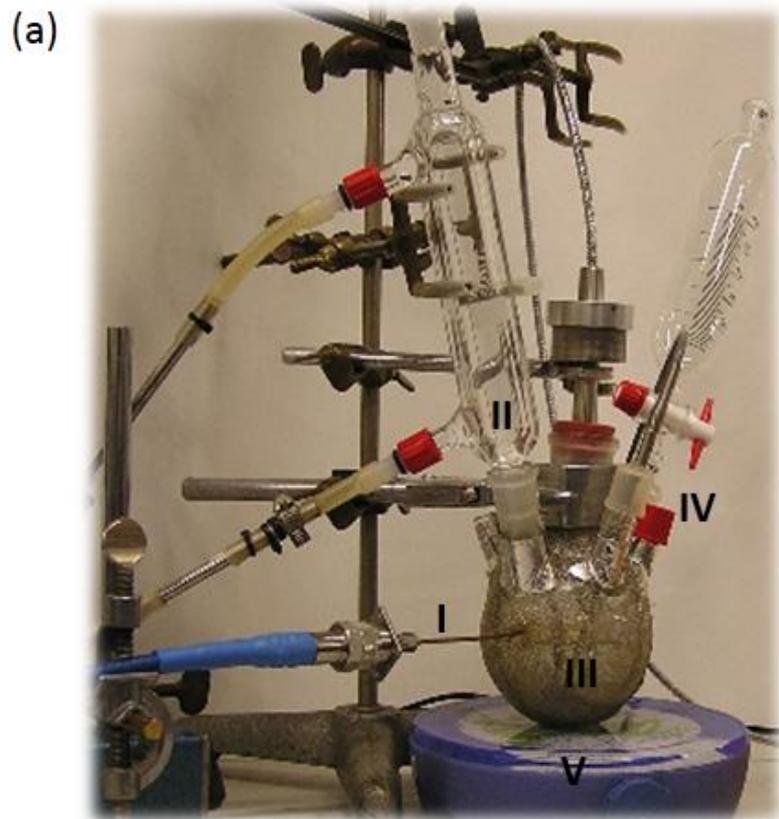
- **Development of One step methodology for the fabrication of polymer based microresonators by in-situ encapsulation of the fluorescent dye through a MW assisted dispersion polymerization process**
 - ✓ An investigation on styrene conversion and Nile red-PS microspheres growth evolution with the MW irradiation time
 - ✓ The study of the effect of the surfactant concentration (polyvinyl pyrrolidone, PVP), heating approach (MW or electrical mantle), solvent (ethanol:water volume ratio) and dye concentration on the morphology, size and particle size distribution of Nile red-PS microspheres
 - ✓ The investigation of the laser dye encapsulation process into the PS microspheres by Uv-vis spectroscopy
- **The evaluation of the Nile red-PS microspheres as WGM- μ Rs**

Polystyrene Microbeads

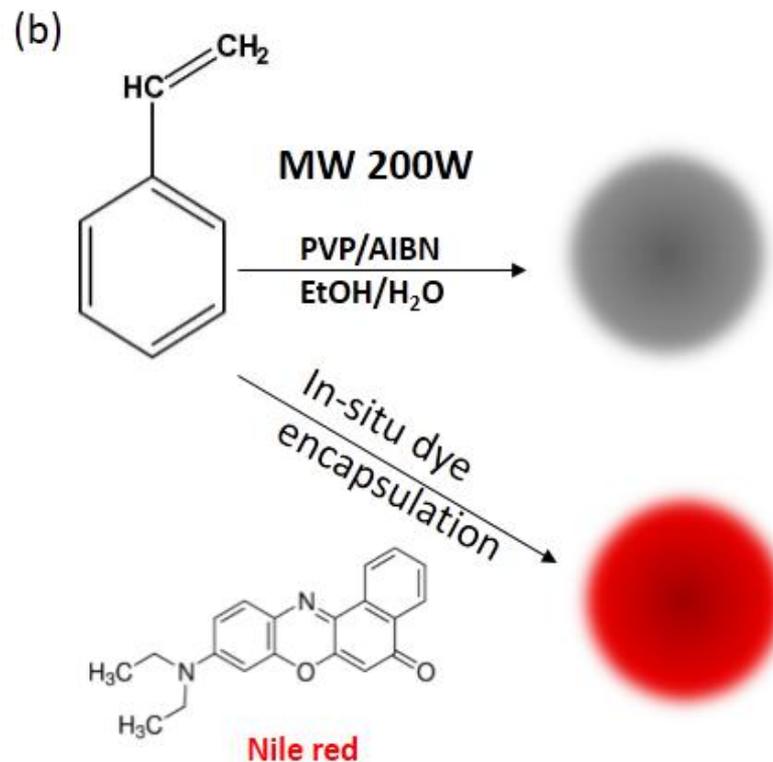


(dye doped polystyrene microspheres)

Free radical
polymerization process



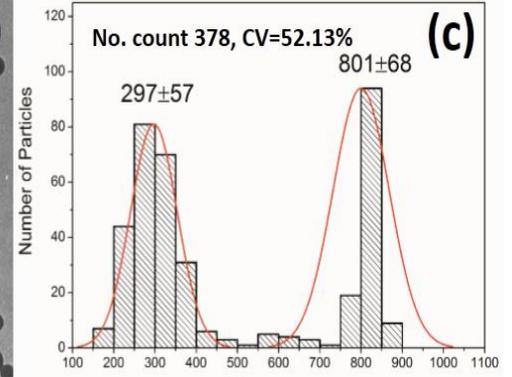
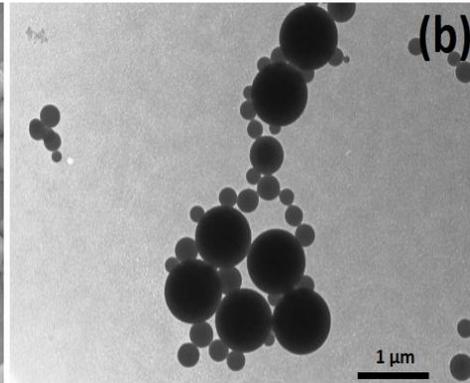
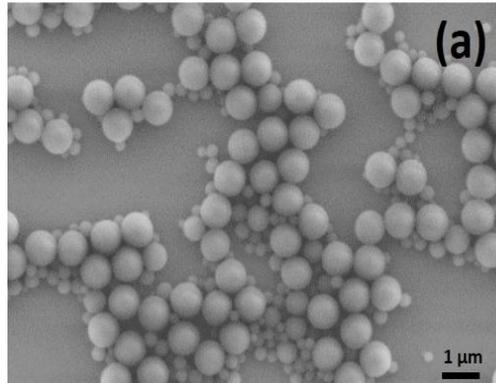
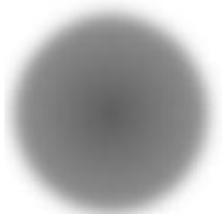
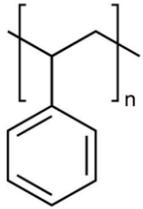
Coaxial antenna (I), reflux system (II), glass reactor (III), N₂ inlet (IV) and stirrer (V).



Polystyrene Microbeads by MW-assisted Polymerization

$t_{rxn}=2$ h, 200W of MW power, 10% of PVP as stabilizer, solvent with 80:20 ethanol/ H_2O vol. ratio

Polystyrene microspheres

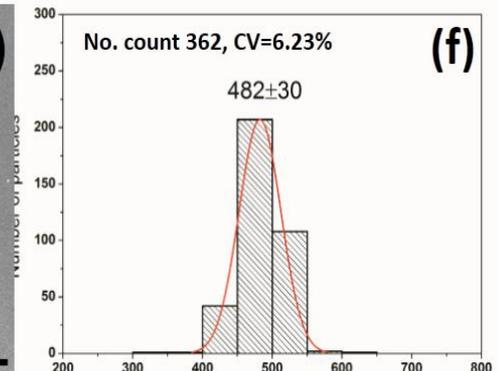
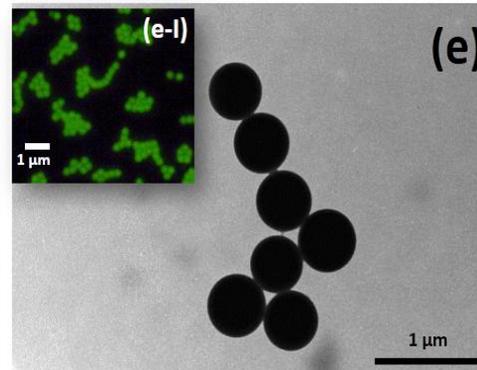
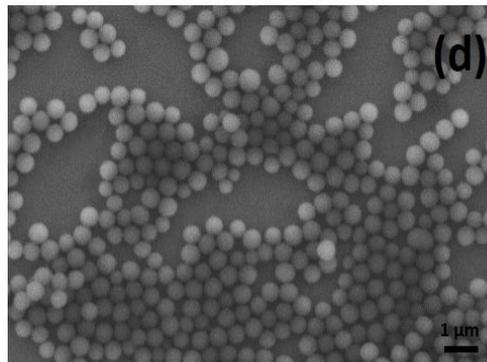
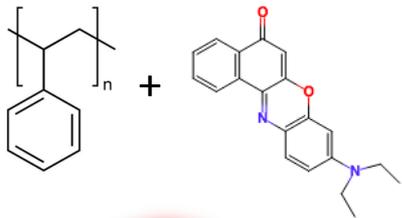


well-defined spherical shape with a broader (bimodal) particle size distribution

(dye doped polystyrene microspheres)

Strong fluorescence

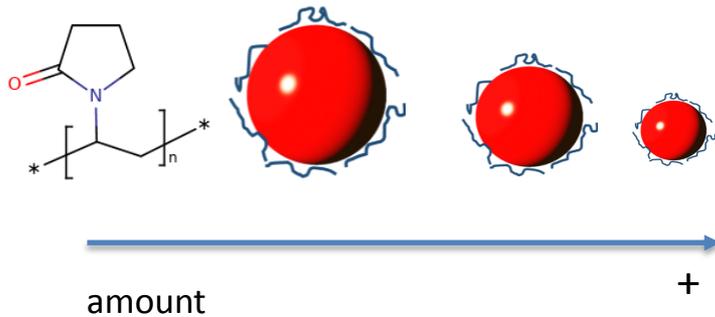
Narrow size distribution



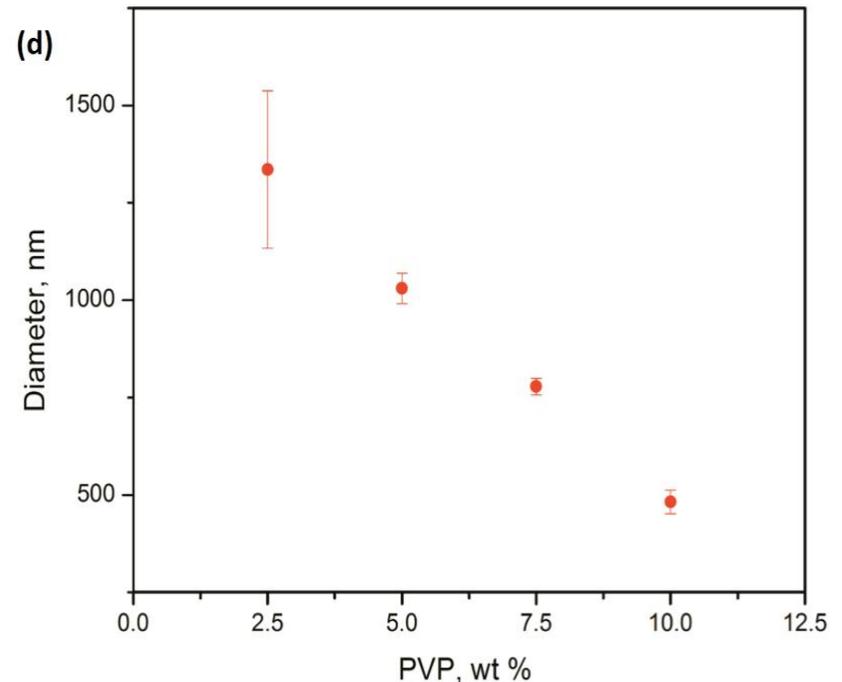
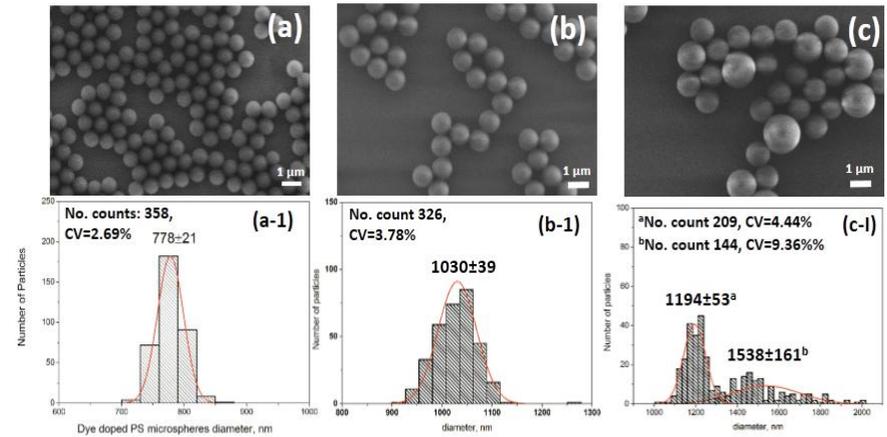
the in-situ NR encapsulation no changes to the spherical morphology and/or the external surface of the microspheres

Polystyrene Microbeads by MW-assisted Polymerization

Modulating the microspheres particle size: the role of PVP



- the size of Nile red-PS microspheres linearly decreased with the increase of PVP concentration
- Polydispersity was also reduced at high amount of PVP



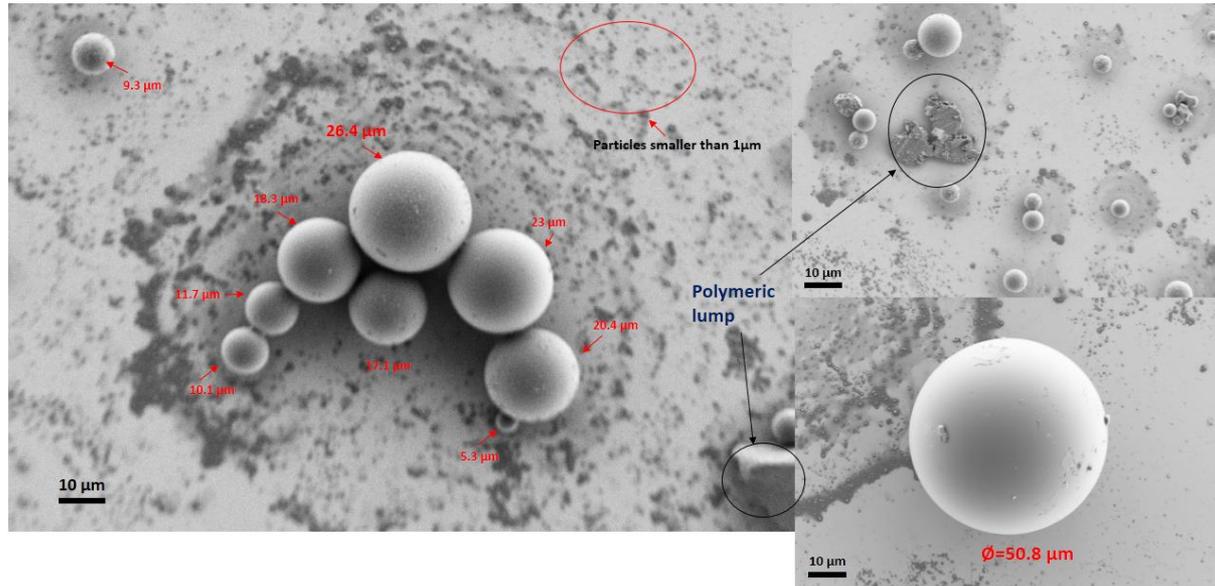
Polystyrene Microbeads by MW-assisted Polymerization

The influence of polarity of the reaction medium (ethanol:water v/v ratio)

- Increments in the amount of water can promote a **better MW absorption system** (due to its high dielectric loss ϵ'')
- Enhancements during the in-situ encapsulation of Nile red can be also induced due to a **confinement effect** (considering the hydrophobicity of styrene-Nile red mixture).

◆ Ethanol:water vol ratio was radically changed from 80:20 to 20:80

- highly polydispersed microspheres with small nanoparticles (from several hundred of nm) up to 20-50 μm

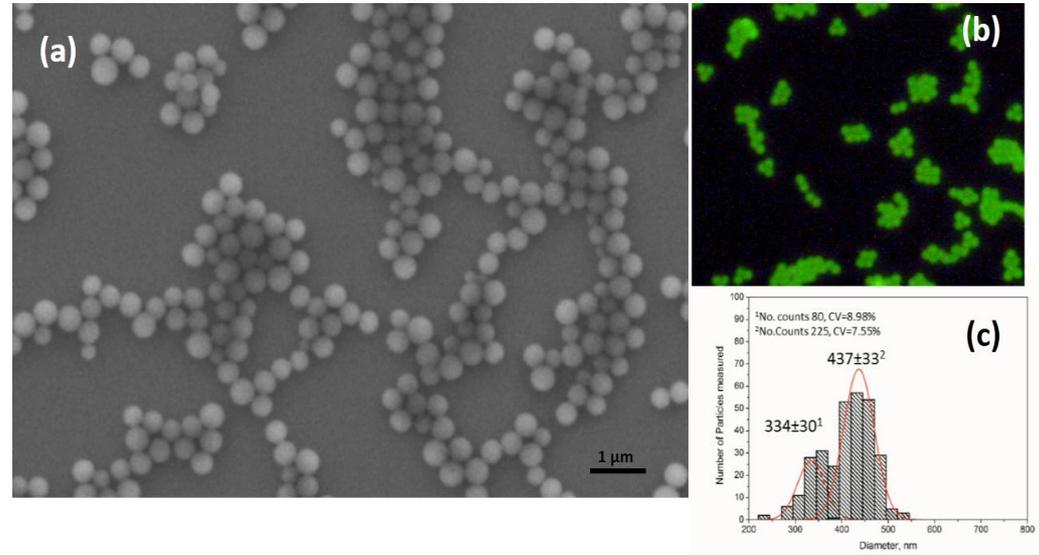
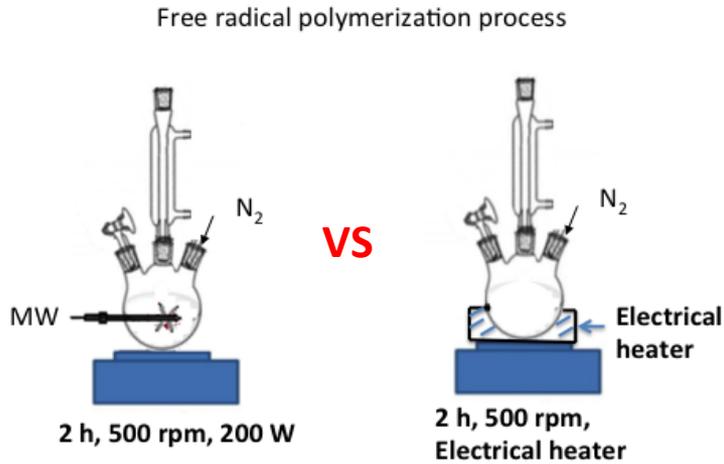


- big size of microspheres and polymeric lumps suggests a strong reaction rate in an **inestable "more" heterogenous polymeric system** due to the fixed amount of PVP and high water content.
- Microspheres kept its **spherical morphology** and under those reaction conditions it could be possible to achieve **high molecular weight Nile-red polystyrene microspheres** with a wide range of sizes

Polystyrene Microbeads by MW-assisted Polymerization

The effect of heating approach during the Nile red-PS microspheres synthesis

PS-Nile red obtained by CH

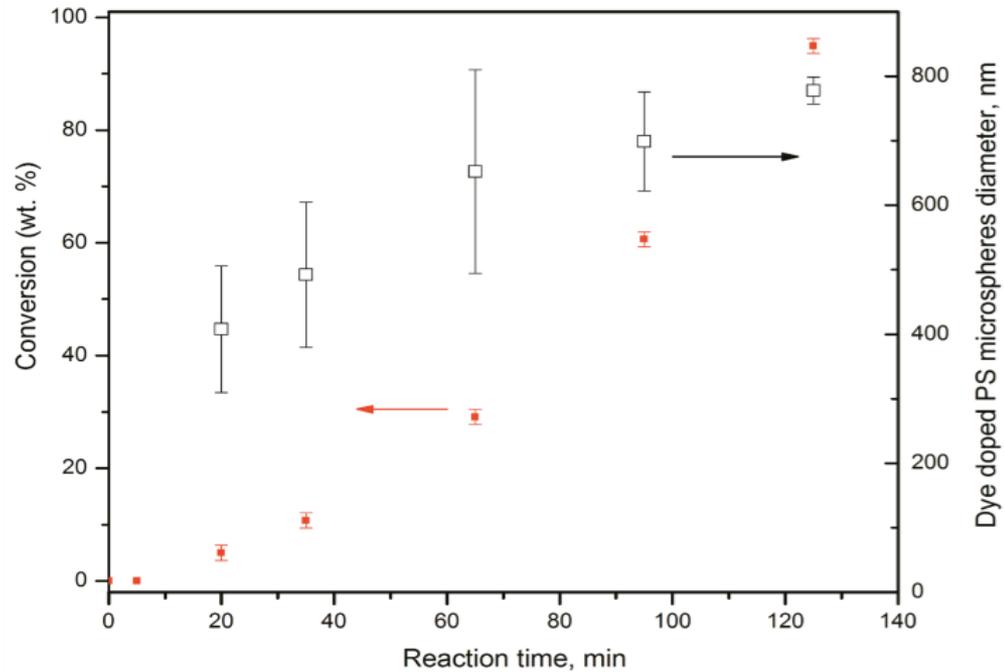


- Nile red-PS microspheres with well defined spherical morphology, slightly small size and broad particle size distribution were obtained.
- the coaxial MW assisted polymerization reaction can produce dye-PS microspheres with **similar or improved properties** than those obtained by conventional heating but with time and energy savings.

Polystyrene Microbeads by MW-assisted Polymerization

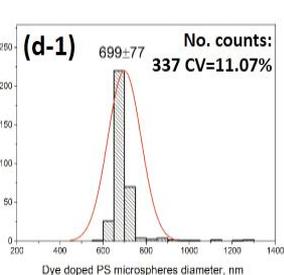
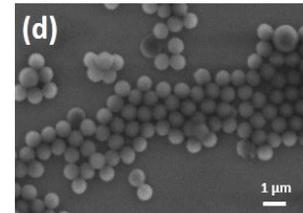
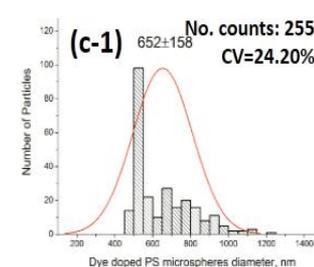
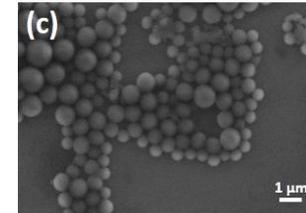
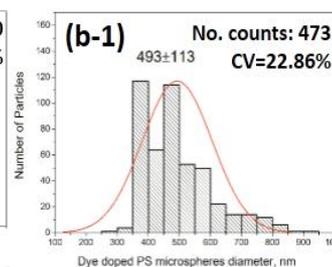
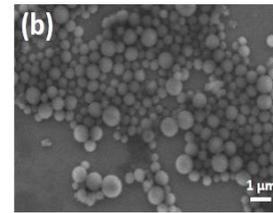
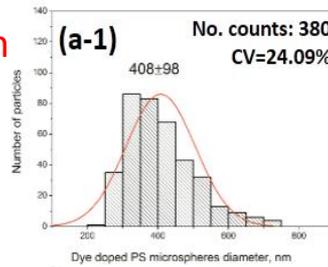
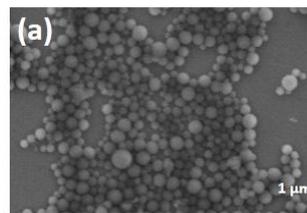
Kinetics of polymerization and Nile red-polystyrene microspheres particle size evolution analysis

- After 2 h of MW irradiation more than **94%** of styrene was polymerized.
- The coaxial MW-assisted polymerization approach thus promoted **high styrene conversion in short reaction time**



A particle growth trend was observed:

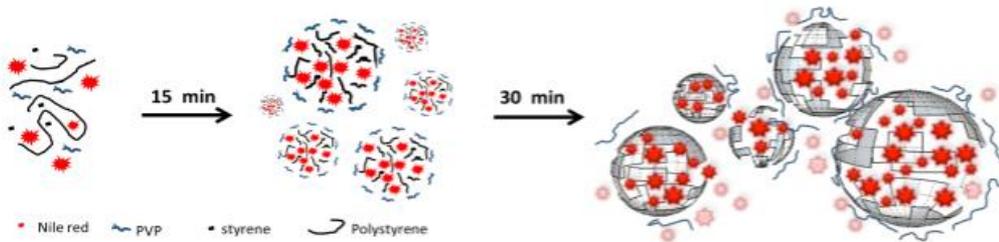
- non-uniform microspheres production during the first 60 min of reaction
- The **particle size distribution** became **narrow** after 90 min of MW irradiation time



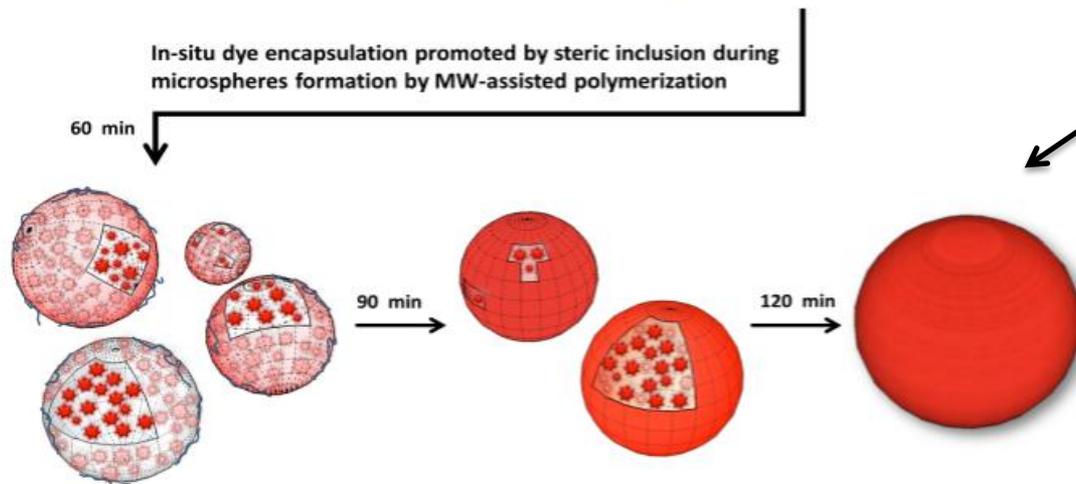
Polystyrene Microbeads by MW-assisted Polymerization

Mechanism of the particle growth

A key step during this possible formation mechanism is the **rapid heating** using MW irradiation that produces many initial nuclei where polymerization-trapping of styrene-nile red can occur.



This fact can explain the high **polydispersity** of the microspheres during the **early stage** of the polymerization.

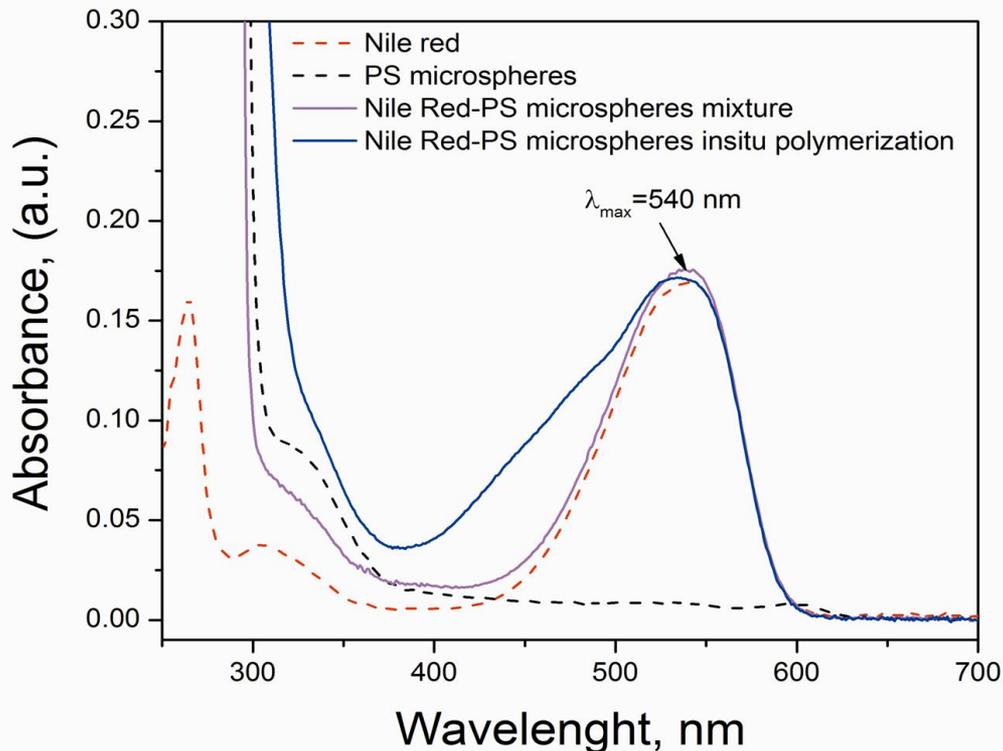


At longer MW irradiation time, the free styrene and Nile red still contained in the continuous phase is then absorbed into the instable smaller nanoparticles, where the **monomer-dye swelled are polymerized and trapped** causing the size increment to the final **stable Nile red-PS monodisperse** microspheres.

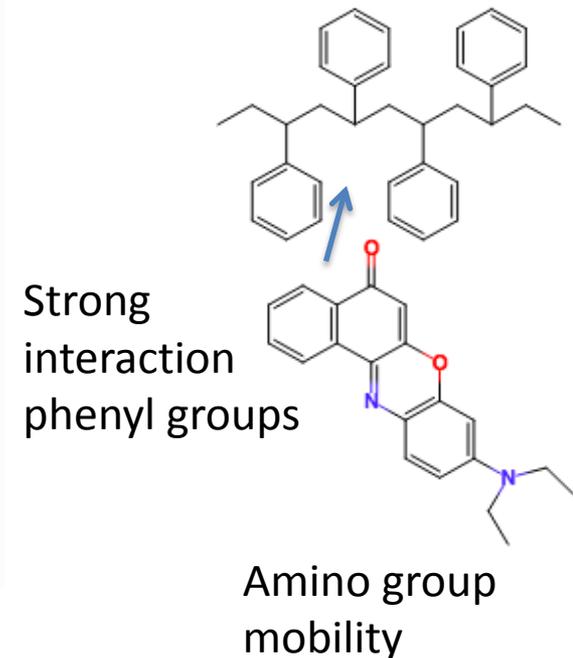
Polystyrene Microbeads by MW-assisted Polymerization

Nile red encapsulation assessment by Uv-vis spectroscopy

High concentration of lasing dye can promote molecule aggregation (due to the aromatic chemical nature of the dye structures) causing fluorescent quenching or lost of lasing efficiency



- ✓ The **maximun amount** achieved of encapsulated dye was promoted by **the self assambled dye-monomer micellar type structures** (favored by similar lipophilic characteristic).



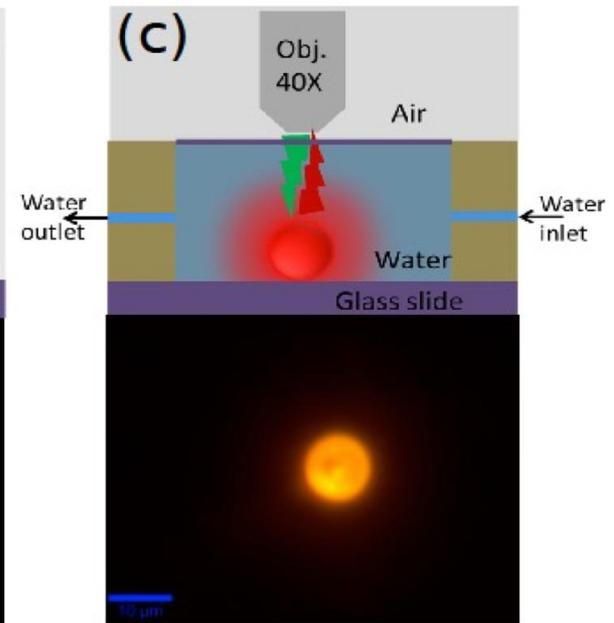
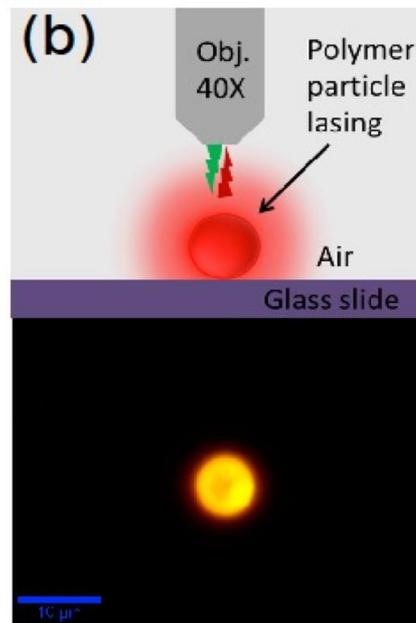
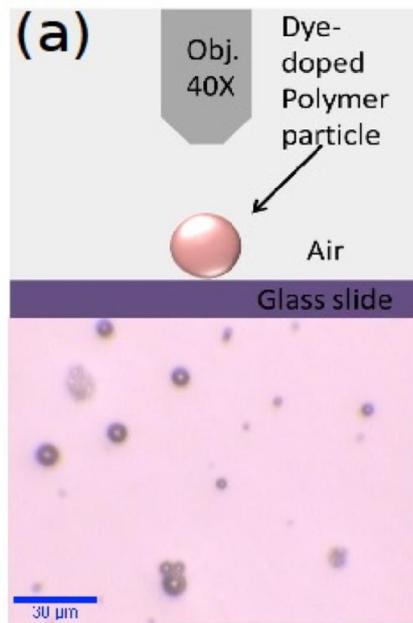
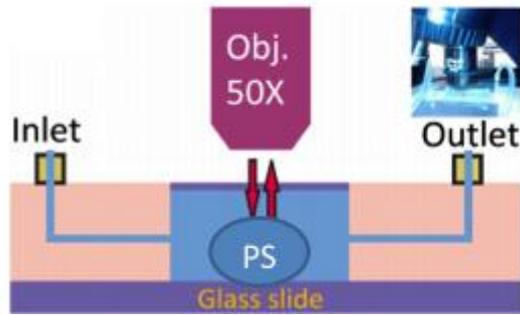
Evaluation of the Nile red-PS microspheres as WGM- μ Rs

PS-Nile red microspheres with diameters of $15 \pm 0.5 \mu\text{m}$, $9.2 \pm 0.2 \mu\text{m}$, $7 \pm 0.1 \mu\text{m}$ and $3.5 \pm 0.1 \mu\text{m}$

Conditions:

Room temperature using a confocal Raman microscope equipped with an excitation light source of 532 nm.

The beam was focused onto a single polymer particle using a 50x long distance objective.



Evaluation of the Nile red-PS microspheres as WGM- μ Rs

The turning point between the fluorescence and the modulated emissions was found at $0.2 \mu\text{W}$ for particles of a ϕ higher than $7 \mu\text{m}$ and $0.7 \mu\text{W}$ for the smallest evaluated particle of $\phi \approx 3.5 \mu\text{m}$

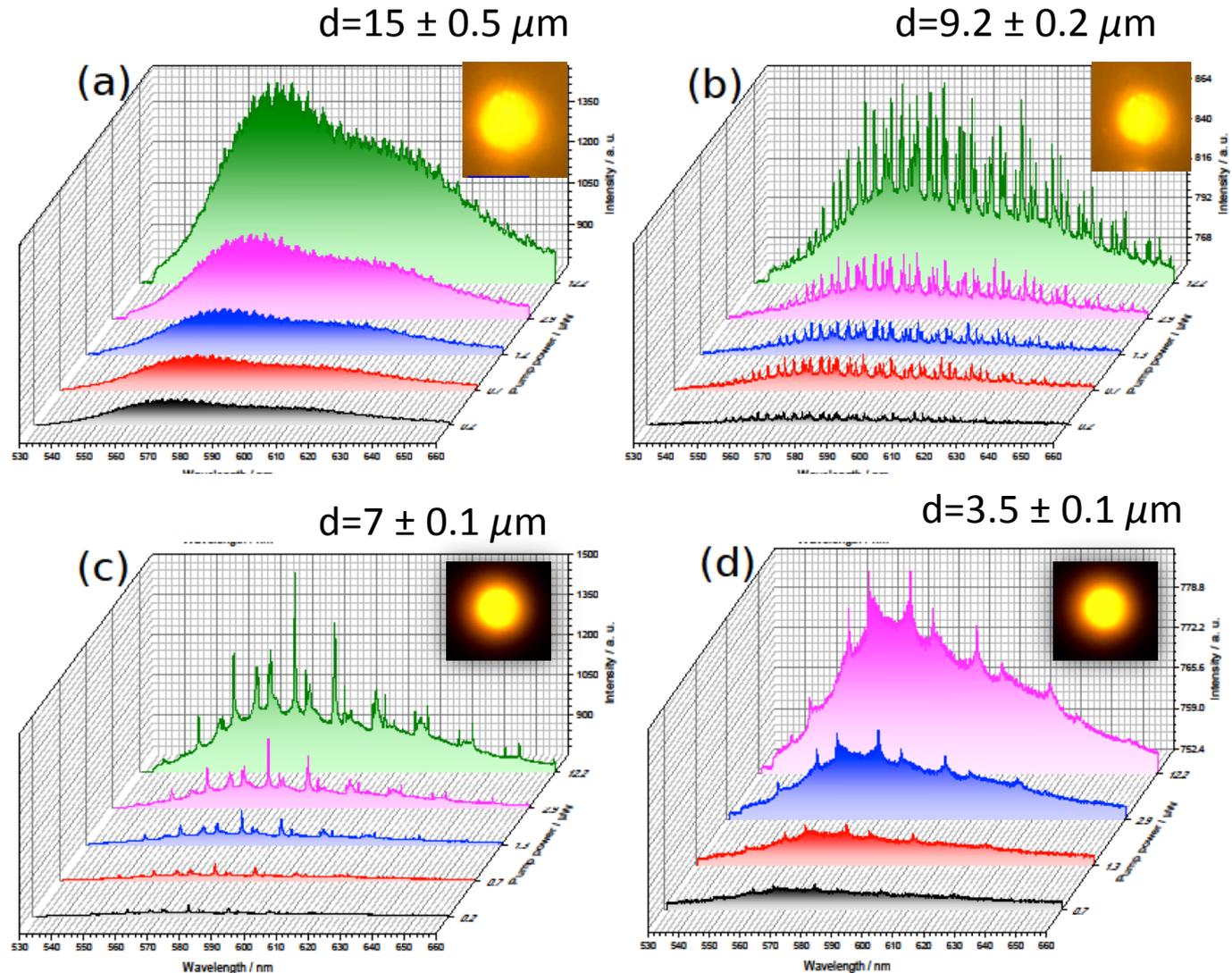
➤ **Threshold values are significantly lower**

NR-PS insitu polymerization
 $0.2 \mu\text{W}$ ($d > 7 \mu\text{m}$)

NR-PS doping by swelling
 $2.4 \mu\text{W}$ ($d > 10 \mu\text{m}$)⁽¹⁾

➤ **The intensity of the modes for all particles increases as the pump power is incremented.**

➤ **The density of modes per spectrum decreases along the decreasing ϕ**



⁽¹⁾A. Francois et al (2015) Applied Phys. Lett. 106, 031104

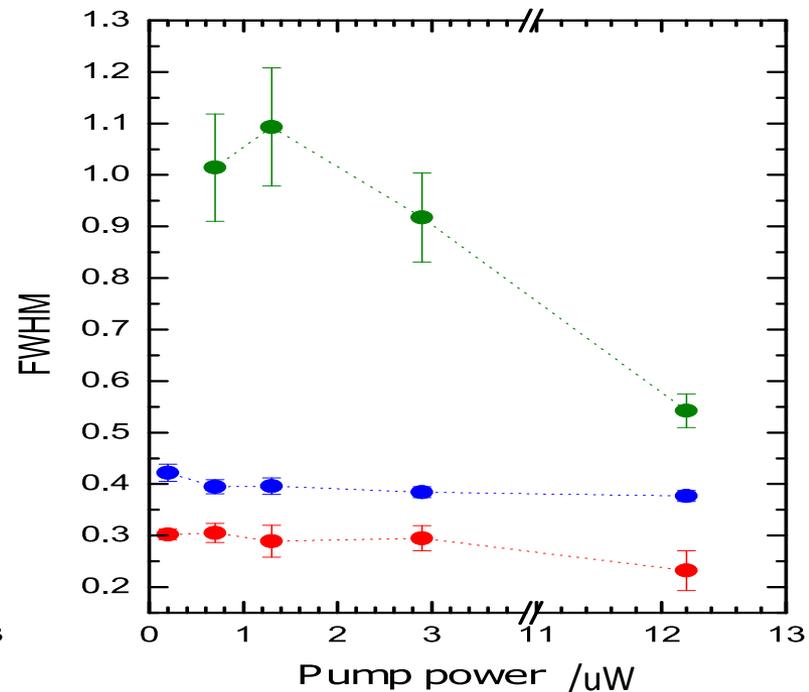
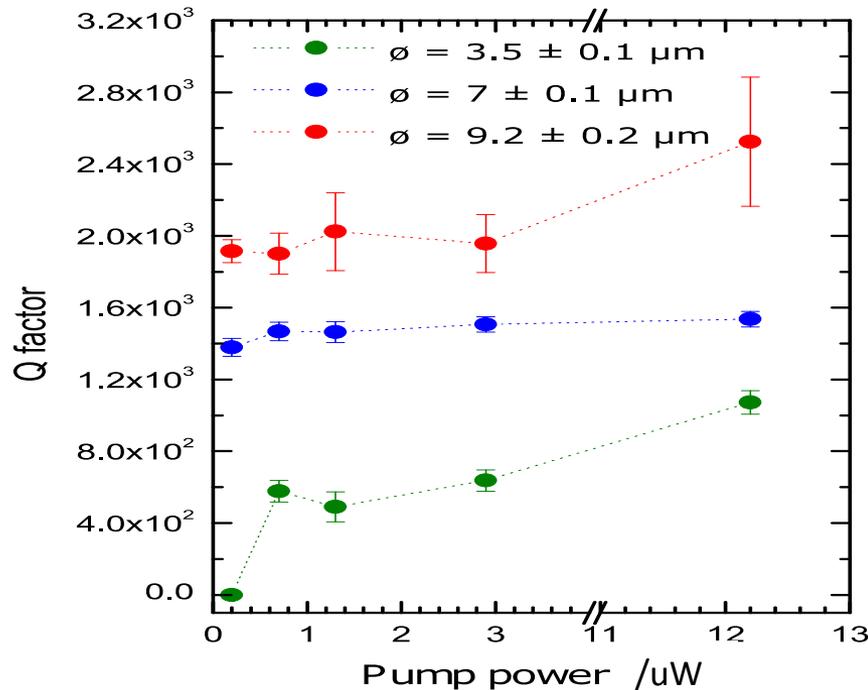
Evaluation of the Nile red-PS microspheres as WGM- μ Rs

- Q factor describes the stored energy in the resonator
- Particles with bigger sizes exhibit higher order of Q

Q factor orders of $10^2 - 10^3$ were found

$$Q = \lambda / \Delta\lambda$$

where $\Delta\lambda$ is the full width at half maximum (FWHM) of the resonance peak occurring at λ



Q factor is essential to [sense refractive index](#), since the detection limit of an optical resonator is set by how precise one can define the mode position λ

Evaluation of the Nile red-PS microspheres as WGM- μ Rs

- microresonators operated at low Q values give a larger spectral shift of the mode position when changing the surrounding medium, this means: spheres with low ϕ offer better resolution of sensitivity (for refractive index sensing).
- Therefore, **microspheres resonators with small sizes** are especially attractive to study. A set of particles were exposed to a drastic decrement in the **diffractive index contrast** by changing the surrounding medium.

➤ **surrounding refractive index**
(label free sensors, cheap,
versatile and fast sensing)

➤ **Water is the base of most of the biological systems**, WGM's of Nile red-PS microspheres in water open a huge application on label free biosensing

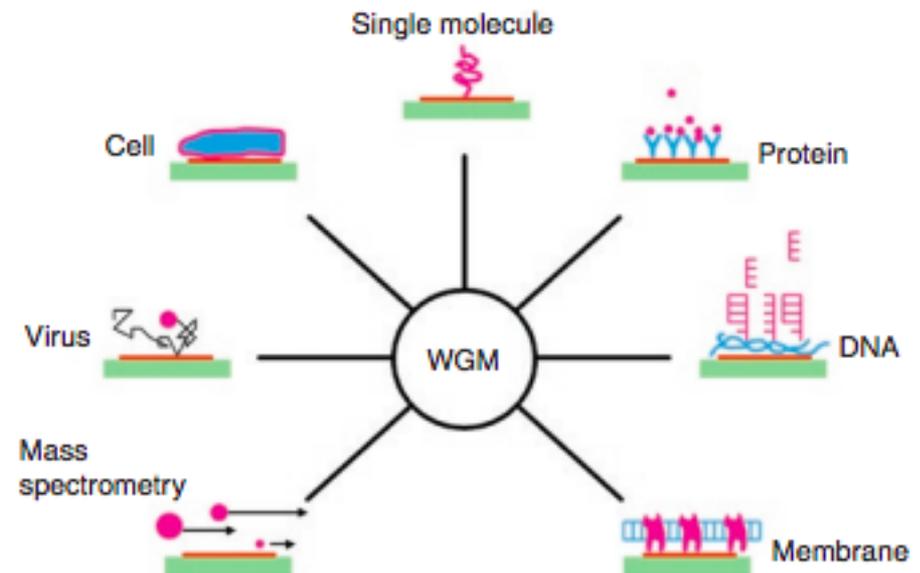
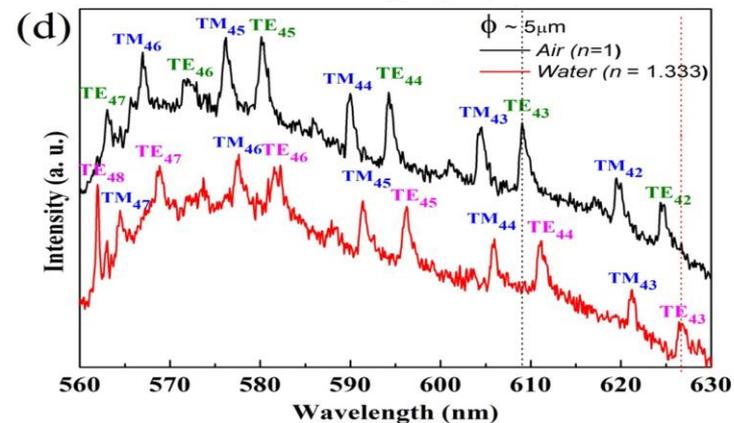
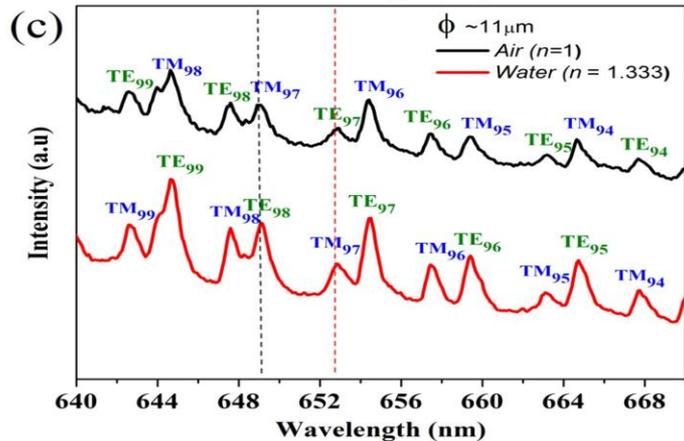
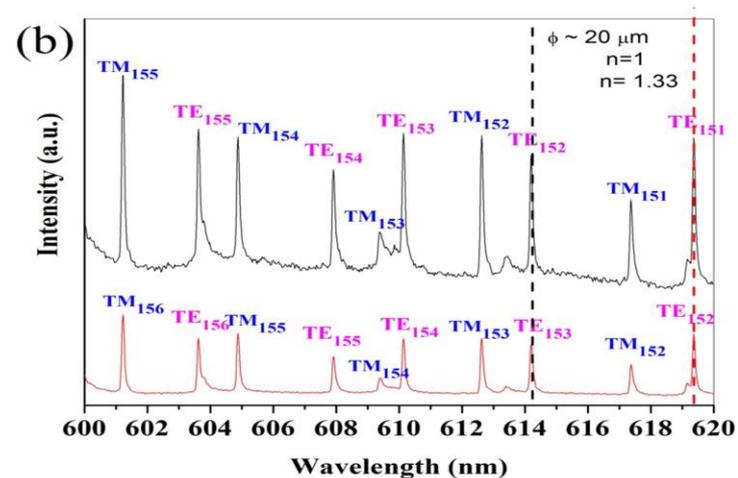
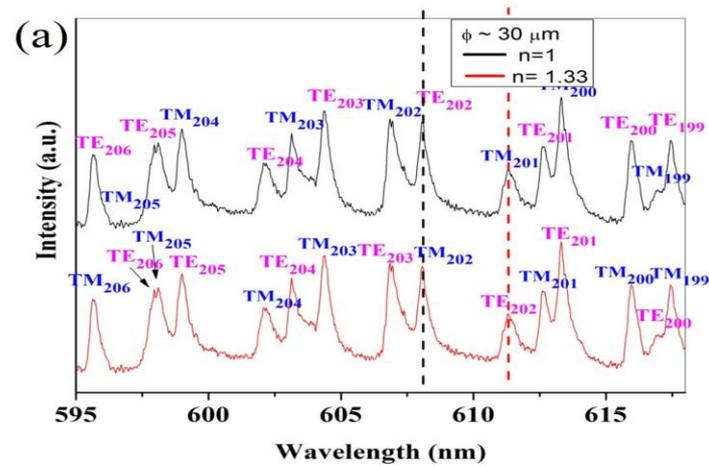


Figure 4 | Applications of WGM biosensors for analysis of various biological materials in different configurations.

Evaluation of the Nile red-PS microspheres as WGM- μ Rs

- WGMs measurements carried out in air and water media to probe diffractive index sensing of microsphere resonators with a ϕ range of $\approx 5 - 30 \mu\text{m}$
- The pump power used for air and water measurements was set to $12.2 \mu\text{W}$ and $42.3 \mu\text{W}$
- the transverse electric (TE) and transverse magnetic (TM) mode numbers were determined by airy approximation.



Evaluation of the Nile red-PS microspheres as WGM- μ Rs

- The experimental peak values of wavelength **well matched** with the calculated one values.
- The **mode shifting (red shift)** was clearly observed **through changing the medium** air to water due to change in the refractive index of the surrounding medium from 1 to 1.33.
- The maximum and minimum mode shifting were observed for the smallest and largest sizes of 5 and 30 μ m microspheres, respectively.

Refractive index Sensitivity (S): $\Delta\lambda / \Delta n$,

where $\Delta\lambda$ is the shifting of wavelength in the particular mode for changing in the refractive index of the surrounding medium and Δn is the change in the refractive index of the surrounding medium.

The maximum sensitivity is calculated for 5 μ m size resonator due to highest mode shifting which comes out about 53 nm / RIU.

S = 53 >> 11 > 16 > 9 nm/RIU for 5, 11, 20 and 30 μ m, respectively

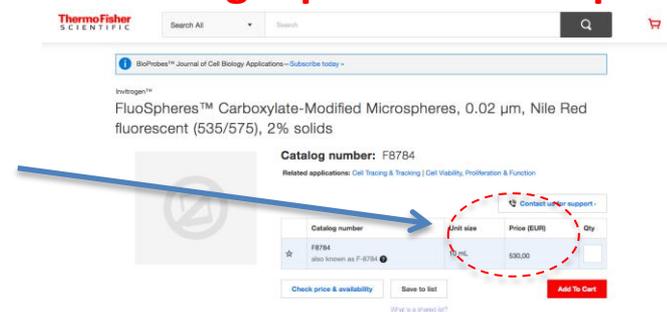
Active WGMS- μ R_s were prepared by a **single step polymerization reaction**.

The direct dye encapsulation promoted by steric inclusion during microspheres formation by MW-assisted polymerization avoid the tedious multi-step doping protocols while the use of organic solvents are also minimized (promoting a **greener fabrication approach**).

The **particle size and particle size distribution** of Nile red-PS microspheres were **easily controlled** by modifying the stabilizer agent concentration and the ethanol: water ratio.

The MW-Assisted polymerization process using the dipole coaxial antenna owns versatility, fast processing times and high yields. This new process enables to produce a high quantity (**millions**) of microspheres in a single step (more than 20g were obtained in one batch experiment) that can be used as **single-particle WGM- μ R**.

Some fluorescent PS particles available: very expensive (530euro 10 ml 2%)

A screenshot of the ThermoFisher Scientific website showing a product page for FluoSpheres™ Carboxylate-Modified Microspheres. The product is described as 0.02 μ m, Nile Red fluorescent (535/575), 2% solids. The catalog number is F8784. The price is listed as 530.00 EUR. A blue arrow points from the text above to the price field in the table. A red dashed circle highlights the 'Add To Cart' button.

Catalog number	Unit size	Price (EUR)	Qty
F8784 also known as F-8784		530.00	

The obtained **microspheres showed to support lasing single-particle WGMs spectra**, particles with \emptyset between ≈ 3 and $30 \mu\text{m}$ were tested as resonators in air and water environments.

This simple new approach of preparing doped particles enables to study resonators of large interval of sizes with **pumping power levels $< 1 \mu\text{W}$** , the lowest value ever reported.

Experiments for refracting index sensing showed that the **sensitivity S can be improved by reducing the size of the resonator and sacrificing Q factor**, to this regard the smallest particle ($\approx 5 \mu\text{m}$) tested here showed a noticeable enhancement value of S , in comparison with bigger ones. This is the smallest polystyrene particle ever reported to sport WGMs in water.

The combination of **low excitation energy and its high sensitivity** factor found for this special particle, open new perspectives to consider such a small polymer particles as a new-scale resonators for **enhancing biosensing applications**.



Thanks for your attention!

Evaluation of the nile red-PS microspheres as WGM- μ Rs

We have considered the airy approximation given in equation (1) for spheres to determine the transverse electric (TE) and transverse magnetic (TM) mode numbers of WGMs of polystyrene microspheres in both water and air as surrounding media [32]:

$$n_r x_l^{(i)} = v + \frac{\alpha_i}{2^{1/3}} v^{1/3} - \frac{mp}{\sqrt{m^2 - 1}} + \frac{3\alpha_i}{10.2^{2/3}} v^{-1/3} + \frac{m^3 p (2p^2 / 3 - 1) \alpha_i}{2^{1/3} (m^2 - 1)^{3/2}} v^{-2/3} + O(v^{-1})$$

where, $p = 1$ for TE and $p = 1/m^2$ for TM polarization and $m (= n_s/n_e)$ is the relative refractive index between resonator and its surrounding medium. Here, $v = l + \frac{1}{2}$, l and i are angular and radial mode order, α_i is the i th zero of the Airy function, the size parameter: $x_l(i) (= 2\pi a/\lambda)$ and, (λ =resonance wavelength).