NanoUp NTF

Multifunctional magnetic, photoluminescent and photocatalytic nano-constructs for bio-medical applications

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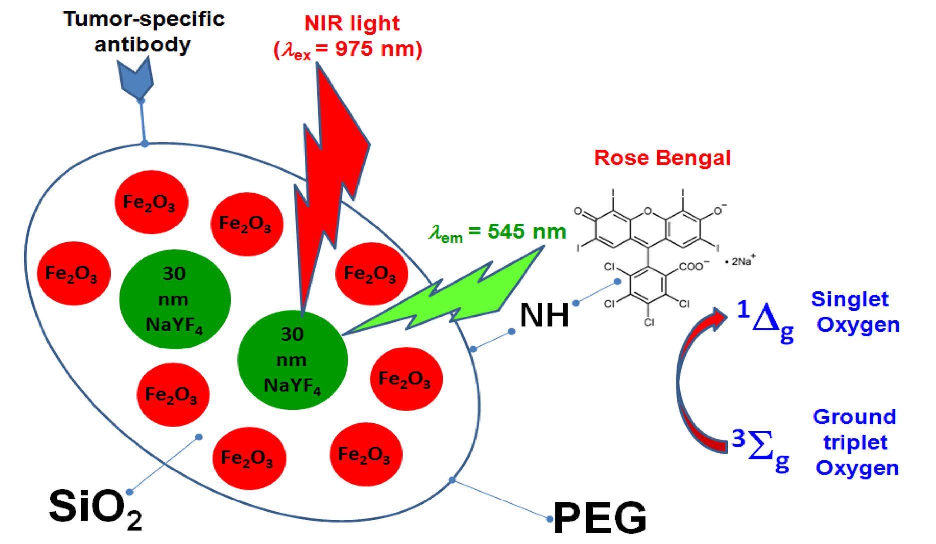
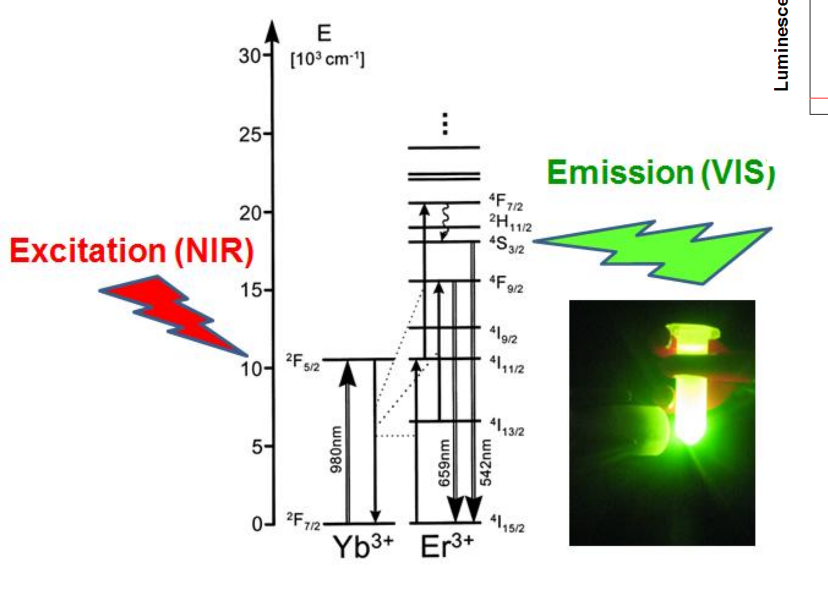
Motivation and challenges of the project 'NanoUp'

The overall goal of this project was to prepare multifunctional ***magnetic***, ***photoluminescent*** and ***photocatalytic*** nanoscale materials, which would combine useful functions of superparamagnetic and near-infrared (NIR)-to-visible upconverting particles. These nanoscale constructs might open new avenues in biomedicine, including simultaneous combination of various therapeutic modalities, such as **photodynamic diagnostic** (PDD) and **photodynamic therapy** (PDT) with A/C driven **hyperthermia** [S. Balivada *et al*. ***BMC Cancer*** 10, 119, 1-9 (2010)].

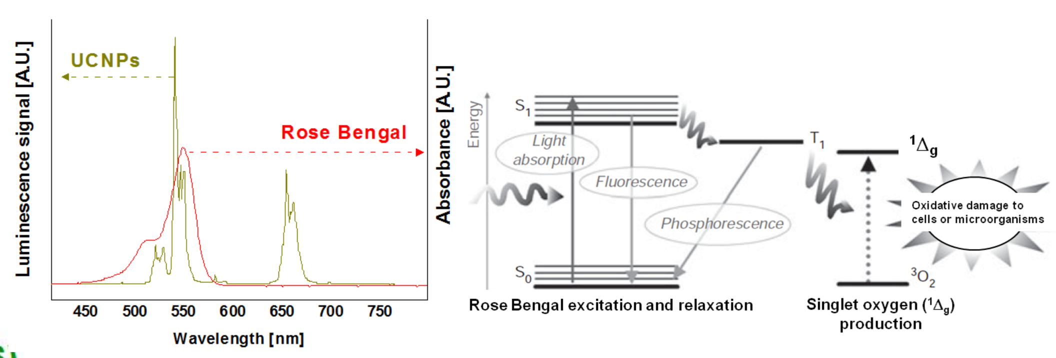


Schematic view of a multifunctional *magnetic*, *photoluminescent* and *photocatalytic* nano-construct targeting specific tumor cells in NIR-based *deep-tissue* PDT & A/C hyperthermia applications.

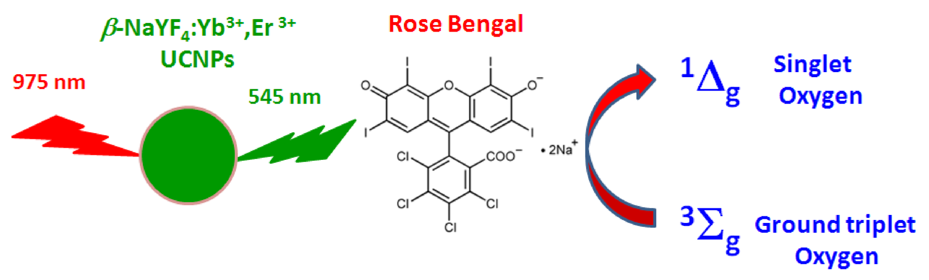
Principles of the *NIR-to-visible* upconversion and 'local' photosensitization of singlet oxygen ($^1\Delta_g$)



Scheme of *NIR-to-visible* upconversion by β-$NaYF_4$:Yb^{3+},Er^{3+} nanoparticles



The perfect overlap of the luminescence spectrum of β-$NaYF_4$:Yb^{3+},Er^{3+} and the absorbance bands of Rose Bengal (left) and the corresponding Jabłoński diagram explaining the formation of singlet oxygen (right).



Scheme of the 'local' *NIR-light-induced* generation of singlet oxygen in the presence of Rose Bengal

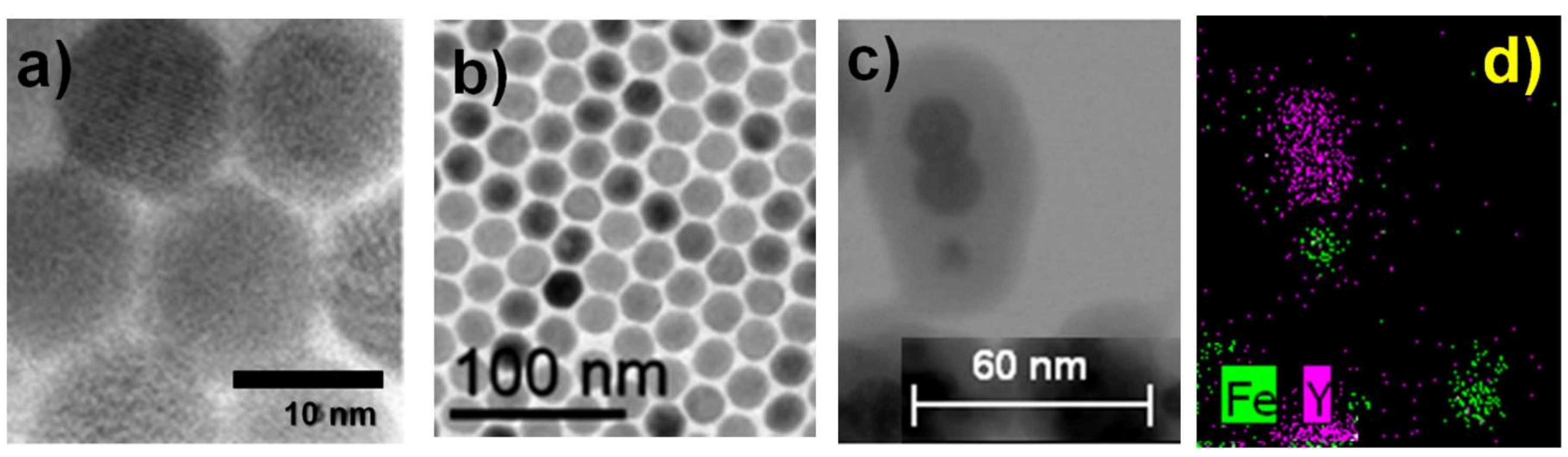
Two technological approaches

Two technological pathways towards obtaining multifunctional nano-constructs were explored:

1. co-encapsulation of commercial 30 nm β-$NaYF_4$:Yb^{3+},Er^{3+} phosphor nanoparticles (UCNPs) with custom-synthesized 10 nm γ-Fe_2O_3 super paramagnetic nanoparticles (SPIONs) in silica (SiO_2) shell using a modified Fink / Stöber method.

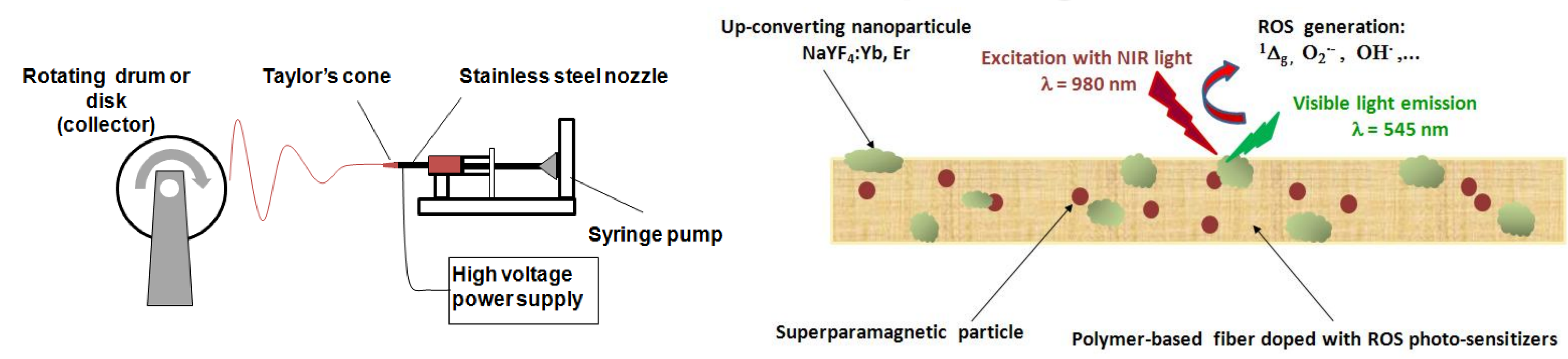
2. co-encapsulation of modified commercial β-$NaYF_4$:Yb^{3+},Er^{3+} phosphor nanoparticles (UCNPs) with custom-synthesized 10 nm γ-Fe_2O_3 super paramagnetic nanoparticles (SPIONs) in a polystyrene (PS) matrix using electro-spinning (E-spinning).

Results: (i) synthesis of $NaYF_4$, γ-Fe_2O_3 @ SiO_2 nano-constructs

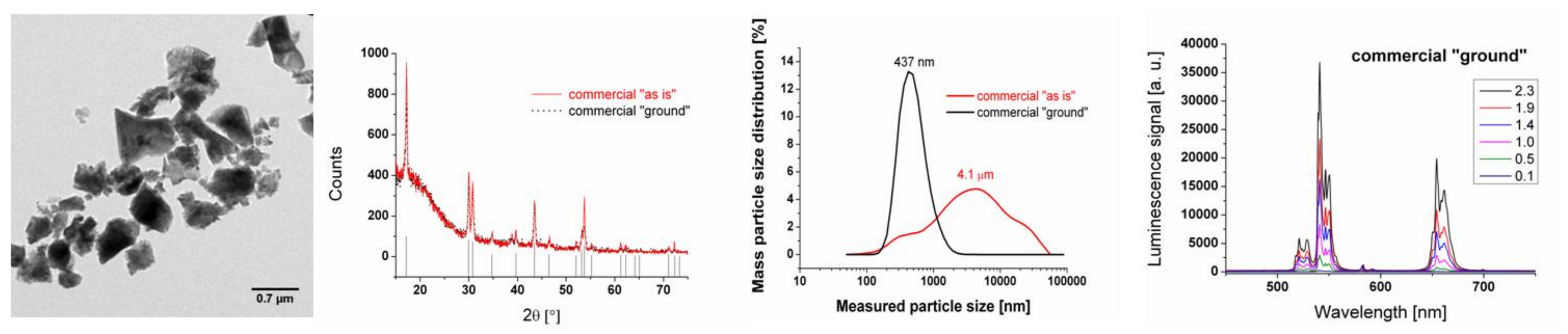


TEM micrographs showing the encapsulation of UCNPs and SPIONs within silica shell ($NaYF_4$ & γ-Fe_2O_3 @ SiO_2): (a) individual custom-synthesized SPIONs, (b) individual commercial 30 nm spherical UCNPs, (c) one SPION and two UCNPs encapsulated in SiO_2, and (d) EDX micrograph showing the elemental analysis of the nano-construct shown in (c).

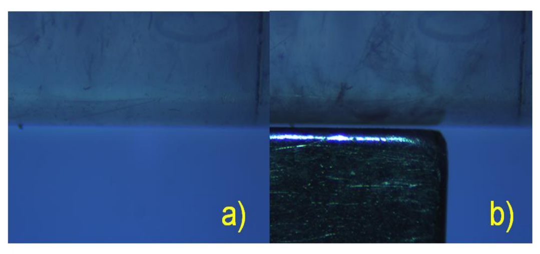
Results: (ii) co-encapsulation of SPIONs and UCNPs in PS matrix *via* E-spinning



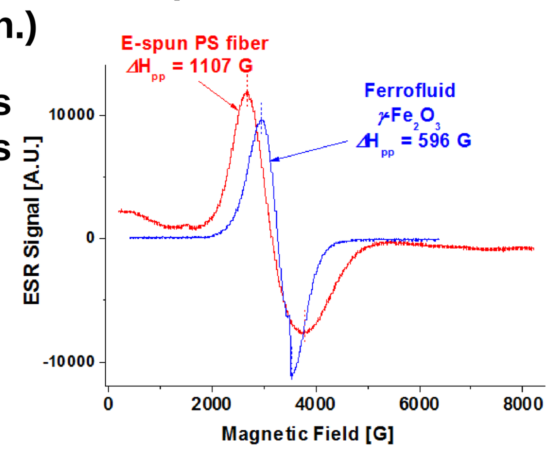
Schematic representations of: the custom-built E-spinning apparatus (left) and a multifunctional *magnetic*, *photoluminescent* and *photocatalytic* PS fiber loaded with SPIONs and UCNPs, also doped with selected sensitizers of singlet oxygen, such as Rose Bengal or fullerene, C_{60} (right).



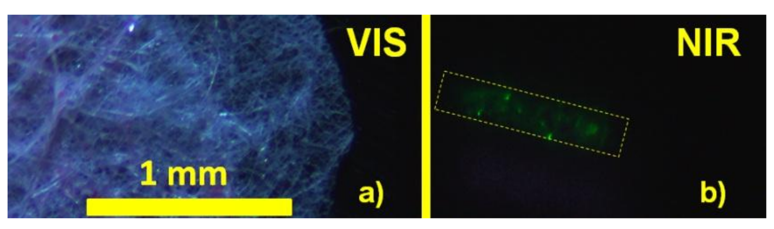
Characterization of the commercial UCNPs used to produce E-spun PS fibers: TEM micrograph of the ground powder, XRD spectra of the ground and 'as is' powders, DLS traces for the ground and 'as is' powders, and UCL luminescence spectra of the ground UCNPs as a function of power of the NIR light laser (from left to right). The *ground-toward-downsizing* UCNPs conserved their excellent upconverting properties.



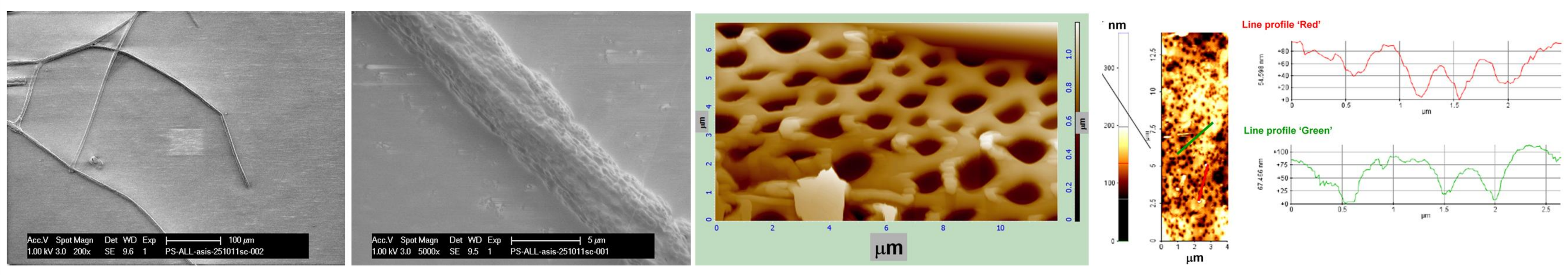
Macroscopic evidence of the magnetic properties of PS E-spun fibers containing SPIONs. *Magnetic-field-induced* movement of fiber fragments in water: in the absence (a) and presence (b) of the magnetic field. (The E-spun PC fibers were suspended in water and cut to smaller fragments by sonication.)



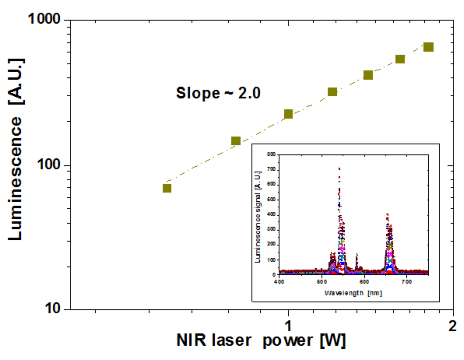
ESR spectra of the original ferro-fluid and of the E-spun PS fibers loaded with SPIONs. The ESR line-width broadens for SPIONs immobilized in the PS matrix [in good agreement with: N. Noginova *et al*., *J. Phys.: Condens. Matter* 19, 246208 (2007)].



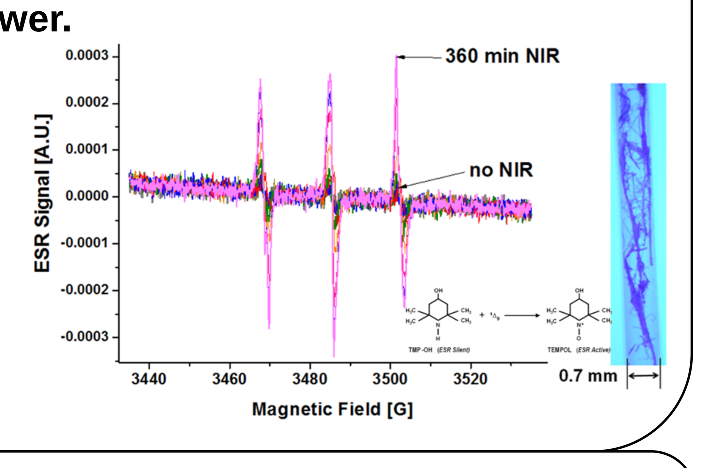
The PS E-spun non-woven fabric under: visible (a) and NIR (b) light.



SEM and AFM images point to a very high porosity of the 'as produced' E-spun PS fibers loaded with UCNPs and SPIONs, which is an asset in photocatalytic processes.



Log-log plot of the upconversion luminescence (UCL) *vs.* excitation power (NIR light, λ_{ex}= 975 nm) for E-spun PS fibers containing UCNPs and SPIONs. Inset: evolution of the UCL spectra of PS fibers as a function of the excitation power.



ESR monitoring of singlet oxygen formation under NIR illumination of E-pun PS fibers containing UCNPs, SPIONs and also doped with Rose Bengal (*via* reactive scavenging of singlet oxygen by TMP-OH).

Conclusions

1. We co-encapsulated UCNPs and SPIONs in silica shell and obtained our first multifunctional nano-constructs. This part of the project is now in progress - towards improvement of the encapsulation yield.
2. We used E-spinning as a 'facile' approach to co-encapsulate the above-mentioned nanomaterials in PS matrix. We demonstrated that the 'as produced' PS fibers reveal promising features of prospective multi-functional nano-constructs. These model constructs might find applications as stimuli-responsive 'smart' materials, including tissue engineering of bio-mimetic scaffolds and designing novel self-healing materials [Q.P. Pham *et al.*, ***Tissue Engineering*** 12 (No.5), pp. 1197-1211(2006)].

Acknowledgments

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