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Multipurpose magnetic-photoluminescent-photocatalytic nanostructures for biomedical applications

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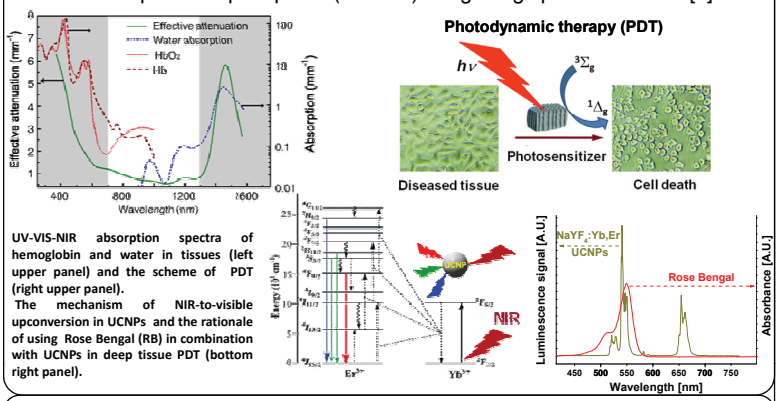
Introduction

Engineered nanoparticles (ENPs), which harbor various functions, have great potential for applications in fields ranging from industry and environment protection to biomedicine. In particular, multipurpose ENPs can find applications in bioimaging, contrast enhancement in magnetic resonance imaging (MRI), as well as in multimodal therapeutic strategies, which combine different modalities, like, *e.g.* **photodynamic diagnostic** (PDD) and **photodynamic therapy** (PDT) with alternating (A/C) magnetic field-driven **magnetic hyperthermia**. Of various multipurpose ENPs, nanoconstructs designed around superparamagnetic nanoparticles of iron oxide (SPIONs) and NIR-light-sensitive upconversion lanthanide-doped nanophosphors (UCNPs) are getting special attention [1].



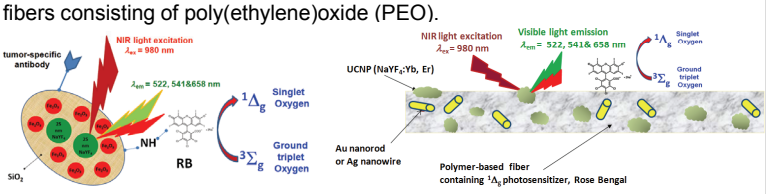
UV-VIS-NIR absorption spectra of hemoglobin and water in tissues (left upper panel) and the scheme of PDT (right upper panel).
The mechanism of NIR-to-visible upconversion in UCNPs and the rationale of using Rose Bengal (RB) in combination with UCNPs in deep tissue PDT (bottom right panel).

Motivation

Current challenges for multifunctional upconversion-based photo-catalytic systems include: pushing up the upconversion luminescence (UCL) efficiency of UCNPs, improving energy transfer from UCNPs the adjacent photosensitizer molecules *via* FRET/LRET mechanisms, and increasing reactive surface for better access of oxygen and other reactive species. Recently, a combination of **localized surface plasmon** resonance (LSPR) effects with up-conversion and FRET/LRET phenomena has also been proposed [2]. Herein, we explored two major fabrication routes towards obtaining multipurpose nanostructures comprising superparamagnetic γ-Fe_2O_3 SPIONs, β-$NaYF_4$:Yb,Er-based UCNPs and noble metal nanoparticles:

(i) a modified **TEOS/Stöber method** to encapsulate SPIONs and UCNPs in SiO_2 shells, which yielded **UCNPs&SPIONs@SiO$_2$** nanoconstructs.

(ii) electro-spinning (ES) to encapsulate SPIONs and UCNPs in polystyrene (PS) matrices, thus obtaining nano/micrometer-sized PS-based fibers. ES was also used to encapsulate UCNPs, Au nanorods and Ag nanowires in polymer fibers consisting of poly(ethylene)oxide (PEO).

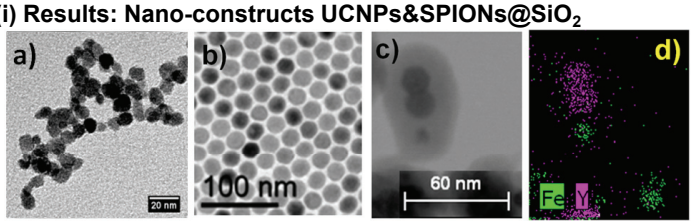


Schematic representation of multifunctional nanoconstructs for biomedical applications: 10 nm γ-Fe_2O_3 SPIONs and 25 nm β-$NaYF_4$:Yb,Er-based UCNPs encapsulated in SiO_2 shels (left panel) and β-$NaYF_4$:Yb,Er-based UCNPs , Au or Ag nanoparticles encapsulated in polymer-based fiber obtained by ES (right panel).

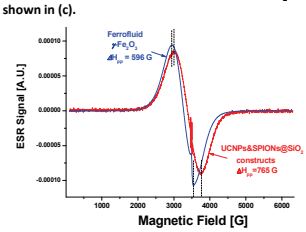
Conclusions

1. UCNPs&SPIONs@SiO$_2$ nanoconstructs revealed both superparamagnetic and NIR-to-visible upconversion properties. Under NIR light illumination (λ_{ex} = 980 nm), they generated singlet oxygen ($^1\Delta_g$) *via* the photodynamic action.
2. The E-spun PS-based fibers revealed superparamagnetic and photocatalytic properties under both visible and NIR light illumination. They may find applications in PDT, magnetic hyperthermia as well as in stimuli-responsive 'smart' materials.
3. The E-spun PEO-based fibers revealed strong photocatalytic properties under visible light illumination. Obtained results also point to a possibility of tailoring the photocatalytic properties *via* plasmon-induced effects, *i.e.* by supplementing the E-spun fibers with noble metal nanoparticles.

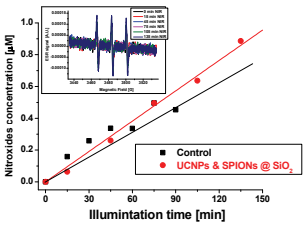
(i) Results: Nano-constructs UCNPs&SPIONs@SiO$_2$



TEM micrographs showing the encapsulation of UCNPs ($NaYF_4$:Yb,Er) and SPIONs (γ-Fe_2O_3) within silica shell, thus forming nano-constructs UCNPs&SPIONs@SiO_2: (a) 10 nm in DIA custom-synthesized SPIONs, (b) 25 nm in DIA commercial 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).

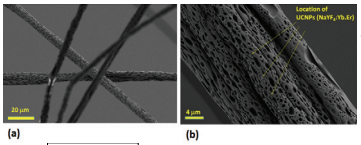


Magnetic properties of UCNPs&SPIONs@SiO_2 nano-constructs measured by ESR: the room-temperature ESR spectra acquired for the original ferrofluid (blue trace) and the aqueous suspension of UCNPs&SPIONs@SiO_2 nano-constructs (red trace). To present the overlapped ESR spectra, the signal amplitude of the ferrofluid was divided by a factor of 10^4.

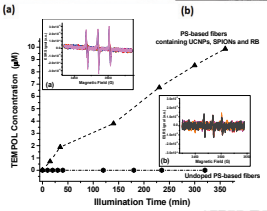


Kinetic plots corresponding to the NIR-light-induced (λ_{ex}=975 nm) formation of singlet oxygen ($^1\Delta_g$) in D_2O for nano-constructs UCNPs&SPIONs@SiO_2 (red dots) and for the control measurement (black squares). Inset: The example time evolution of the ESR spectra observed during 135 min of NIR illumination of nano-constructs UCNPs&SPIONs@SiO_2. 100 μM Rose Bengal and 100 mM TMP-OH were used as $^1\Delta_g$ photo-sensitizer and $^1\Delta_g$ scavenger, respectively. The NIR laser power was set at 2.57 W.

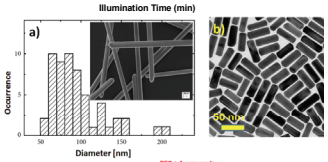
(ii) Results: co-encapsulation of UCNPs, SPIONs and metal nanoparticles in polymer matrices by E-spinning



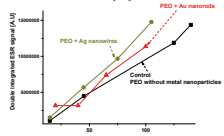
The morphology of E-spun polystyrene (PS) -based fibers containing co-encapsulated UCNPs and SPIONs: (a) SEM image of the fiber network; (b) SEM image of an individual fiber. [3]



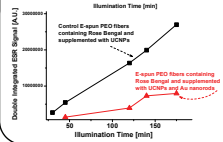
The ESR assay of the photodynamic formation of singlet oxygen in D_2O under the NIR light excitation of PS-based E-spun fibers loaded with UCNPs, SPIONs and RB (black triangles) and the control trace acquired for the undoped PS-based E-spun fibers (black hexagons). In both cases, the PS-based fibers were immersed in 50 mM solution of TMP-OH in D_2O. Insets: (a) the time evolution of the ESR signals of TEMPOL under NIR light illumination of PS-based E-spun fibers loaded with UCNPs, SPIONs and RB; (b) the time evolution of the ESR signals of TEMPOL under NIR light illumination of PS-based E-spun fibers without UCNPs. [3]



Noble metal nanoparticles used as plasmonic nanofillers in this study: (a) custom-synthesized silver nanowires having diameters in the range 50-150 nm and average length of 3-30 μm [4] and (b) commercial monodispersed gold nanorods with ~10 nm diameter and ~67 nm length (aspect ratio 6.7), A12N-10-1064, from Nanopartz™ (USA).



Preliminary results of testing plasmon-induced effects in the presence of metallic nanoparticles of Au and Ag in the liquid phase, *i.e.* in the precursor liquid used for ES of polymer fibers. The liquid PEO (solution in EtOH/H_2O) is supplemented with either Au nanorods or Ag nanowires. The PEO solution contains also 50 μM concentration of singlet oxygen ($^1\Delta_g$) generator, Rose Bengal. Generation of $^1\Delta_g$ is followed by ESR under NIR light illumination at λ_{ex} = 980 nm (1W NIR laser diode). The liquid sample was illuminated and measured in 0.7 mm ID capillary.



Preliminary results of testing plasmon-induced effects due to the presence of gold nanoparticles in E-spun polymer fibers based on PEO. The E-spun fibers are immersed in Toluene in 2 mm ID capillary. Generation of $^1\Delta_g$ in Toluene was monitored by ESR under NIR light illumination λ_{ex} = 980 nm (NIR laser diode, 1 W). Toluene contained 100 mM concentration of TMP, which served as a scavenger of singlet oxygen.

References

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Acknowledgments

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