

PHOTOACTIVE NANOFIBER MATERIALS

Jiří Mosinger

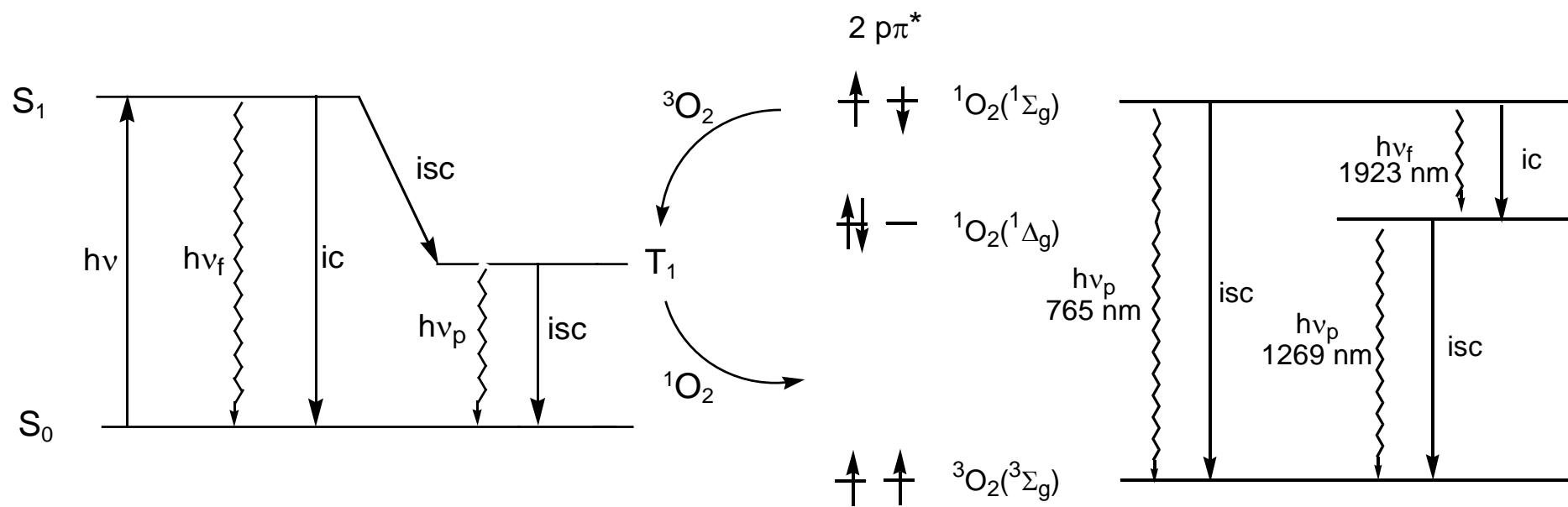
Research group: Photochemistry and Supramolecular Chemistry of Porphyrinoids

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Mechanism of photosensitized production of ${}^1\text{O}_2$

Electronic transitions of O_2



ic – internal conversion, isc – intersystem crossing,
 $h\nu_f$ – fluorescence, $h\nu_p$ – phosphorescence

Nanofibers with encapsulated nonpolar photosensitzers

Properties of ${}^1\text{O}_2$:

Strong oxidation effect

Strong cytotoxic effect

Short lifetime (activity "in situ")

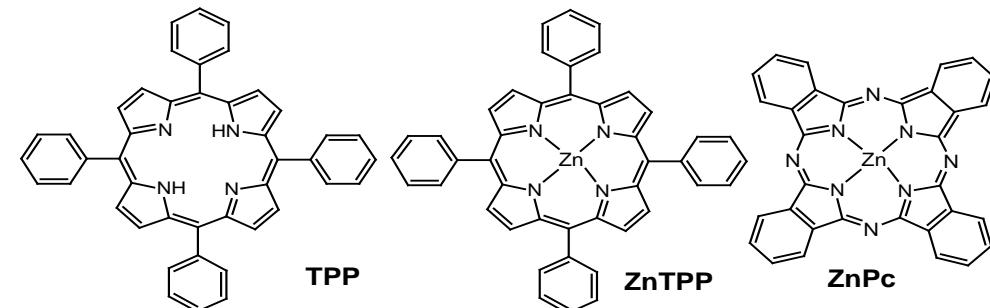
Properties of nanofiber materials:

Optical transparency

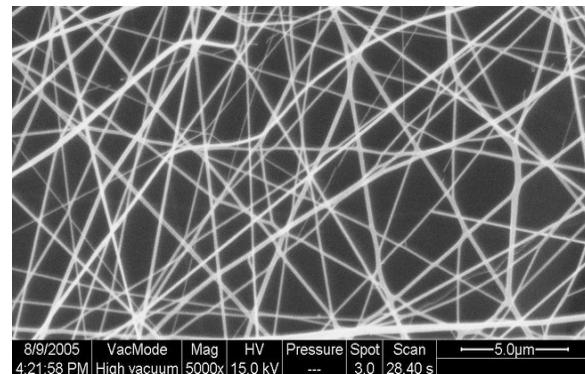
High oxygen permeability/diffusion

Large surface

Ability to detain bacteria or other pathogens on nanoporous surface



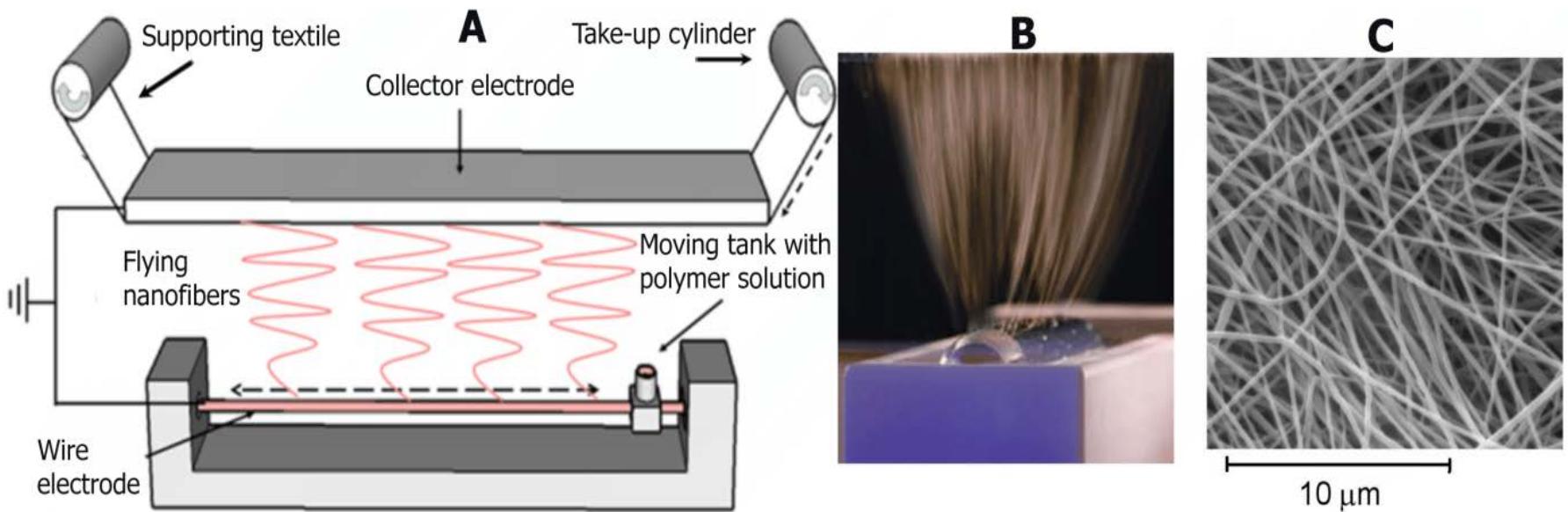
1-5 wt %



Nanofiber diameter: 150-350 nm

Novel photoactive
nanomaterials

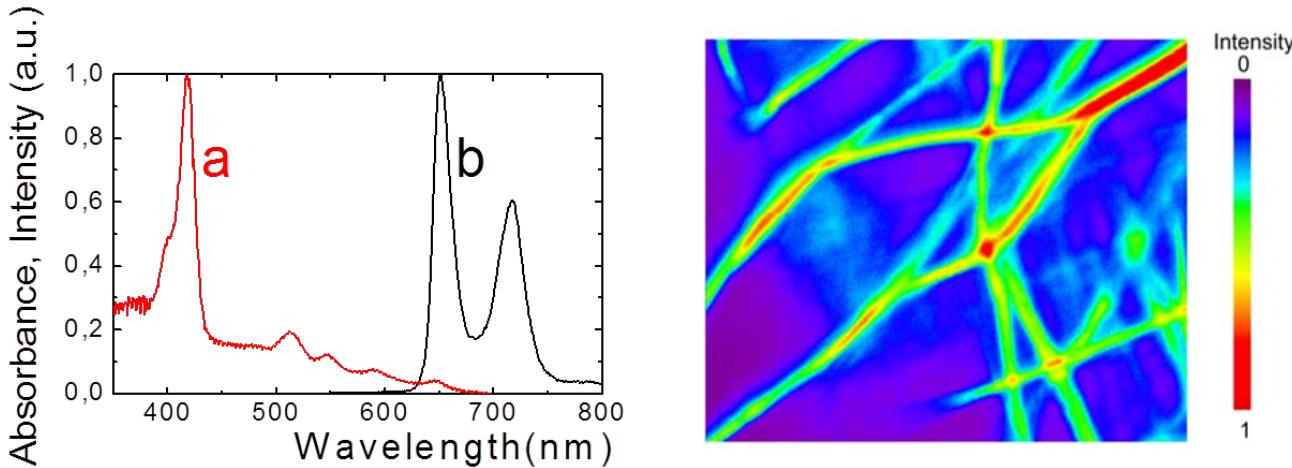
Electrospinning



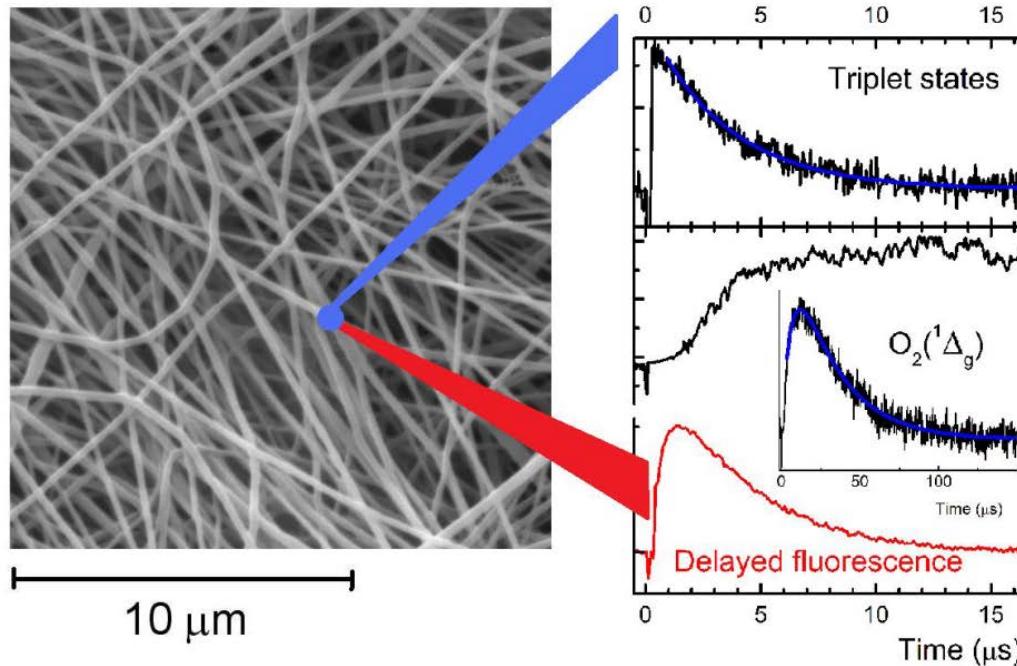
A: Scheme of an industrial electrospinning device Nanospider™.

B: Electrospinning device consisting of a roller electrode immersed in a tank with polymer solution. Flying nanofibers from a charged roller are placed on a grounded collector electrode. **C:** SEM of resulting nanofiber material.

Application of steady-state spectroscopy

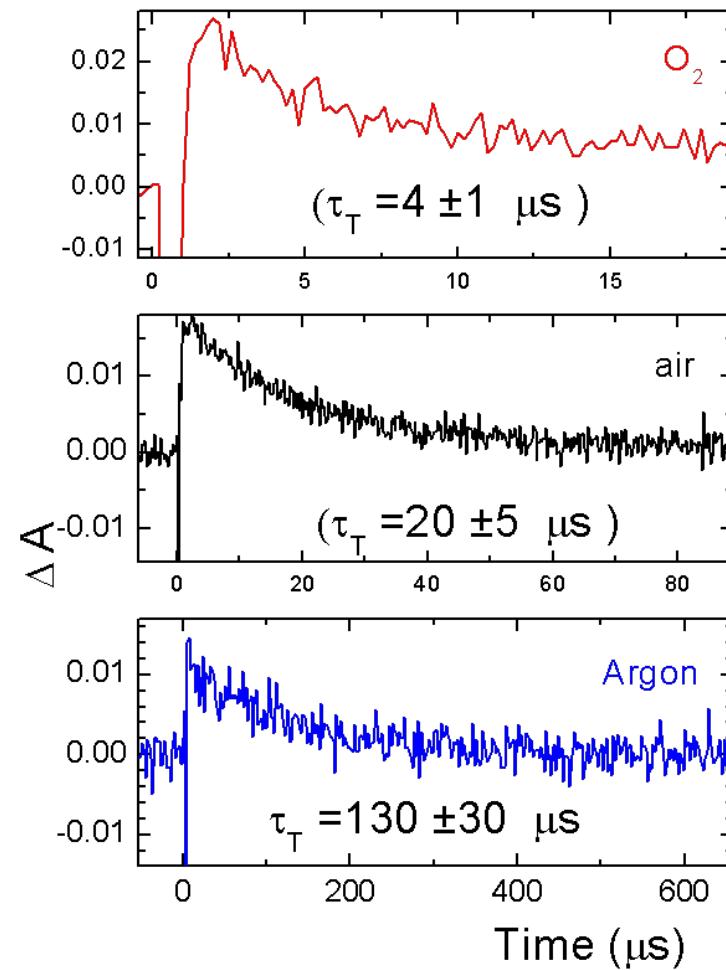


Application of time-resolved spectroscopy



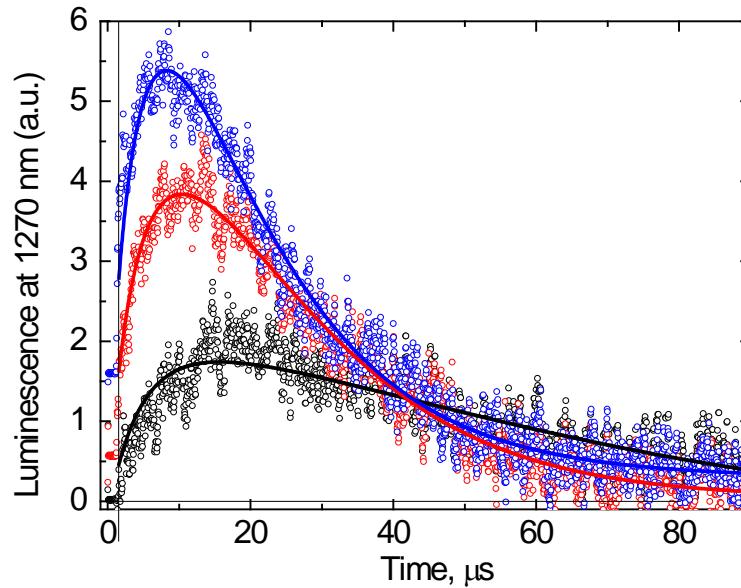
Kinetics/lifetimes of T-states

$$[A^T] = [A_0^T] \exp(-t/\tau_T)$$



Kinetics/lifetime/diffusion pathway of $\text{O}_2(^1\Delta_g)$

$$[\text{O}_2(^1\Delta_g)] = A_{\text{SO}} \tau \Delta / (\tau T - \tau \Delta) (\exp(-t/\tau T) - \exp(-t/\tau \Delta))$$



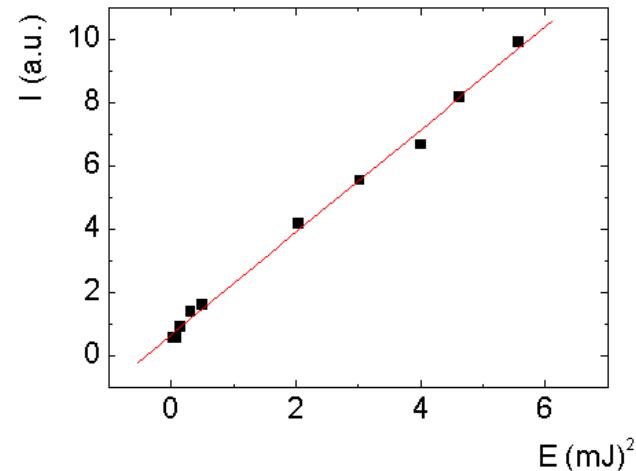
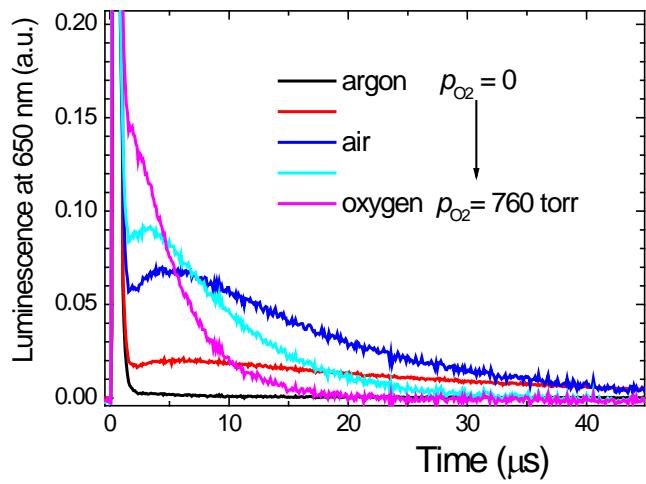
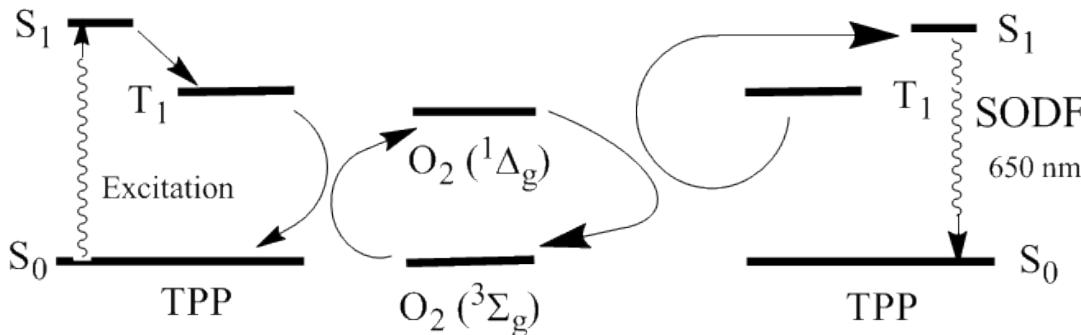
Time–resolved phosphorescence of $\text{O}_2(^1\Delta_g)$ at 1270 nm at oxygen pressure 100 (blue), 60 (red) and 13.3(black) kPa of oxygen

$\sim 20 \mu\text{s}$ (air); $D_0 \sim 1.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (PUR)

Diffusion pathway: $l_r = (6D_0\tau_\Delta)^{1/2} \sim 115 \text{ nm}$

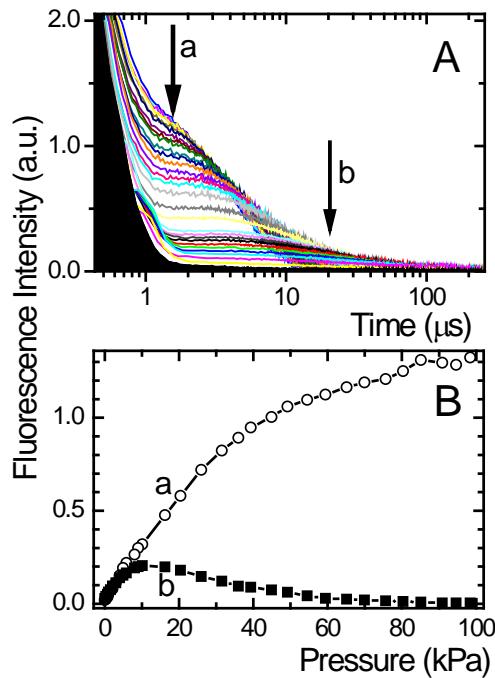
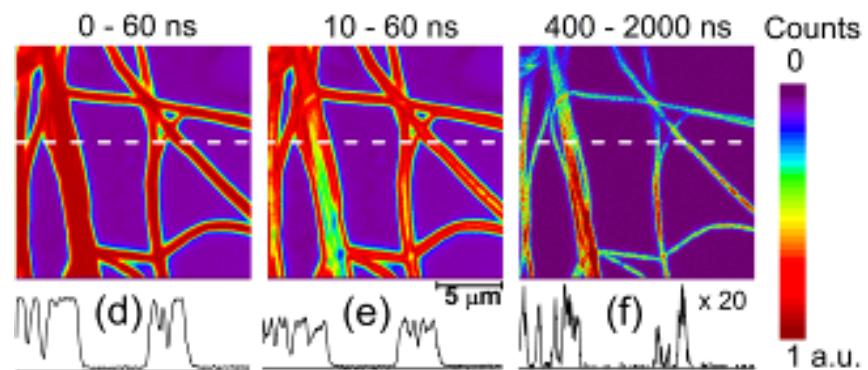
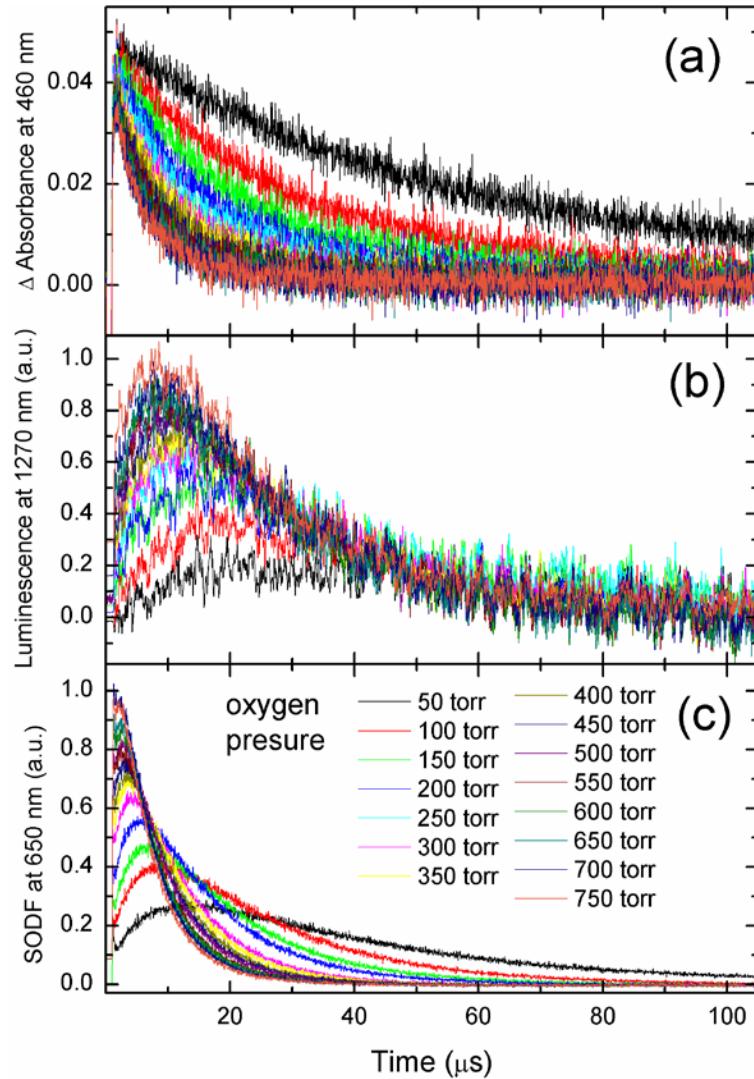
Photooxidation effect ONLY on the surface !

SODF („Singlet Oxygen sensitized Delayed Fluorescence“)

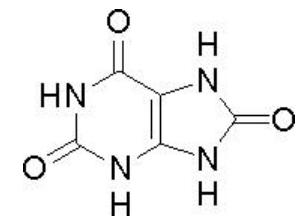
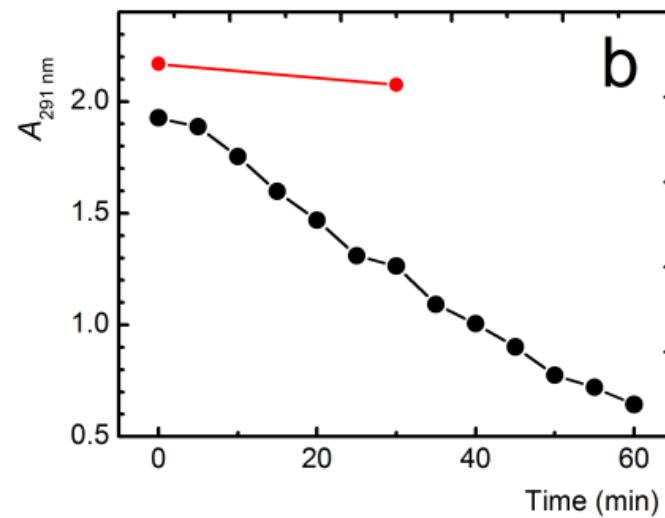
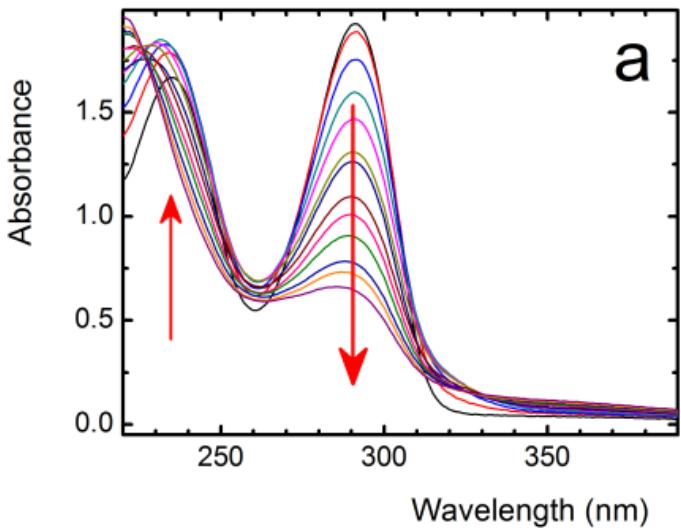


Detection and imaging of O₂/O₂(¹Δ_g) by SODF

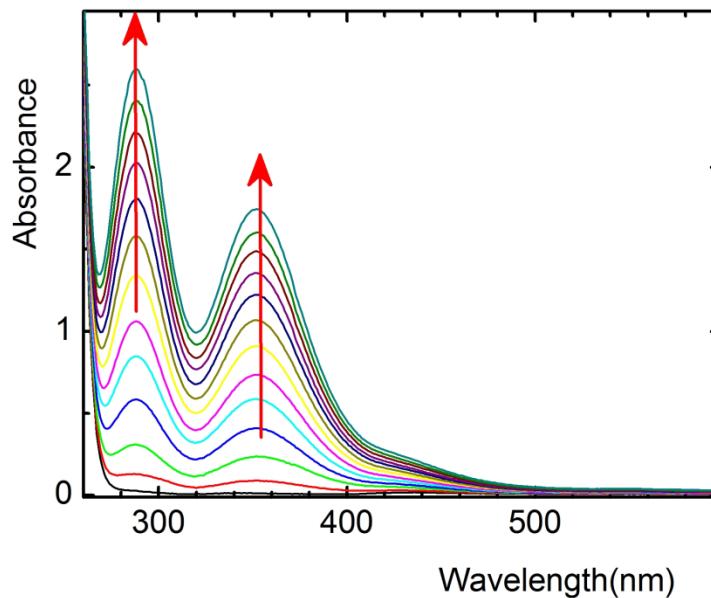
$$I_{\text{SODF}} = A_{\text{SODF}} \tau \Delta / (\tau T - \tau \Delta) (\exp(-t/\tau T) - \exp(-t/\tau \Delta))$$



Photooxidation of organic/inorganic substrates



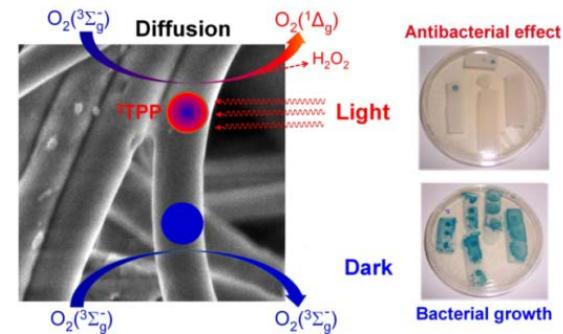
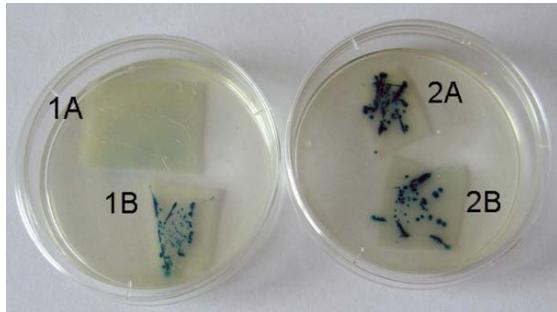
Uric acid
photooxidation



Iodide
photooxidation

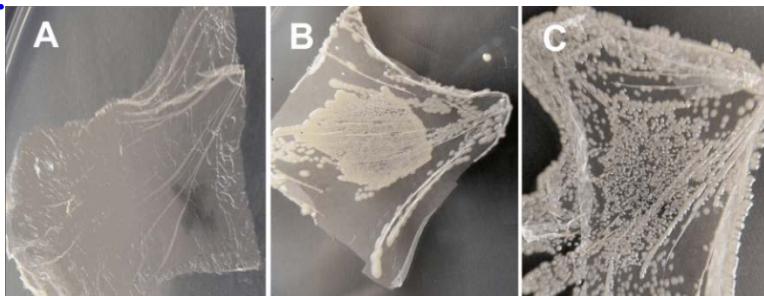
Antibacterial surface

*Escherichia coli, Staphylococcus aureus,
Pseudomonas aeruginosa*



Escherichia coli DH5α+
plasmid pGEM11Z
X-gal (5-bromo-4-chloro-3-indolyl- β -D-galactopyranosid)

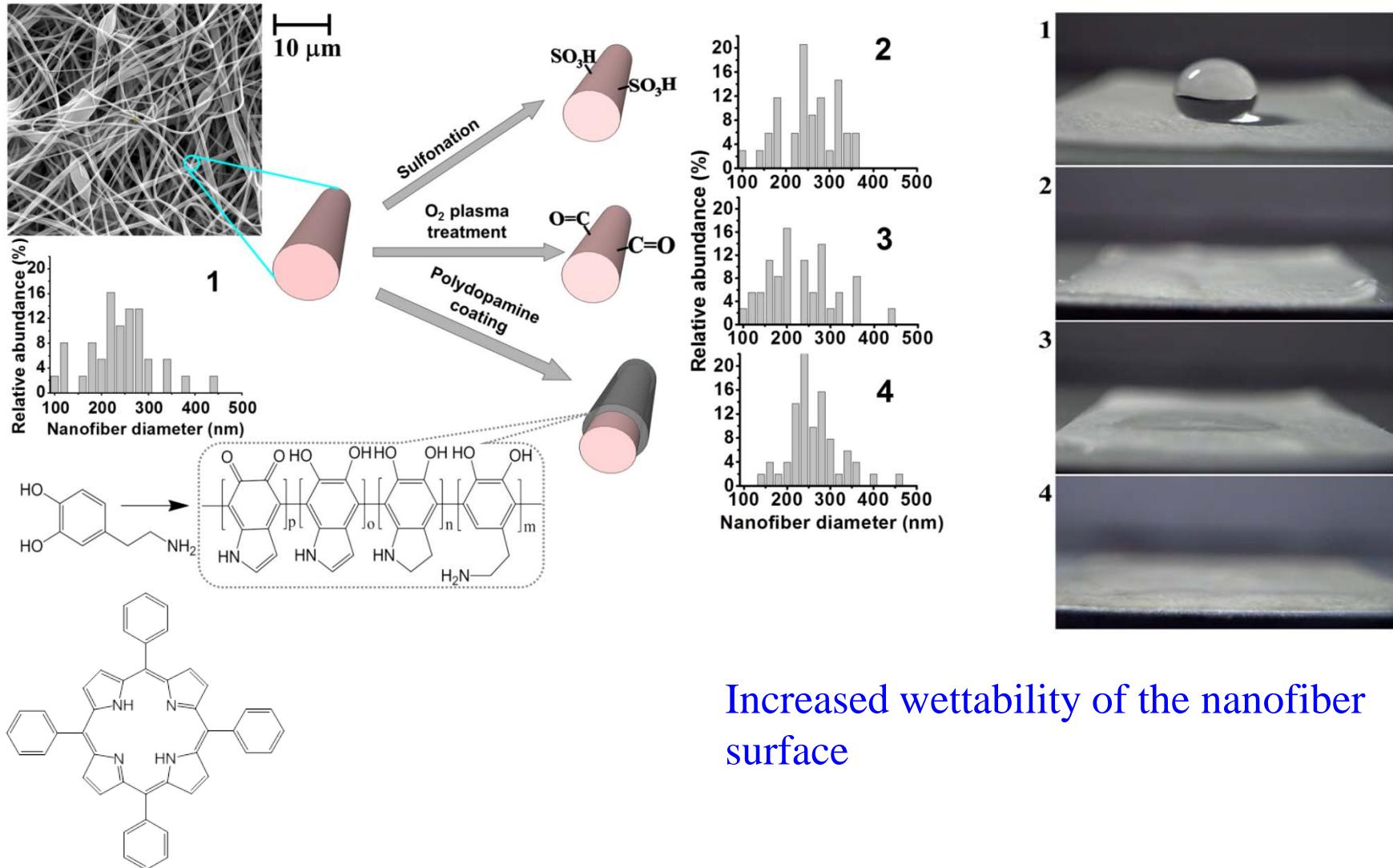
The antibacterial effect of Tecophilic™ nanofiber membrane with encapsulated 1% ZnTPP to *E. coli DH5a*. Agar plates with pieces of nanofiber membrane with encapsulated ZnTPP (**A**) and without photosensitizer (**B**) inoculated with *E. coli* exposed to white light (left, **1**) and kept in the dark (right, **2**).



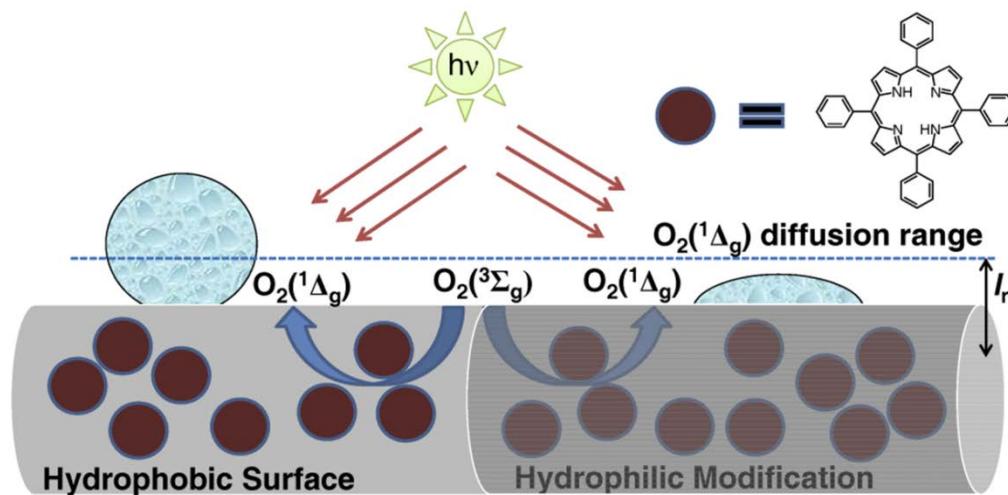
Staphylococcus aureus

The antibacterial effect of PCL nanofiber membrane with encapsulated 1% TPP. *Staphylococcus aureus* inoculated on surface of nanofiber membrane doped with photosensitizer (A) or without photosensitizer (B) and 30 min irradiated by white light. Inoculated doped nanofiber membrane left in the dark (C).

Nanofiber materials with encapsulated nonpolar photosensitizer and surface modifications



Enhanced antibacterial effect on the surface of nanofiber materials with post-processing surface modifications



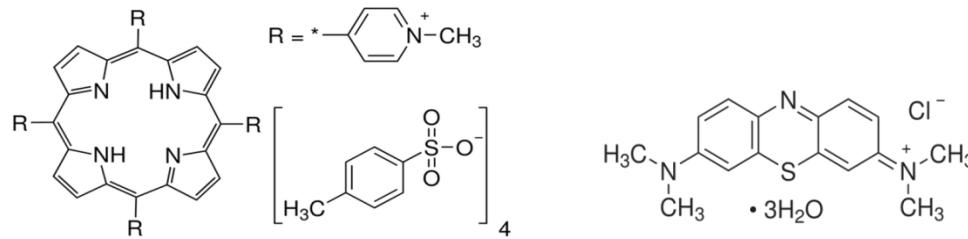
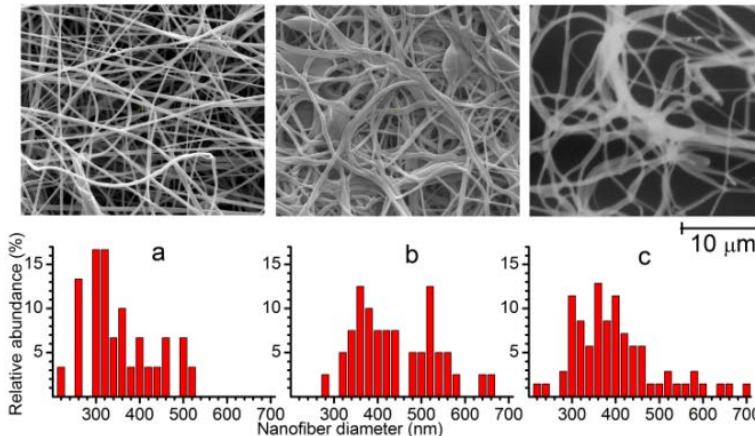
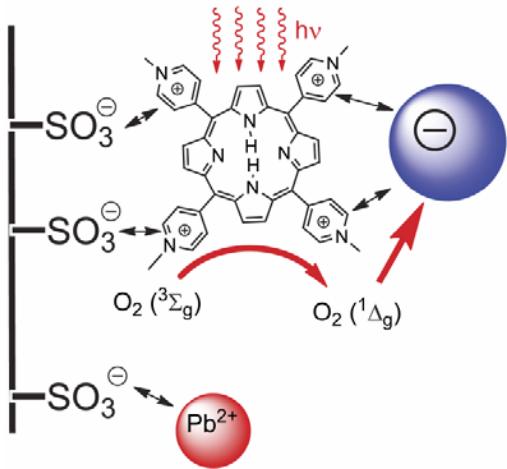
Light-activated, sterile nanomaterials for medical applications



Clinical photographs of a patient with leg ulcers treated with illuminated PU (Tecophilic) nanofiber membrane with encapsulated TPP at the beginning of curing (A), after 15 (B) and 42 (C) days of the treatment.

Multifunctional photoactive nanofiber materials with externally bonding photosensitizer(s)

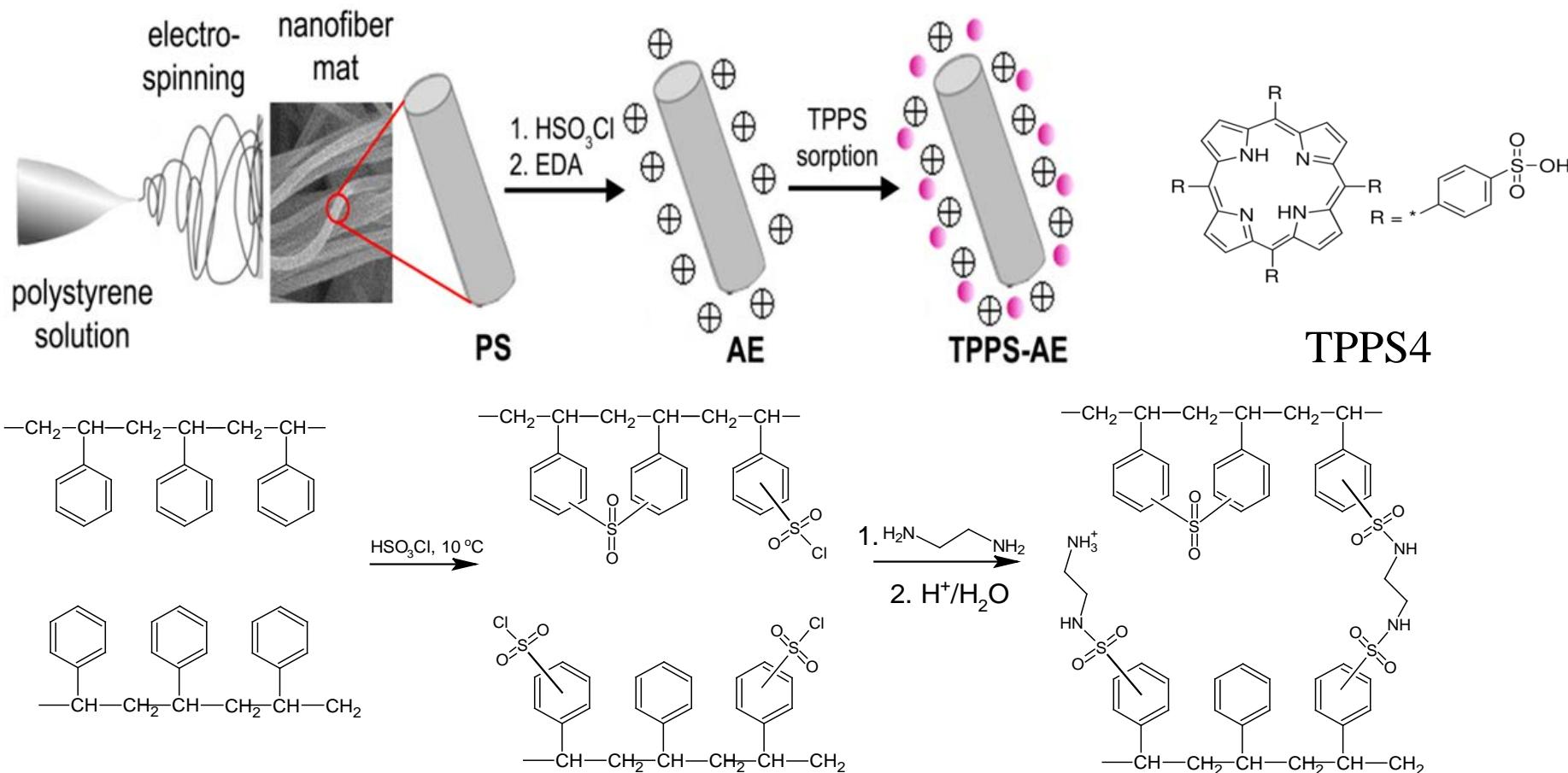
I) Photoactive cation exchange materials



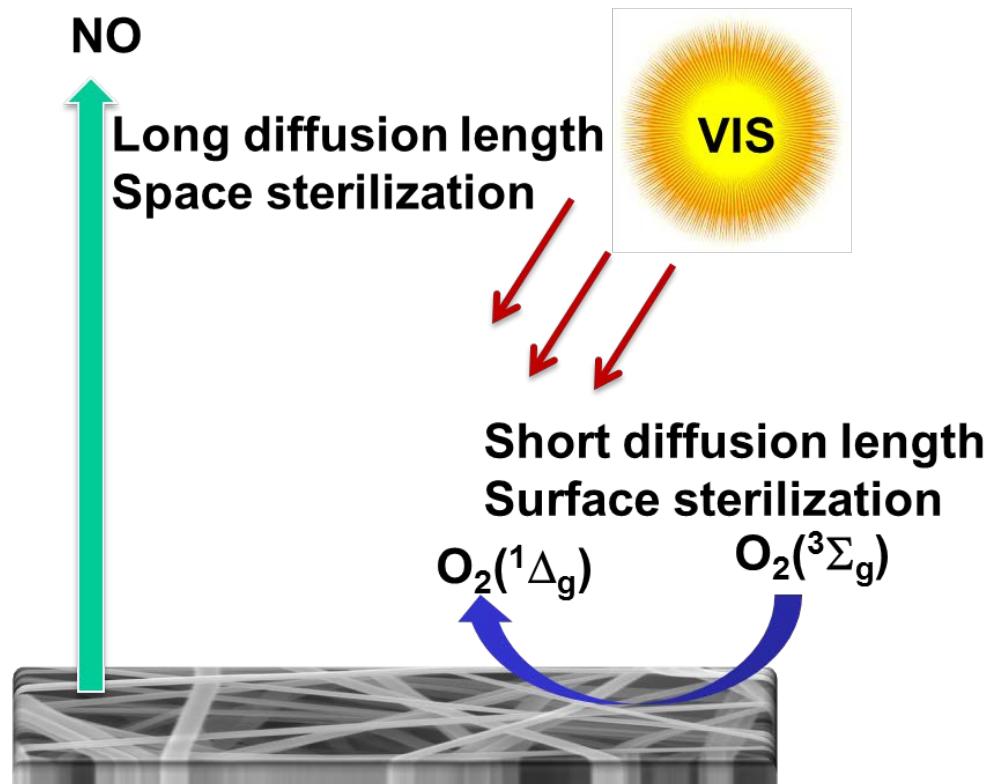
TMPyP

MB

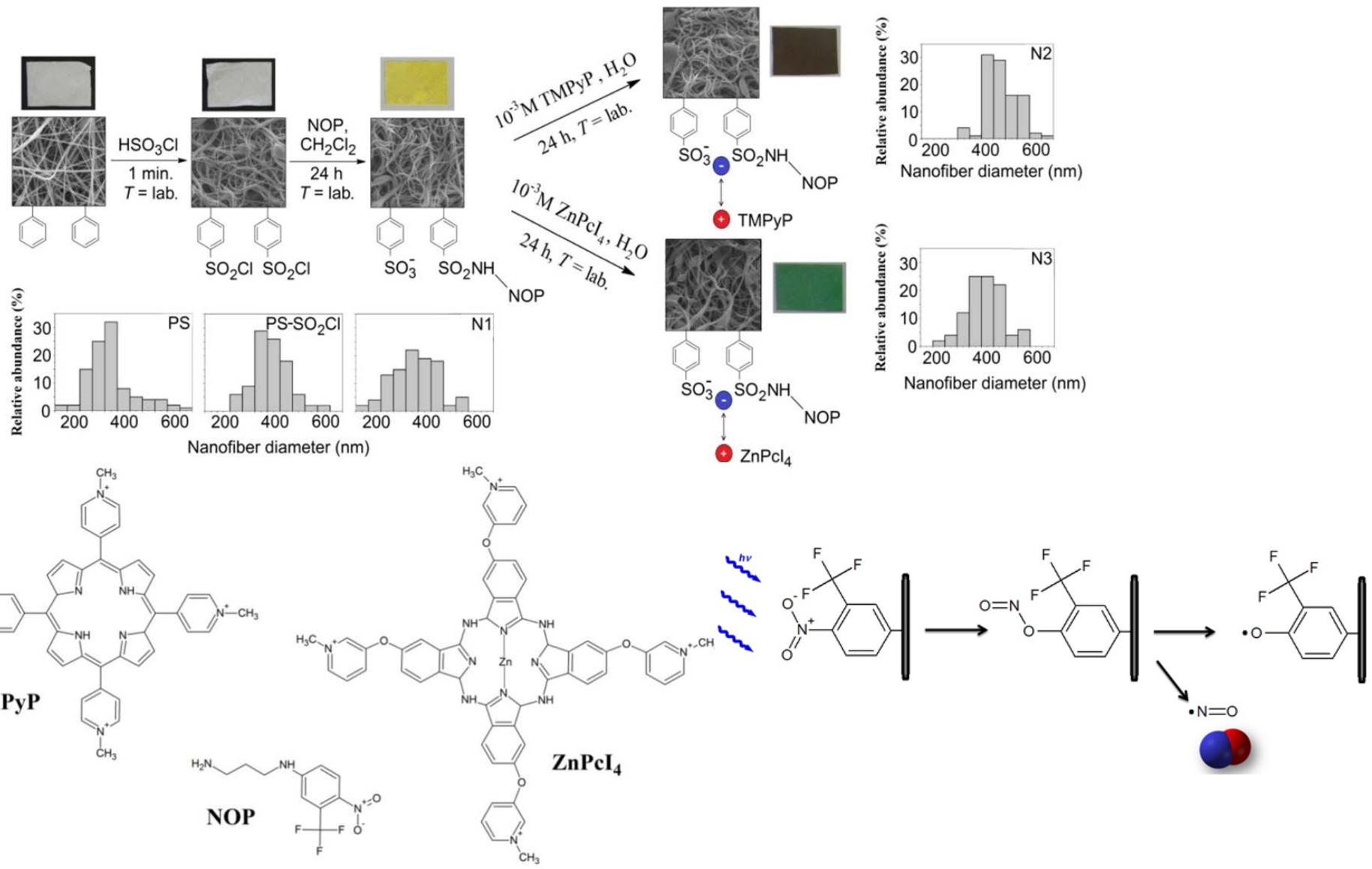
II) Photoactive anion exchange materials



Nanofiber materials for visible light driven simultaneous generation of NO and $O_2(^1\Delta_g)$



Preparation/characterization

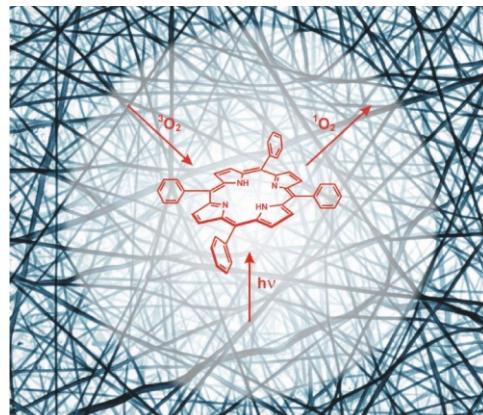


Conclusion

**Strong photooxidation & phototoxic effect on
surface of nanofiber materials**



**Sterile nanomaterials for medical applications
(wound covering, surgical mask, oxygen sensors...)
activated by visible light (daylight)**



Acknowledgment

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Thank you for your attention !