Direct optical detection of singlet oxygen in silicon nanocrystal systems

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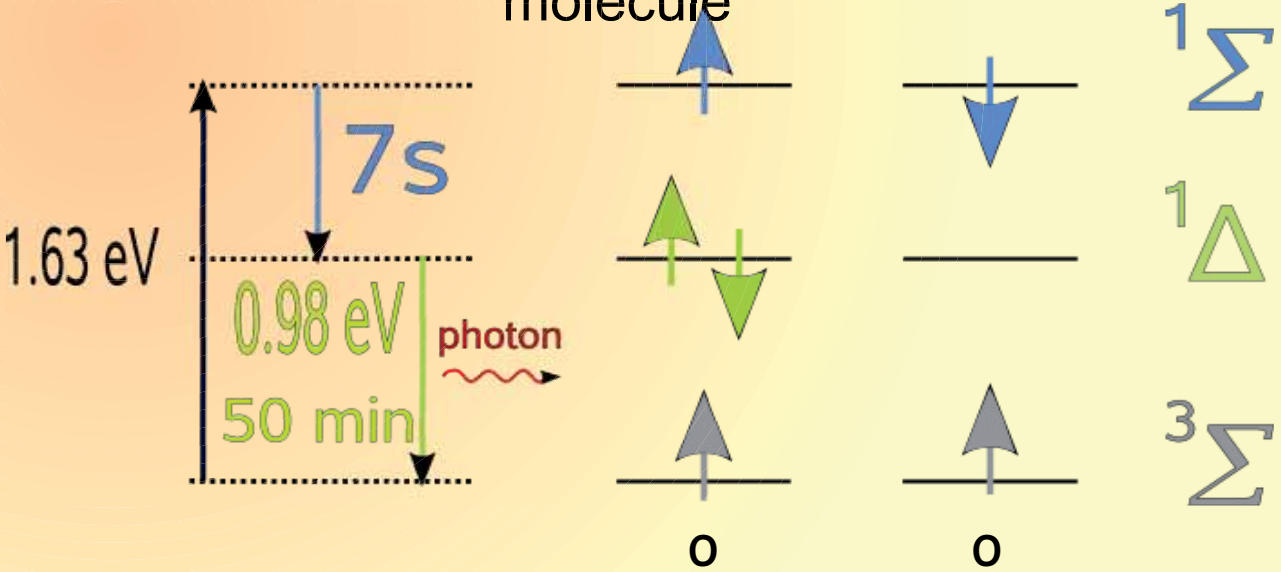
Electronic structure of an isolated oxygen molecule



Transitions to the singlet states are forbidden in dipole-dipole approximation by the spin selection rule. Some photosensitizers are required to make them more probable. Various photoexited dye molecules or **silicon nanocrystals (nc-Si)** can act as photosensitizers.

A luminescence of oxygen in $^1\Delta$-state is one of the most useful

Application of singlet oxygen in photodynamic therapy (PDT)

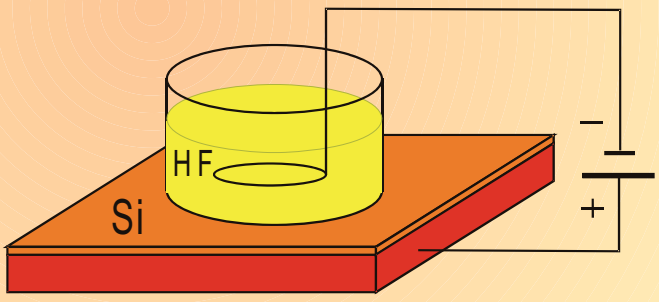
Singlet oxygen has very high chemical activity: it's a thousandfold more than for molecular oxygen. PDT is a method based on cytotoxic properties of singlet oxygen. The main area of PDT applications is oncology.

Stages of PDT:

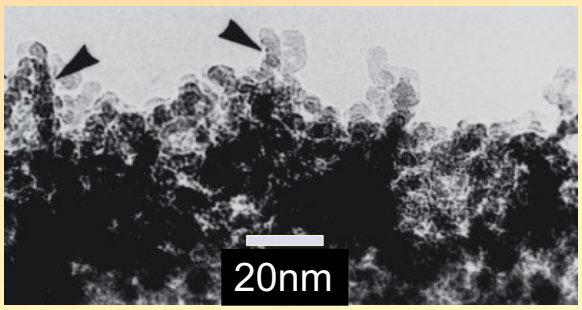
- Injection of preparation to the tissue
- Exposure the tissue under laser light, which leads to singlet oxygen generation.
- Death of irradiated cells via necrosis or apoptosis.
- Washout of medication

Disadvantages of dye photosensitizers: high toxicity, fast diffusion throughout organism, stability of photosensitizing properties, difficulties on providing selectivity of action

Formation of porous silicon (PSi)



$HF:C_2H_5OH = 1:1$



TEM-image of microporous luminescent silicon.

A. G. Cullis and L. T. Canham, Nature London, 1991 .

PSi layers have been prepared by electrochemical etching of **100** oriented, Boron-doped bulk Si wafers in a 1:1 by volume mixture of hydrofluoric acid (HF) 50 wt % in water and ethanol .

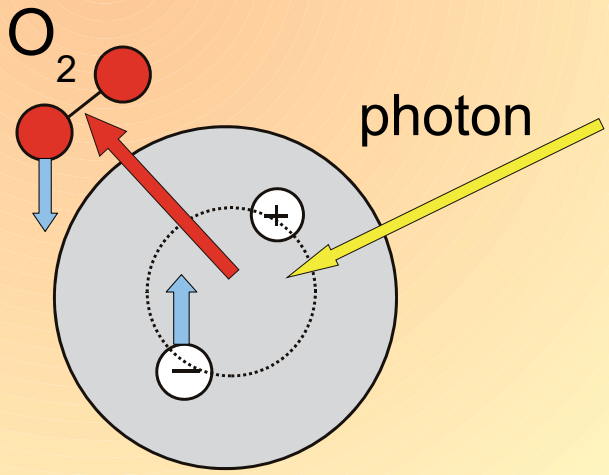
Etching time – 1 hour.

Current density – 60 mA/cm^2.

*Resistivity - 10 Ом*см (100)*

There is very efficient visible photoluminescence (PL) in PSi in contrast with bulk Si. It's due to recombination of quantum-confined carriers coupled in exitons.

Energy transfer from exitons confined on nc-Si to oxygen molecule



There are 3 path of exitons' recombination:

1) Radiative recombination which leads to PL

2) Nonradiative recombination on defects

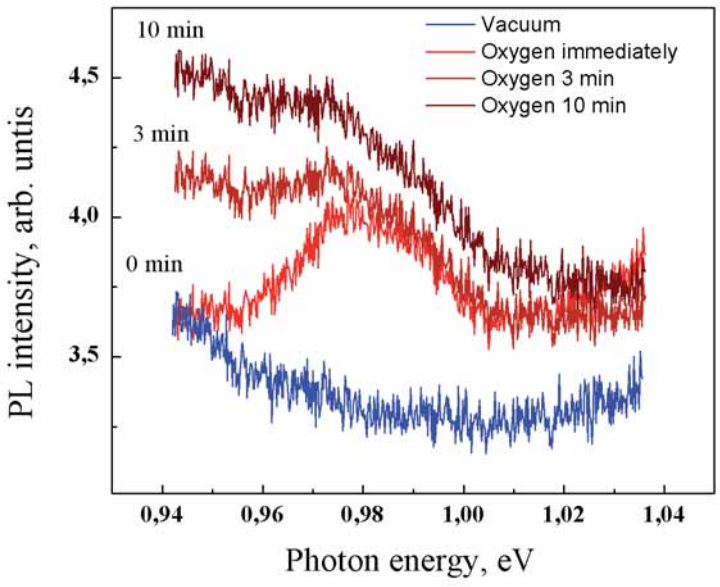
3) Nonradiative energy transfer to molecular oxygen

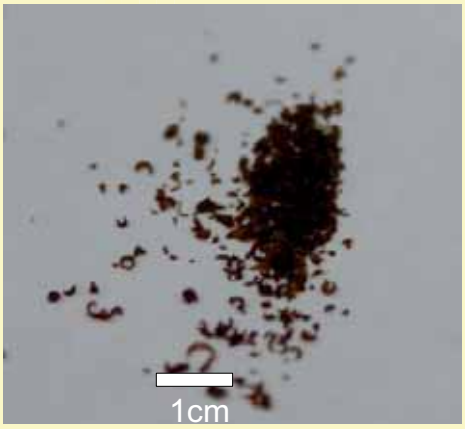
The last one can be described by Dexter direct electron exchange mechanism: molecule and exiton swap their electrons with different spin orientation, so spin of each electron remains unchanged, but the whole spin of oxygen molecule

No direct measurement has proved presence of singlet oxygen in PSi layers in oxygen ambient at room temperature yet.

Singlet oxygen luminescence in PSi layers

Initial PSi

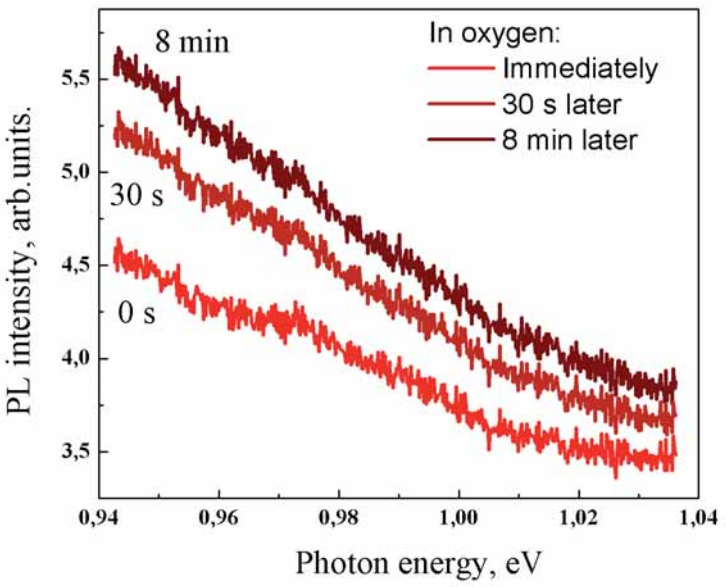


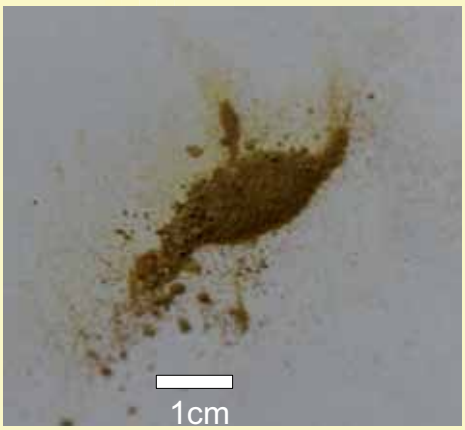


PL spectra: wide band — defects of nc-Si and narrow line — singlet oxygen luminescence.

Intensity of the singlet oxygen luminescence is decreasing in time while defects' PL is going to be brighter. New defects is suggested to be superoxide molecules bound to nc-Si.

Milled PSi layers

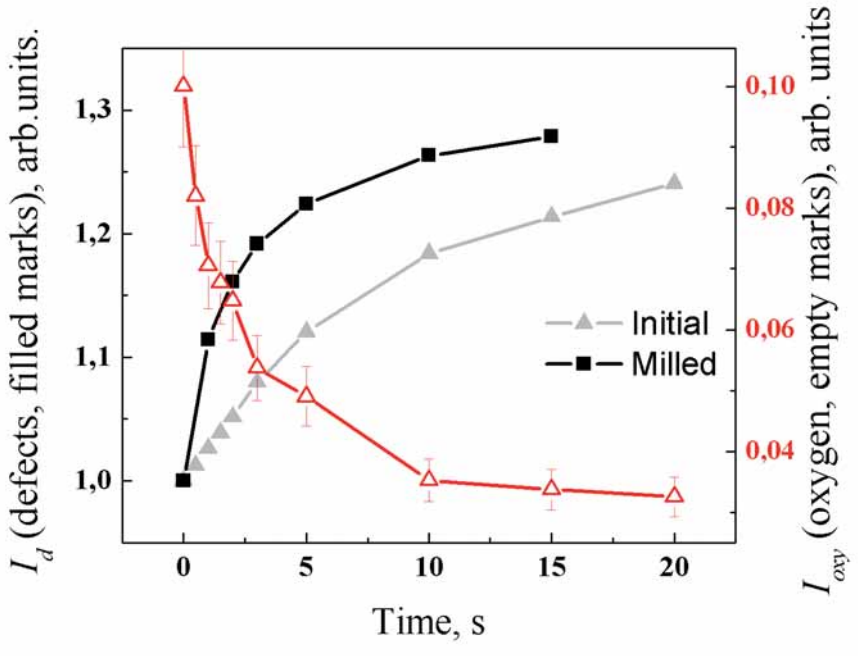




PSi layers is needed to be milled in order to delivery them into living tissues and cells.
Average size of granulas is 600 nm.

Milled PSi emits light more efficiently, and therefore it produces more singlet oxygen. In spite of it, amount of the singlet oxygen in milled PSi is much fewer than in intial PSi.

Correlation of nc-Si defects with the quantity of the singlet oxygen



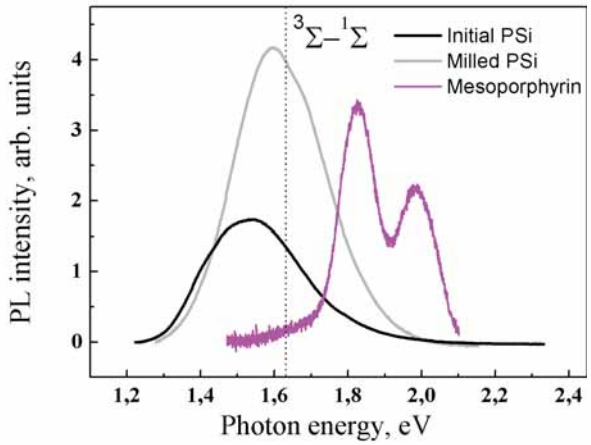
Amount of defects anticorrelates with amount of singlet oxygen. Therefore new defects is beleived to be cause of quenching singlet oxygen luminescence.

Singlet oxygen molecules interacts stronger with silicon surface in milled PSi, because silicon granulas are nearer to each other on it in comparison with

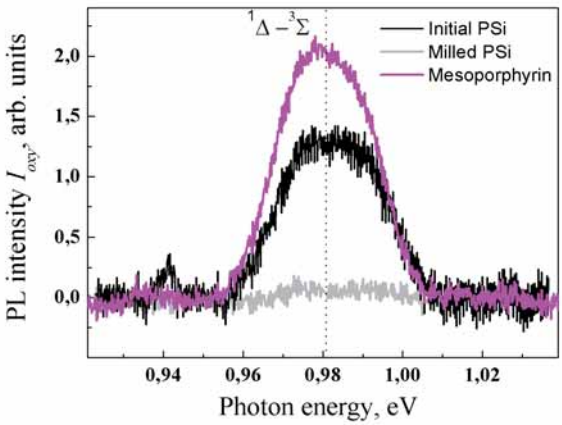
The way to prevent singlet oxygen molecules from quenching by nc-Si defects is making granulas smaller and increasing

Comparison with dye molecules (mesoporphyrin)

Visible



Infrared



Photosensitizing properties of PSi and dye molecules are comparable. Singlet oxygen lifetime can be estimated from these spectra with the help of simple calcualtions. This lifetime is around **15 ms**, it's significantly greater then singlet oxygen lifetime in biological systems (1 — 100 ns).

Conclusions

- The presence of singlet oxygen in porous silicon layers in oxygen ambient at room temperature has been detected for the first time
- Intensity of singlet oxygen luminescence decreases in time due to generation of new defects (superoxide)
- Milling of porous silicon layers leads to decrease of singlet oxygen quantity
- Without regard to these negative effects photosensitizing properties of porous silicon and dye molecules are comparable

Acknowledgements

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Thank you for attention!