Porous Silicon: A versatile material for applications from wound care to drug delivery to water purification

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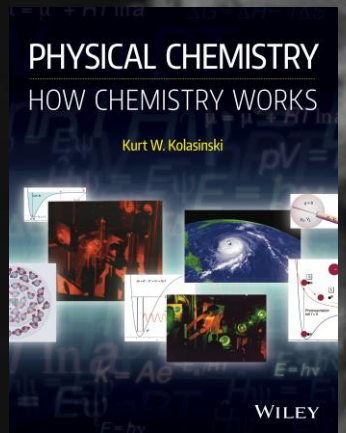
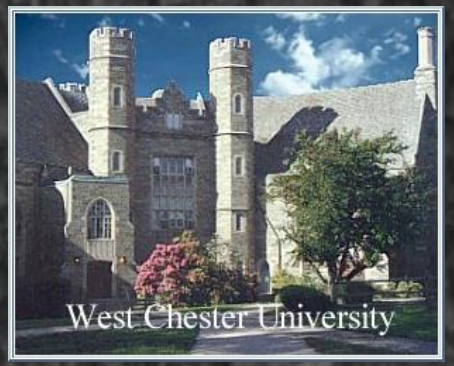
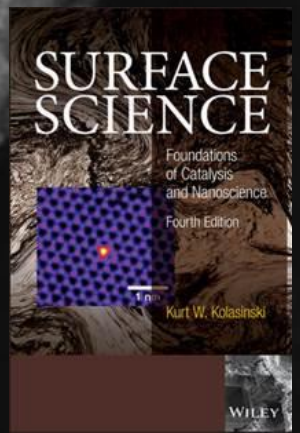


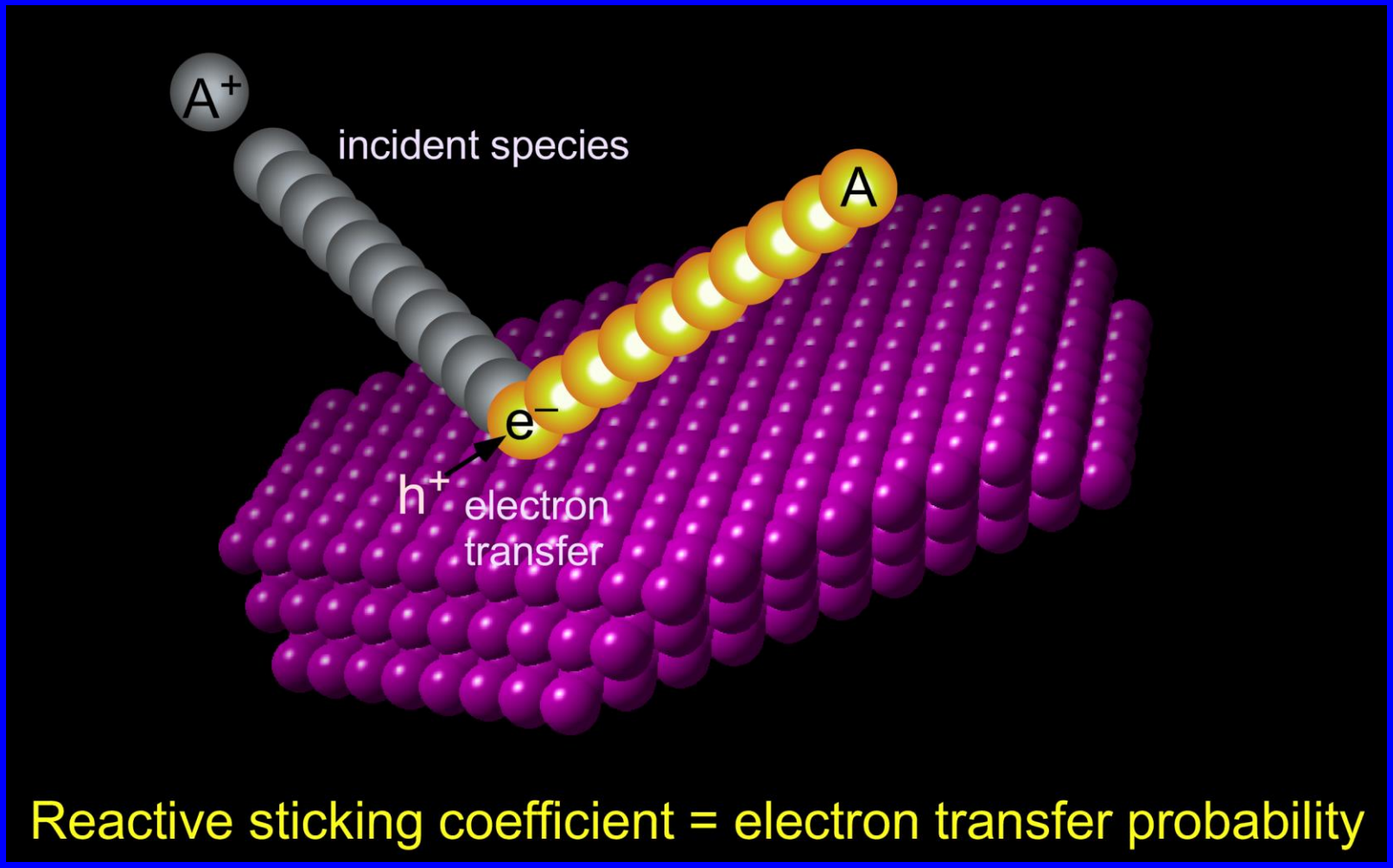




Motivation

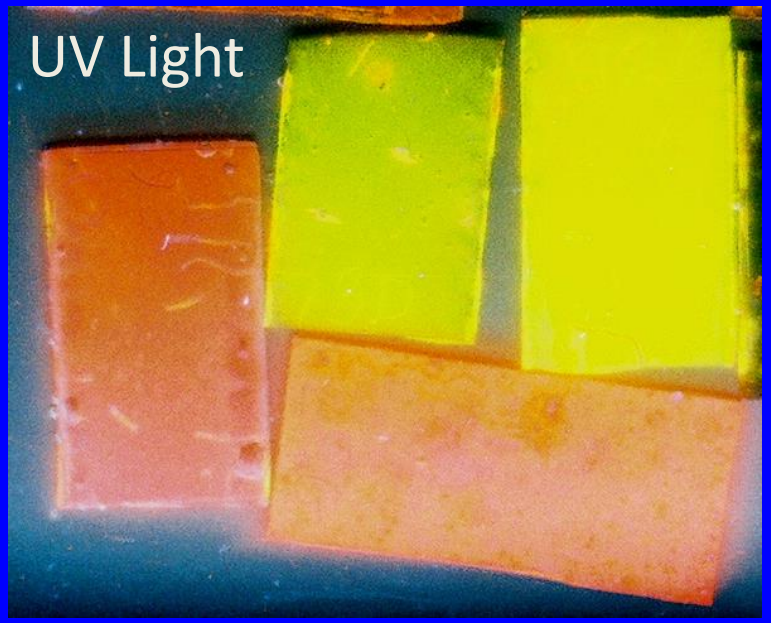
- Make better batteries
- Cure cancer
- Brew better beer
- Change the world

The surface scientist in me asks, how often does a molecule hitting the surface exchange an electron?

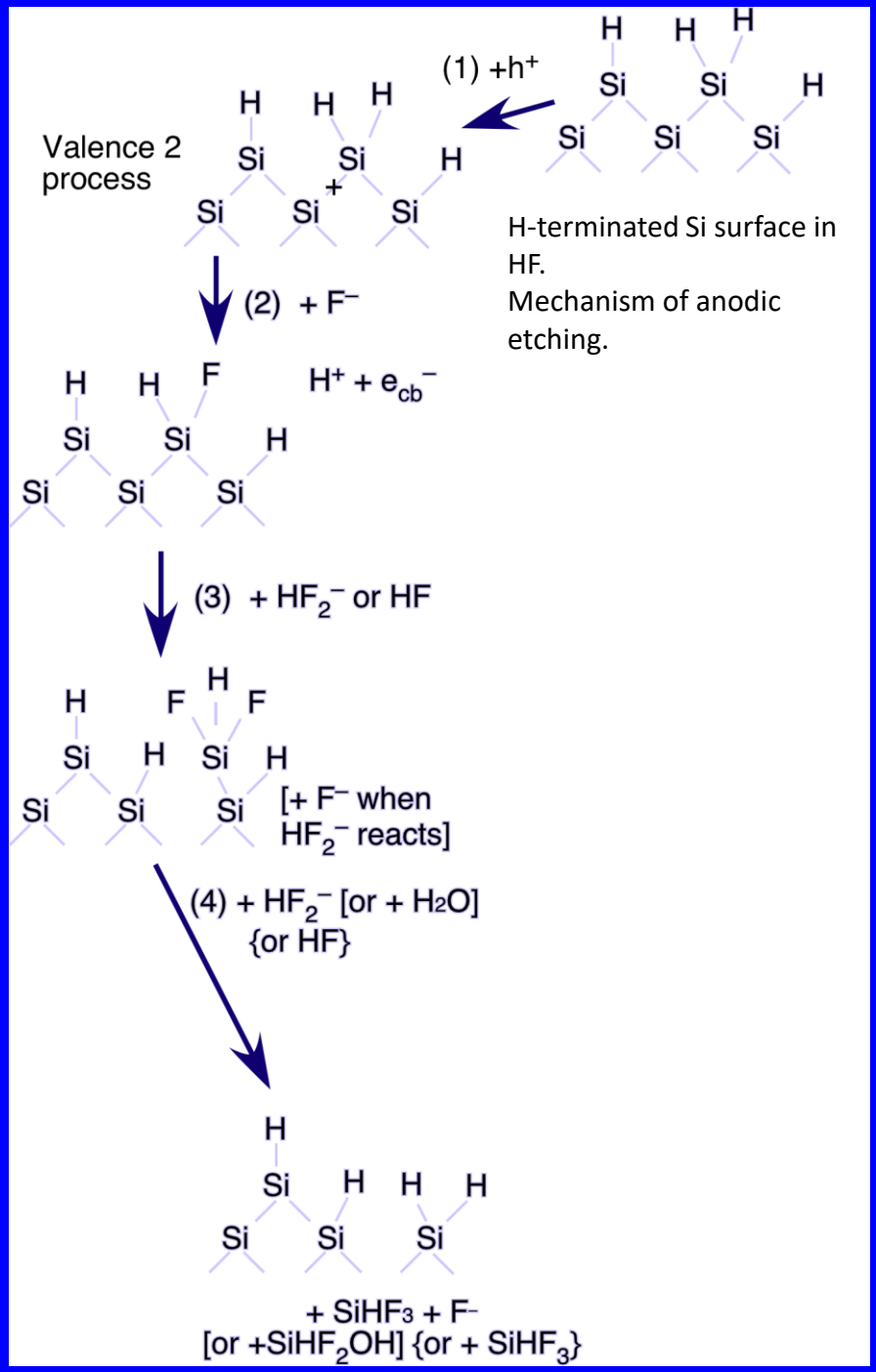


KW Kolasinski, JW Gogola, WB Barclay, *A test of Marcus theory predictions for electroless etching of silicon*, J. Phys. Chem. C 2012, 116, 21472–21481

Quantum Confinement and Photoluminescence



- Nanostructuring of silicon turns it into a material that emits visible light when illuminated
- Why do small (<5 nm) Si particles emit light and can we can control it?



H-terminated Si surface in HF.
Mechanism of anodic etching.

What is the sequence of chemical reactions that leads to the etching of Si and why are these reactions self-limiting?

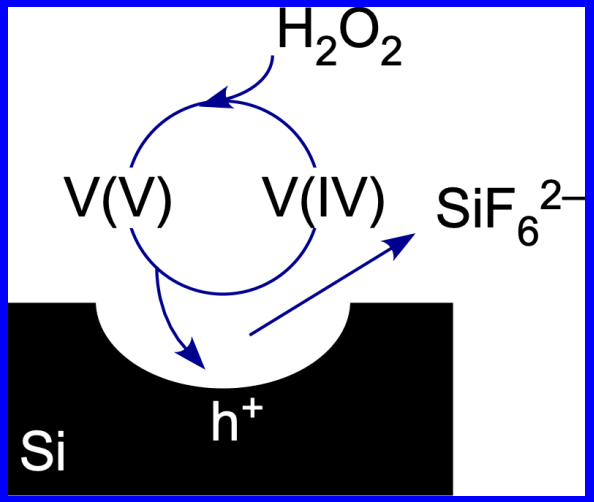
Gerischer, Allongue, & Costa Kieling, Ber. Bunsen-Ges. Phys. Chem. 97 (1993) 753

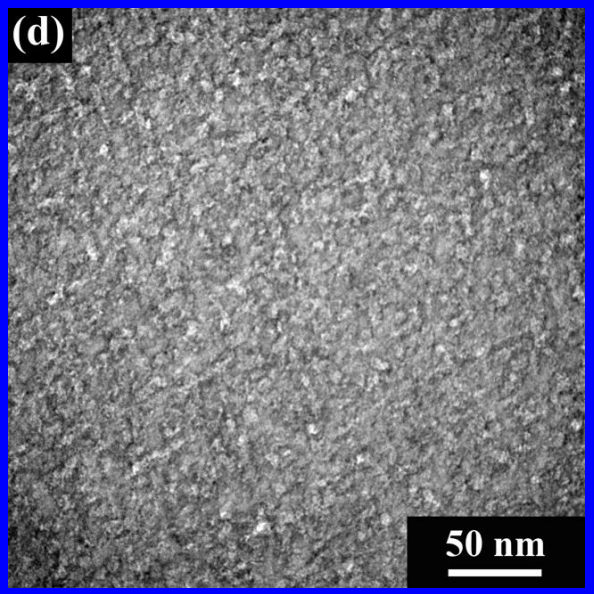
Kooij & Vanmaekelbergh, J. Electrochem. Soc. 144, 1296 (1997).

Kolasinski, Phys. Chem. Chem. Phys. 5 (2003) 1270

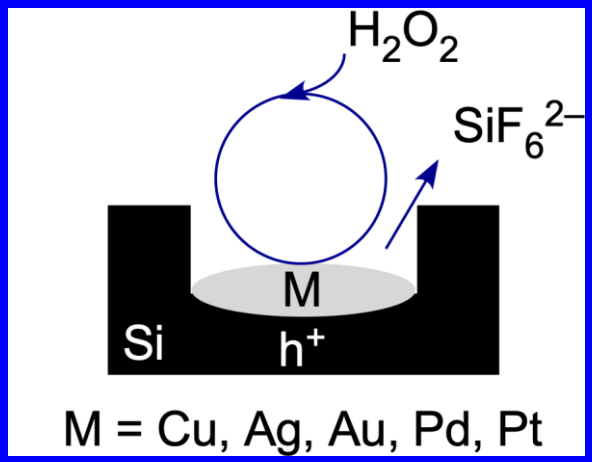
Kolasinski, Surf. Sci 603 (2009) 1904

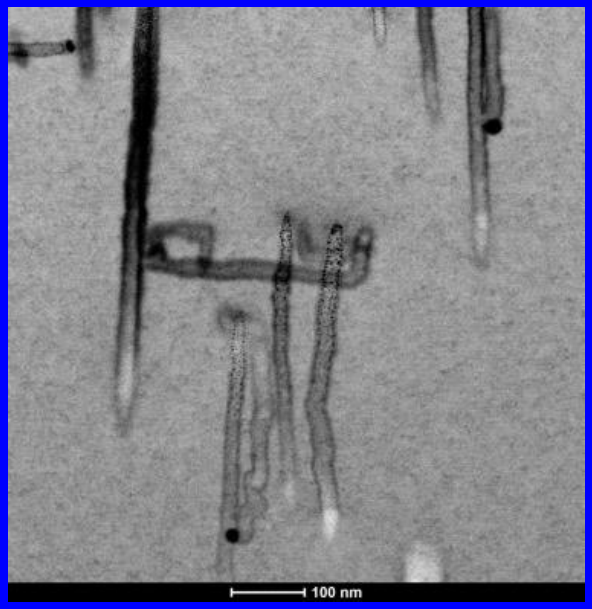
Regenerative Electroless Etching (ReEtching)





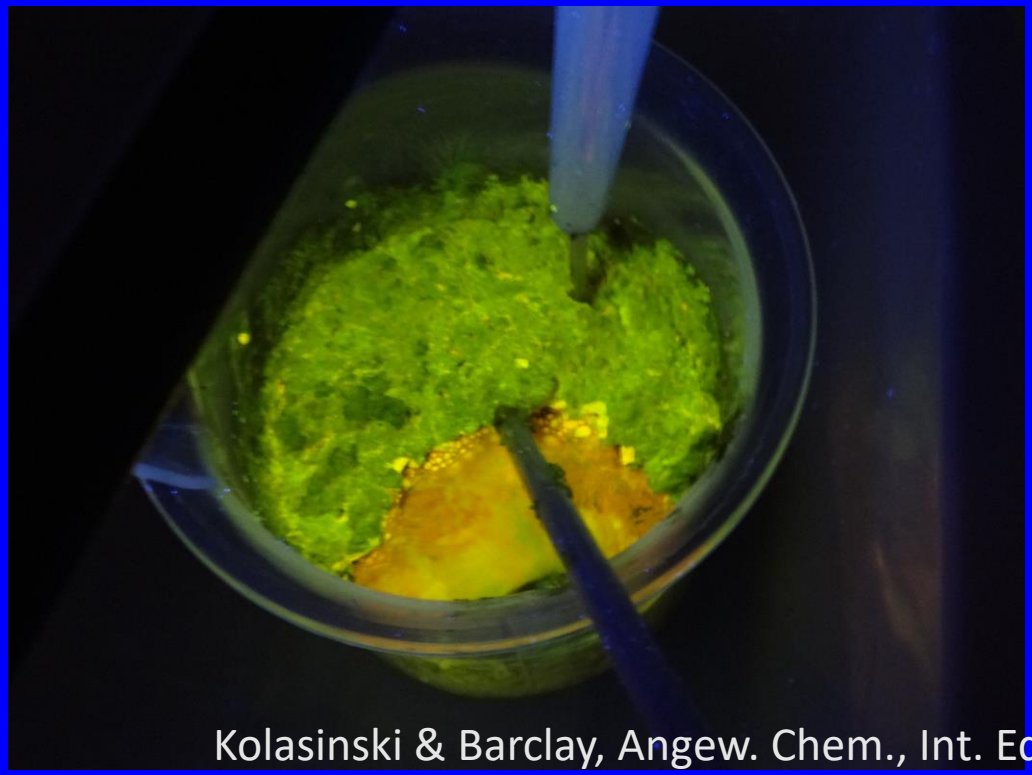
Metal Assisted Catalytic Etching (MACE)





Kolasinski, Unger, Ernst, Aindow, Frontiers in Chemistry 2019, 6, 651

Using electroless etching in the ReEtch process it is now feasible to generate porous silicon powders in quantities limited only by the size of your beakers from metallurgical grade Si. Furthermore problems with thermal budget and foaming can be alleviated by this new $V_2O_5 + H_2O_2 + HF$ method. Foaming is reduced and homogeneity is enhanced by addition of acetic acid.

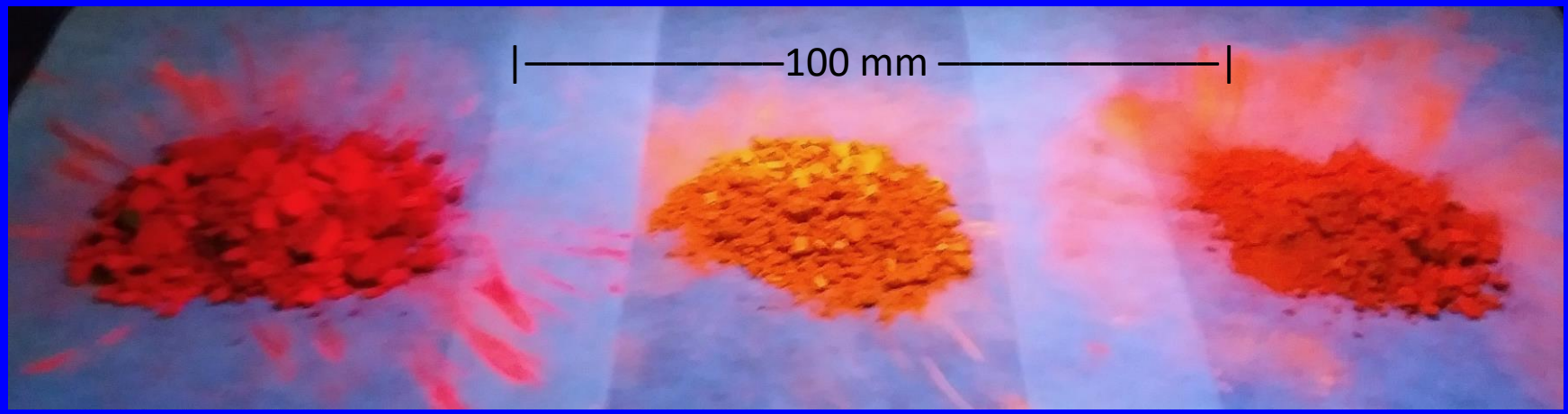


Kolasinski & Barclay, Angew. Chem., Int. Ed. Engl. 52 (2013) 6731

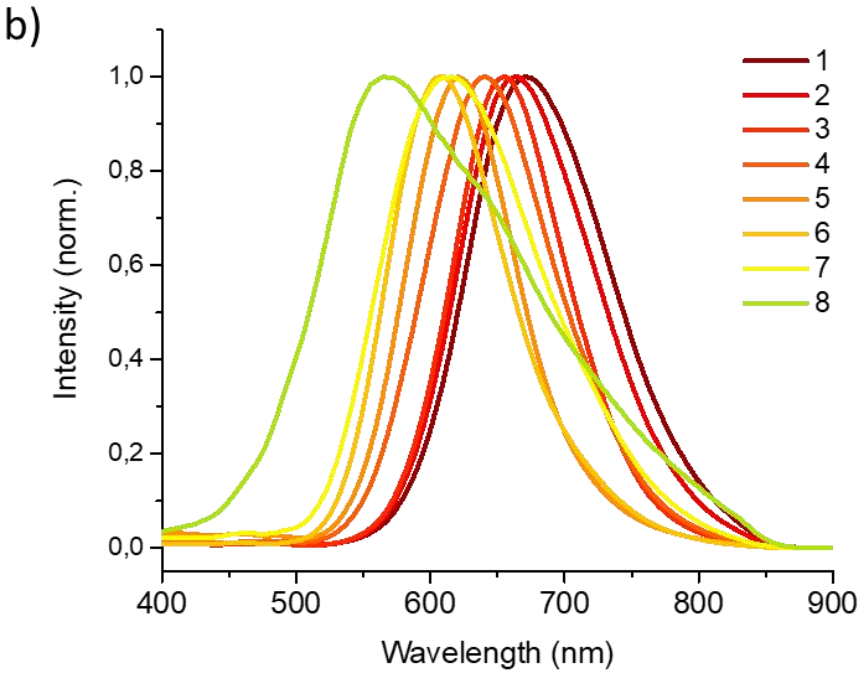
Green to red photoluminescence under UV illumination during etching of metallurgical grade Si in $V_2O_5 + HF(aq)$

KW Kolasinski, NJ Gimbar, H Yu, M Aindow, E Mäkilä, J Salonen, Angew. Chem., Int. Ed. Engl. 2017, 55, 624-627

ReEtching leads to brilliant photoluminescence



Photoluminescence from RaPSi can be tuned across the whole of the visible spectrum by control of the etching parameters



Mäkilä, Anton Willmore, Yu, Irri, Aindow, Teesalu, Canham, Kolasinski, Salonen, ACS Nano 2019, 13, 13056-13064.

Stability of the photoluminescence intensity of COOH-RaPSi nanoparticles immersed into PBS buffers with pH 7.4 and 5.5 at 37 °C for three weeks. The hydrosilylation stabilizes the visible photoluminescence such that the strong red PL at 650 nm can be observed over the course of days or weeks depending on the pH

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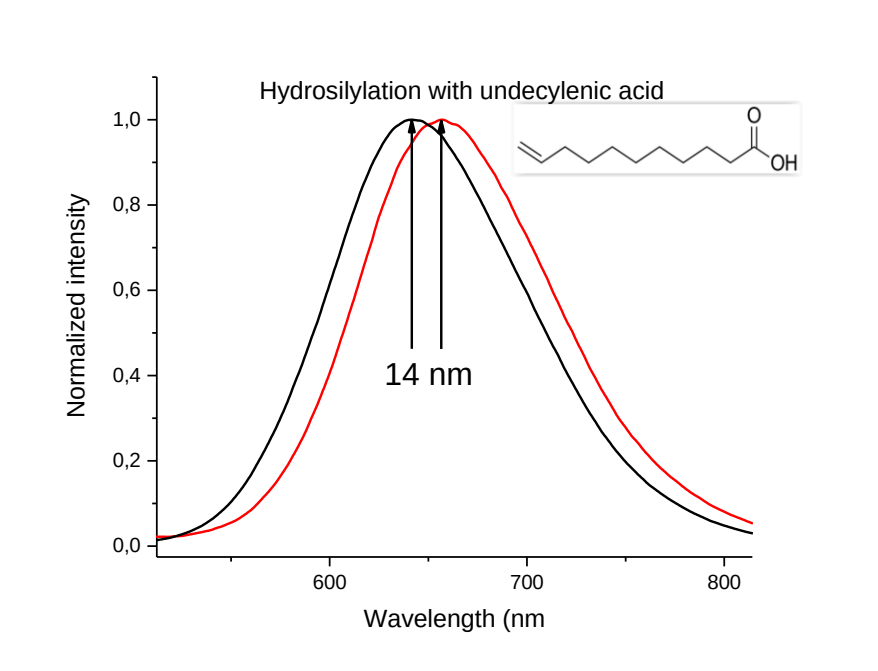
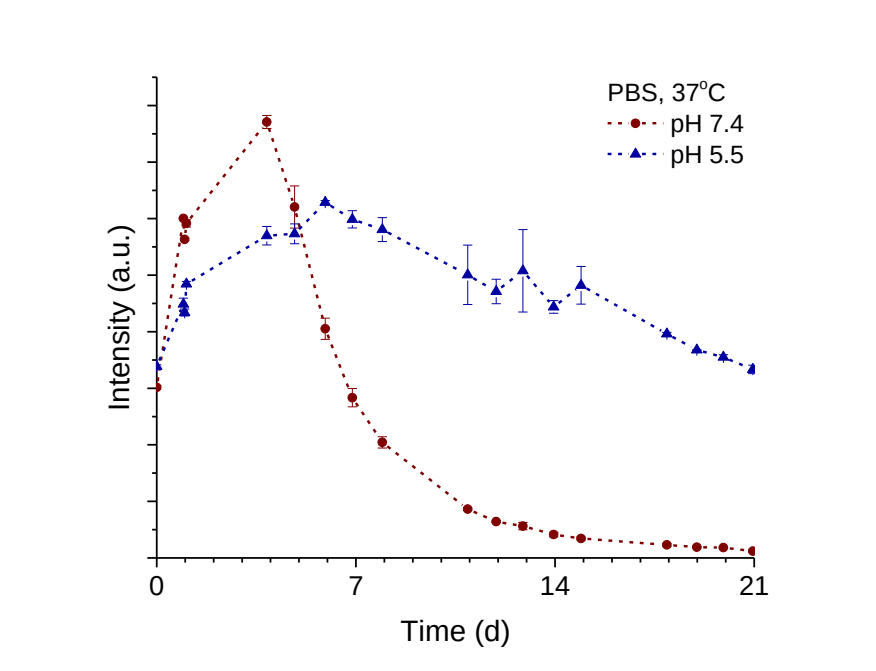
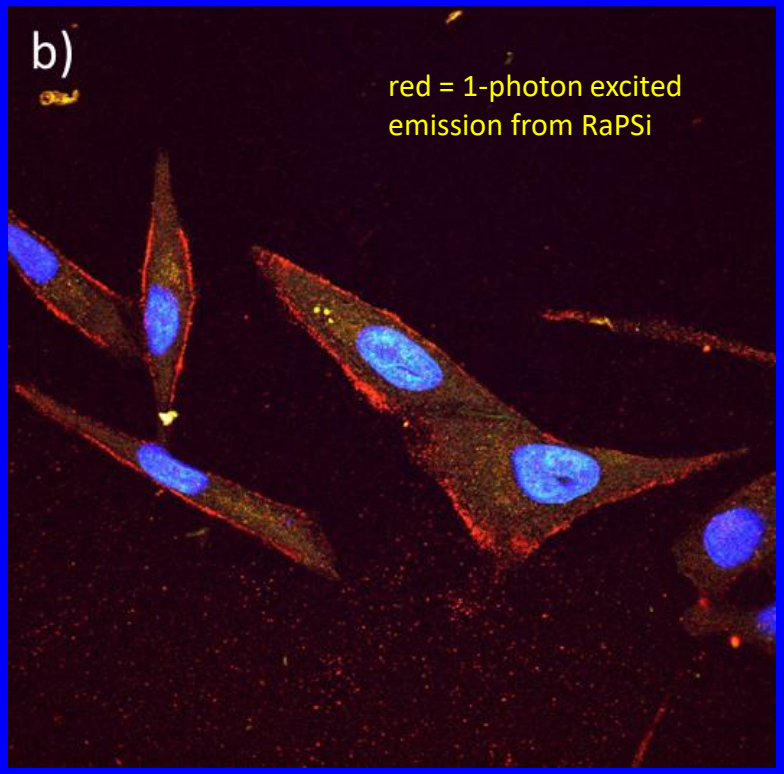


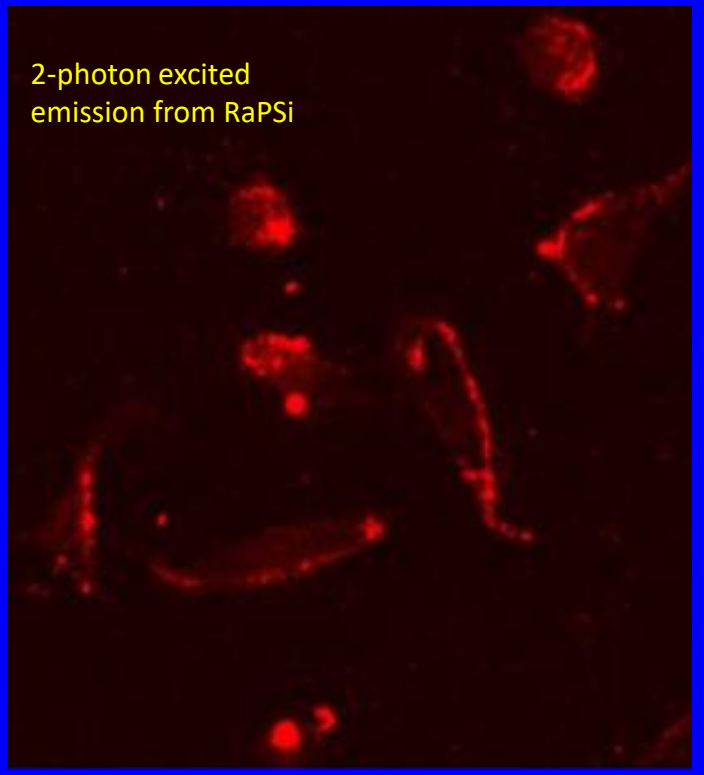


phosphate buffered saline solution = PBS

COOH-RaPSi = undecylenic acid terminated RaPSi

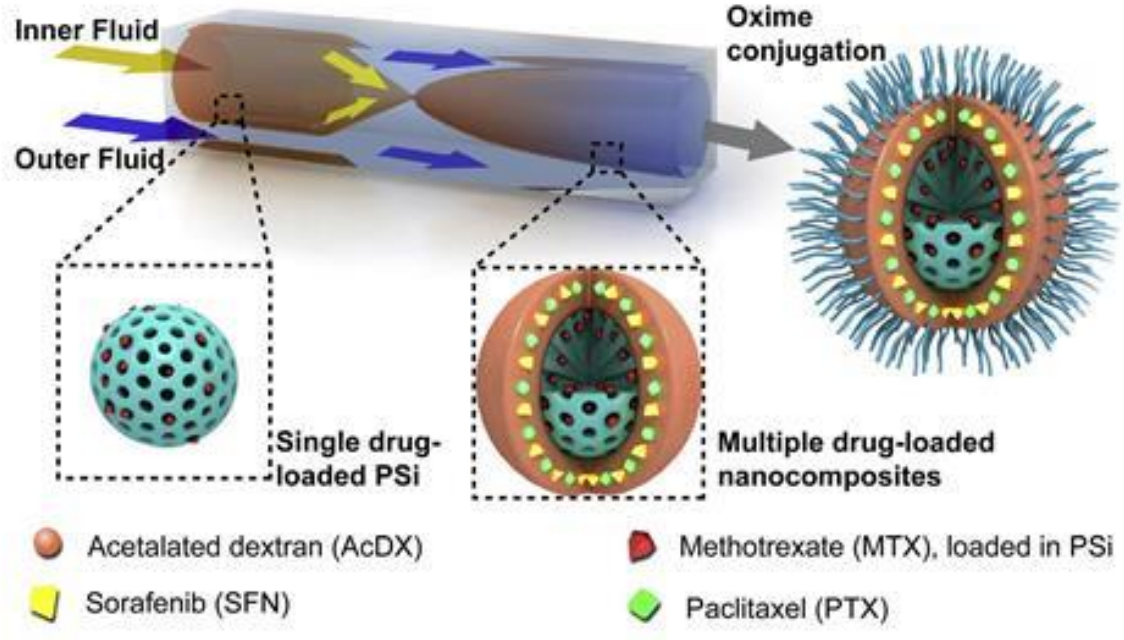
Photoluminescence can either be excited with 1 or 2 photons

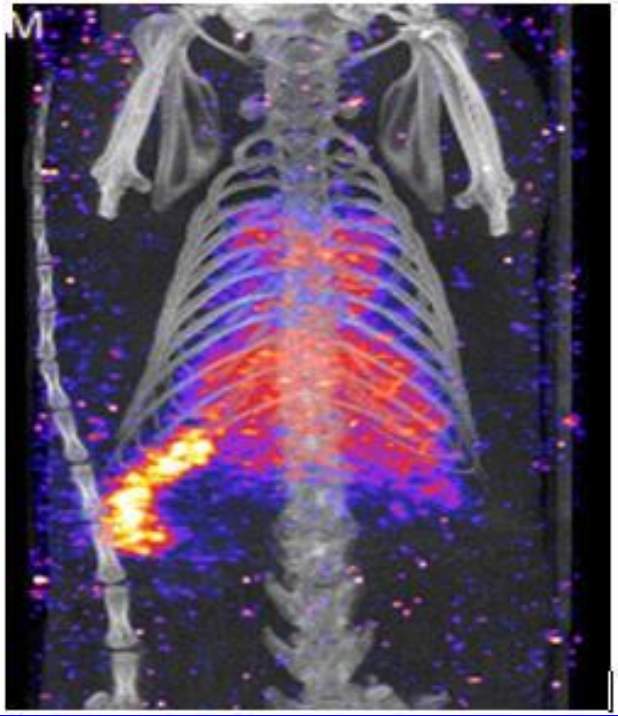




Confocal microscopy images of PPC-1 cells (human prostate carcinoma tumor cells) incubated with FAM-RPARPAR modified COOH-RaPSi nanoparticles.

Theranostics



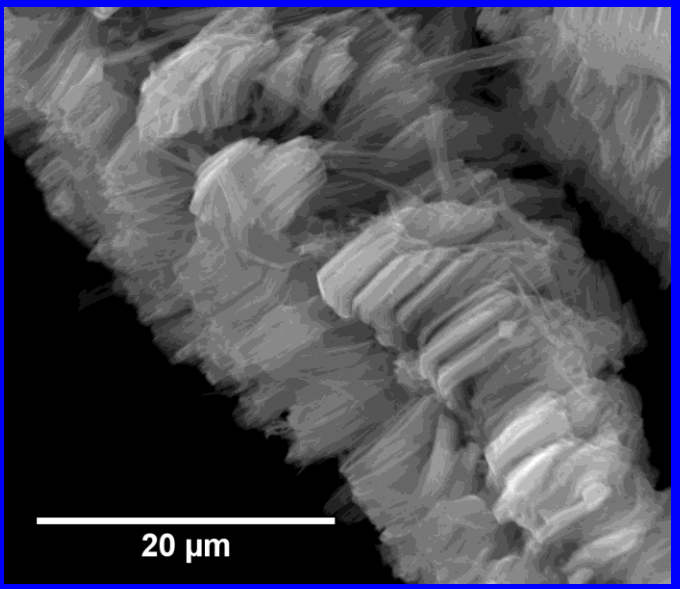


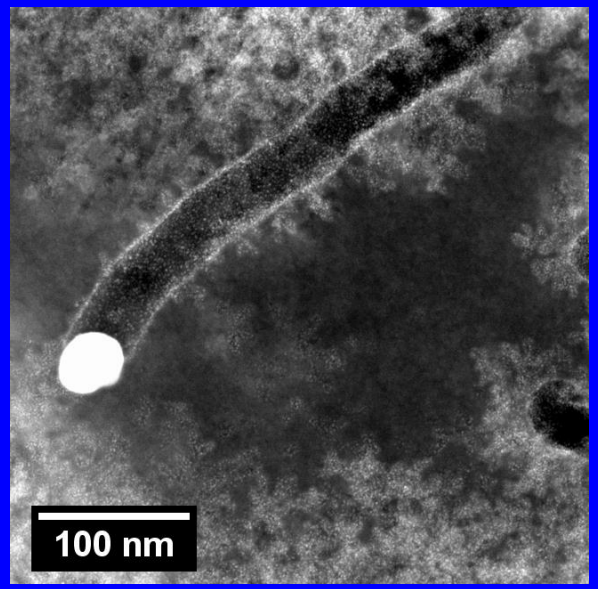
Hélder Santos (Helsinki), Jarno Salonen (Turku)

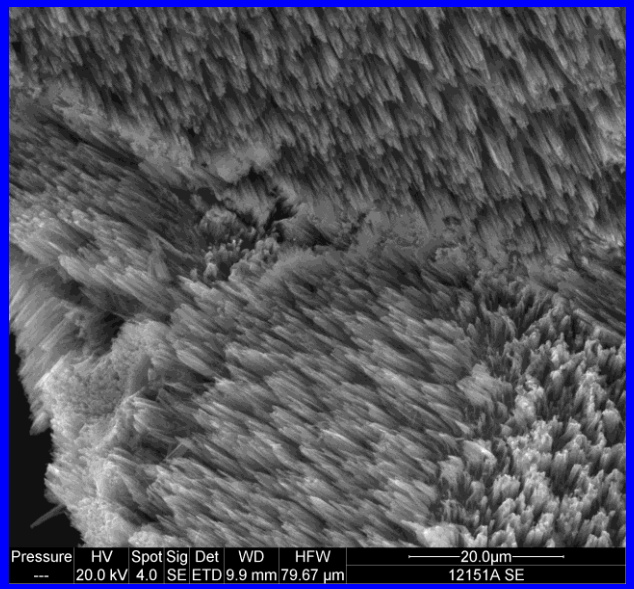
Vesa-Pekka Lehto (Kuopio) MRI contrast agent

Porous Si (Psi) is resorbable, that is, it is degraded into $Si(OH)_4$, some of which is taken up in, e.g. bones, some of which is excreted. 3–15 nm pores can be loaded with a drug or radionuclide. The Si surface is readily functionalized with selective targeting moieties, which means that after injection the nanoparticles preferentially concentrate at tumors as demonstrated by the fluorescence image. The therapeutic payload is then selectively delivered.

- Pore size is tunable and metal nanoparticles can either be left in or dissolved
- Cu, Ag, Pt, Pd, Au
- Cu and Ag exhibit antimicrobial action
- Rough surface enhance cell attachment

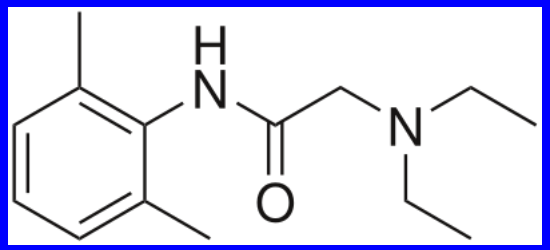




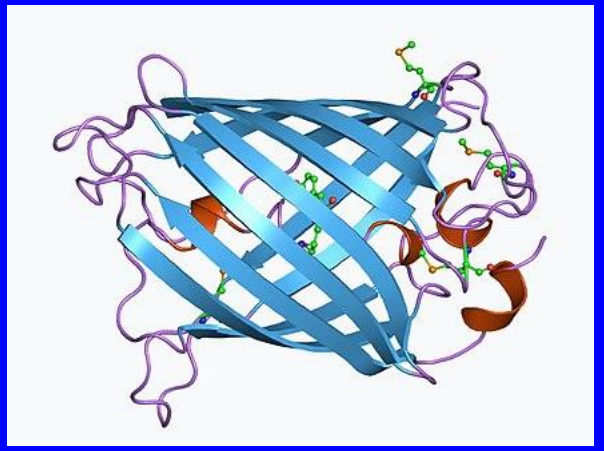


Tamarov, Swanson, Unger, Kolasinski, Ernst, Aindow, Lehto, Riikonen, ACS Appl. Mater. Interfaces 2020, 12, 4787-4796.

Small molecule drug
roughly 1 x 0.3 nm



Large molecule drug
(protein)
> 4 x 3 nm



While 3-4 nm pores are acceptable for accepting small molecules, larger 10–15 nm pores are required for larg molecule drugs. It may also be important to change pores walls from hydrophobic to hydrophilic or to terminate them with specific functional groups such as –COOH.