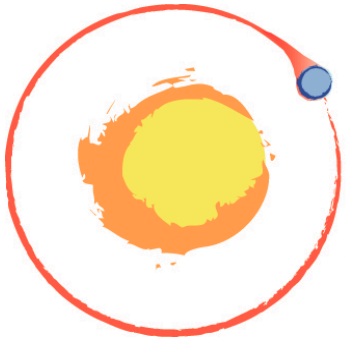
UNIVERSITY OF ICELAND

Summer School on
'Materials for the hydrogen economy'
Reykjavik, 17-21 August 2010



SOLAR HYDROGEN

2010-08-17

PHOTOINDUCED PROCESSES AT SURFACES AND NANOSTRUCTURES

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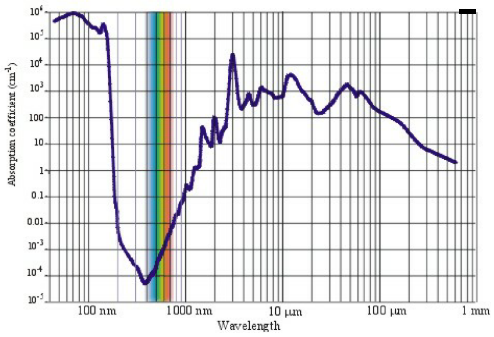
How to split water with low energy photons?

MODIFY!

- WATER,
- SURFACE,
- PRODUCTS



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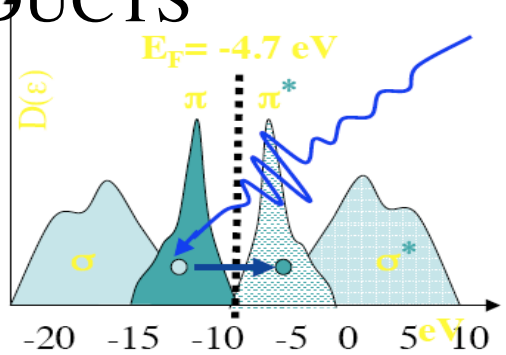

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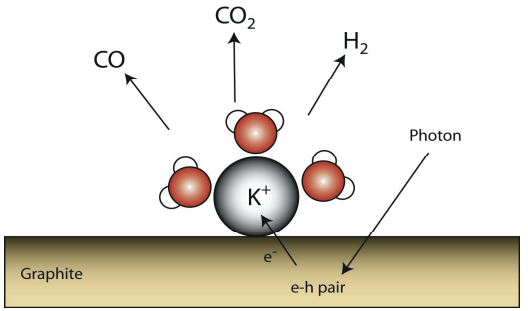
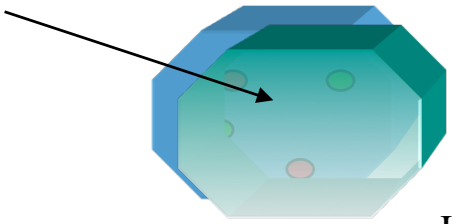
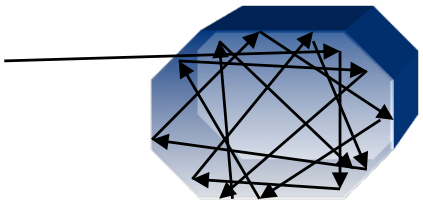
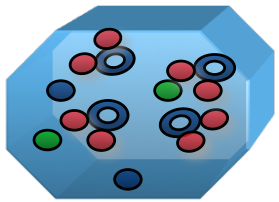






Light capture



Products capture

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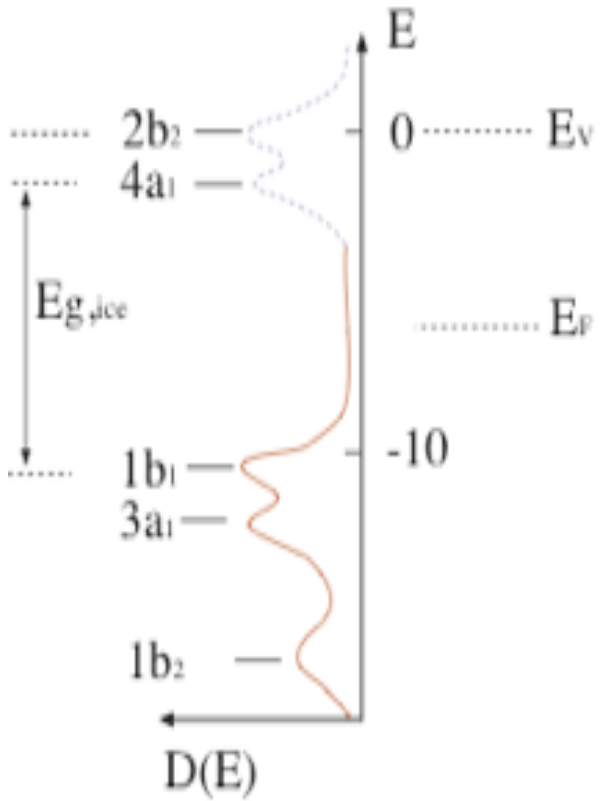
Outline

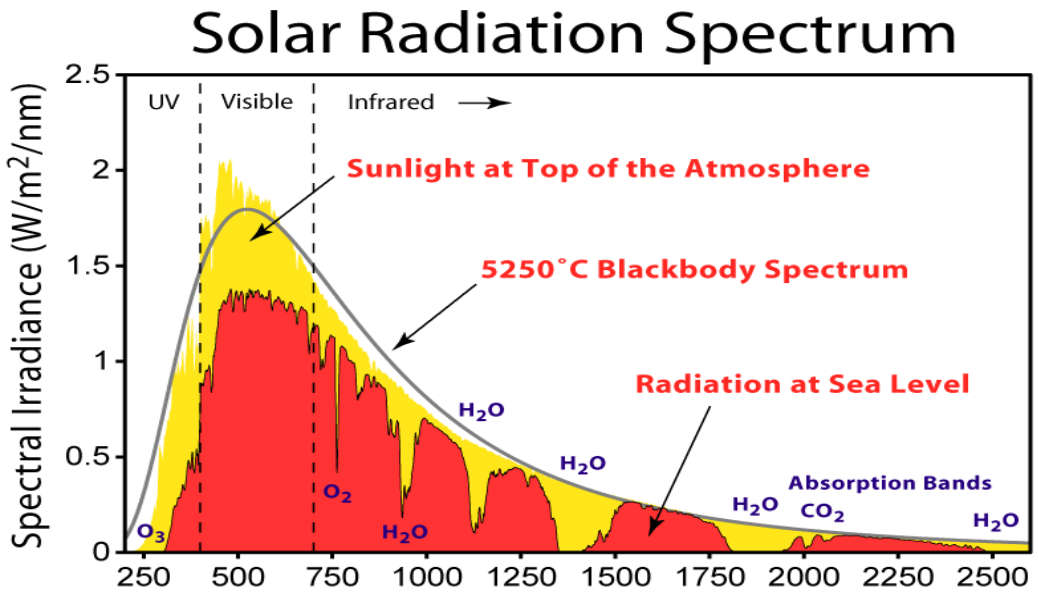
PART II - Nanotech approaches:

- **Tuning of optical and electronic properties**
- **Micro - and nanostructures for light management**
- **Control of structure and morphology**
- **Control of the reaction environment and volume**
- **Fabrication of model systems & theoretical modeling**
- **Progress in R&D;**
- **Summary**

Tuning of optical and electronic properties

"The absorption spectrum of the system must overlap the emission spectrum of the sun".





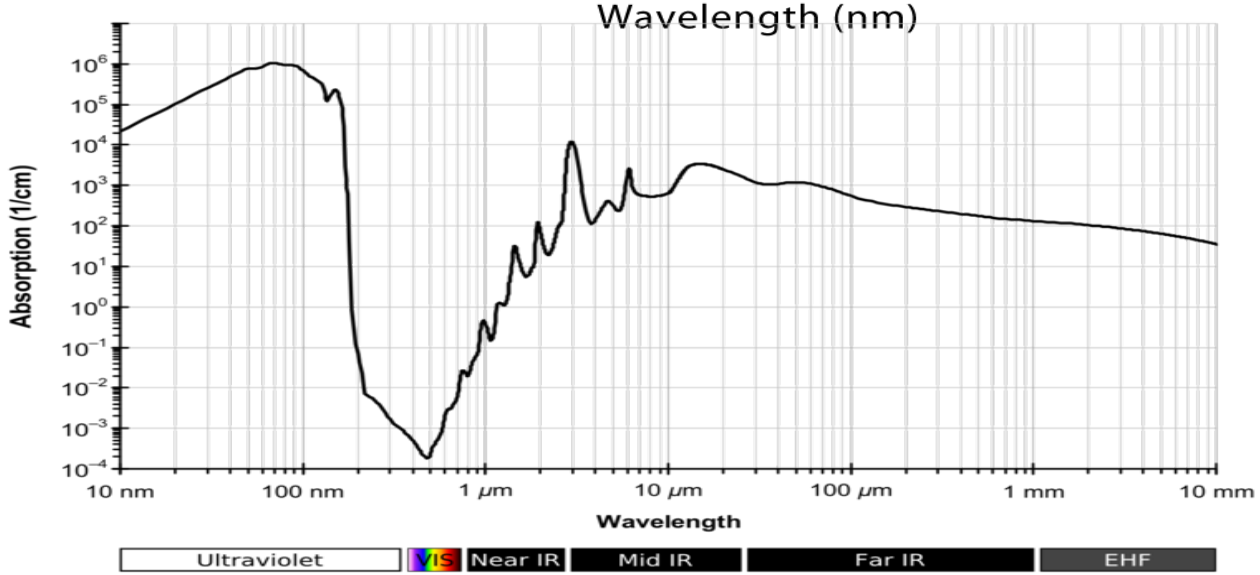


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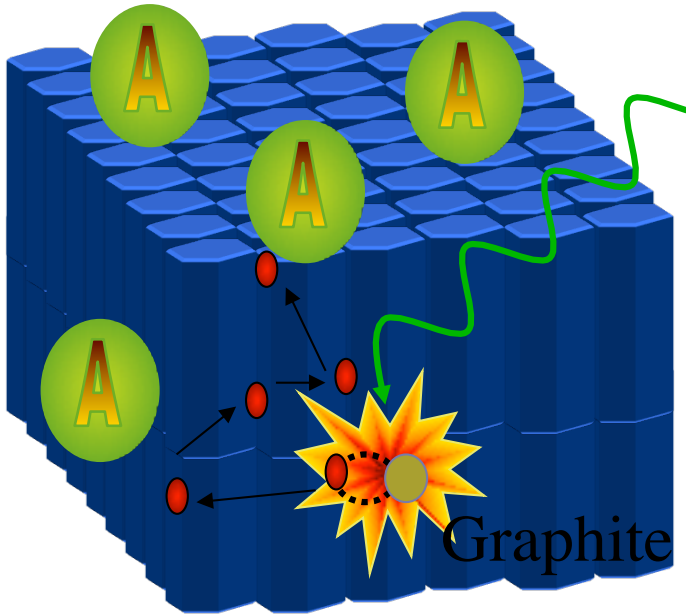
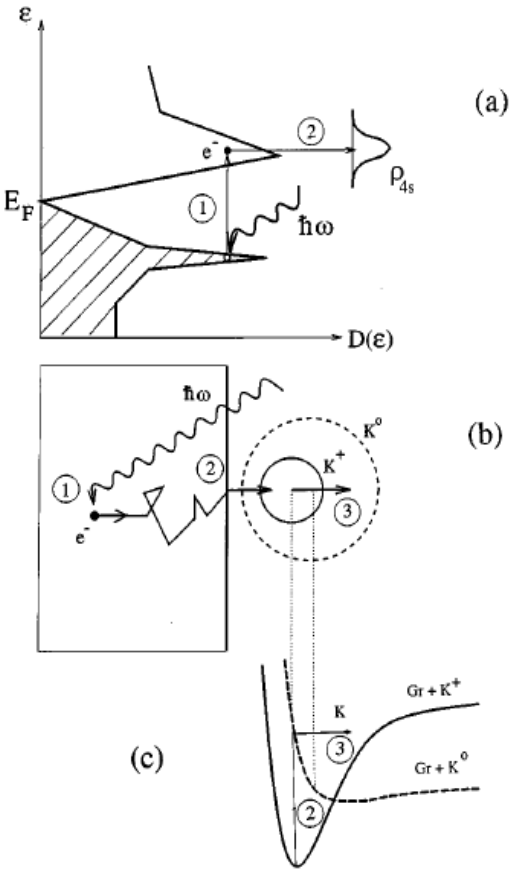
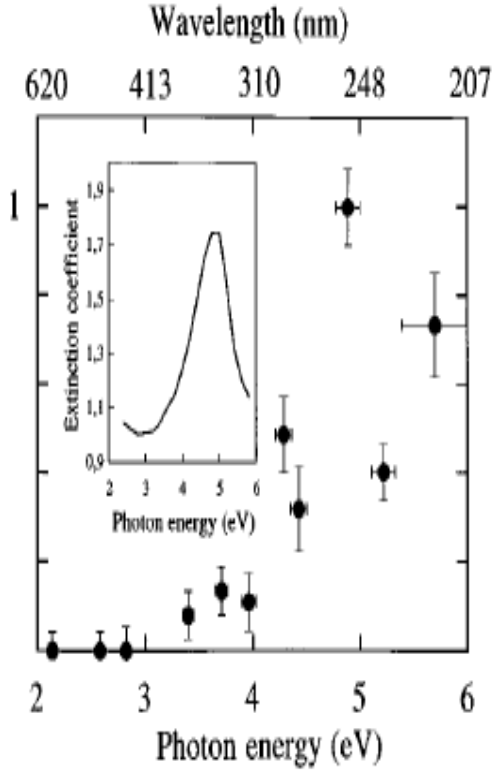
PHOTO DESORPTION/ PHOTO MANIPULATION OF ALKALI ATOMS







Bo Hellsing et al., *J. Chem. Phys.* **106** (3), 982, 1997

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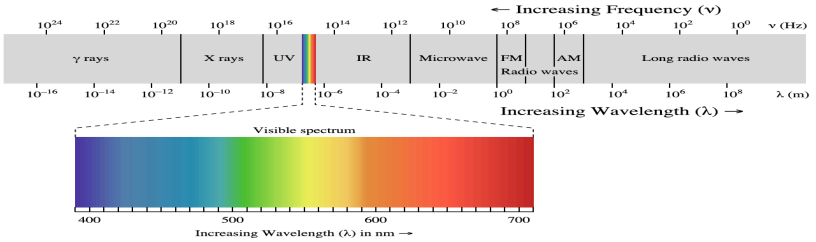
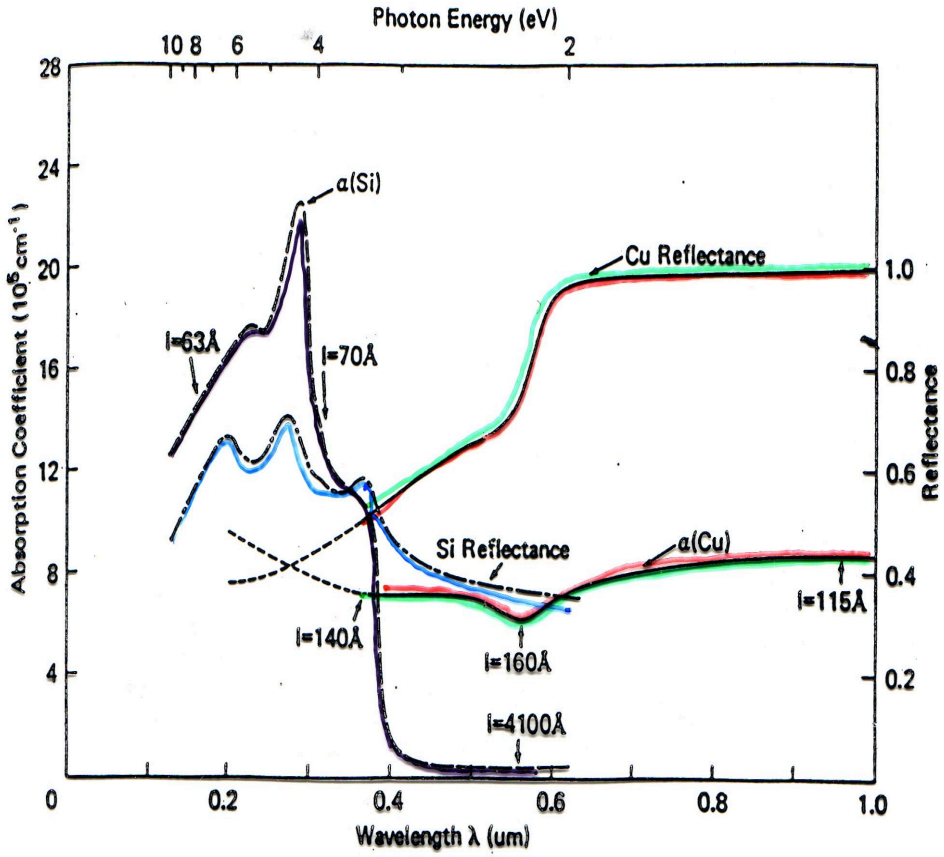
Light on Surfaces ("nano")

(i) the wealth of new, often of resonance character phenomena, observed when the object size and the electromagnetic field periodicity (wavelength) match.

(ii) the energetic of important chemical transformations, e.g. bond breaking and bond formation, are in this range (0.5 – 6.5 eV).

(iii) ability to manipulate materials on nanoscale.





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Tuning of optical and electronic properties

- Bandgap engineering,
- Doping,
- Multiple excition generation,
- Charge carrier separation and transport,
- Nanocomposites (e.g. semiconductor-semiconductor, semiconductor-metal, …),
- Co-catalysts…

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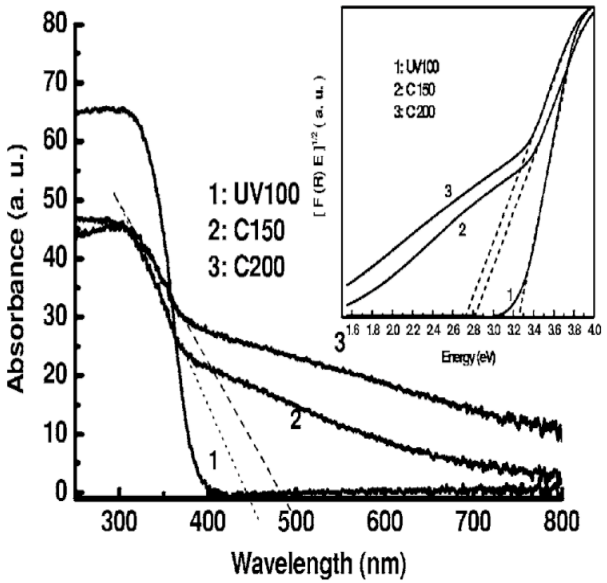
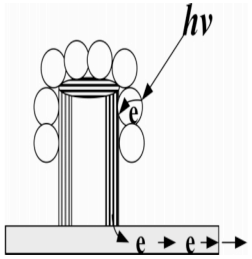
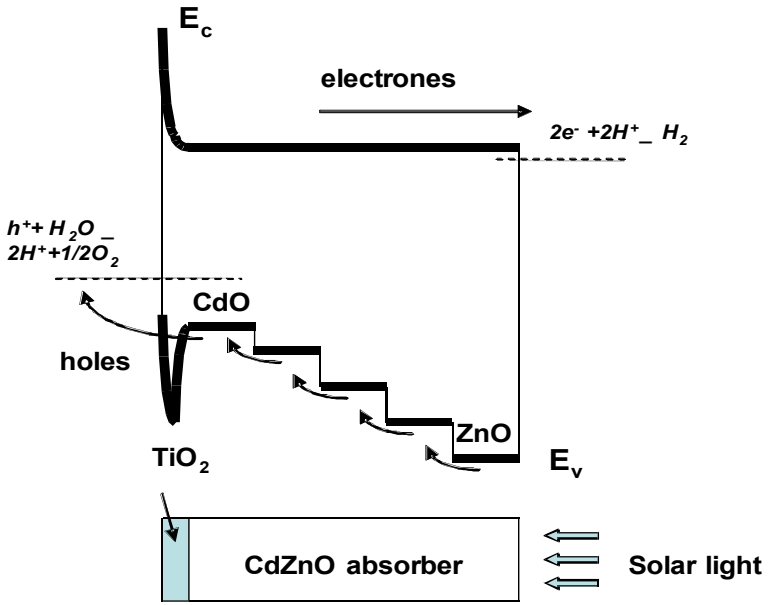
Tuning …



Appl. Phys. Lett. 89, 131919 (2006)



J. Phys. Chem. C, Vol. 111, No. 35, 2007



© A. Kuznetzov et all.

at UiO: - Developing a synthesis technology for growth of ZnO nanorods arrays with engineered band gaps.

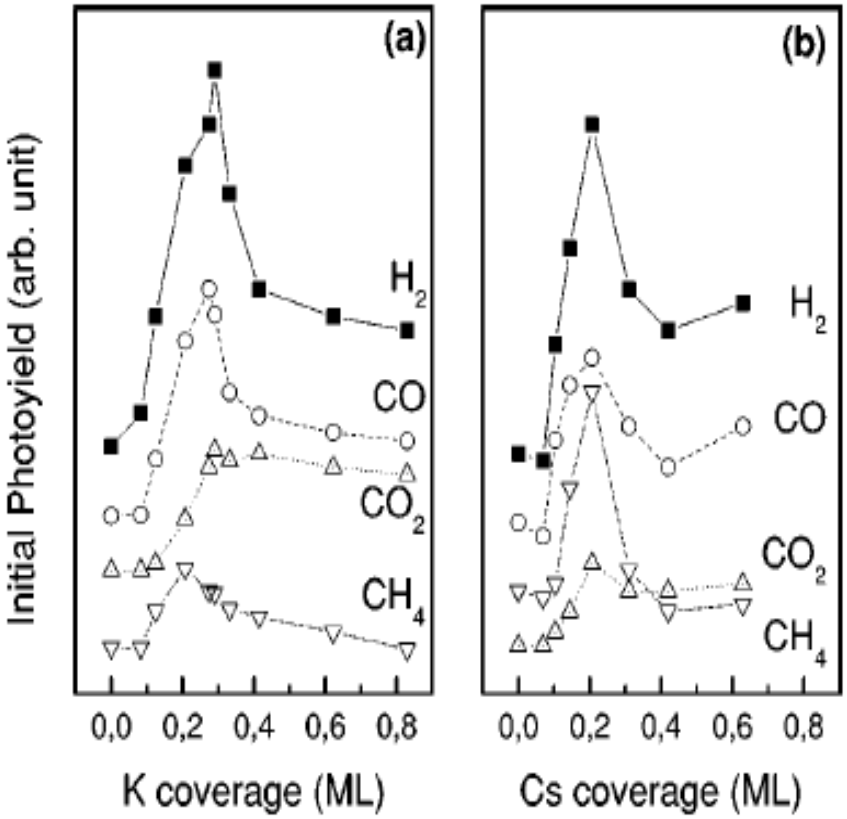
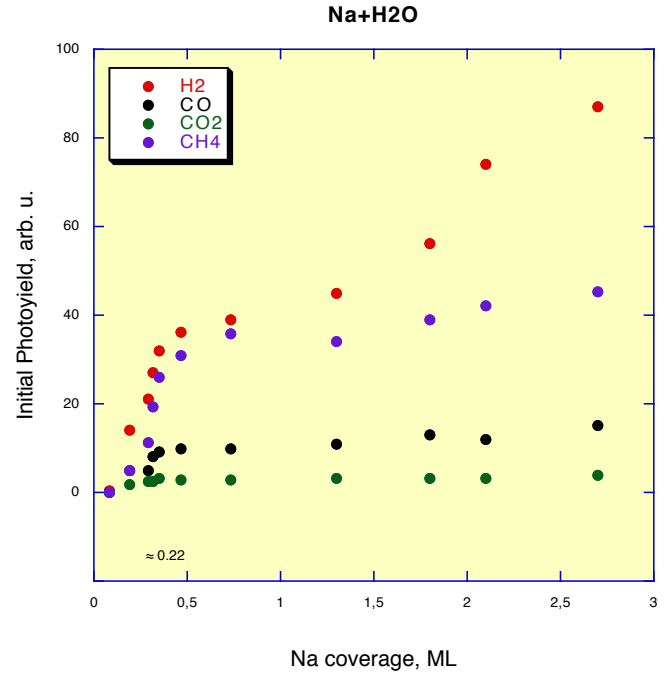
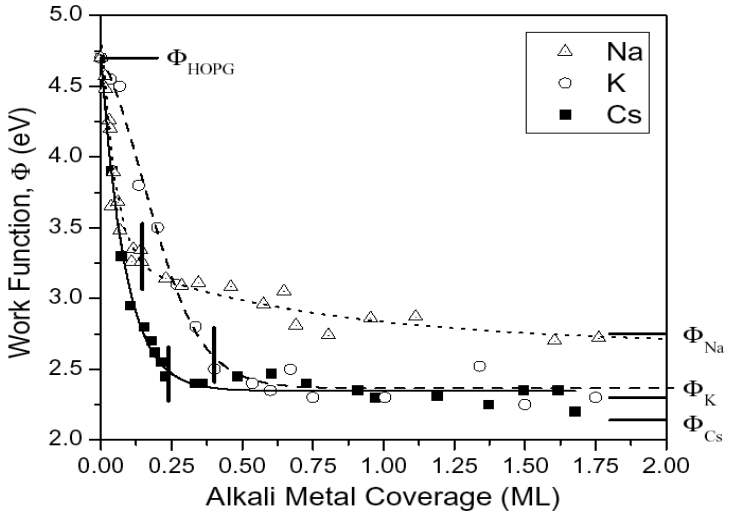


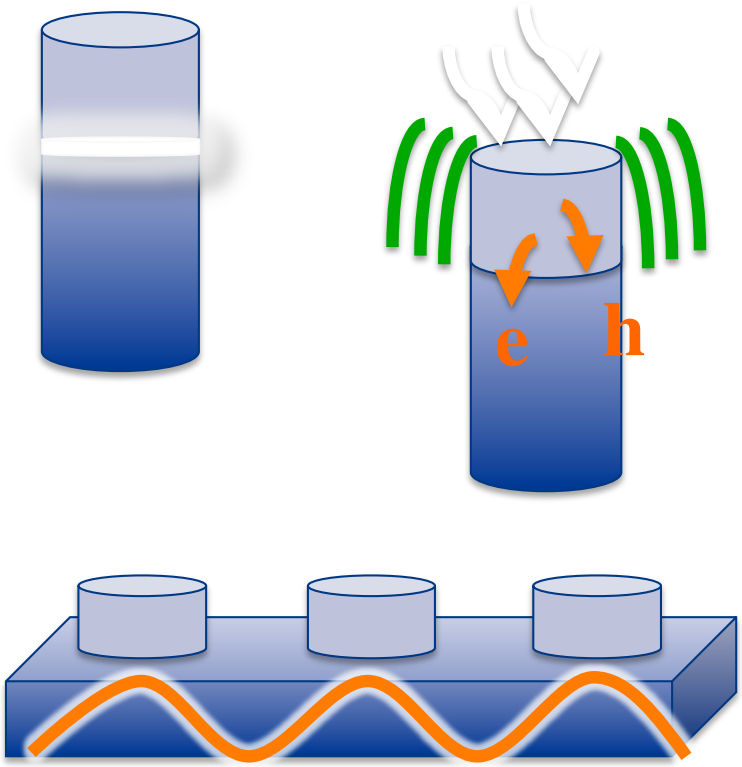
FIG. 4. Variation of the initial photo-yield of H_2, CH_4, CO, and CO_2 as a function of the AM pre-coverage for K (a), and Cs (b) co-adsorbed with H_2O on graphite (0001).





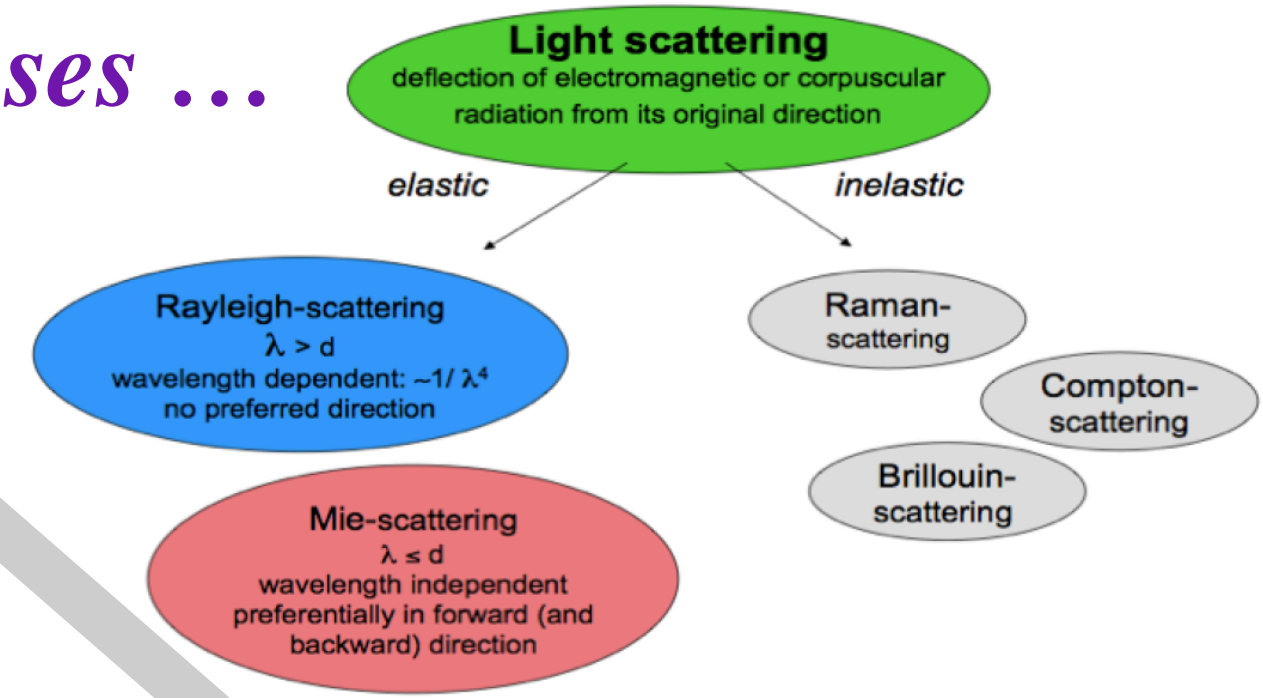
•Micro- and nanostructures for light management

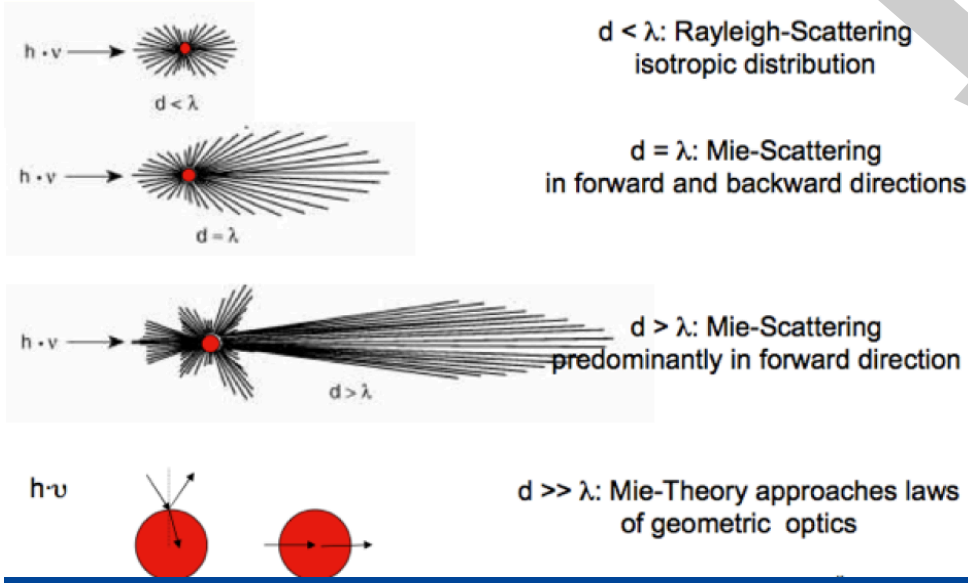
- Optically active metal nanoparticles (plasmonics),
- Waveguiding,
- Whispering gallery modes,
- Scattering structures / centers
- …



Optical processes …

- **Absorption**
- **Reflection**
- **Refraction**
- **Diffraction**





d < λ: Rayleigh-Scattering
isotropic distribution

d = λ: Mie-Scattering
in forward and backward directions

d > λ: Mie-Scattering
predominantly in forward direction

d >> λ: Mie-Theory approaches laws of geometric optics

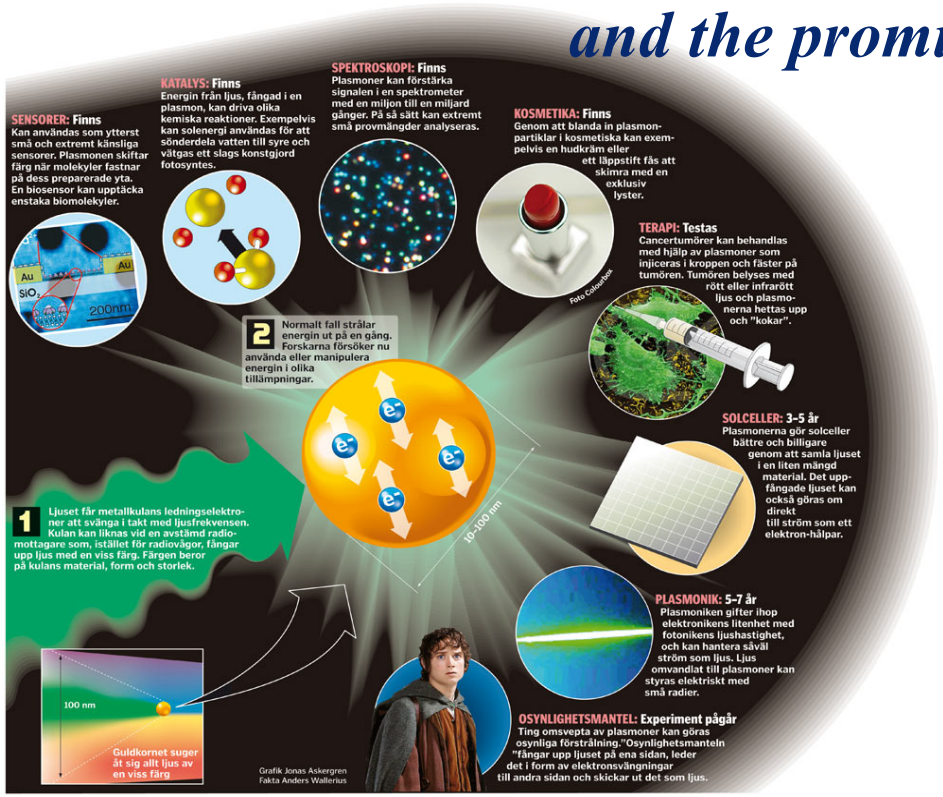
- **For large objects each effect is distinct;**
- **For small lengths (objects) the difference between these effects is blurred!!!**

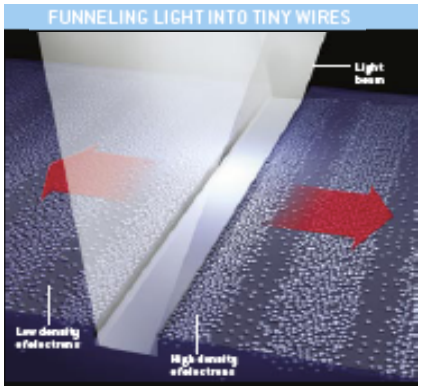
Beginnings of nanoscience and technology…

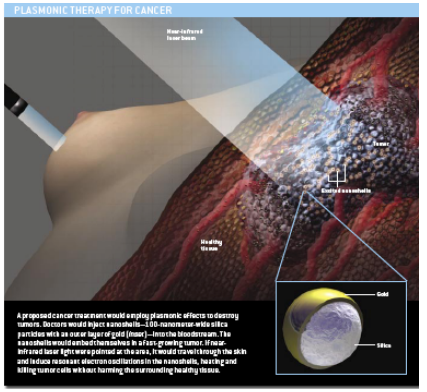
The birth of Sant Eligio – patron saint of the goldsmiths.Niccolo da Varallo, 1480-1486 *(Fabbrica del Duomo di Milano)*

The Lycurgus Cup ***(British Museum; 4th century A. D.)***

and the promises…







Harry Atwater, *Sci American* **56**

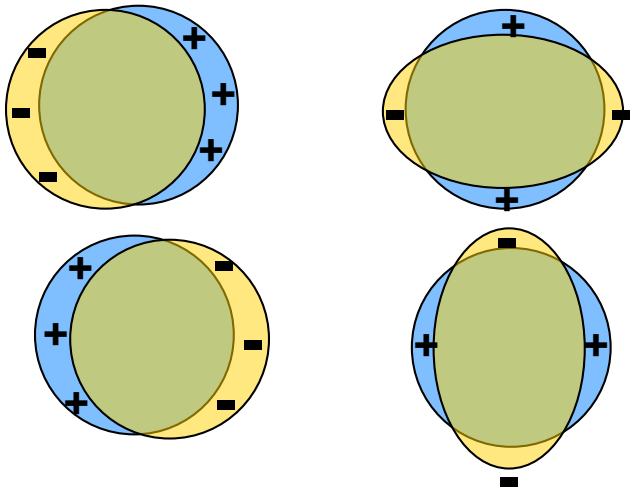
What is the origin of the color?

Answer: "surface plasmons"

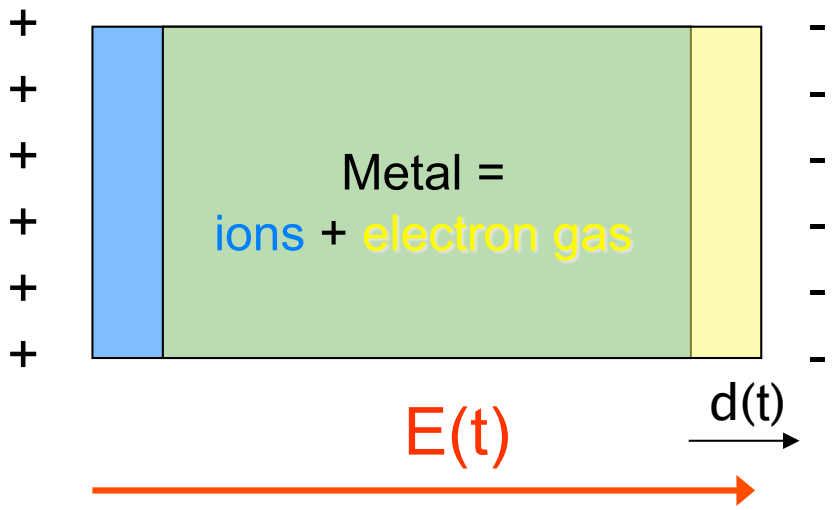
A plasmon is an incompressible self-oscillation of the conduction electrons in a nanoparticle

Sphere plasmons

Dipolar (l=1) Quadrupolar (l=2)



Bulk plasmon



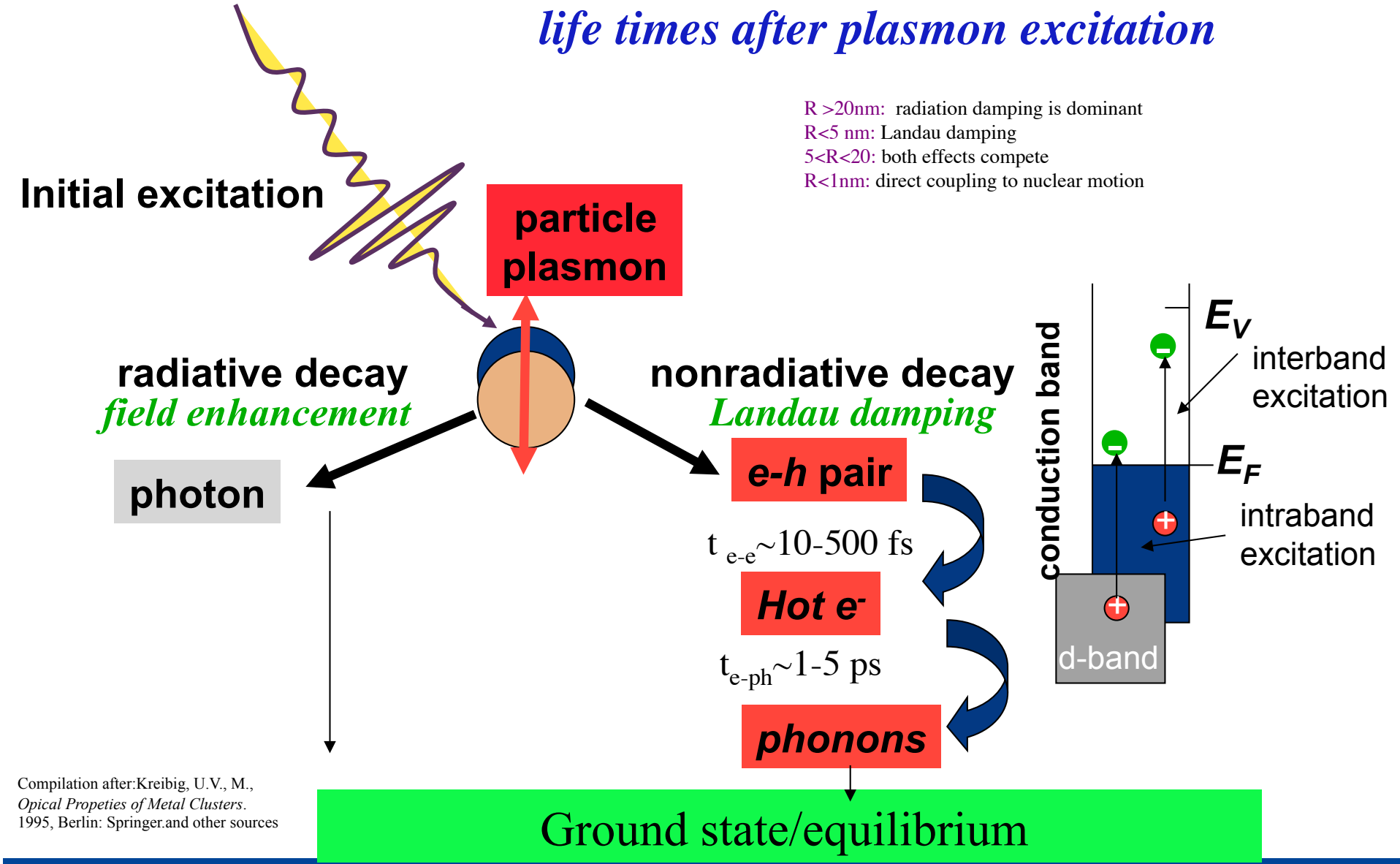
For small nanoparticle, incident E&M wave looks like dipolar field and only couples to plasmons with a dipole moment (l=1).

Since ***all*** conduction electrons are involved in the oscillation, plasmons interact ***strongly*** with resonant light.

The surface charges can induce **large** local electric fields at ω_{PL}

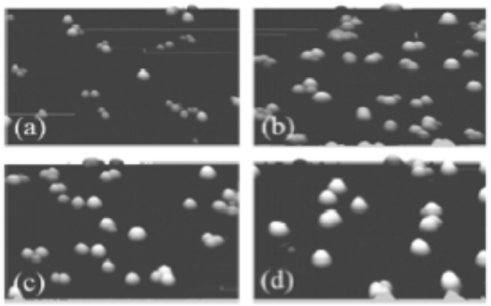
Decay channels and typical life times after plasmon excitation

R >20nm: radiation damping is dominant
R<5 nm: Landau damping
5<R<20: both effects compete
R<1nm: direct coupling to nuclear motion

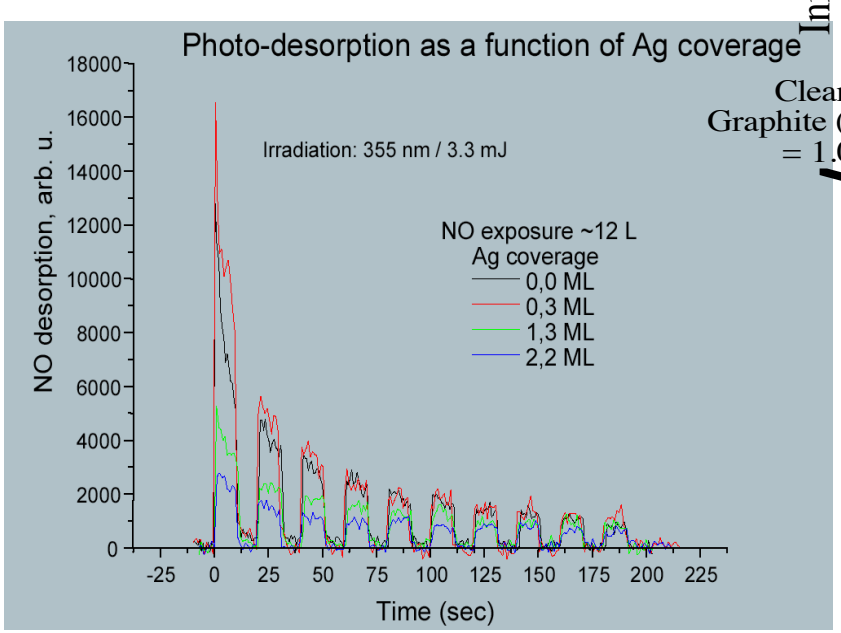


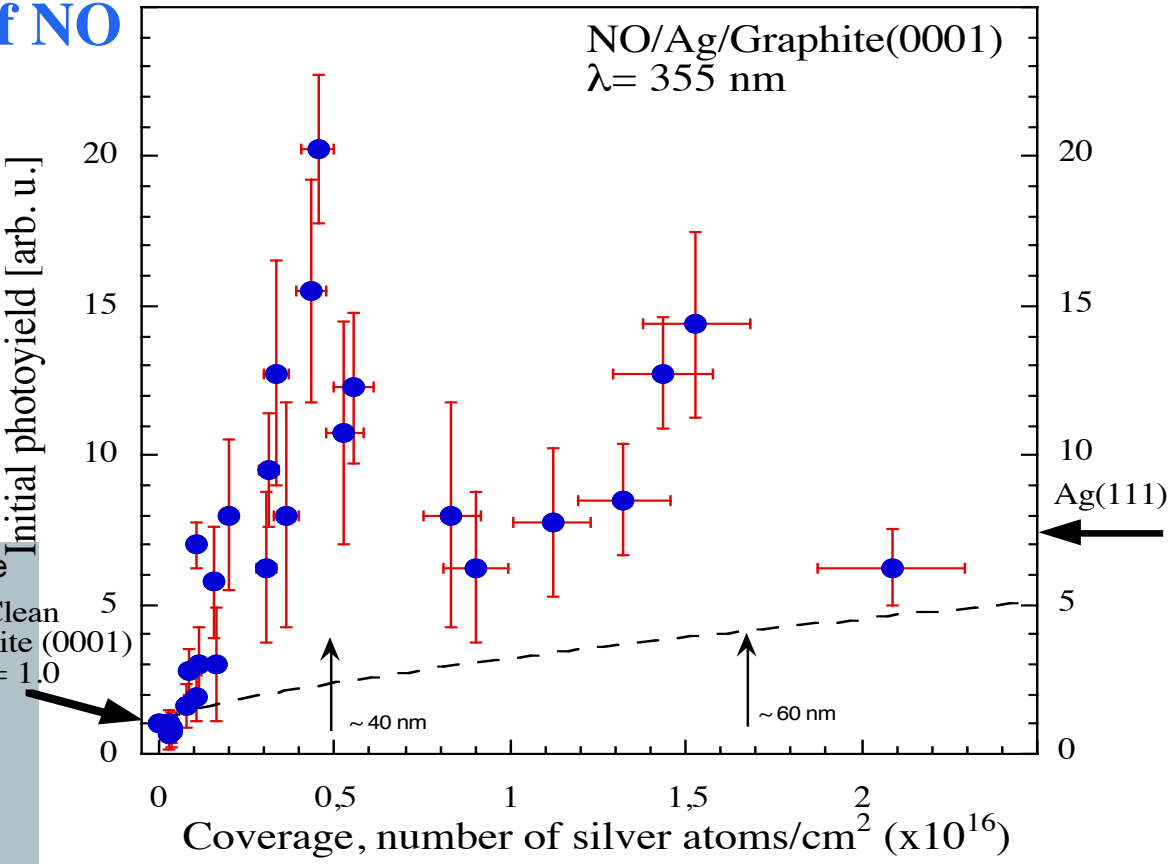
Compilation after:Kreibig, U.V., M., *Opical Propeties of Metal Clusters*. 1995, Berlin: Springer.and other sources

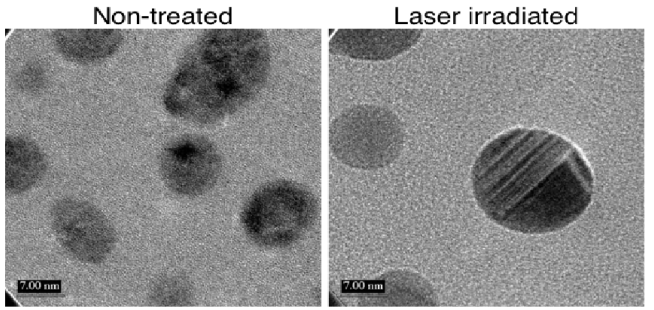
Plasmon mediated desorption of NO



Ag/ Graphite: STM images (150x150 nm) taken from H.Hövel et al Appl. Phys. A72, 295 (2001)







Surface Sci. 593 (2005) 235

TEM images (L: Eurenius) of Ag clusters before and after irradiation with 355 nm pulsed laser irradiation with subthreshod intensity.

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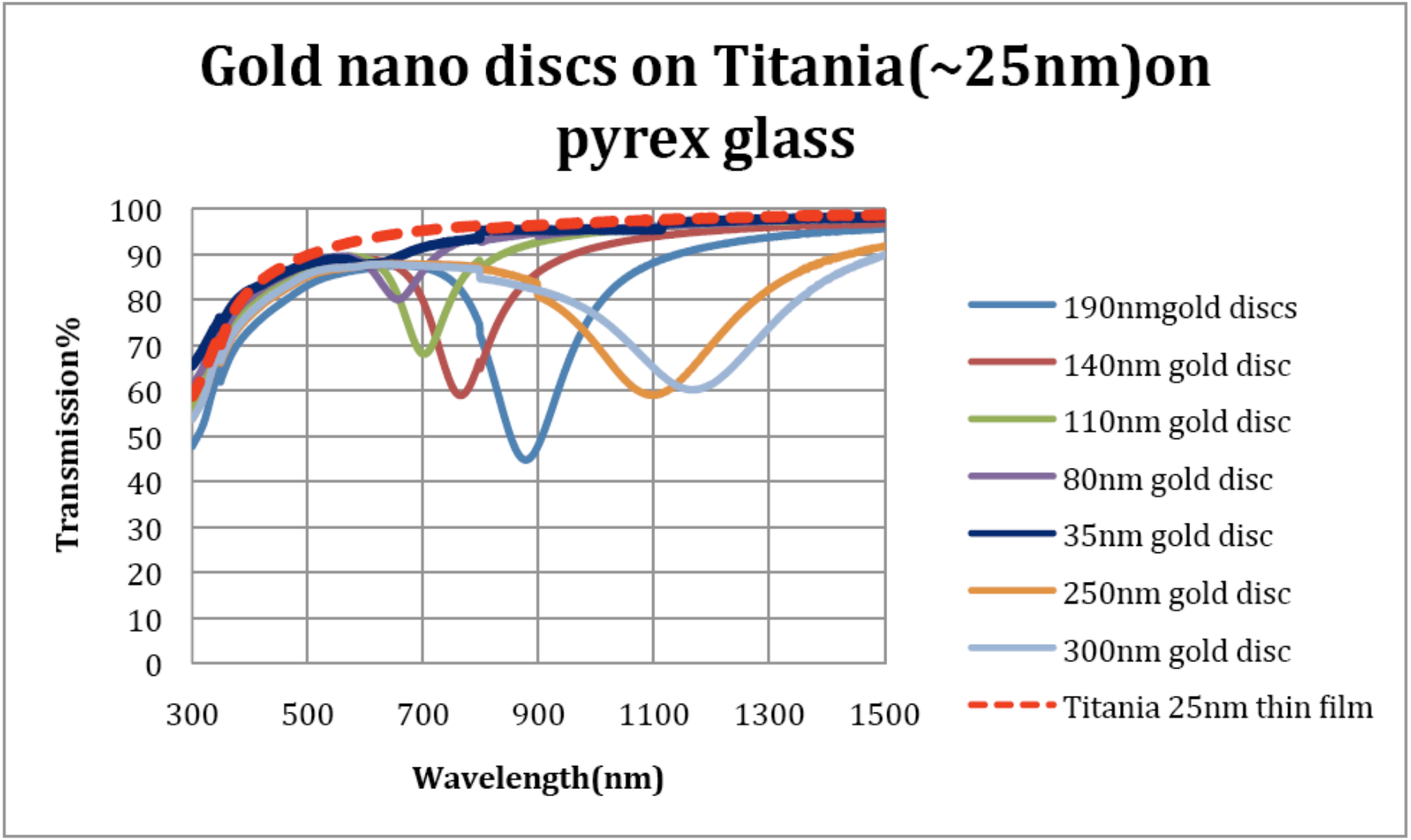
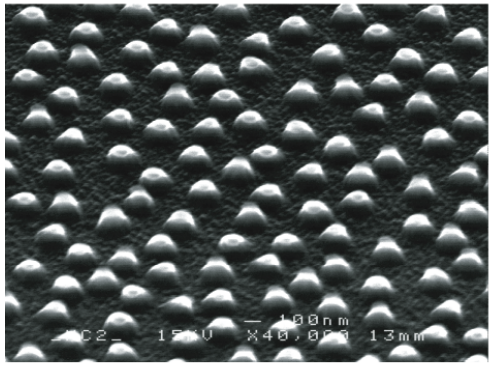
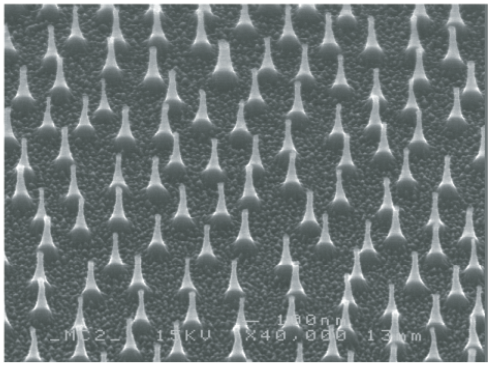

Gold nano discs on Titania(~25nm)on pyrex glass
Transmission%
100
90
80
70
60
50
40
30
20
10
0
300
500
700
900
1100
1300
1500
Wavelength(nm)
190nmgold discs
140nm gold disc
110nm gold disc
80nm gold disc
35nm gold disc
250nm gold disc
300nm gold disc
Titania 25nm thin film

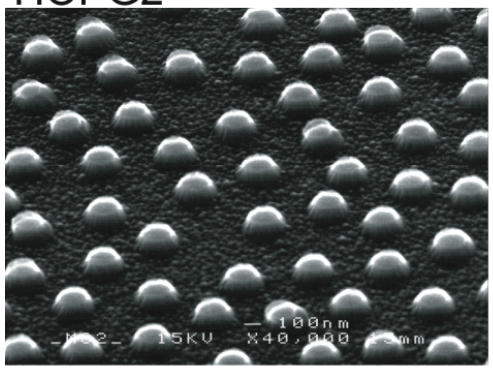
HOPG1



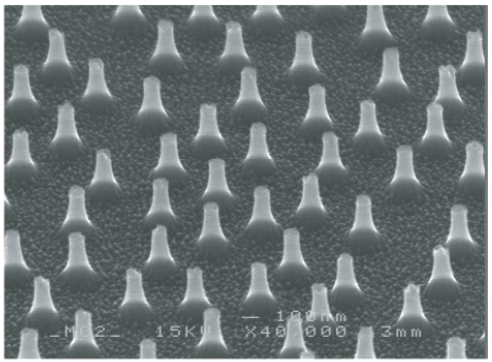
GC1



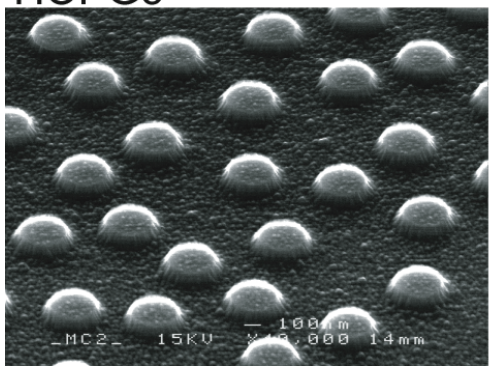
HOPG2



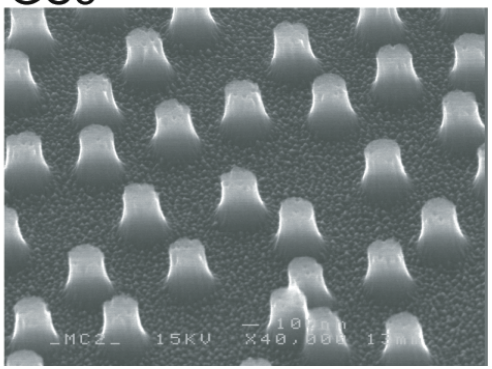
GC2

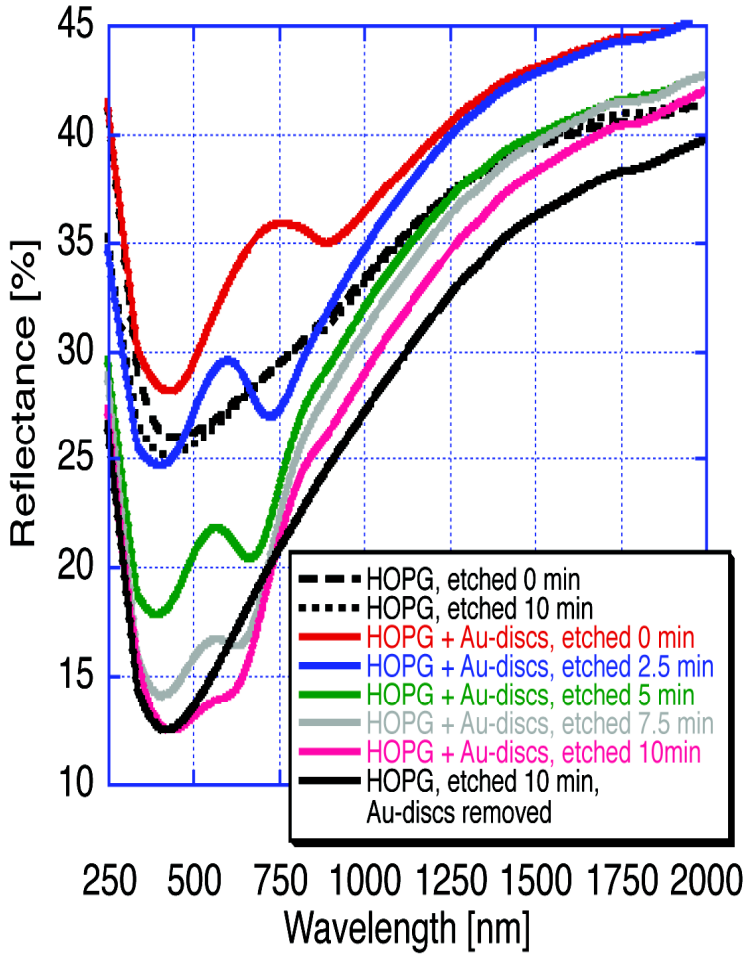


HOPG3



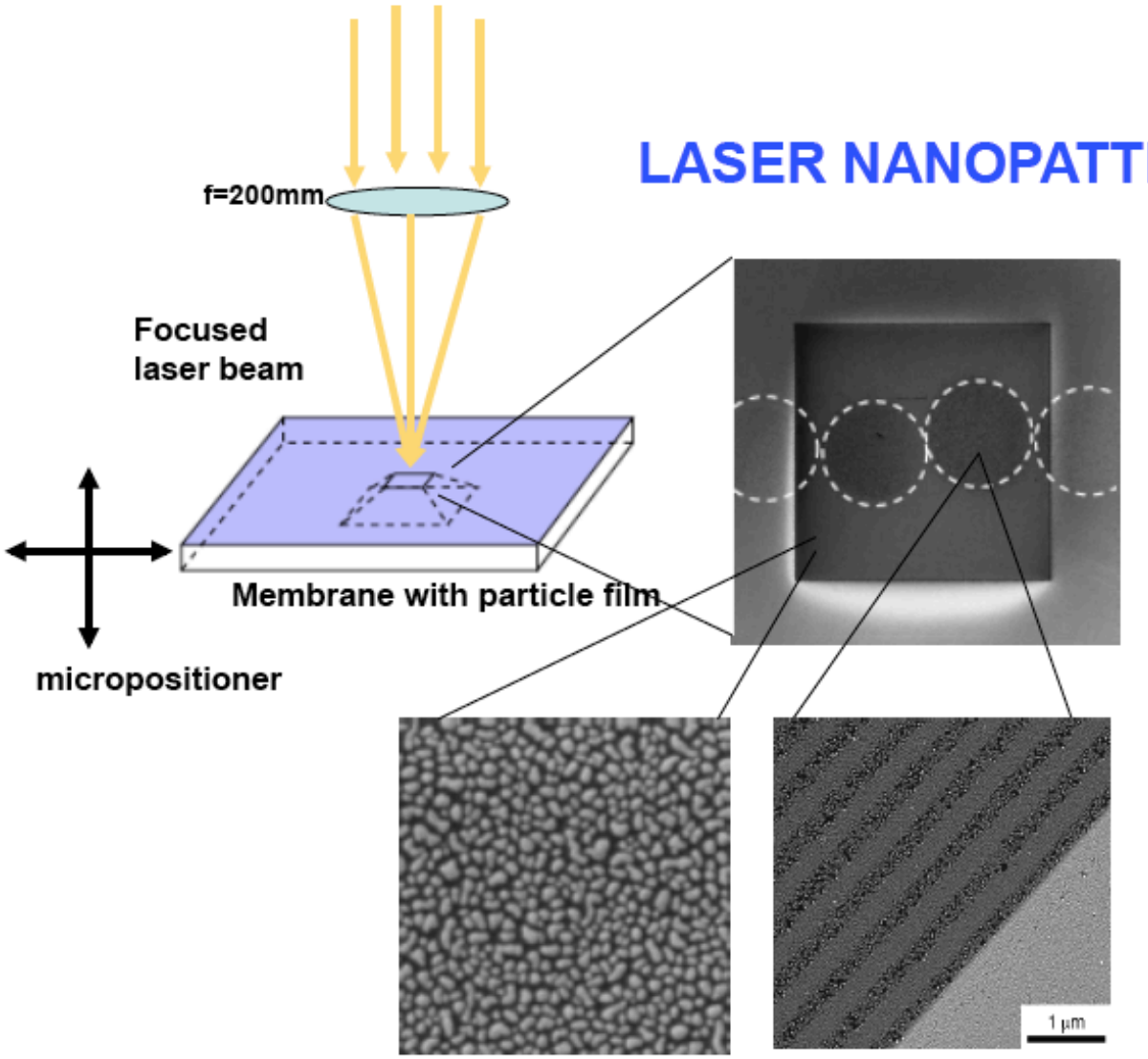
GC3





H. Fredriksson et al.

LASER NANOPATTERNING



L. Eurenius, *Nature Photon.* **2,** 360 (2008).

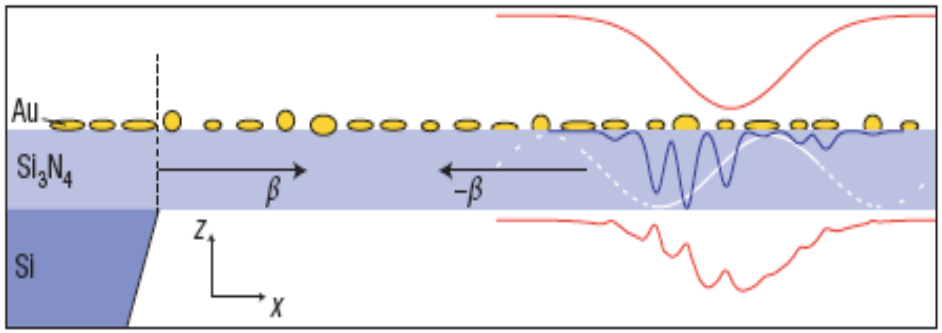


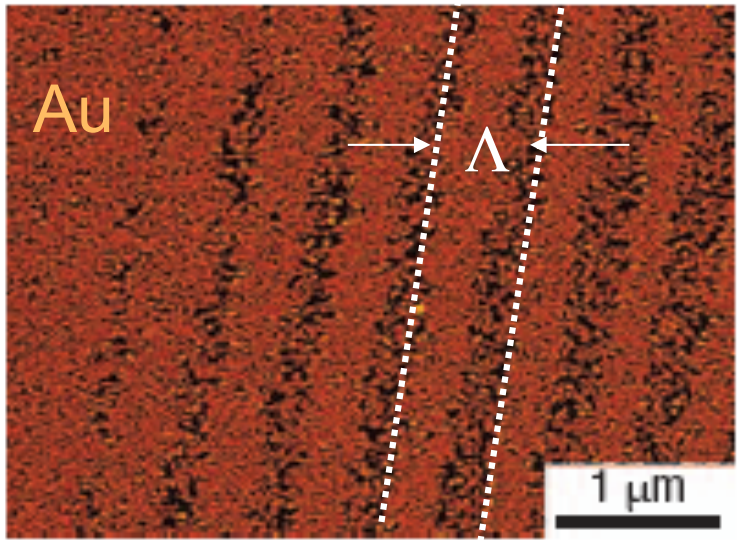
Table 1 Observed grating periods in gold nanoparticle films formed for different irradiation wavelengths. No pattern formation was observed after irradiation with 355-nm photons.

Wavelength (nm)	Grating period (nm)	
	TE mode	TM mode
532	460	520
590	510	630
640	560	680

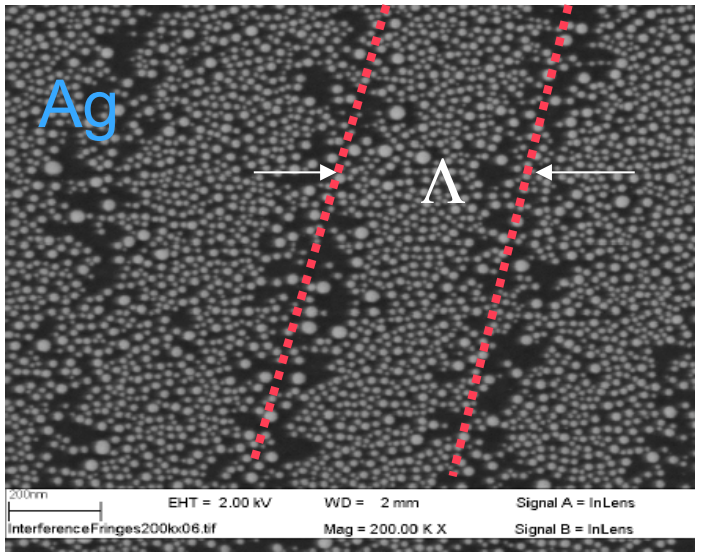
$$\frac{E_0^2 + E_{wg}^2}{2} + E_0 E_{wg} \cos\left[\left(k_{0x} - k_{wg}\right)x + \varphi_0 - \varphi_{wg}\right]$$

Table 2 Observed grating periods in gold nanoparticle films formed for different angles of incidence at an irradiation wavelength of 532 nm.

Incident angle (°)	Grating period (nm)	
	Far edge	Near edge
15	360	600
30	320	780
45	280	860–1,200



$$\Lambda = 2\pi / | k_{0x} - k_{wg} |$$



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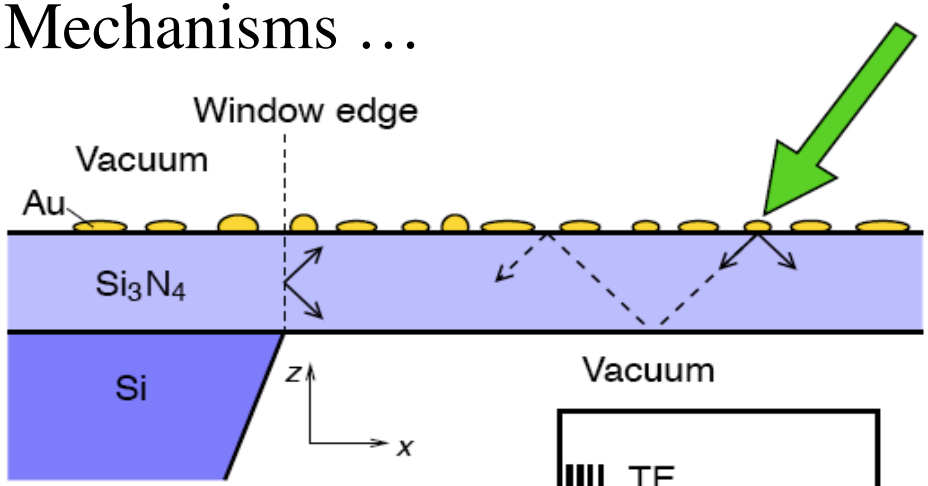
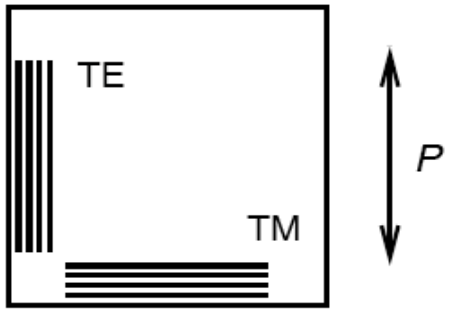
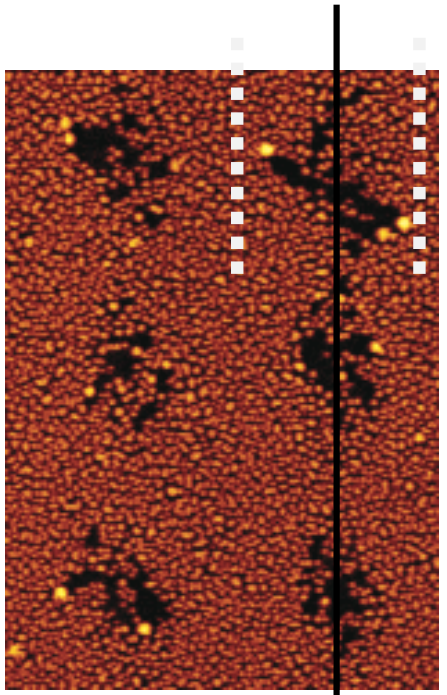
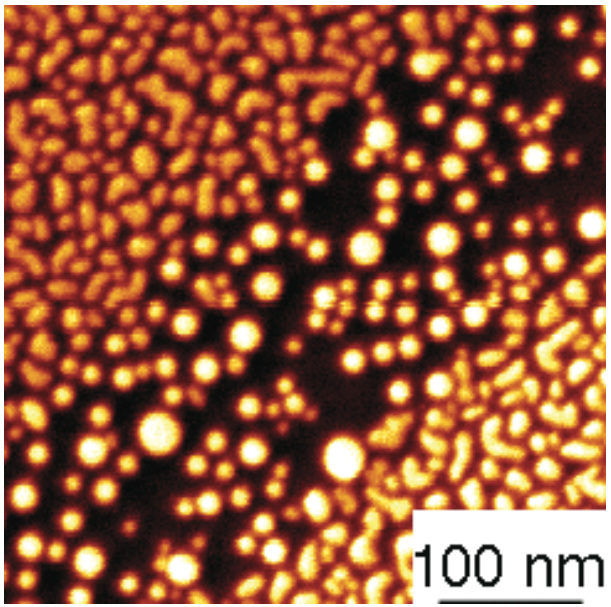
Mechanisms …

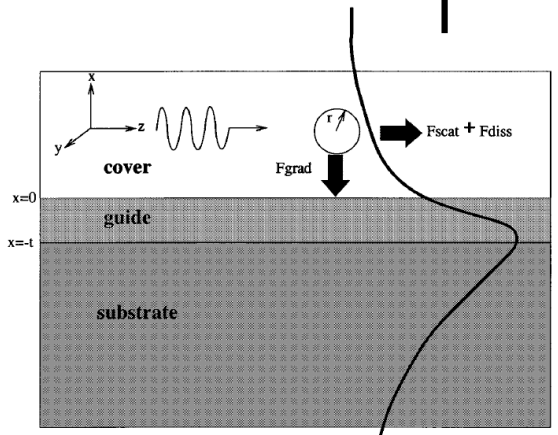




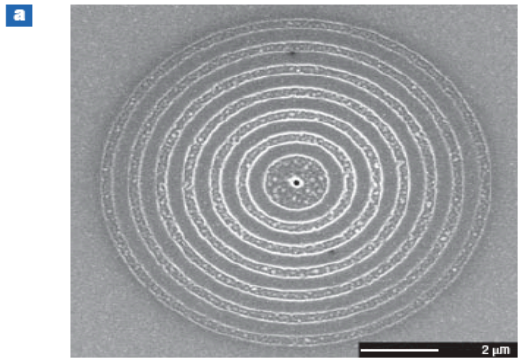


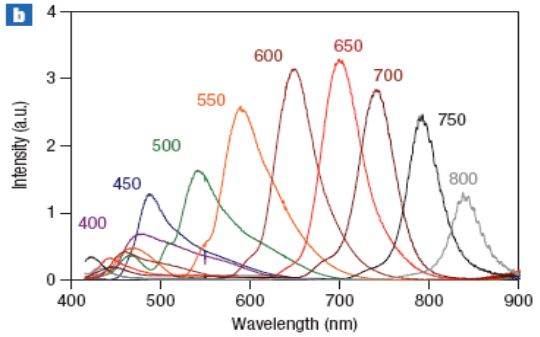
$$F = \alpha\nabla(E_{tot}^2)/2$$

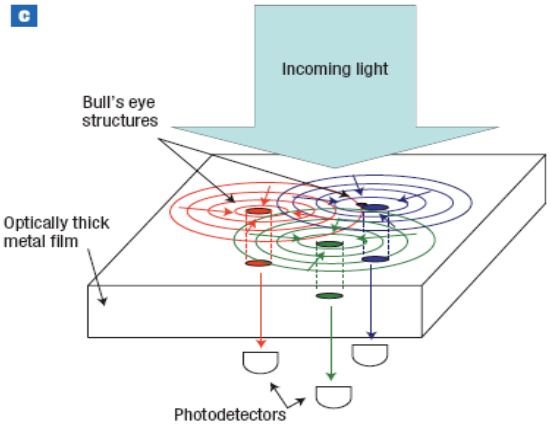




L. N. Ng et al, J. LIGHTWAVE TECHNOLOGY, VOL. 18, NO. 3, 388, MARCH 2000







Plasmonic photon sorters for spectral and polarimetric imaging

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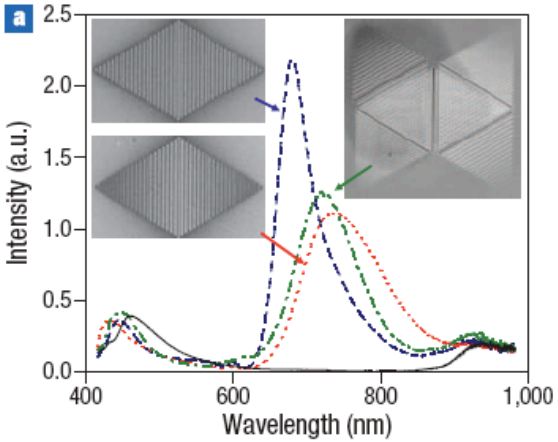
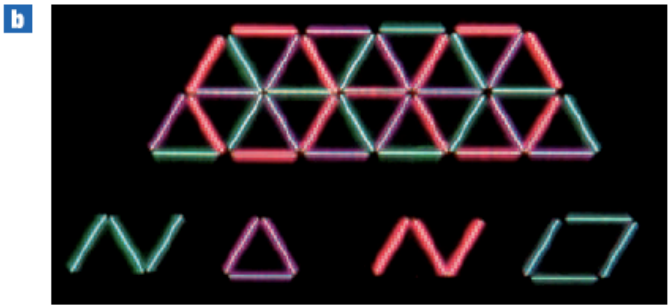
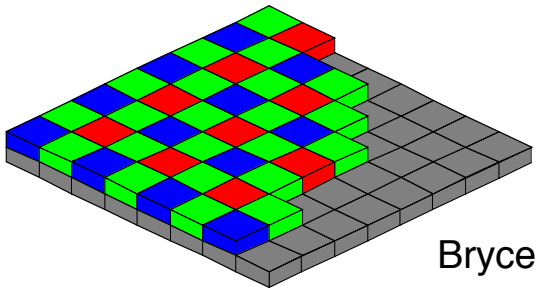
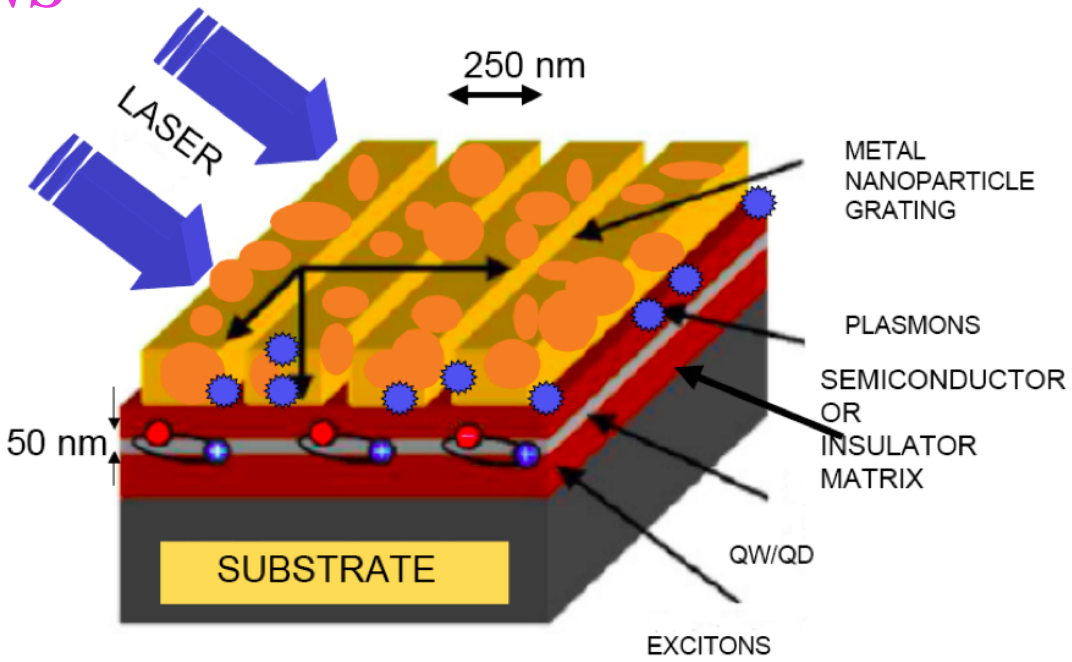


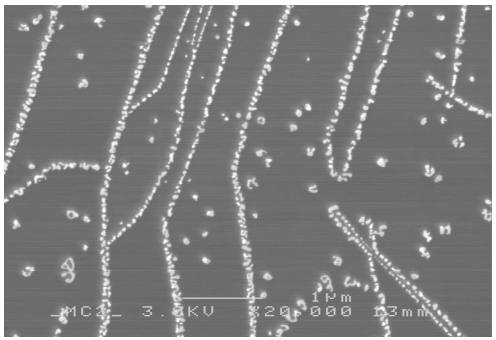




Bryce E. Bayer

- Metamaterials for enhanced photon capture - ***PLEXITONS***

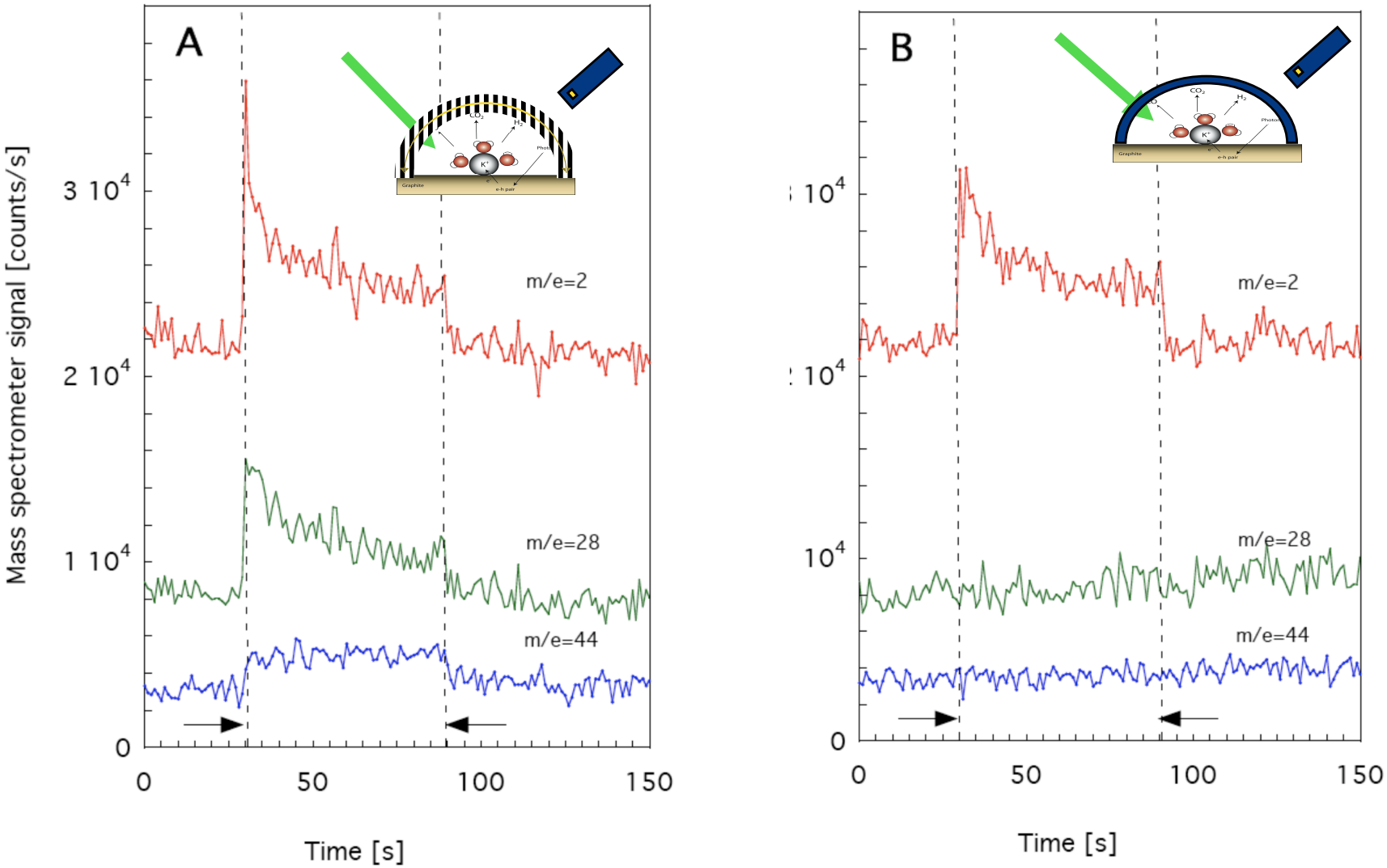


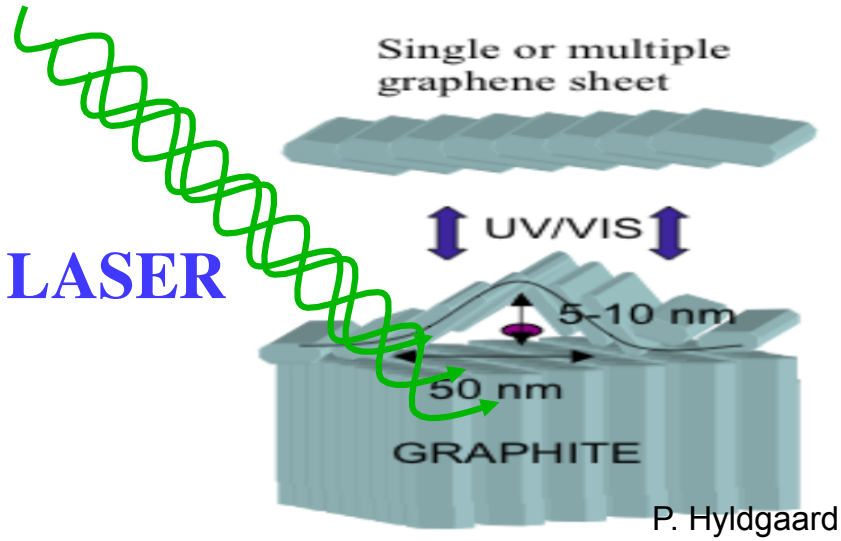


Ag clusters on HOPG

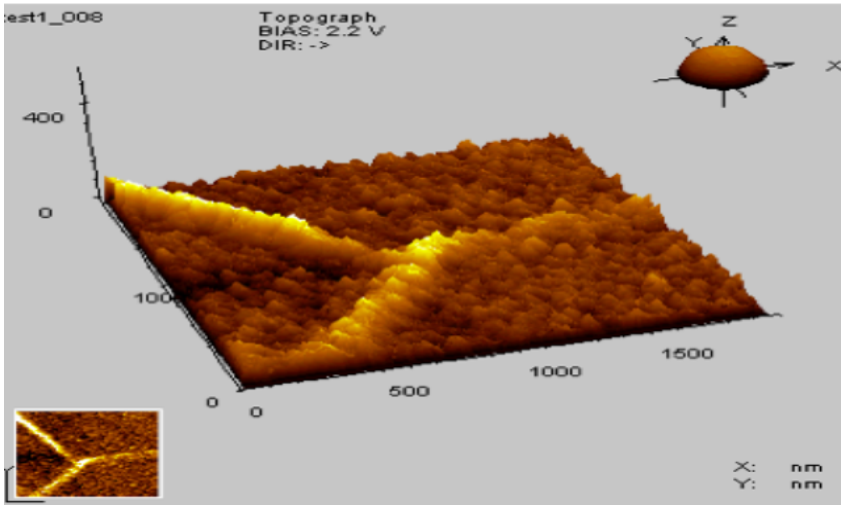
•Control of the reaction environment and volume

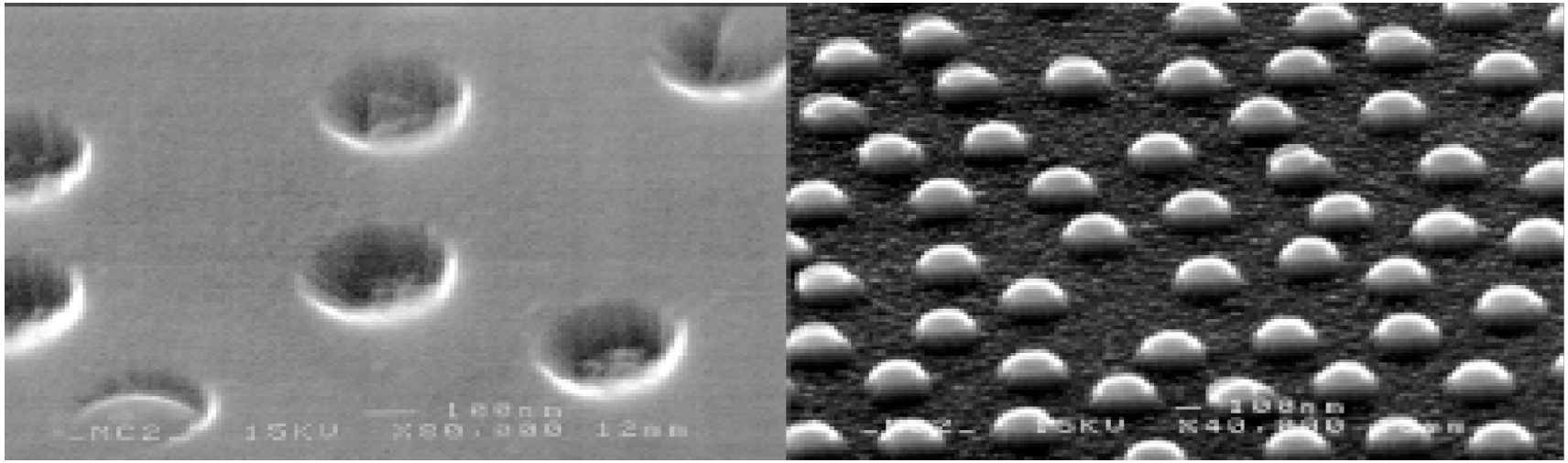
- Confinement of reactants and reaction products,
- Nanoreactors


A
B
Mass spectrometer signal [counts/s]
3 10^4
2 10^4
1 10^4
0
m/e=2
m/e=28
m/e=44
0
50
100
150
Time [s]



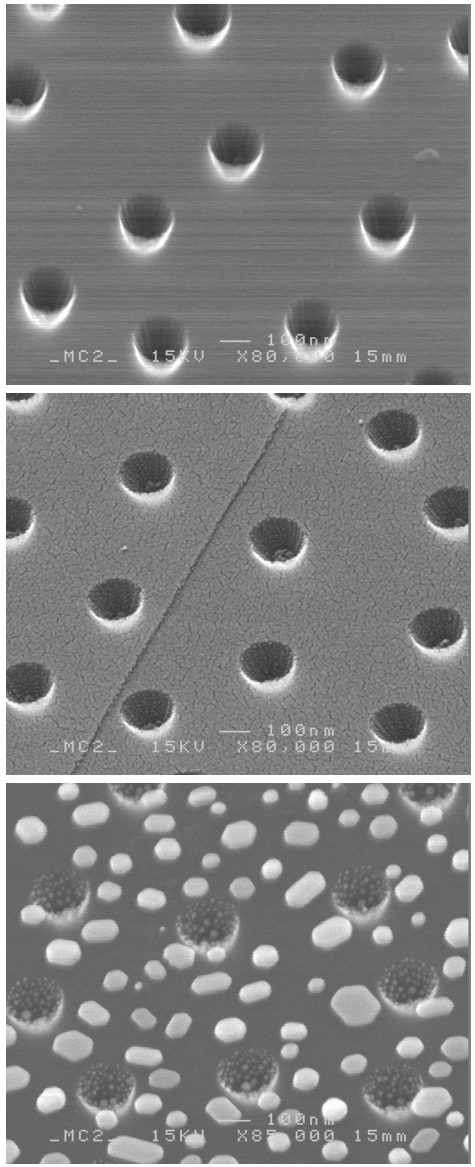
P. Hyldgaard et al.





AFM scan over exfoliated HOPG surface obtained by irradiation with a single 4 ns laser pulse (0.8 mJ/cm^2 290 nm photons). SEM images of nanofabrivcated graphite samples (H. Fredriksson): 190 nm pits (bottom left) and cones.

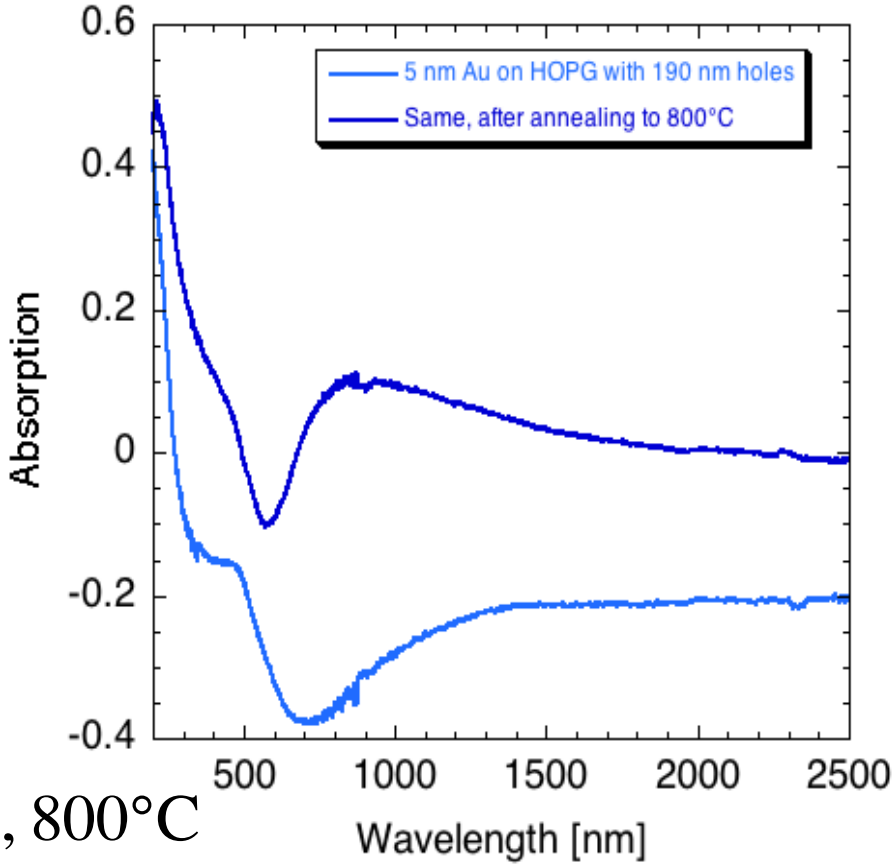
120 nm holes in HOPG + Ag



As prepared

With 5 nm Au

After annealing, 800°C



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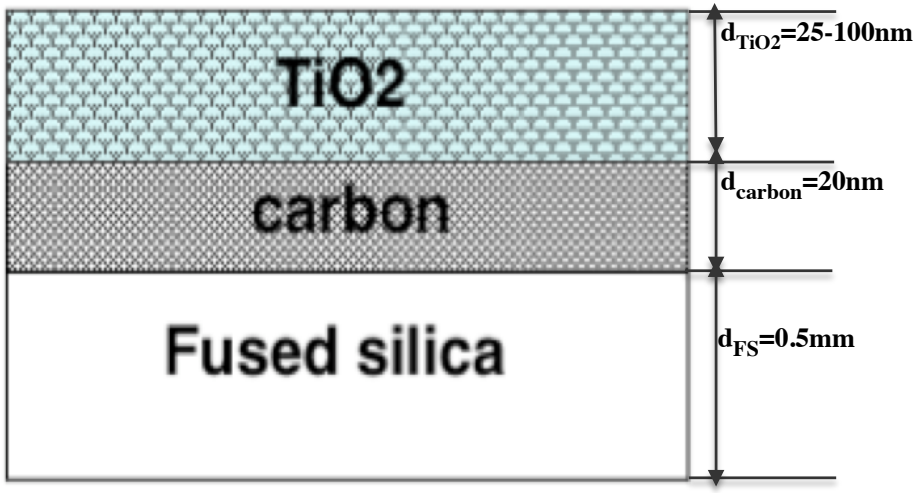
Control of structure and morphology

- High surface area structures,
- Nanotube arrays,
- Core-shell architectures,
- Controlled wetting properties,
- Controlled porosity
- …

Schematic of the sample

R. Sellappan



Why thin film?

◆Reduced recombination probability

◆Less transport path for charge carriers

CARBON

E-beam evaporation
Source material= Graphite
Post-deposition annealing= 800°C in Argon atmosphere.

Titania

DC reactive magnetron sputtering
Post-deposition annealing= 500°C in Argon atmosphere.

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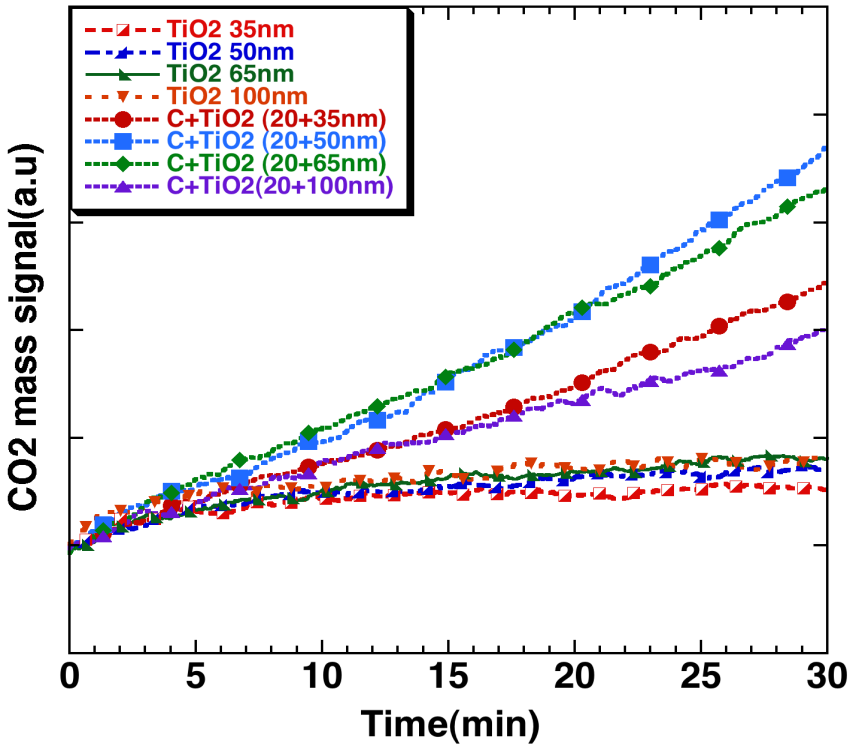
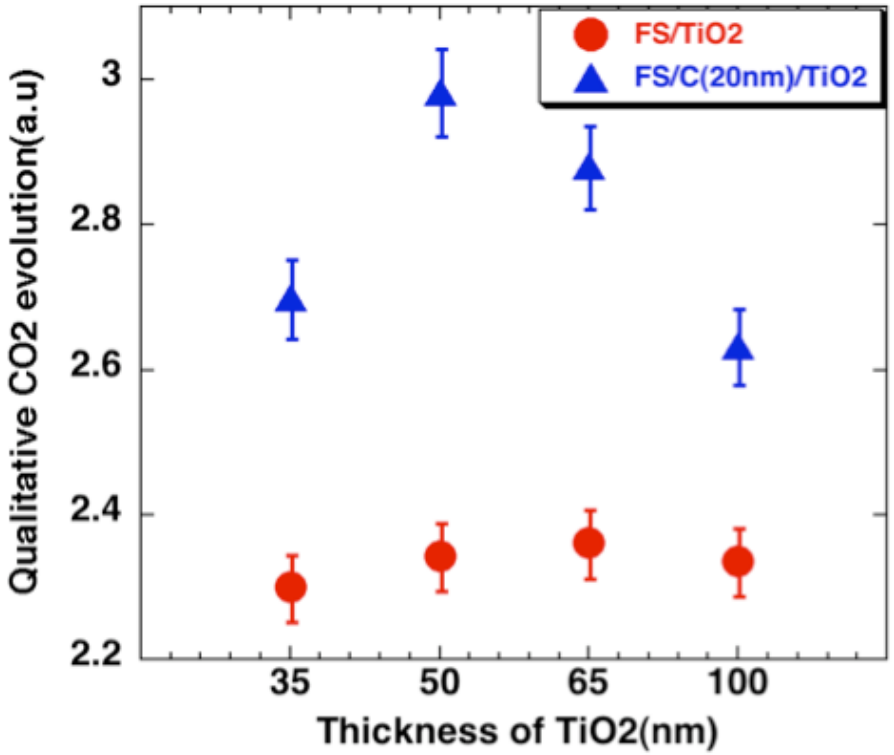
Thickness dependence of the photocatalytic results





FS= Fused Silica (substrate)
C=carbon

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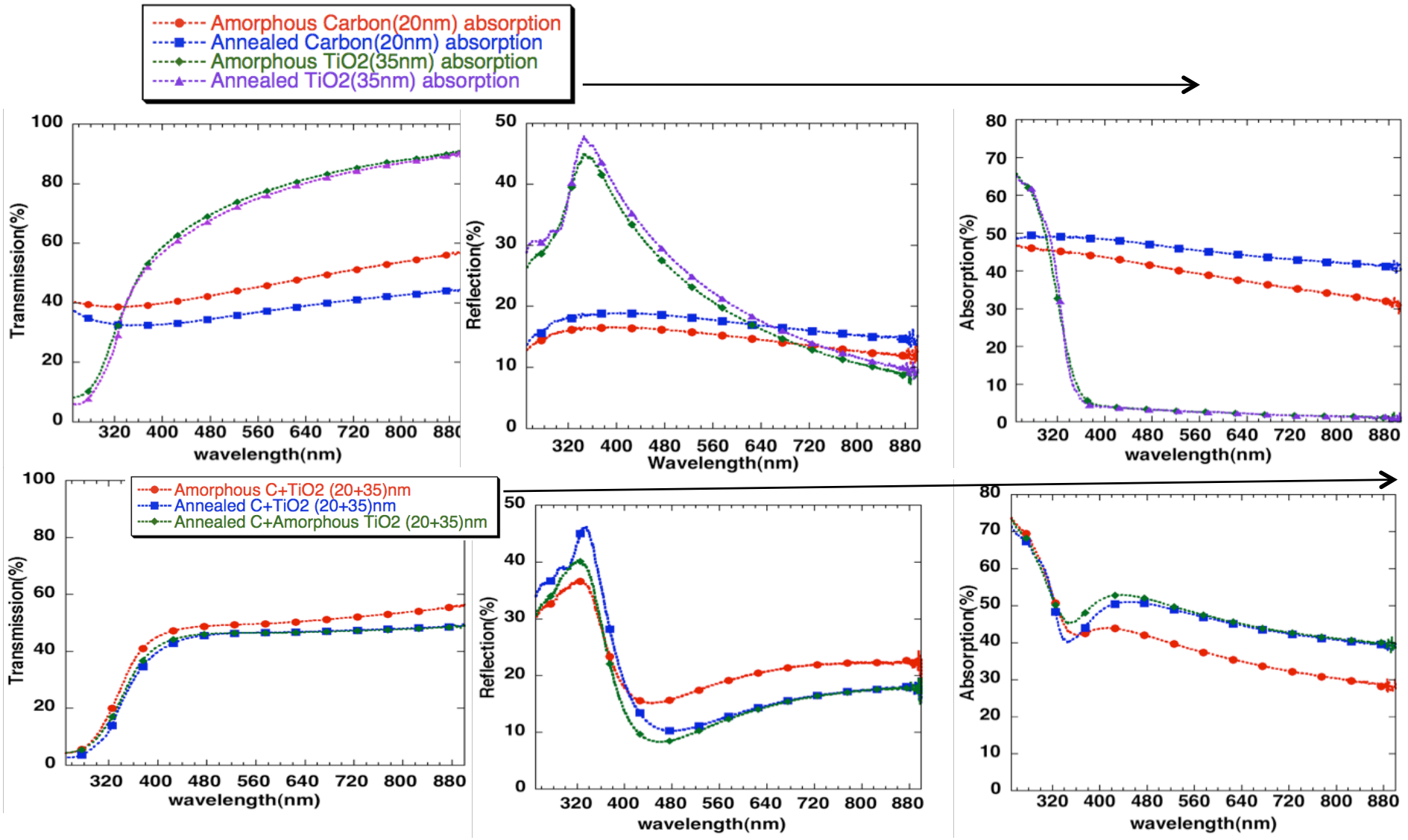
Optical absorption



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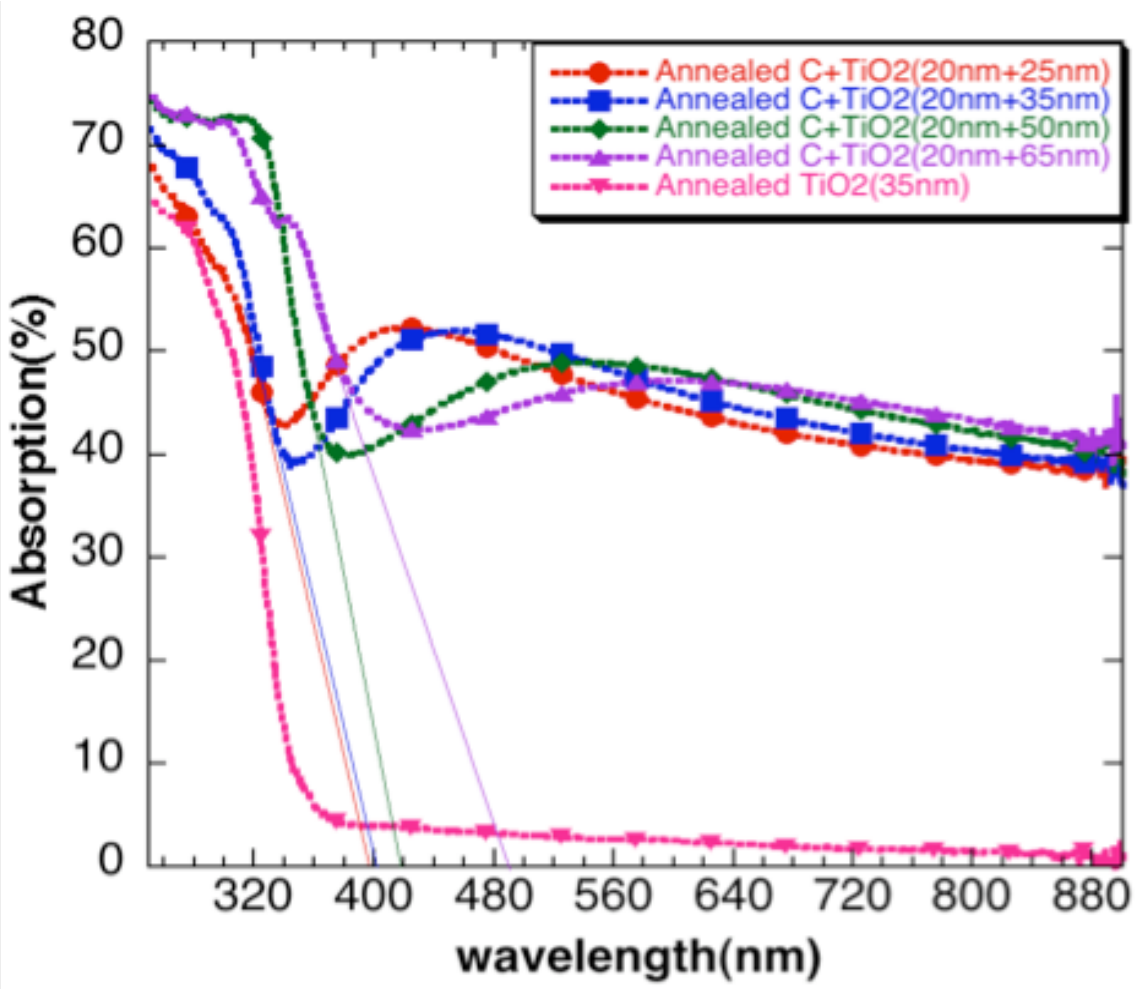
Optical absorption



- Increase in absorption in the visible regime as well as in the UV.
- Absorption tail of TiO_2 redshifts for the combined films.
- Correlation between the increase in absorption and enhanced activity.
- Availability of more optically active volume

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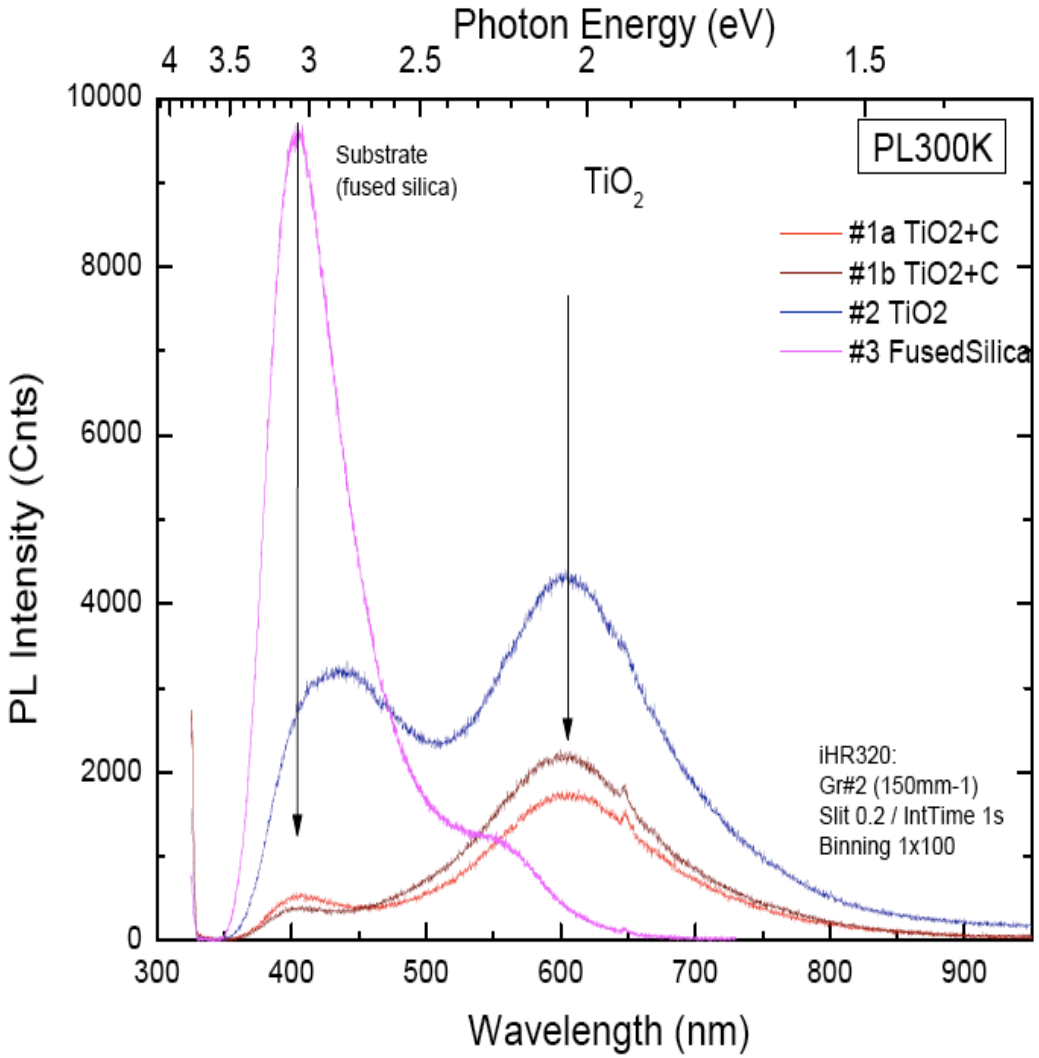
Composite TiO_2/carbon nanofilms: PL

A. Kuznetzov et al.



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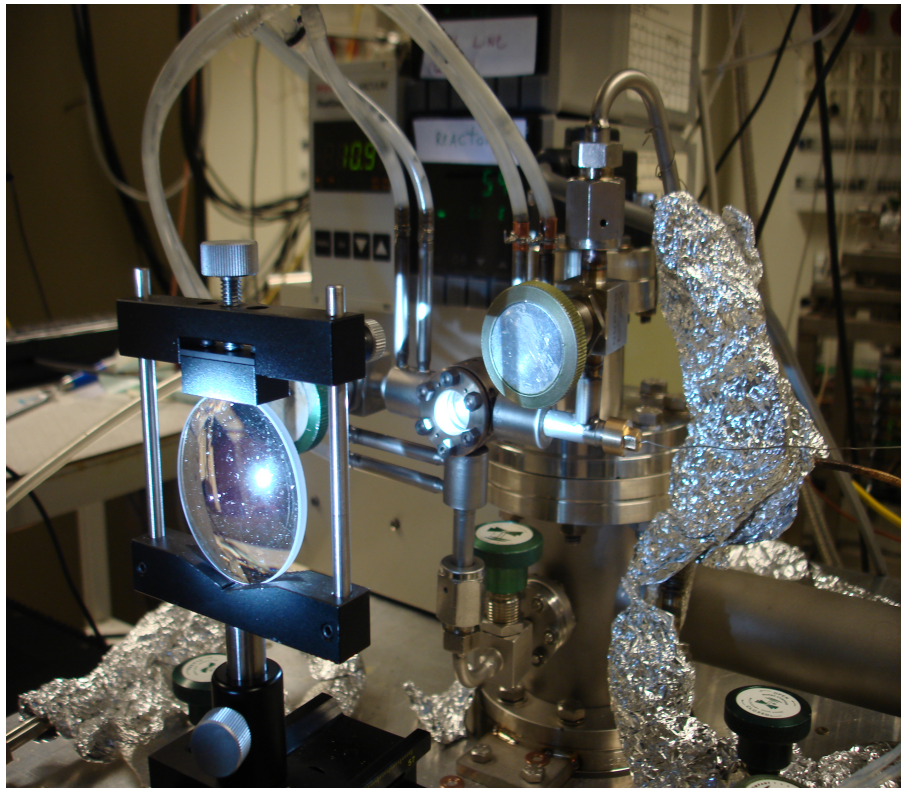
Photocatalytic measurement



- Hg lamp =100W
- Focused UV light(385nm) =120mW/cm^2
- Temperature= 16°C under dark and 5°C increase during illumination
- Batch mode

Reactants= Methanol and oxygen
Products= carbon dioxide and water (not shown)
In-situ mass spectrometer

$$2CH_3OH+3O_2 \longrightarrow 2CO_2+4H_2O$$

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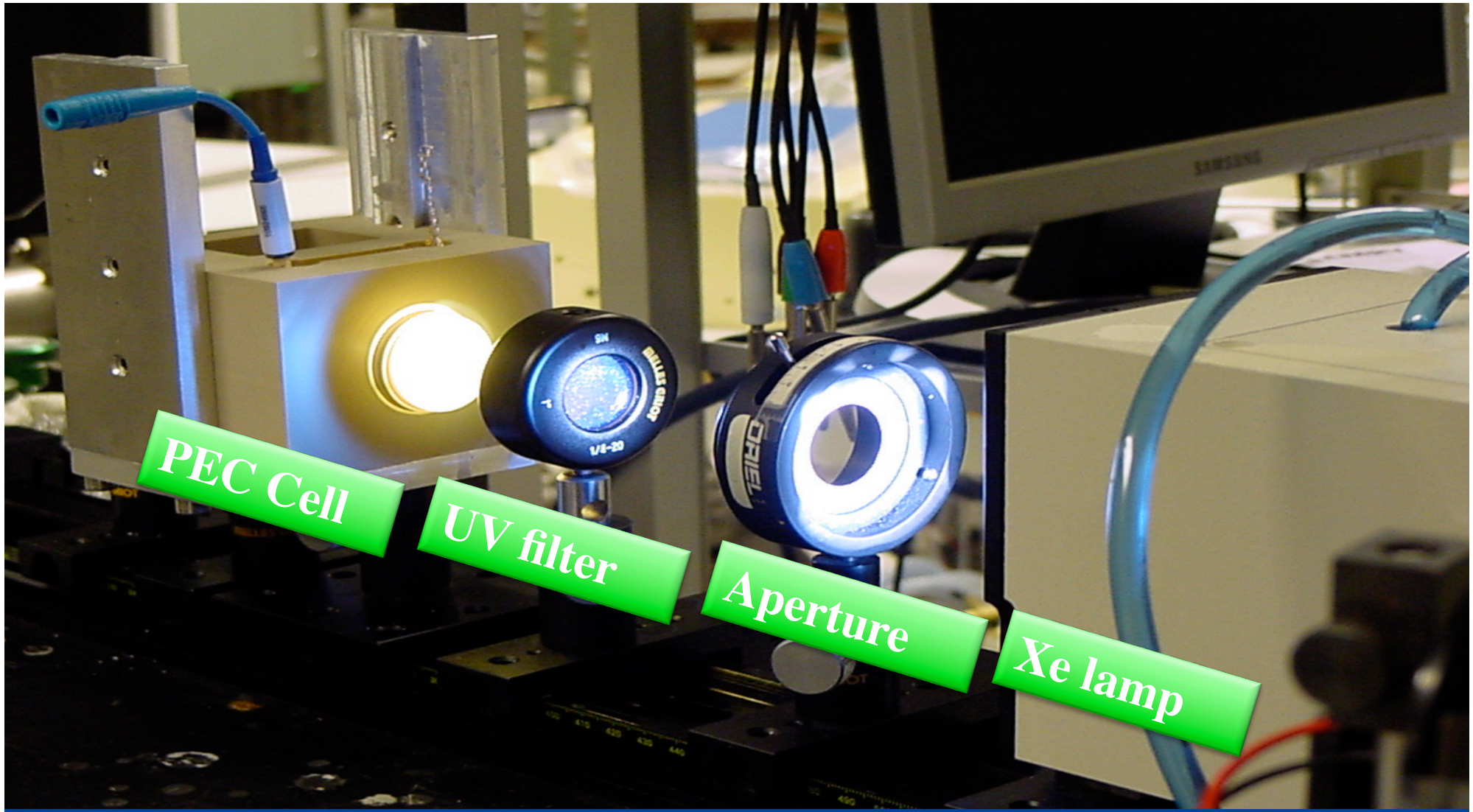
Photoelectrochemical measurements



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Fabrication of model systems & theoretical modeling

Fabrication methods …

Fabrication of model systems & theoretical modeling

E-BEAM LITHOGRAPHY

- Superb control of feature size and spacing;
- Possible to fabricate ordered arrays of nanoparticles;
- Slow and expensive.

COLLOIDAL LITHOGRAPHY

- Not so good control on particle size and distribution;
- Random arrays only;
- Fast and cheap.

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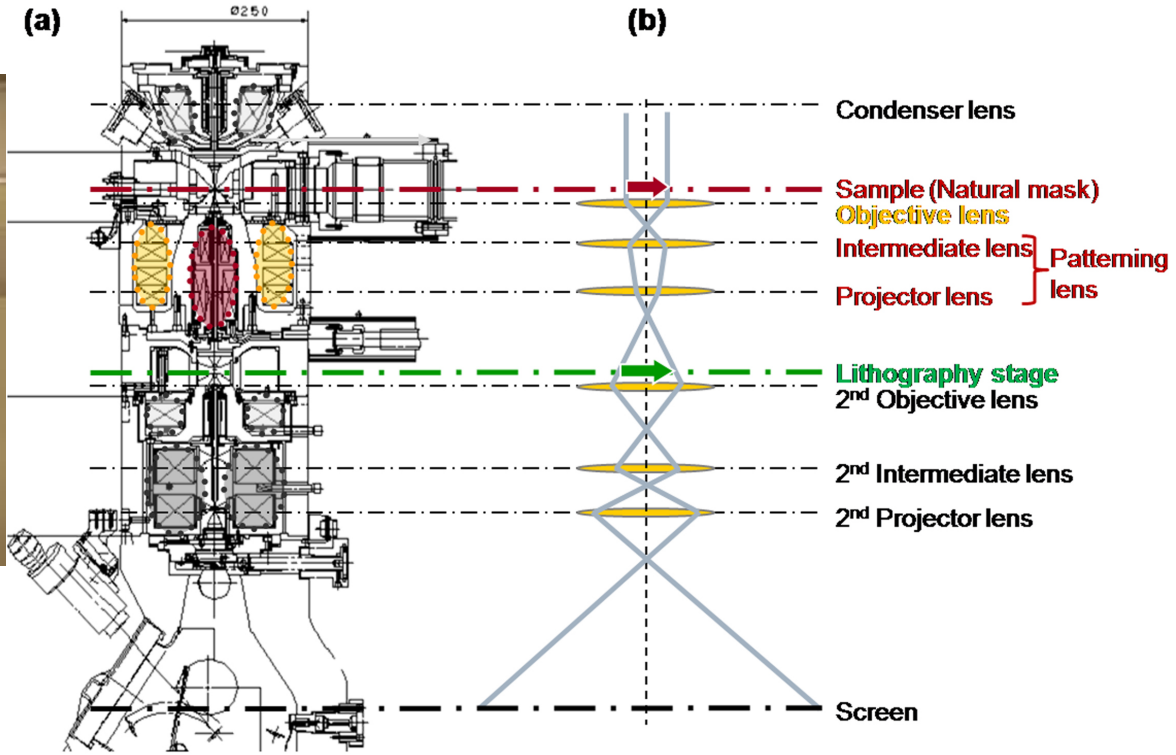
• e-beam lithography

EBL - JEOL JBX-9300FS



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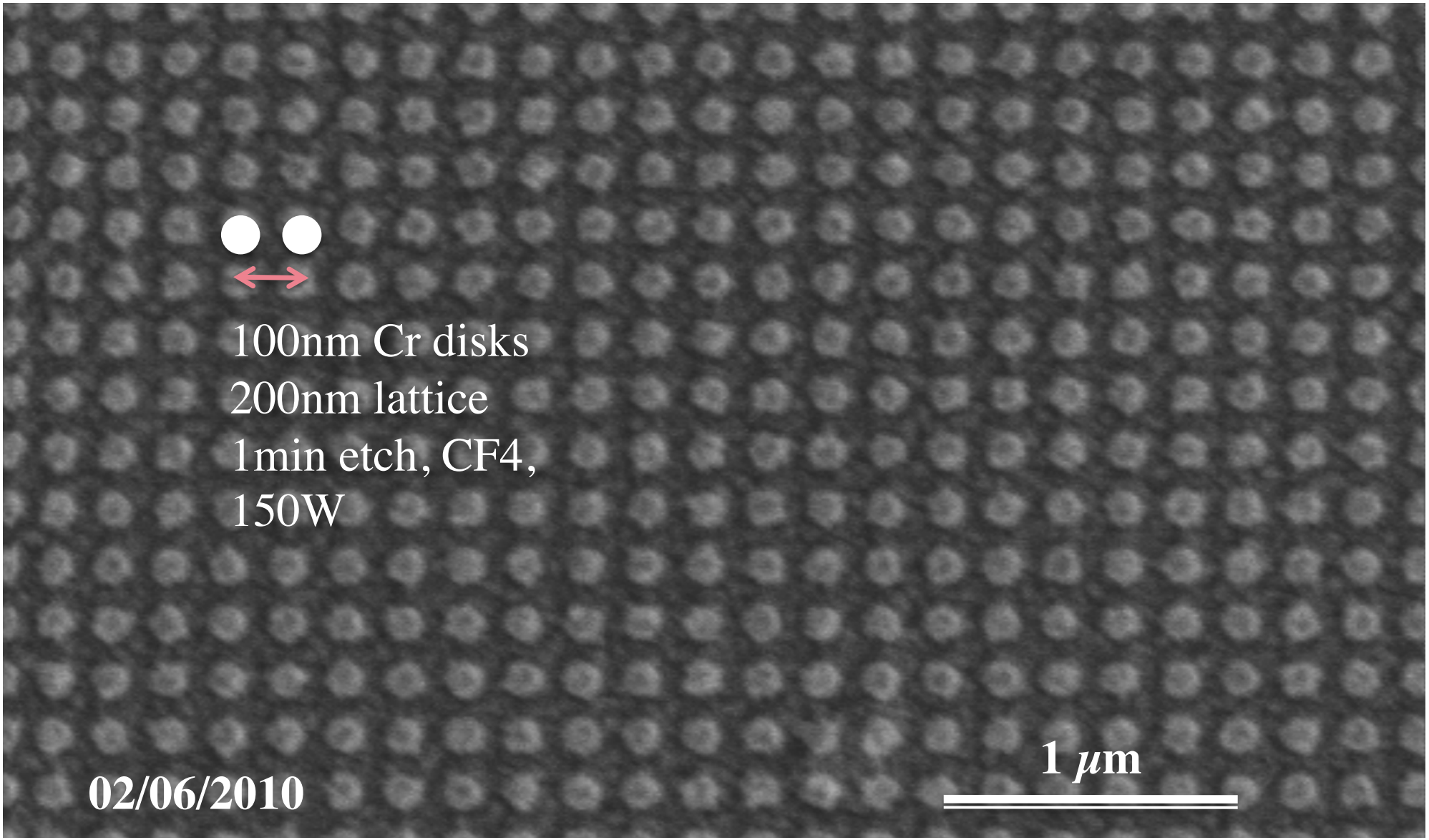
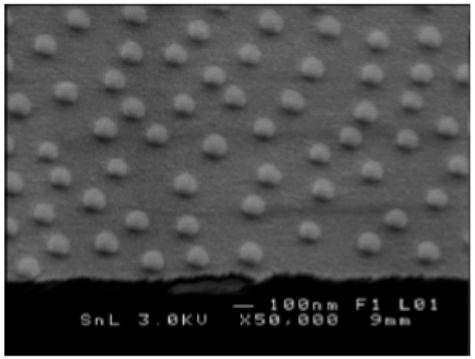
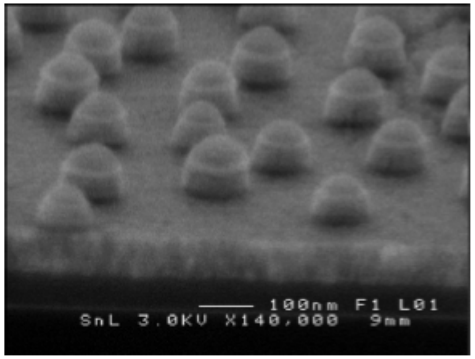
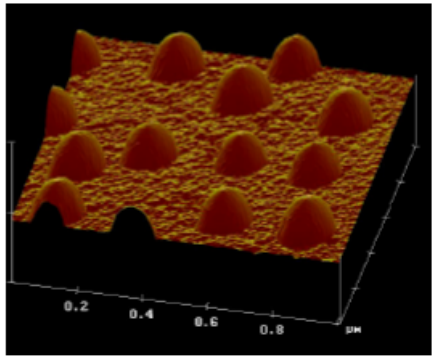

100nm Cr disks
200nm lattice
1min etch, CF4,
150W
02/06/2010
1 μm

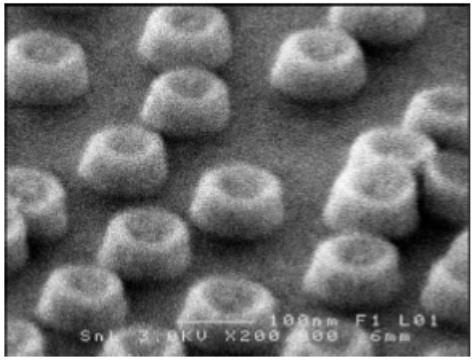
Preparation-3

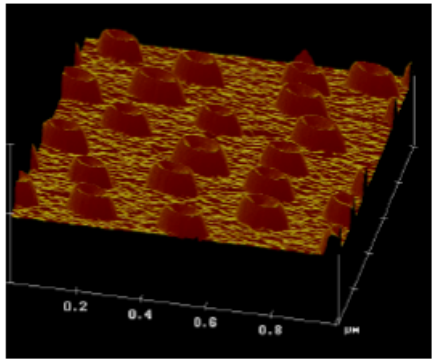
Colloidal Lithography

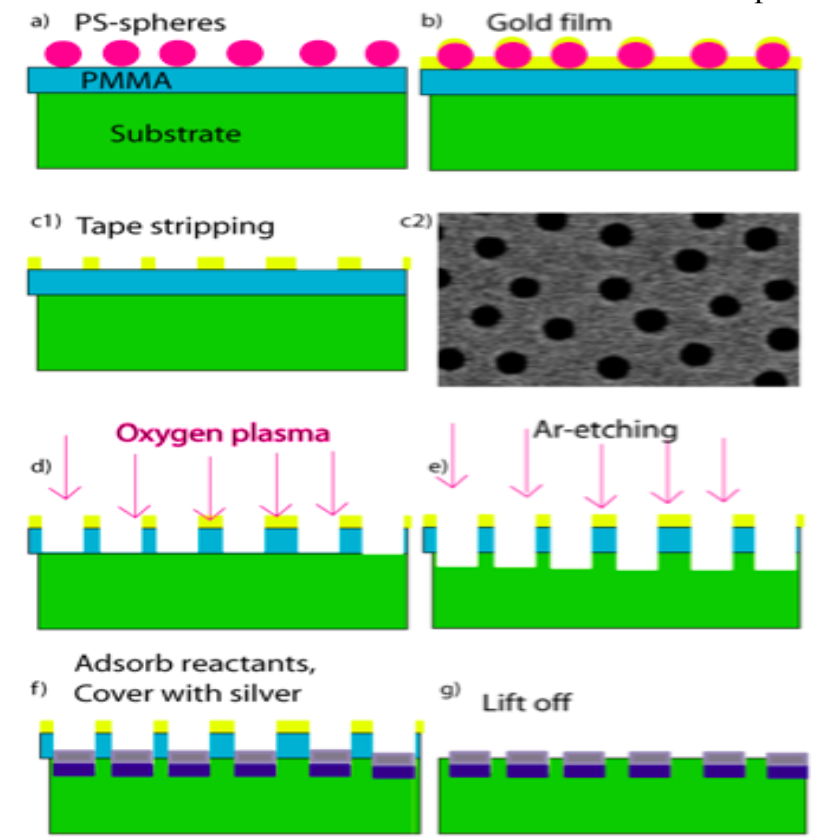












(a) Electrically charged, self-assembling polystyrene spheres are adsorbed on spin coated over substrate polymer film. (b) A thin Au film is evaporated. (c) The polystyrene spheres are removed with solvent or tape stripping leaving a thin perforated film on top of the polymer. (c2) SEM image of the perforated film. (d) The sample is etched in directed oxygen plasma that removes the polymer not covered by the thin film. (e) Pits are dug into the substrate using ion etching. (f) One or several reactants are adsorbed on the surface, followed by evaporation of a metal. (g) The polymer film is lifted of in a solvent leaving the reactants trapped in little cavities sealed with a metal particle.

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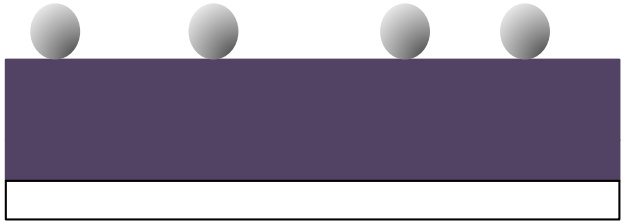
How to nanostructure Fe?

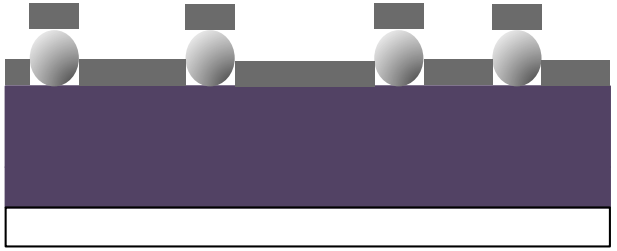
→ additive process with Colloidal Mask Lithography

1. resist spinning & baking

2. colloidal particles deposition

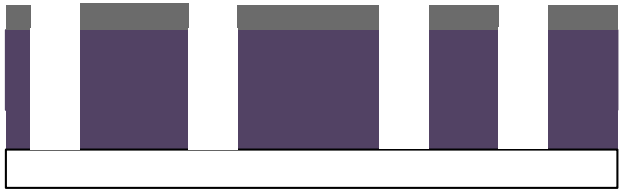


3. Cr mask deposition

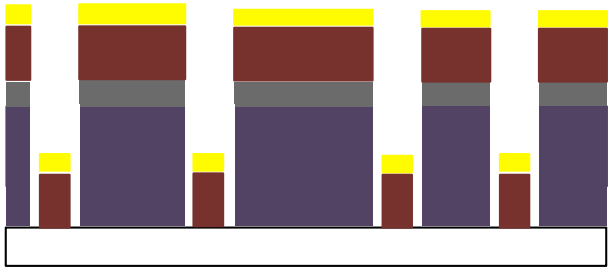


4. collodial particles removal by tape stripping

5. resist etching



6. Fe and noble metal deposition



7. liftoff

→ to final oxidation

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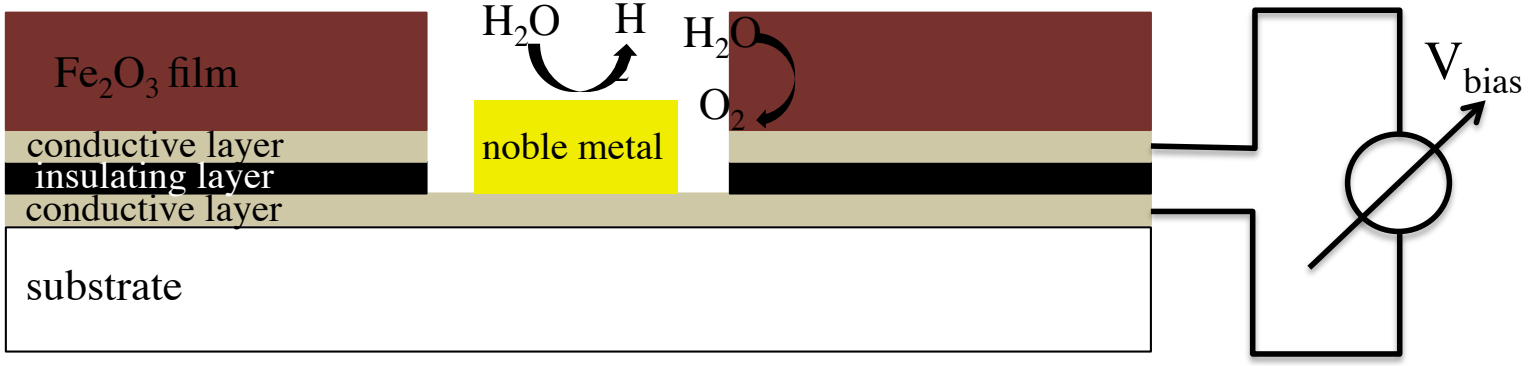
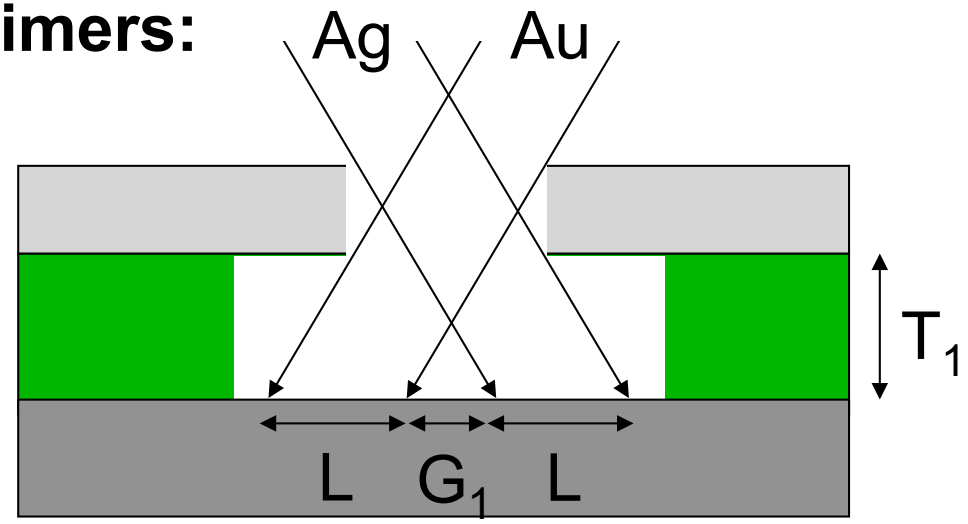
NANO photoelectrochemical cells

Fe_2O_3 films with metallic nanoparticles in nanocavities

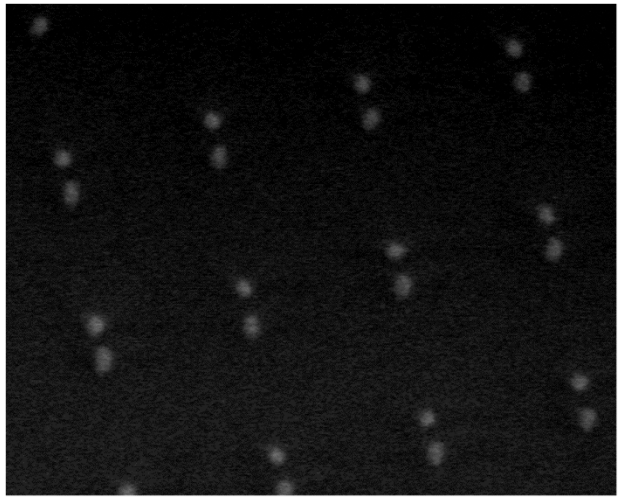


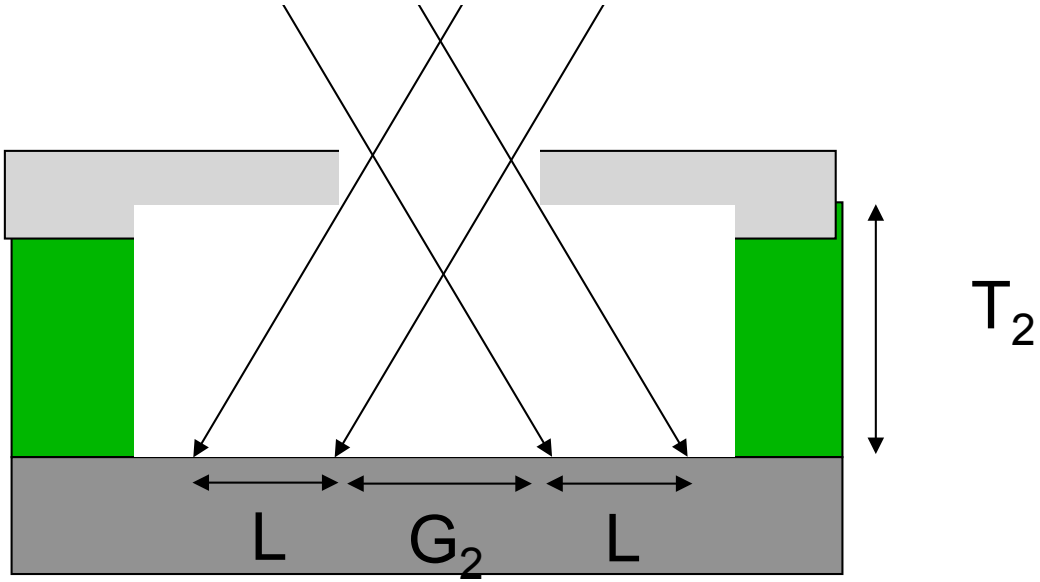
©Beniamino Iandolo

Dimers:

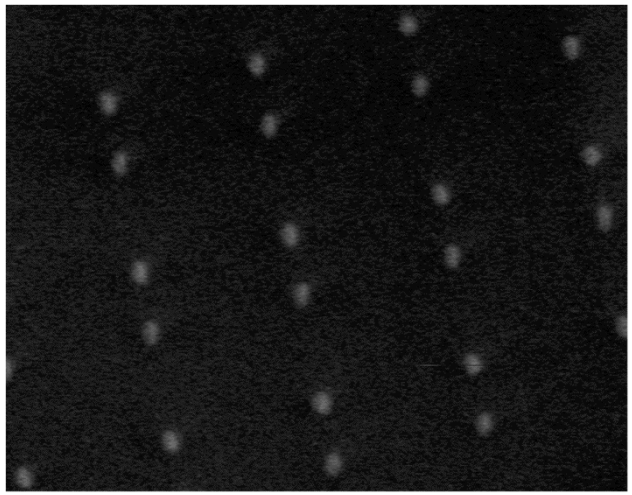


G_1 = 53nm





G_2 = 118nm



Made so far: 25nm < G < 300nm

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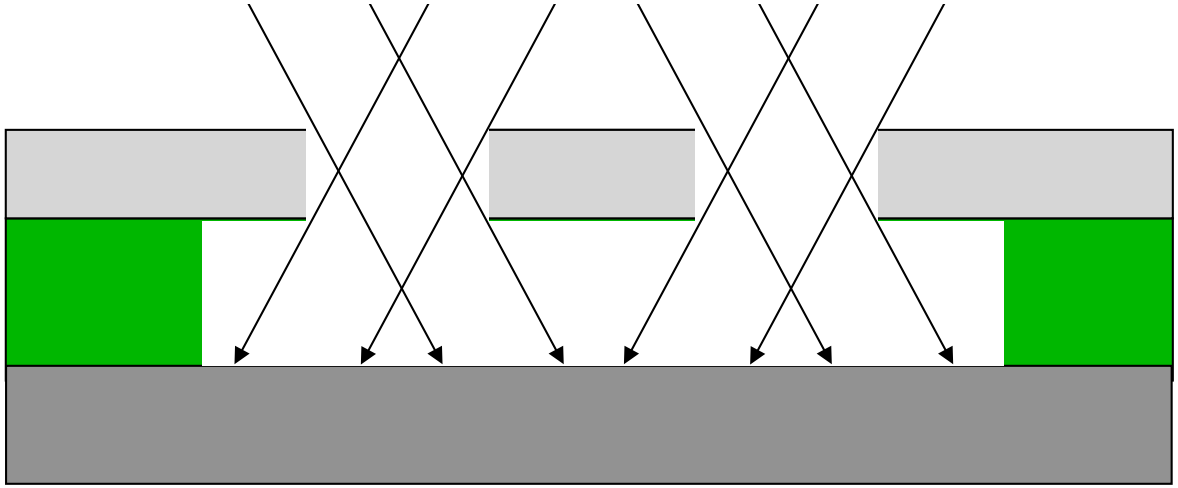
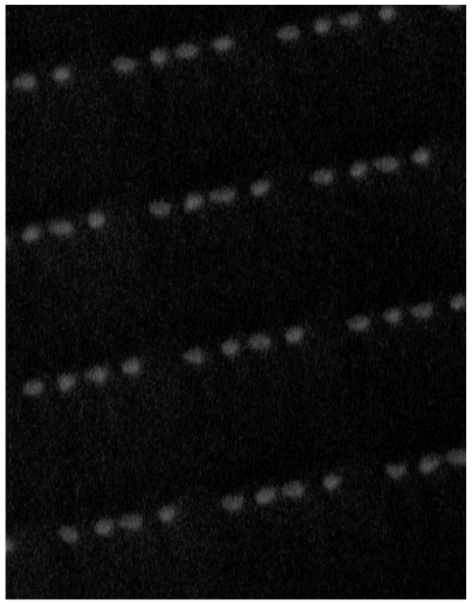
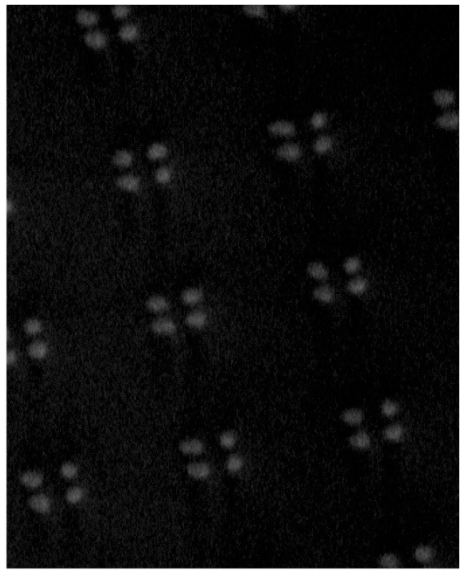
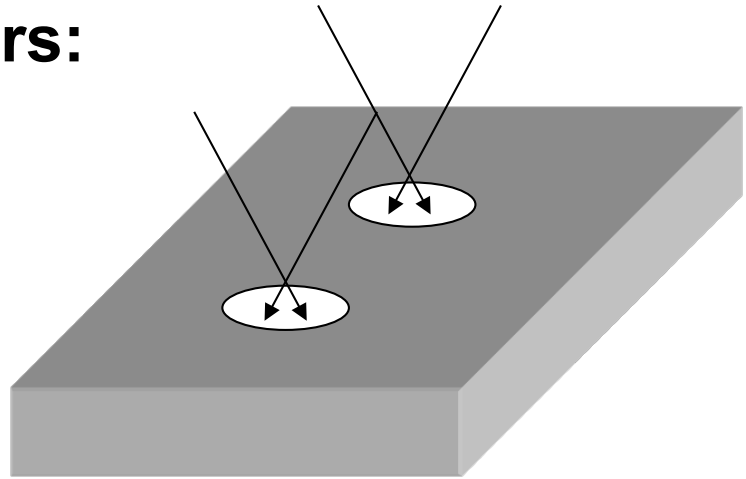
Chains $(Au\text{-}Ag)_n$ or $(Au\text{-}Au\text{-}Ag\text{-}Ag)_m$:







Tetramers:



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- **Progress in R&D;**
- **Summary**

Nanotechnology enables new hydrogen production methods

- More efficient use of diffuse solar energy
- Spill over to solar electricity production
- Potential applications in wind farms, and other renewable sources
- Improvements on cost in traditional methods
- Much applied research needed to bring these new application to economic reality.

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… It seems clear that a creative breakthrough will result from the the intriguing basic research conducted over the last decade in the nanotech area…

…. The countries having access to this PEC technology are likely to form the OPEC of the near future…

U.S. **DOE Energy Efficiency and Renewable Energy (EERE) Home Page: http://www.eere.energy.gov/**

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Gustav Edman

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VETENSKAPSRÅDET
THE SWEDISH RESEARCH COUNCIL

Photo Nano

GÖTEBORGS UNIVERSITET

INNER ERA-NET
Innovative Energy Research

The Northern European Innovative Energy

Research Programme (N-INNER)

”Solar Hydrogen”

THANK YOU FOR YOUR ATTENTION!

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Specific references, part II

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