Fabrication and Application of Micro/Nano Coatings by Convective Assembly

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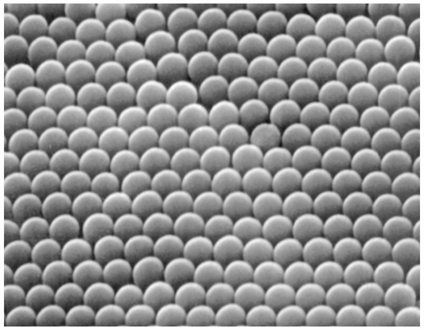
Peter M. Tessier



Colloidal Self-assembly: Problems

- The particles move in chaotic world dominated by Brownian motion and interactions that are often difficult to control
- Defects are nearly omnipresent
- Colloids are not readily compatible with conventional photonic and electronic materials and fabrication processes
- The assembly times are too slow for practical technologies
- The conventional and some unconventional lithographic methods are pretty good and evolve in 3D
- So far, very few practical results have come from the hyped promises

Rationale for research in nanocoating applications

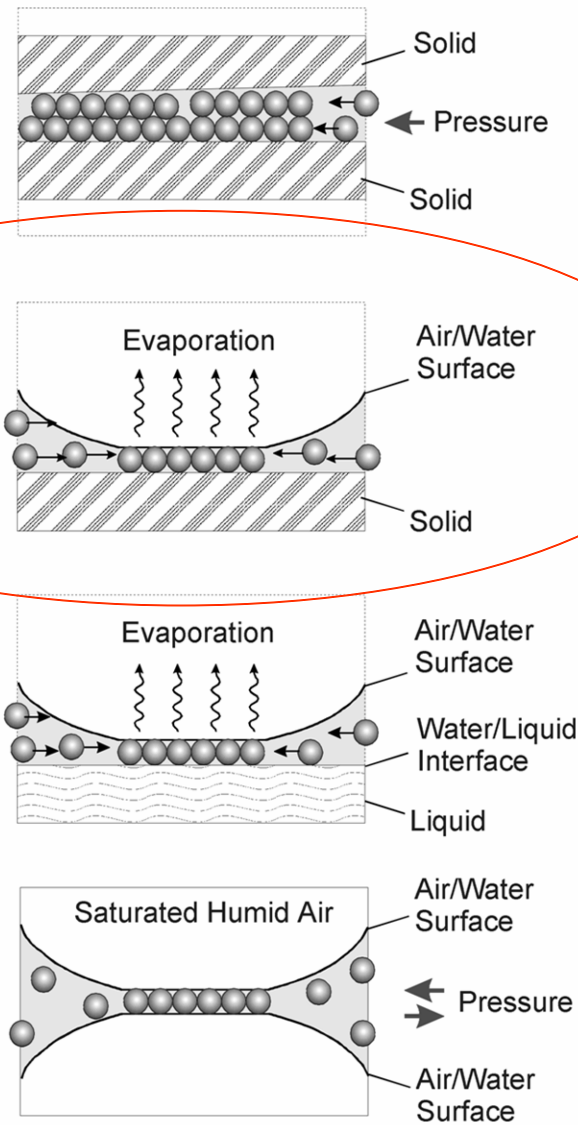
- Forget the full photonic bandgap
- Find simple, cost-effective applications - e.g. large scale coatings
- Find applications where nanoparticle structures work better than microfabricated ones – e.g. SERS substrates
- Look for new functionality

Overview of our research directions

- Antireflective coatings from silica microspheres
- Conductive semitransparent coatings from gold nanoparticles
- Nanomagnetic coatings based on encapsulated ferritin
- Templated hierarchically porous gold substrates for SERS

Colloidal assembly techniques in 2D liquid films

O. Velev, *Chp 3*. Handbook of Surfaces and Interfaces of Materials (2001).



Films between solid plates

Pieranski, *Contemp. Phys.* **24**, 25 (1980).
Park and Xia, *Langmuir* **15**, 266 (1999).

Wetting films on solid surfaces

Denkov, Velev et al., *Nature* **361**, 26 (1993); *Langmuir* **8**, 3183 (1992).
Jiang et al. (Colvin), *Chem. Mater.* **11**, 2132 (1999).

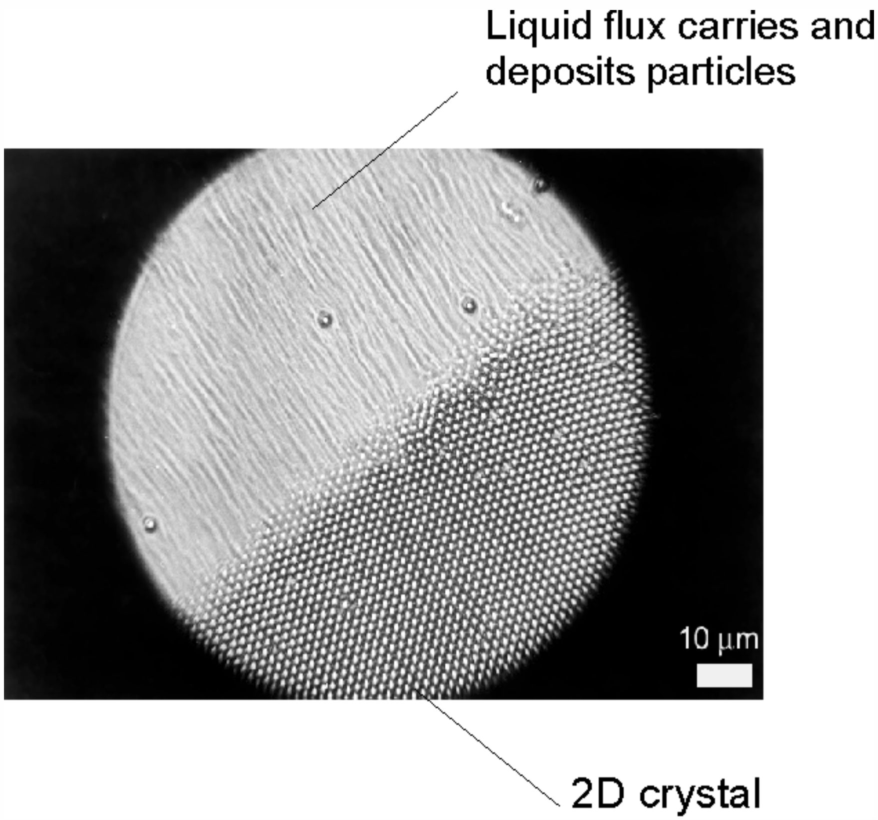
Wetting films on liquid interfaces

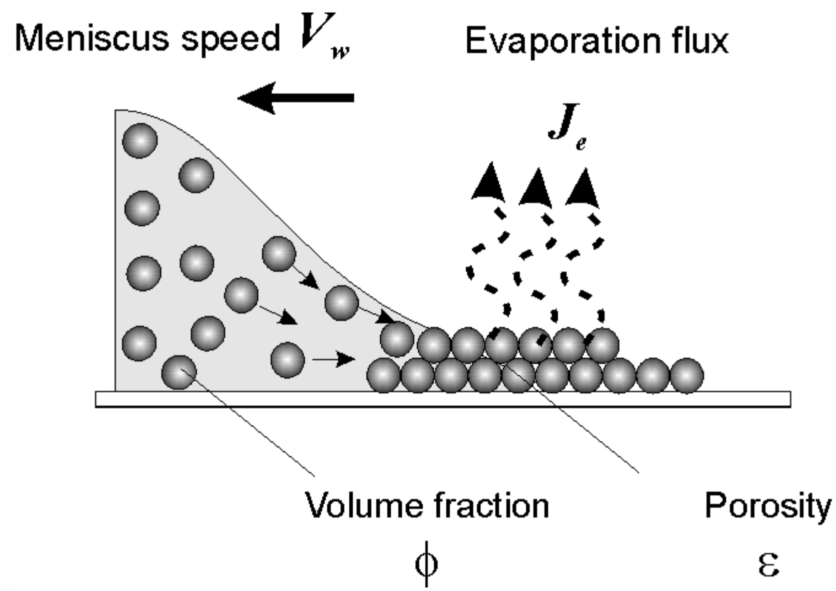
Lazarov et al., *J. Chem. Soc. Faraday Trans.* **90**, 2077 (1994).

Free foam films

Velikov and Velev, *Langmuir* **14**, 1148 (1998).

2D crystallization via convective assembly



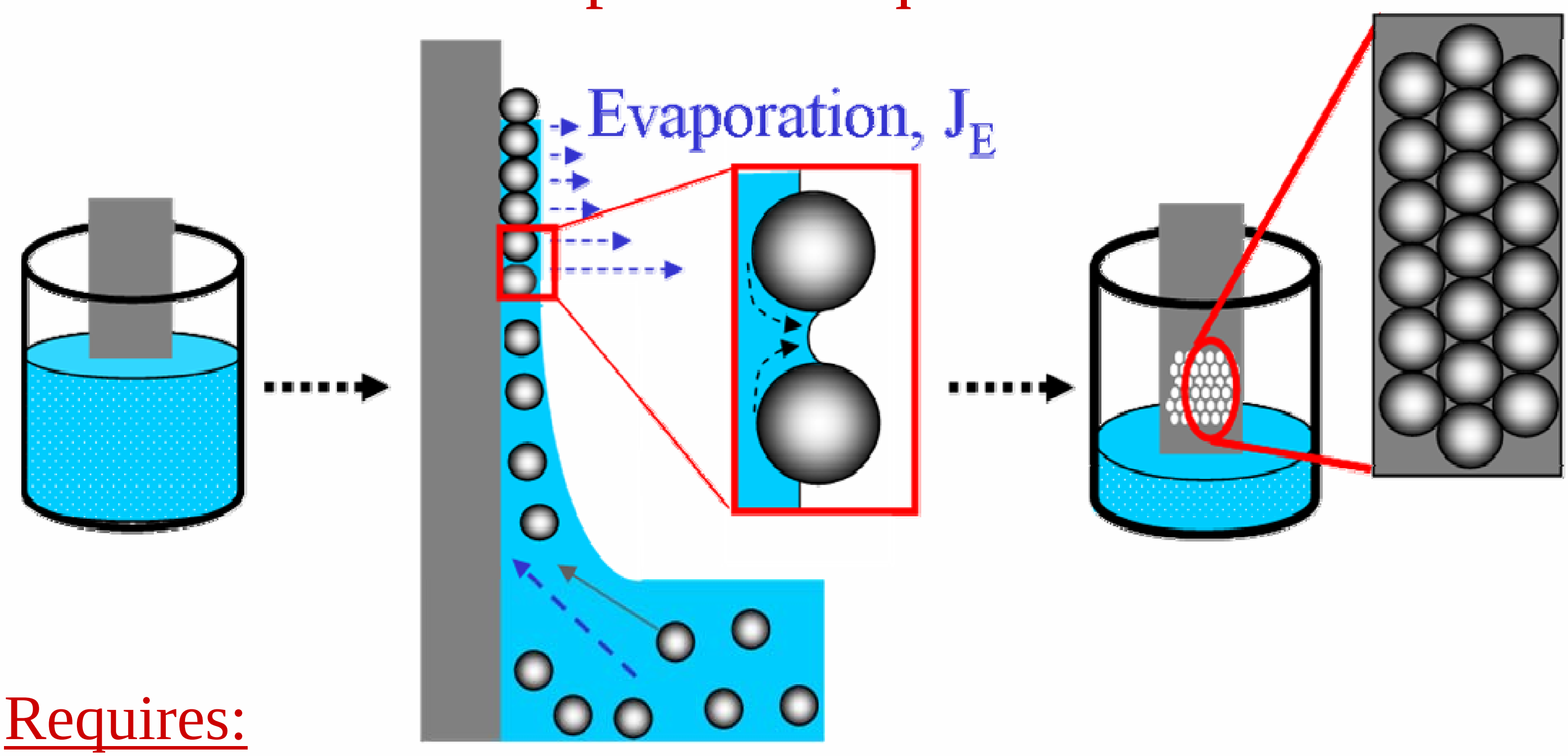


$$V_w = \frac{\beta \; J_e \, \phi}{h_k \,(1-\varepsilon)(1-\phi)}$$

Denkov, Velev et al.,
Nature, **361**, 26 (1993)
Langmuir, **8**, 3183 (1992)

Convective assembly by dip-coating

Common and simple technique



Requires:

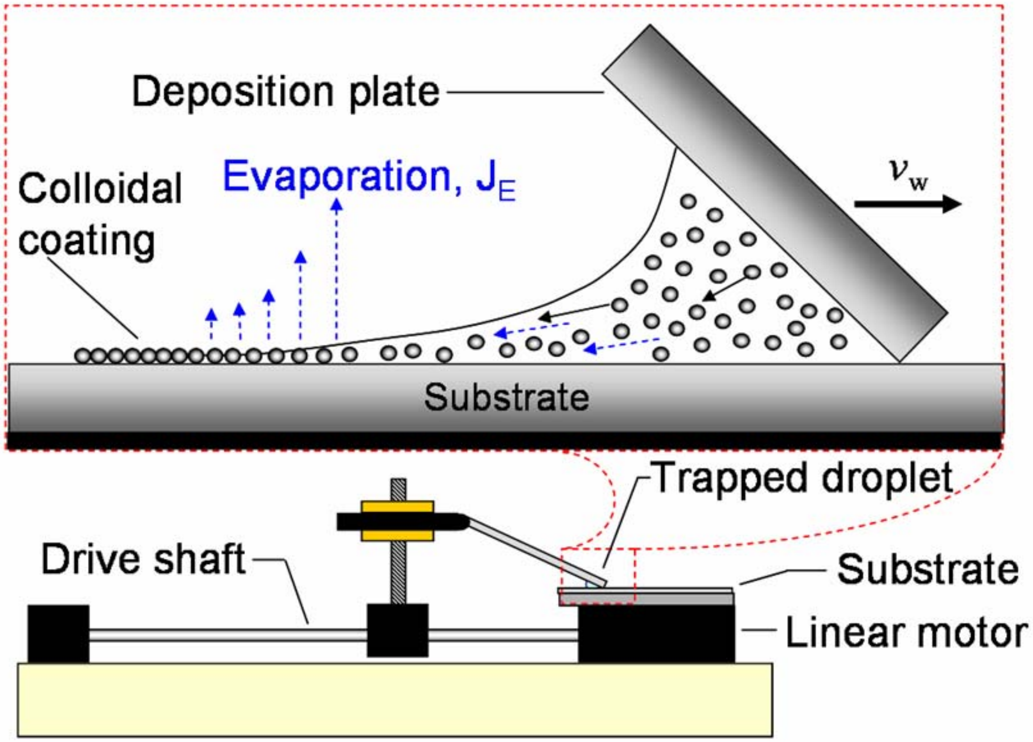
- long times scales
 ~ many hours → days (even weeks)
- large quantities
 (wasteful → coats container too)

Jiang et al. (Colvin), *Chem. Mater.* **11**, 2132 (1999).

Drawbacks & Solutions

Conventional convective assembly limitations	Possible improvements
Slow deposition speeds ~ hours to days	Speed up deposition by working at high vol. fractions
Requires high volumes, and has low efficiency	Conserve volume with new deposition technique
Control is required…	Develop operational process control diagrams
Applied on a case to case basis	Develop generic system for coating any suspension

Rapid deposition of 2D crystal coating of particles
(convective assembly at high volume fractions)



cm² coatings from μL drops in minutes

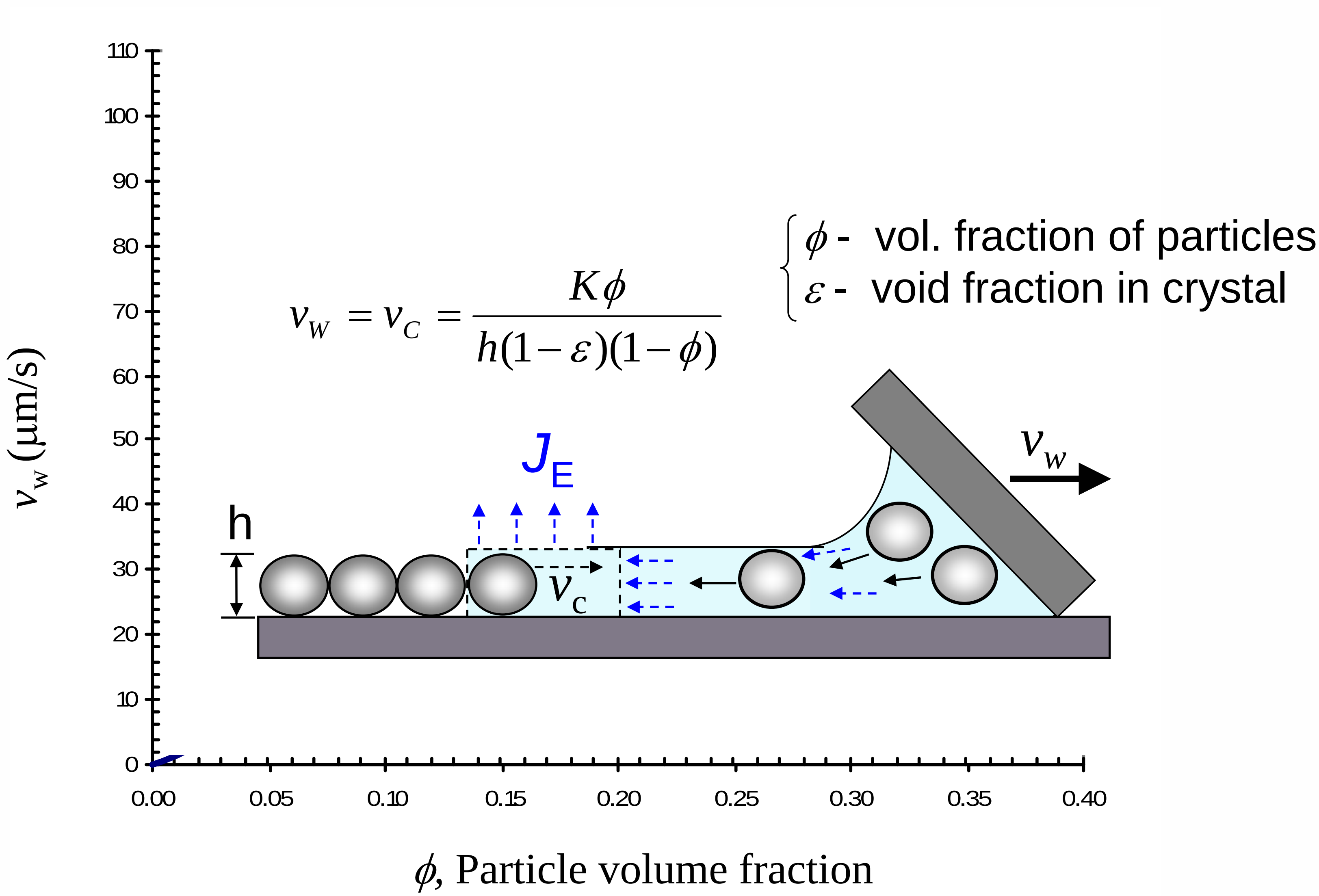
1.1 μm latex crystal viewed with:

- Ambient light

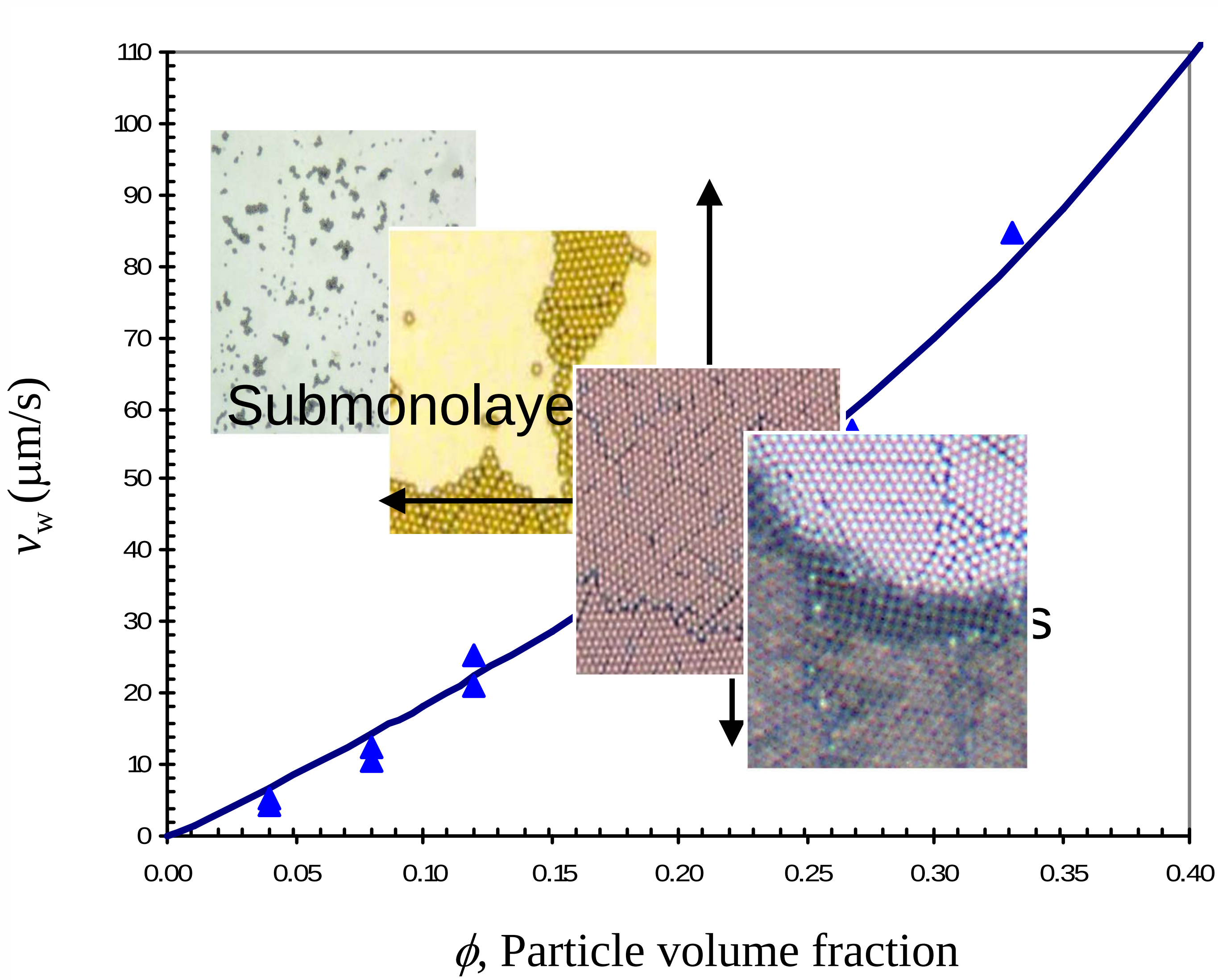
- Low angle Light transmission

1cm

Modeling the process of colloidal crystal film deposition

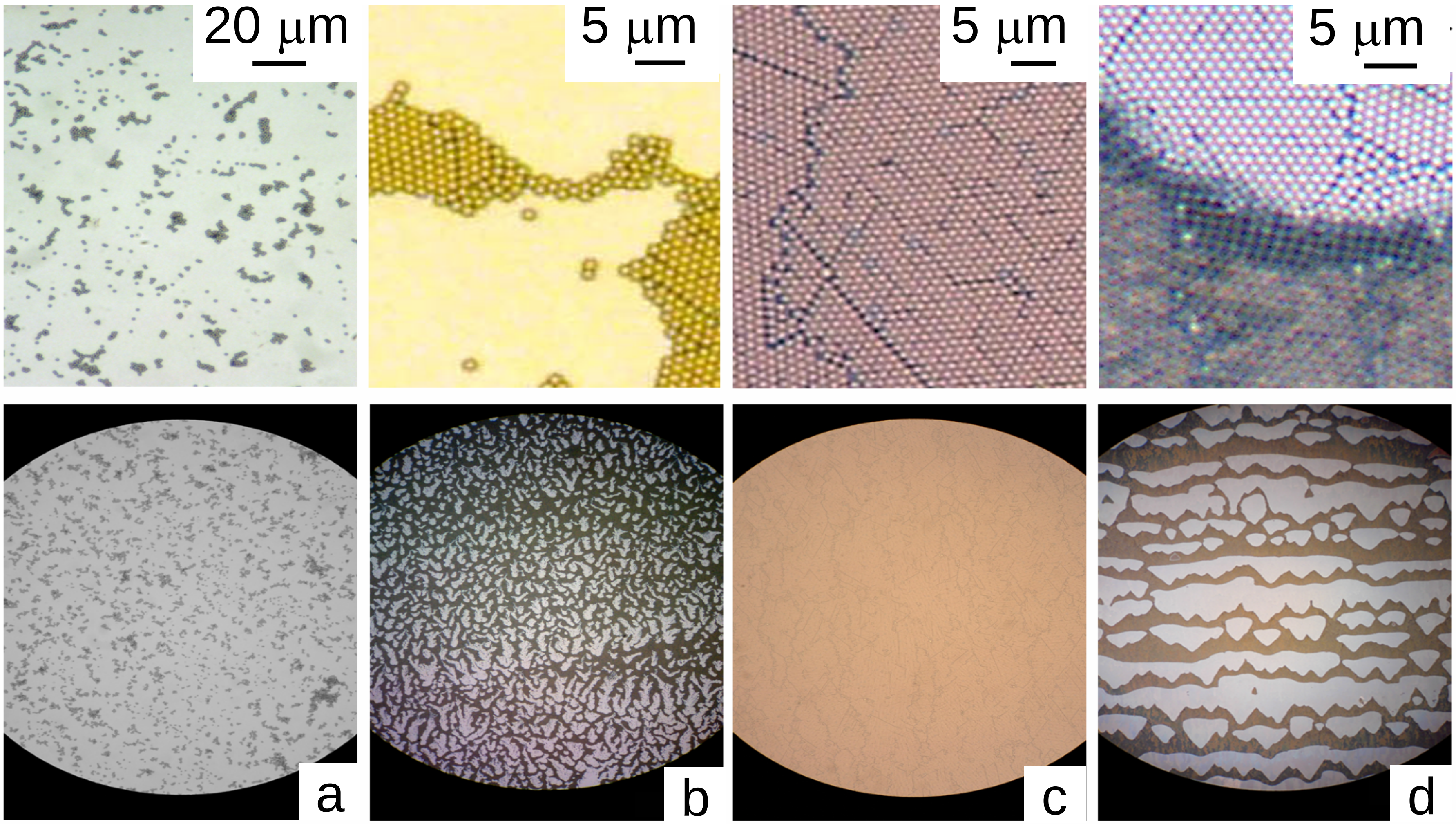


Effect of varying deposition speed and volume fraction

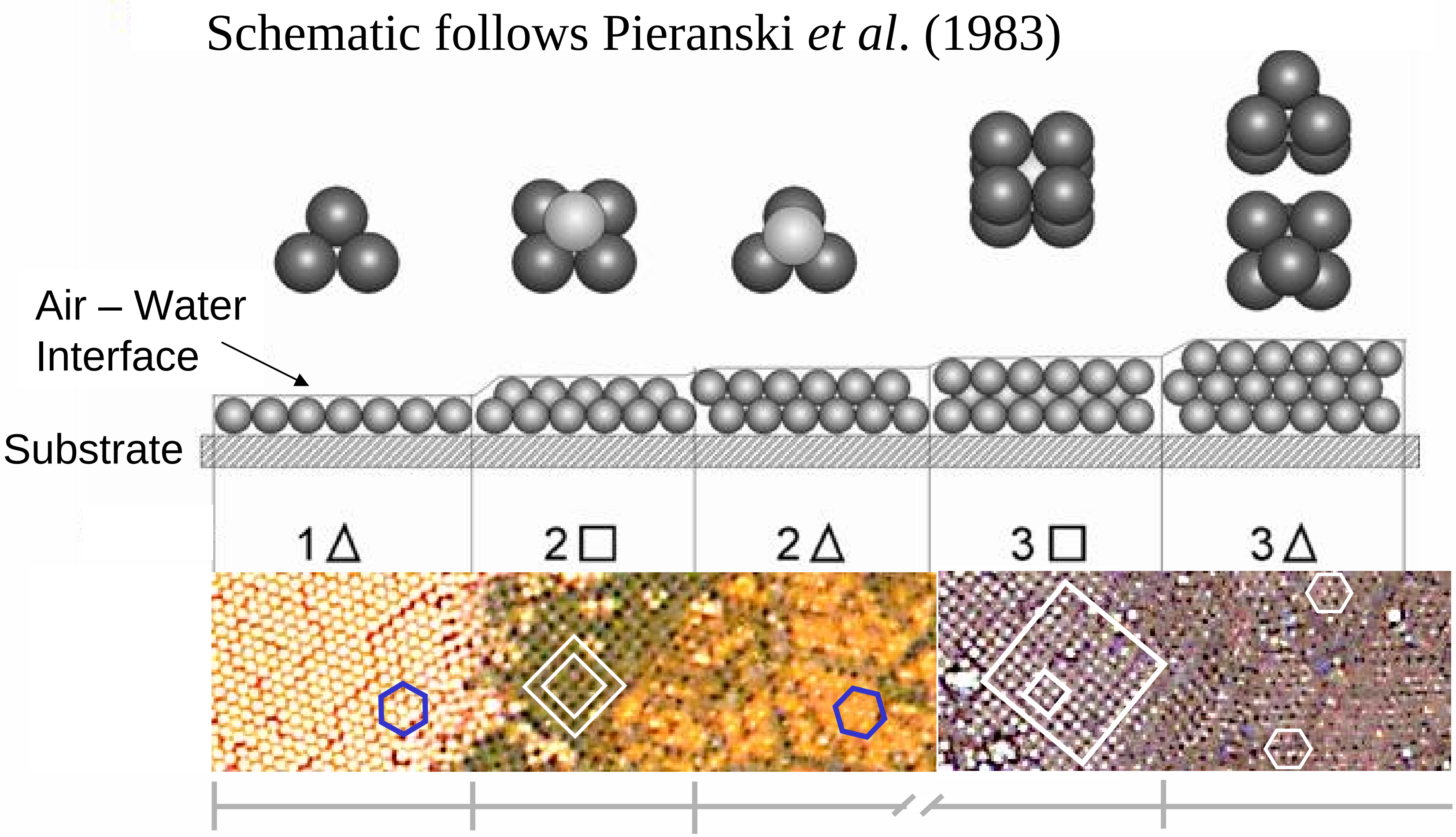


Effect of varying deposition speed

Decreasing deposition speed →

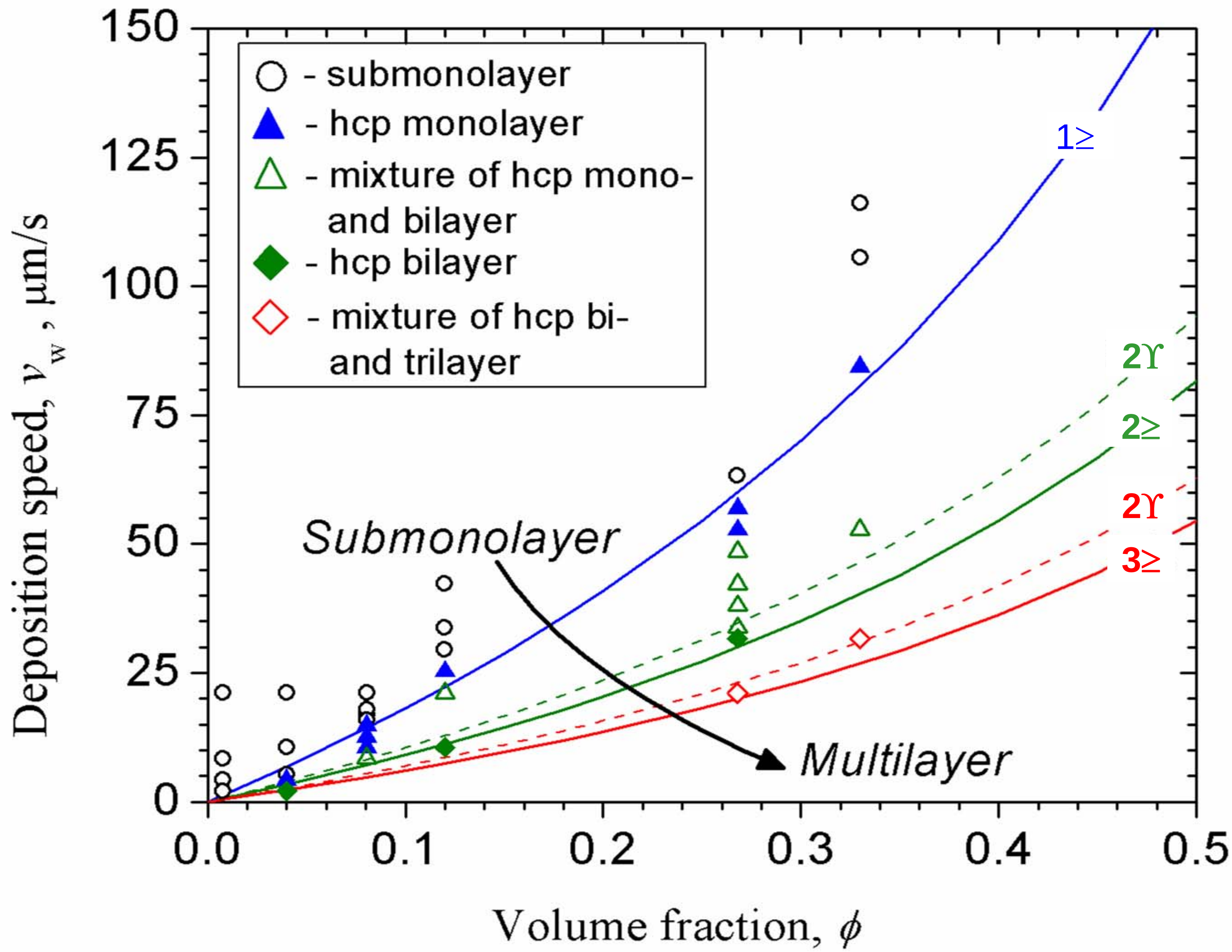


Structural transitions in 2D colloidal crystal films of varying thickness



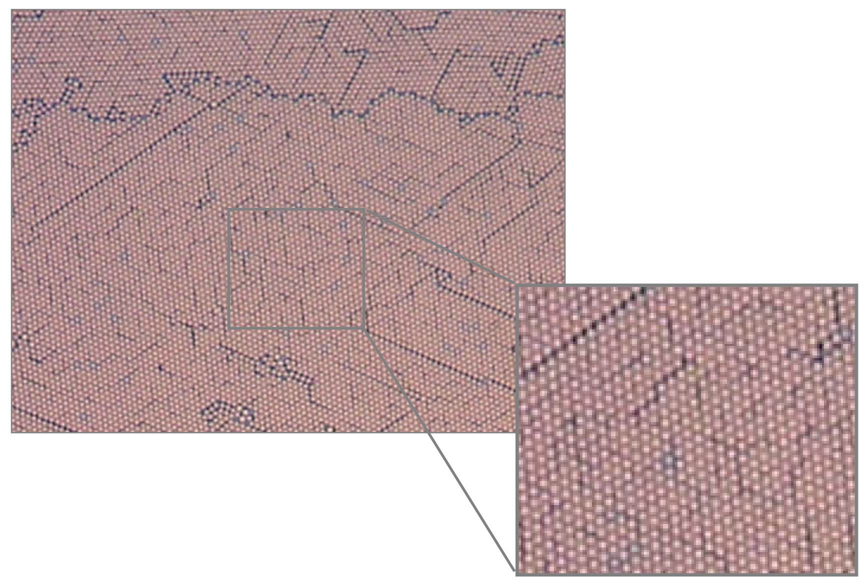
- 1.1μm PS latex microsphere coating data
- Colored polygons are to aid the eye

Process 'phase' diagram for 30% RH



Conclusions from process diagram

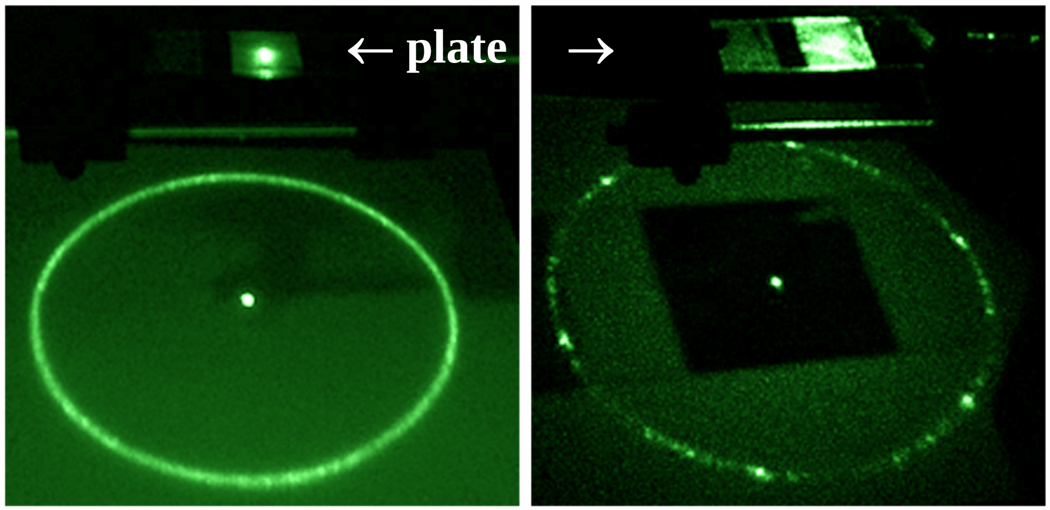
- Process parameters (v_w and ϕ) dictate coating structure and thickness
- ϕ offers better control in sustaining the coating structure
- Cannot coat infinitely fast; limited to $v_w < 150$ μm/s for monolayer
- Best coatings achieved for: $0.10 < \phi < 0.40$
- Slow and difficult to control crystallization beyond 3△



Prevo and Velev, *Langmuir* **20**, 2099 (2004).

Crystal 2D domain symmetry and size via the diffraction pattern

4 mm beam | **150 μm beam**



Von Laue equation for 2D point scatterers

$$h = \frac{n\,\lambda_c}{\sin\theta}$$

Corrected for the refractive index of the composite media

$$\lambda_c = \frac{\lambda_o}{\left(\phi\, n_p^2 + (1-\phi)\, n_w^2\right)^{1/2}}$$

Corrected for refraction on exiting the plate

$$\sin\theta = \frac{n_{cell}}{n_{air}}\sin\theta_{meas}$$

Measured lattice spacing = **939 nm**

Lattice spacing from particle size = **953 nm**

Potential uses for nanocoatings

silica spheres

Photonics and optical

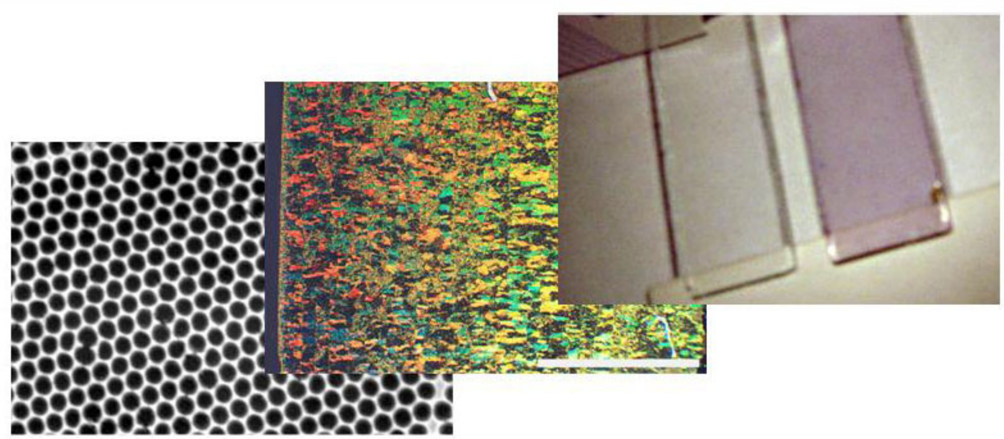
- Light filters and mirrors
- SERS enhancement
- Reflective / Antireflective films
- Energy harvesting
- Decorative materials
- Wave guides

Electronic

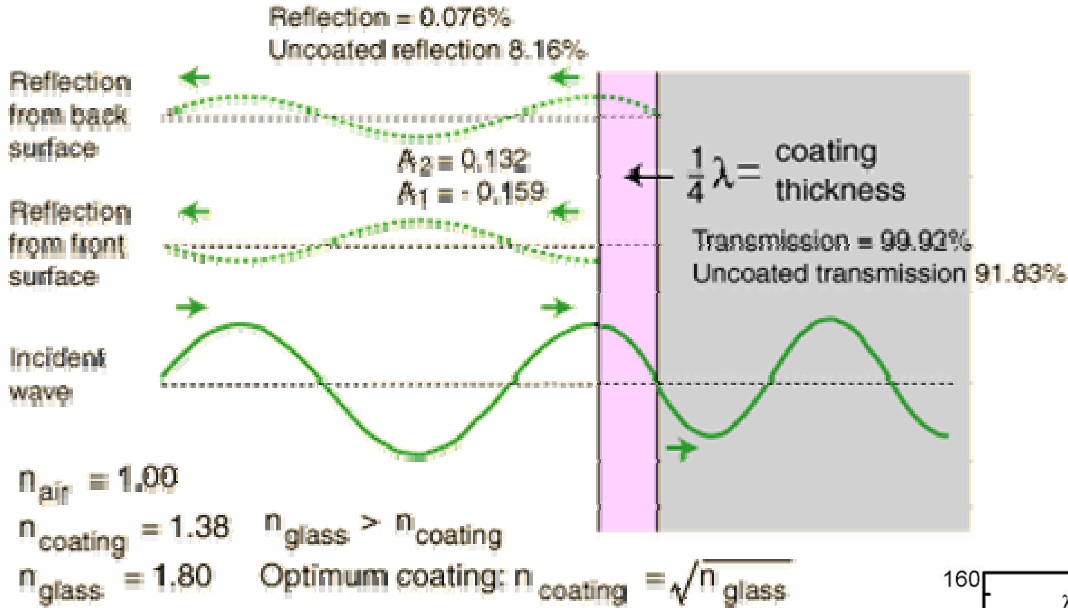
- Vacuum deposition alternative
- Low dielectric materials
- Conductive / semiconductive porous materials
- Non-ohmic switches
- Nanomagnetic coatings

Catalytic

- Uniform micro/nano-porous supports



Dielectric sphere crystal application:
Anti-reflective coatings

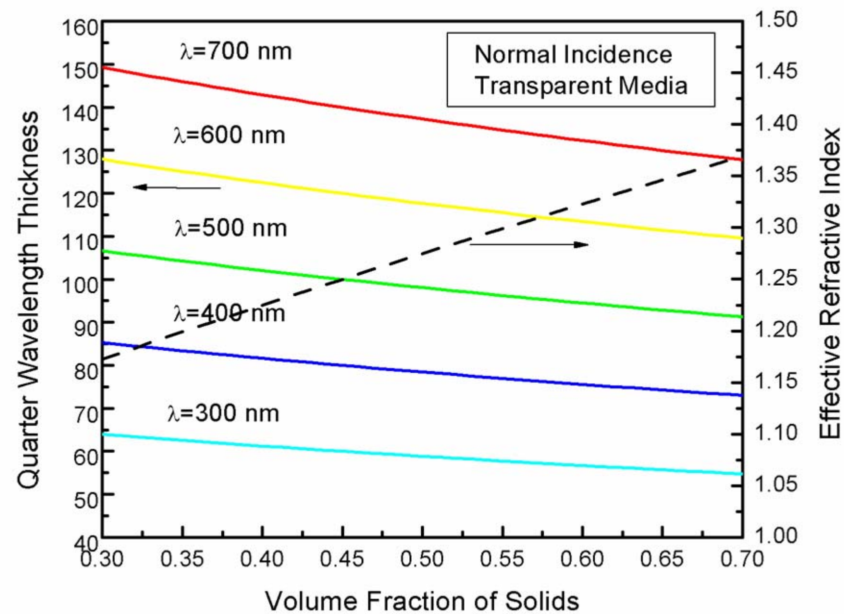


http://hyperphysics.phy-astr.gsu.edu/hbase/phyopt/antiref.html

For plain glass optimal coating refractive index

$n_{eff} \approx 1.25$

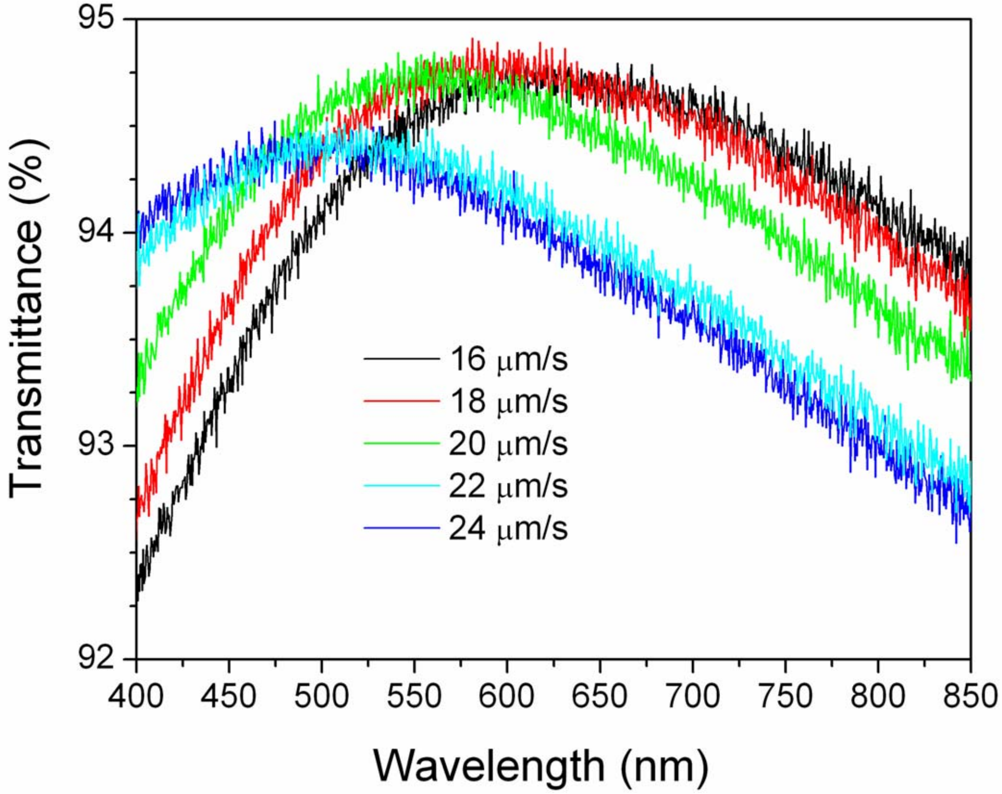
$$n_{eff} = (\phi\, n_p^2 + (1-\phi) n_w^2)^{1/2}$$

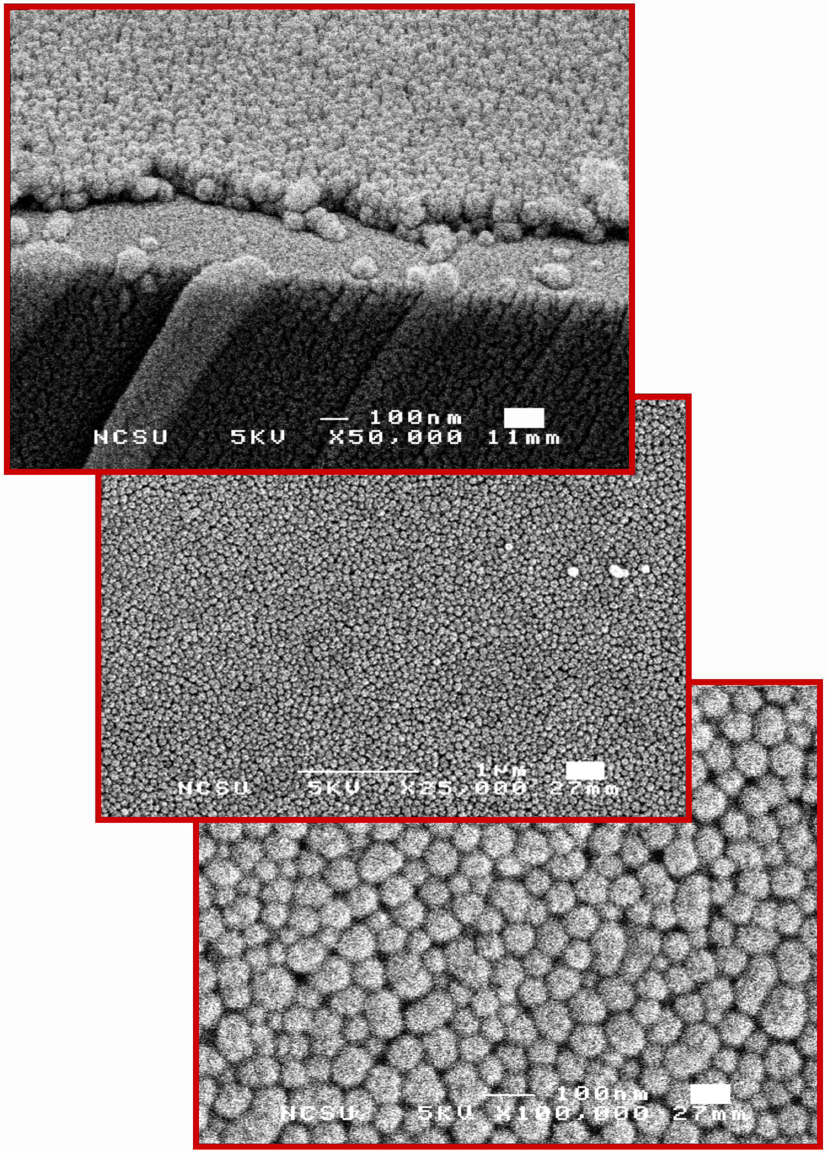


The desired thickness and refractive index of the film can be achieved by using coatings from silica spheres

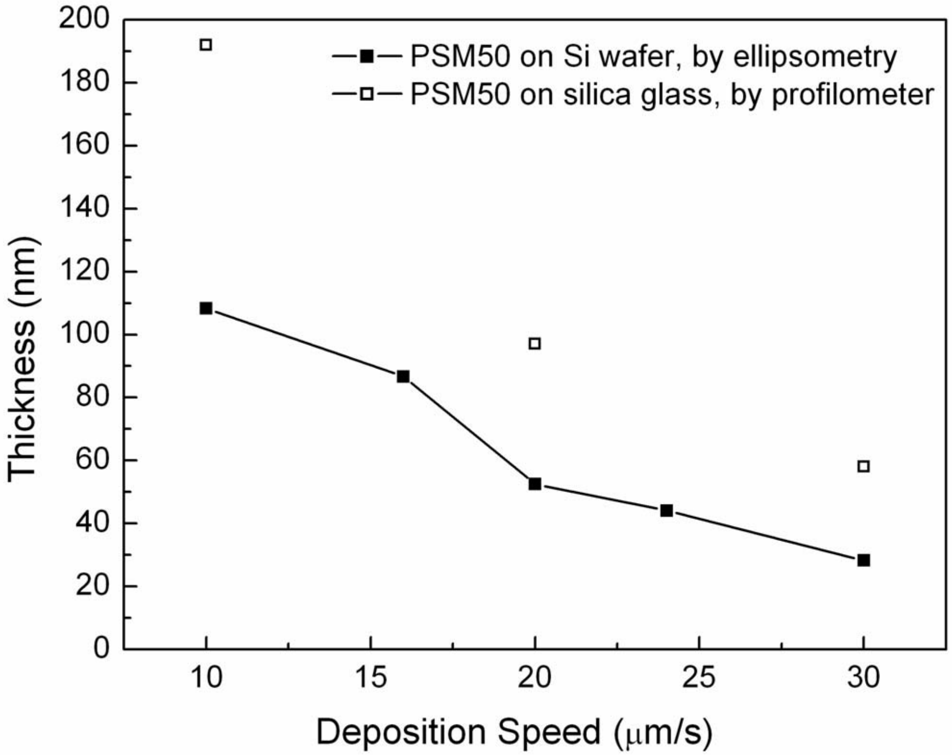
Silica sphere coatings: Transmittance and structure

50 nm silica deposited from
6 % solids (aq) dispersions





Effective silica film thickness measured by ellipsometry and profilometry



- Maxwell Garnett effective media approximation used to obtain film thickness from ellipsometric data
- Layer model: film thickness and volume fraction of particles fitted
- Ellipsometry data yielded filling fractions of 60 – 70% (good correspondence with estimated range)

Antireflection efficiency > 80% of nanocoatings on glass and silicon made by very simple and inexpensive technique

Potential uses for nanocoatings

Au nanoparticles

ferritin

Photonics and optical

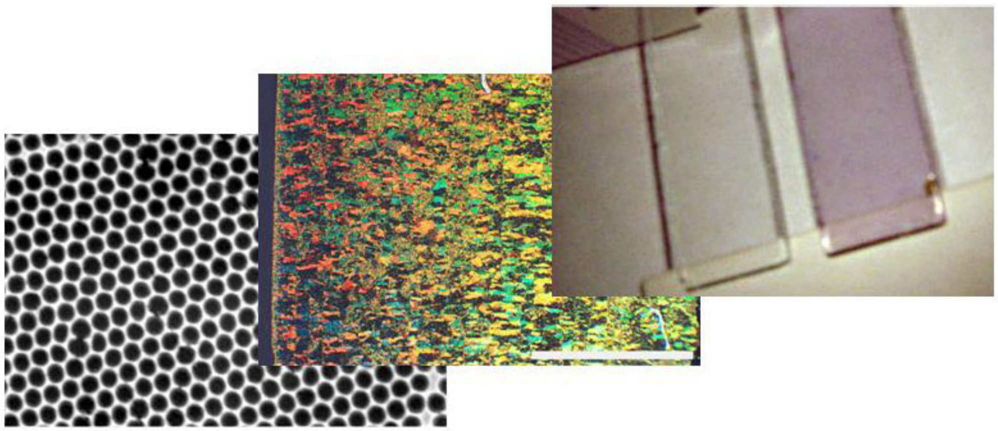
- Light filters and mirrors
- SERS enhancement
- Reflective / Antireflective films
- Energy harvesting
- Decorative materials
- Wave guides

Catalytic

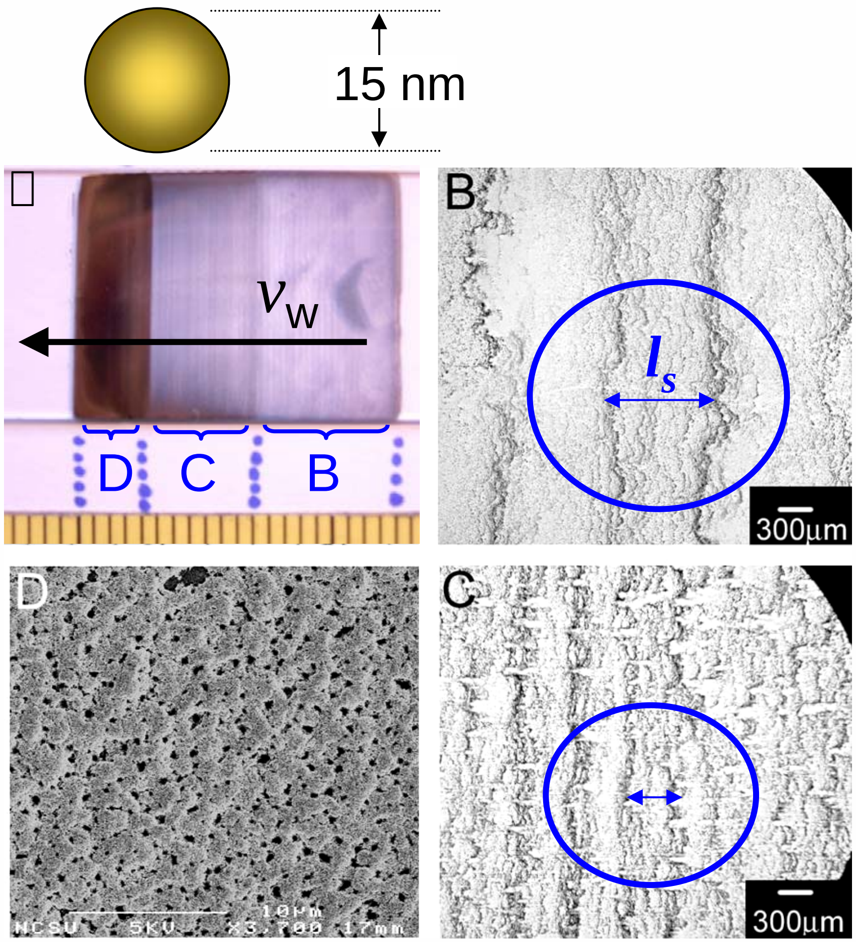
- Uniform micro/nano-porous supports

Electronic

- Vacuum deposition alternative
- Low dielectric materials
- Conductive / semiconductive porous materials
- Non-ohmic switches
- Nanomagnetic coatings



Gold nanoparticle deposition

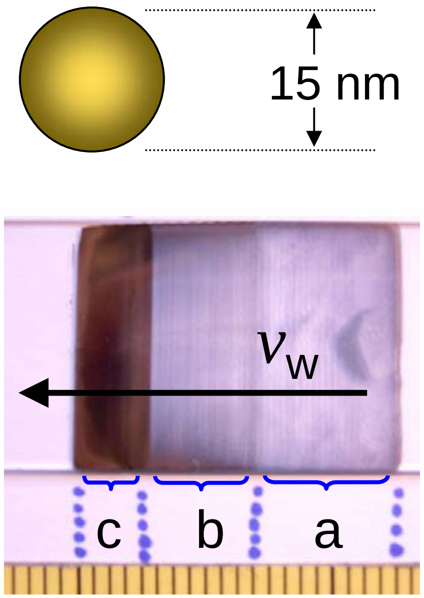


B) 40 μm/s
C) 20 μm/s
D) 4 μm/s

- Deposition technique works for gold nanoparticles
- Deposition speed governs coating surface coverage (v_w decreases for B - D)
- Scaling for submonolayer striping effect:

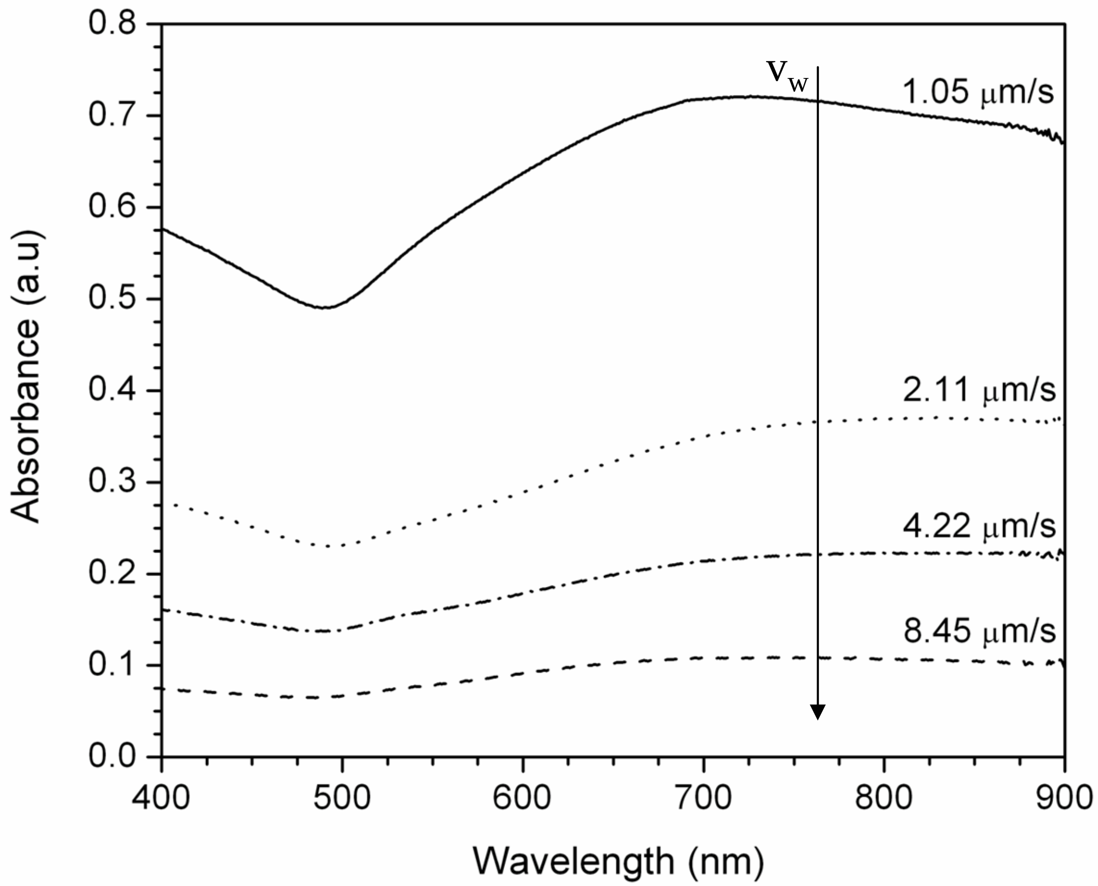
Gold nanoparticle coatings: Optical Density

2-3 wt % gold



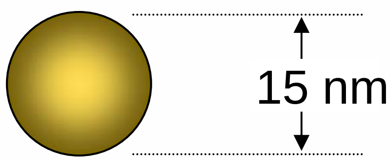
a) 40 μm/s
b) 20 μm/s
c) 4 μm/s

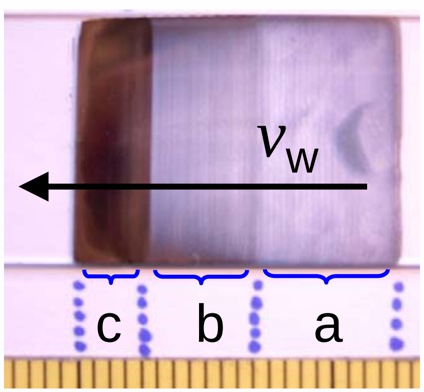
OD controllably changes with deposition speed



Gold nanoparticle coatings: Summary

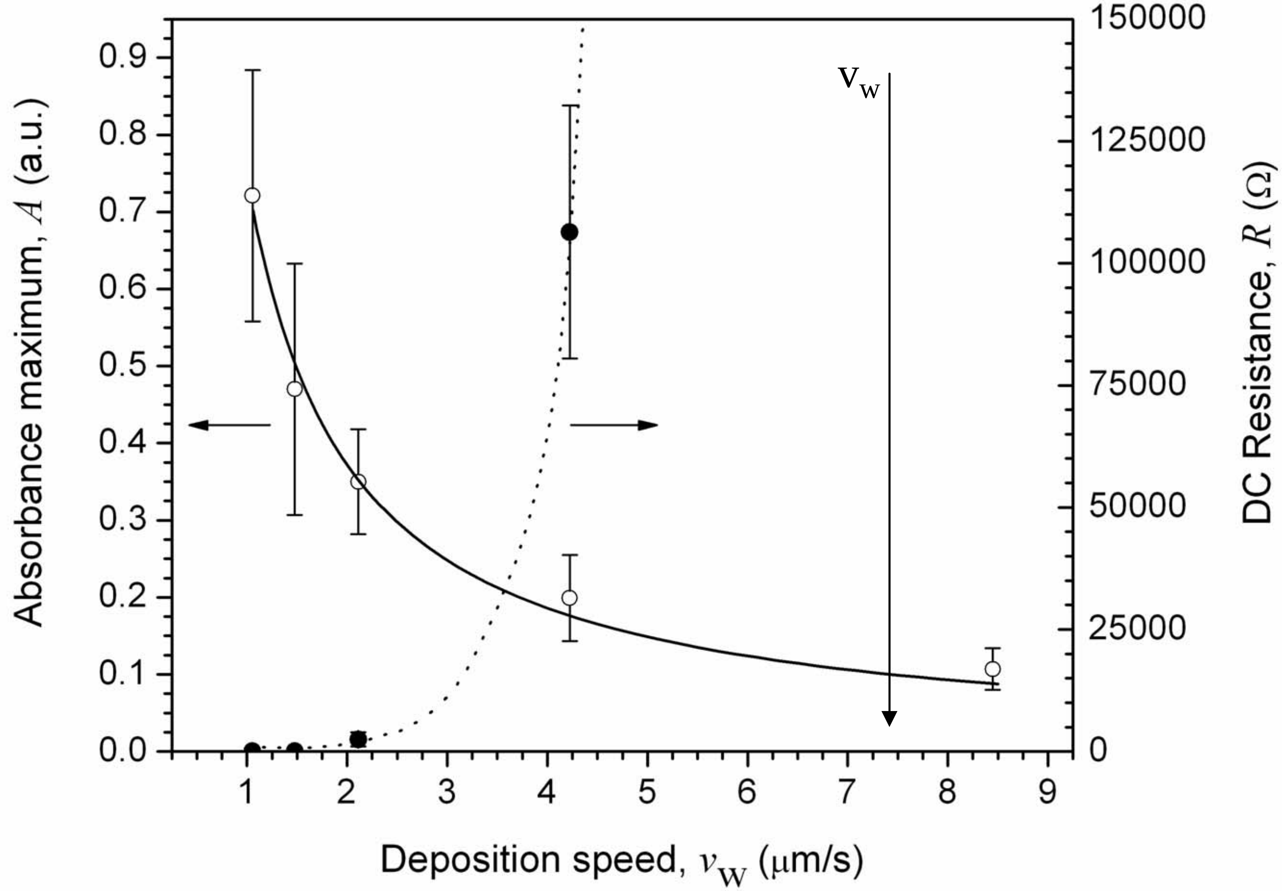
2-3 wt % gold





a) 40 μm/s
b) 20 μm/s
c) 4 μm/s

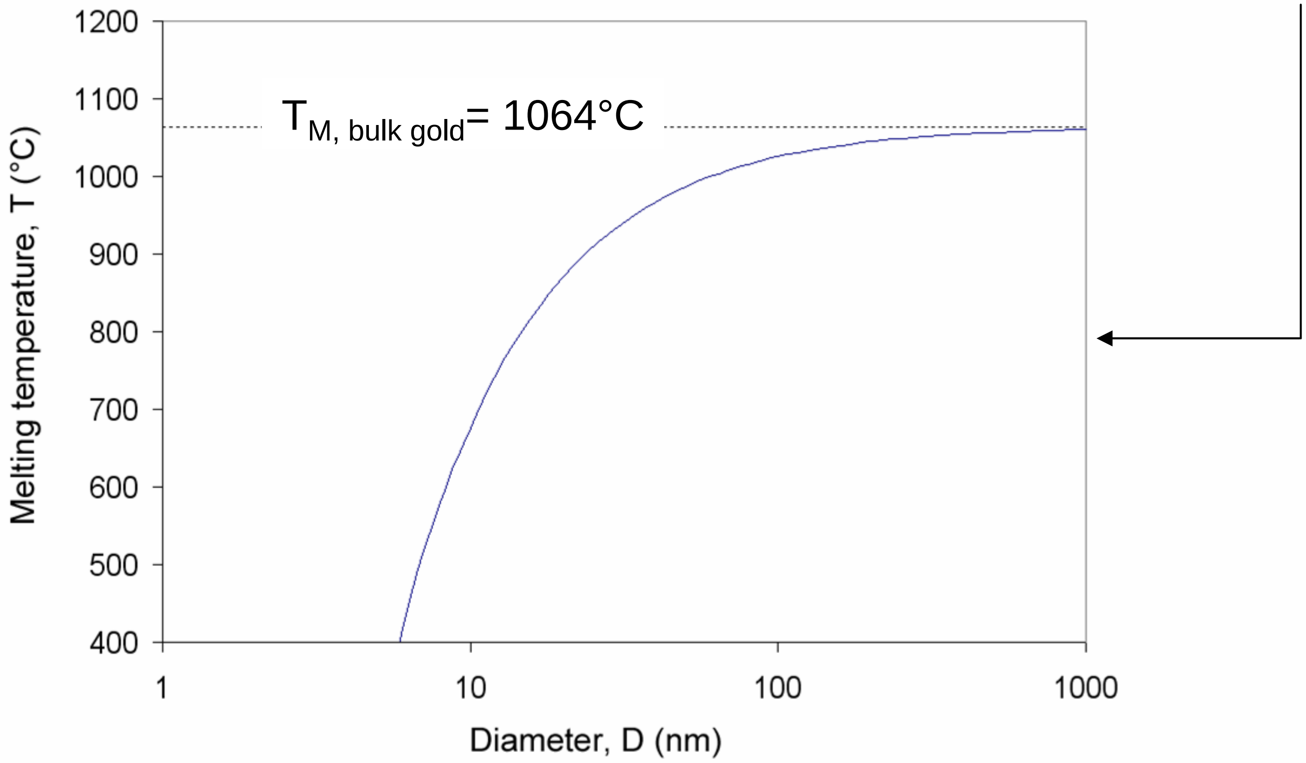
Absorbance scales inversely with deposition speed and is related to electric conductance



Modifying nanocoatings by heat treatment

- Reduced energy requirements for nanocoating processing
- Nanoparticles have lower melting pts. (predicted by Kelvin equation):

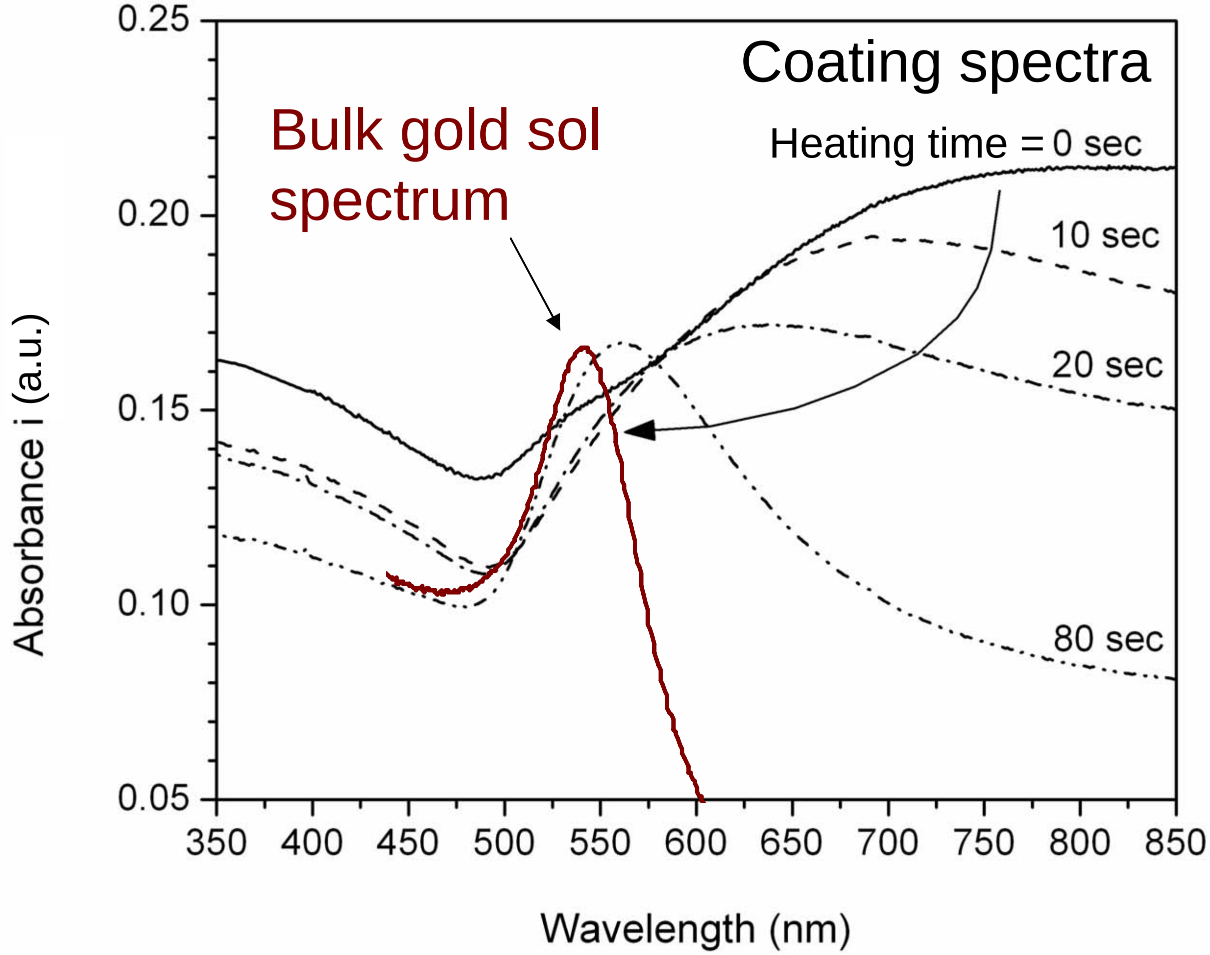
$$\ln \frac{p_r(s)}{p_0(s)} = \frac{2\gamma V_M}{RTr} \xrightarrow{\textit{Pawlow expansion}} T(d) = T_{M,\,bulk}\left(1 - \frac{4}{\rho_s\, d\, \Delta H_M}\left[\gamma_s - \gamma_l\left(\frac{\rho_s}{\rho_l}\right)^{2/3}\right]\right)$$



Thermal modification of gold nanocoatings

Evolution of coating spectra upon heating

- Blue shift saturated out after 2 minutes of heating

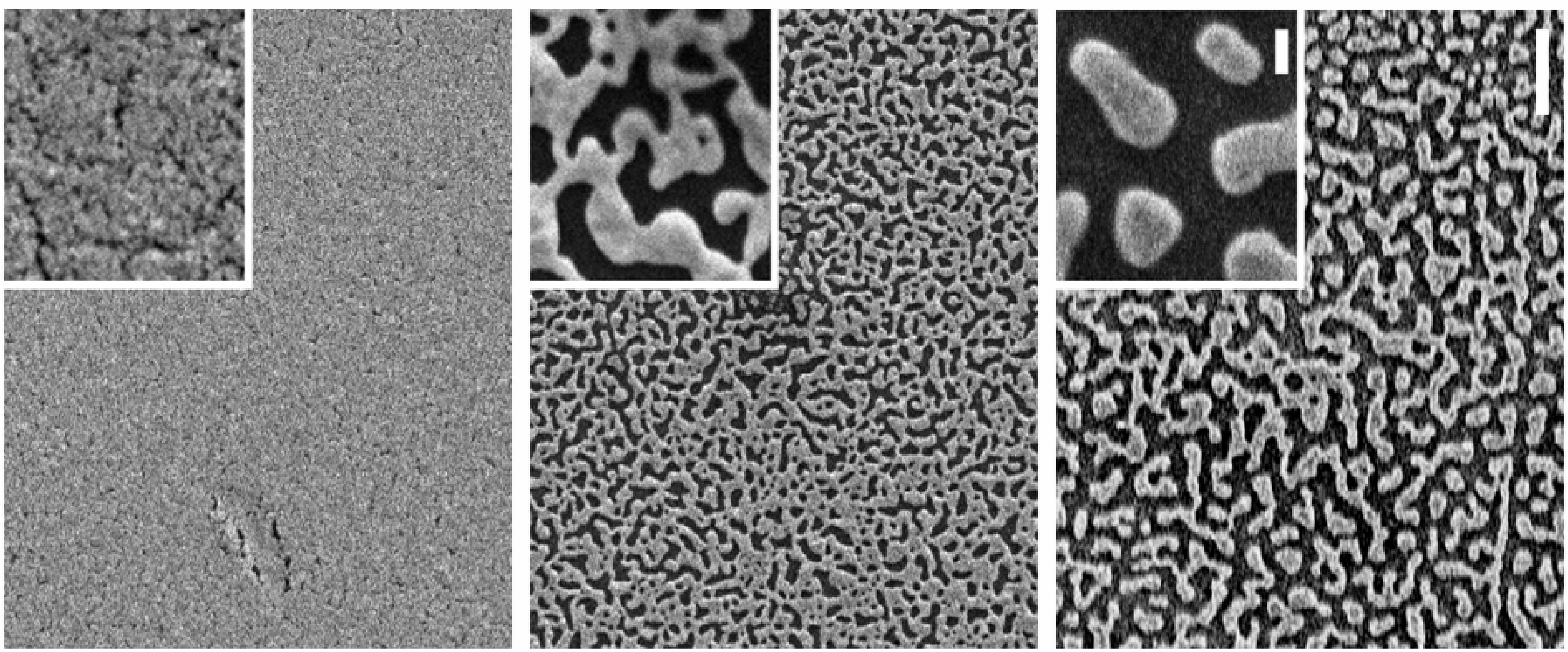


Prevo et al., submitted (2004).

Effect of heating on film structure

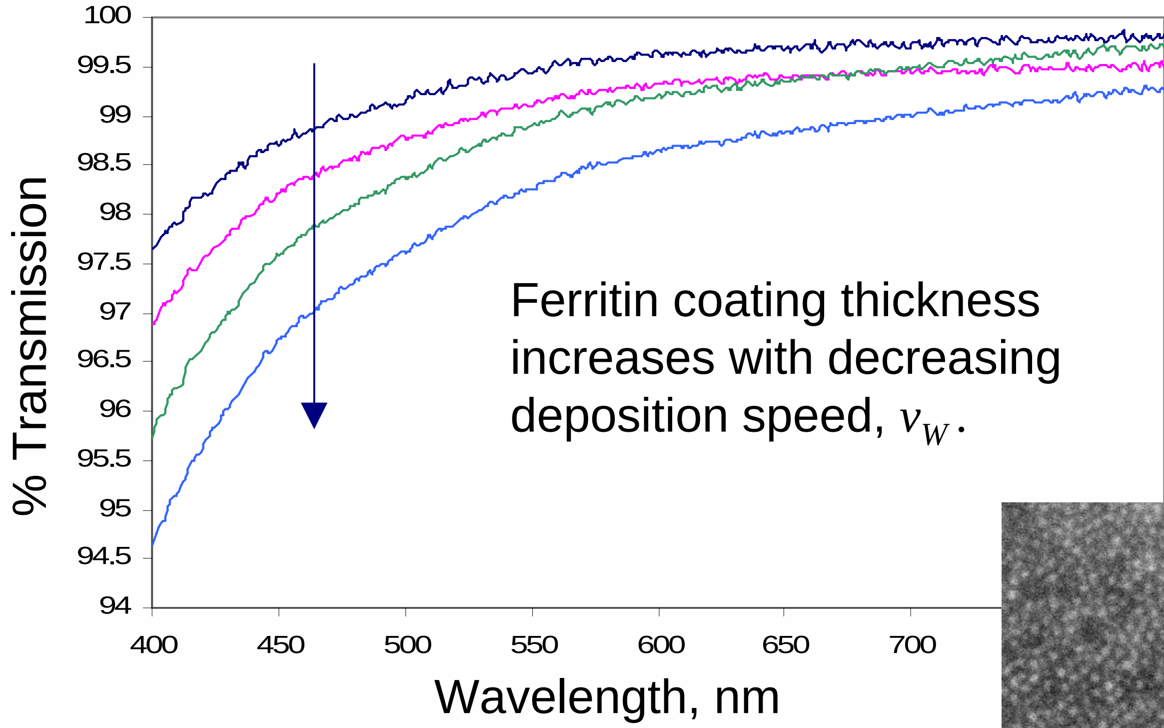
Initial coating composed of inter-connected aggregated nanoparticles

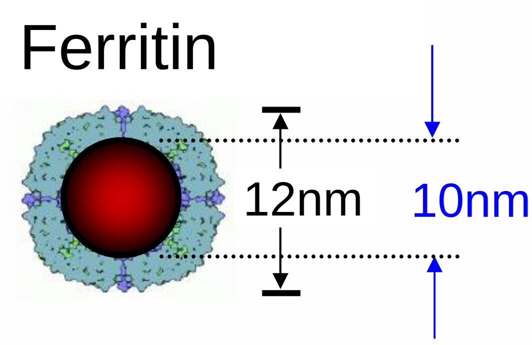
Heating breaks up the network into discontinuous gold islands

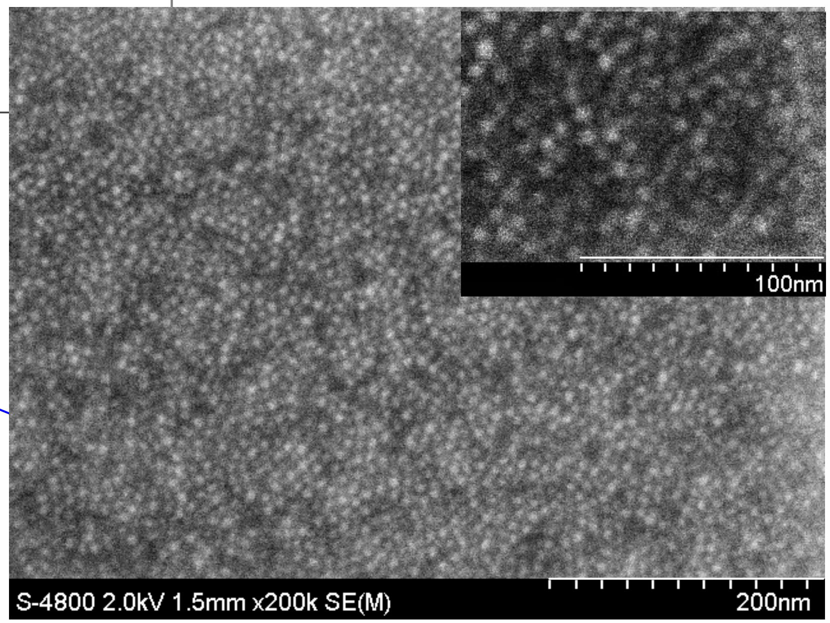


Images obtained via SEM (Large scale = 1μm, inset scale = 100 nm)

Deposition of biomolecule nanocoatings: Ferritin



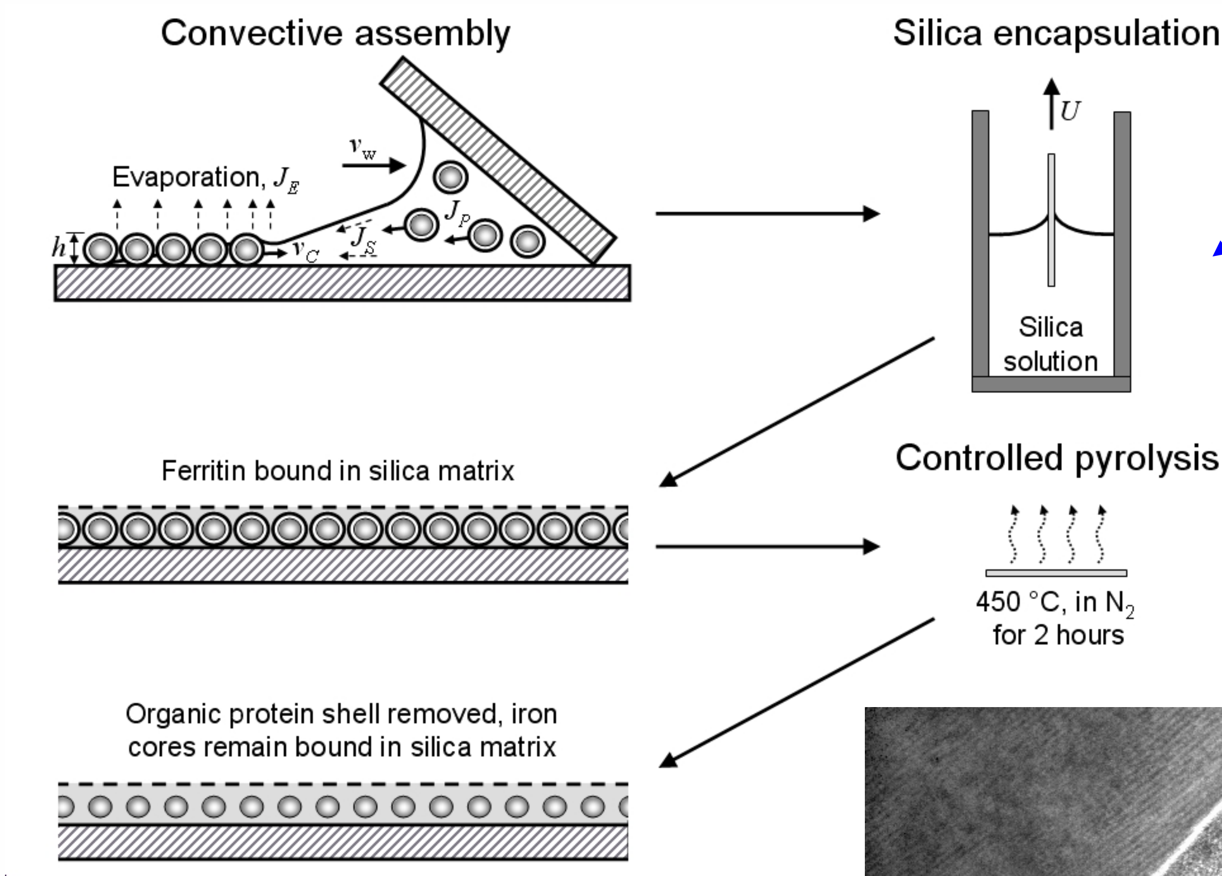




SEM reveals local ordering of ferritin

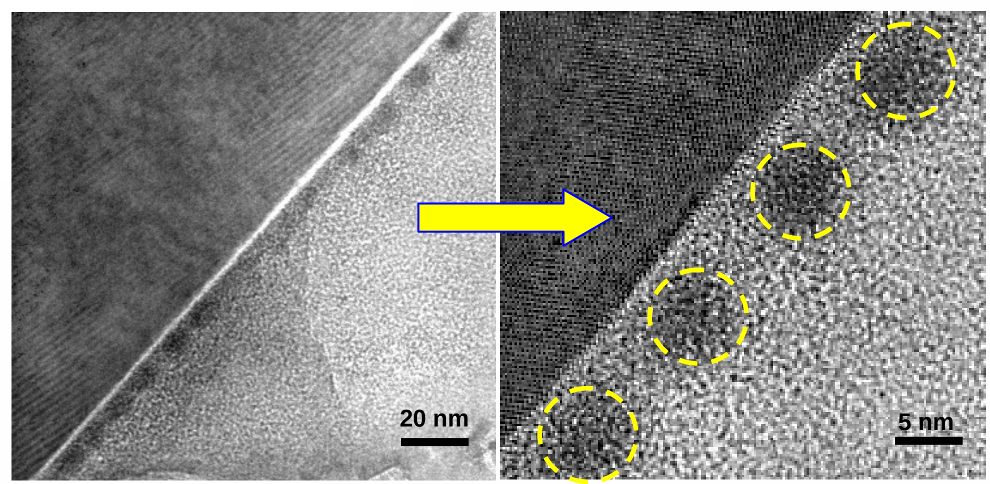
Collaboration with Z. Yuan and P. Atanassov, Univ. of New Mexico

Ferritin nanocoatings: Combining with dip coating to make silica-encapsulated nanomagnets



Combining convective deposition and dip-coating

SEM shows encapsulated ferritin nanomagnet cores



Yuan et al., submitted (2004).

Summary - nanocoatings

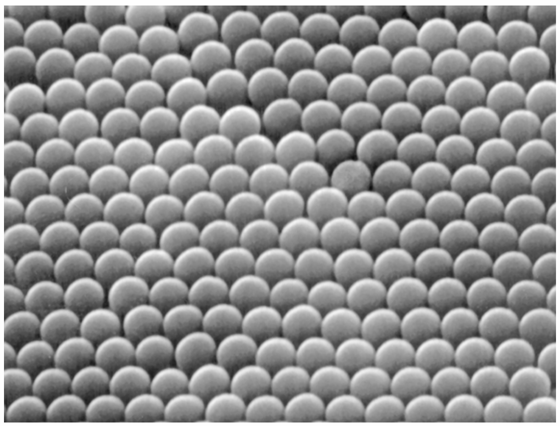
Gold nanocoatings

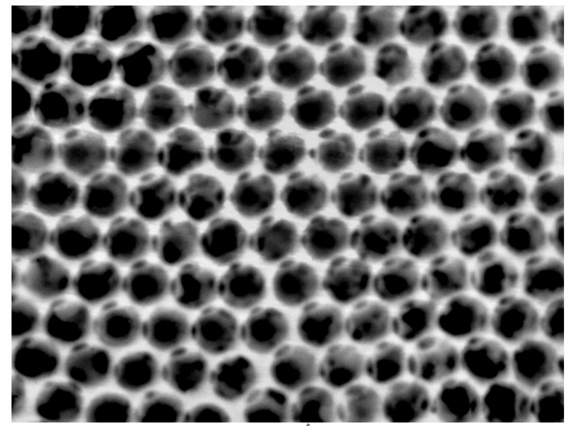
- Simple, rapid & cost effective
- Alternative to CVD
- Semitransparent, controlled reflectance and electric conductivity
- Structure, optical and electronic properties can be additionally modified by heat treatment

Ferritin nanocoatings

- Method works with large protein molecules
- Can be combined with dip-coating
- Solid films of magnetic nanodomains obtained

“Inside-out" templating:
Structured porous materials via colloidal crystals

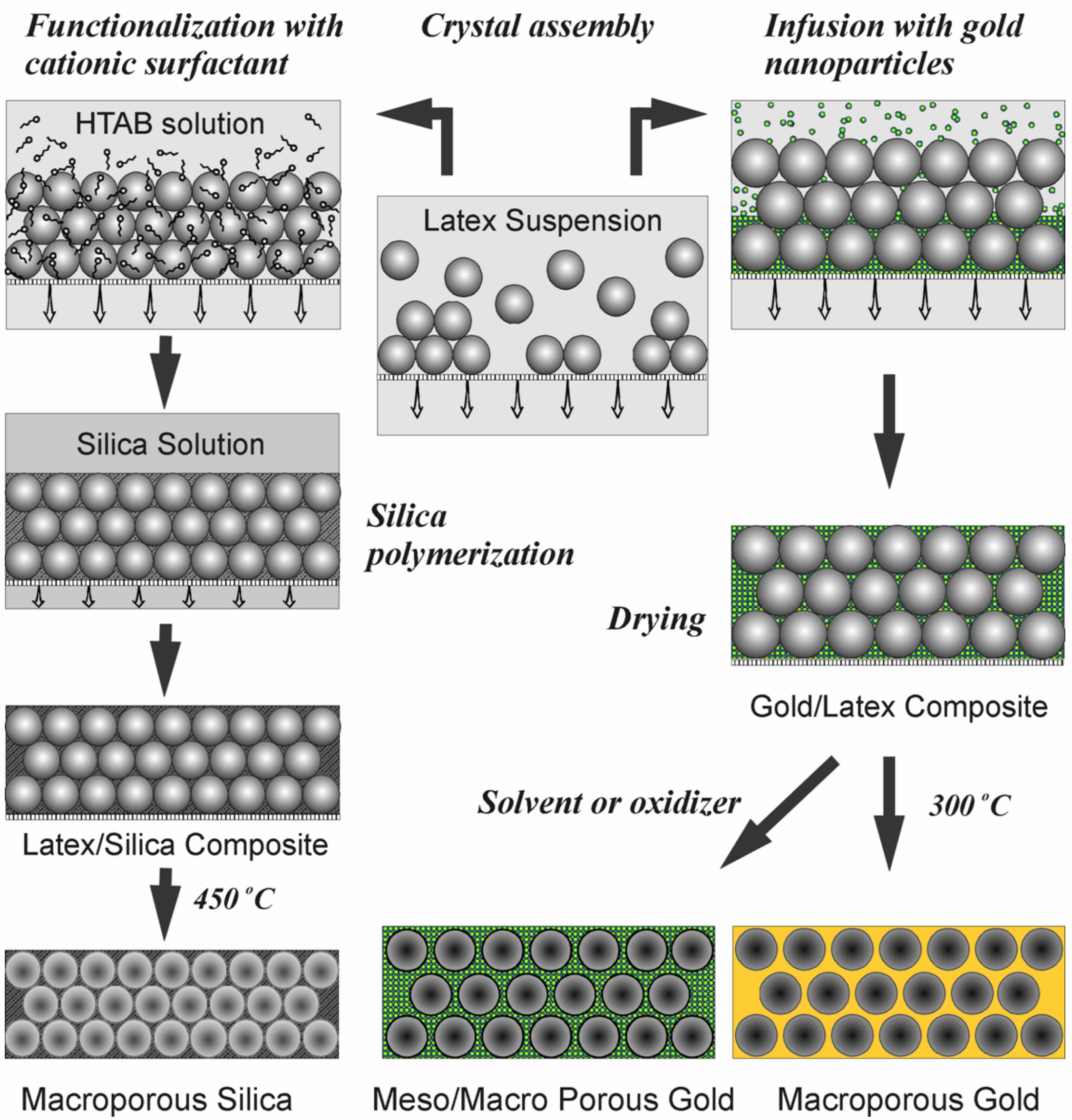




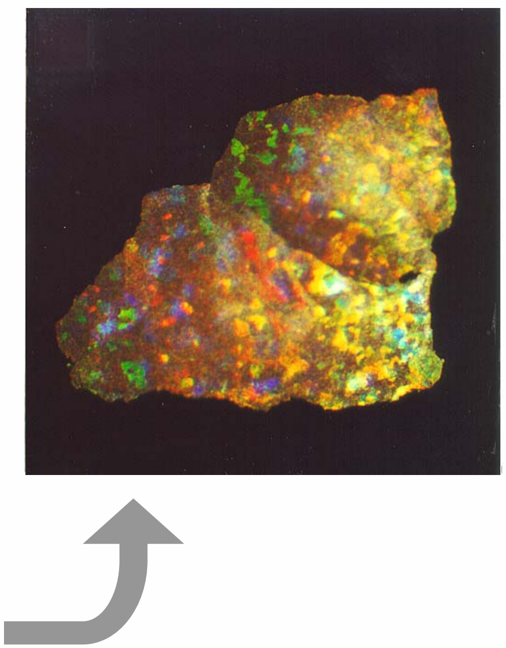
Velev *et al.*
Nature, **389**, 447 (1997).

“Inverse opals”: A full photonic bandgap material ….. at n ≥ 3

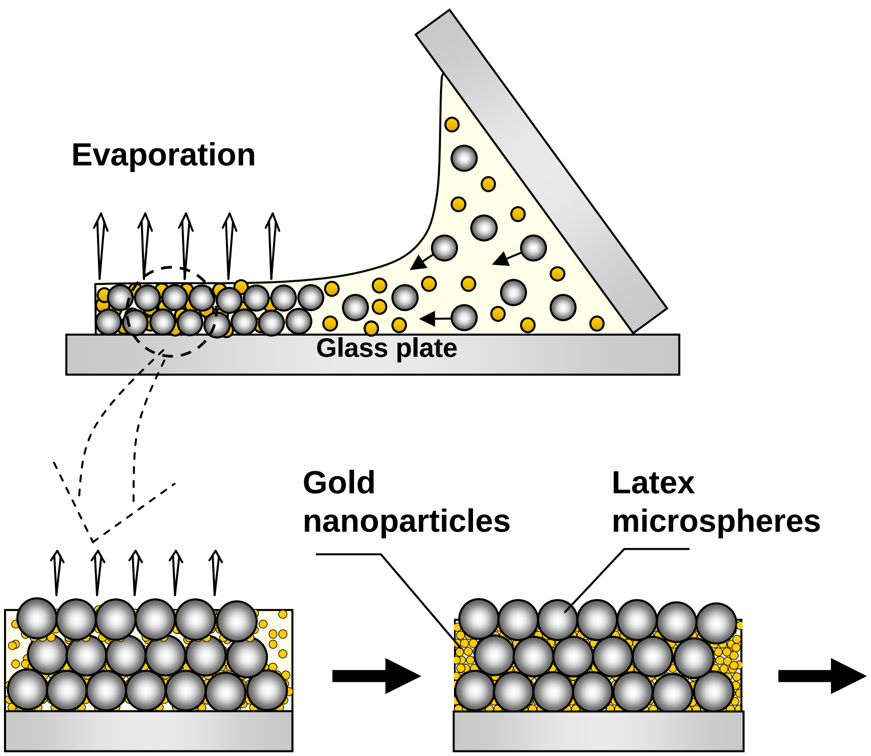
Examples of how the "replication" of crystals works



Velev *et al.*
Nature, **389**, 447 (1997).
Nature, **401**, 548 (1999).
Adv. Mater., **12**, 531 (2000).



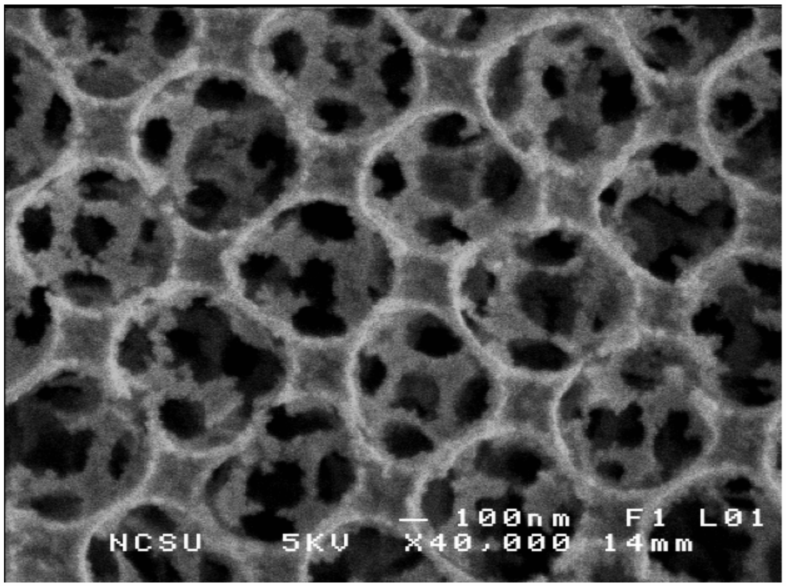
“Inside-out" templating:
Structured metallic films via colloidal crystals



Single-step deposition

Porosity on two length scales

1. Aggregated Au nanoparticles (~12 nm)
2. Aggregated latex microspheres (650 nm)

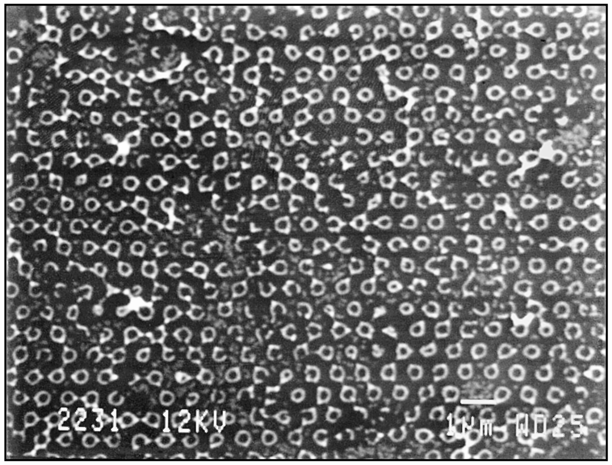


Nanostructured gold film (SEM)

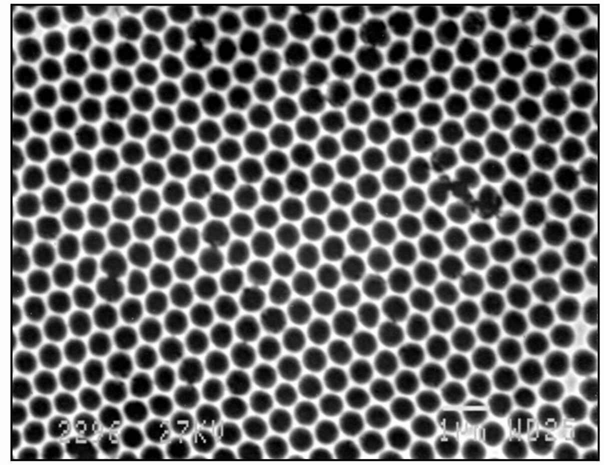
Velev et al.,
J. Am. Chem. Soc., **122**, 9554 (2000).
Adv. Mater, **13**, 396 (2001).

"Inside-out" templating:
Structured metallic films via colloidal crystals

Gold submonolayer

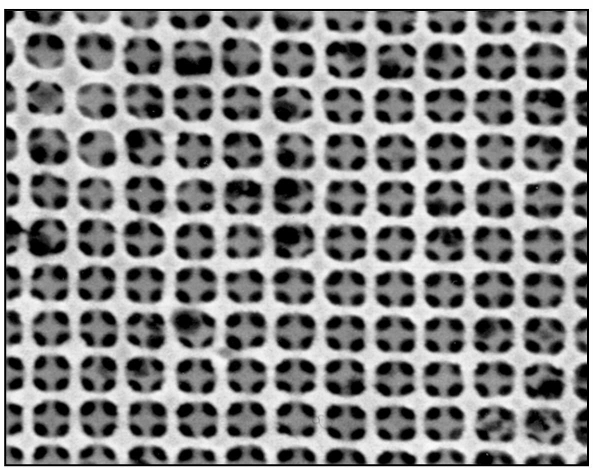


Gold monolayer

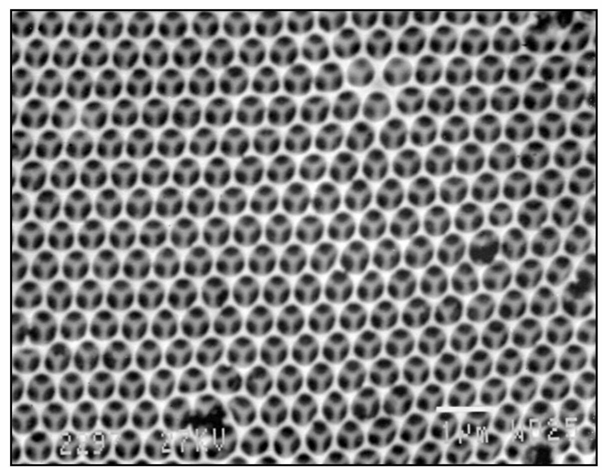


1 μm

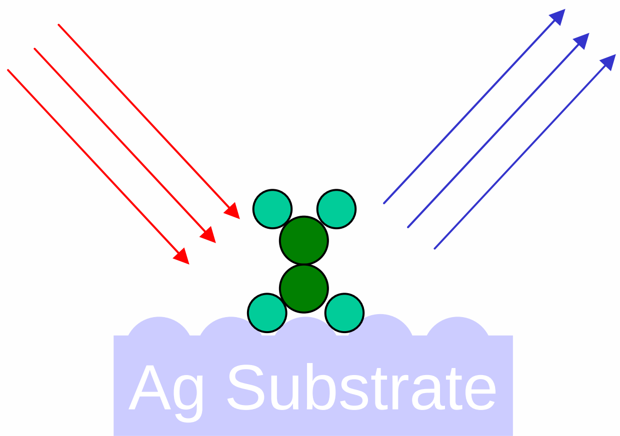
Square bilayer

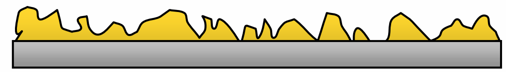


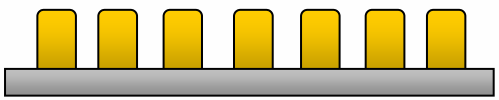
Hexagonal bilayer

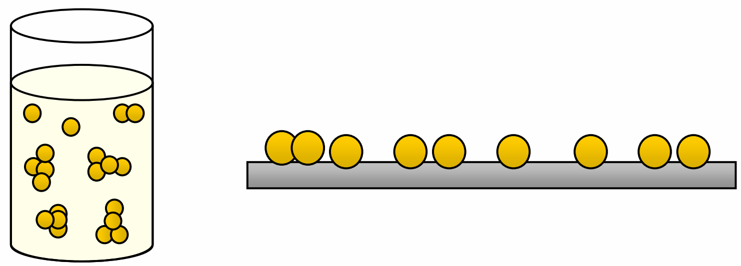


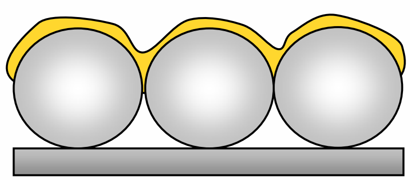
Surface Enhanced Raman Scattering (SERS):
Interfacing photonics with chemistry

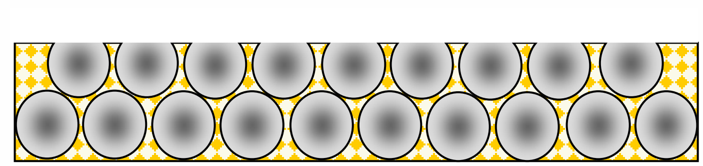



Electrochemically roughened metal

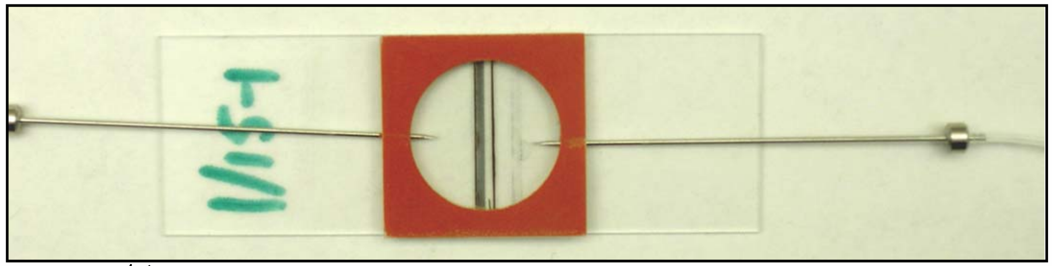

Microfabricated metal structures

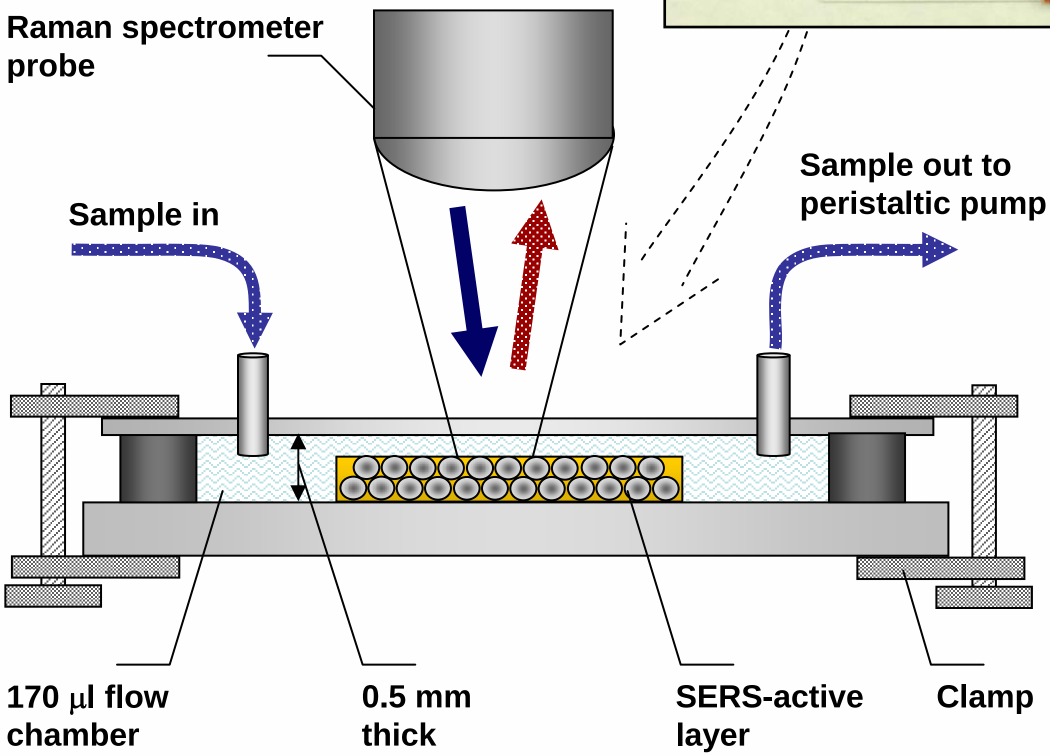

Nanoparticles in solution or on substrates


Metal deposition on microspheres


Au nanoparticles templated by 3D colloidal crystals

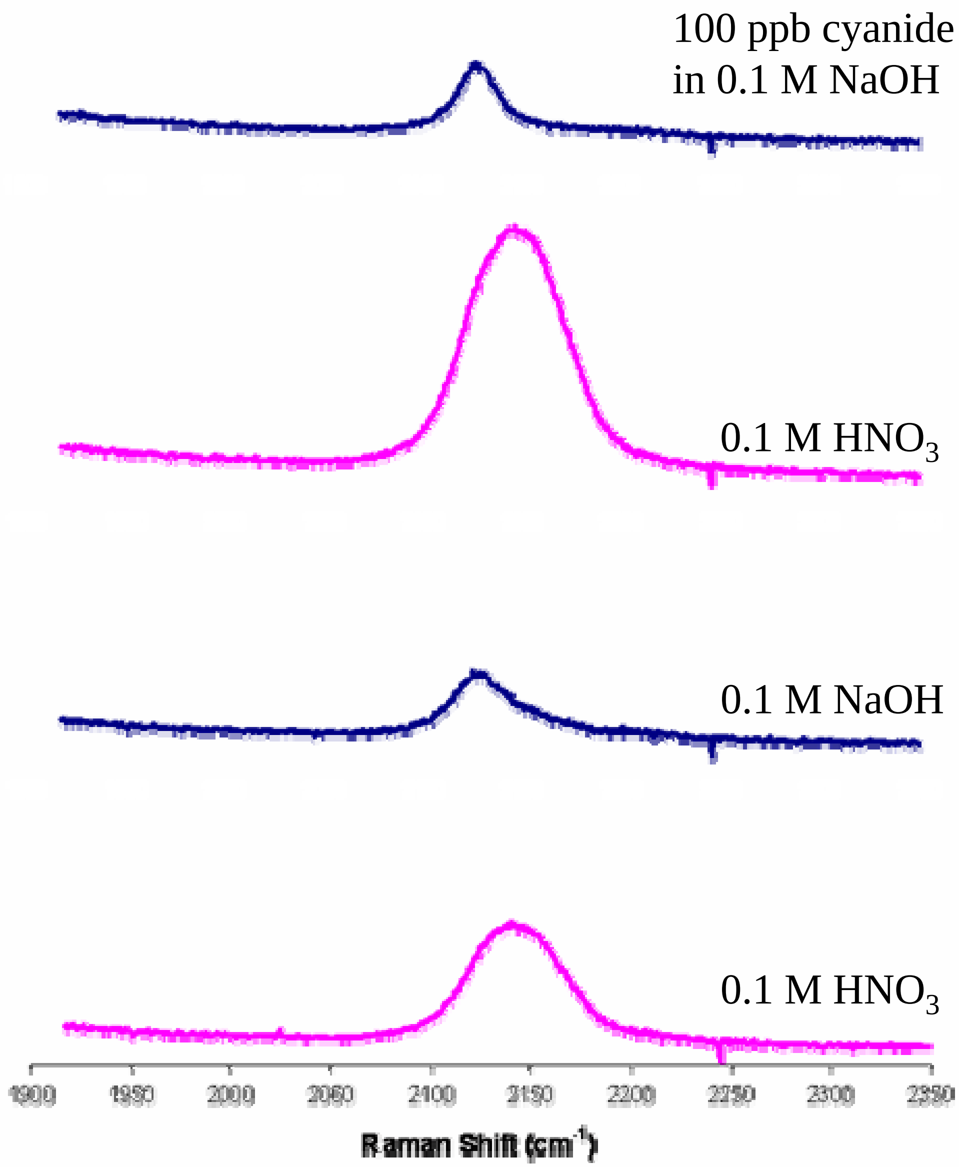
Incorporating SERS substrates in flow microchamber





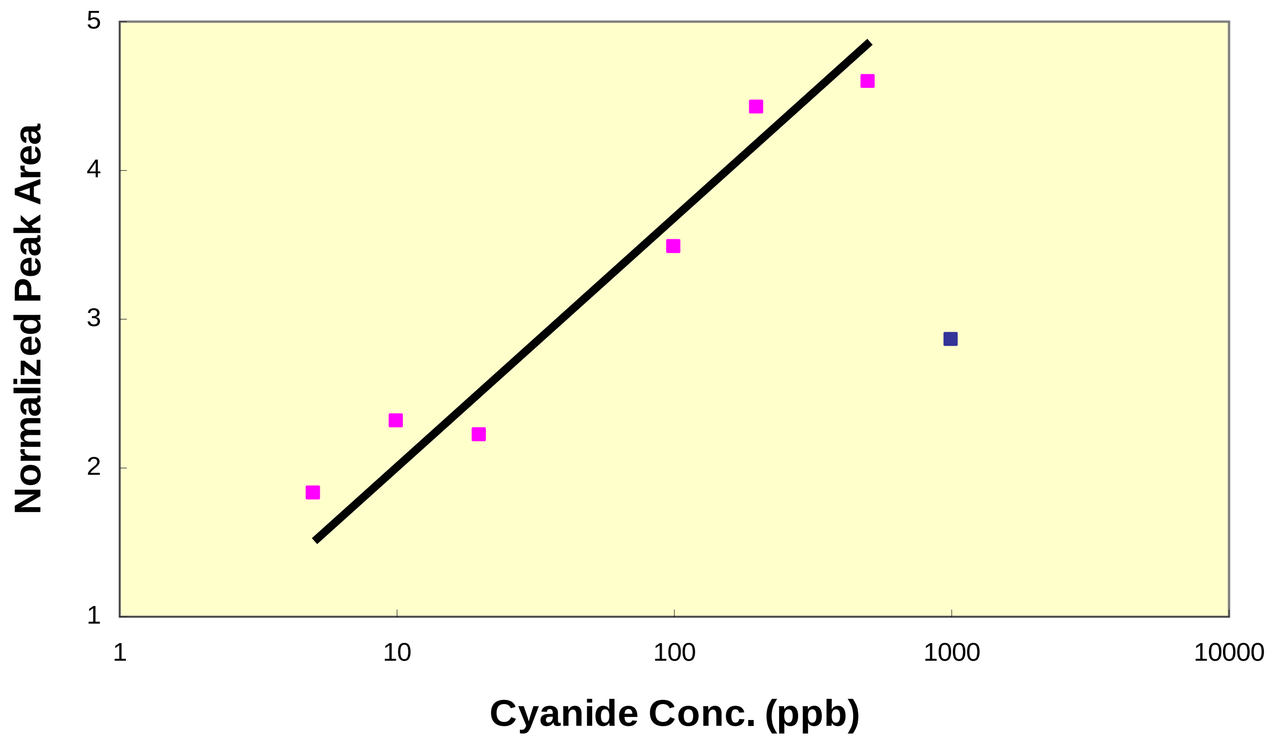
- Cell holds 170 μl, response in < 3 min
- Excitation λ = 785 nm

SERS on-line measurements: Switchable media enhancement



- Changing pH *without* adsorbing new CN^- leads to strong enhancement of the peak intensity
- Process can be repeated multiple times by flowing different solutions
- Likely associated with changes in the orientation of the adsorbed molecules

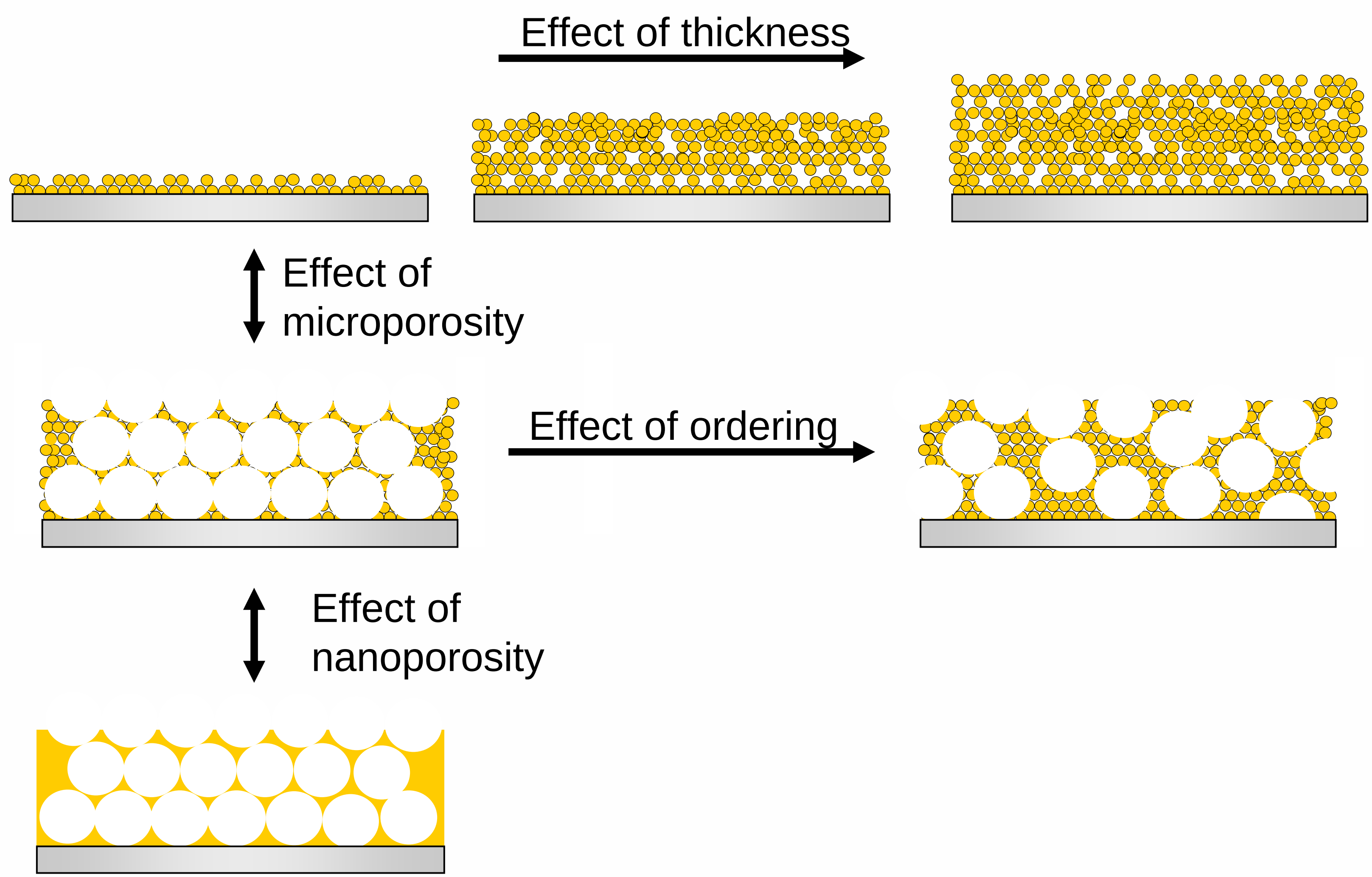
SERS on-line measurements: precise estimate of LOD



$$\theta = \frac{K\,c}{K\,c + 1}$$

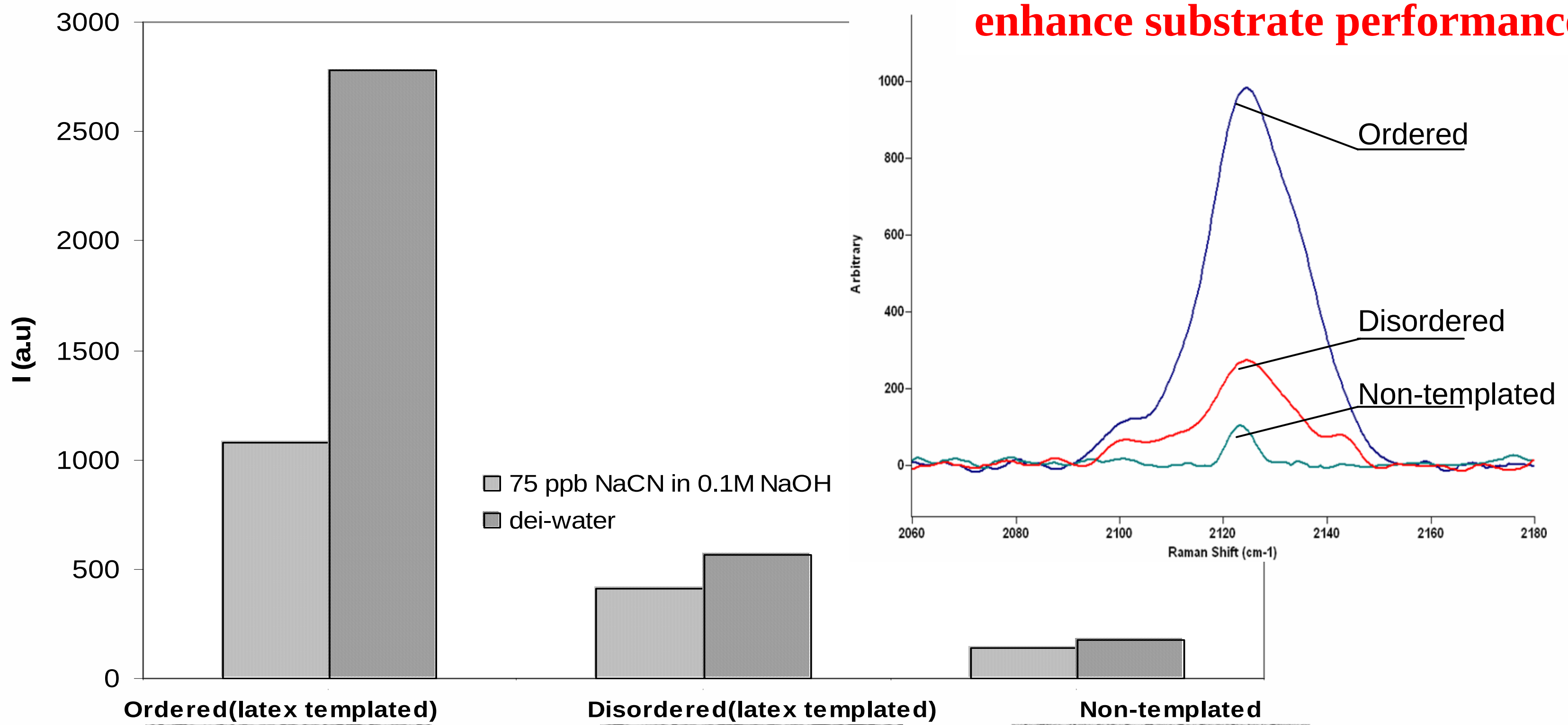
- Peak area proportional to the logarithm of the concentration (Langmuir isotherm)
- Sodium cyanide monolayer forms on the gold surface at bulk solution concentration = 500 ppb (corresponds to Gao and Weaver, 1989)
- Gold begins to dissolve above 500 ppb of sodium cyanide (decrease in Raman signal)

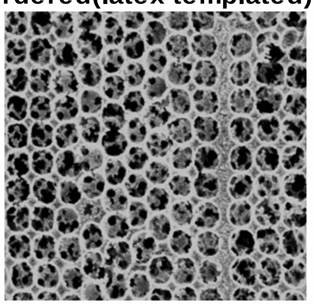
Substrate design for SERS performance evaluation

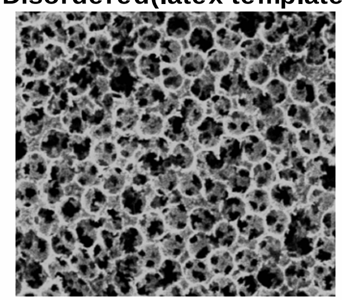


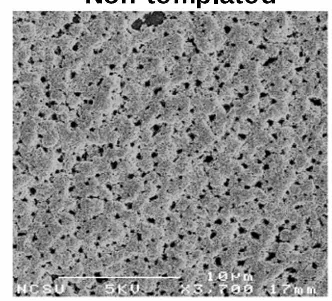
Effect of substrate structure on SERS signal

Ordering and microporosity enhance substrate performance

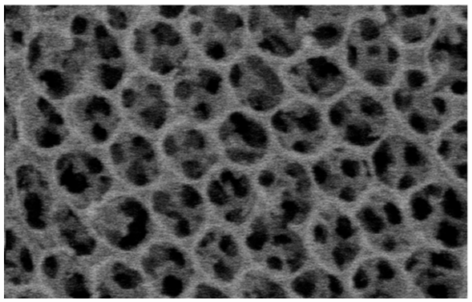




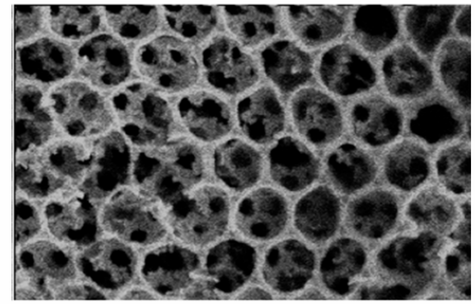




Impact of controlled nanoporosity on SERS response



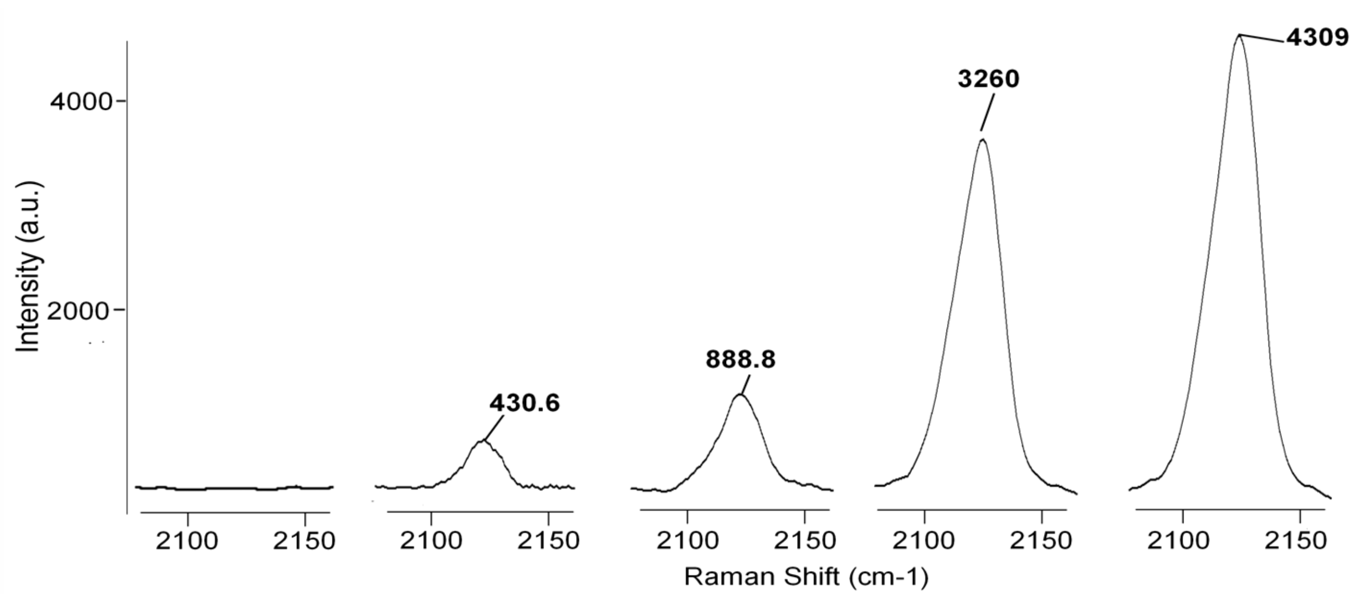
Annealing reduces the substrate performance due to reduction in nanoporosity (microporosity retained)



Annealed

Temp. ←

Non-annealed

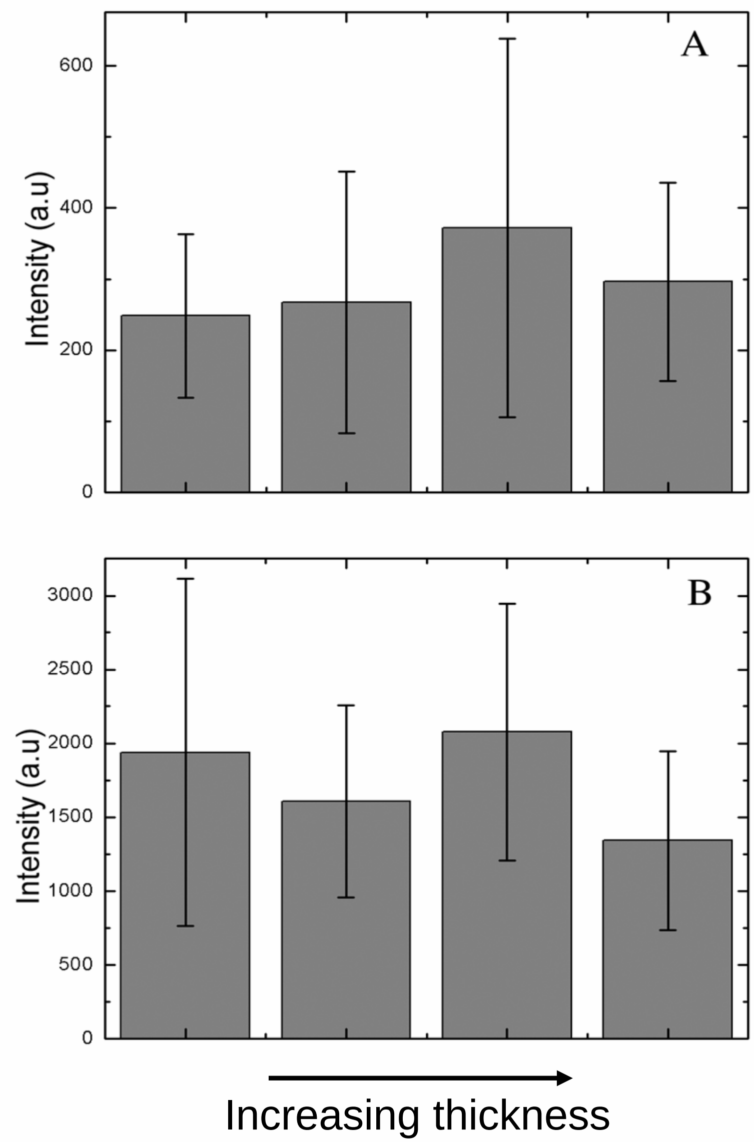


Effect of film thickness on SERS performance

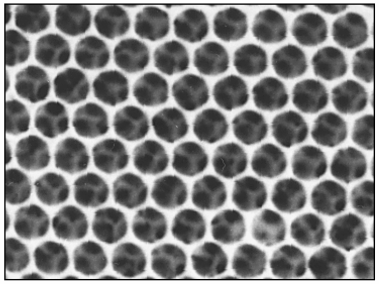
No increase in performance by adding more material

Likely because optical accessibility of analyte does not increase with Au particle loading

Kuncicky et al., submitted (2004).



Summary:
Structured metallic films as SERS substrates

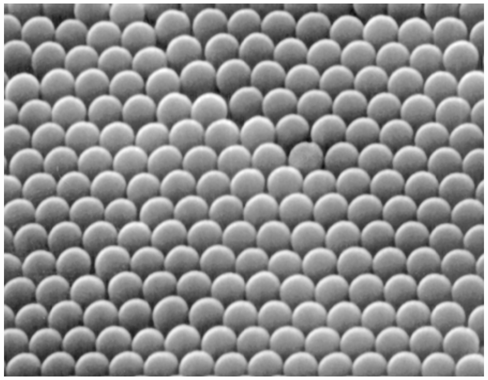


- **Advanced metal nanoparticle structures can be formed by simple and inexpensive colloidal templating (no microfabrication or vacuum deposition required)**
- **These hierarchically porous gold films serve as excellent SERS substrates**
- **The structures can be integrated into flow chambers for continuous sensing**
- **The SERS performance is increased both by the long-range ordered macropores and high nanoparticle porosity**
- **The samples are very reproducible and require very small amount of metal**

Tessier et al. *Appl. Spectr.* **56**, 1524 (2002).
Kuncicky et al., submitted (2004).

Final message

Nanocoatings by self-assembly have high technology potential, but research needs to be done above and beyond the current state of the art



- Developed new techniques
  - Simple, rapid & cost effective
  - Applicable to any type of particles
- Proved new applications
  - Antireflective coatings from silica microspheres
  - Conductive semitransparent coatings from gold nanoparticles
  - Nanomagnetic coatings of encapsulated ferritin
  - Templated hierarchically porous gold substrates for SERS

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