Nanoparticle Synthesis in Reverse Micelles

Nicola Pinna

Max Planck Institute of Colloids and Interfaces

e-mail: pinna@mpikg-golm.mpg.de - http://www.pinna.cx

Plan

1. Reverse Micelles

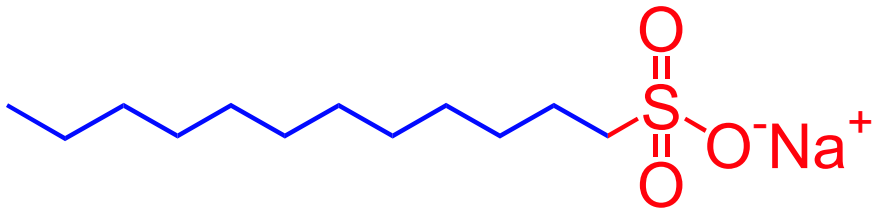
   - Surfactants in Solutions
   - Reverse Micelles
   - Synthesis of Particles

2. Examples

   - Semiconductors
   - Metals
   - Oxides

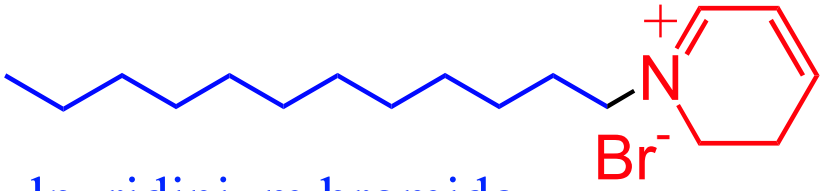
Surfactants in Solution

- Anionic



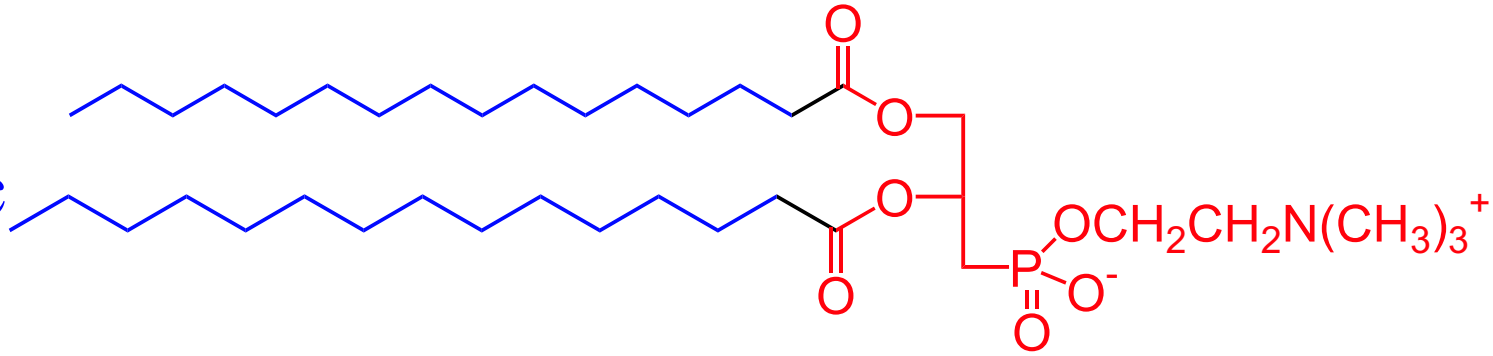
Sodium dodecylsulfate (SDS)

- Cationic



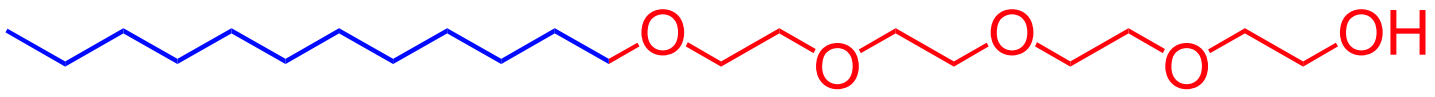
Cetylpyridinium bromide

- Zwitterionic



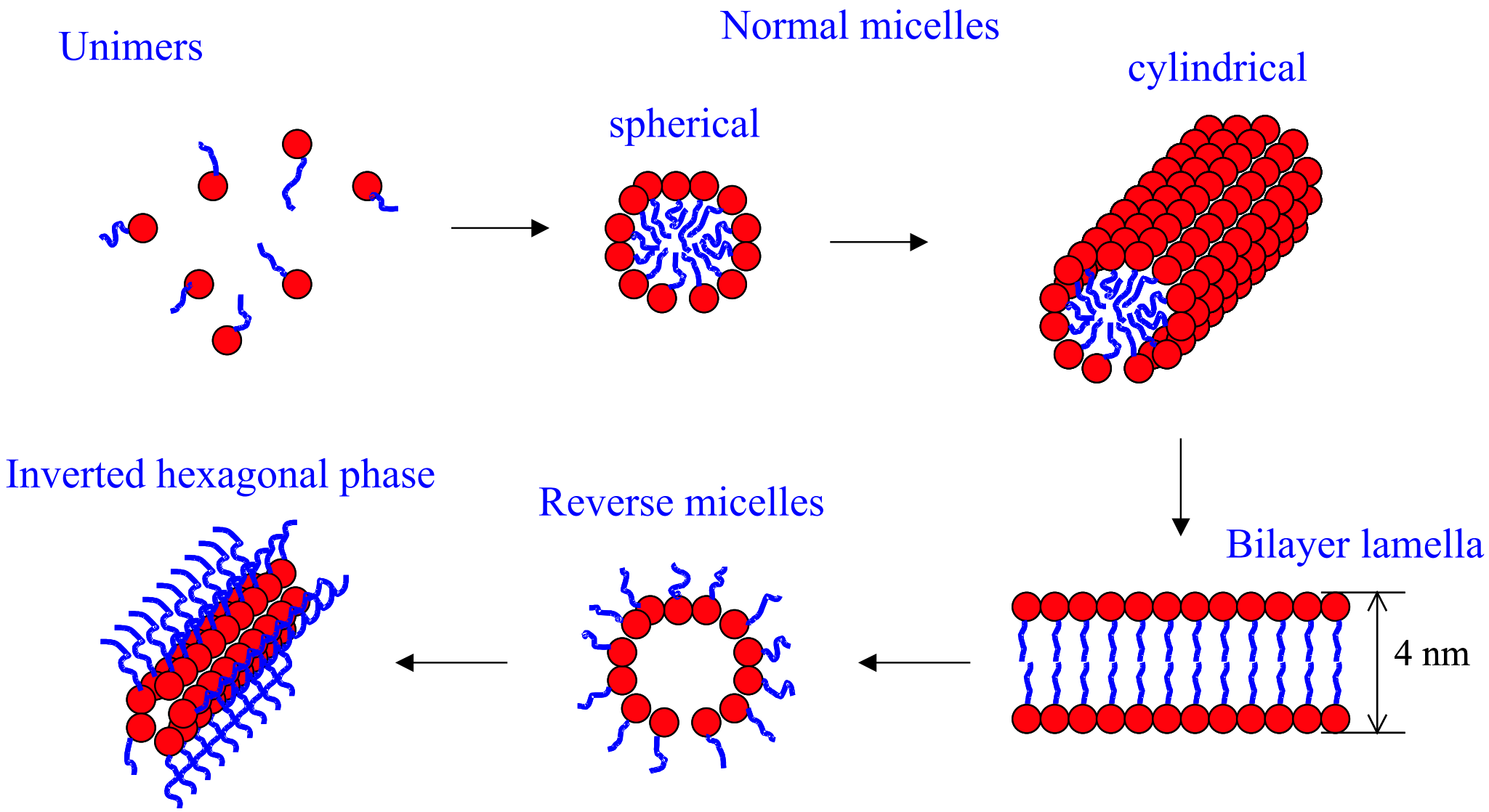
Dipalmitoylphosphatidylcholine (lecithin)

- Nonionic

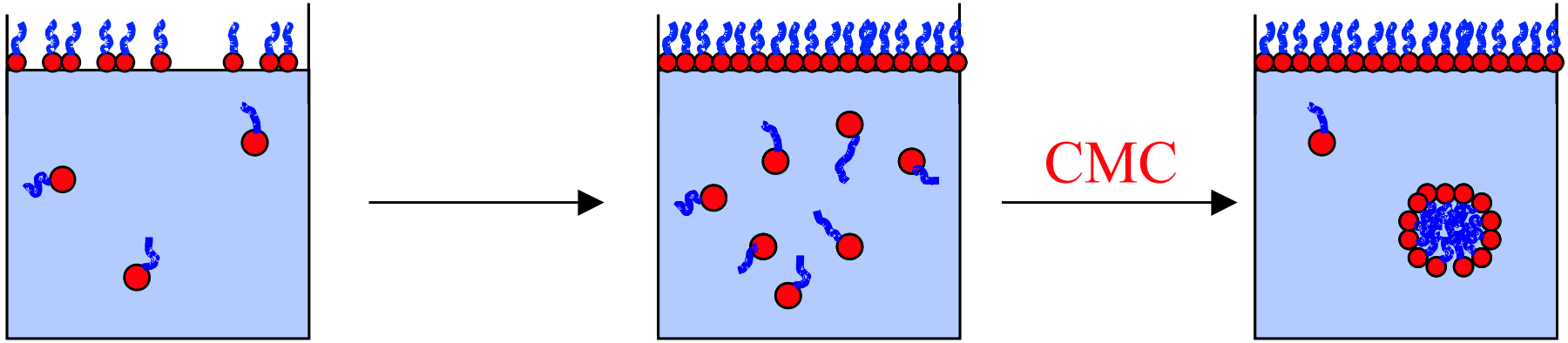


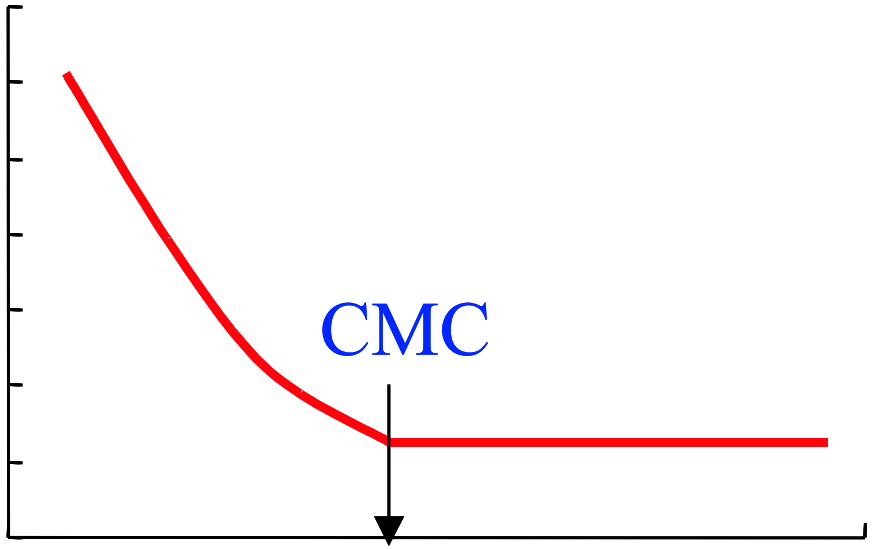
Polyoxyethylene(4) lauryl ether (Brij 30)

Surfactants in Solution



Surfactants in Solution





- Below CMC only unimers are present
- Above CMC there are micelles in equilibrium with unimers

Packing parameter (shape factor)$= V/al$

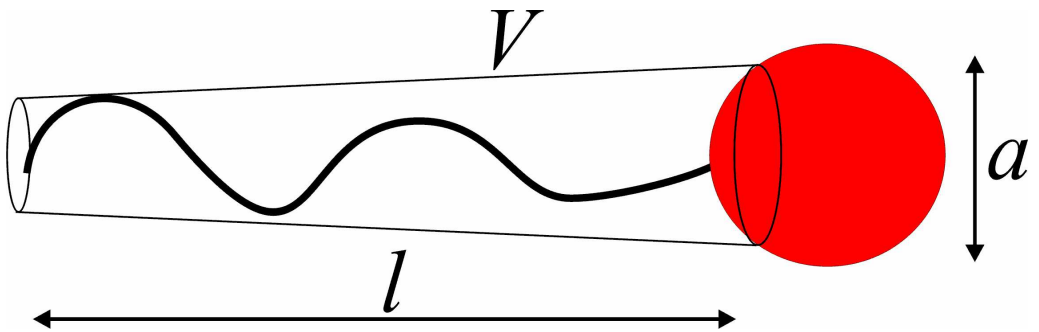
V Volume of the tail

a Cross sectional surface of the polar head

l Length of the hydrophobic tail

Table 4.3 Surfactant packing parameter range for various surfactant aggregates

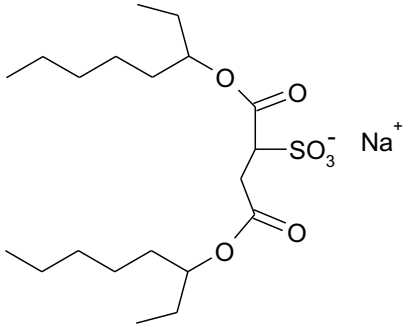
Spherical micelles	$V/al < 1/3$	
Cylindrical micelles	$1/3 < V/al < 1/2$	
Vesicles, flexible bilayers	$1/2 < V/al < 1$	
Lamellae, planar bilayers	$V/al \approx 1$	
Inverse micelles	$V/al > 1$	

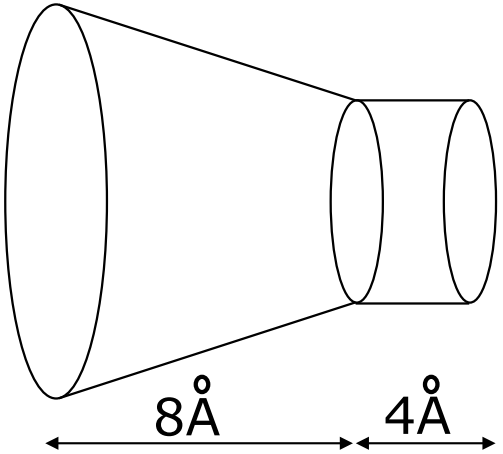


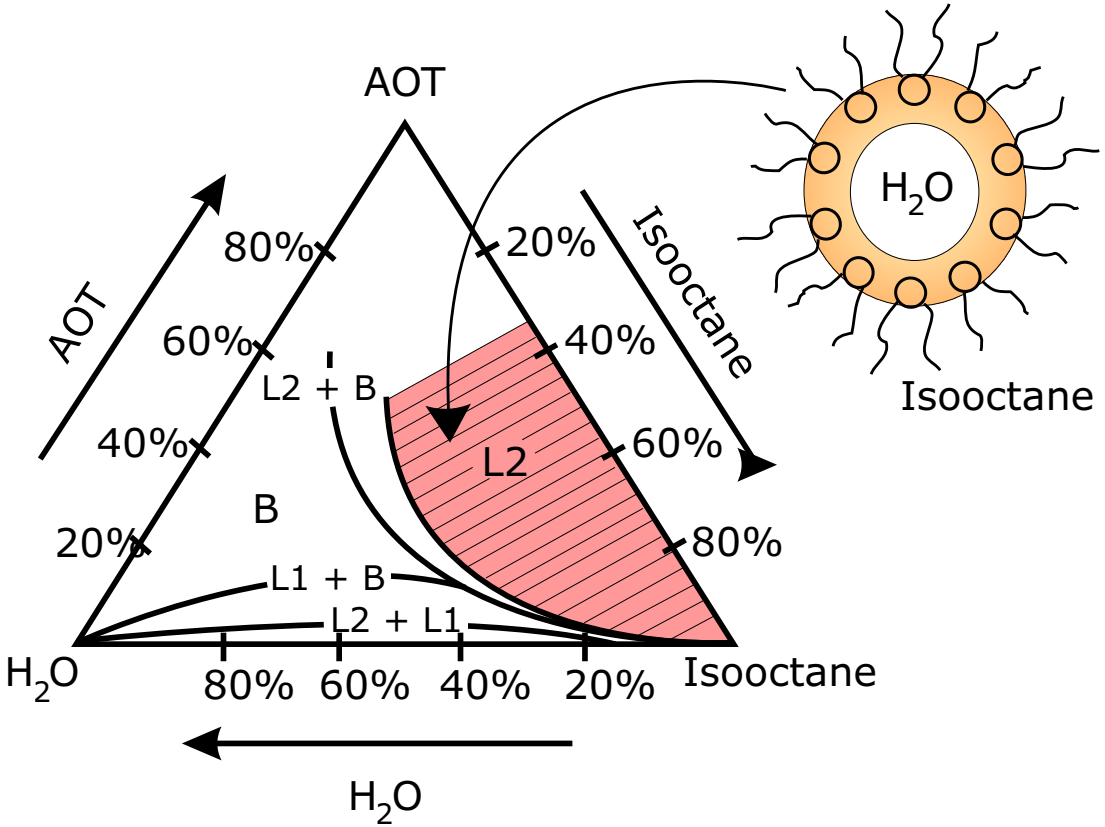
Reverse Micelles

Water in oil microemulsion

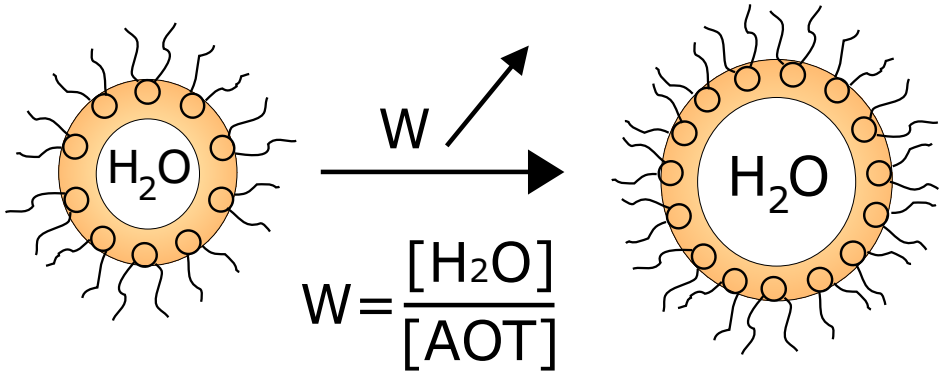
Surfactant = AOT



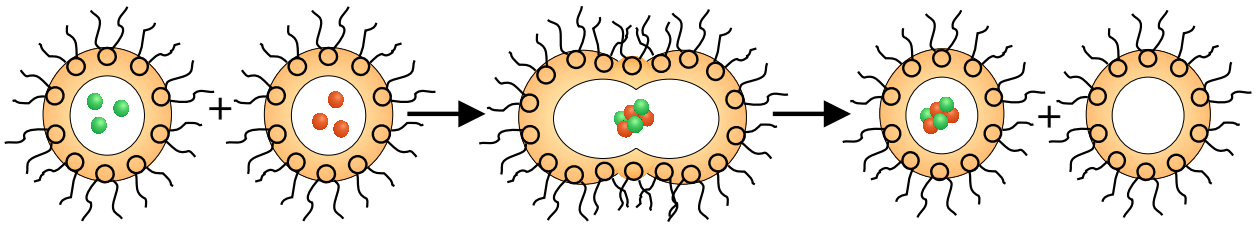




Reverse Micelles



Water amount $\longrightarrow$ size of the micelles

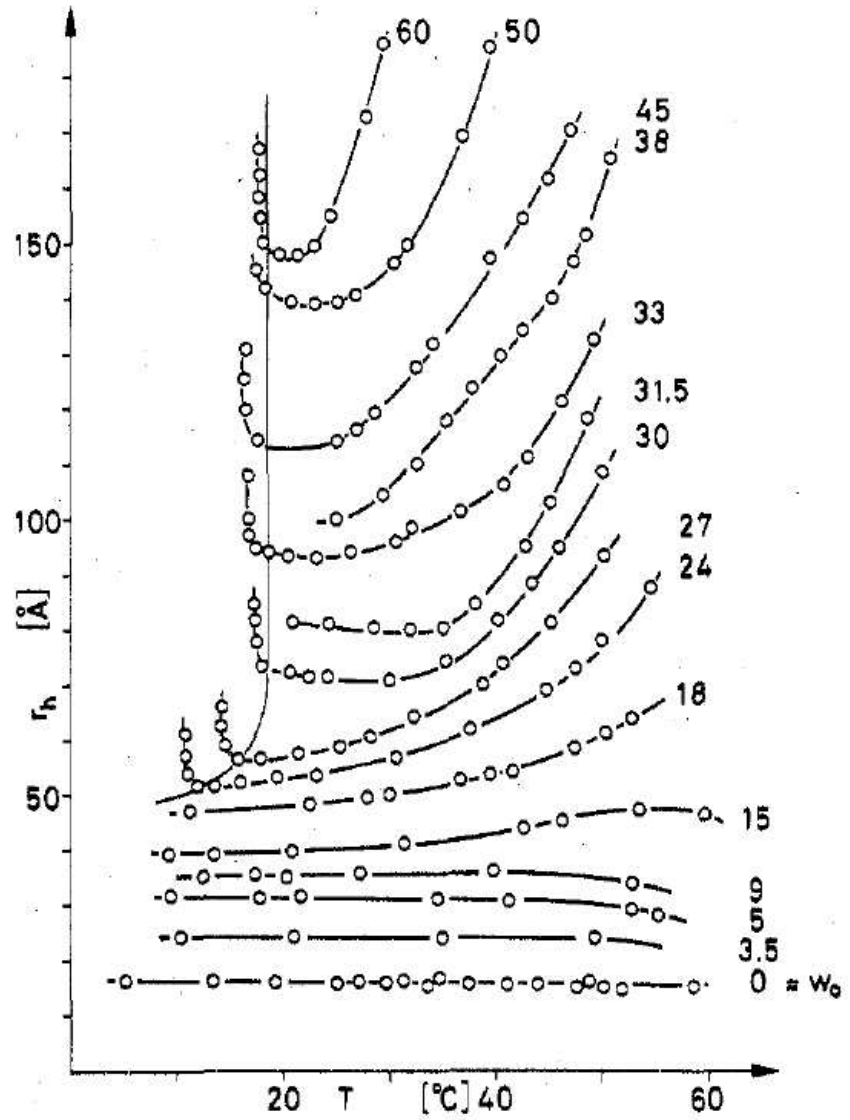


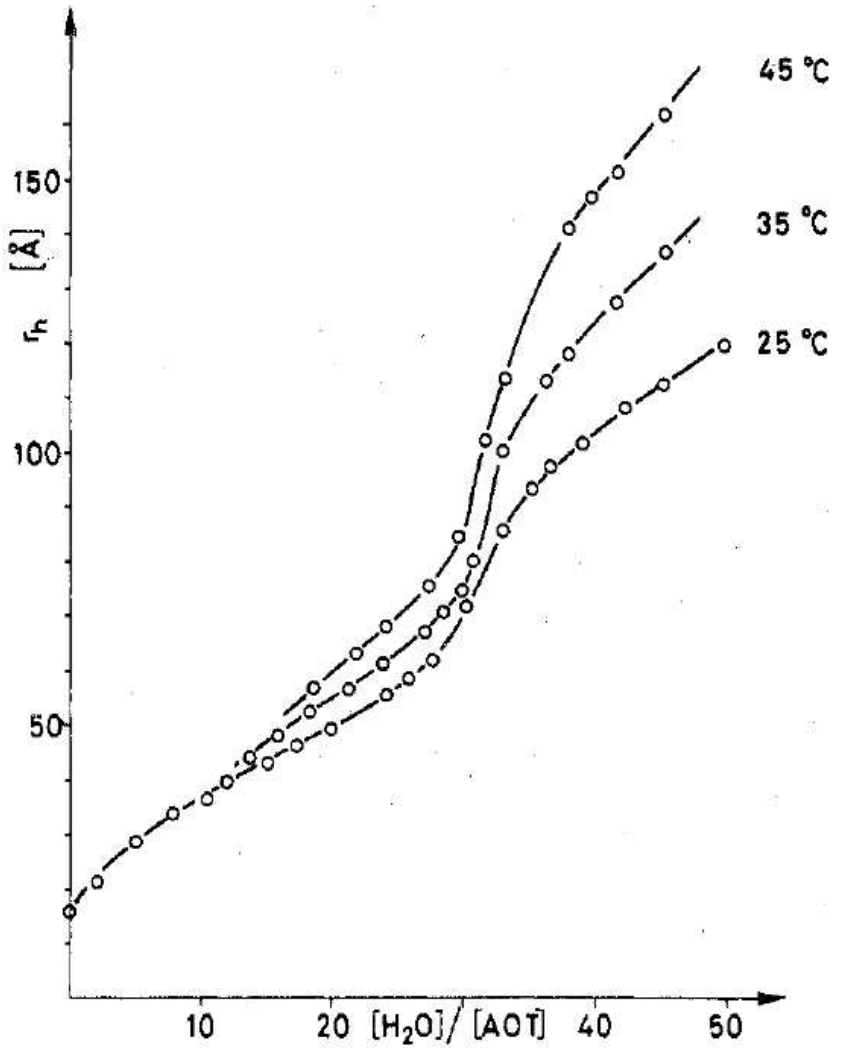
Collisions between micelles $\longrightarrow$ Exchange of the water content

---

$\longrightarrow$ Chemical Reactions: Coprecipitation, Reduction, Hydrolysis-Condensation

Reverse Micelles





M. Zulauf, H.-F. Eicke, J. Phys. Chem. 83, 4, 1979

First Synthesis

First review article about particles formations in microemulsions

- Atomic and molecular clusters in membrane mimetic chemistry Janos H. Fendler, Chem. Rev.; 1987; 87(5); 877-899.

- Cadmium sulfide of small dimensions produced in inverted micelles
  P. Lianos, J. K. Thomas, Chem. Phys. Lett. 1986, 125, 299
  CdS nanoparticles from AOT/H_2O/Heptane reverse micelles, coprecipitation between $Cd(ClO_4)_2$ and Na_2S

- Photosinsitiezed charge separation and hydrogen production in reversed micelle entrapped platinized colloidal cadmium sulfide
  M. Meyer, C. Wallberg, K. Kurihara, J. H. Fendler, Chem. Comm. 1984, 90
  CdS nanoparticles from AOT/H_2O/isooctane reverse micelles, coprecipitation between $CdCl_2$ and H_2S

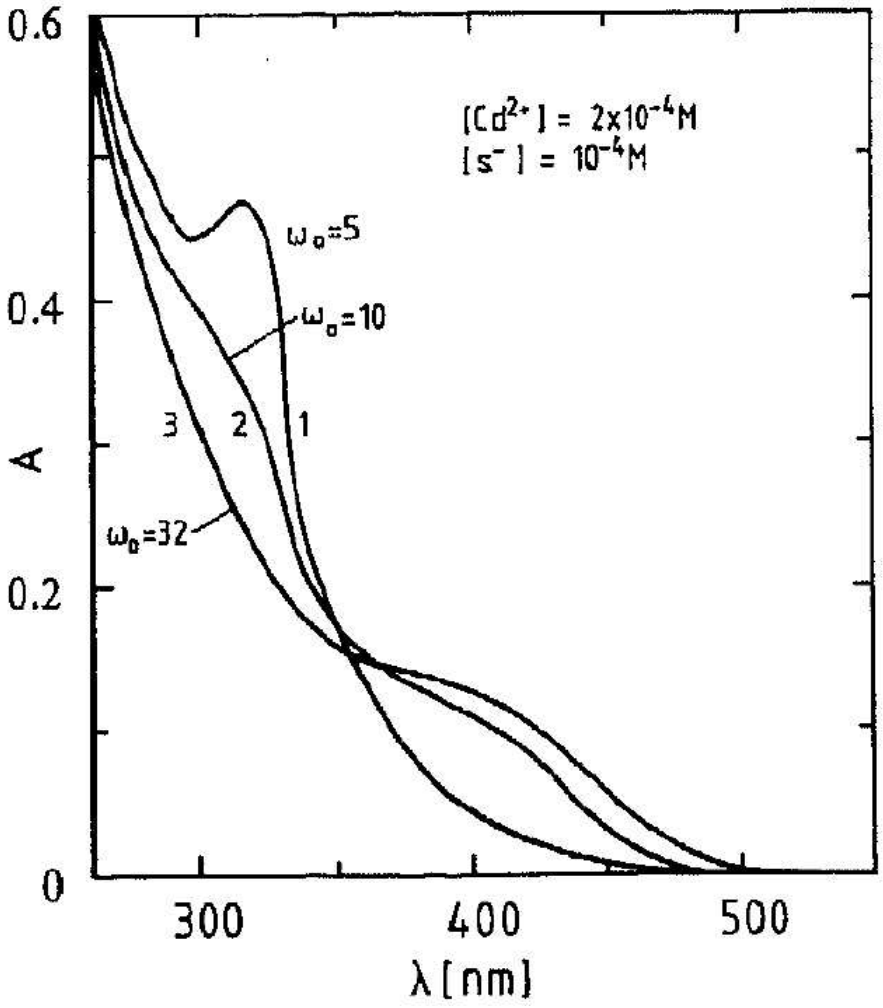
- Synthesis of cadmium-sulfide insitu in reverse micelles and in hydrocarbon gels
  C. Petit, M. P. Pileni, J. Phys. Chem. 1988, 92, 2282
  CdS nanoparticles from AOT/H_2O/isooctane reverse micelles, coprecipitation between $Cd(NO_3)_2$ and Na_2S

- The preparation of monodisperse colloidal metal particles from microemulsions
  M. Boutonnet, J. Kizling, P. Stenius, G. Maire, Colloids Surf. 1982, 5, 209
  Pt, Pd, Rh, Ir 3-5 nm particles prepared by reduction of metal salts in reverse micelles: Hexadecyltrimethylammonium Chloride (CTAB)/octanol/H_2O

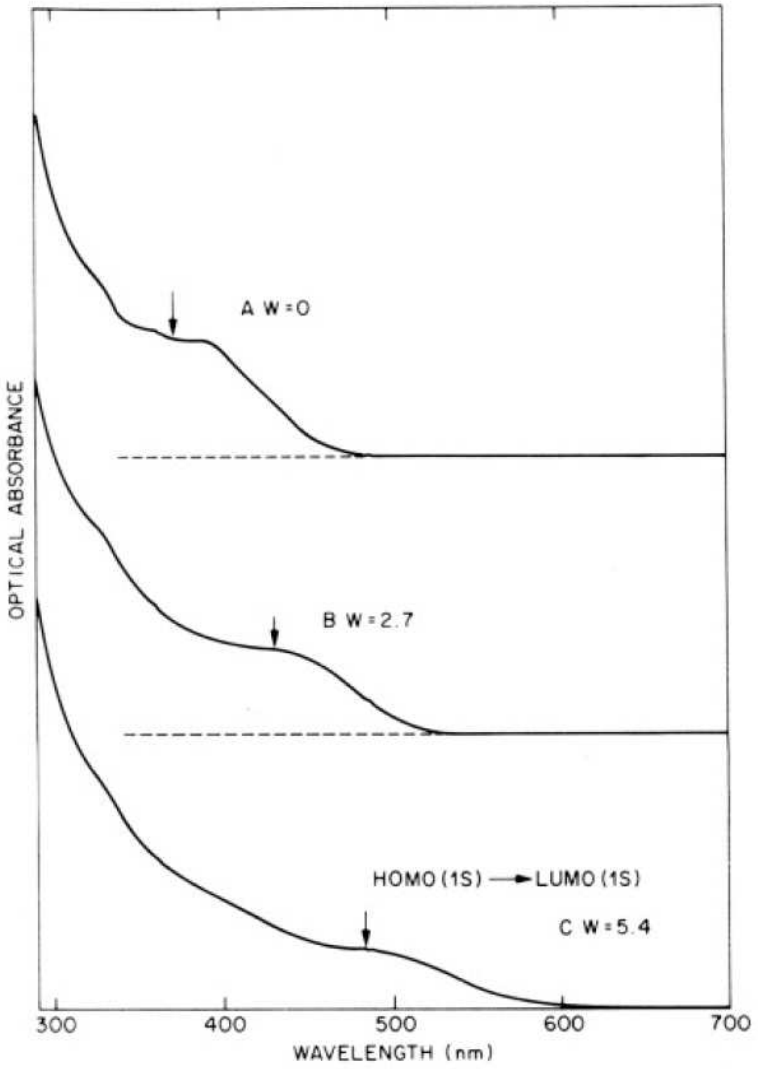
The general approach consist on mixing 2 micellar solutions containing the cations and the anions

$\longrightarrow$ Fast reaction, spherical particles

First Synthesis



P. Lianos, J. K. Thomas, Chem. Phys. Lett. 1986, 125, 299



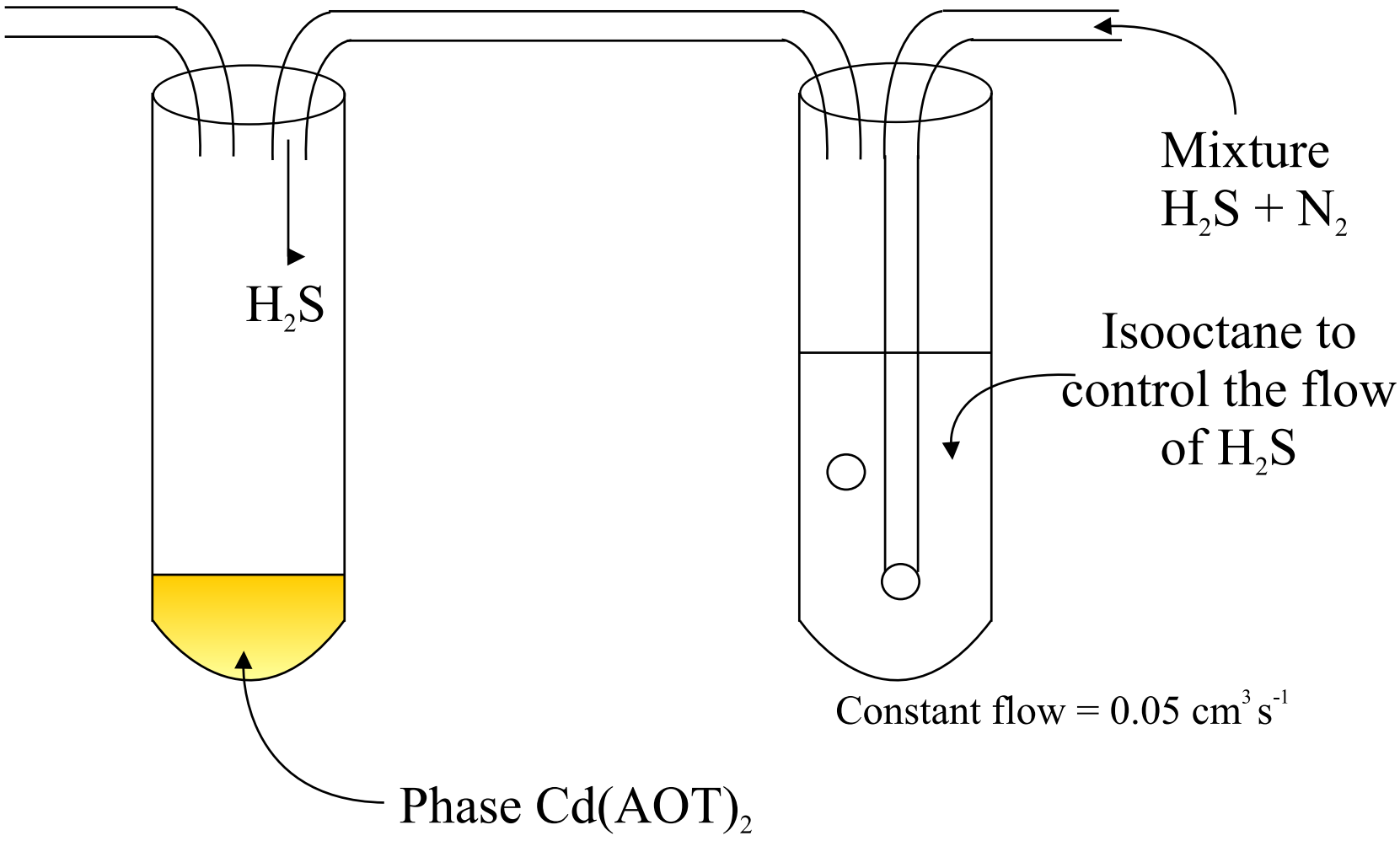
M. L. Steigerwald, et al. J. Am. Chem. Soc.; 1988; 110(10); 3046-3050

Modern Examples

Synthesis and Characterization of non spherical nanoparticles made in reverse micelles

- Semiconductors - CdS nanoparticles and nanotriangles - Coprecipitation
- Oxides - V_2O_5 nanorods and nanowires - Hydrolysis-Condensation
- Metals - Silver nanoparticles and nanodisks - Reduction

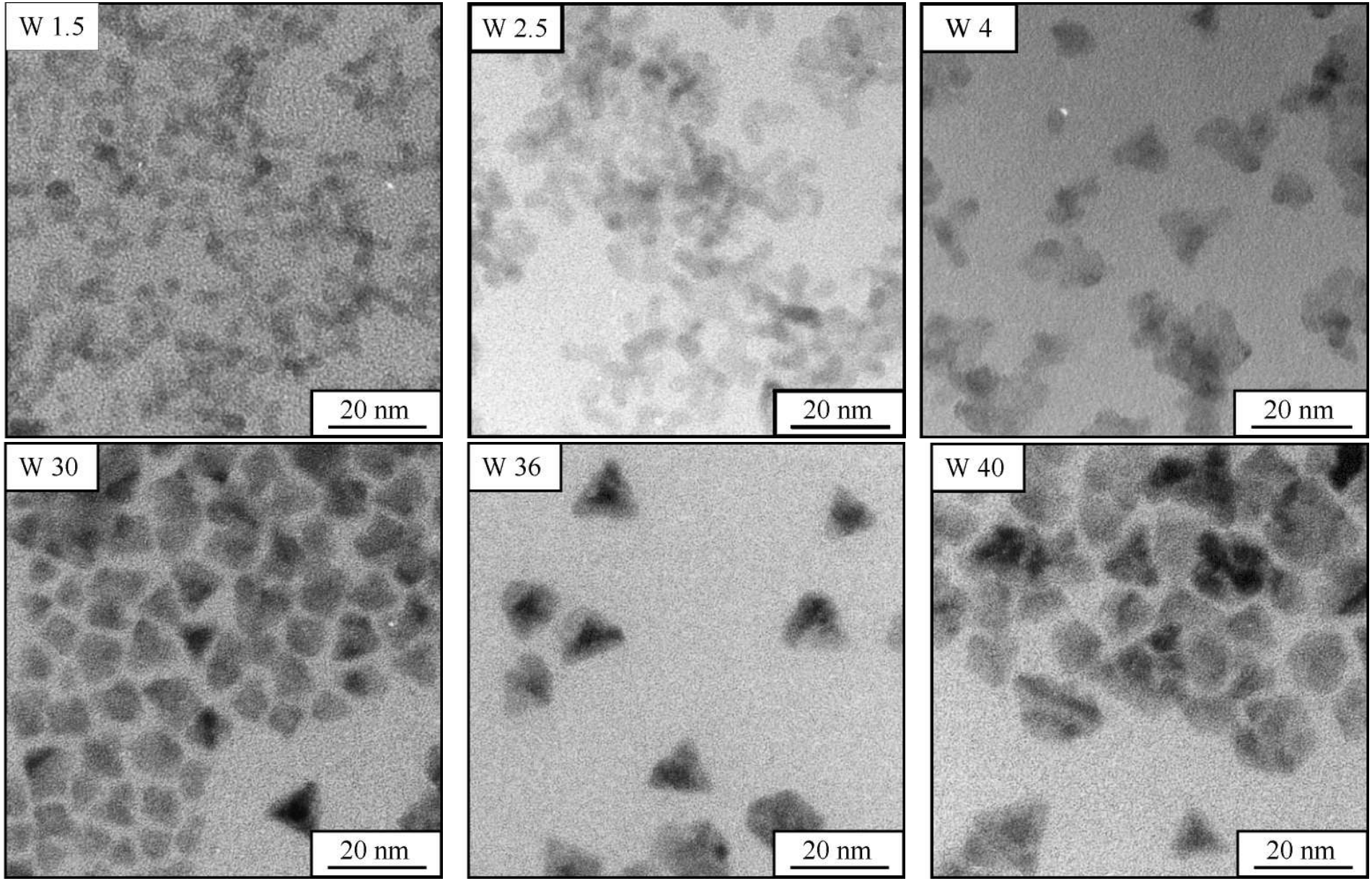
Coprecipitation



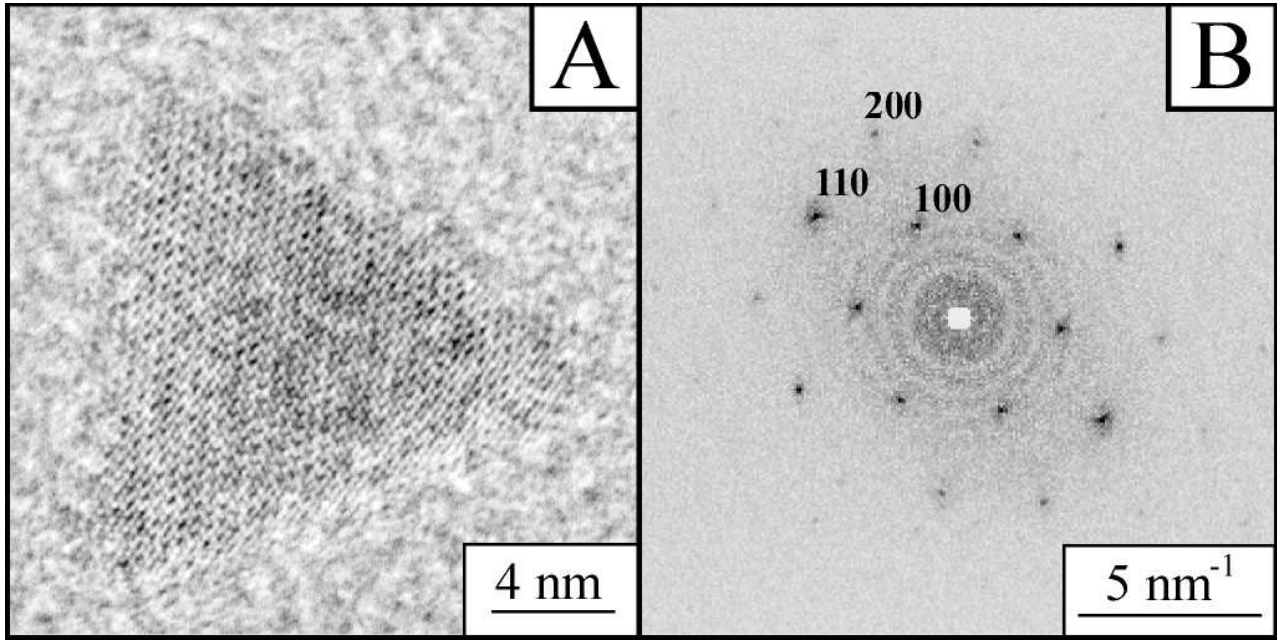
N. Pinna, K. Weiss, J. Urban, M. P. Pileni, *Adv. Mat,* **2001**, *13,261*

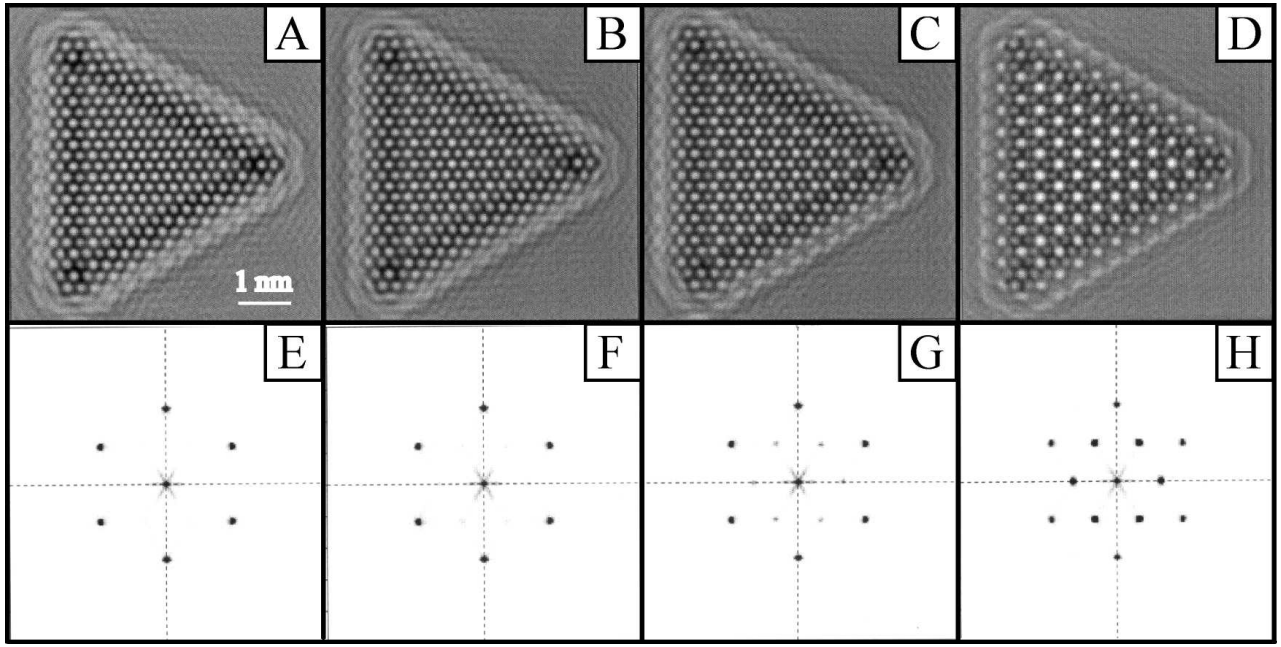
N. Pinna, K. Weiss, H. Sack-Kongehl, W. Vogel, J. Urban, M. P. Pileni, *Langmuir* **2001**, *17, 7982*

TEM

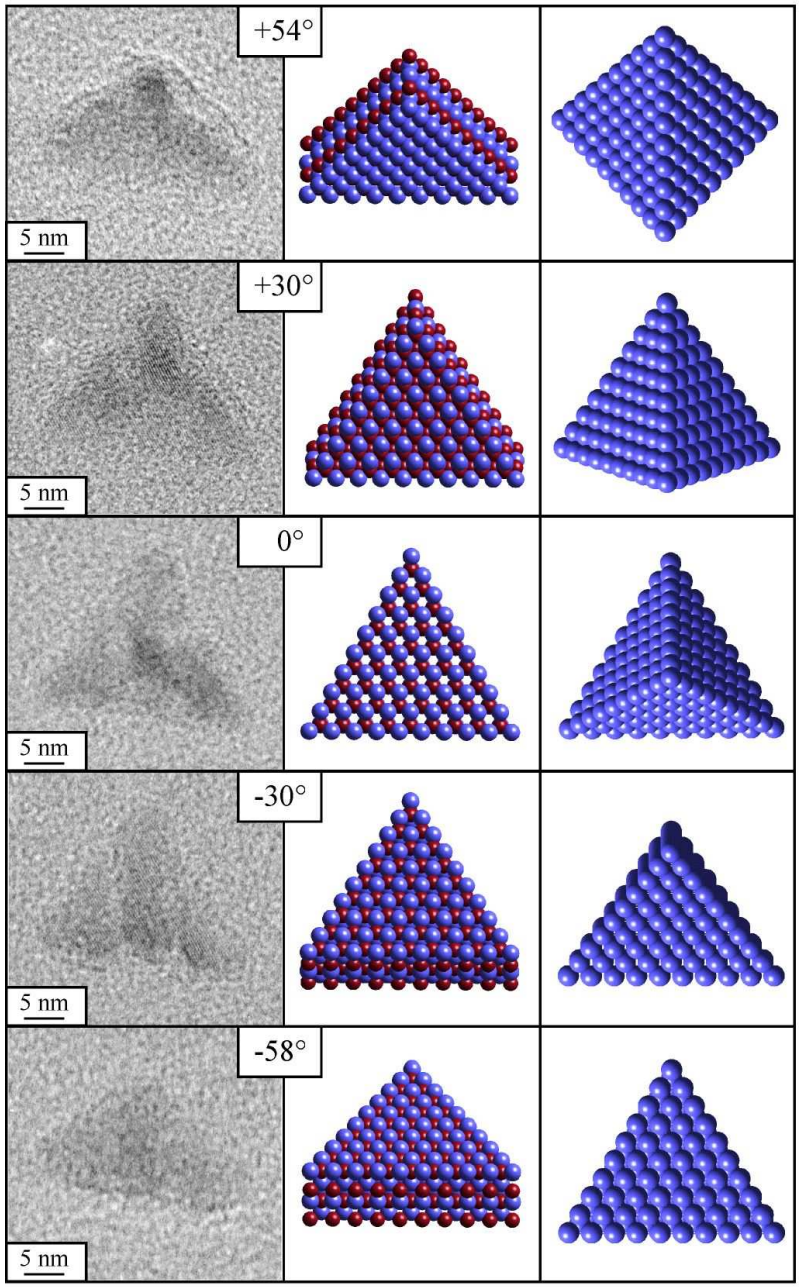


HRTEM

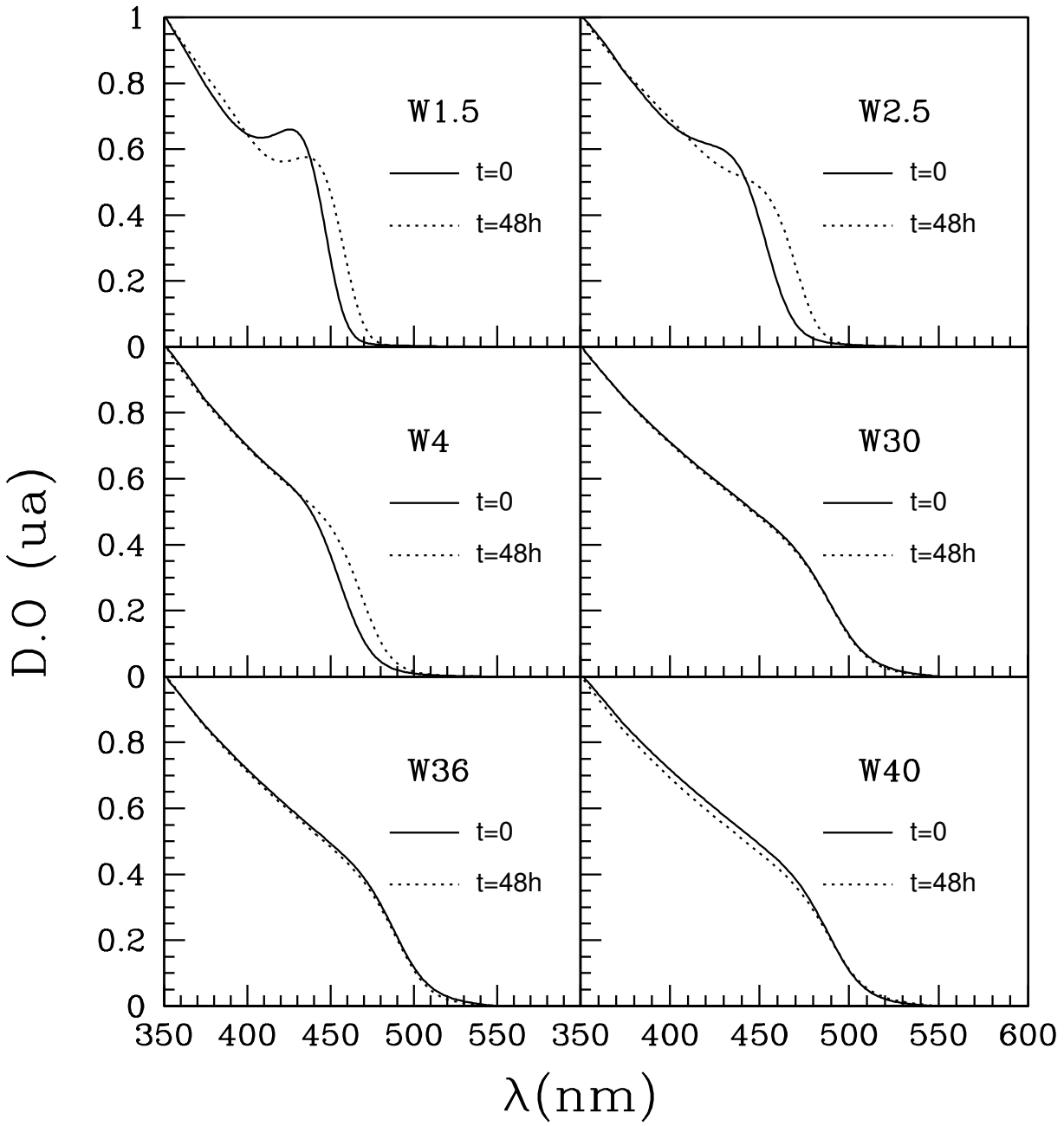




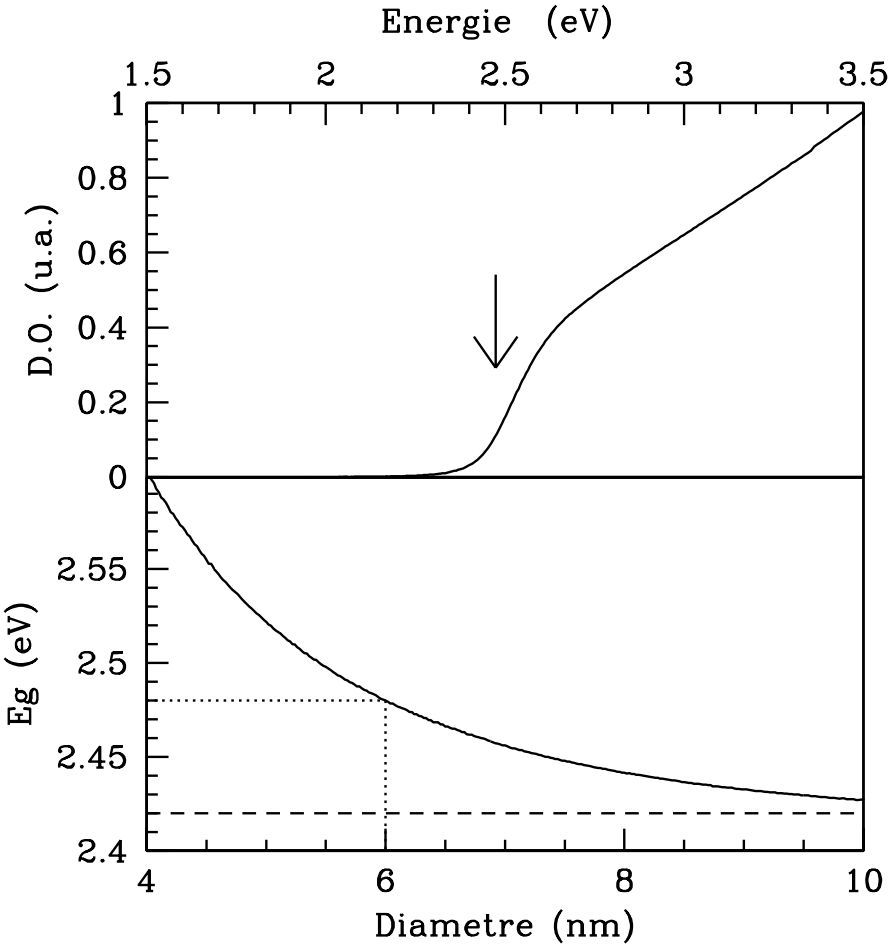
Shape Determination

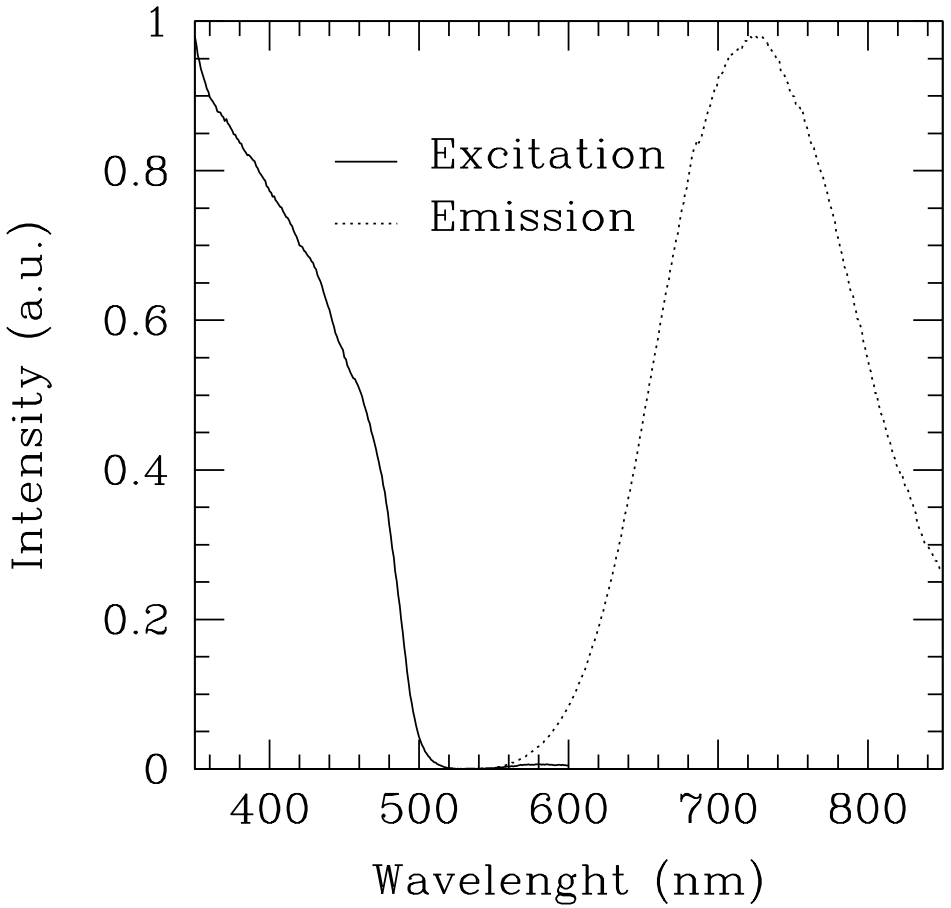


Optical Properties



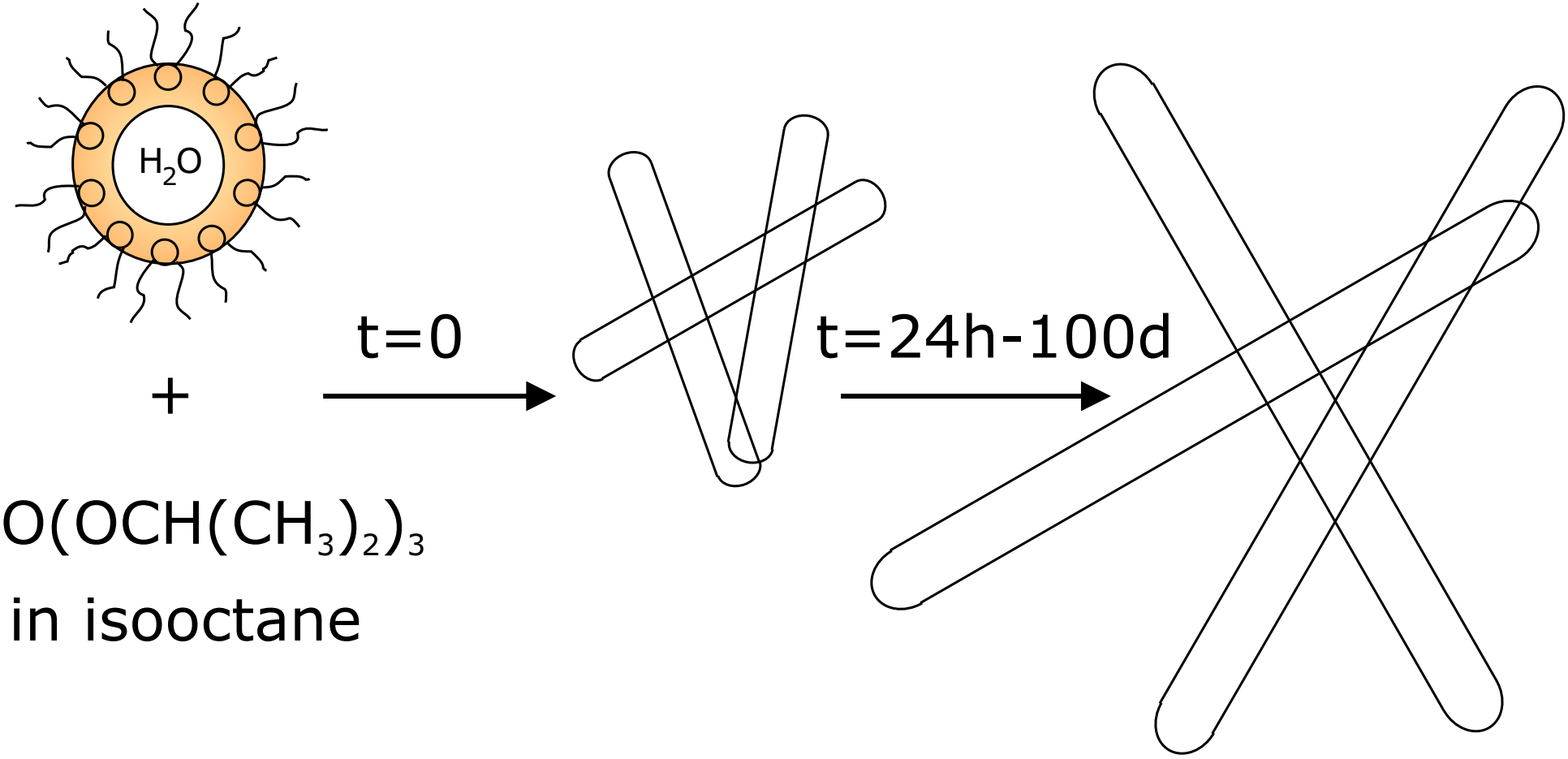
Optical Properties





Hydrolysis-Condensation

$$2VO(OR)_3 + 3H_2O \rightarrow V_2O_5 + 6ROH \qquad R{=}CH(CH_3)_2$$

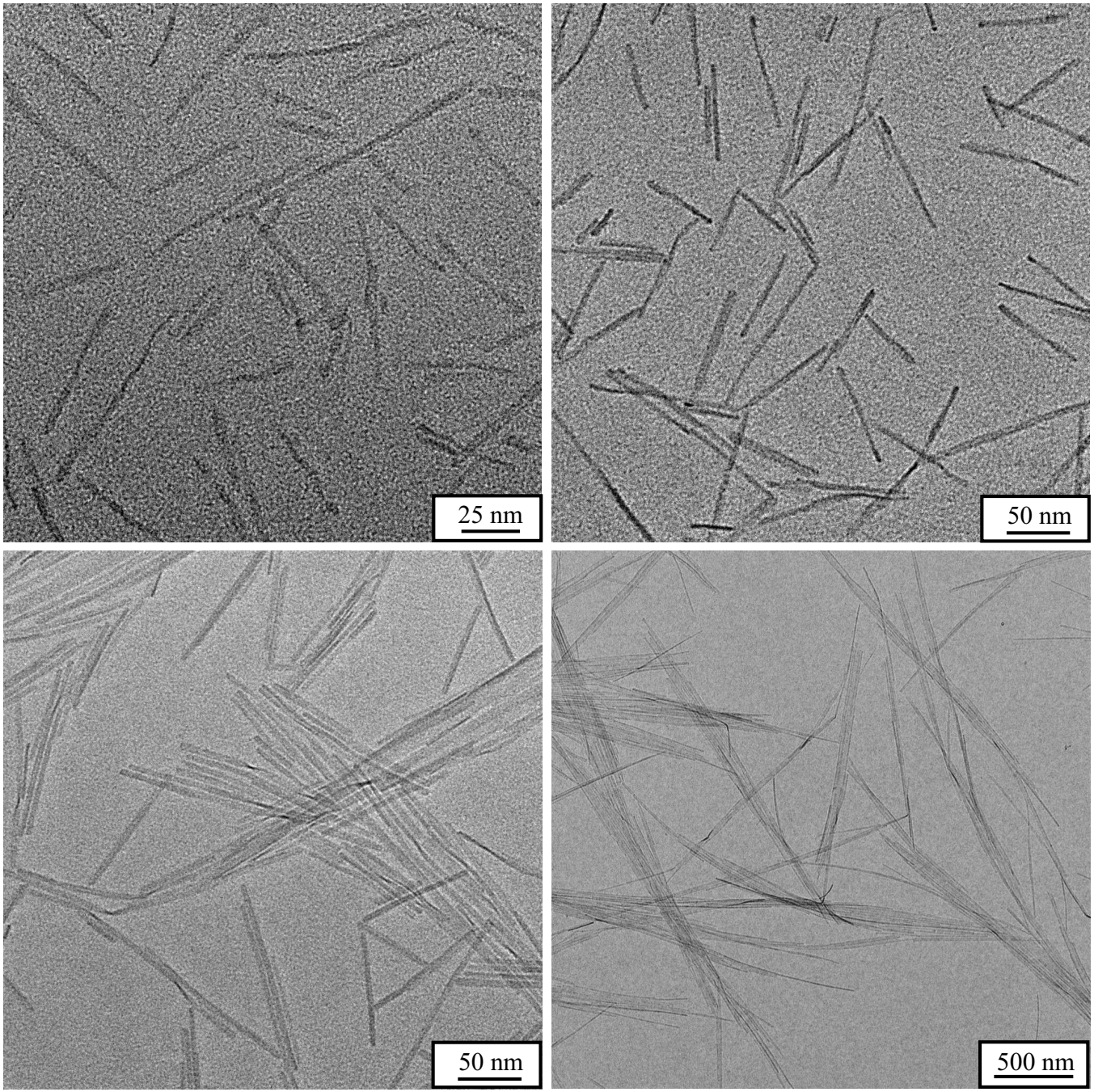


N. Pinna, U. Wild, J. Urban, R. Schlögl. Adv. Mat. 15(4), 329, 2003

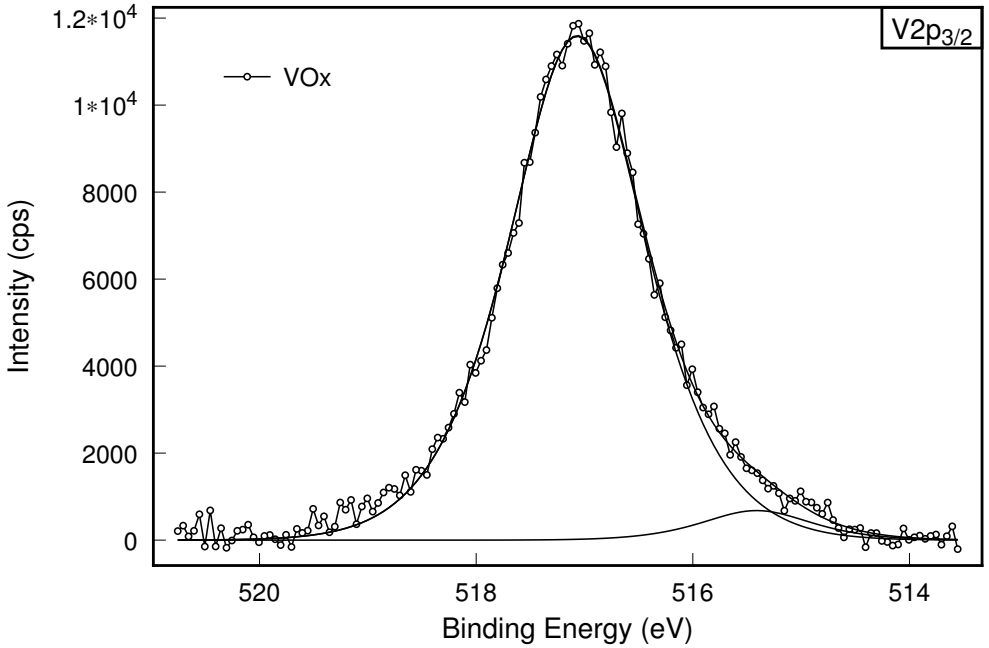
N. Pinna, M. Willinger, K. Weiss, J. Urban, R. Schlögl, Nano Lett, 3, 1131, 2003

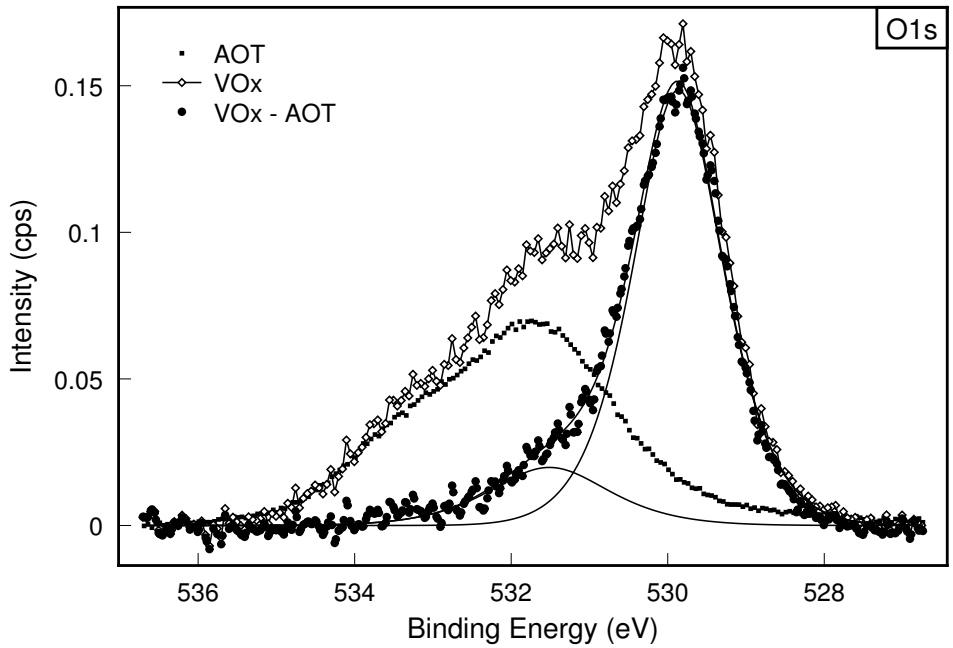
M. Willinger, N. Pinna, D.S. Su, R. Schlögl, Phys. Rev. B, 69, 155114, 2004

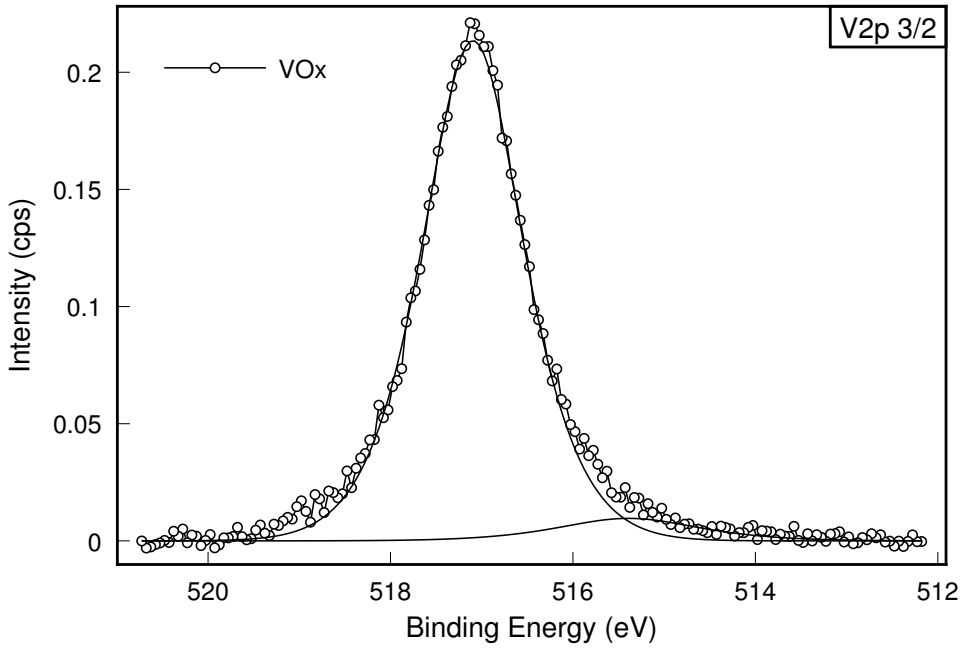
V_2O_5 Nanorods and Nanowires

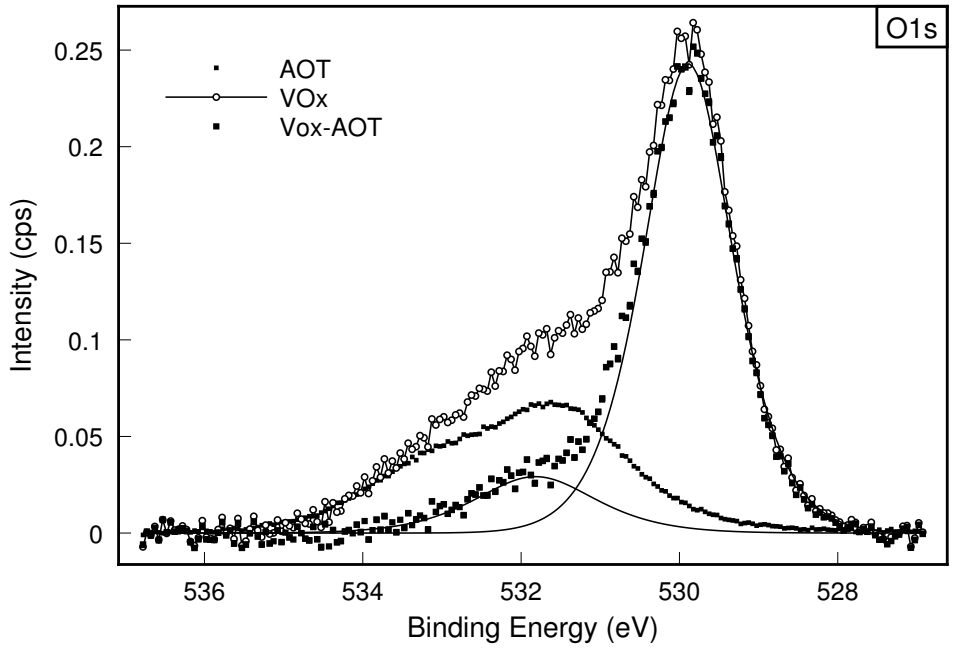


XPS

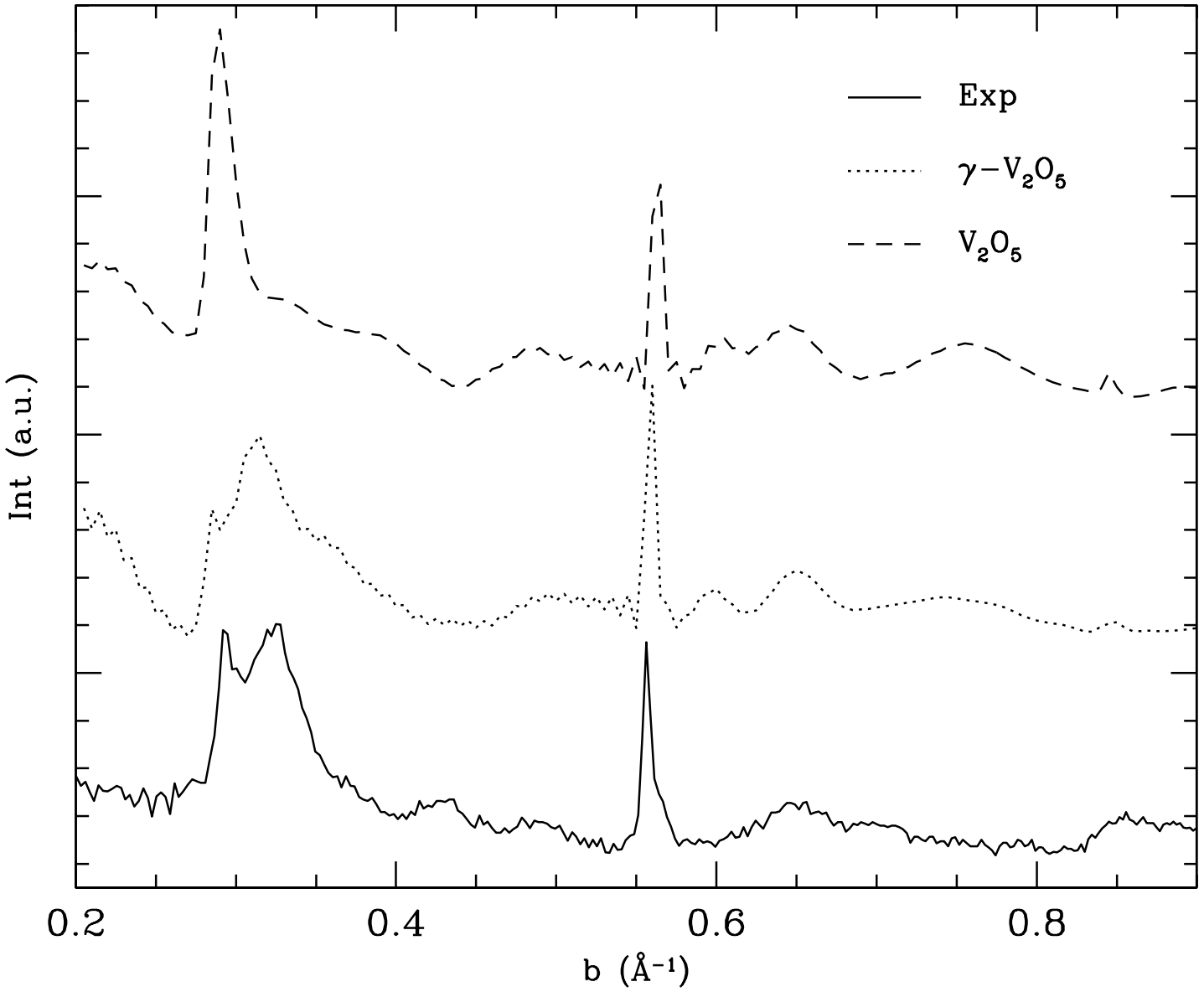

V2p3/2
VOx
Intensity (cps)
Binding Energy (eV)
1.2*10^4
1*10^4
8000
6000
4000
2000
0
520
518
516
514


O1s
AOT
VOx
VOx - AOT
Intensity (cps)
Binding Energy (eV)
0.15
0.1
0.05
0
536
534
532
530
528


V2p 3/2
VOx
Intensity (cps)
Binding Energy (eV)
0.2
0.15
0.1
0.05
0
520
518
516
514
512


O1s
AOT
VOx
Vox-AOT
Intensity (cps)
Binding Energy (eV)
0.25
0.2
0.15
0.1
0.05
0
536
534
532
530
528

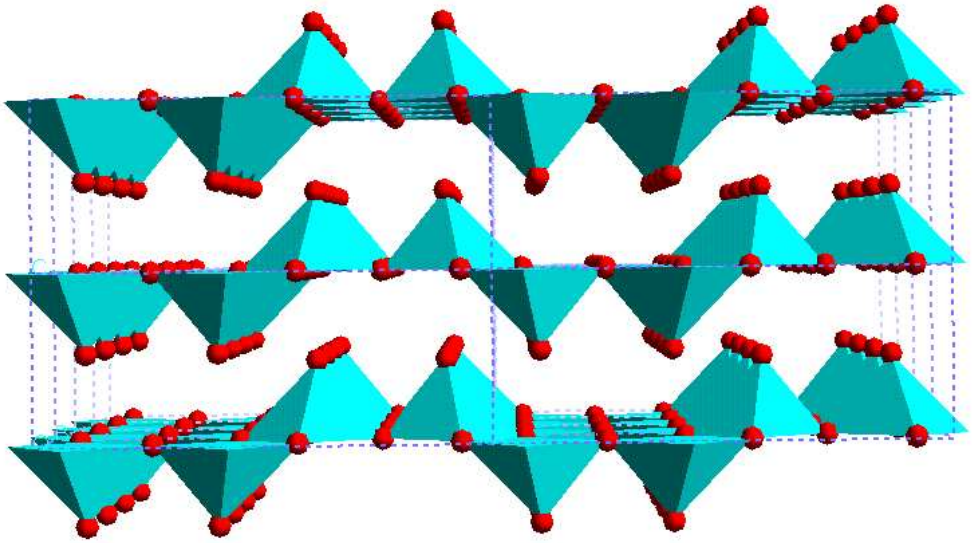
XRD



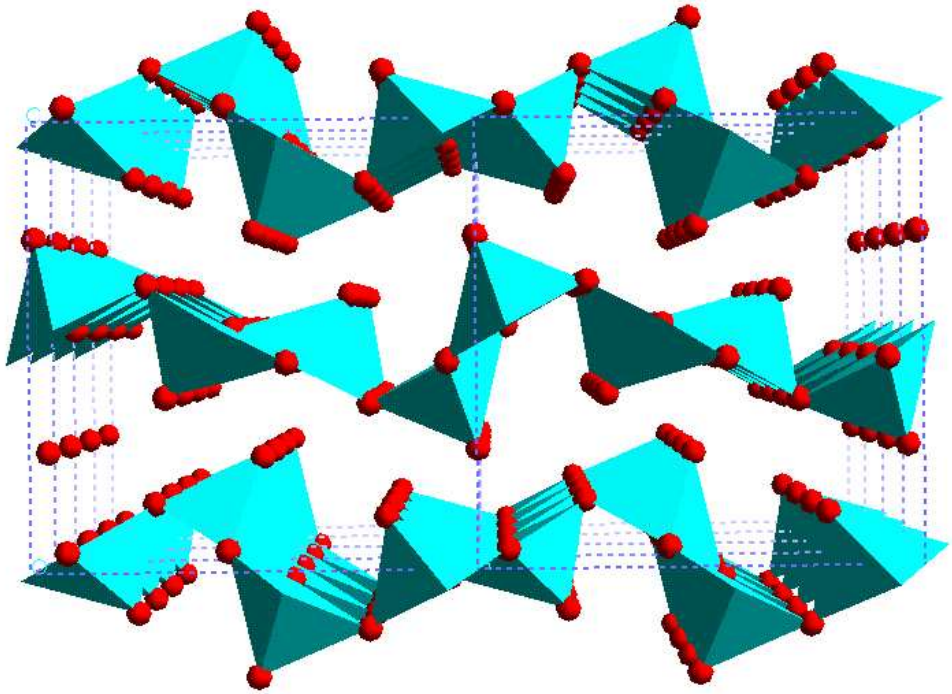
$$I_N(b) = \sum_{n,m\neq n}^{N} f_n f_m \frac{sin(2\pi b r_{nm})}{2\pi b r_{nm}} \qquad b = \frac{1}{d} = \frac{2sin\vartheta}{\lambda}$$

Structures

α-V_2O_5

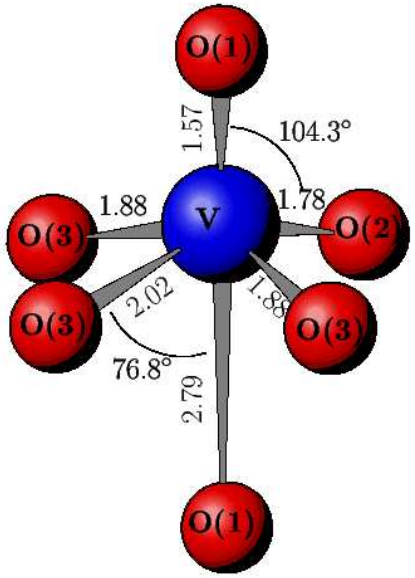


γ-V_2O_5



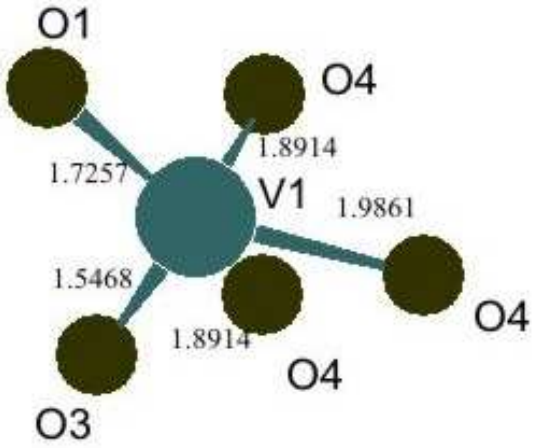
Structures

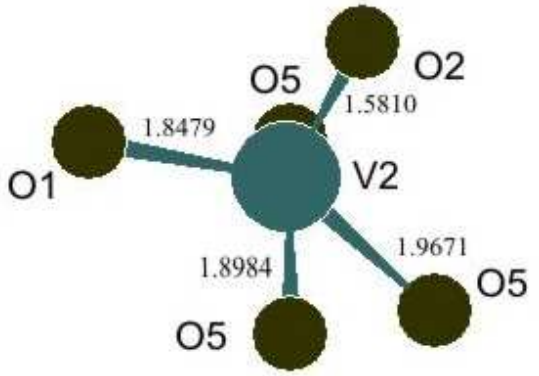
α-V_2O_5



Atom1	Atom2	Distance (Å)
V	O1	1.5759
V	O2	1.7783
V	O3	2.0176
V	O3	1.8776

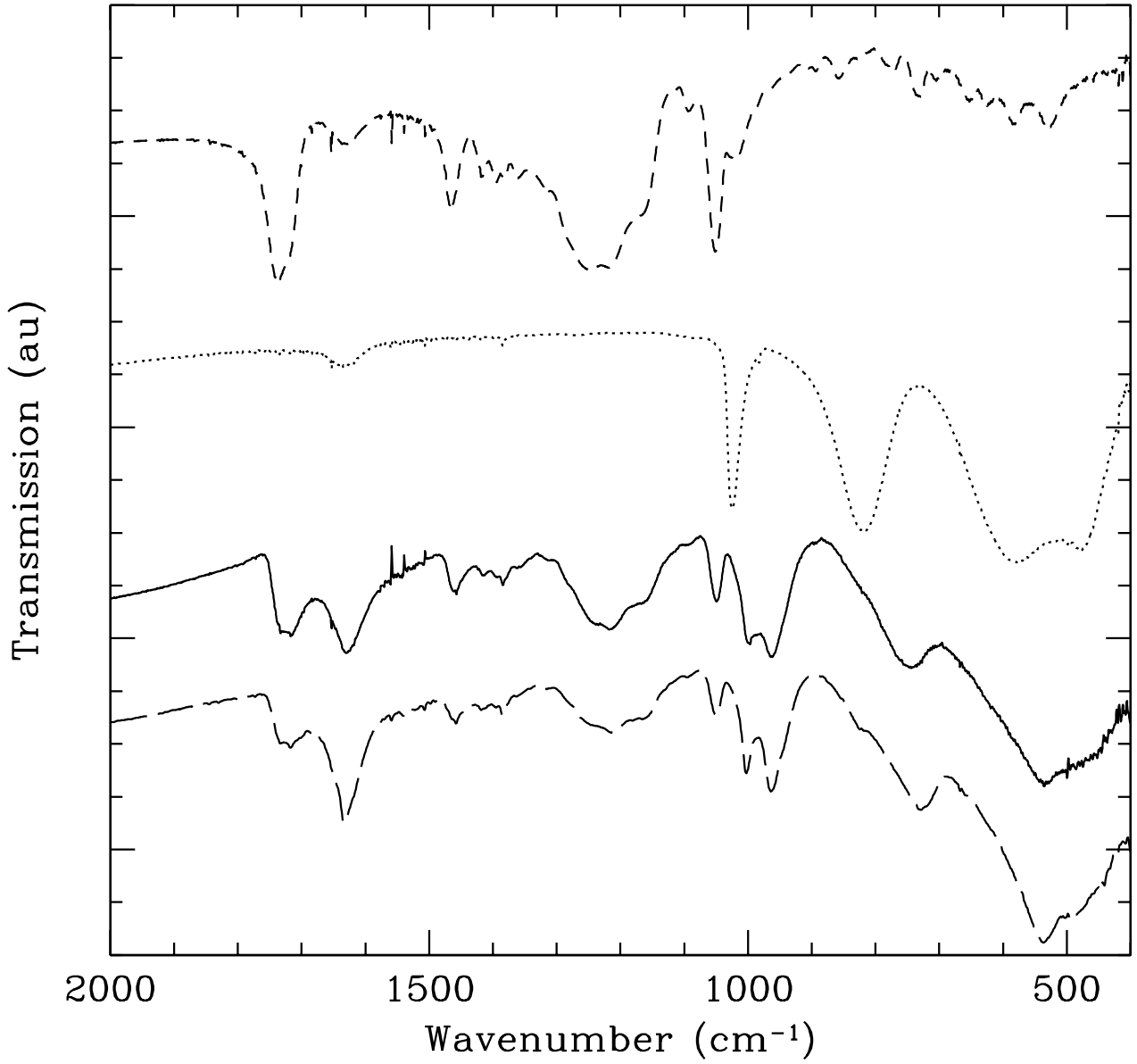
γ-V_2O_5





Atom1	Atom2	Distance (Å)
V1	O1	1.7257
V1	O3	1.5468
V1	O4	1.8914
V1	O4	1.9861
V2	O1	1.8479
V2	O2	1.5810
V2	O5	1.8984
V2	O5	1.9671

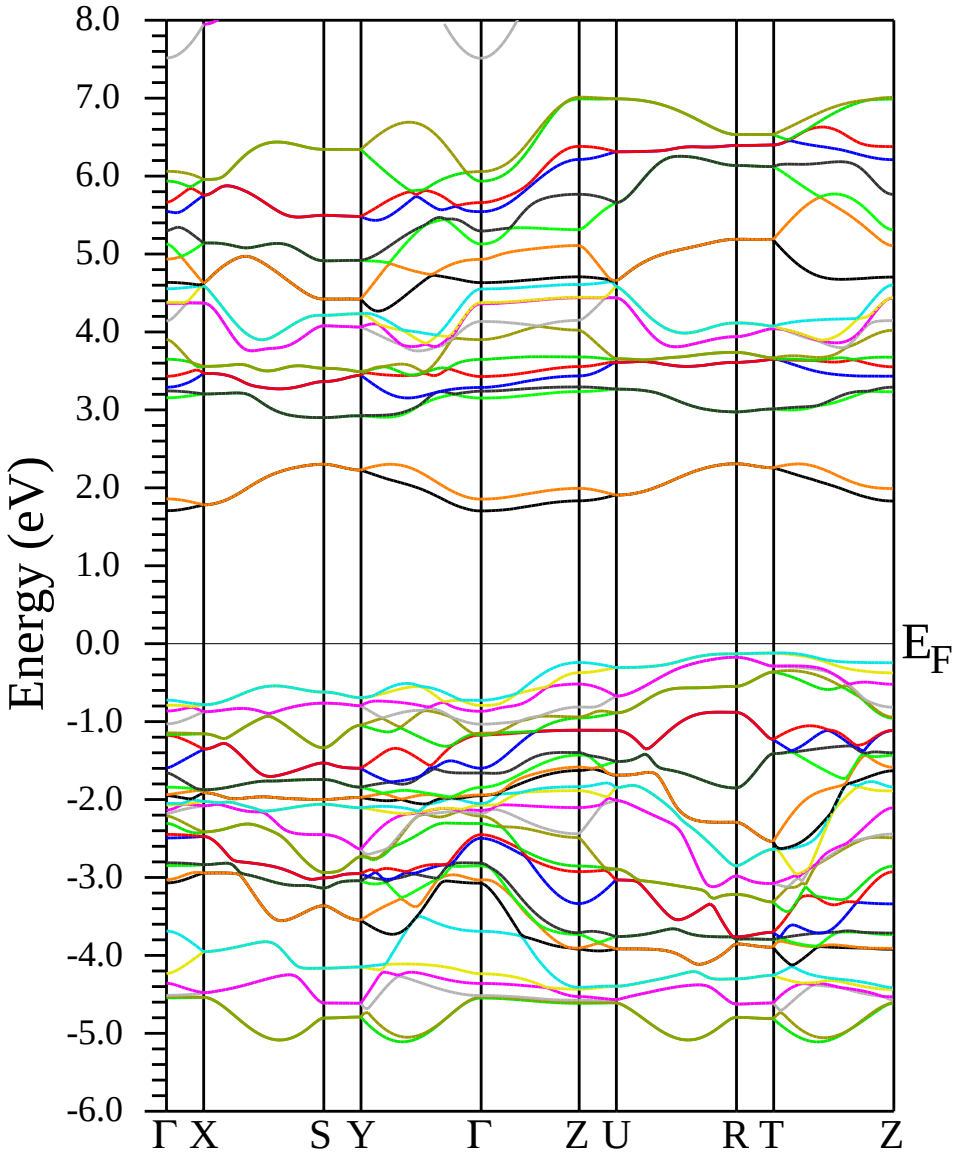
FT-IR



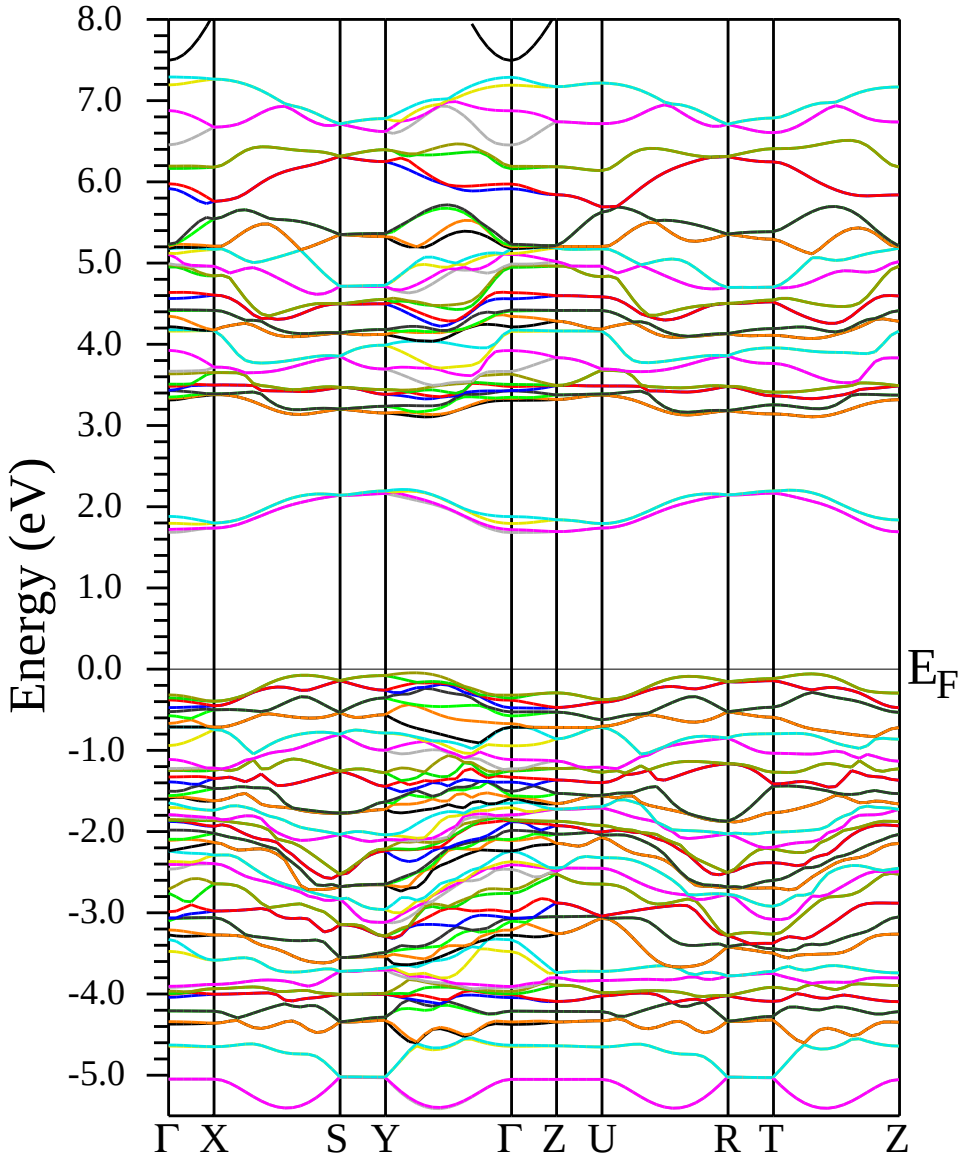
- - - AOT · · · α-V_2O_5 Bulk — γ-V_2O_5 24h – – γ-V_2O_5 100d

Band structure

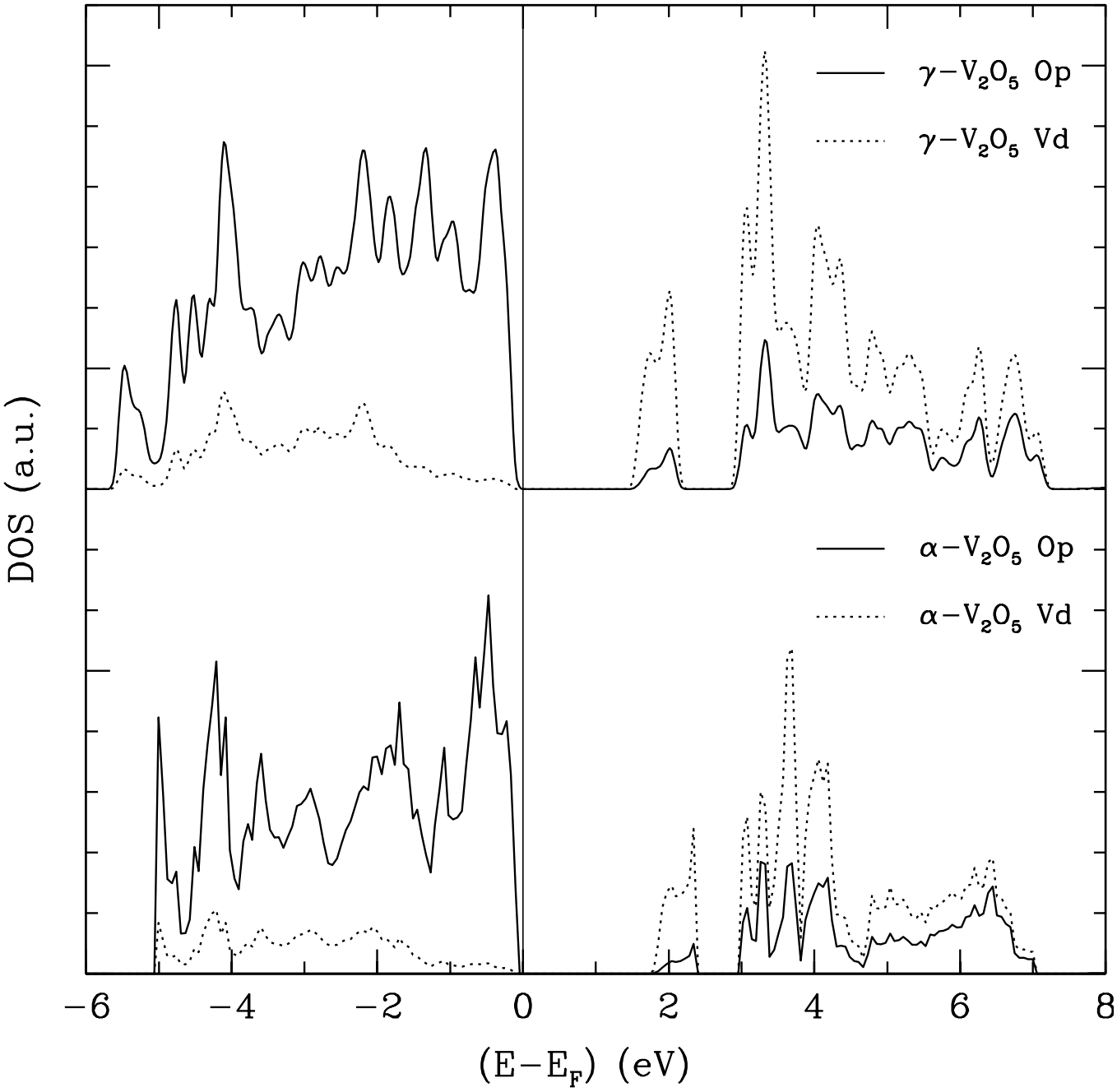
α-V_2O_5



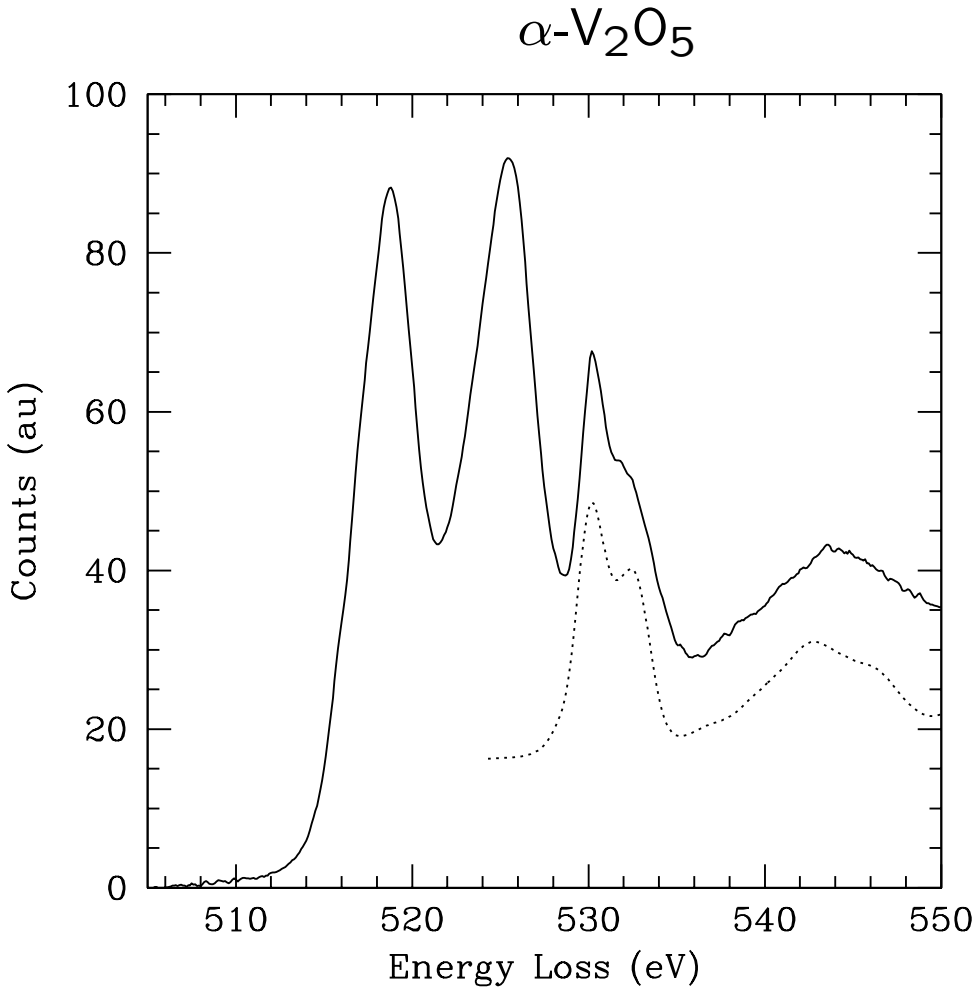
γ-V_2O_5

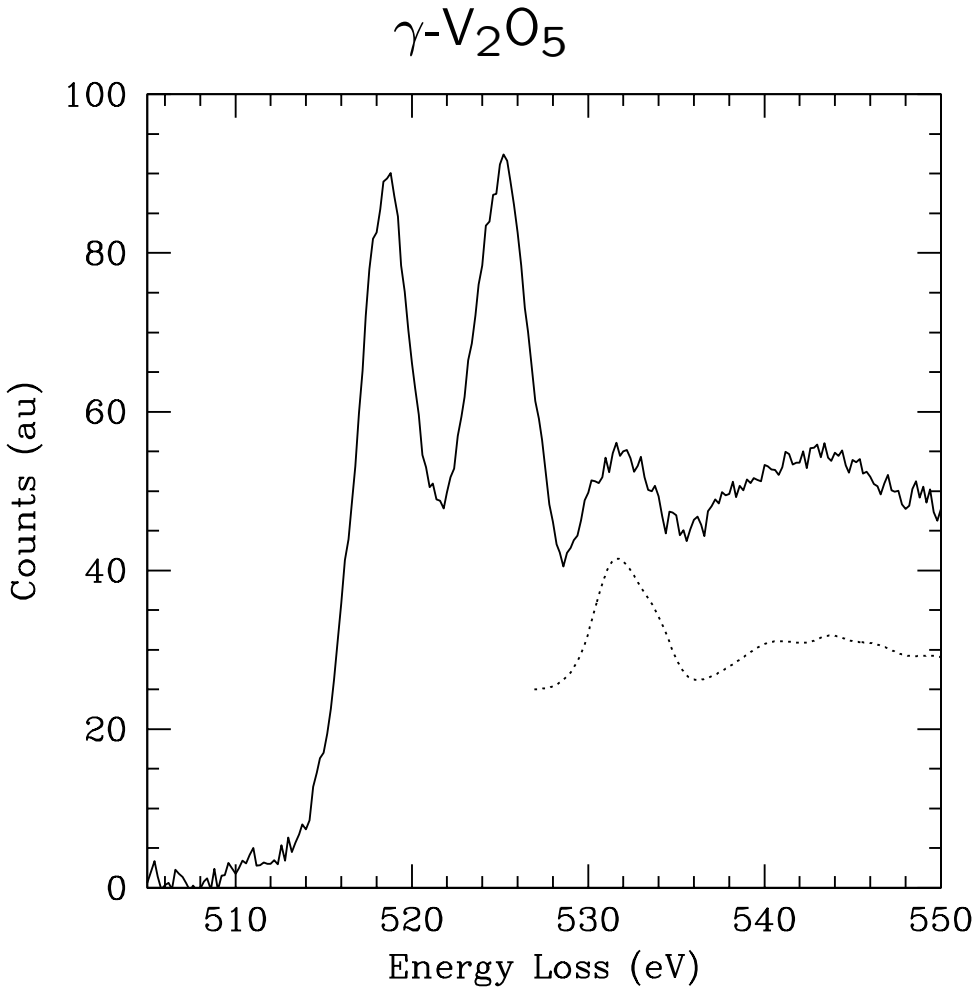


DOS

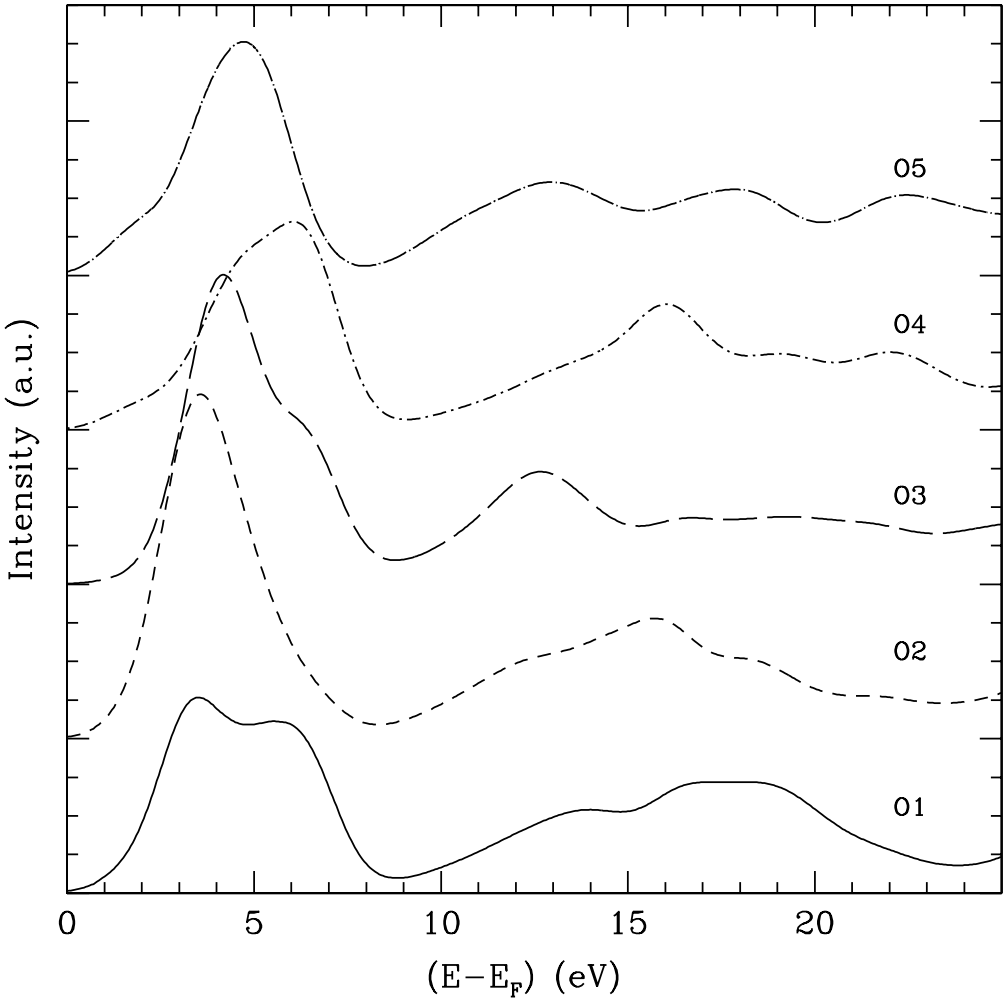


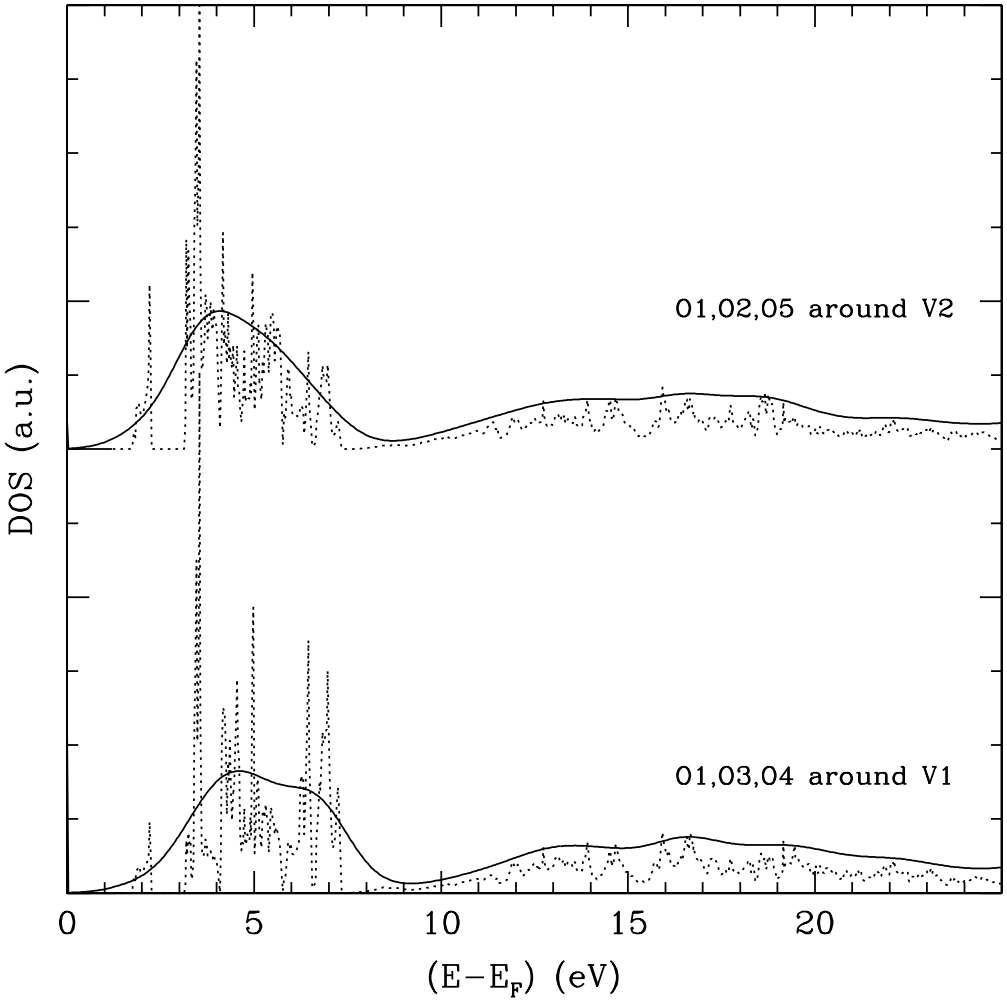
Electron Energy Loss Spectrometry



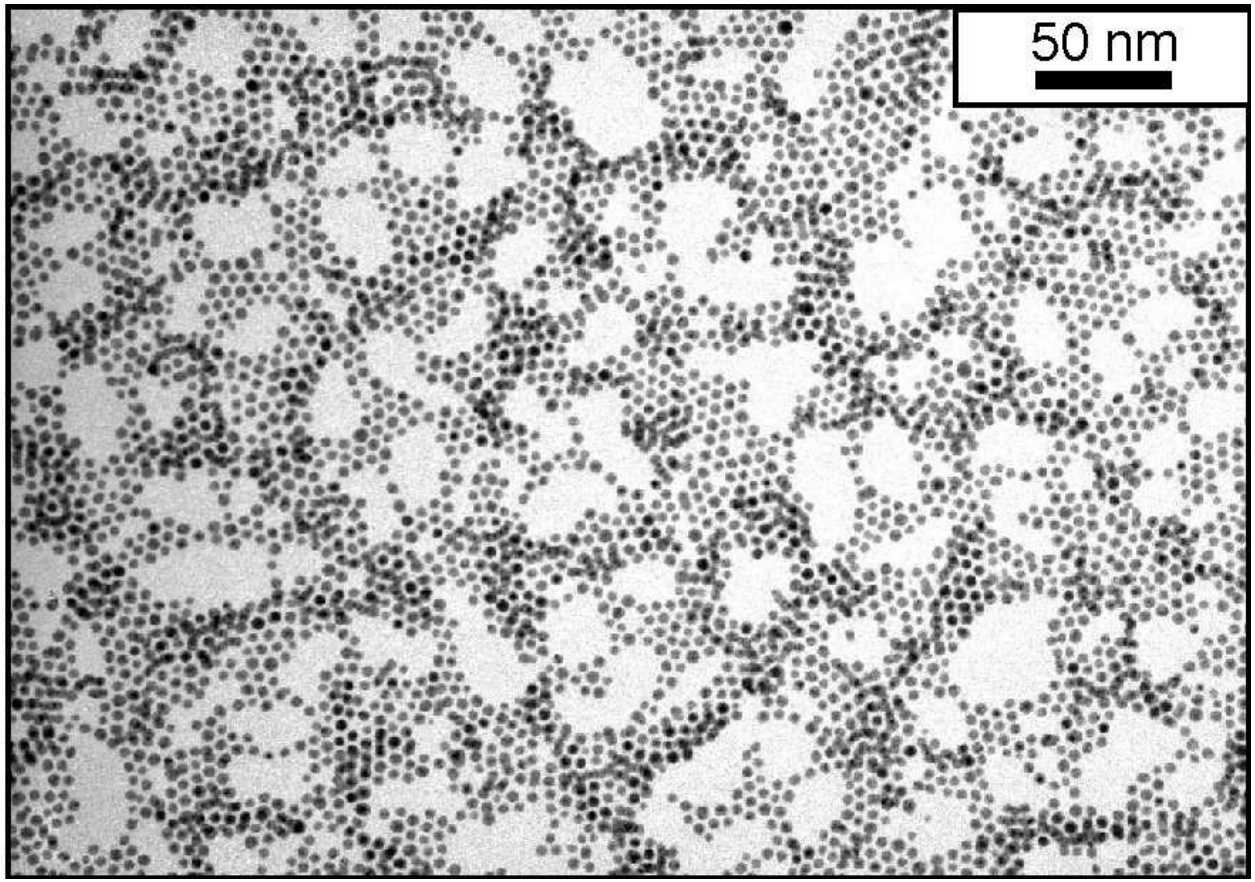


Electron Energy Loss Spectrometry





Reduction



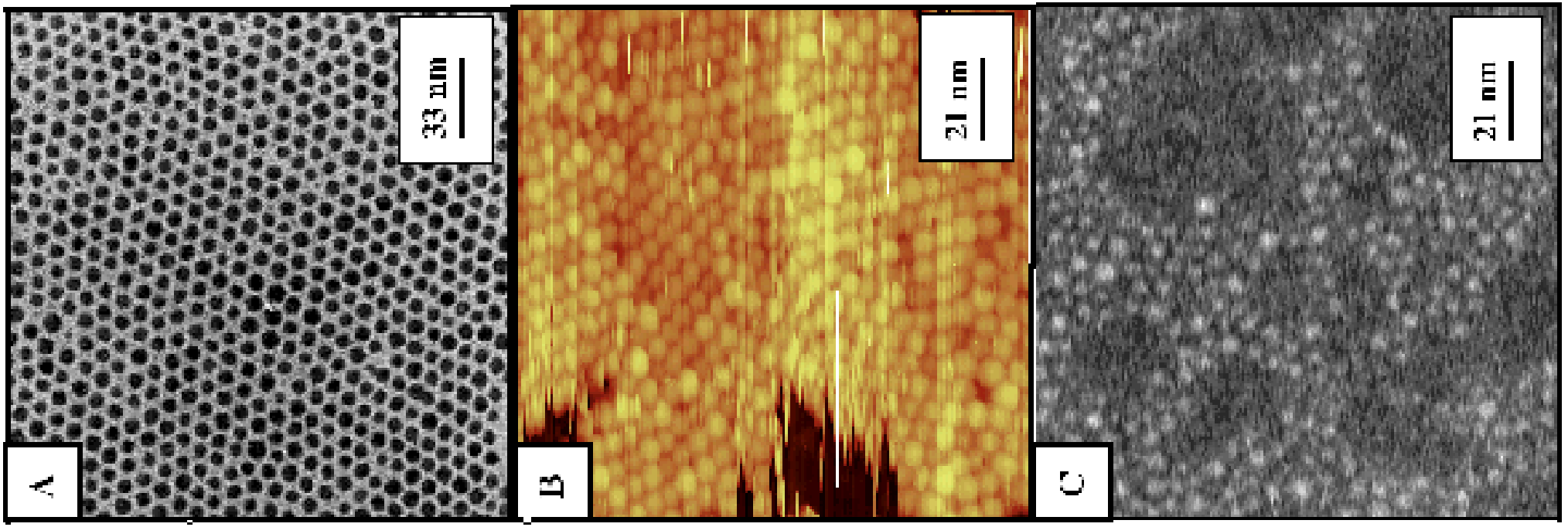
1 - 60% Ag(AOT) - 40% Na(AOT) O.1 M - W=2

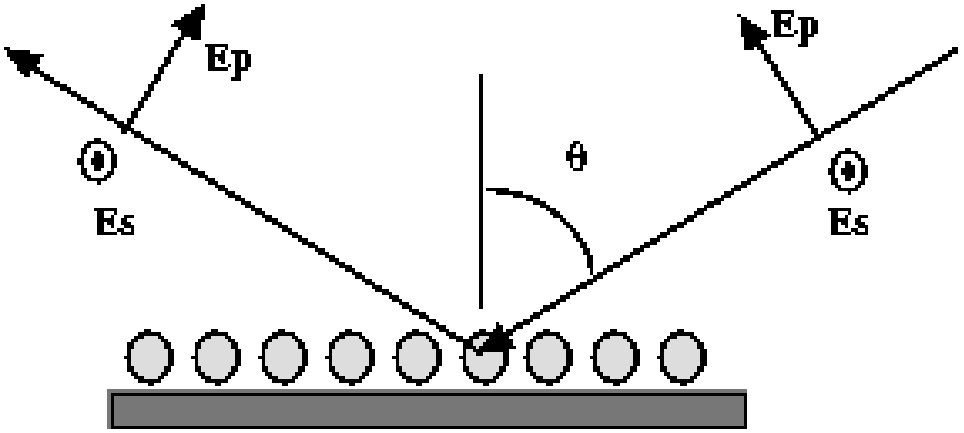
2 - Na(AOT) O.1 M - N_2H_4 - $[N_2H_4]/[AOT]=1.44$

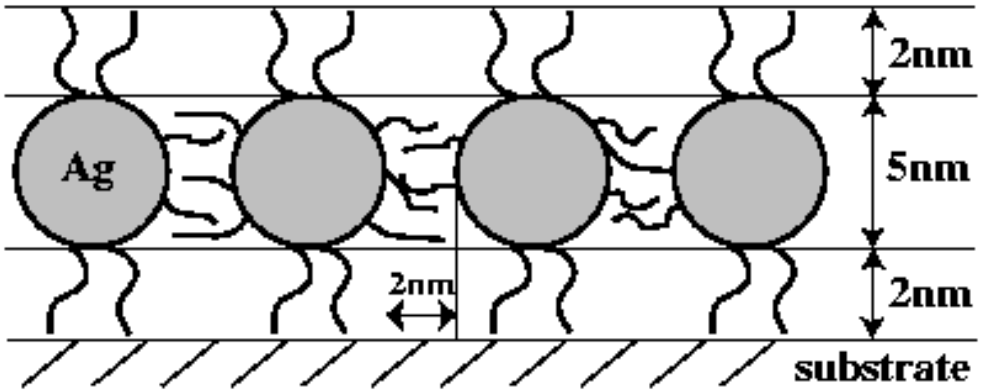
$$2\ N_2H_4 + 4Ag^+ \rightarrow N_2 + 4H^+ + 4Ag^0$$

A. Taleb, C. Petit, M. P. Pileni, Chem. Mater. 1997, 9, 950

Silver Nanoparticles



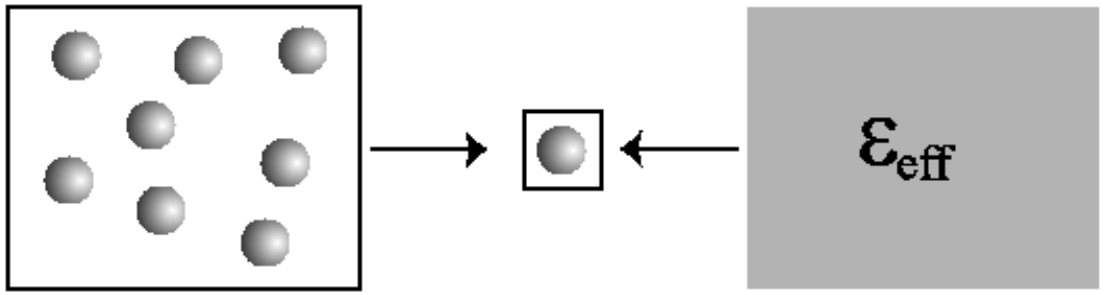




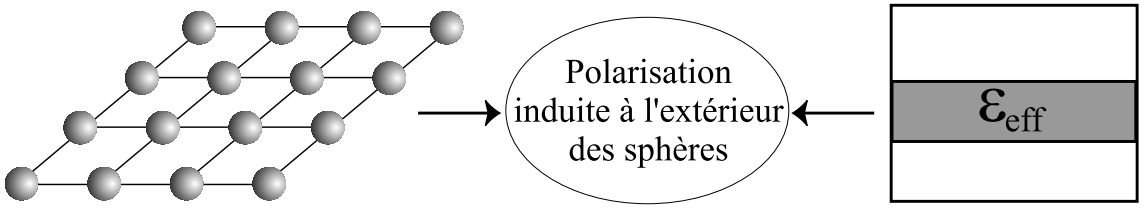
N. Pinna, M. Maillard, A. Courty, V. Russier, and M. P. Pileni, *Phys. Rev. B* **2002**, *66, 045415*

Optical Properties

Maxwell-Garnett



2D Generalisation

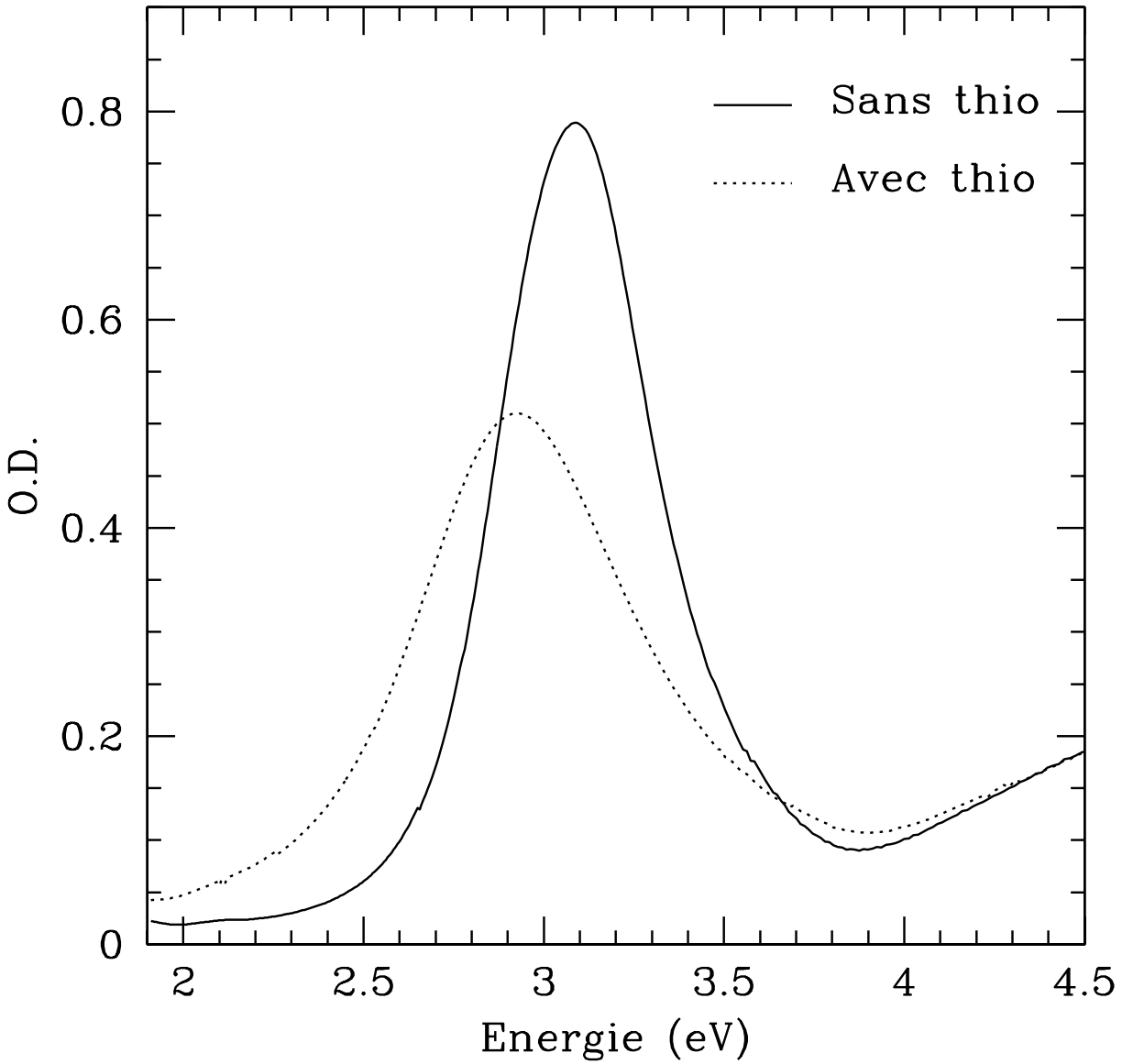


Dipolar Fields: $\sum_x = \frac{1}{2}S_0 \quad ; \quad \sum_z = -S_0 \quad ; \quad S_0 = \sum_j' = \frac{1}{(r_{ij}/d)^3}$

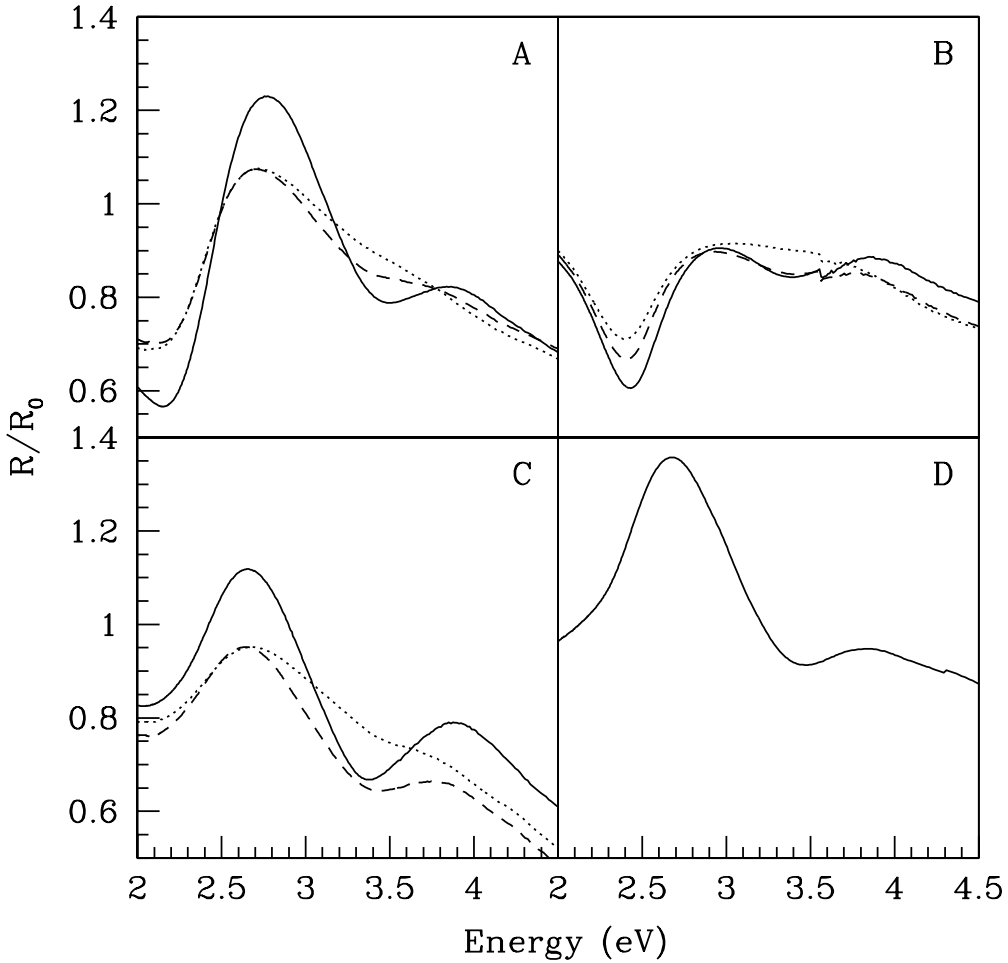
$$\frac{\varepsilon^x_{eff}}{\varepsilon_m} = \frac{1-(\lambda\tilde{\alpha}/8)(S_0/2)+2\gamma(2a/d)^2\tilde{\alpha}}{1-(\lambda\tilde{\alpha}/8)(S_0/2)} \quad ; \quad \frac{\varepsilon^z_{eff}}{\varepsilon_m} = \frac{1+(\lambda\tilde{\alpha}/8)S_0}{1+(\lambda\tilde{\alpha}/8)S_0-2\gamma(2a/d)^2\tilde{\alpha}}$$

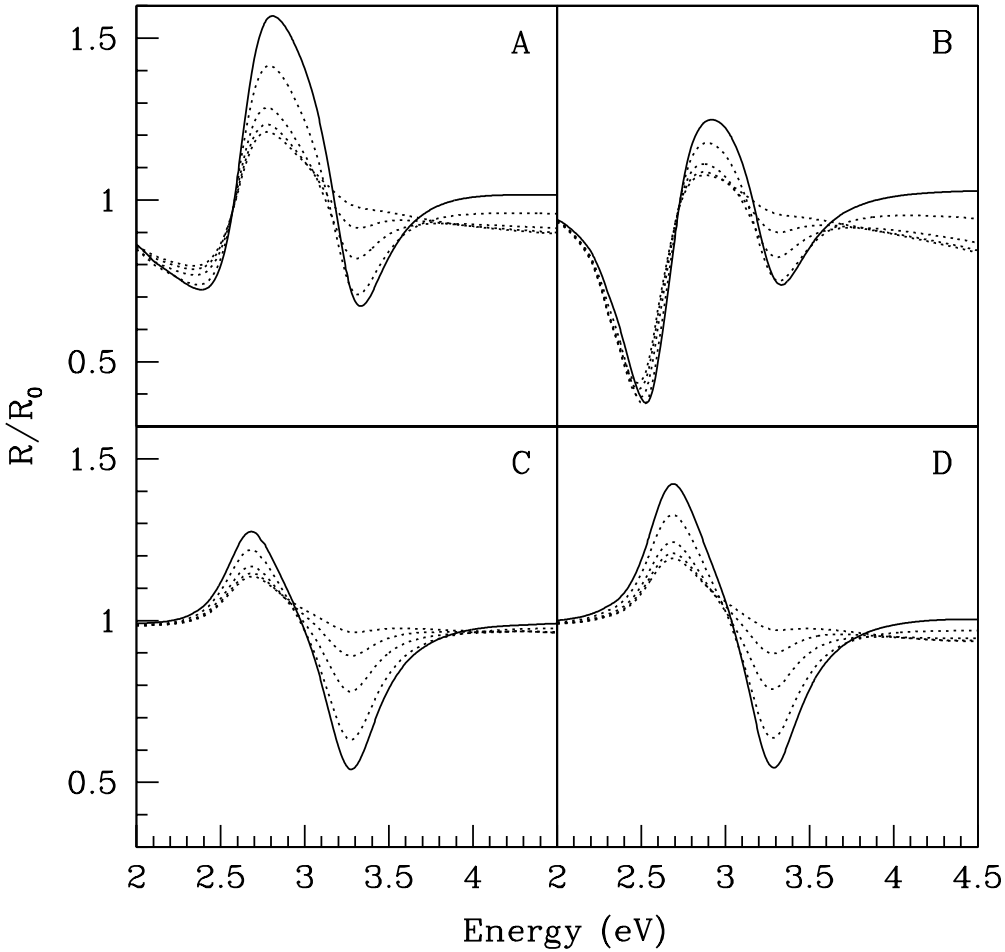
$$\lambda = (2a/d)^3 \quad ; \quad \tilde{\alpha} = \frac{\varepsilon_s(\omega)-\varepsilon_m}{\varepsilon_s(\omega)+2\varepsilon_m} \quad ; \quad \gamma = f_s/(2a/d)^2$$

Optical Properties

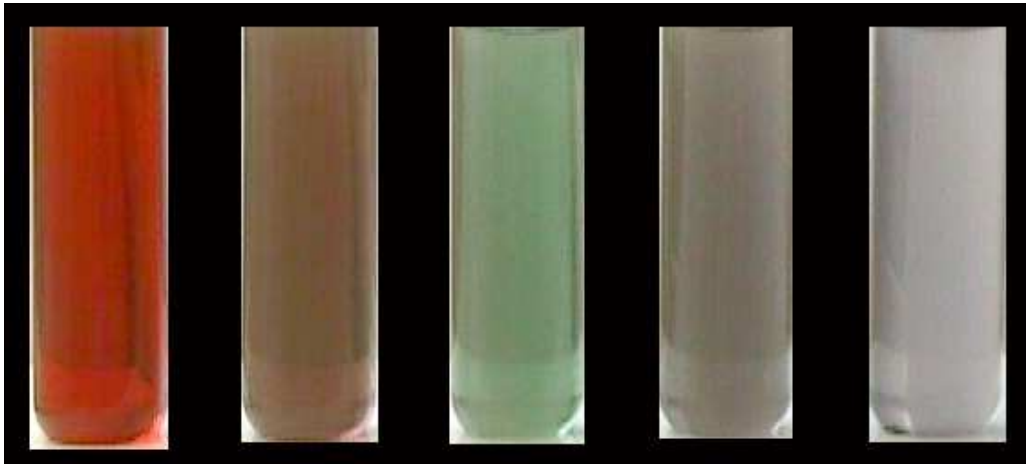


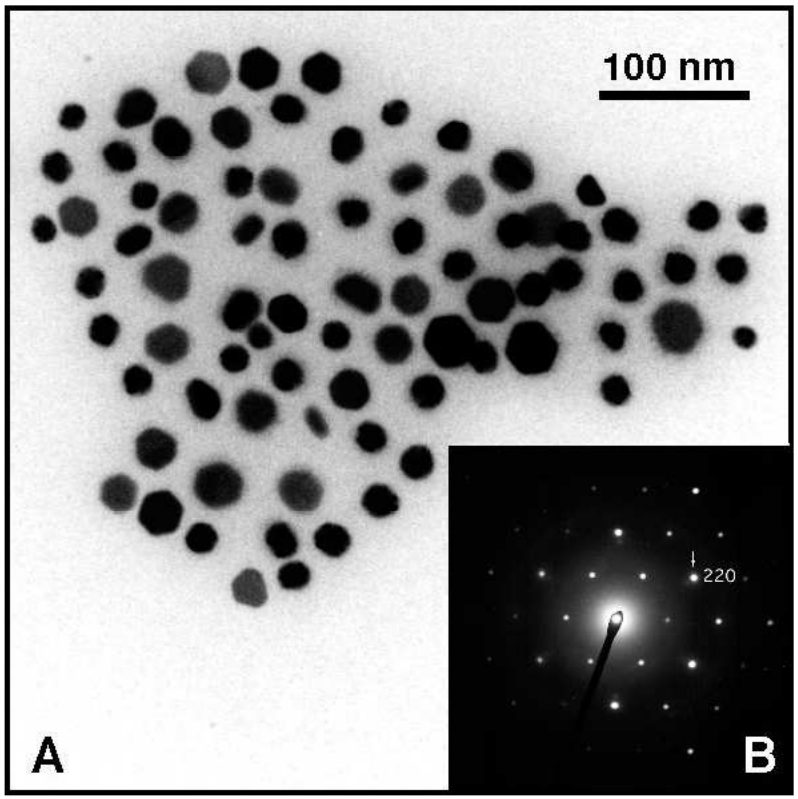
Optical Properties





Silver Nanodisks





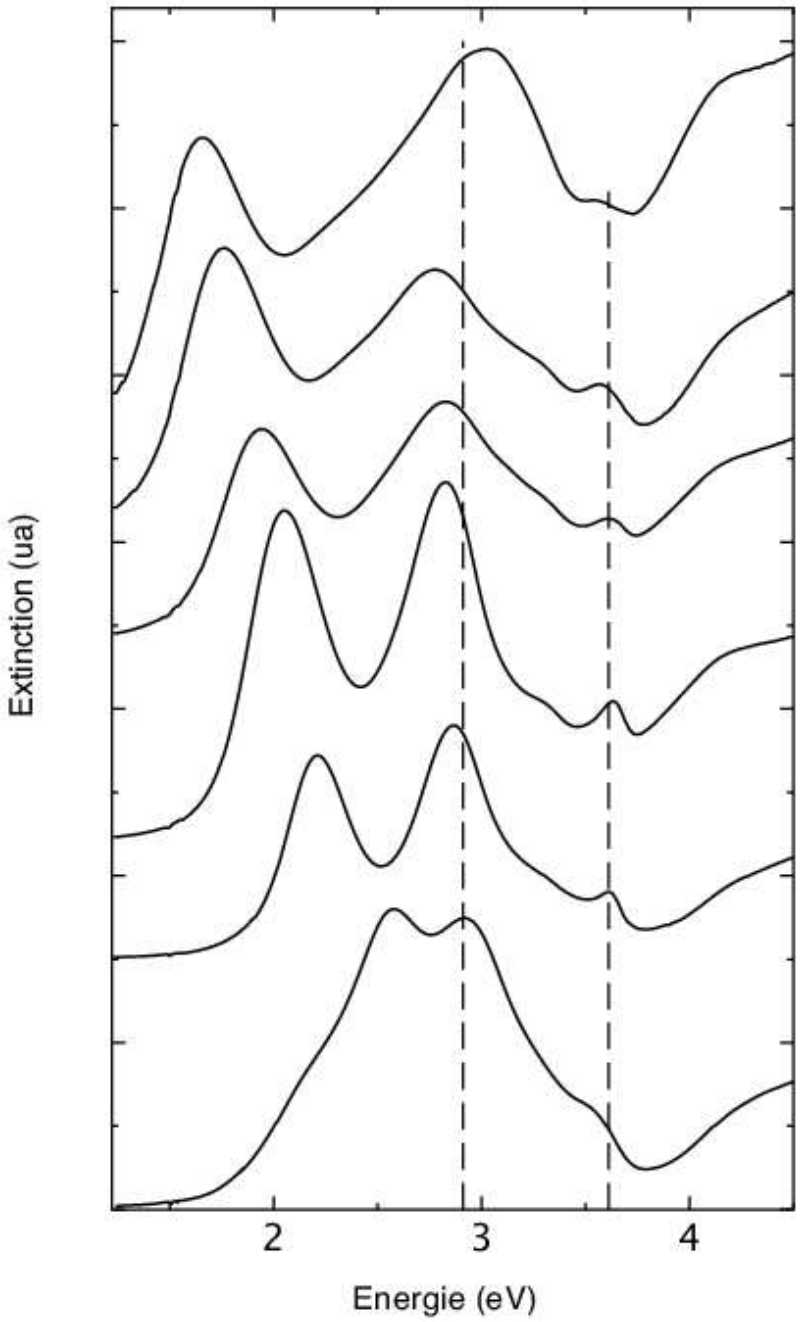
1 - 60% Ag(AOT) - 40% Na(AOT) O.1 M - W=2

2 - Na(AOT) O.1 M - N_2H_4 - $4.1 < [N_2H_4]/[AOT] < 16.5$

$$2\ N_2H_4 + 4Ag^+ \rightarrow N_2 + 4H^+ + 4Ag^0$$

M. Maillard, S. Giorgio, M.P. Pileni, Adv. Mater. 14, 1084, 2002

Optical Properties



Conclusion

- The reverse micelle technique permits the synthesis of many inorganic materials
- Size and shape control
- Homogeneous products
- Low polydispersity
- Small quantities and difficult to scale up

Acknowledgements

- M. Willinger - First DFT calculations of γ-V_2O_5 Structure
- K. Weiss, H. Sack-Kongehl - Transmission electron microscopy
- U. Wild - XPS mesurements
- Dr. M. Maillard, Dr. V Russier - Optical properties of silver nanoparticles
- Prof. J. Urban, Prof. R. Schlögl, Prof. M. P. Pileni