Inorganic Laminar Semiconductors

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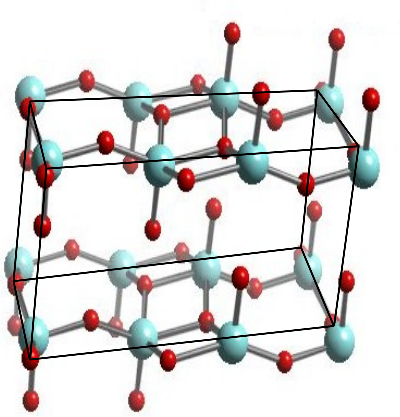
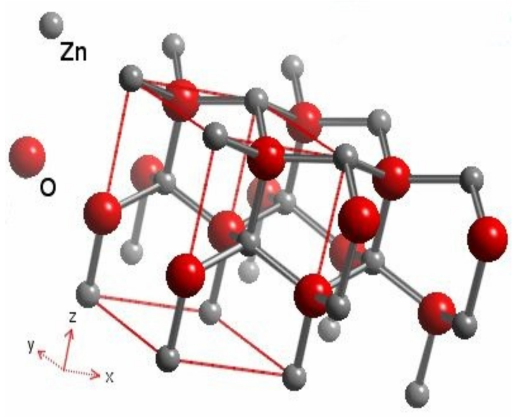
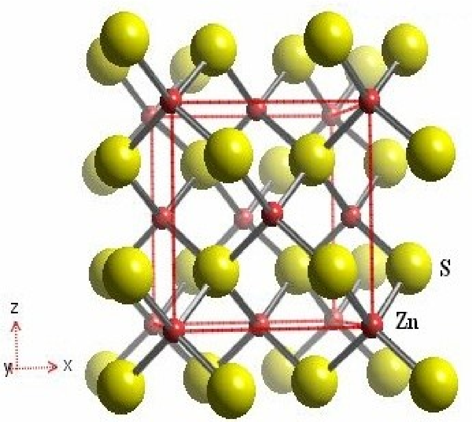
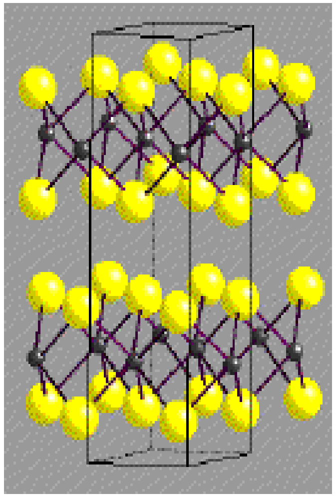
IRELAC - EULA-NETCERMAT SEMINAR
Brussels, February 28, 2013

INORGANIC SEMICONDCUTORS
Crystal Structures





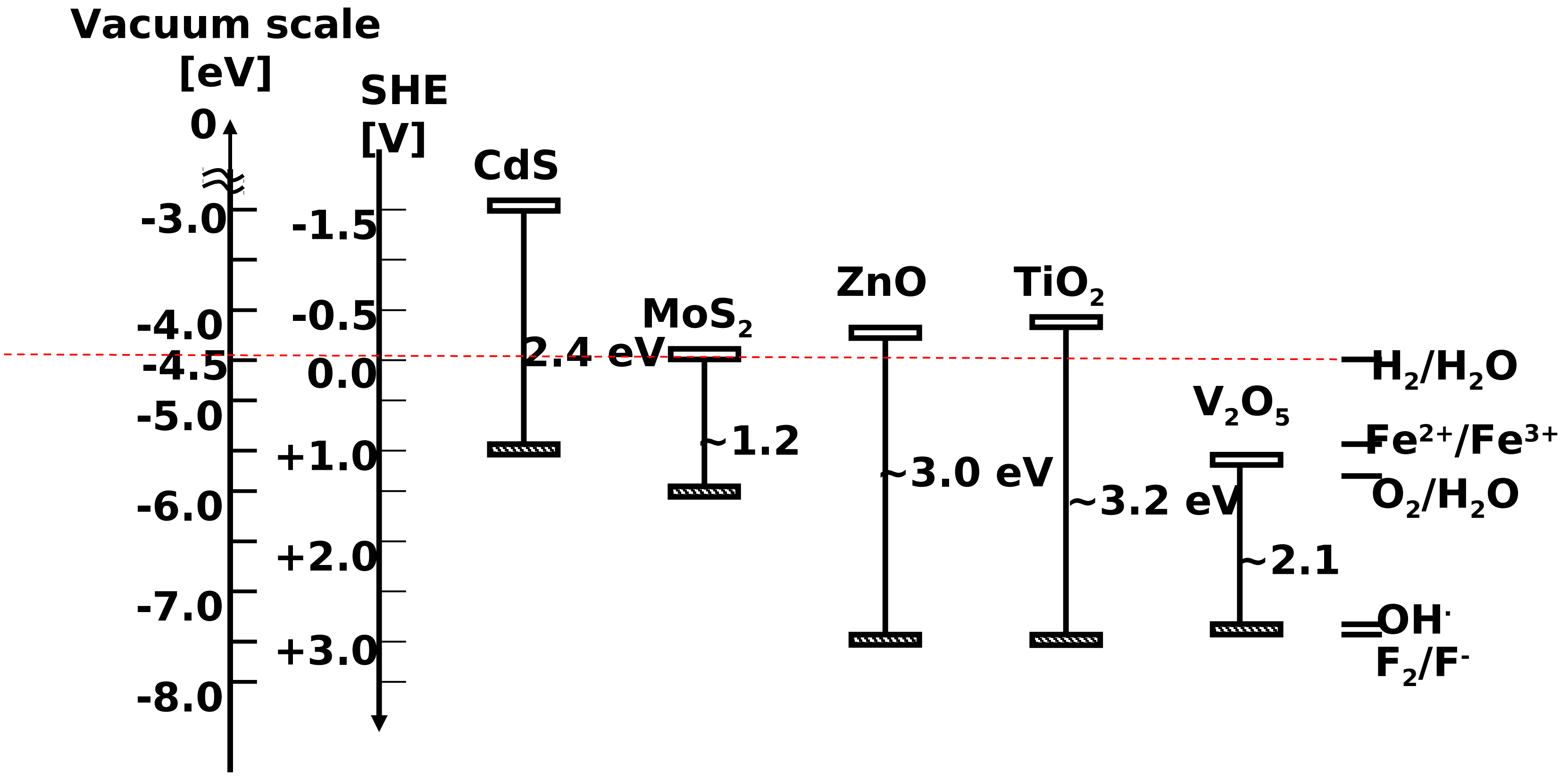




V_2O_5 **ZnO** **ZnS** **MoS_2**

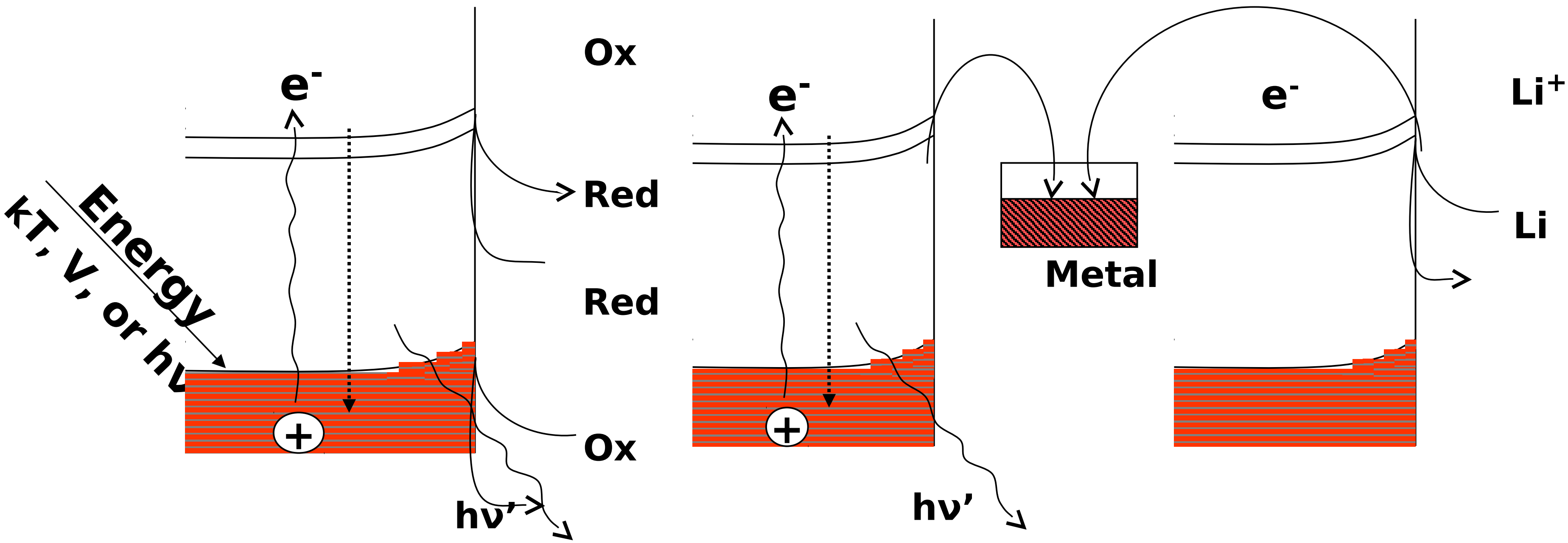
Ionic-Covalent Networks
Inherent atomic distribution and symmetry
Electronegativity, size, oxidation states of components

INORGANIC SEMICONDCUTORS
Electronic Structure



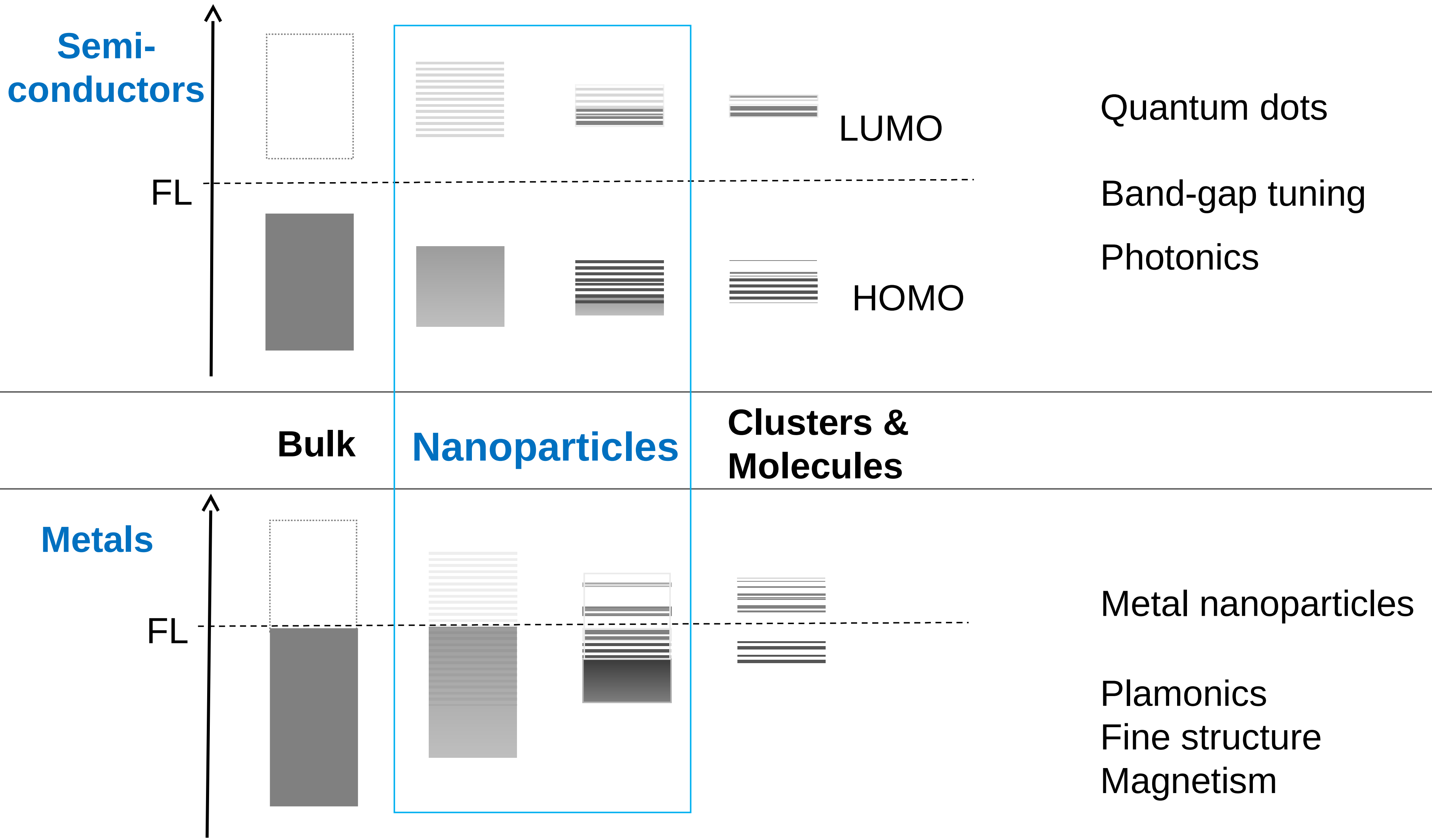
INORGANIC SEMICONDCUTORS
Physicochemical Properties

Electron and/or Hole Chemical Potential
Energy of Valence and Conduction Band
Band Gap – Separation of Hole/Electron Pair - Surface Area

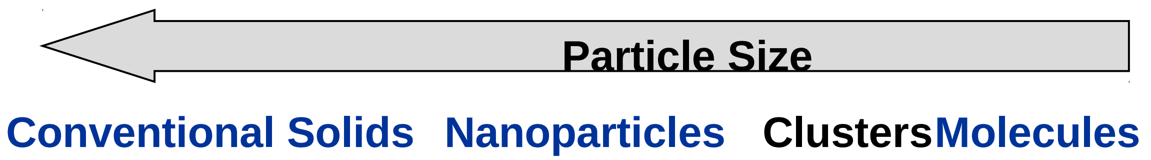


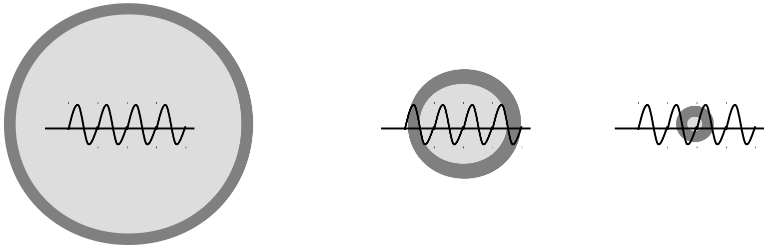
Photocatalysis **Photovoltaics** **Electrochemistry**

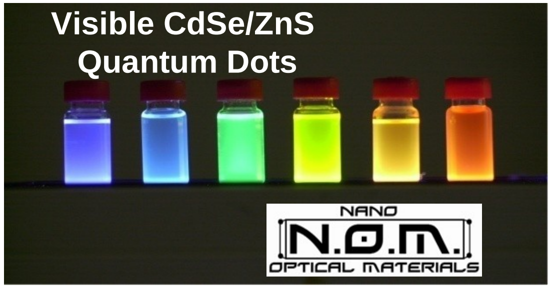
Particle Size & Elecronic Structure

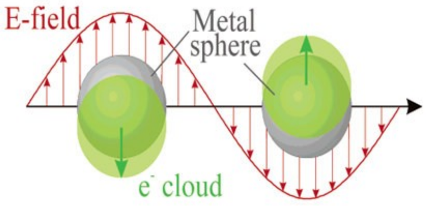


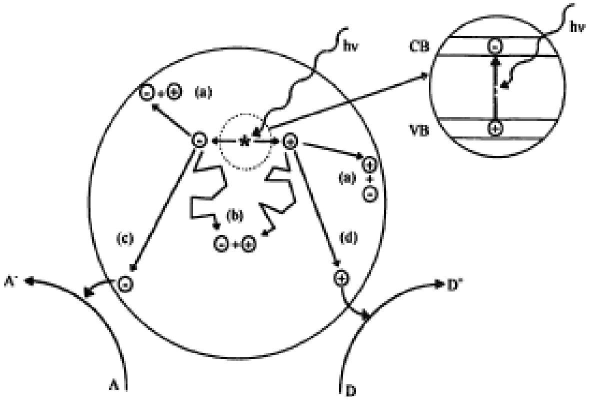
Nanoparticle Size & Spectroscopic Properties

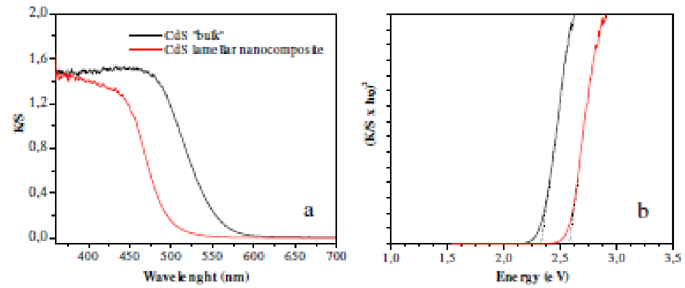


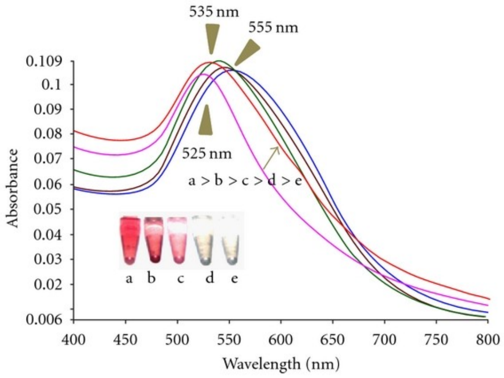


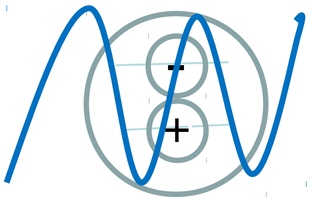




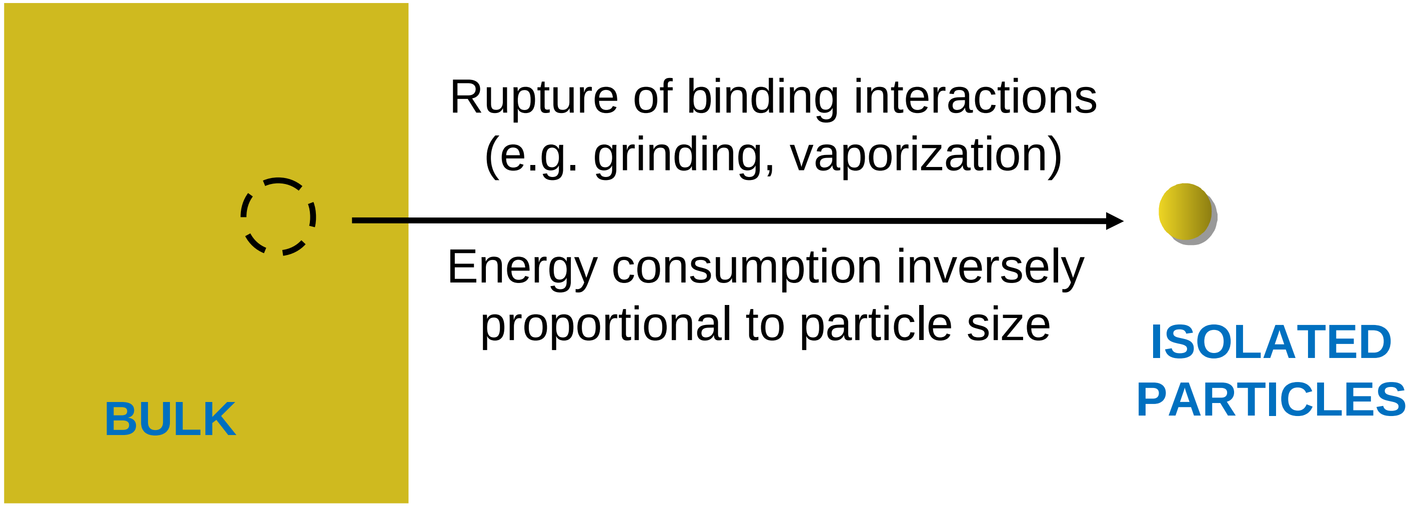


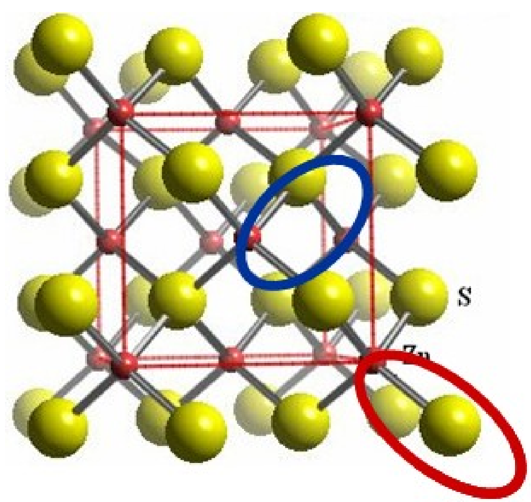


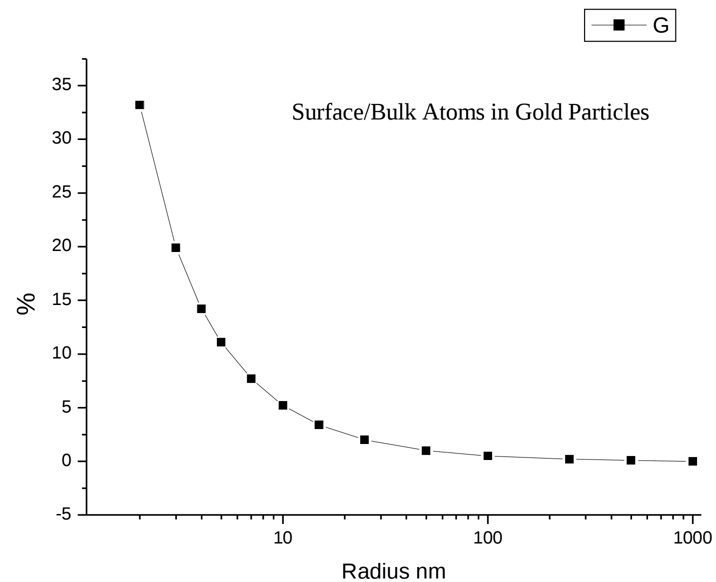




Exciton, De Broglie wave







- **NANO-SPECIES ARE INTRISICALLY INESTABLE OBJECTS**
- **MAJOR CONTRIBUTION IS SURFACE ENERGY**
- **NANOOBJECTS ARE ENERGETICALLY NON HOMOGENEOUS SPECIES**

Nanoscience and nanotecnology: a revolution in natural sciences ?

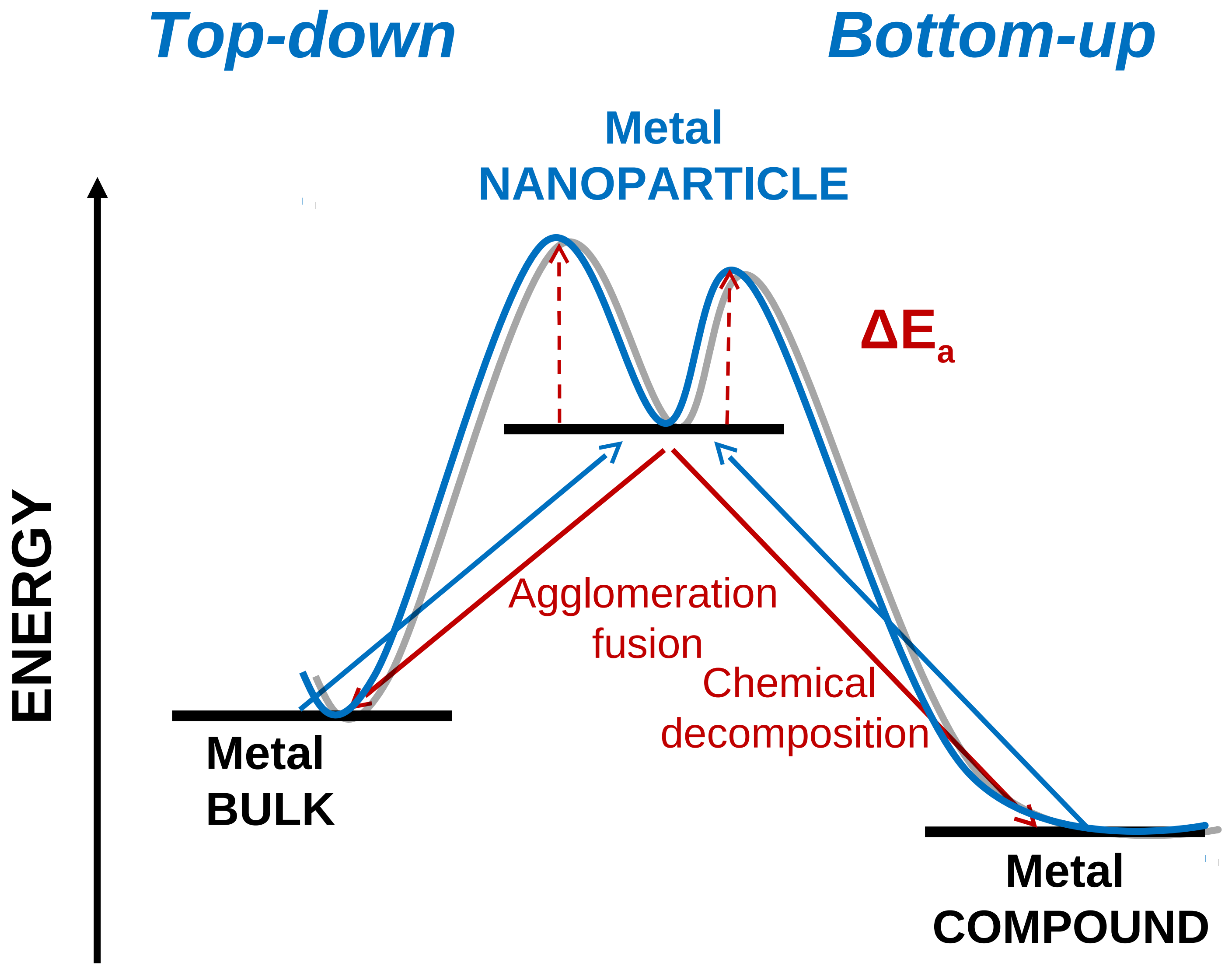
Research of solids with sizes of the order of the nanometers
Challenges to physical and chemical knowledge

Corroboration of theoretical predictions from the physics of solids
A bridge between atoms - molecules and solids
Window for knowledge on properties of thin films and catalysts

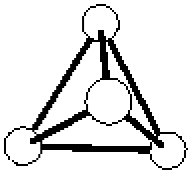
Great potential for multiple applications

…

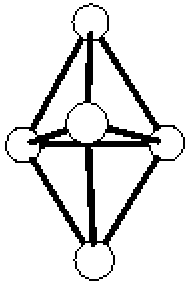
NANOPARTICLE STABILIZATION



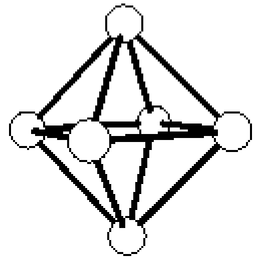
MOLECULAR CLUSTERS



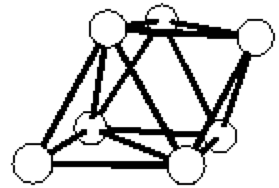
$Ir_4(CO)_{12}$



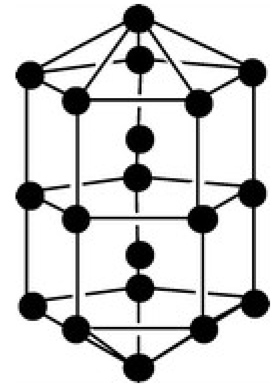
Pb_5^{2-}



Nb_6Cl_{14}



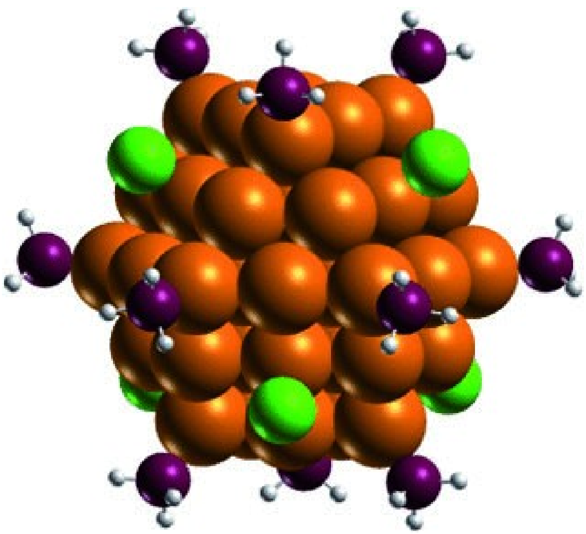
$Os_7(CO)_{21}$

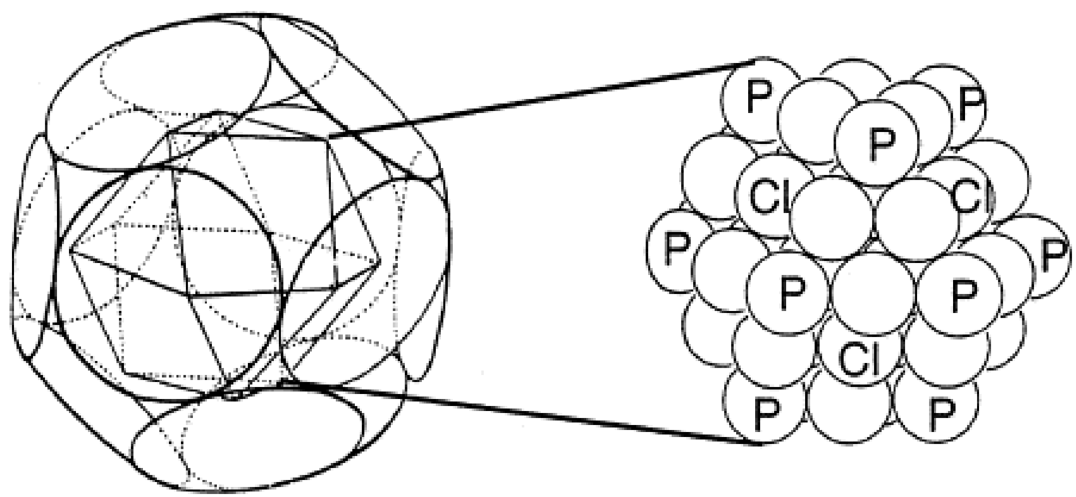


$[Pt_{19}(CO)_{22}]^{4-}$

$[Au_{12}Ag_7(PPh)_{10}]^{2+}$

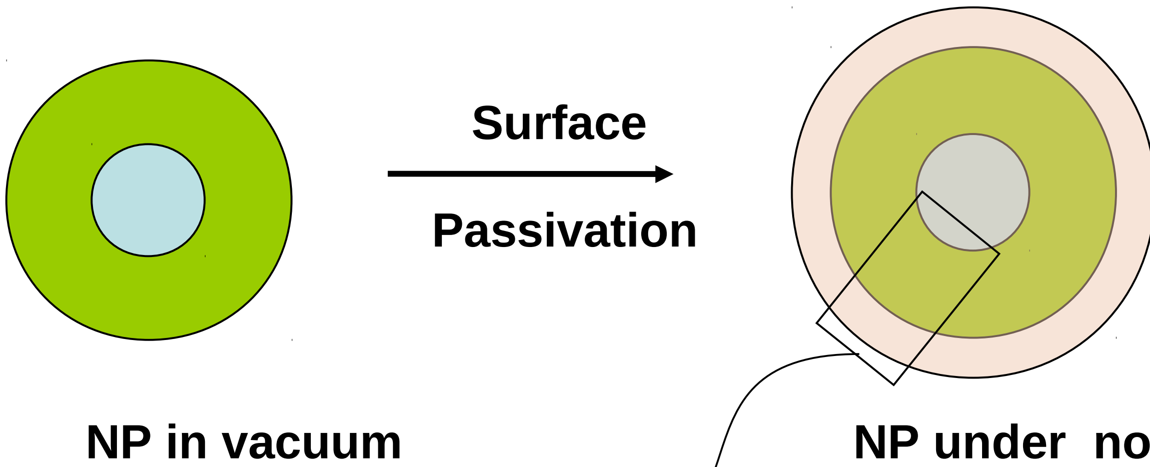
$Au_{55}[P(C_4H_5)_3]_{12}Cl_6$

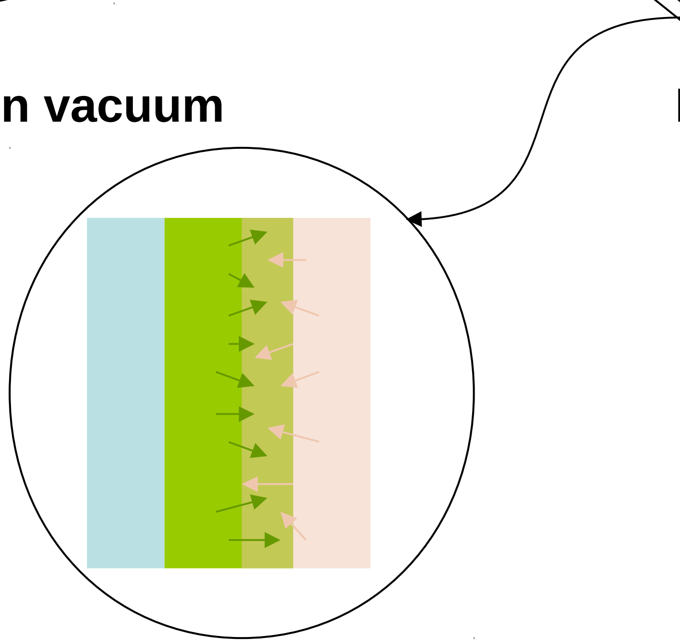




G. Schmid, A. Lehnert, *Angew. Chem. Int. Ed. Engl.* 1989, *28*,

Behavior of Nanoparticles in Normal Chemical Environments





Chemical interactions
Interface defects
Synergic effects
New Properties

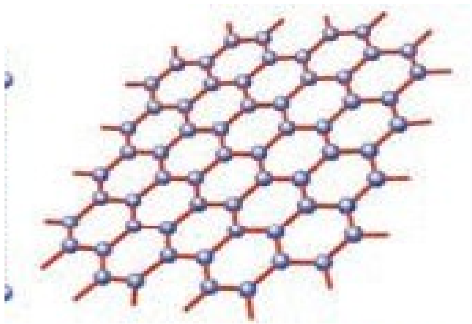
Molecular Interface Engineering
Regulation of Properties
Tailor-Made Materials

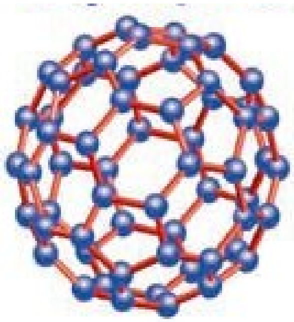
An special case

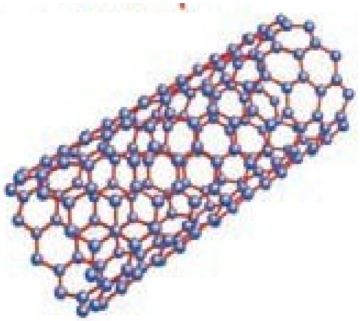
Layered solids – anisotropic nanomaterials

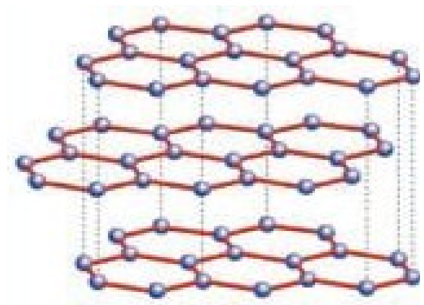
Best example Carbon derivatives

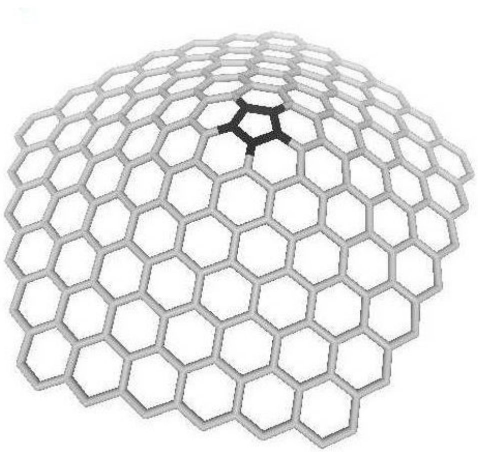
Stability of two dimensional nanoparticles

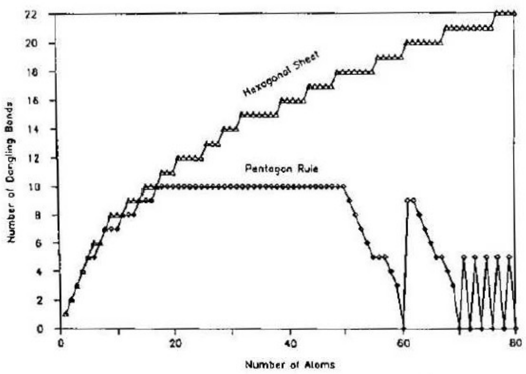


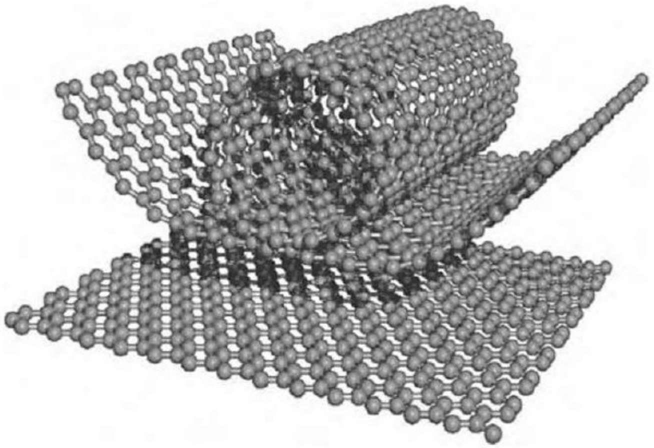




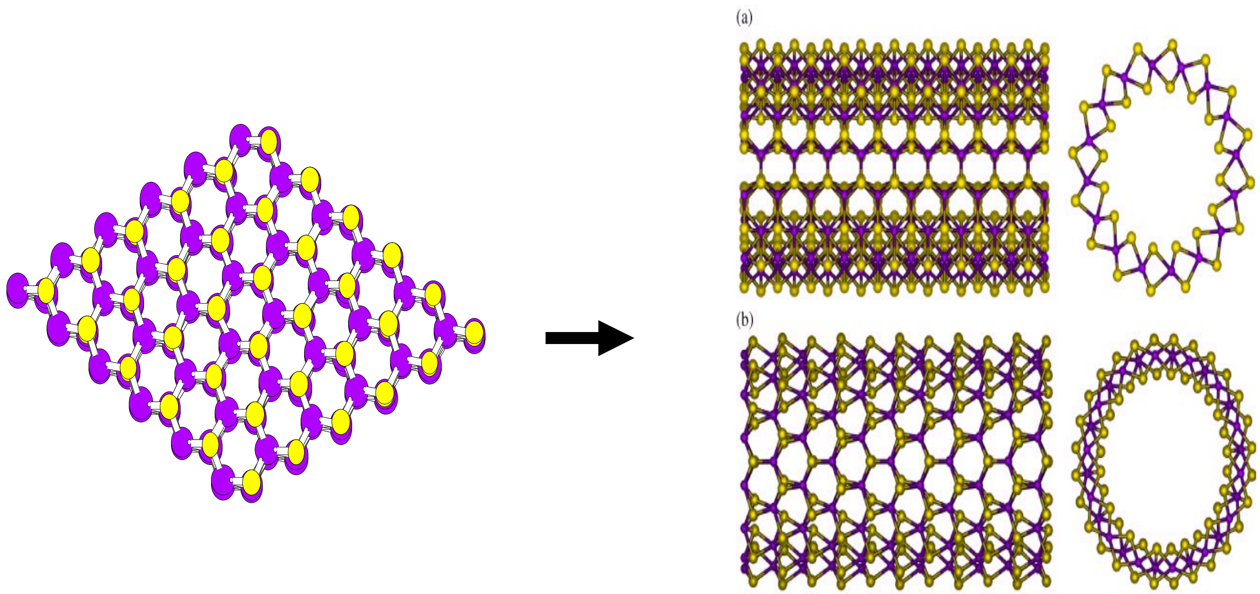








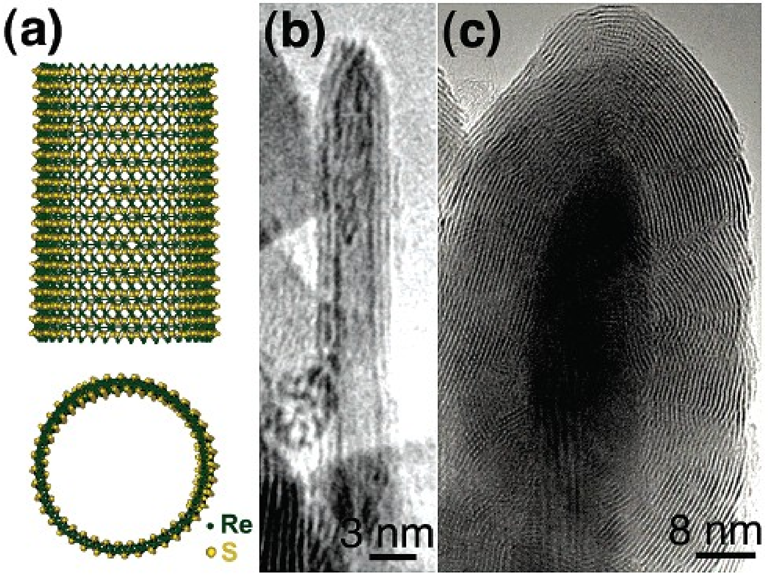
INORGANIC FULLERENES



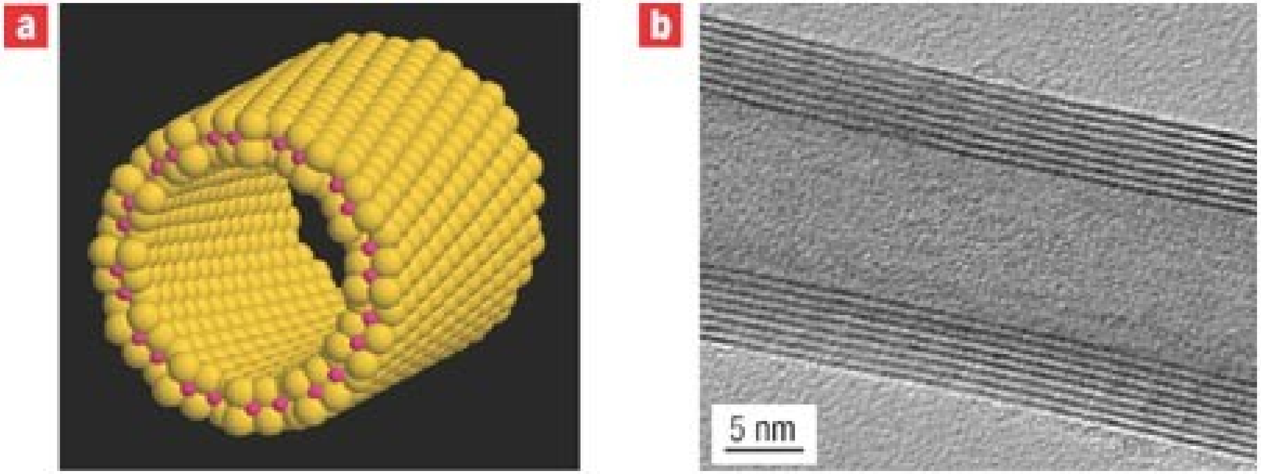
INORGANIC FULLERENES

ReS_2

Coleman et al., J. Am. Chem. Soc. 124, 11580 (2002)



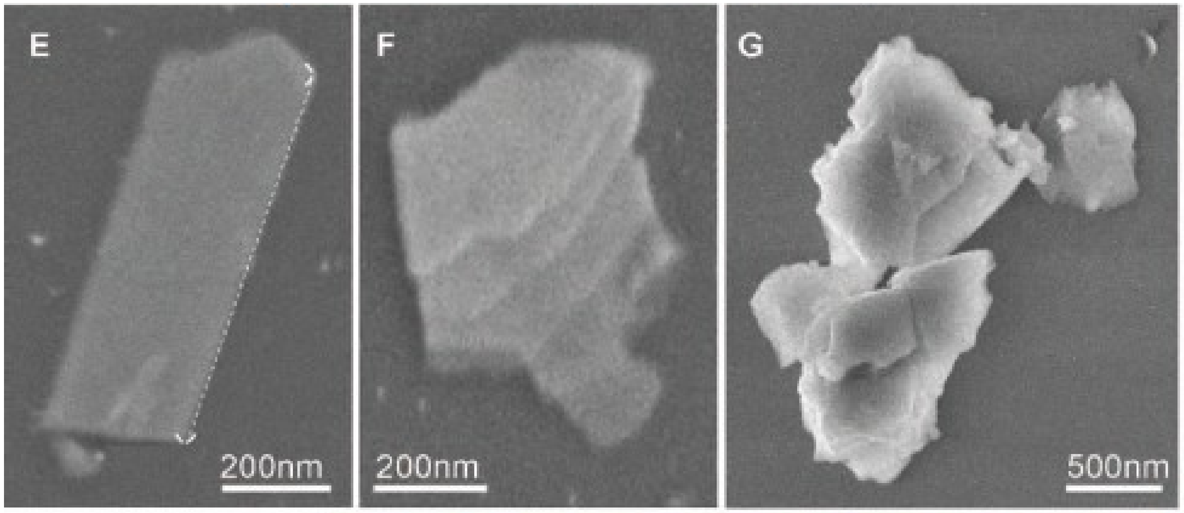
WS_2



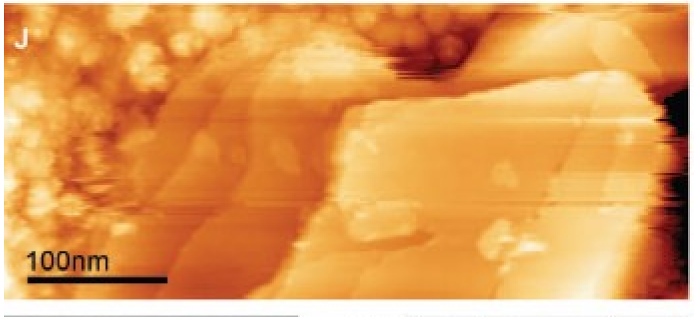
R. Tenne, Nature nanotech. 1, 102, 2006

MoS_2 Graphene-like Nanosheets

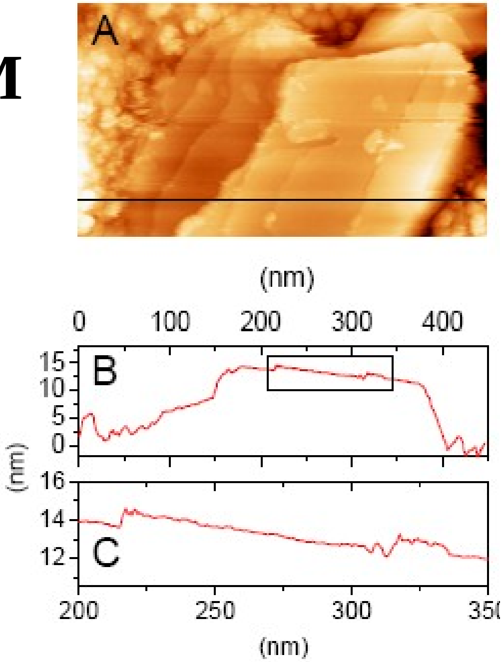
SEM



AFM



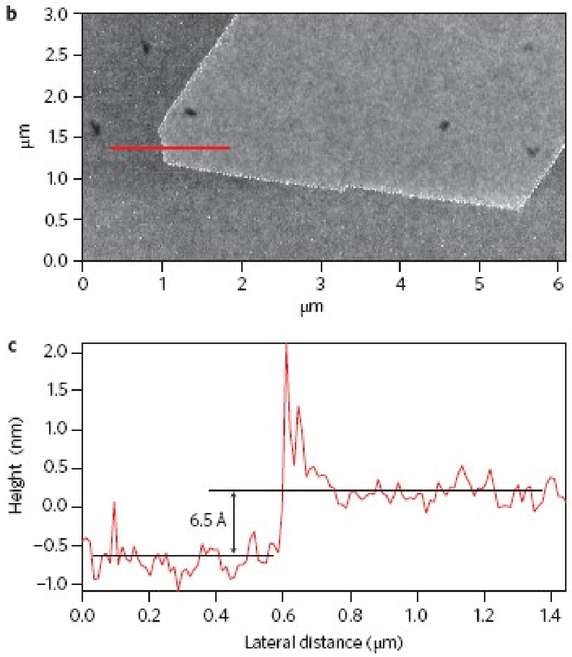
STM

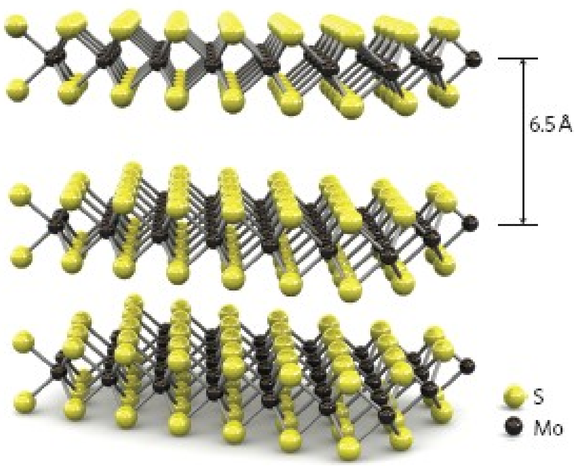


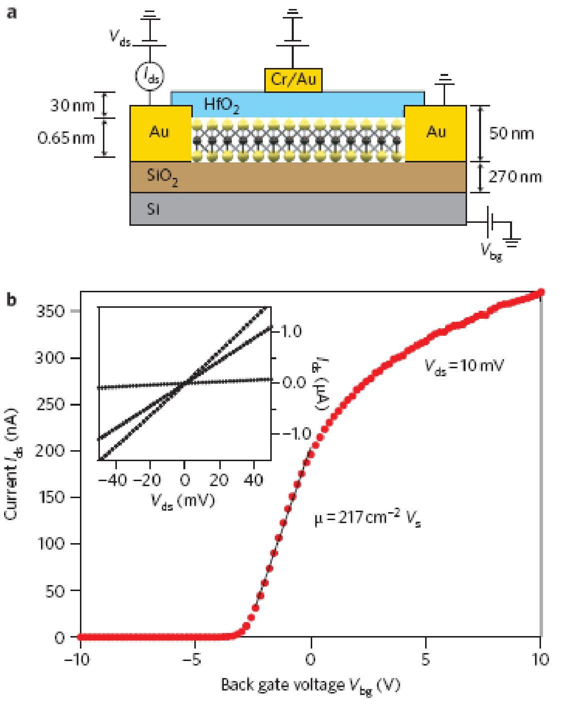
Coleman et al., *Science* 331, 568 (2011)

Inorganic Semiconductor Single Layers

Single-layer MoS_2 transistors

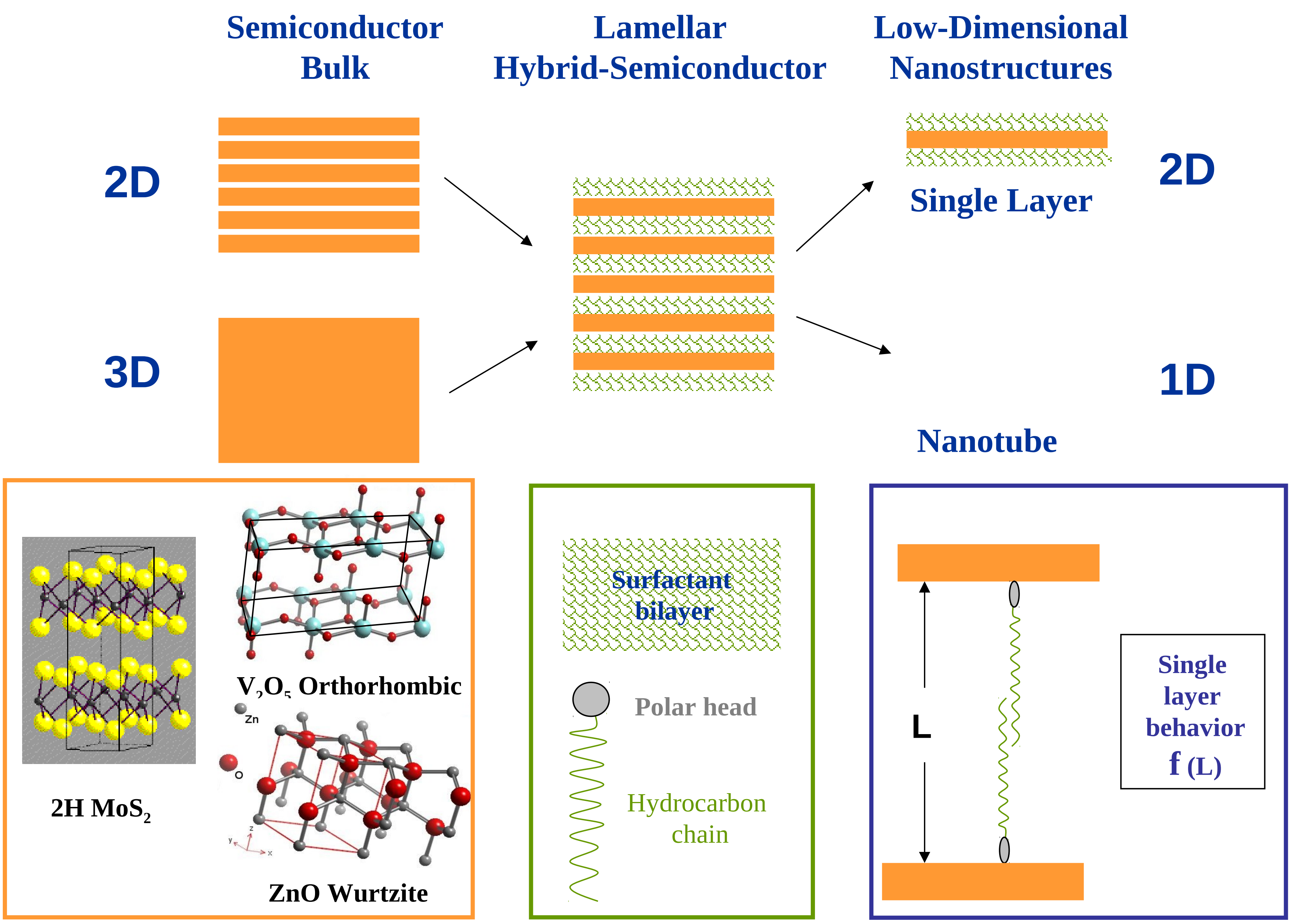






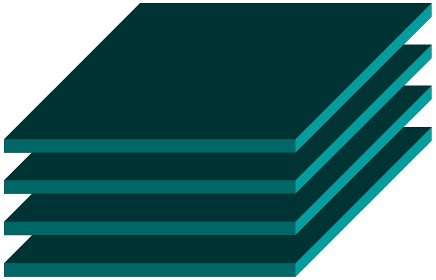
Radisavljevic et al., Nature Nanotech., 2011

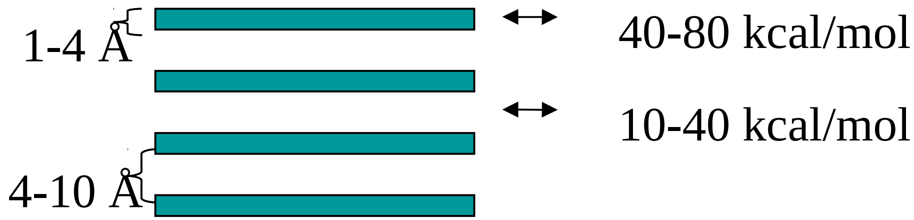
OUR APPROACH



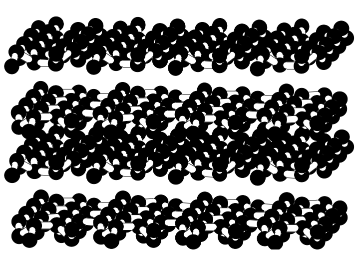
Layered Solids

Two phase systems: **Nano heterogeneity**

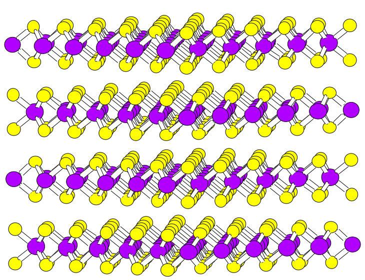




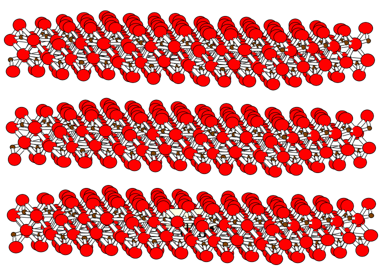
Exampl



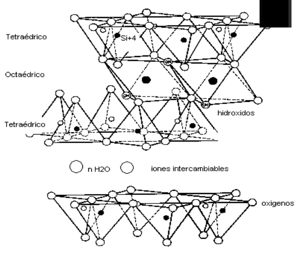
Graphite



MoS_2

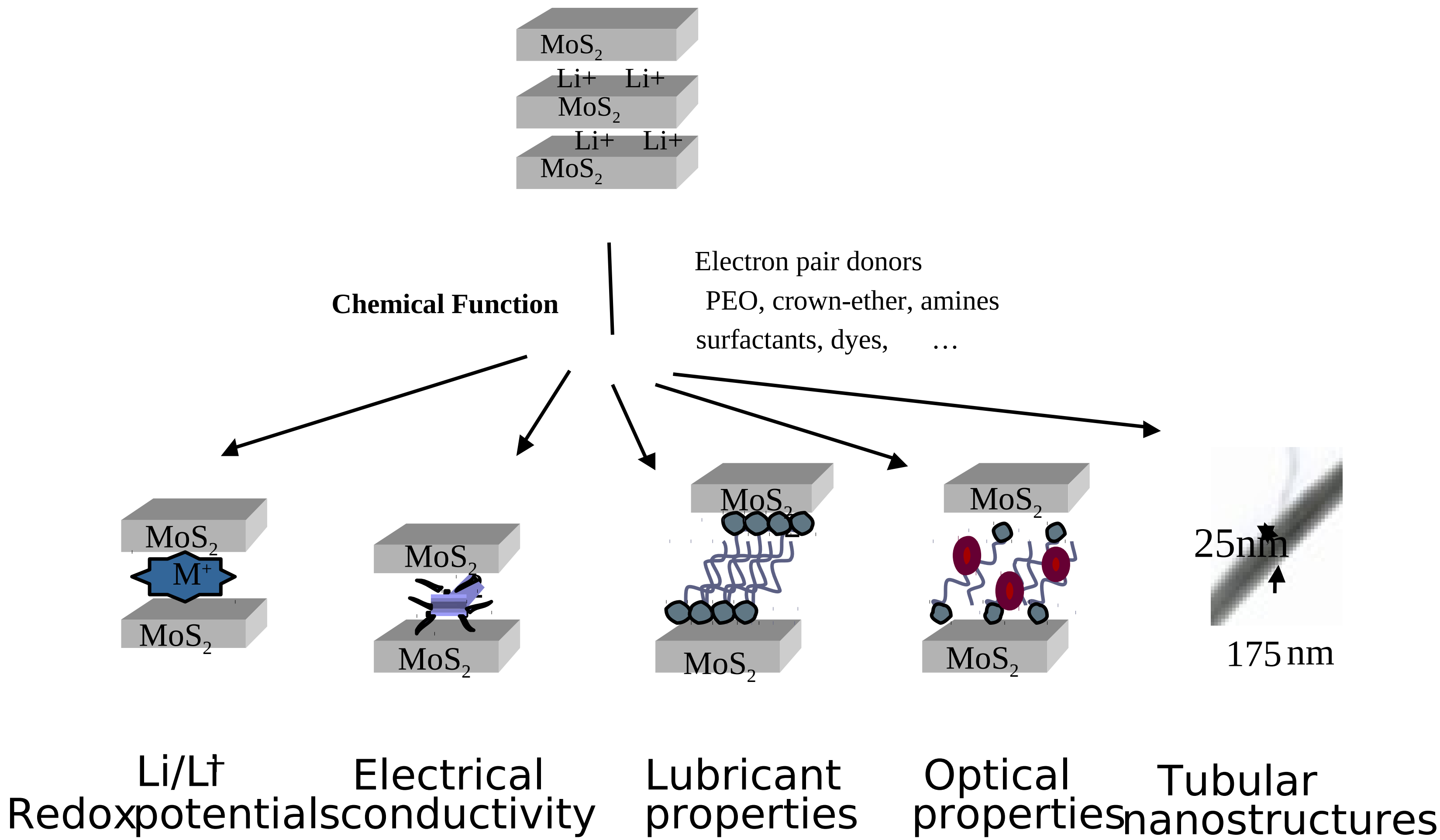


V_2O_5 xerogel

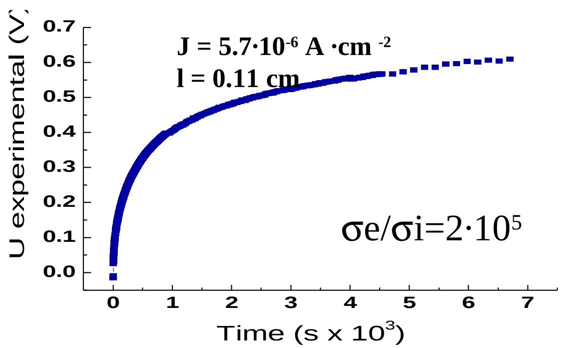


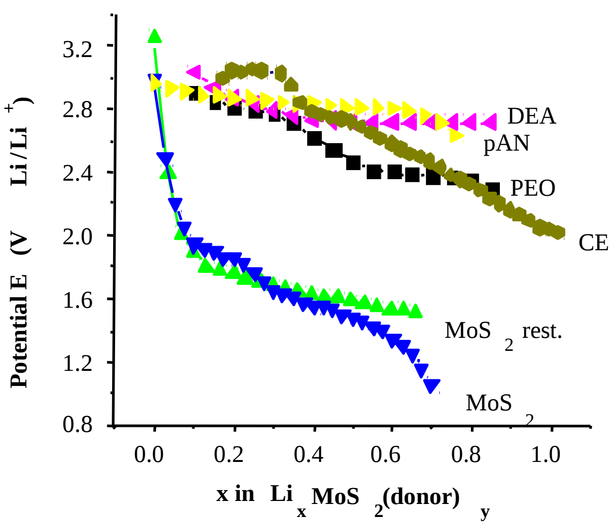
Aluminosilicate

MoS_2-Based Organic-Inorganic Nanocomposites



Electrical and Electrochemical Properties of MoS_2 Nanocomposites





Electronic Conductivity and Lithium Diffusion Coefficients at 298 K

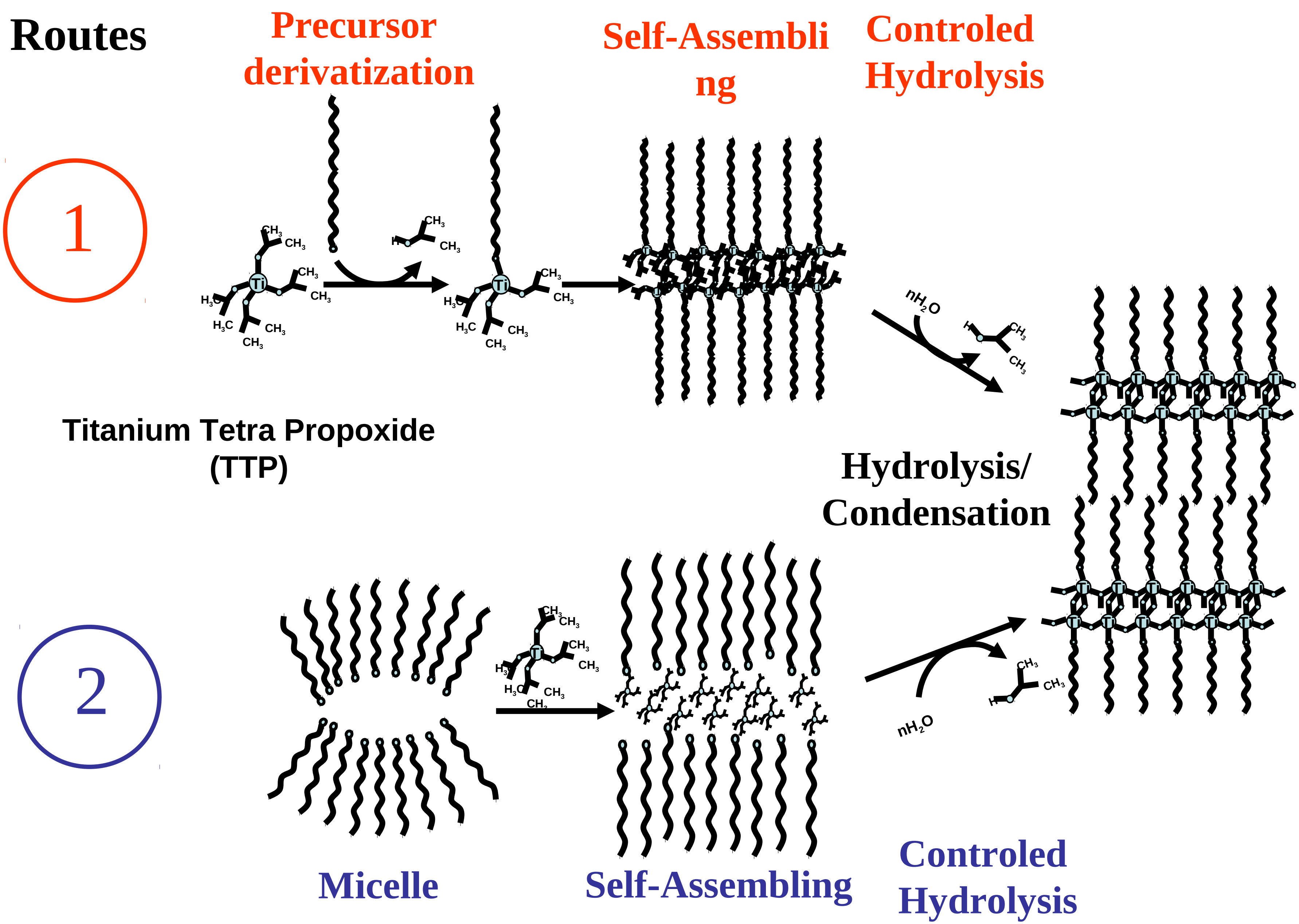
Compound	σ ($S \cdot cm^{-1}$)	D ($cm^2 s^{-1}$) x=0.2
MoS_2	$2.1 \cdot 10^{-6}$	$1.4 \cdot 10^{-13}$
$Li_{0.1}MoS_2(PEO)_1$	$6.6 \cdot 10^{-3}$	$2.0 \cdot 10^{-12}$
$Li_{0.32}MoS_2(12\text{-}CE\text{-}4)_{0.186}$	0.085	$2.6 \cdot 10^{-12}$
$Li_{<0.1}MoS_2(DEA)_{0.3}$	0.251	$1.5 \cdot 10^{-11}$

Solid State Ionics, 85,225 (1996)
J.Phys Chem Solids, 58, 1457 (1997)
Electrochim. Acta 2006.

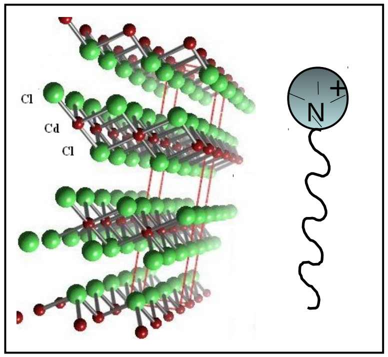
Instable Semiconducting Layered Structures (e.g. TiO_2)

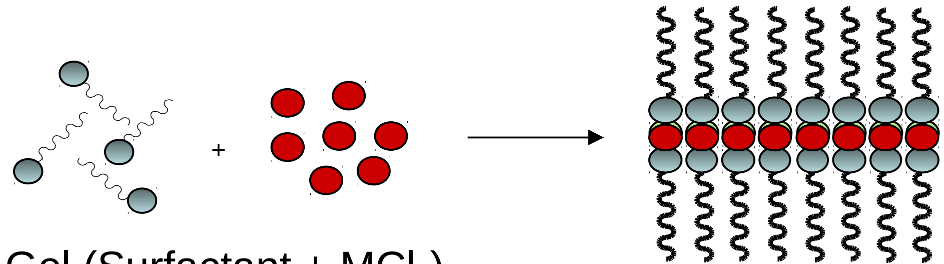
Synthesis Strategies

Two Routes

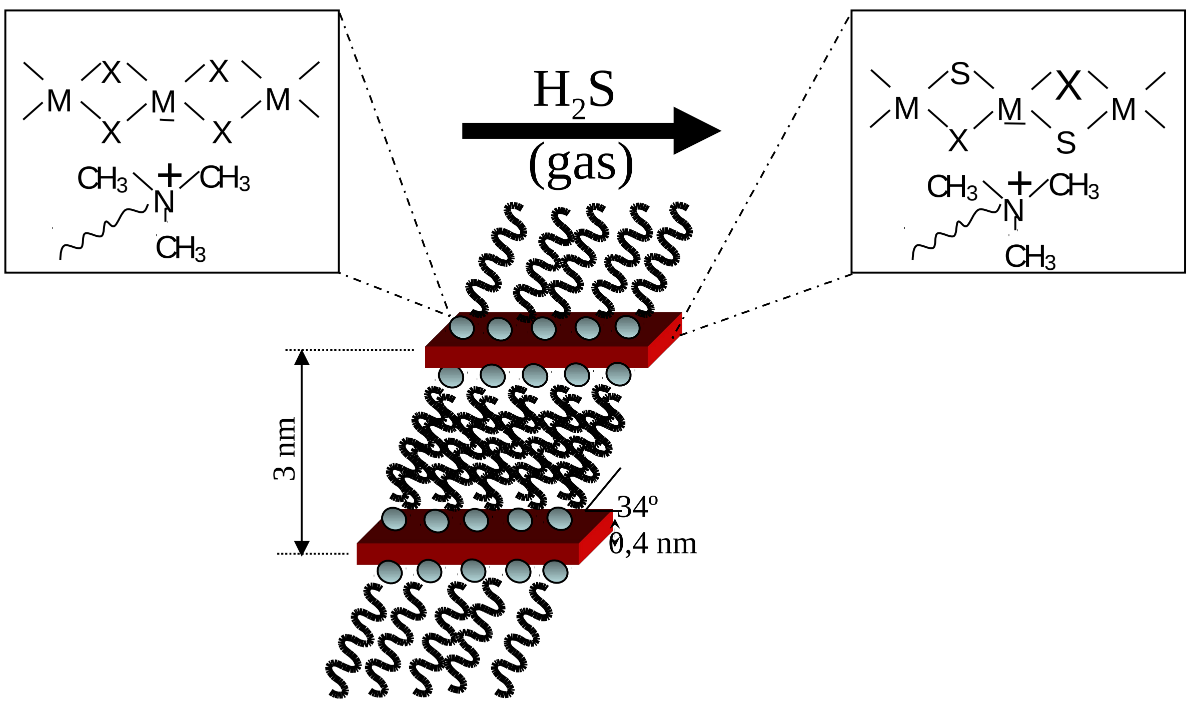


Instable Semiconductor Layered Structures (e.g. ZnS, CdS)
Synthesis Strategies





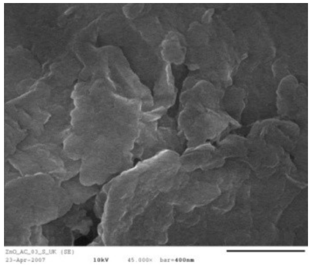
Gel (Surfactant + MCl_2)
M= Cd, Zn

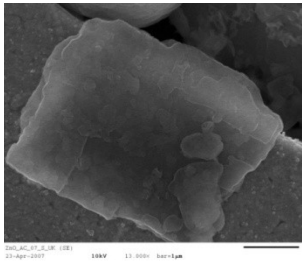


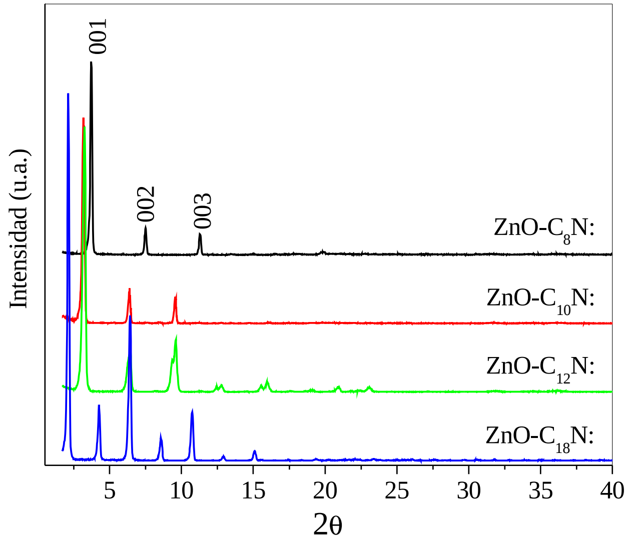
Commensurate Layered Organic-Inorganic Nanocomposites

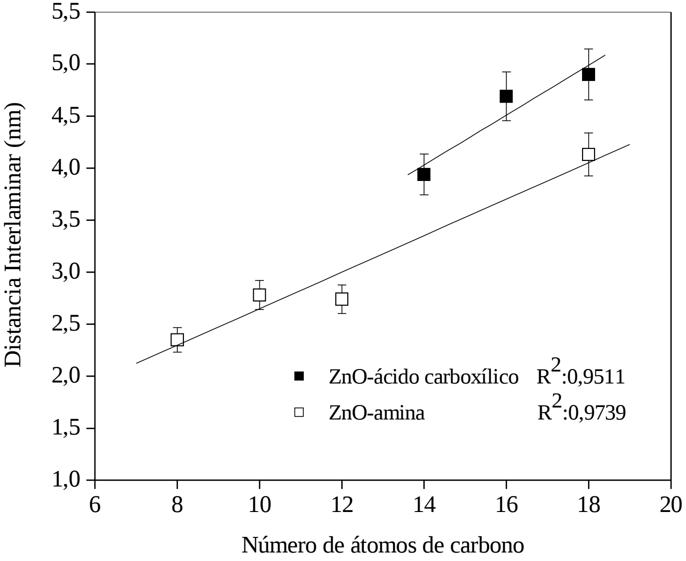
"Bulk"

Stoichiometry	*DRX* *Δd(nm)*
$(ZnO)_1H_{0,17}(C_{14}H_{27}O_2)_{0,17} \cdot 0,01H_2O$	3,94
$(ZnO)_1H_{0,36}(C_{16}H_{31}O_2)_{0,36} \cdot 0,7H_2O$	4,69
$(ZnO)_1H_{0,91}(C_{18}H_{35}O_2)_{0,91} \cdot 7,1H_2O$	4,90
$(ZnO)_1(OH)_{1,01}(C_8H_{17}NH_3)_{1,01} \cdot 0,02H_2O$	2,35
$(ZnO)_1(OH)_{1,07}(C_{10}H_{21}NH_3)_{1,07} \cdot 0,3H_2O$	2,78
$(ZnO)_1(OH)_{1,05}(C_{12}H_{25}NH_3)_{1,05} \cdot 0,22H_2O$	2,74
$(ZnO)_1(OH)_{1,25}(C_{18}H_{37}NH_3)_{1,25} \cdot 0,06H_2O$	4,13
$(ZnO)_1H_{0,21}(C_{16}H_{33}SO_3)_{0,21} \cdot 0,05H_2O$	4,70



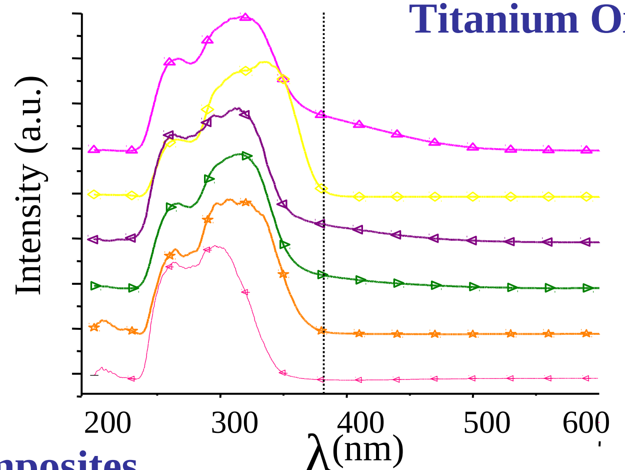






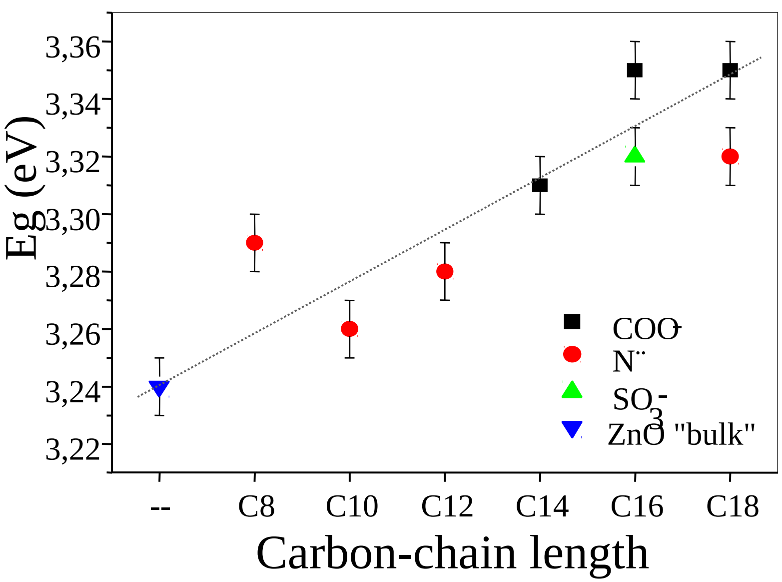
Confinement Effects
Band Gap Regulation

Titanium Oxide Nanocomposites



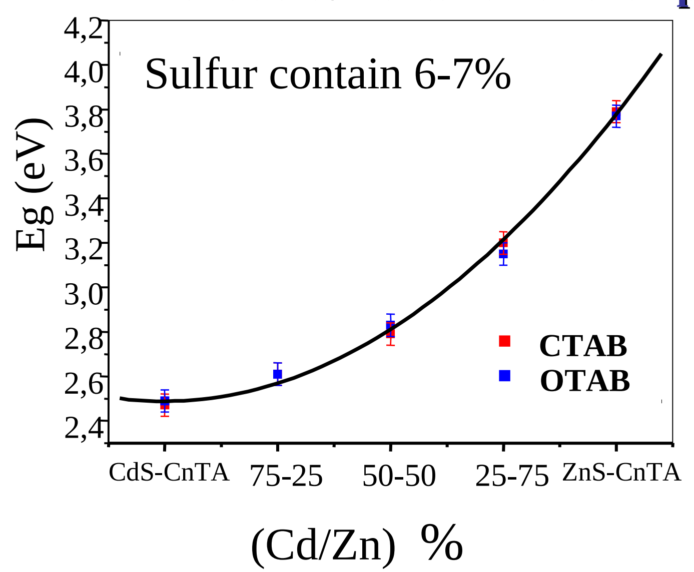
Band Gap	
TiAAc	3.42
TiOPh	2.51
BTO	3.55
TiOC8	3.58
TiSC8	3.45
TiAcP	3.50
TiHDA	3.70
TiLec	3.15
TiO_2 rutilo	3.06

ZnO Nanocomposites



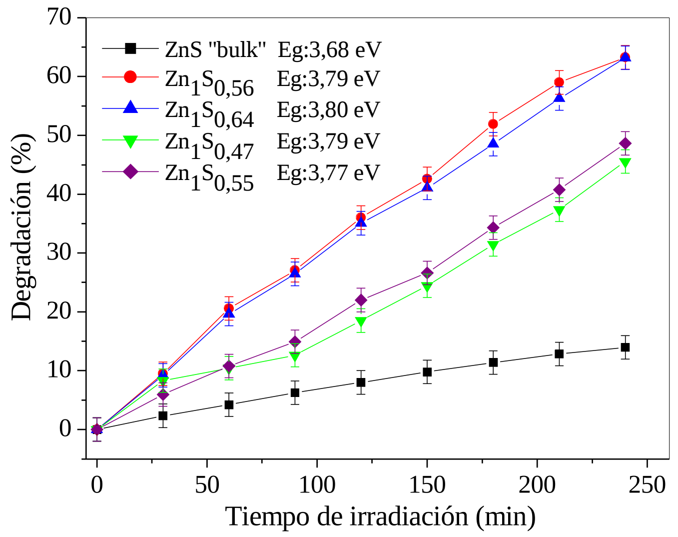
E_g=f(Surfactant)

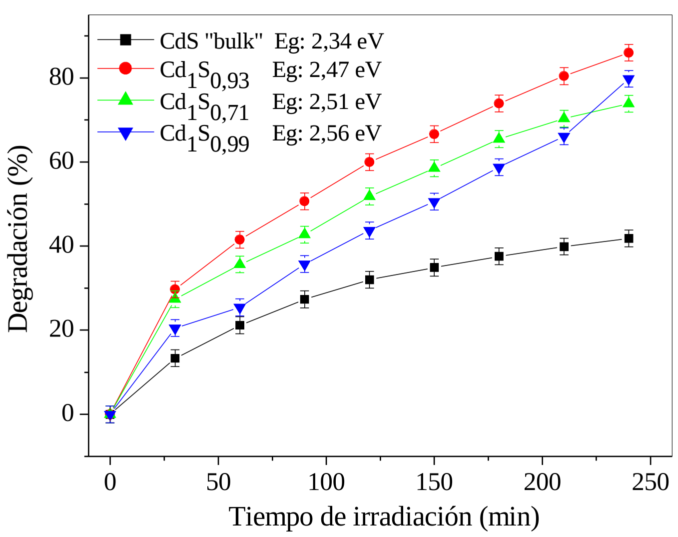
ZnS-CdS-surfactant Nanocomposites

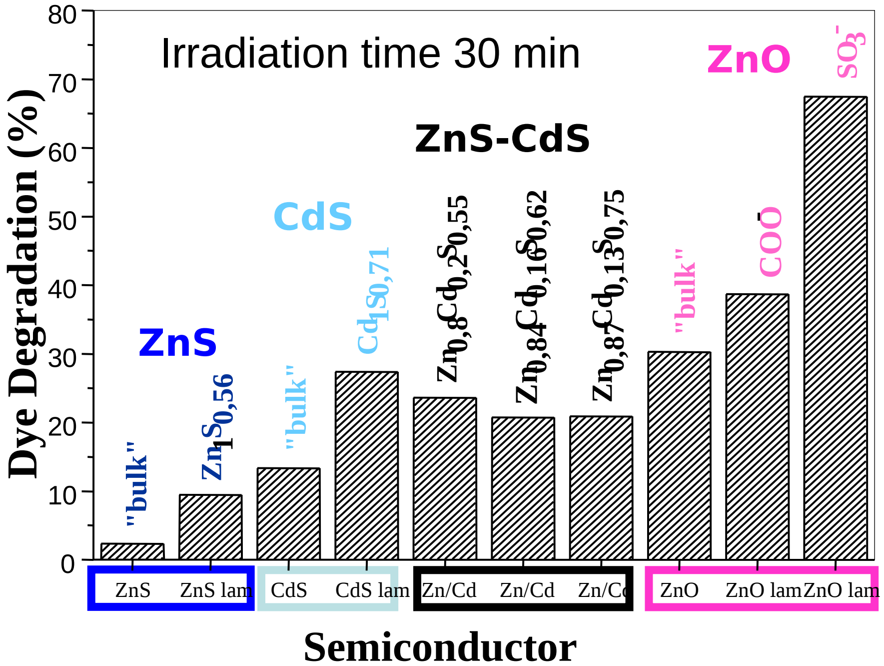


E_g=f(Zn/Cd)

Photocatalytic Activity





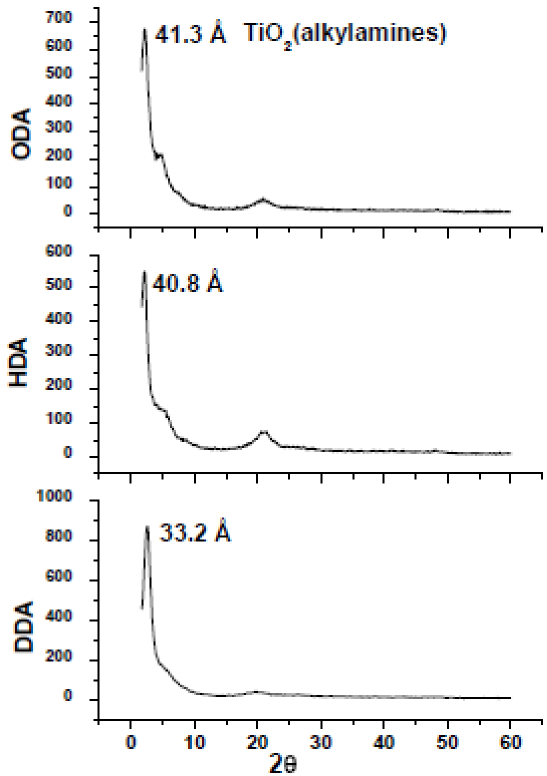


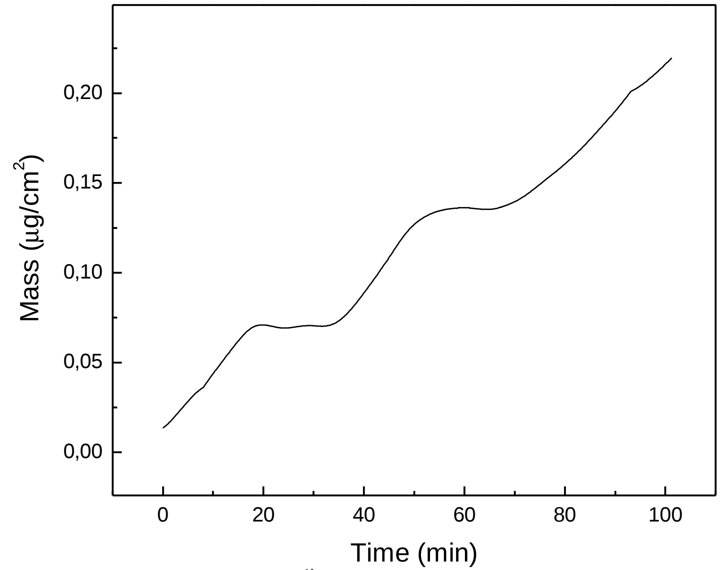
Single Layers and Thin Films

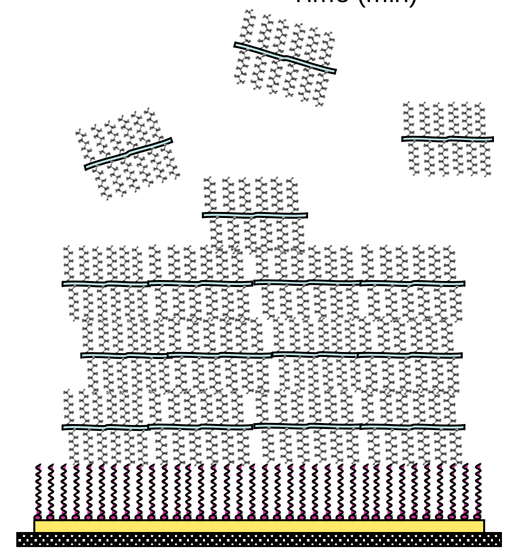
ZnO –Carboxilic Acid Nanocomposites

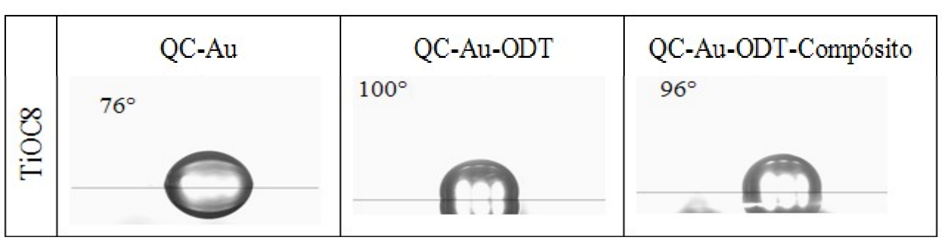
TiO_2-Based Single Layer Semiconductors

TiO_2-Amine nanocomposites



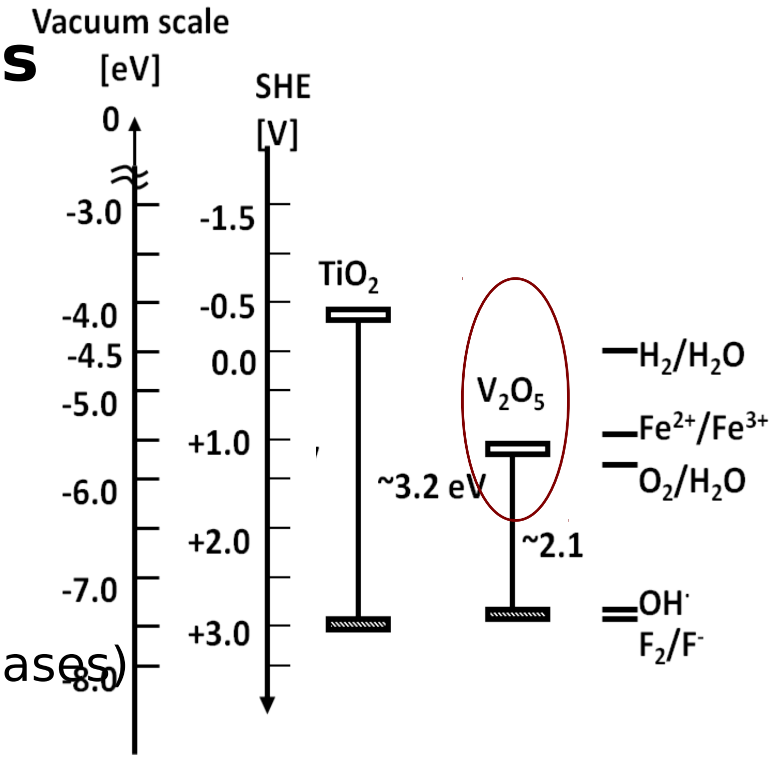






VANADIUM PENTOXIDE-NANOSTRUCTURES

Mixed-Valence nanostructures



Electronic structure of Vanadium Oxide

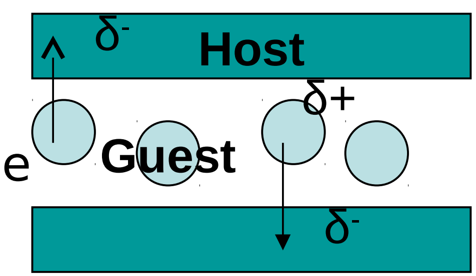
•Energy of Valence Band
•Band Gap

Partial reduction of V(V) → V(IV)

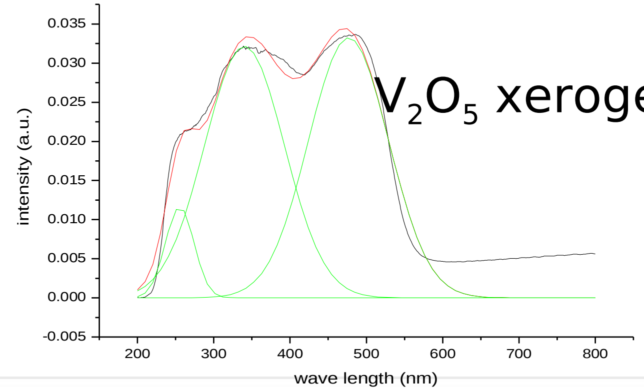
uest-Host charge transfers
lectron donors or electron-pair donors (Lewis bases)

olvent (e.g. Water Alcohols)
lectropositive metals (e.g. Lithium)
emplates (Anphiphiles)

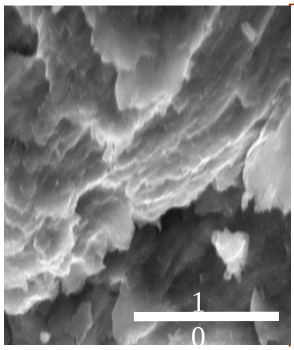
eaction conditions like temperature and reaction time

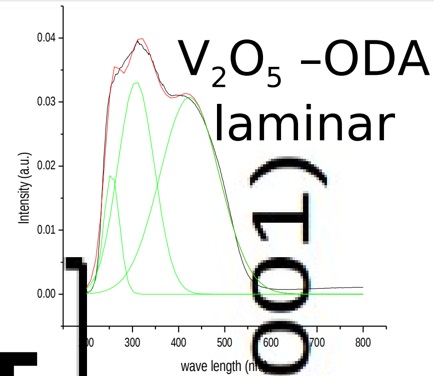


Xerogel

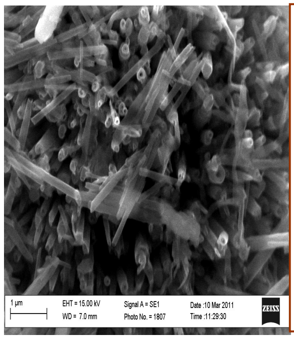


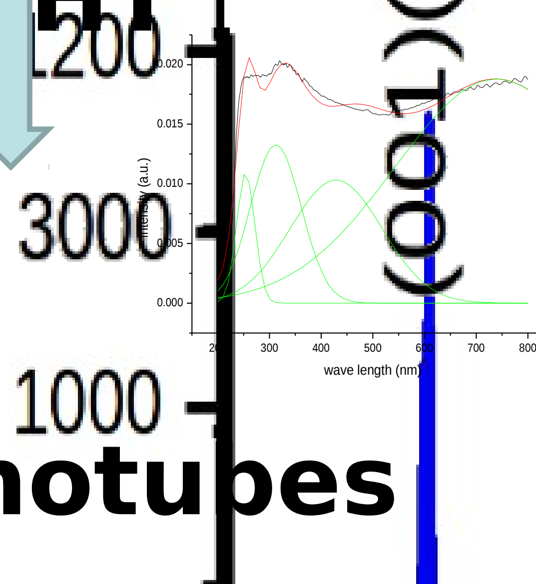
Laminar

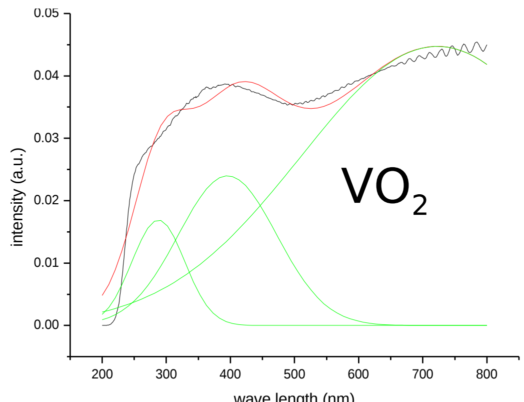




HT

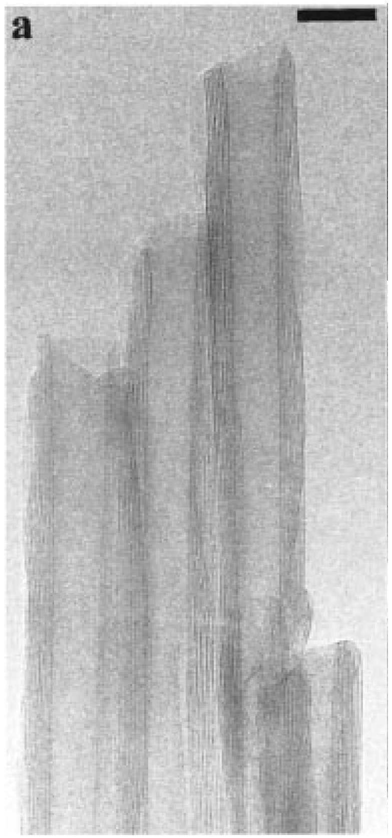


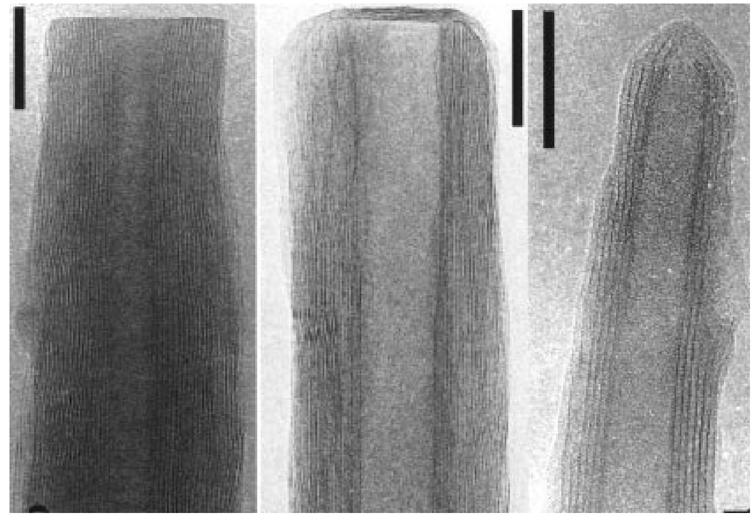


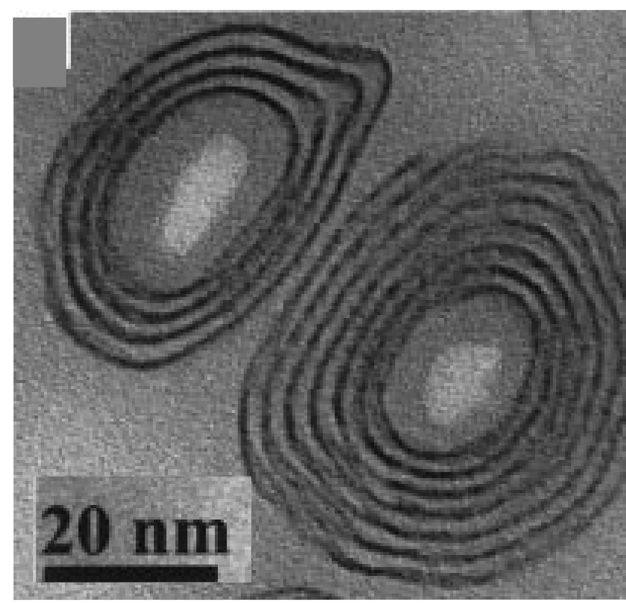


Nanotubes

VANADIUM OXIDE NANOTUBES







Spahr, M. E.; Bitterli, P.; Nesper, R.; Mu¨ller, M.; Krumeich, F.; Nissen, H.-U. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1263.
Nesper, R.; Muhr, H.-J. *Chimia* **1998**, *52*, 571.

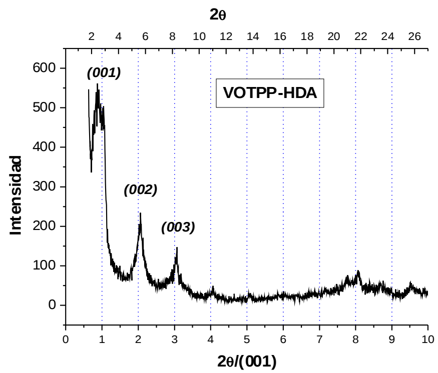
VO_x NANOTUBES
Three Dimensional Arrangements

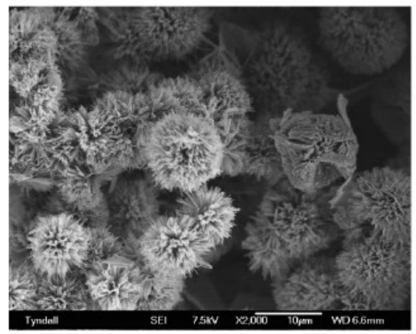
Vanadium Triisopropoxide (VOTPP) + H2O+ amine

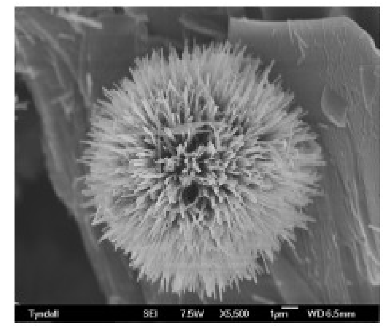
Hydrothermal treatment

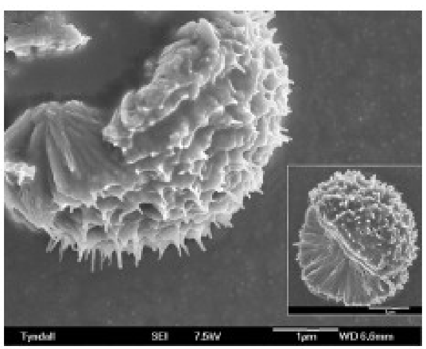
120-180 C
2-8 days

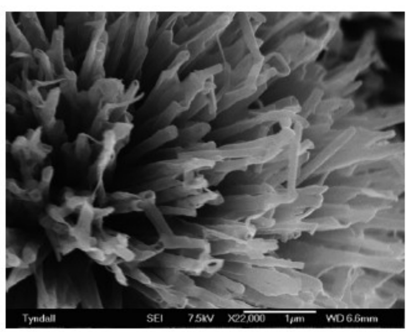
NANOURCHINS

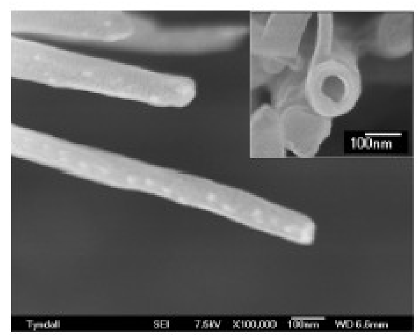


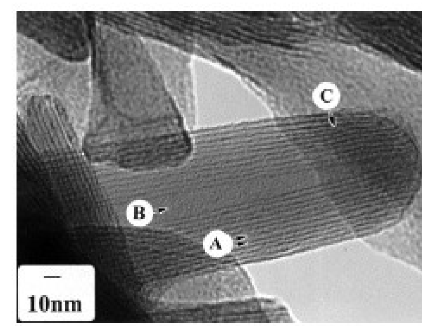




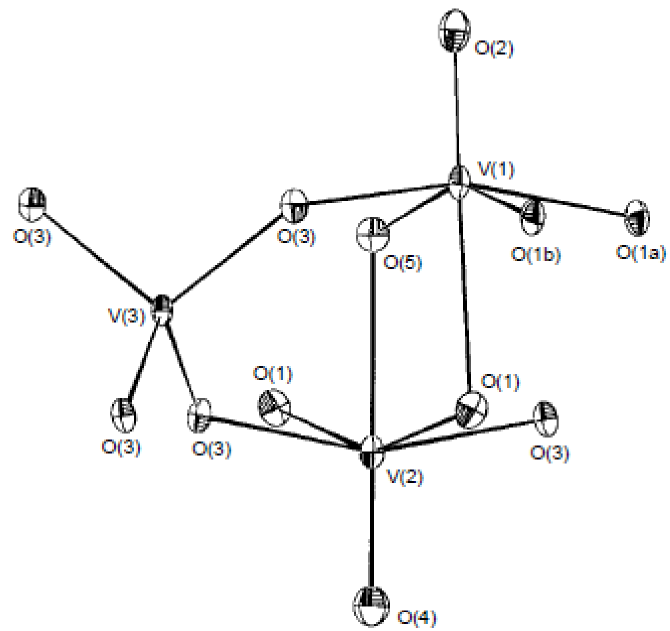


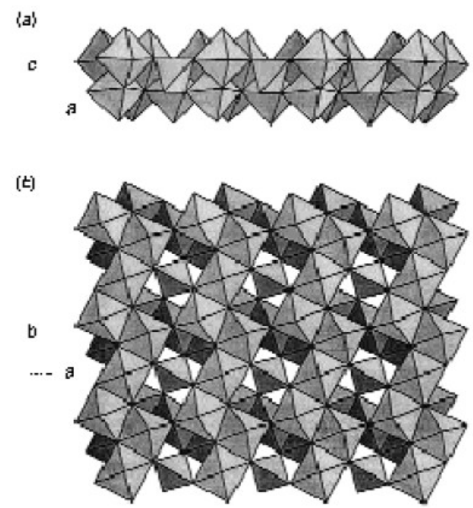




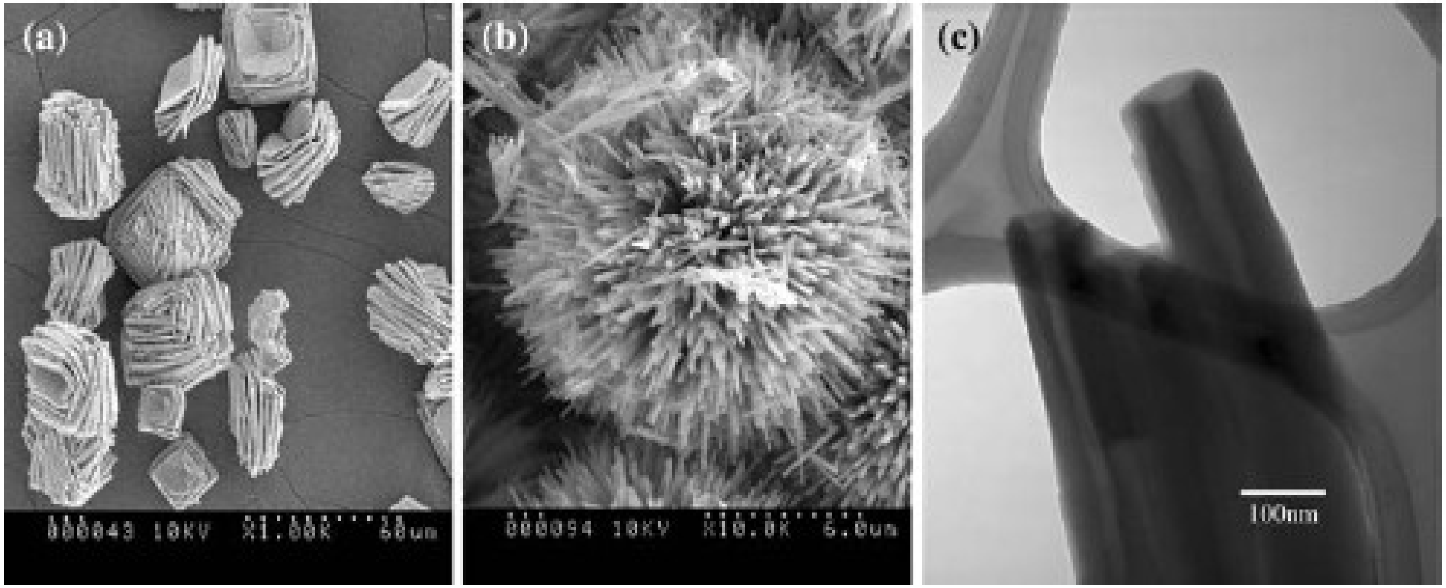


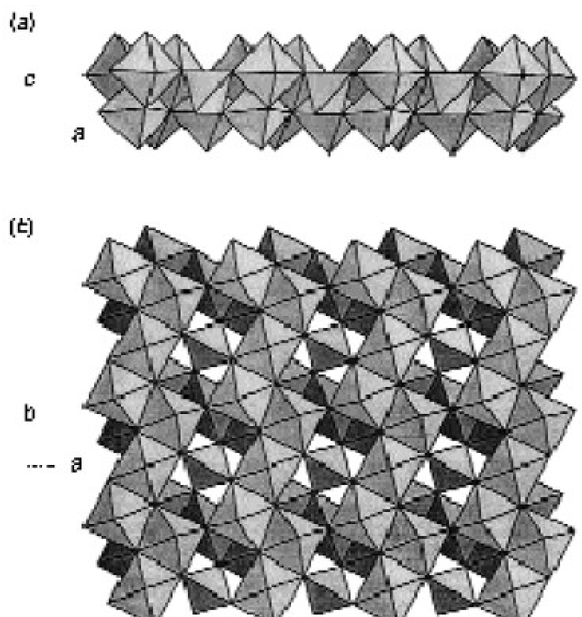
Layered mixed-valence oxide $BaV_7O_{16}\cdot nH_2O$





Wang et al 1989, ***Chem. Commun*., 1009**

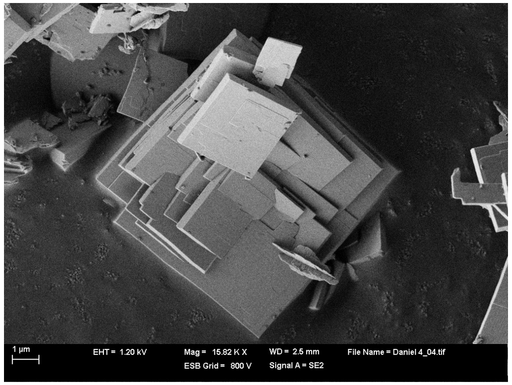

(a)
000043 10KV X1.00K 60um
(b)
000094 10KV X10.0K 6.0um
(c)
100nm

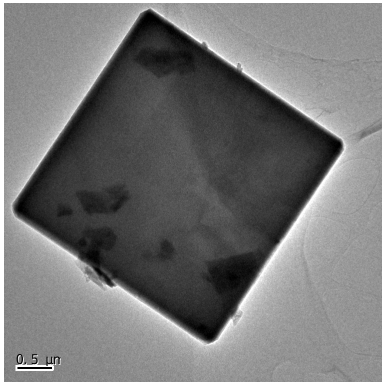

(a)
c
a
(b)
b
a

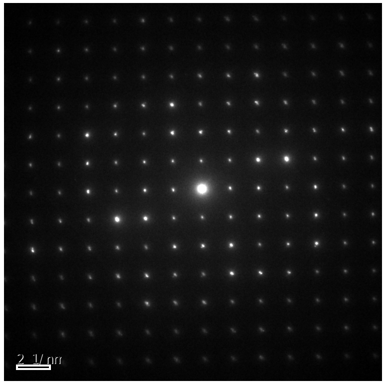
$V_7O_{16}^{2-}$

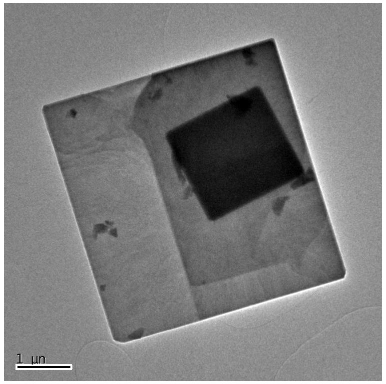
Vanadium Oxide Micro-Squares

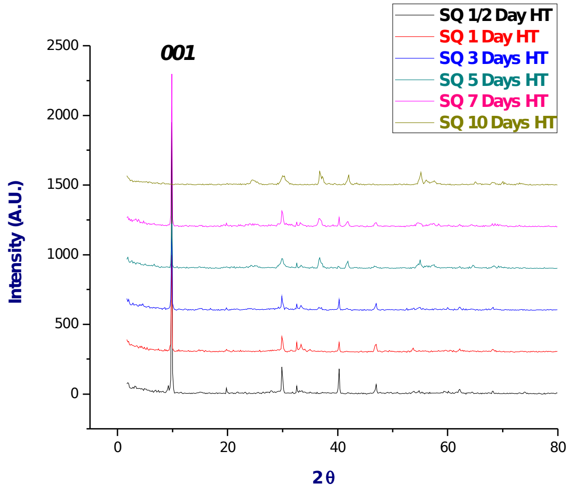
$(NH_4)_2V_7O_{16}$

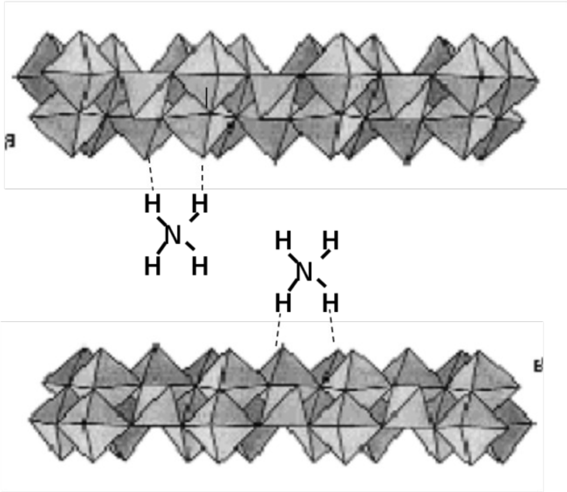












Some conclusions

Formation of graphene-like structures is a relevant approach for the stabilization of nanostructured inorganic semiconductors.

Layered semiconductors maintain in a great extend the electronic properties of their corresponding parent compounds

Vanadium oxide micro-squares open a new window for designing new template free layered products

Thank you for your attention !!!