Nanotechnology in the life sciences

A FRONTIS LECTURE SERIES

organized by

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Nanotechnology in the life sciences

February 13	13:30	Pieter Stroeve-Size, measurement and sensing
	14:30	Mieke Kleijn (WUR)- Surface forces using AFM
February 20	13:30	Pieter Stroeve- (Bio)materials
	14:30	Ernst Sudholter (WUR)- Hybrid organic semiconductor FETs
February 27	13:30	Pieter Stroeve- Self-assembly of molecular structures
	14:30	Richard Schasfoort (U Twente)- Surface modification and microfabrication strategies
Friday, March 5	**13:30**	**Pieter Stroeve- Nanotechnology and the environment**
	14:30	**Keurentje (TU Eindhoven)- Micellar systems for nanoscale engineering of reaction and separation processes**
Friday, March 12	13:30	Pieter Stroeve- Life sciences and medicine
	14:30	A.J.W.G. Visser (WUR)- Single-molecule fluorescence in microfluidic devices

Nanotechnology and the environment

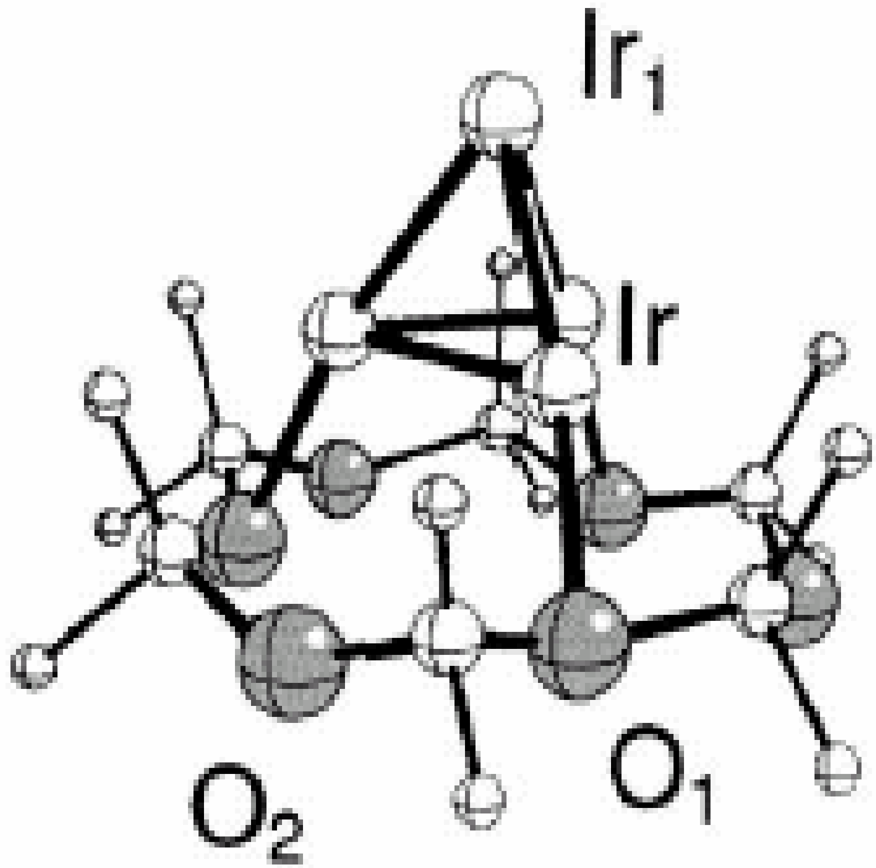
Focus: nanoparticles

- catalysis
- materials (nanocomposites)
- biomineralization and nanoparticles
- environmental remediation with nanoparticles
- health effects of nanoparticles in the environment

Molecular clusters of noble metal supported on porous inorganic oxides

- optimum metal cluster size is about 4-10 metal atoms
- increase surface area for reaction
- increase catalytic activity
- reduce temperature
- reduce the amount of noble metals needed
- porous support can sieve reactants
- extensive use in industry
- catalytic converters in automobiles (reduce environmental pollutants)

Ir_4 cluster supported at the six-ring of zeolite NaX. Bottom Ir atoms form covalent bonds with oxygen atoms

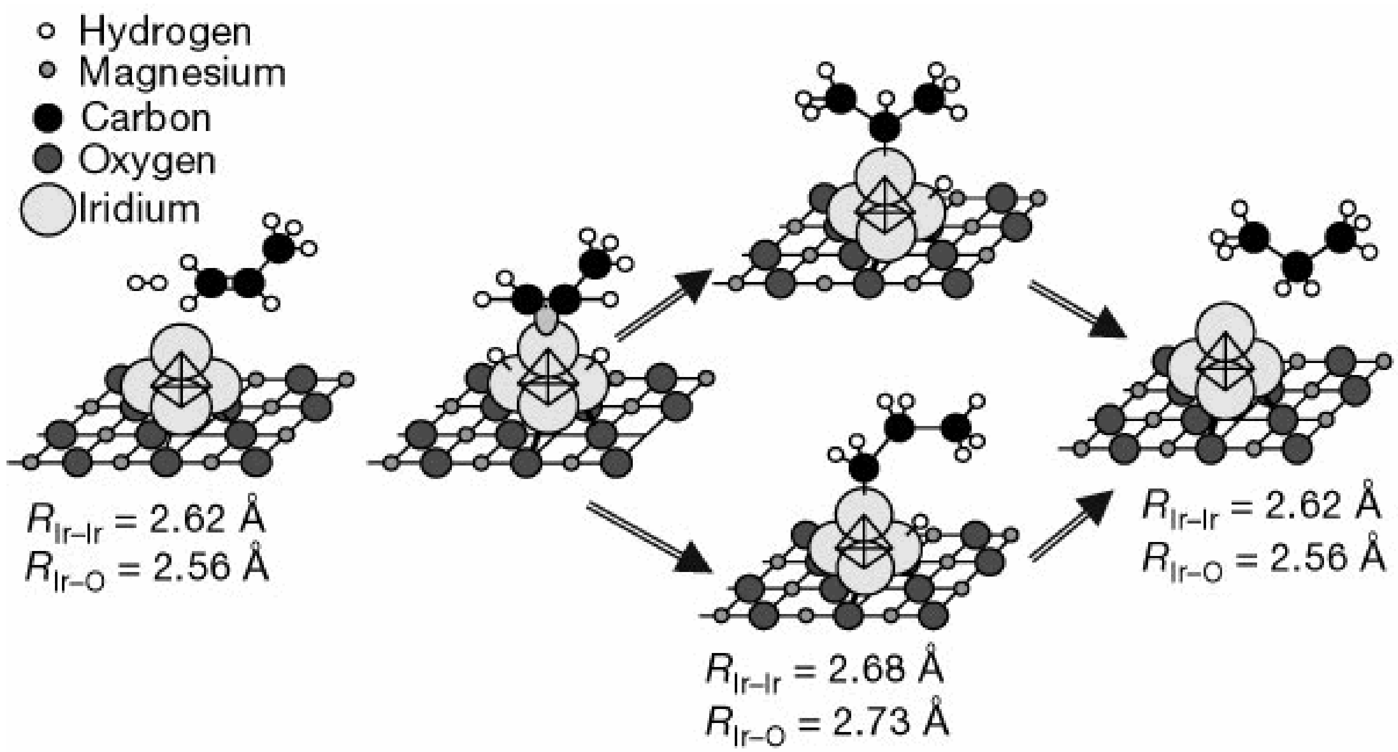


B.C. Gates, J. Phys. Chem., 1999

Alkene hydrogenation catalyzed by supported metal cluster Ir_4 on MgO

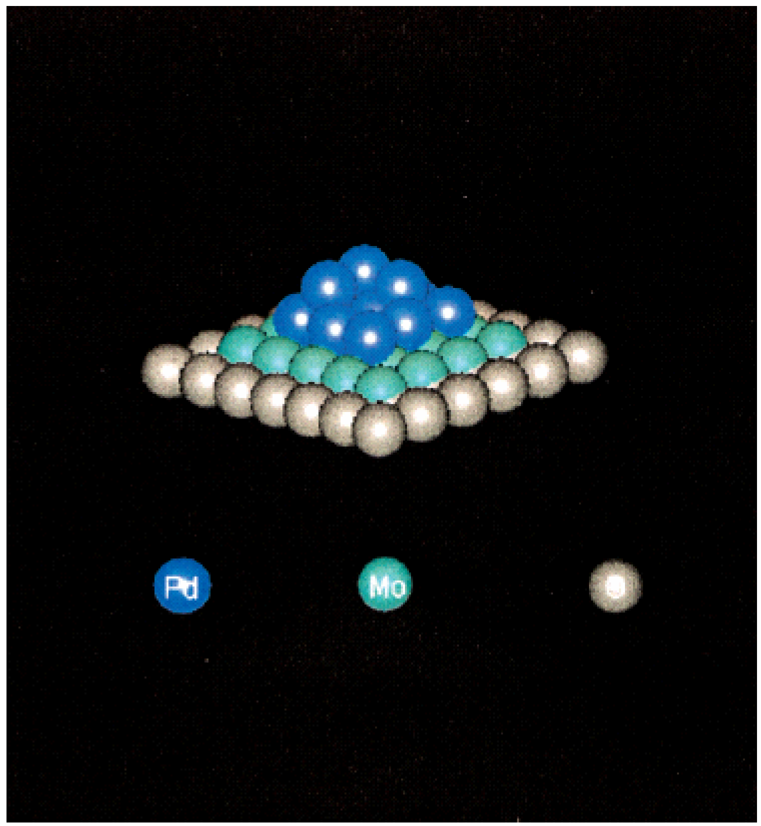
Schematic representation of the hydrogenation of propene on MgO-supported Ir_4. Propene is initially bonded to the cluster then hydrogenated to give 1-propyl or 2-propyl, which is hydrogenated
to give propane. The Ir–Ir and longer (non-bonding) Ir–O distances change as shown.

B.C. Gates, Nature 2002

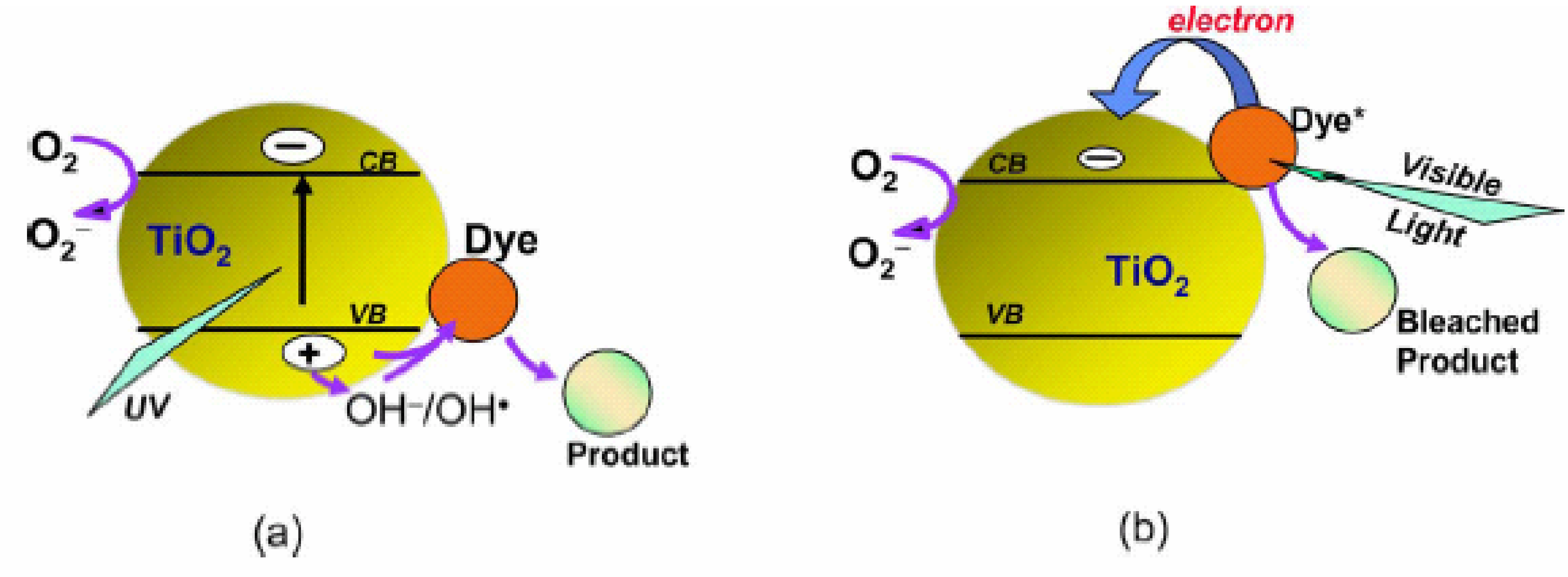


Supported bimetallic clusters

Catalytic behavior of supported metal is influenced by size of metal particle, interactions with the support and second catalytic material. Second metal interact through electronic interactions or direct bonding of the reactants.



Photoinduced charge transfer with semiconductor nanoparticles



(a) bandgap excitation; (b) sensitized charge injection by excited adsorbed dye molecules. CB=conduction band, VB=valence band

P.V. Kavat and D. Meisel, C.R. Chimie, 2003

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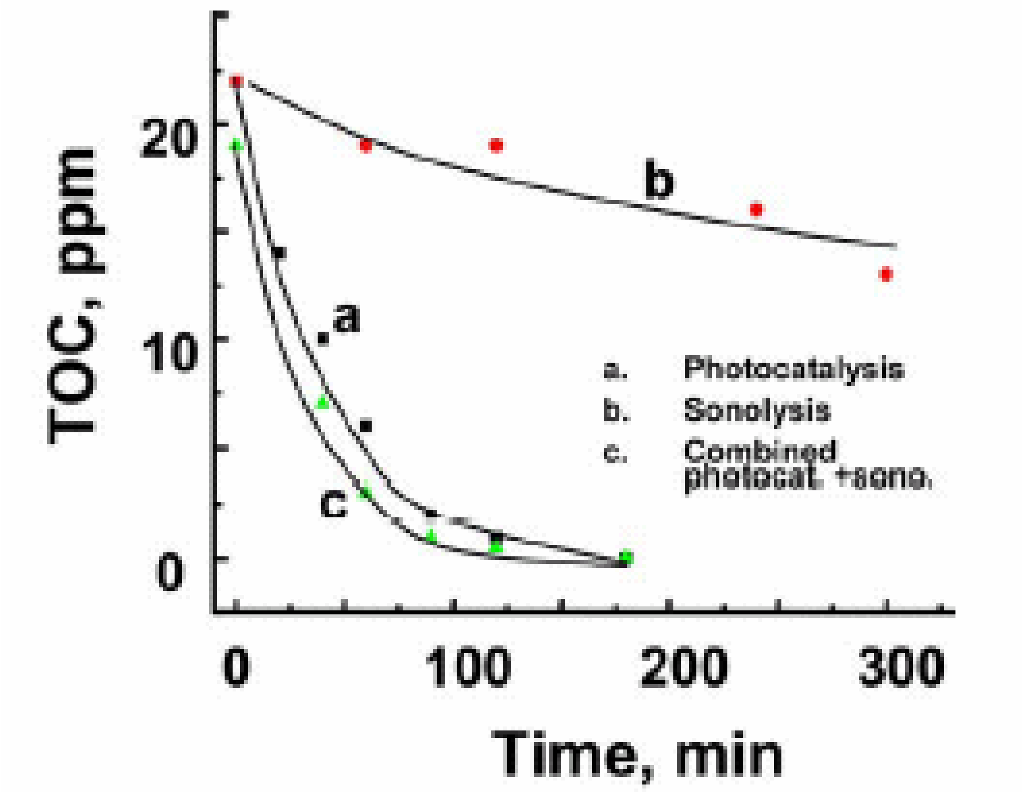
Degradation of total organic carbon TOC with TiO_2 nanoparticles

a) photocatalysis, b) sonication, and c) combined

P.V. Kamat and D. Meisel, C. R. Chimie, 2003



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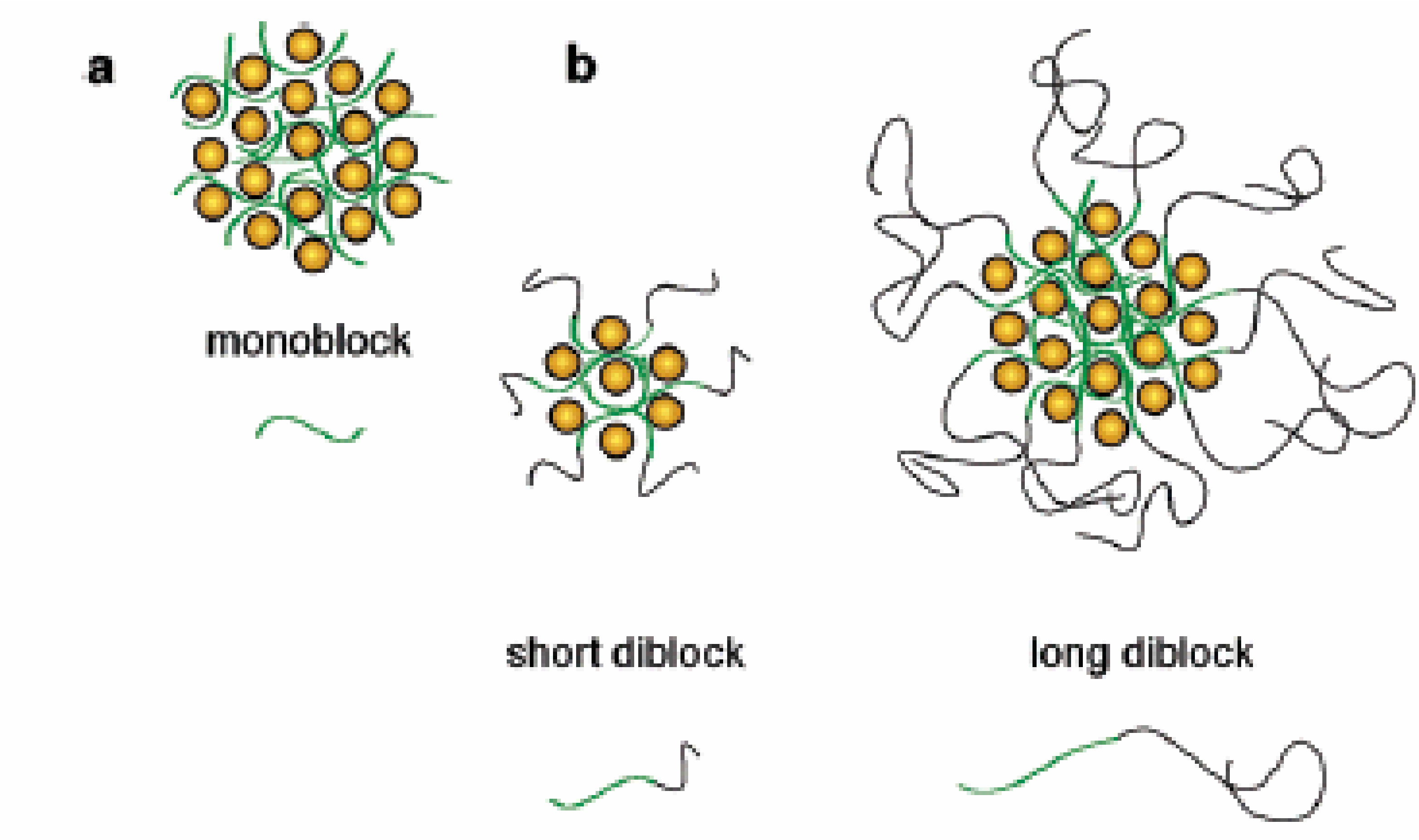
Nanocomposites formed from reactive nanoparticles and diblock polymers



Nanotechnology and the environment

- catalysis
- ➔ materials: nanocomposites
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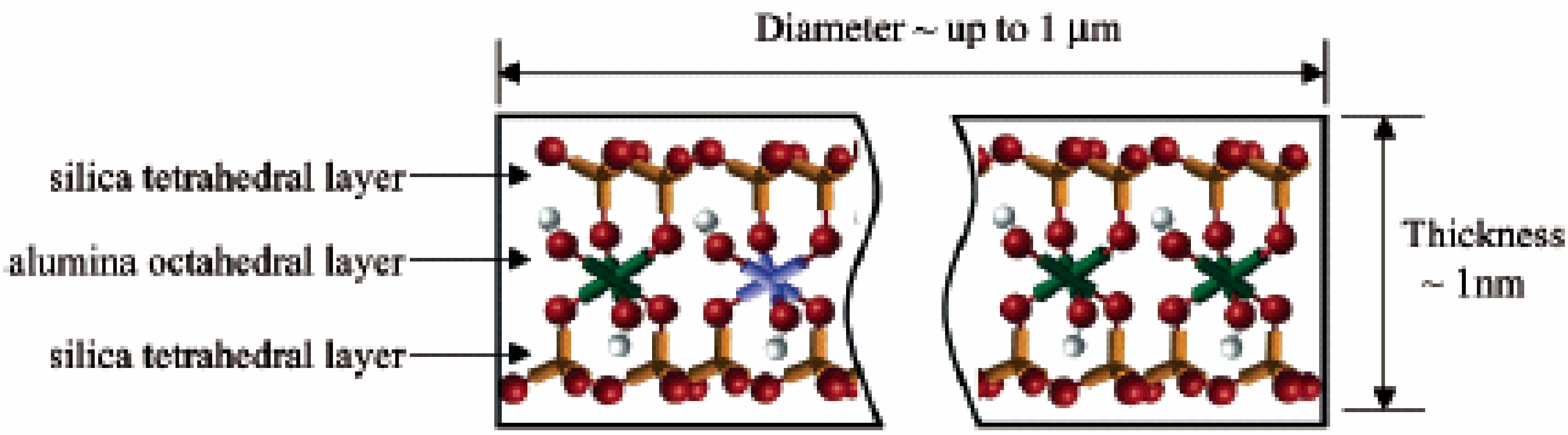
- health effects of nanoparticles in the environment

Nanocomposites and the environment examples:

- barrier films for food packaging
- catalytic materials for environmental remediation
- sensors for environmental monitoring
- controlled release of pesticides
- coatings
- catalytic converters on cars
- low weight, high strength materials
- filtration and purification

Nanoparticles of clay are used in polymer composites

Montmorrillonite clay plate



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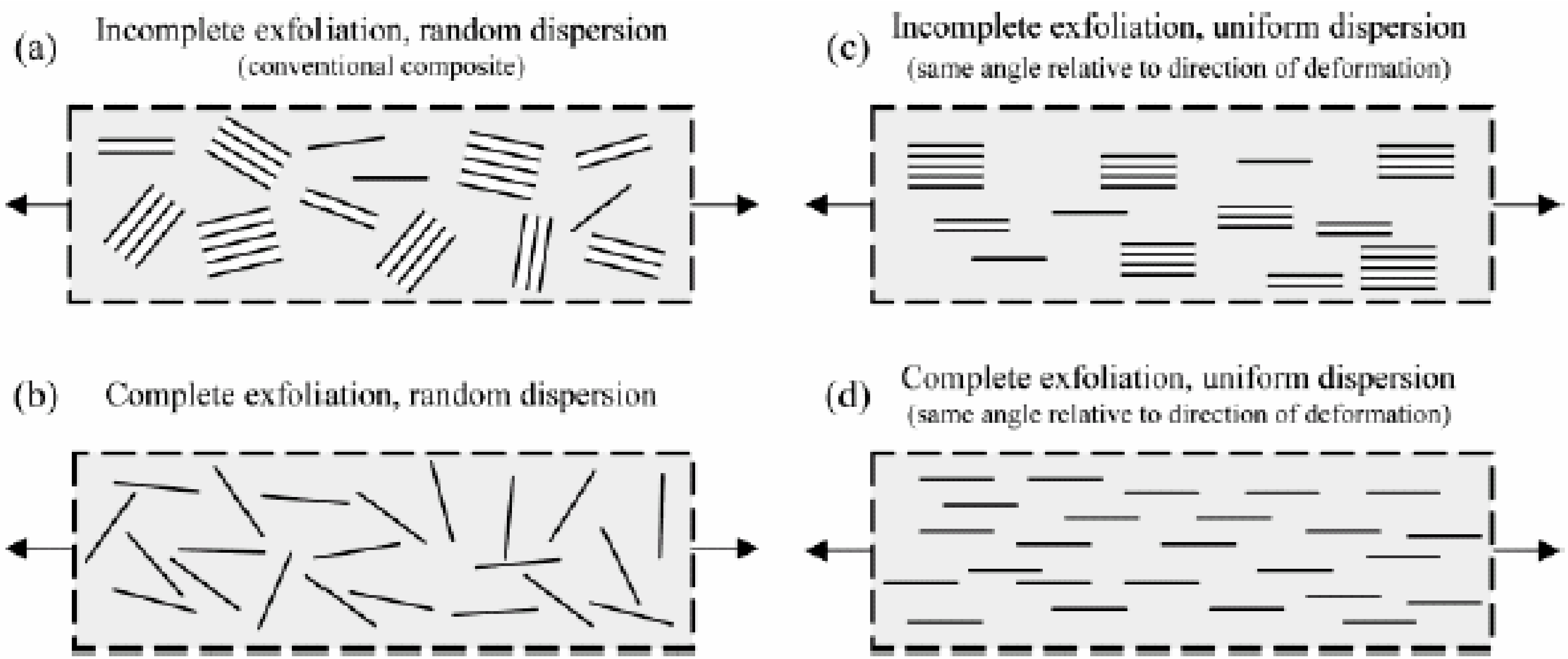
Nanotechnology and the environment

Exfoliated and uniform dispersed nanoclay platelets gives improved mechanical properties with relatively low loading (1-6 % nanoclay)

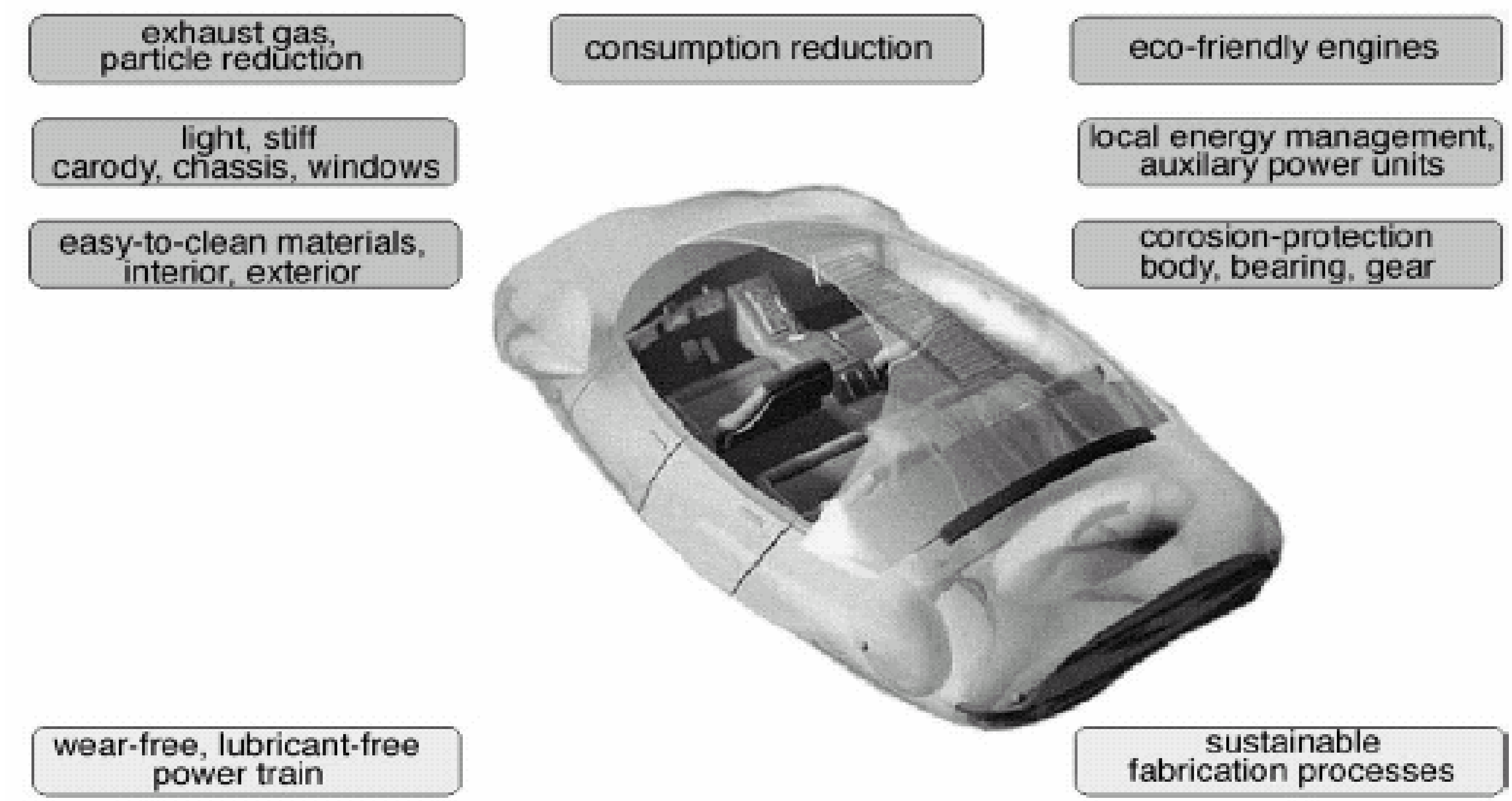


Current use of nanotechnology in production of materials for vehicles

- **antireflection coatings (multiple monolayers on glass)**
- **catalytic converters**
- **sun protecting glaze (infrared reflecting nanolayers imbedded in glass)**
- **thermoplastic nanocomposites (light exterior parts)**

Future use of nanotechnology in automobiles

Presting and Konig, Mat Sci & Engr C, 2003



Material properties of polymer composites with 1% or 6% of clay platelets

1

S.N. Lloyd & L.B. Lave, Envir. Sci. and Technol., 2003

Projected Values of Variables Used To Predict Young's Modulus

variable	description	lower bound	upper bound
E_{matrix}	Young's modulus of polypropylene matrix	1.1 GPa (*18*)	1.55 GPa (*18*)
E_r	ratio of platelet to matrix modulus	100 (*16*)	100 (*16*)
A_r	aspect ratio of platelet (diameter/thickness)	100 (*16*)	1000 (*16*)
ϕ	volume ratio of platelets in matrix	1% (*16*)	6% (*16*)
N	number of platelets per stack	5 (*16*)	1 (*16*)
S	inter-platelet spacing	0.3 nm(*19*)	7 nm (*20*)
T	thickness of the platelet	0.95 nm (*21*)	1 nm (*19*)
Young's modulus of the clay–polypropylene composite		1.4 GPa	10.3 GPa

Fuel savings, toxic release and CO_2 reduction for use of nanocomposites for body panels of vehicles

S.N. Lloyd & L.B. Lave, Envir. Sci. and Technol., 2003

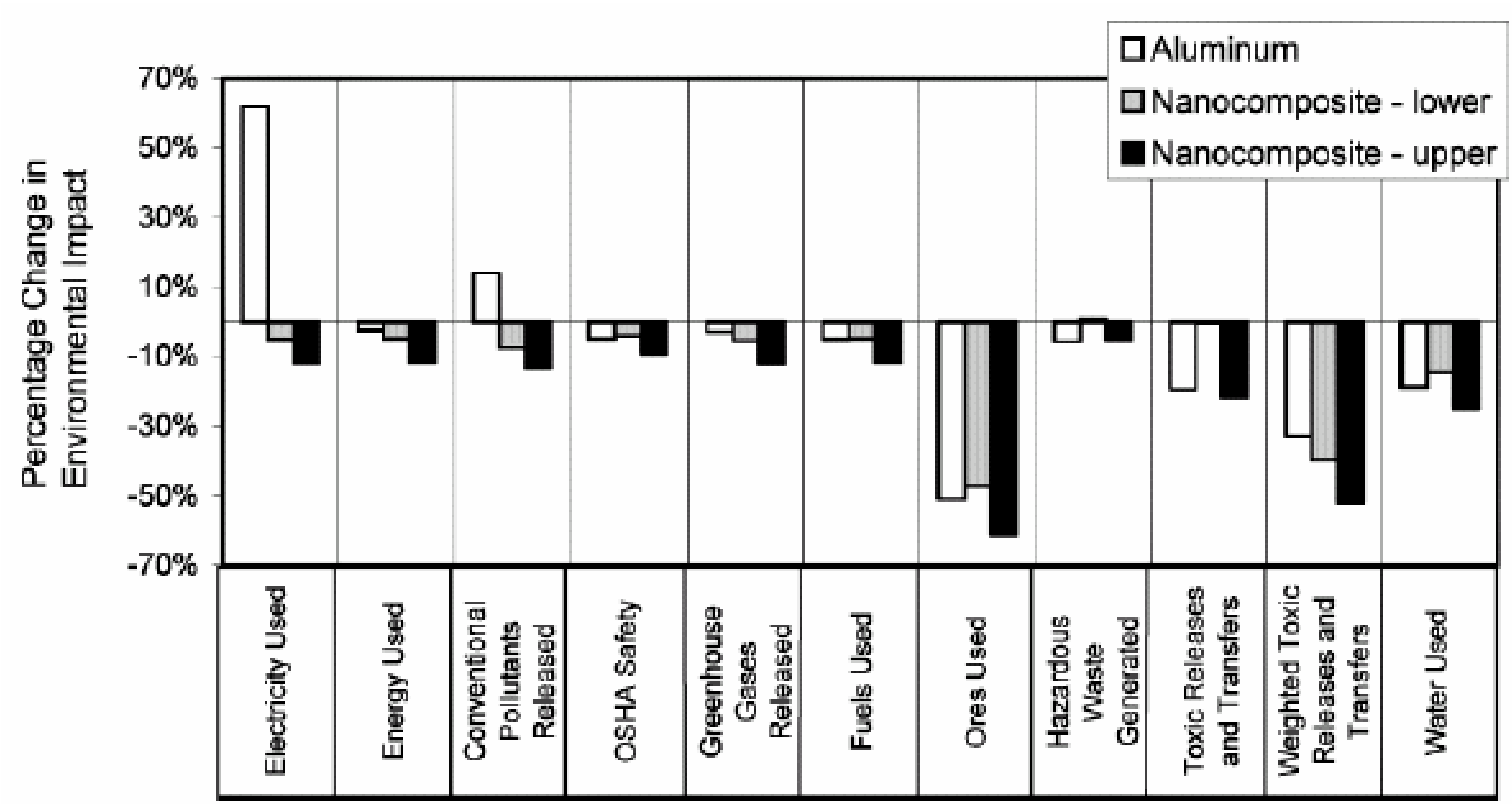
TABLE 5. Change in Life Cycle Environmental Impact from Substituting Nanocomposites or Aluminum for Steel in Body Panels for One Year's Fleet of Vehicles in the United States (16.9 Million Vehicles)[a]

effects	aluminum	nanocomposite lower	nanocomposite upper
electricity used (M kw-h)	48 000	−4 000	−9 200
energy used (TJ)	−51 000	−100 000	−240 000
conventional pollutants released (t)	320 000	−170 000	−300 000
OSHA safety (fatalities)	−4	−3	−7
greenhouse gases released (t of CO_2 equiv)	−3 800 000	−7 200 000	−16 000 000
fuels used (t)	−100 000	−99 000	−230 000
ores used, at least (t)	−5 300 000	−4 900 000	−6 300 000
hazardous waste generated (RCRA, t)	−1 900 000	360 000	−1 800 000
toxic releases and transfers (t)	−13 000	−110	−14 000
weighted toxic releases and transfers (t)	−56 000	−68 000	−88 000
water used (billion gal)	−150	−120	−200

[a] See www.eiolca.net for explanations of the valuation and weighting.

nanocomposites for 16.9 M vehicles gives reduced pollution

S.N. Lloyd & L.B. Lave, Envir. Sci. and Technol., 2003



Nanotechnology and the environment

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- toxicity of nanoparticles

Biomineralization: magnetite nanoparticles formed in bacteria

Crystal morphologies and intracellular organization of magnetite nanoparticles inside magnetotactic bacteria:

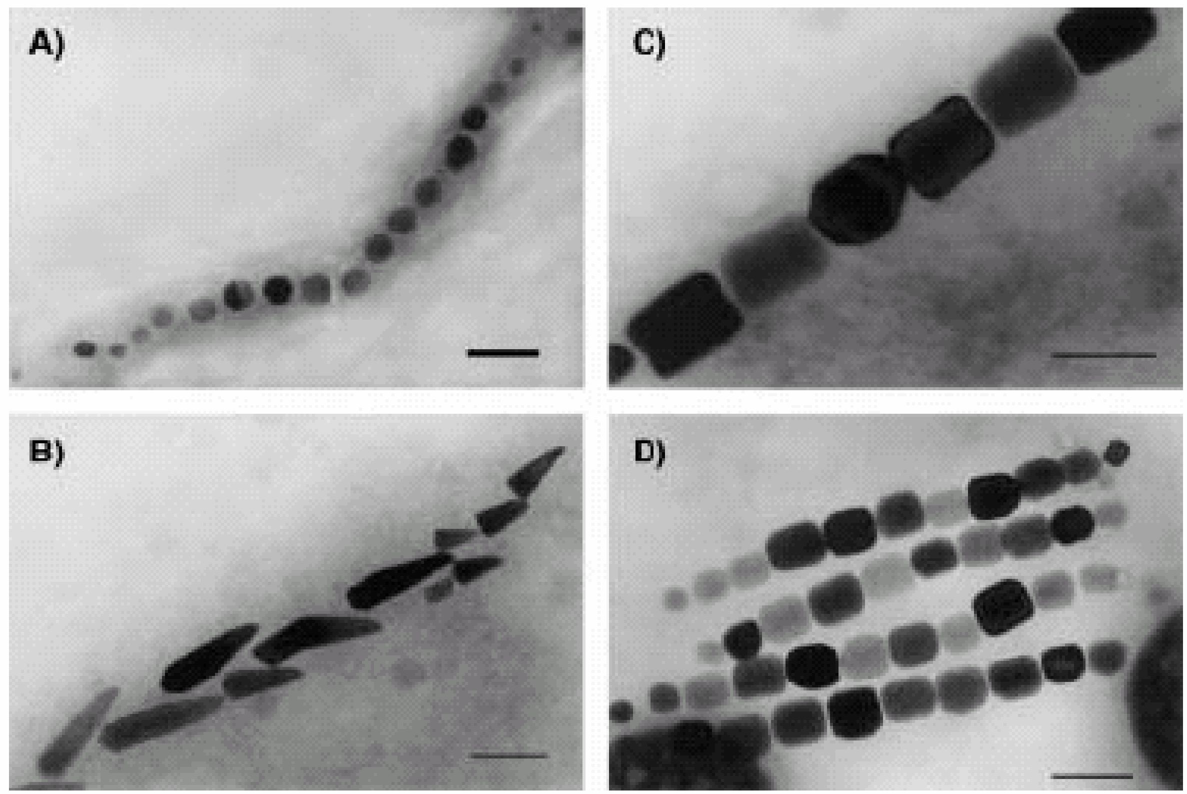
a) cubooctahedral

b) bullet-shaped

c-d) pseudohexaganol

Bars are 100 nm

E. Bauerlein, Angew Chemie Int Ed, 2003



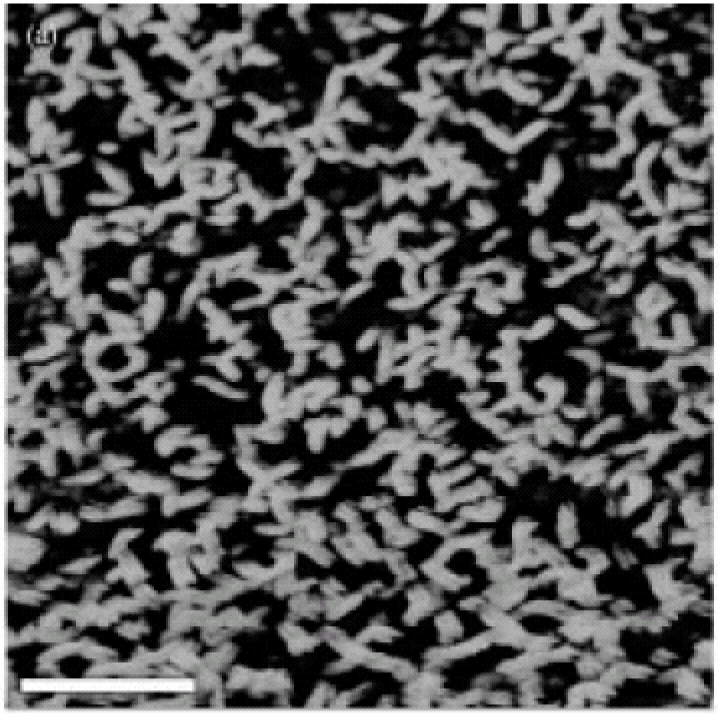
"Biomineralization inspired" research on nucleation of nanoparticles

Influence on nucleation and growth

- **surface chemistry**
- **soluble additives**
- **particle-based additives**
- **biopolymers as soluble additives**
- **synthetic polymers as soluble additives**
- **polymeric templates**

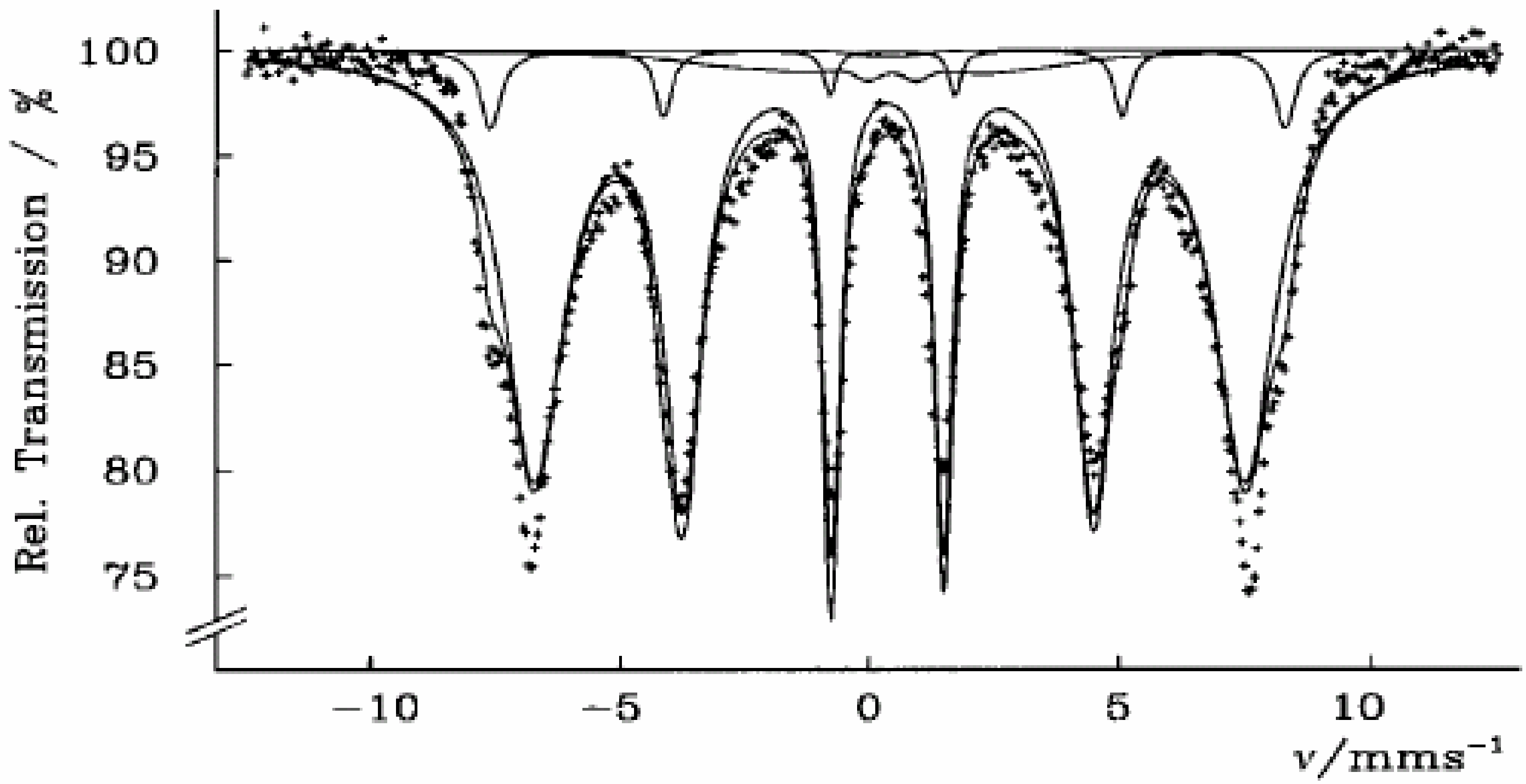
Heterogeneous nucleation of lepidocrocite γ-FeO(OH) on MDS SAM surface

Tapping mode AFM top view. Bar corresponds to 500 nm. MDS is 3-mercaptodecane sulfonic acid. **M. Nagtegaal, P. Stroeve et al., Chem. Eur. J., 1999.**



Lepidocrocite formed on SAM

Mossbauer spectra of ^{57}Fe-labeled lepidocrocite from an MPS SAM surface. Data were acquired at 20K. **M. Nagtegaal, P. Stroeve et al., Chem. Euro. J., 1999.**



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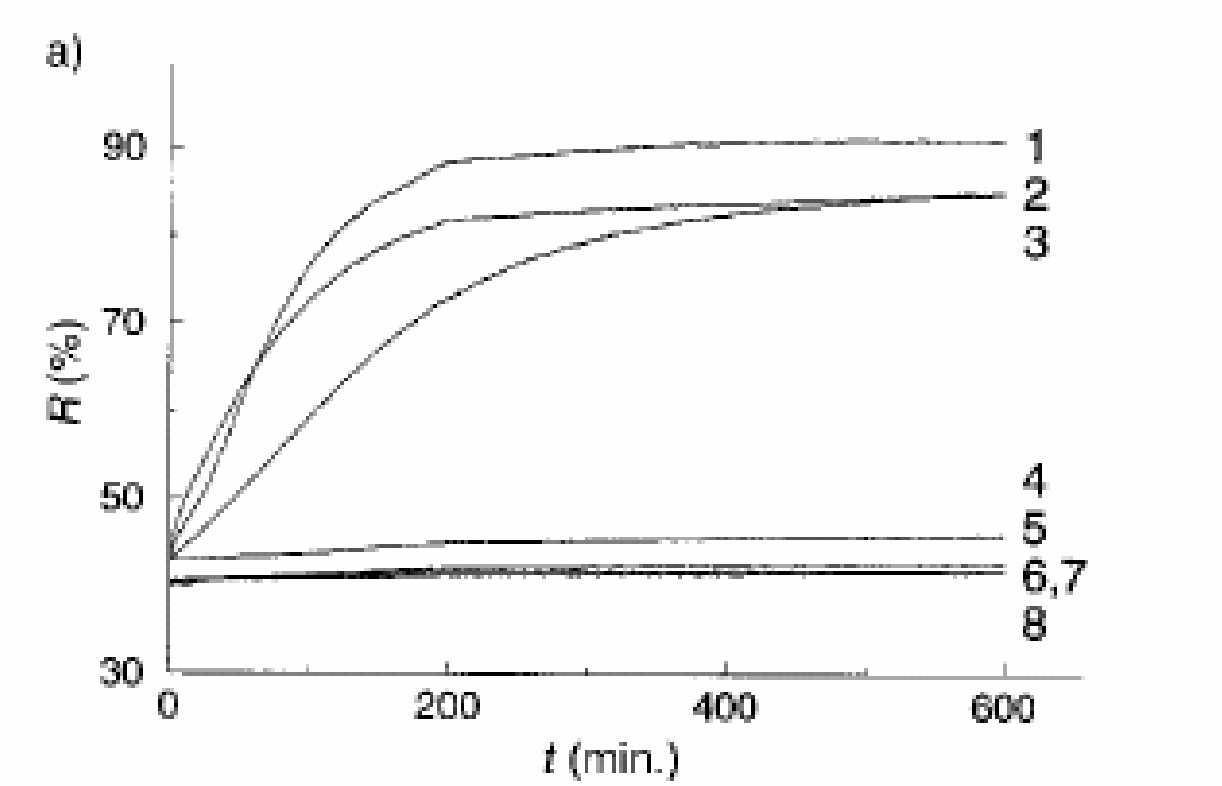
SPR reflectivity vs. time of SAM surfaces exposed to 2 mM Fe^{+3} solutions at pH 2.86

Traces correspond to different SAMs: 1 Au; 2 MDS; 3 MPS; 4 MHA; 5 MUDO; 6 MUDP; 7 cysteamine; 8 MHD.

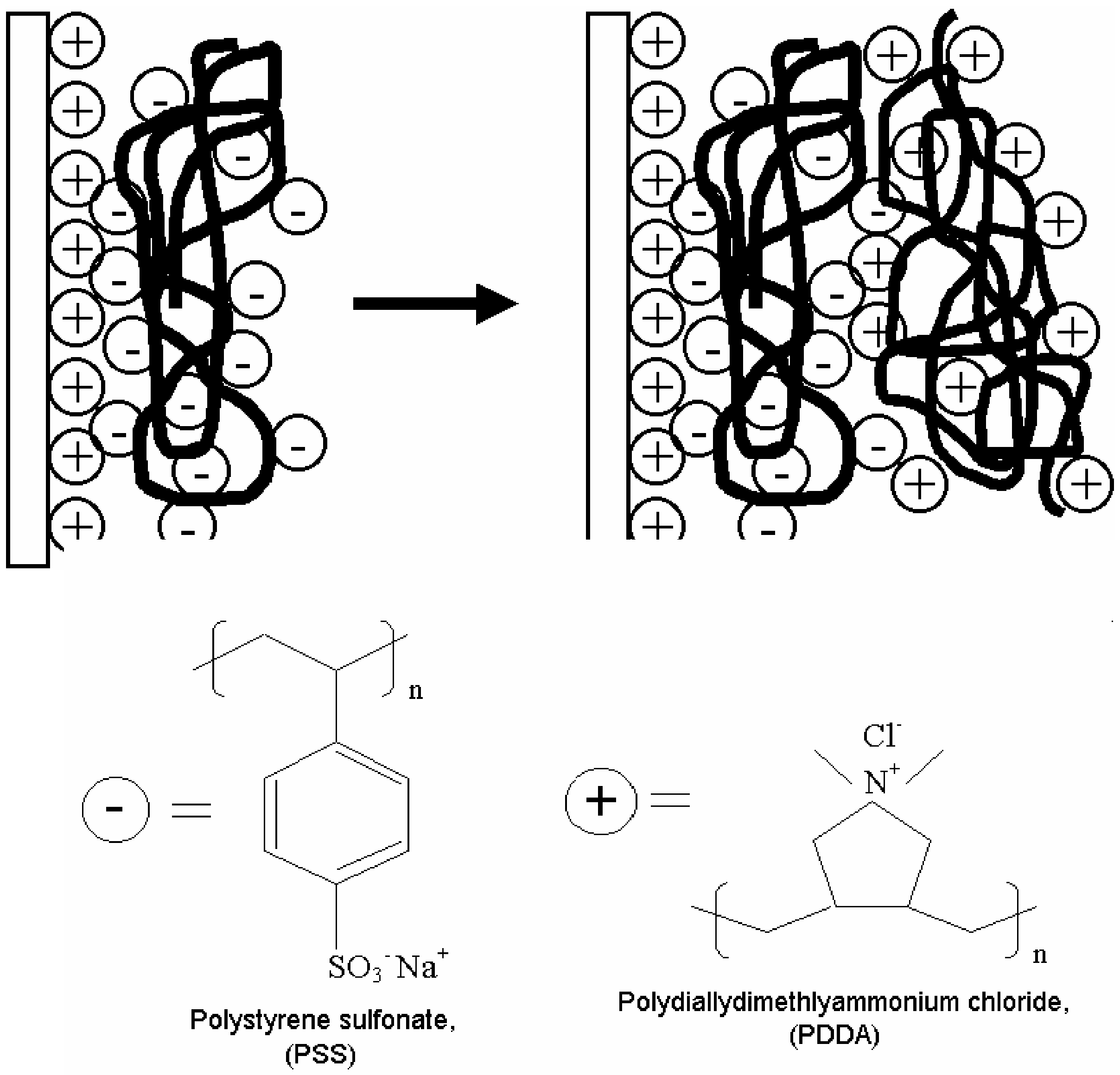


Thiols and their abbreviations

M. Nagtegaal, P. Stroeve et al., Chem. Eur. J., 1999

	Formula	Abbrevation
3-mercaptopropane sulfonic acid	$HO_3S(CH_2)_3SH$	MPS
10-mercaptodecane sulfonic acid	$HO_3S(CH_2)_{10}SH$	MDS
11-mercapto undecanol	$HO(CH_2)_{11}SH$	MUDO
hexadecanethiol	$H_3C(CH_2)_{15}SH$	MHD
16-mercaptohexadecanoic acid	$HOOC(CH_2)_{15}SH$	MHA
2-mercapto ethylamine hydrochloride	$Na^+H_3NCl^-(CH_2)_2SH$	Cysteamine hydrochloride
11-mercapto-1-undecane phosphonate	$H_2O_3P(CH_2)_{10}SH$	MUDP

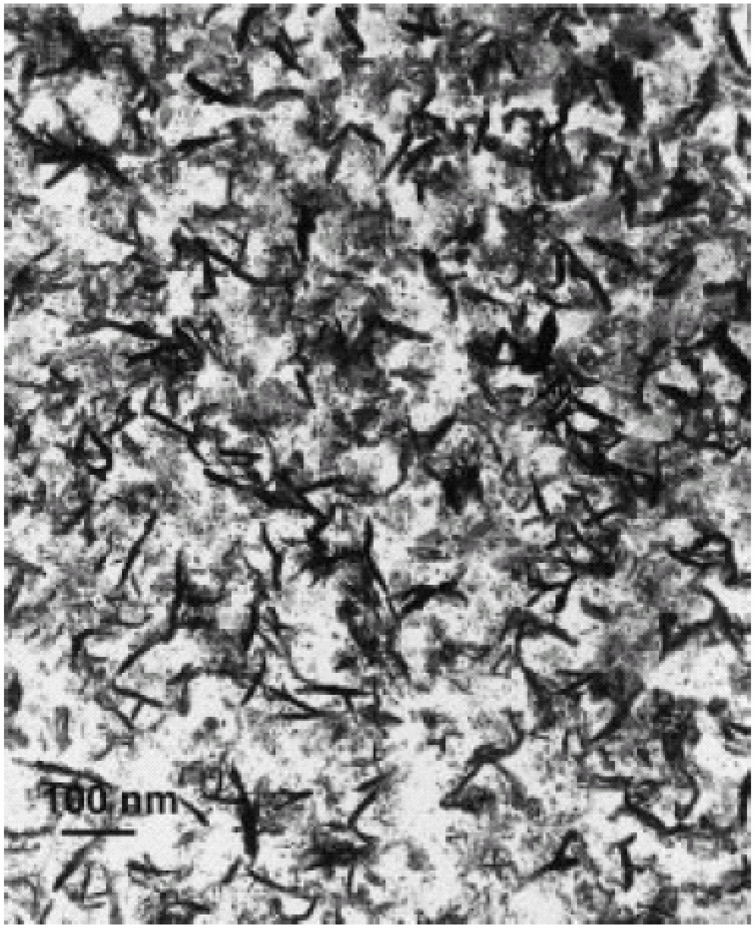
LbL deposited polyions as ultrathin films for absorption and reaction



Ultrathin LbL polyion film with nucleated akaganeite nanoparticles

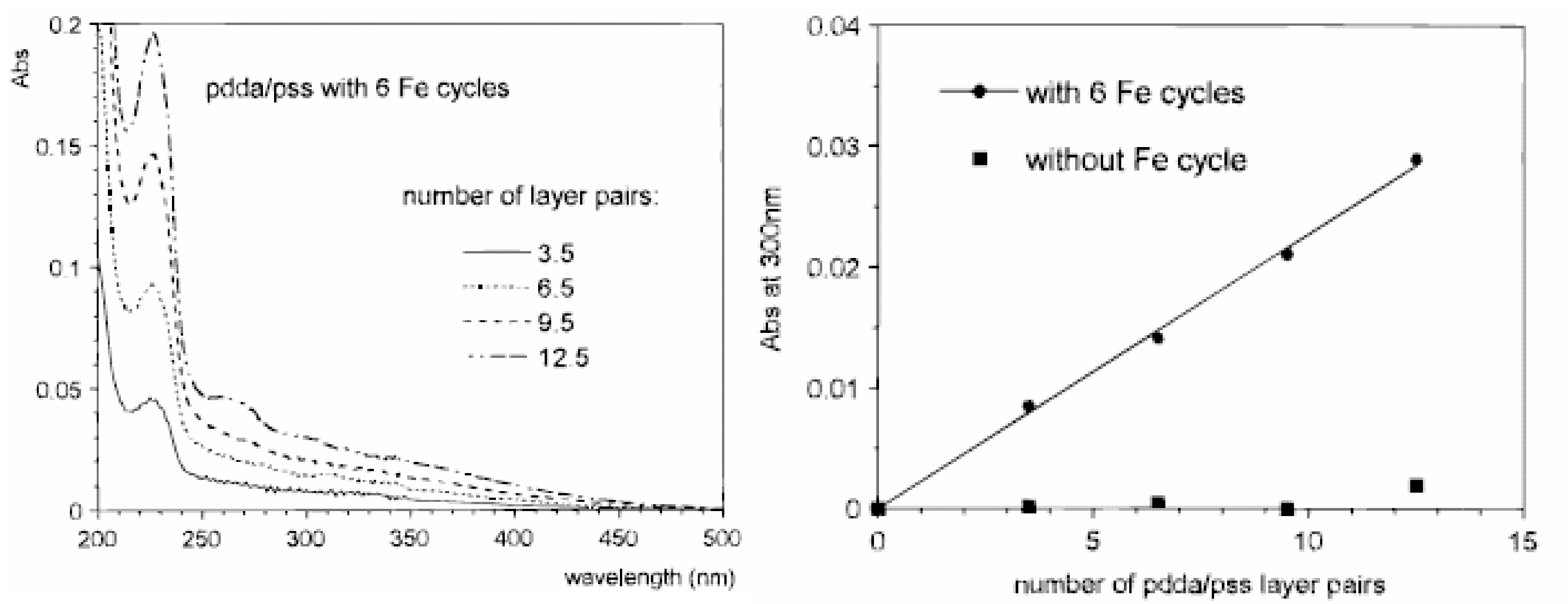
3.5 layer pairs; 3 cycles of absorption-oxidation; bar is 100 nm

S. Dante, P. Stroeve et al., Langmuir, 1999



UV-vis spectroscopy of LbL films used to follow akaganeite growth

Six Fe^{+2} absorption-oxidation cycles



Nucleation of nanoparticles in layer by layer PDDA-PSS ultrathin films

L. Zhang, P. Stroeve et al., Langmuir, 2001

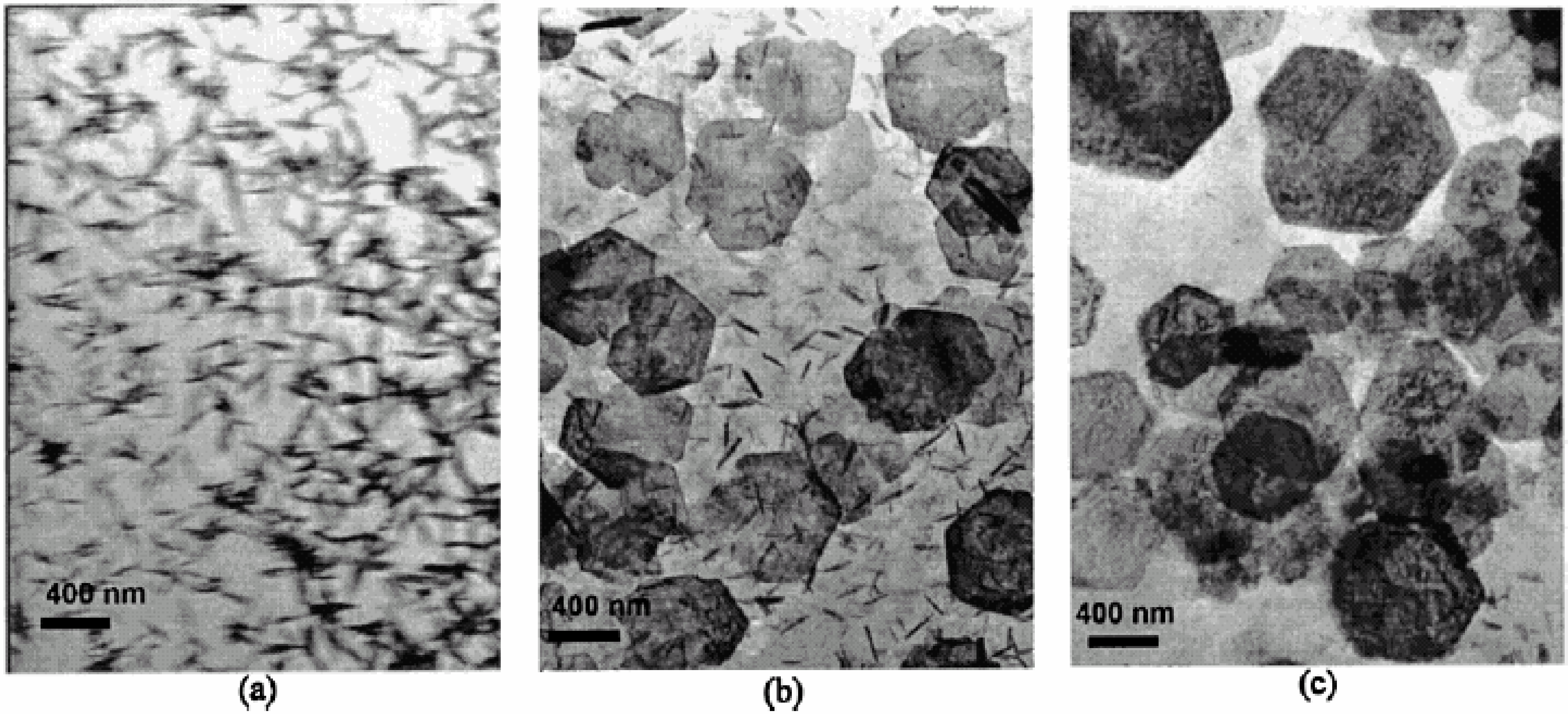


Figure 5. TEM micrographs of a 3.5 layer pairs of PDDA−PSS films at different stages of the absorption−hydrolysis process: (a) 2 cycles in a nitrogen-enriched environment, (b) 4 cycles in an oxygen-enriched environment, and (c) 8 cycles in an oxygen-enriched environment. The concentrations of cobalt chloride and sodium hydroxide solutions were 4 and 10 mM, respectively.

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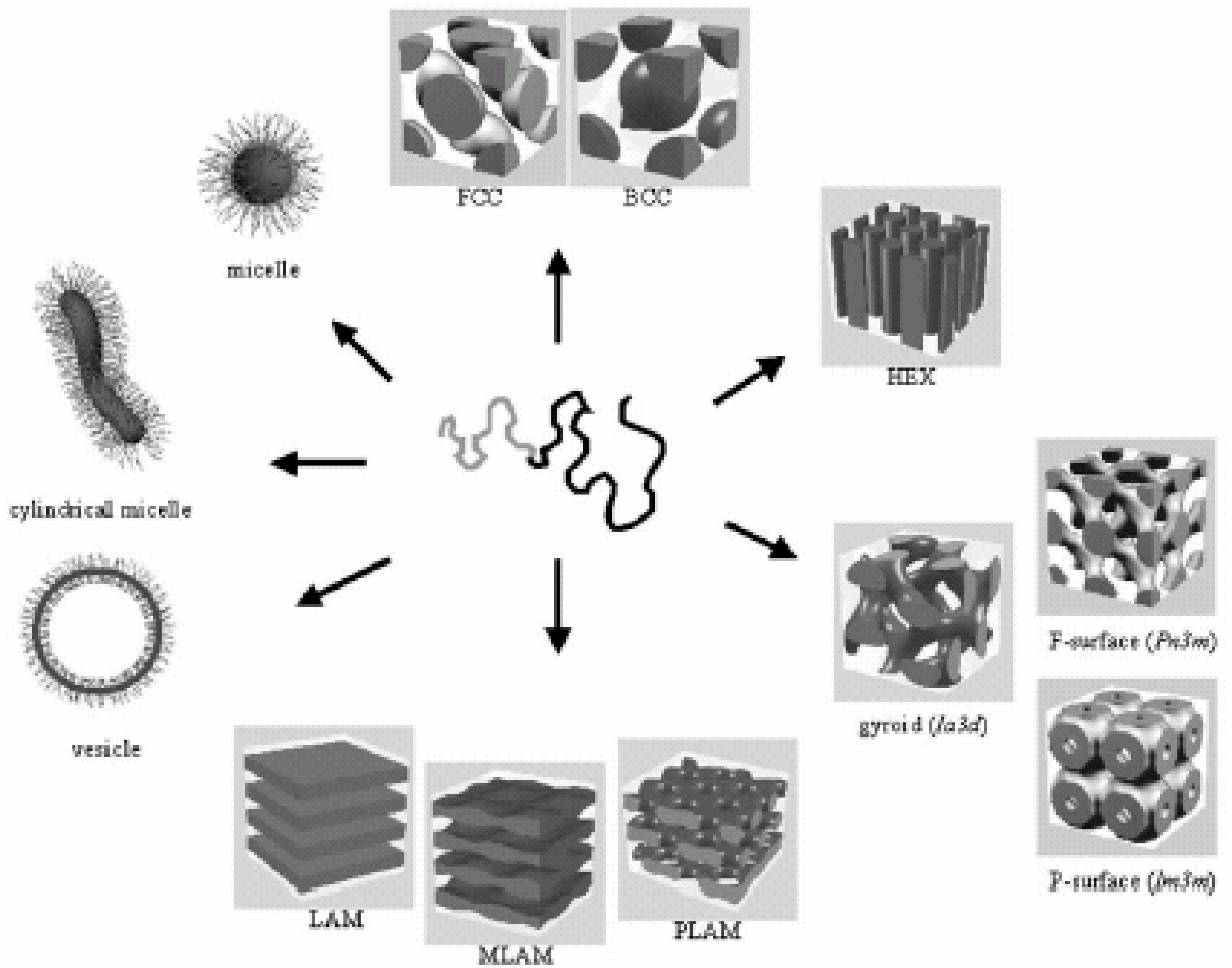
Diblock copolymers as templates for nanoparticle nucleation and growth

S. Forster and M. Konrad, J. Mat. Chem., 2003



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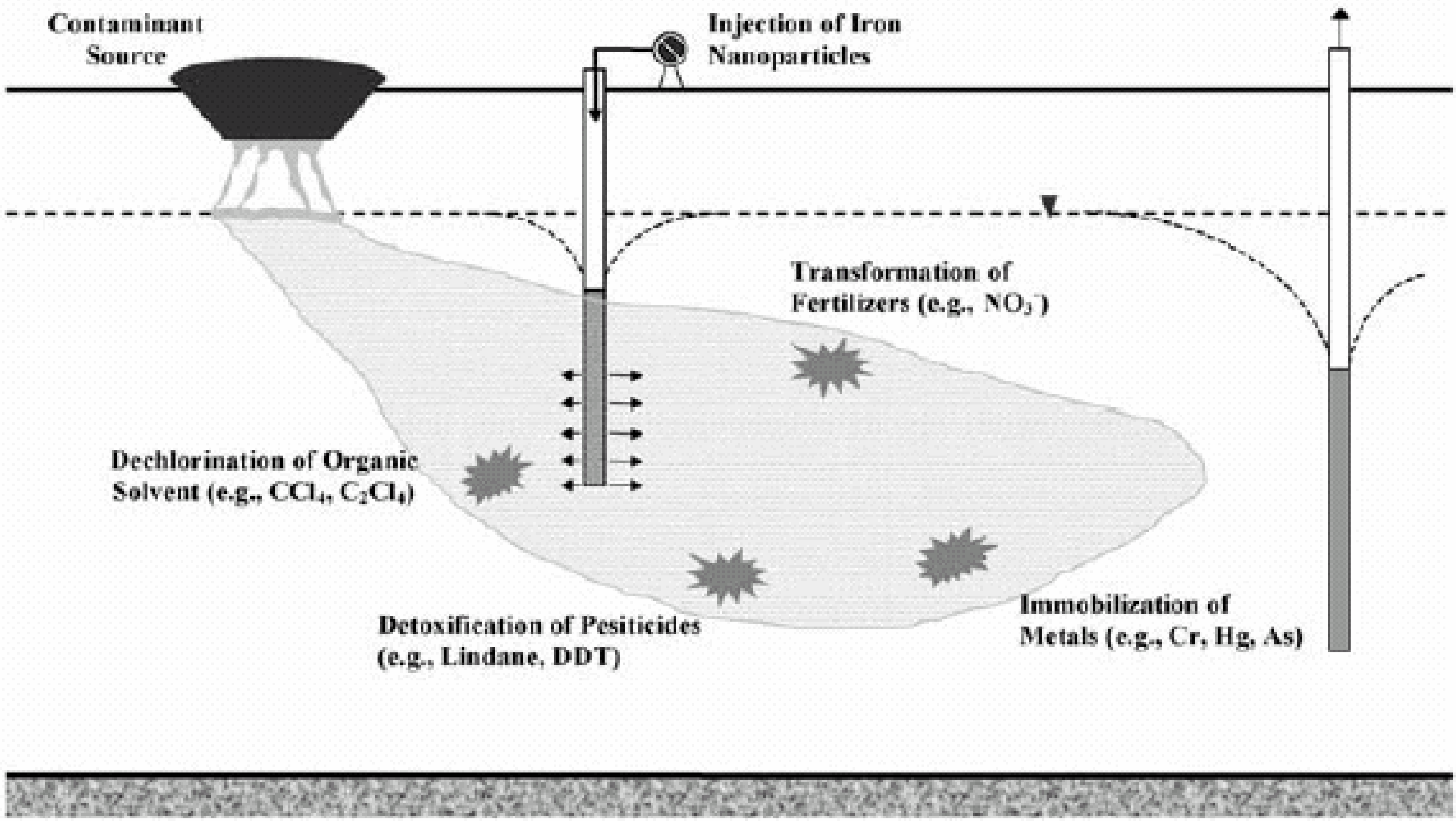
Environmental remediation

Use of iron and iron oxide nanoparticles for in situ remediation: reaction and adsorption. W.-X. Zhan, Nanoparticle Res., 2003



There are 16 different iron oxides

	Chemical formula	Common name	Color	Crystal system	Type of magnetism
Oxides:	α-Fe_2O_3	Haematite	red	trigonal	weakly ferro-magnetic
	β-Fe_2O_3	(synthetic)			
	γ-Fe_2O_3	Maghemite	reddish-brown	cubic or tetragonal	ferrimagnetic
	ε-Fe_2O_3	(synthetic)			
	Fe_3O_4	Magnetite	black	cubic	ferrimagnetic
	FeO	Wustite	black	cubic	antiferro magnetic
Oxide Hydroxides	α-FeOOH	Goethite	yellow-brown	orthorombic	antiferro magnetic
	β-FeOOH	Akaganeite	yellow-brown	tetragonal (monoclinic)	antiferro magnetic
	γ-FeOOH	Lepidocrocite	orange	orthorombic	antiferro magnetic
	δ-FeOOH	(synthetic)	red brown	hexagonal	ferrimagnetic
	δ'-FeOOH	Feroxyite	red brown	hexagonal	ferrimagnetic
	High pressure FeOOH	(synthetic)		orthorombic	
	$Fe_{16}O_{16}(OH)_y(SO_4)_z$ nH_2O	Schwertmannite	yellow-brown	tetragonal	
Hydroxides	Fe_5HO_8 4H2O	Ferrihydrite	red brown	hexagonal	speromagnetic
	$Fe(OH)_3$	Bernalite	greenish	orthorombic	
	$Fe(OH)_2$		white	hexagonal	

Contaminants that can be treated by iron oxide and iron nano particles

Chlorinated methanes
- Carbon tetrachloride (CCl_4)
- Chloroform ($CHCl_3$)
- Dichloromethane (CH_2Cl_2)
- Chloromethane (CH_3Cl)

Chlorinated benzenes
- Hexachlorobenzene (C_6Cl_6)
- Pentachlorobenzene (C_6HCl_5)
- Tetrachlorobenzenes ($C_6H_2Cl_4$)
- Trichlorobenzenes ($C_6H_3Cl_3$)
- Dichlorobenzenes ($C_6H_4Cl_2$)
- Chlorobenzene (C_6H_5Cl)

Pesticides
- DDT ($C_{14}H_9Cl_5$)
- Lindane ($C_6H_6Cl_6$)

Organic dyes
- Orange II ($C_{16}H_{11}N_2NaO_4S$)
- Chrysoidine ($C_{12}H_{13}ClN_4$)
- Tropaeolin O ($C_{12}H_9N_2NaO_5S$)
- Acid Orange
- Acid Red

Heavy metal ions
- Mercury (Hg^{2+})
- Nickel (Ni^{2+})
- Silver (Ag^+)
- Cadmium (Cd^{2+})

Trihalomethanes
- Bromoform ($CHBr_3$)
- Dibromochloromethane ($CHBr_2Cl$)
- Dichlorobromomethane ($CHBrCl_2$)

Chlorinated ethenes
- Tetrachloroethene (C_2Cl_4)
- Trichloroethene (C_2HCl_3)
- *cis*-Dichloroethene ($C_2H_2Cl_2$)
- *trans*-Dichloroethene ($C_2H_2Cl_2$)
- 1,1-Dichloroethene ($C_2H_2Cl_2$)
- Vinyl chloride (C_2H_3Cl)

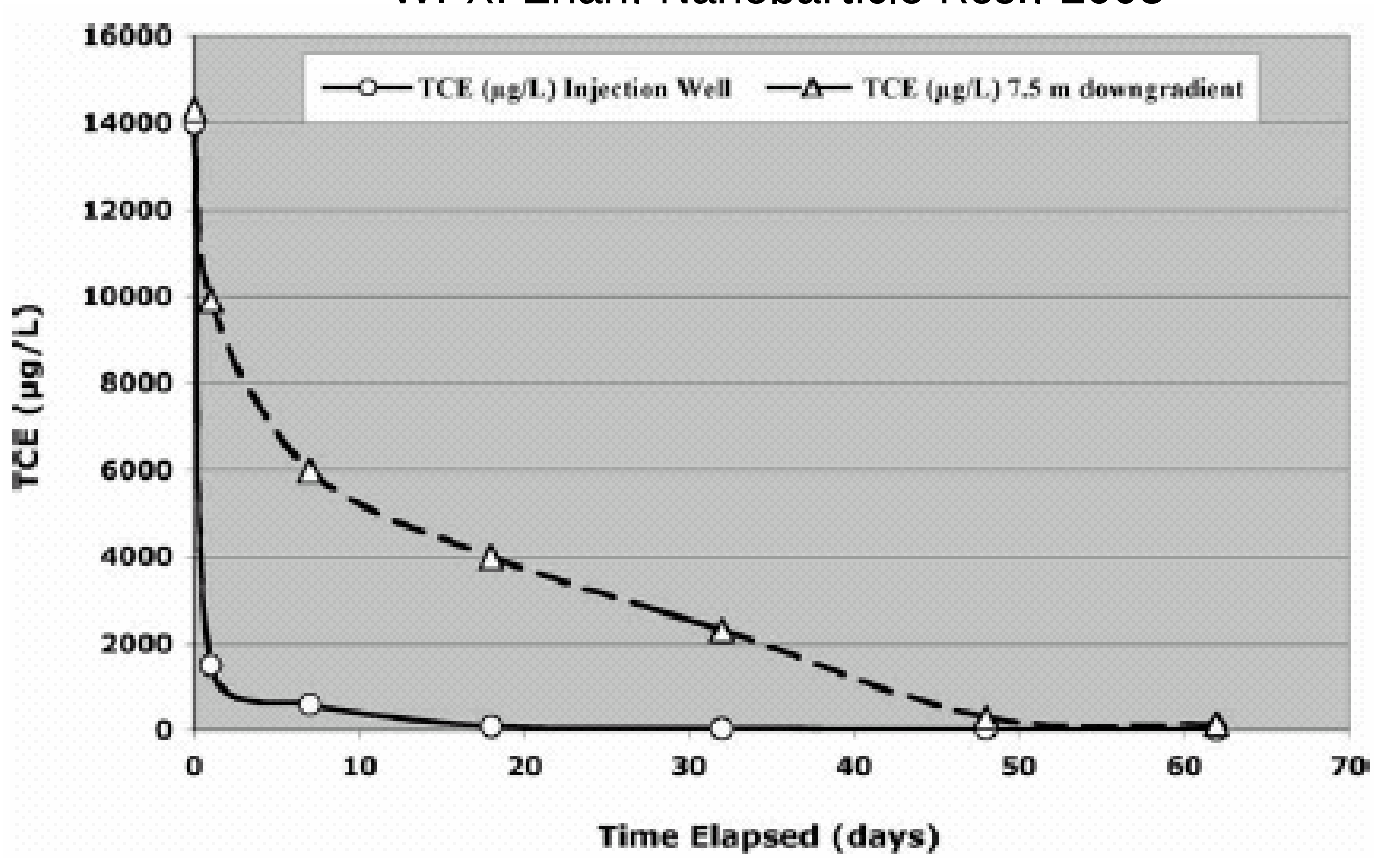
Other polychlorinated hydrocarbons
- PCBs
- Dioxins
- Pentachlorophenol (C_6HCl_5O)

Other organic contaminants
- N-nitrosodimethylamine (NDMA) ($C_4H_{10}N_2O$)
- TNT ($C_7H_5N_3O_6$)

Inorganic anions
- Dichromate ($Cr_2O_7^{2-}$)
- Arsenic (AsO_4^{3-})
- Perchlorate (ClO_4^-)
- Nitrate (NO_3^-)

Reduction of tetrachloroethylene (TCE) following in situ application of nanoscale iron particles

W.-X. Zhan. Nanoparticle Res.. 2003



Reduction of TCE following the *in situ* application of nanoscale iron particles.

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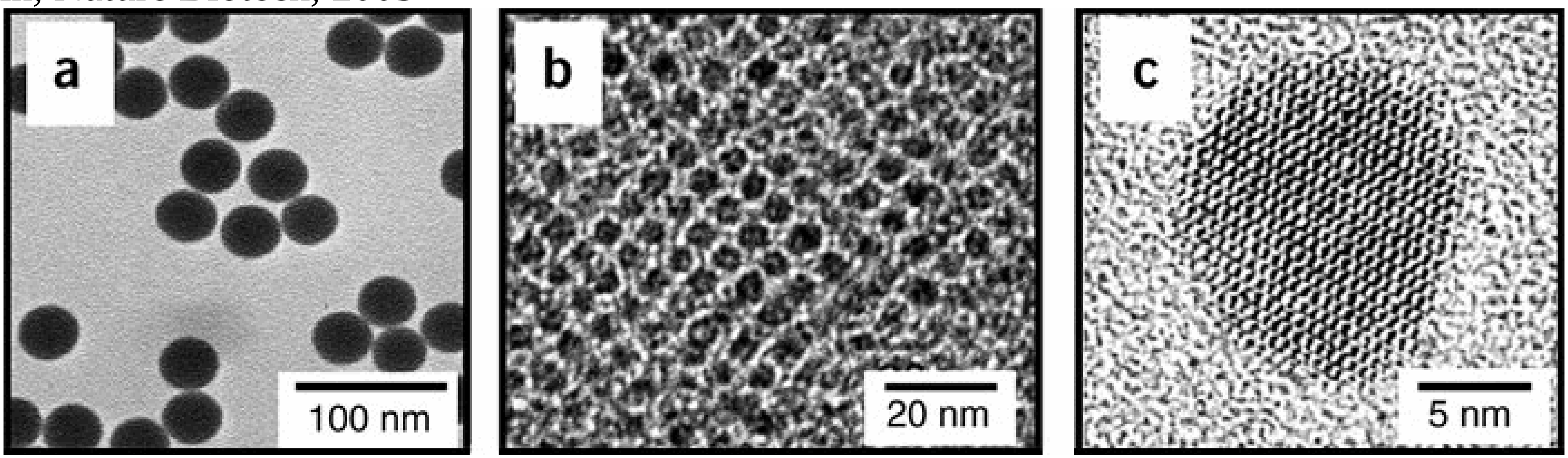
TEM of engineered nanoparticles

(**a**) Nanosized silica particles produced by the hydrolysis of silicon alkoxides. The high uniformity of these samples is a characteristic feature of many nanomaterials where control of size is necessary to define properties.

(**b**) Nanocrystalline magnetite (Fe_3O_4). This close-packed array of nanocrystals, with an average diameter of 4 nm, was formed as a drop of dispersed nanocrystals dried onto a TEM support grid. The particles are not touching because of the presence of a surface passivating agent, oleic acid.

(**c**) High-resolution transmission electron micrograph of a single TiO_2 nanocrystal.

V. Colvin, Nature Biotech, 2003



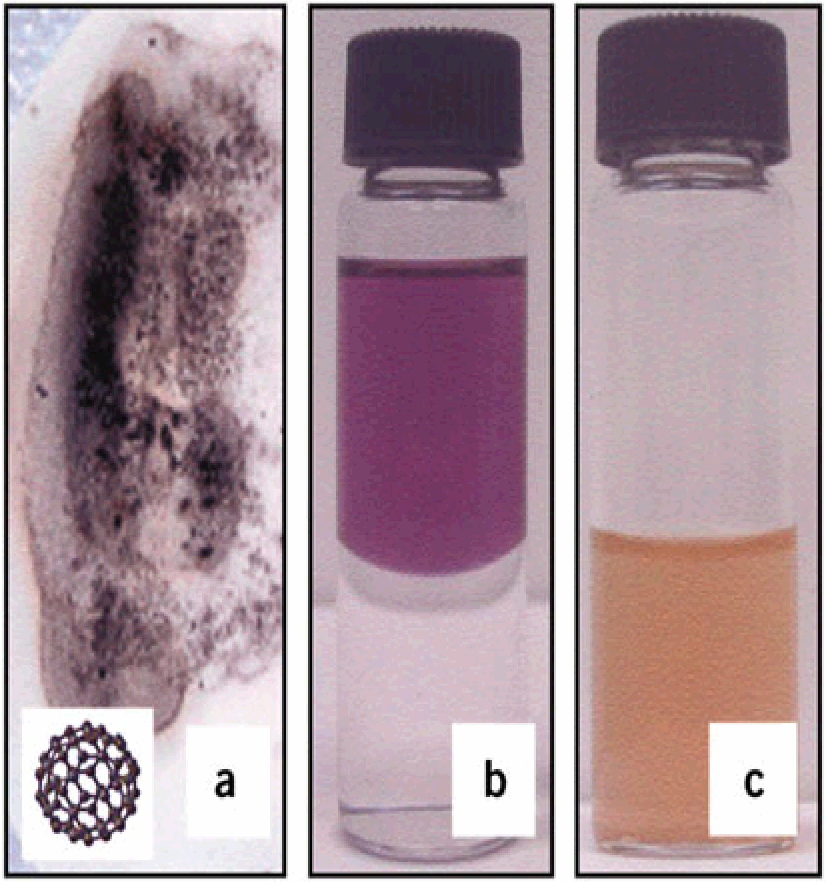
The diverse formats of engineered nanomaterials

(**a**) C_{60} dried onto filter paper is a black powder (inset: molecular structure of C_{60}).

(**b**) Fullerenes are easily dissolved in nonpolar solvents and form a purple solution (top layer).

(**c**) With relatively mild chemical treatments, such as evaporation of the nonpolar phase, C_{60} becomes water stable in the yellow solution. The material is present as colloidal aggregates that contain between 100-1,000 fullerene molecules.

V. Colvin, Nature Biotech, 2003



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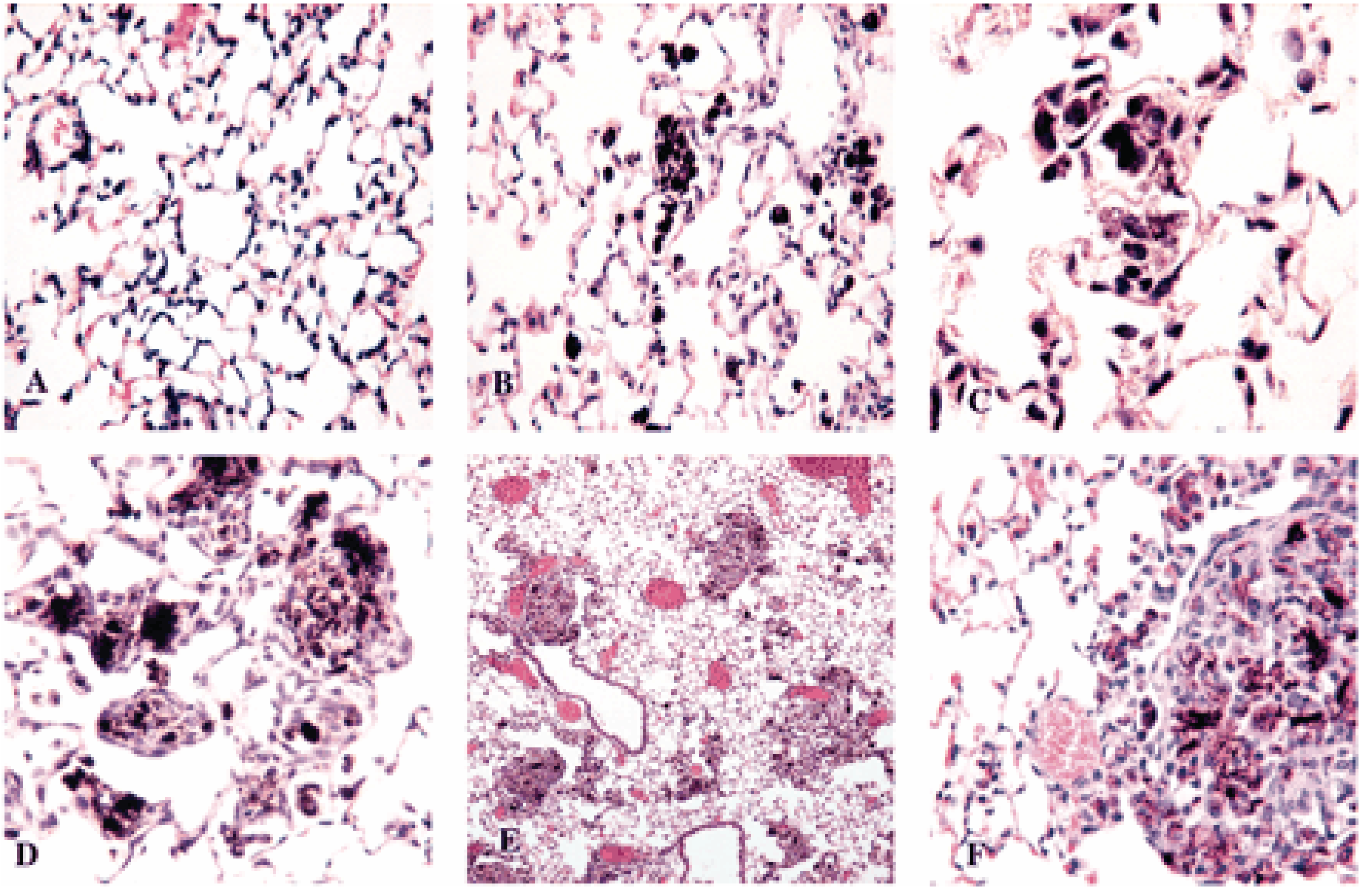
Pulmonary toxicology of SWCNT: RNT (raw), PNT(purified), CNT (nickel)

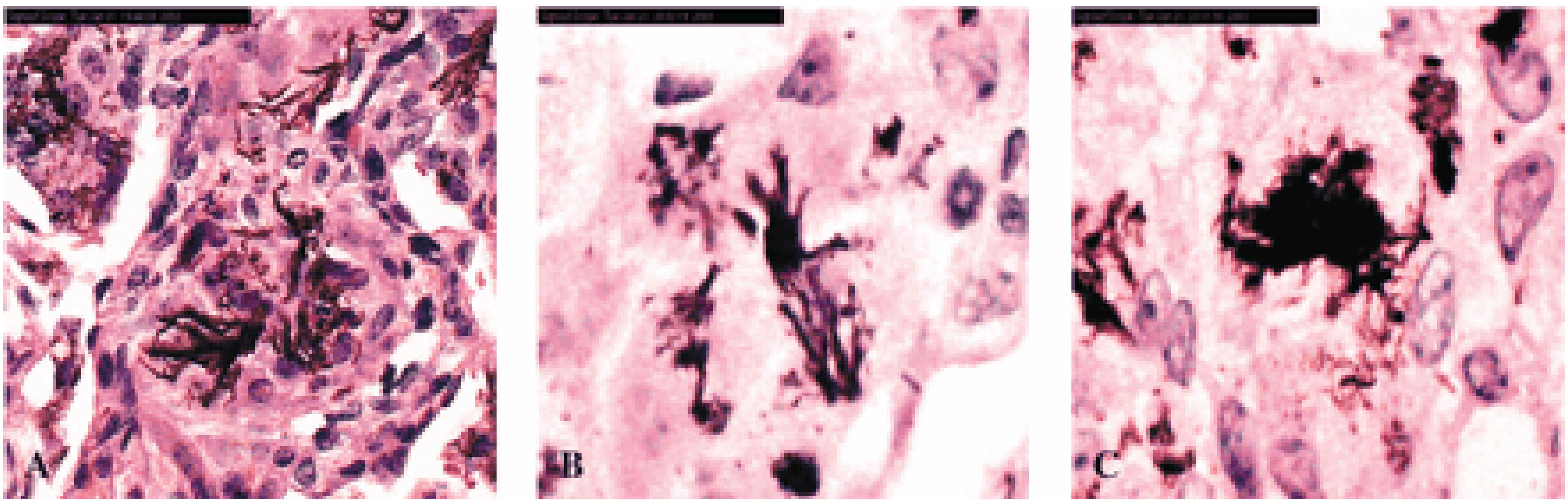
Lung tissue from mice instilled with 0.5 mg of a test material per mouse and euthanized 90 d after the single treatment. (A) Carbon black. Particles scattered in alveoli. (B) Quartz. Shows an aggregate of inflammation cells (lymphocytes) around an area surrounded by quartz particle-containing macrophages. (C) CNT. Granulomas contained black particles. (D) RNT. Granulomas at low magnification. (E) RNT. A granuloma at a high magnification. (F) PNT. A large granuloma underwent degeneration with necrosis. Magnifications 40 to 200x.

C.W. Lam et al., Tox. Sci., 2004



Pulmonary toxicology of SWCNT: RNT (raw), PNT (purified)

Lung tissues from mice instilled with 0.5 mg of NT per mouse and euthanized 90 d after the single treatment showing presence of NT fibers. (A) RNT. NT fibers in a granuloma. (B) PNT. NT fibers in a granulomas. (C) PNT. Clumps of NT fibers in a granuloma. (Magnification 900x). C.W. Lam et al., Tox. Sci., 2004



Nanotechnology and the environment

Closing comments

- Nanotechnology has had a significant impact on the environment and offers potential for reduction of the use of fuels, CO_2 generation, and environmental pollution.
- Increased use of nanoparticles may cause release of some nanoparticles in the environment. The effects of nanoparticles on the environment and health are not known. Question: are soft particles more benign than hard particles?