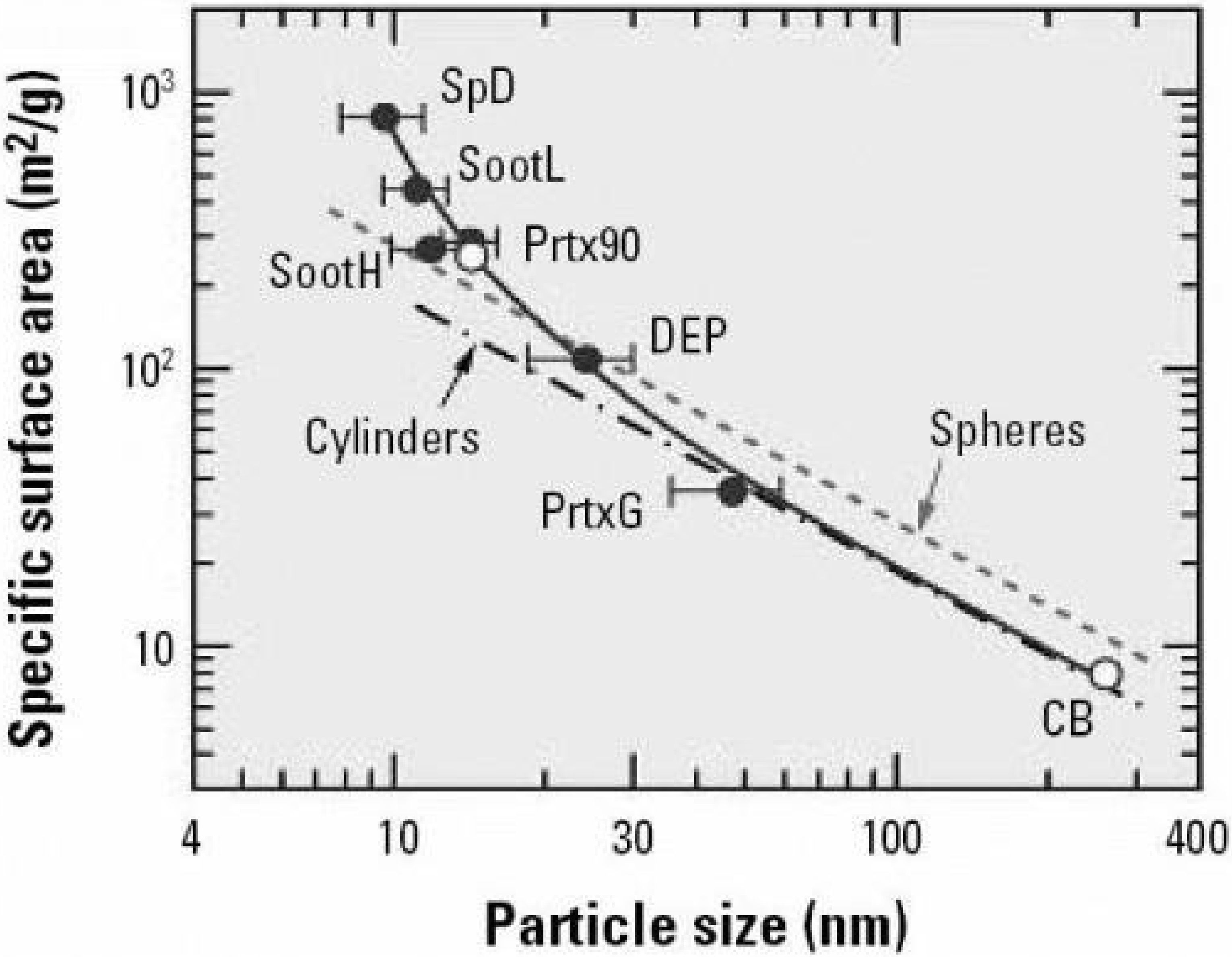
Environmental Impacts of Nanoparticles: The Good, the Bad and the Beautiful

Dr. James Kubicki
Professor of Geosciences
College of Earth and Mineral Sciences
and
The Earth & Environmental Systems Institute

Surface area increases dramatically with size



openi.nlm.nih.gov/detailedresult.php?img=1831520_ehp0115-000187f4&req=4

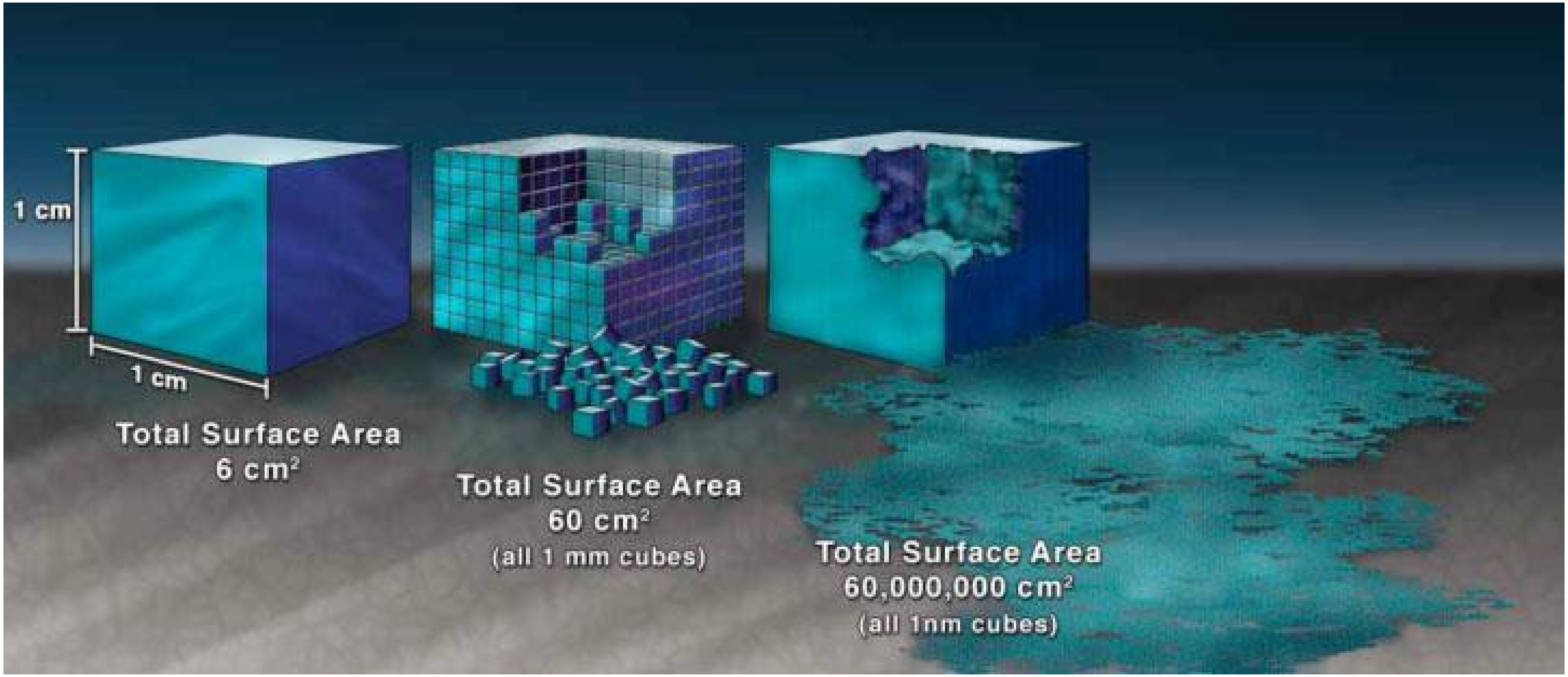


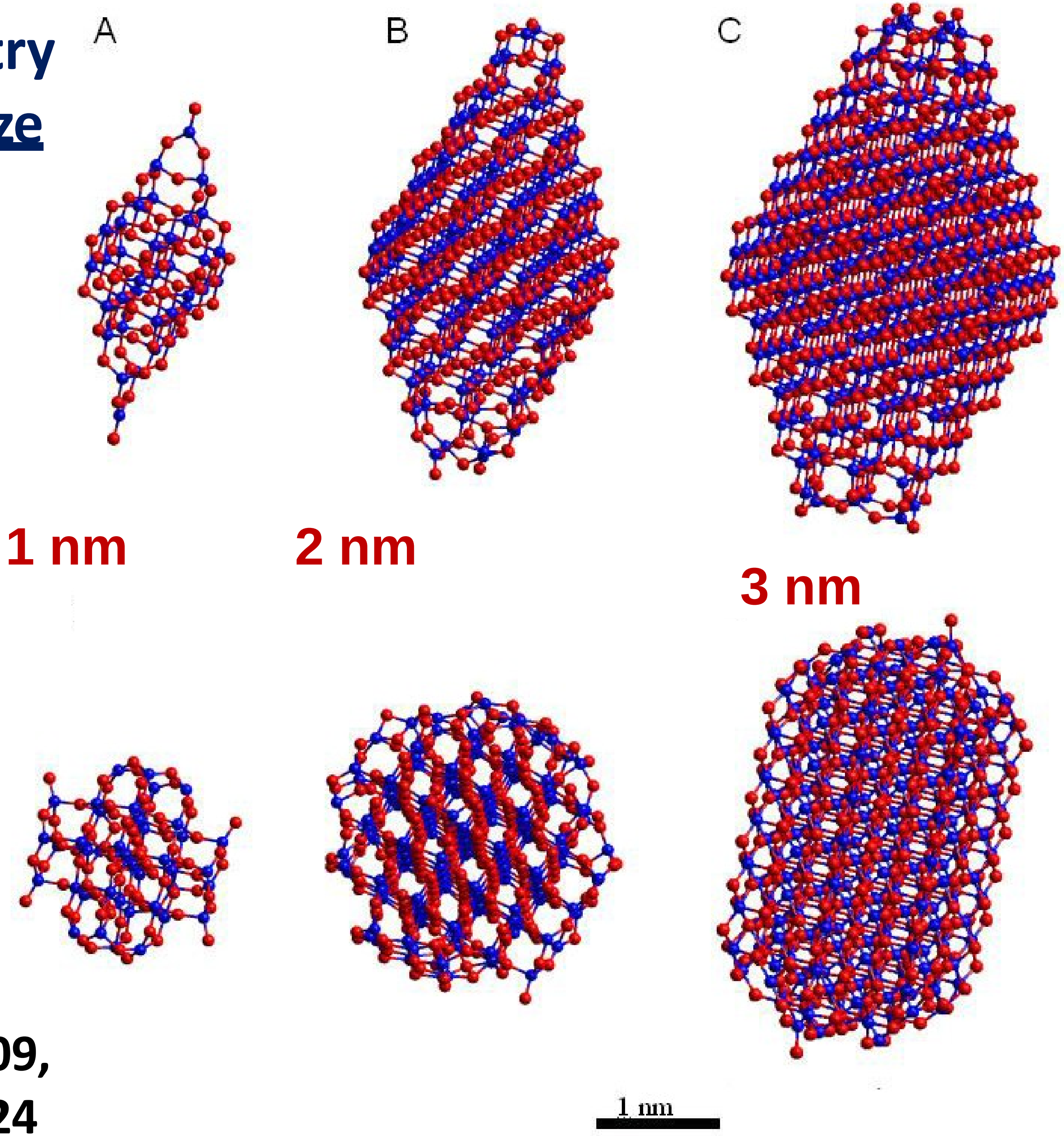
Illustration demonstrating the effect of the increased surface area provided by nanostructured materials

www.nano.gov/nanotech-101/special

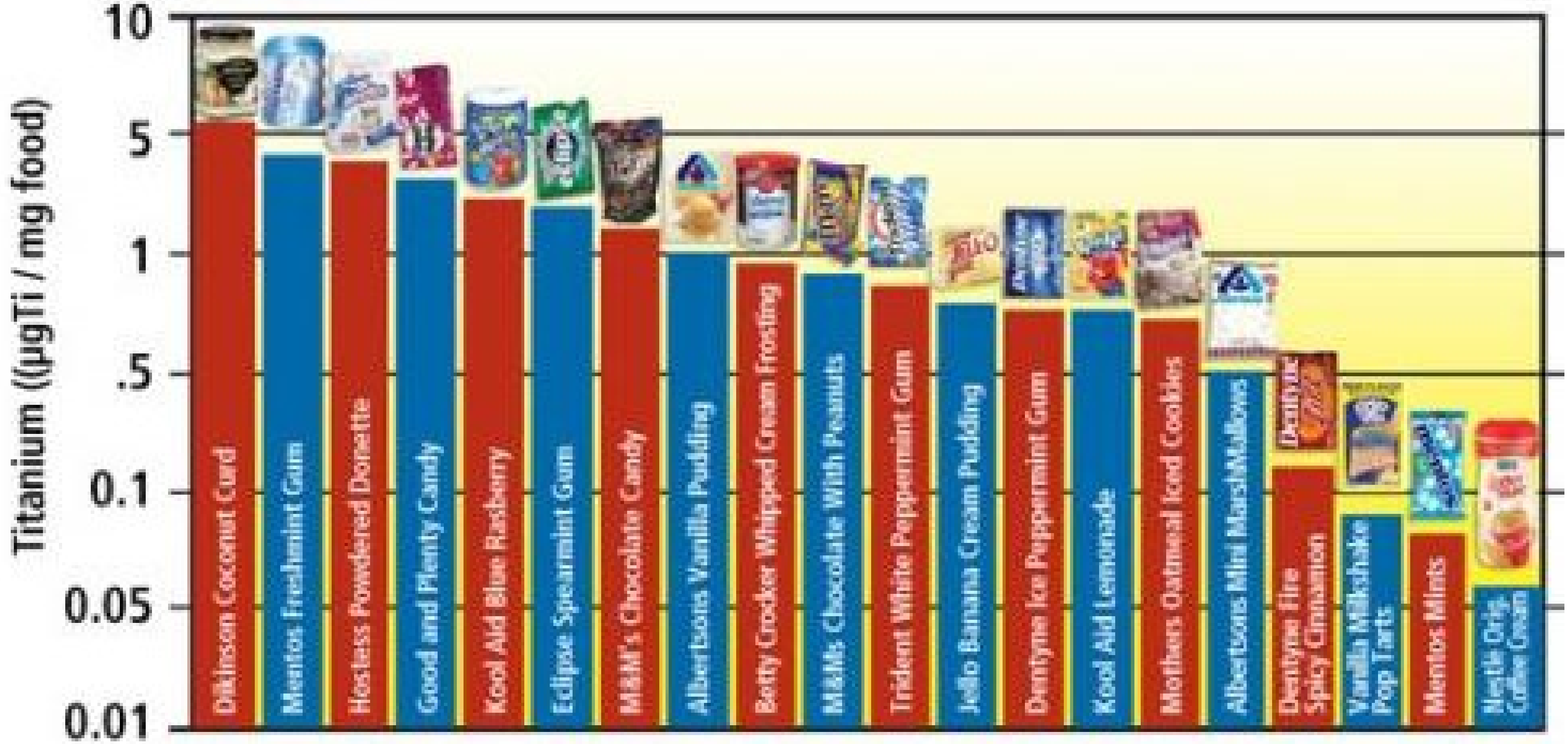
Surface chemistry changes with size

Anatase

Rutile



Hummer et al., 2009, JPC C, 113, 4240-424



Titanium dioxide is added to a huge swath of products in nano form including paints, paper and plastics but also lends white pigment to most toothpastes and many processed foods, including Mentos, Trident and Dentyne gum, M&Ms, Betty Crocker Whipped Cream Frosting, Jello Banana Cream Pudding, Vanilla Milkshake Pop Tarts and Nestlé Original Coffee Creamer. - See more at: www.emagazine.com/magazine/eating-nano#sthash.W9agPXVz.dpuf

www.emagazine.com/magazine/eating-nano

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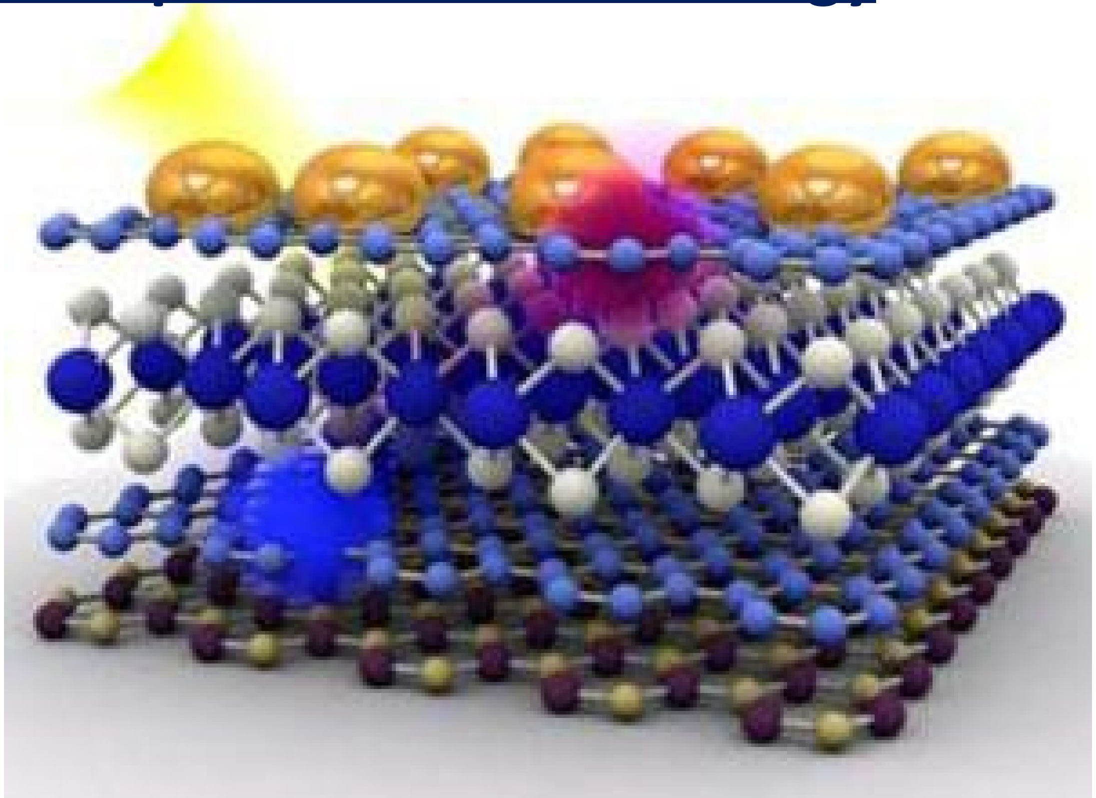
www.emagazine.com/magazine/eating-nano

Inventory of nanoparticle occurrence

	Manufactured 	Incidental (D) 	Incidental (I) 	Natural 
Au	✓			✓
Ag	✓	✓		✓
Fe	✓			
FeOx	✓	✓	✓	✓
TiO_2	✓	✓		✓
SiO_2	✓	✓	✓	✓
CeO_2	✓	✓		✓
ZnO	✓	✓		✓
C60	✓	✓		✓
CNT	✓	✓		

Nanoparticles in solar energy



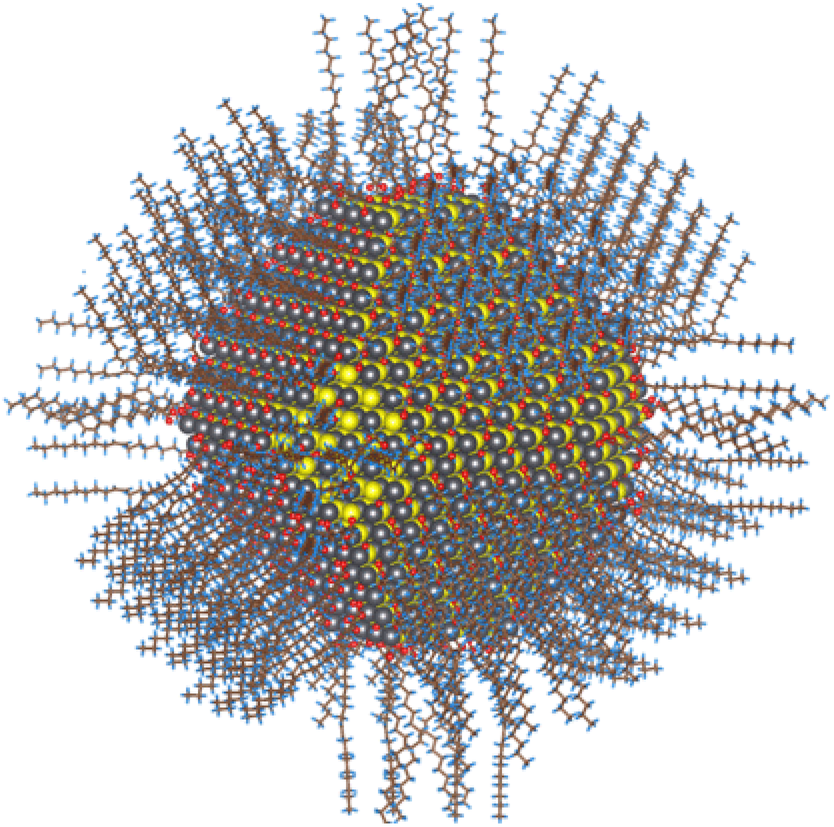
The incredibly thin cell. Graphene (light blue); dichalcogenide (white+blue); nanoparticles (gold); boron nitride (purple+beige) © Science/AAAS

An international team of researchers has constructed an [atom thin photovoltaic device] with unusually high quantum efficiency – a measure of the photons converted into charge carrying electrons – of 30%.

www.rsc.org/chemistryworld/2013/05/solar-panel-photovoltaic-slims-down-atom-thick-graphene

Nanoparticles in solar energy

This new form of solid, stable light-sensitive nanoparticles, called colloidal quantum dots, could lead to cheaper and more flexible solar cells, as well as better gas sensors, infrared lasers, infrared light emitting diodes and more. The work, led by post-doctoral researcher Zhijun Ning and Professor Ted Sargent, was published this week in the journal *Nature Materials*.



The image shows complete atomistic model of the colloidal lead sulfide (selenide) nanoparticle also known as quantum dot.

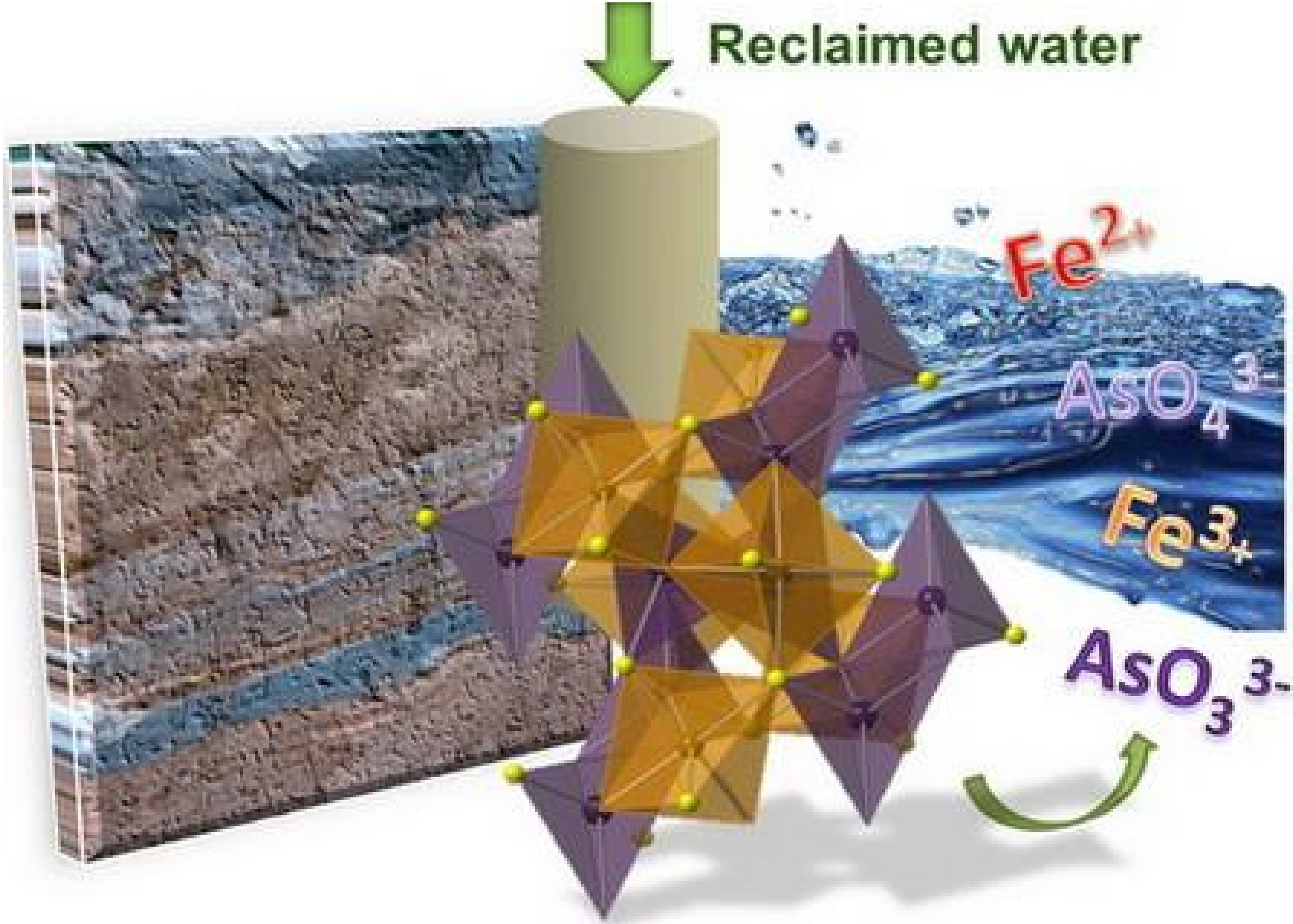
genefan.com/news.php?item.956.11

Nanoparticles used for water treatment

Extreme arsenic lesions on feet

http://phys4.harvard.edu/%7Ewilson/arsenic/arsenic_project_introduction.html

Nanoparticles of iron oxides adsorb arsenic



Neil et al., J. Environ. Monitoring, 2012, 14, 1772

NANOTECH ON TAP

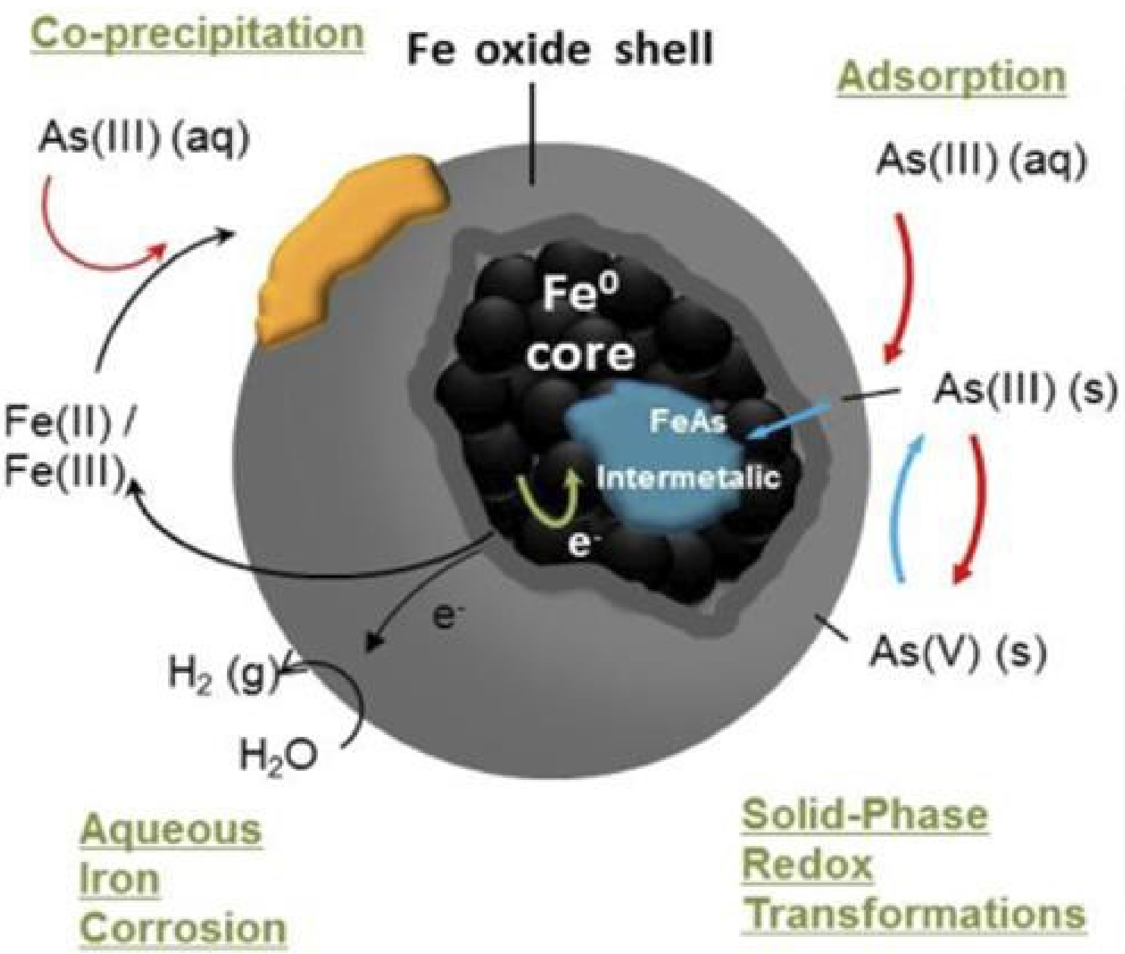
Indian technology offers **CLEAN WATER** at low cost

CEN.ACS.ORG NOV 10, 2014

INVENTORS The InnoNano Team in front of a water treatment tank that uses the materials they developed. From left, Anshup, holding a cartridge of ferric oxyhydroxide-chitosan nanocomposite; Chaudhary; Anil Kumar; Pradeep; and Sankar.

GROUNDWATER in West Bengal naturally contains arsenic, causing ailments including skin diseases and cancer. Thanks to nanotechnology, thousands of people there have gained access to arsenic-free water since 2013, with the installation of treatment tanks using porous granules developed by a team at the Indian Institute of Technology (IIT), Madras, led by chemistry professor Thalappil Pradeep.

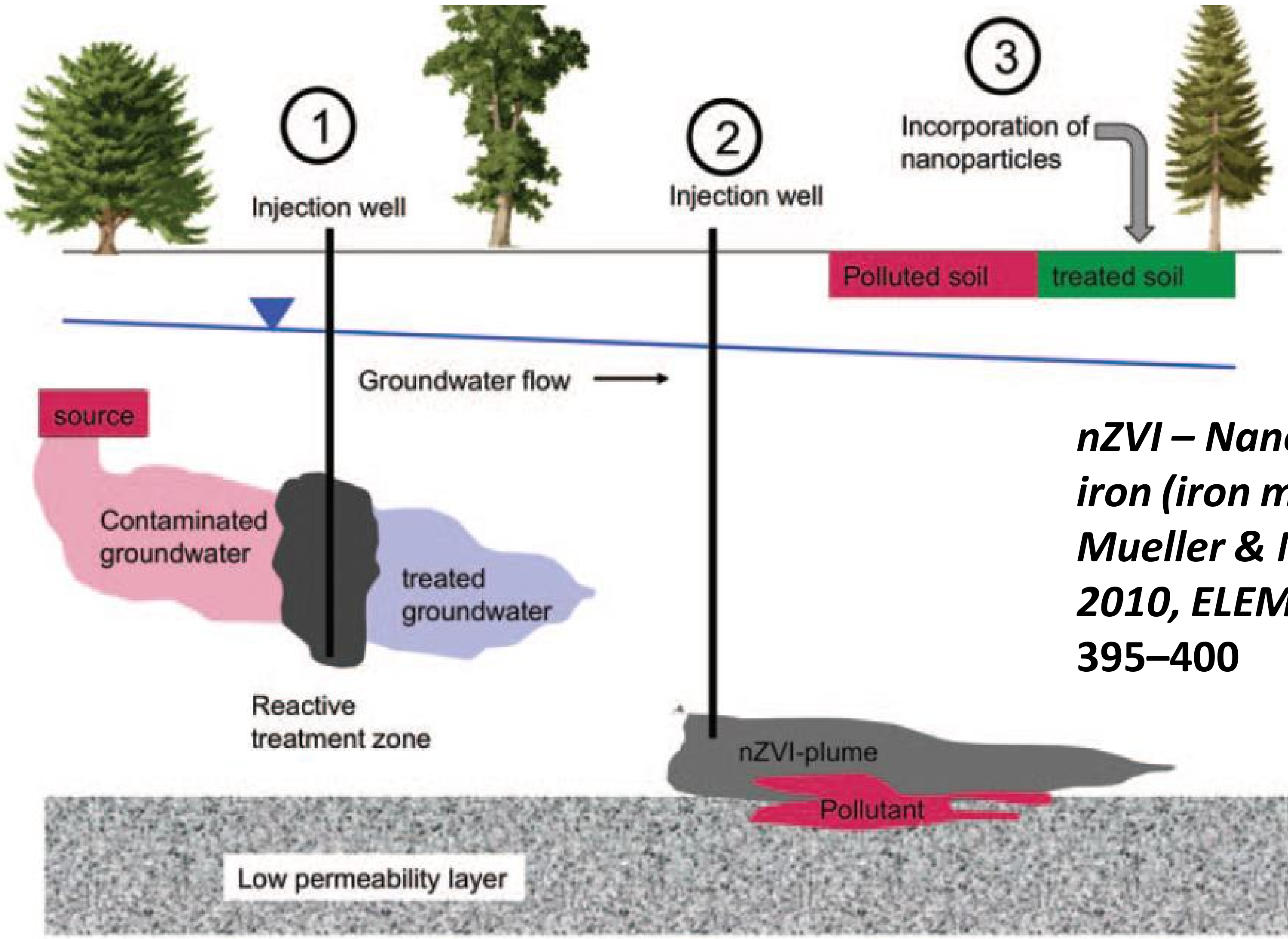
Nanoparticles of iron oxides and metal break down contaminants



Iron oxide nanoparticles can enhance iron-reducing bacteria that also reduce and immobilize uranium. Fe metal nanoparticles are effective reductants for the dehalogenation of chlorinated solvents and reduction of Cr(VI), and also U(VI) under anoxic conditions.

www.princeton.edu/cbe/people/faculty/koel/group/research/solid-surface-structure/

In situ technologies used to treat polluted groundwater and soils: injection of nZVI to form a reactive barrier; injection of mobile nZVI to form an nZVI plume; incorporation of NP into topsoil to adsorb or degrade pollutants



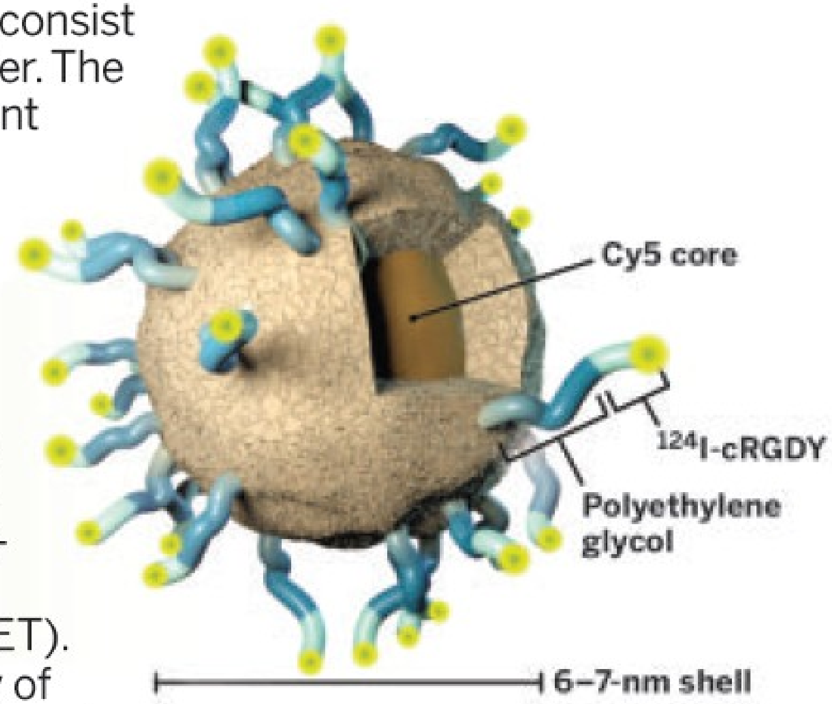
nZVI – Nano zero-valent iron (iron metal NPs)

***Mueller & Nowack, 2010, ELEMENTS*, 6, 395–400**

TINY PARTICLES TESTED IN HUMANS

CEN.ACS.ORG
NOVEMBER 3, 2014

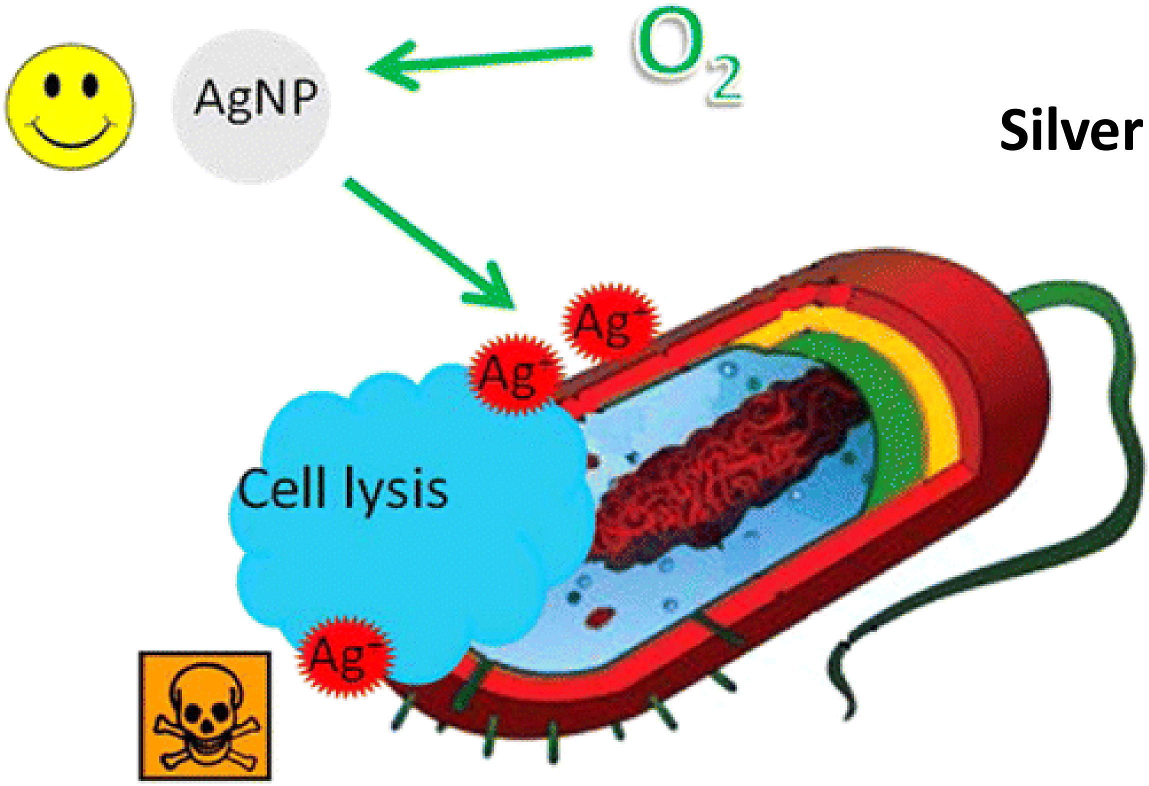
The nanoparticles known as C dots have been studied in humans, marking the first time this type of ultrasmall inorganic particle has made the leap from animal tests to people (*Sci. Transl. Med.* 2014, DOI: 10.1126/scitranslmed.3009524). C dots, known formally as Cornell dots for the university where they were first developed, consist of silica nanoparticles 6–7 nm in diameter. The nanoparticles encapsulate the fluorescent dye Cy5, which allows researchers to track them using fluorescence methods. The C dots have a coating of polyethylene glycol, which prevents them from getting caught in the liver. The radiolabeled cyclic peptide ^{124}I-cRGDY also decorates the nanoparticle surface. The cyclic peptide targets integrin present in high concentration on certain cancer cells, and iodine-124 can be tracked using positron emission tomography (PET). Researchers led by Michelle S. Bradbury of Sloan Kettering Institute for Cancer Research and Ulrich Wiesner of Cornell University tested the C dots in five patients with terminal melanoma. They found that the particles were not toxic and were excreted intact by the kidneys and bladder, thanks to their small size.—BH



Functionalized silica nanoparticles can be used for PET imaging of certain cancers in people.

SCI. TRANSL. MED.

Nanoparticles of silver are anti-bacterial agents



Silver kills germs by ion emission

This work suggests that AgNP morphological properties known to affect antimicrobial activity are indirect effectors that primarily influence Ag^+ release. Accordingly, antibacterial activity could be controlled (and environmental impacts could be mitigated) by modulating Ag^+ release, possibly through manipulation of oxygen availability, particle size, shape, and/or type of coating.

Xiu et al., 2012, Nano Lett., 12, **4271–4275**

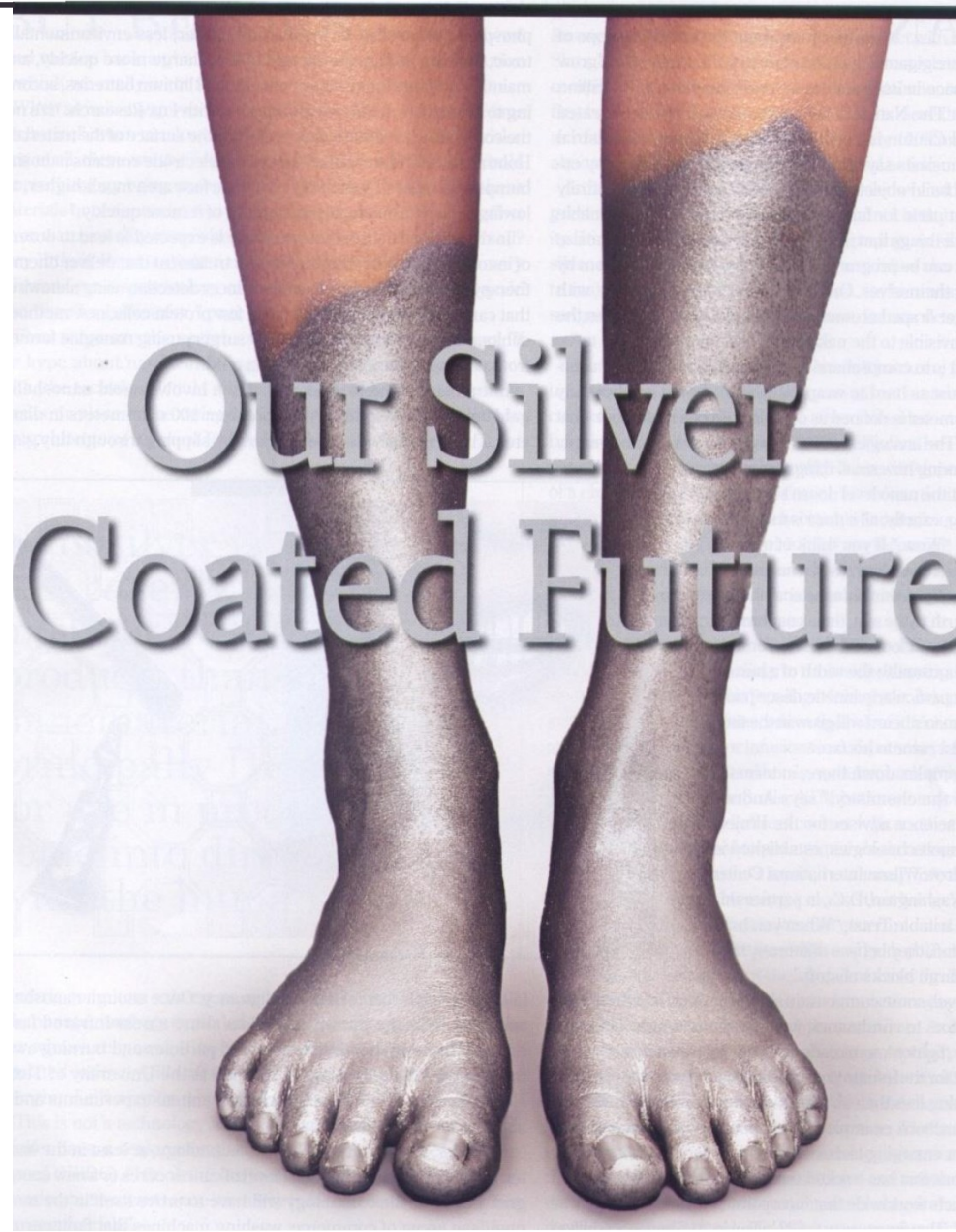
DOI: 10.1021/nl301934w

nanoparticle-blog.com/

Our Silver-Coated Future

BY ROBIN MARANTZ HENIG

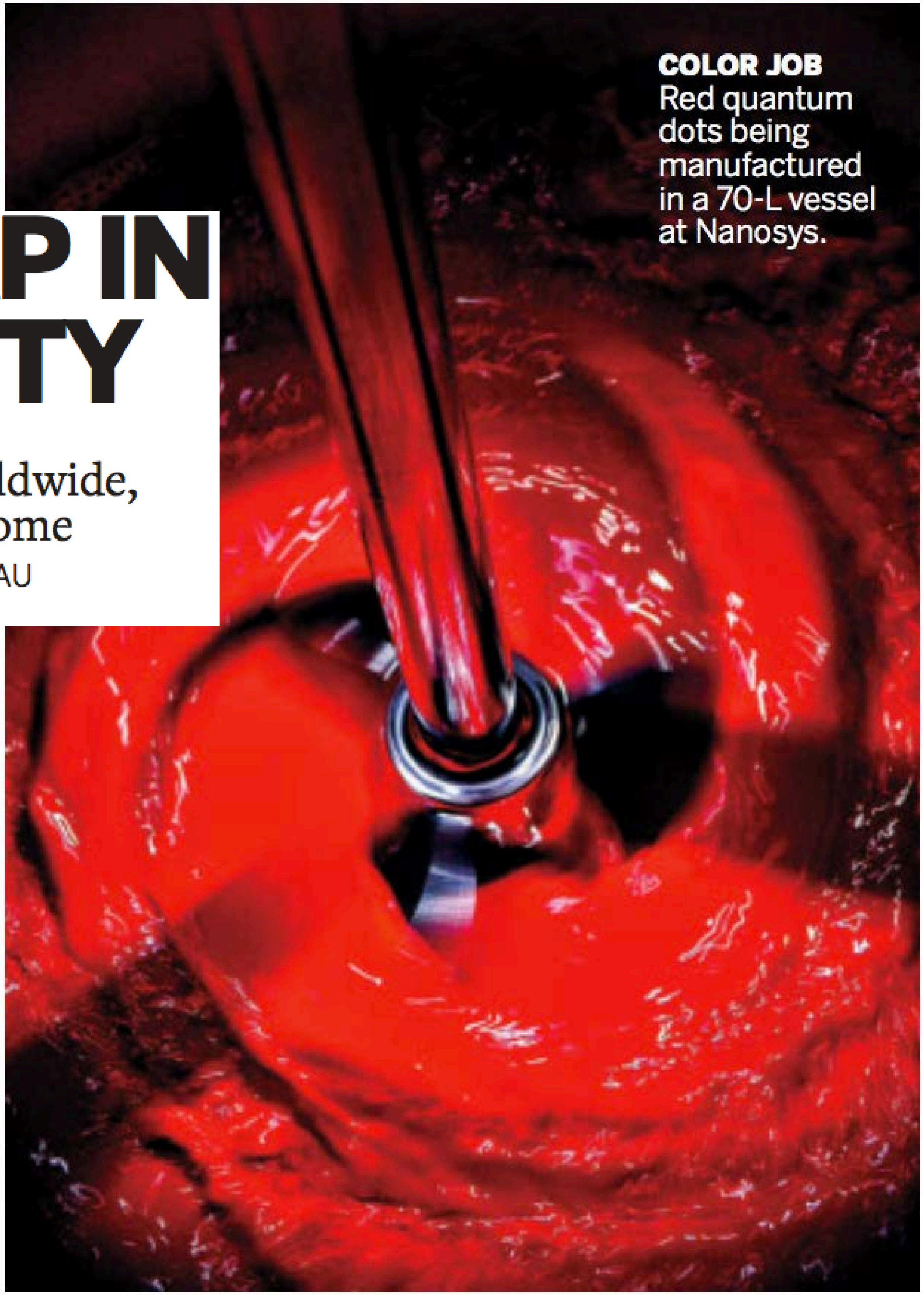
PHOTOGRAPHS BY EVA KOLENKO



A QUANTUM LEAP IN DISPLAY QUALITY

Quantum dots are improving screens worldwide, but their **CADMIUM CONTENT** worries some

MICHAEL MCCOY, C&EN NORTHEAST NEWS BUREAU



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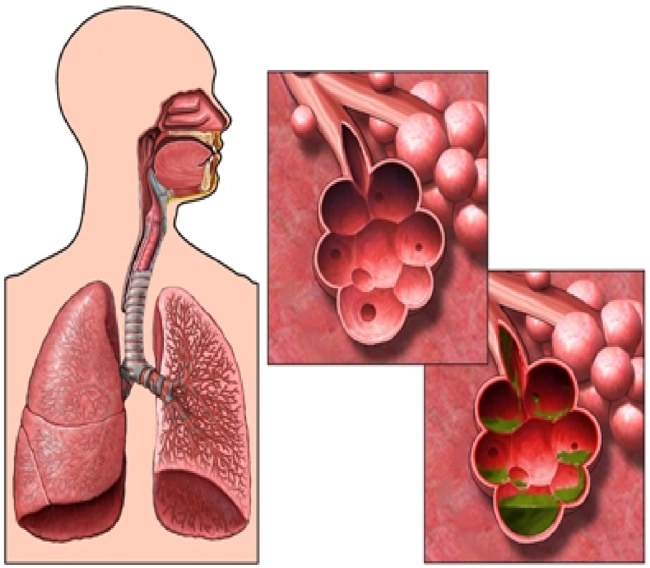
NOVEMBER 10, 2014

Why is Cd attentuation important?



trialx.com/curetalk/wp-
content/blogs_dirf7/files/2011/05/di
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ic.ucsc.edu/~flegal/migrated/etox8
0e/SpecTopics/itaiitaipic
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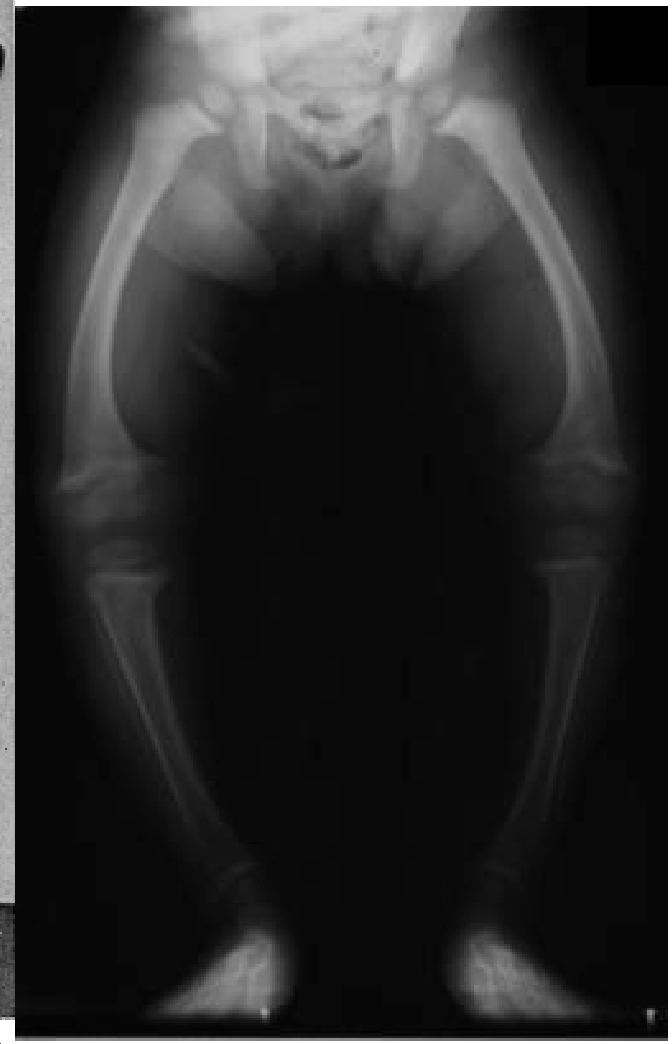
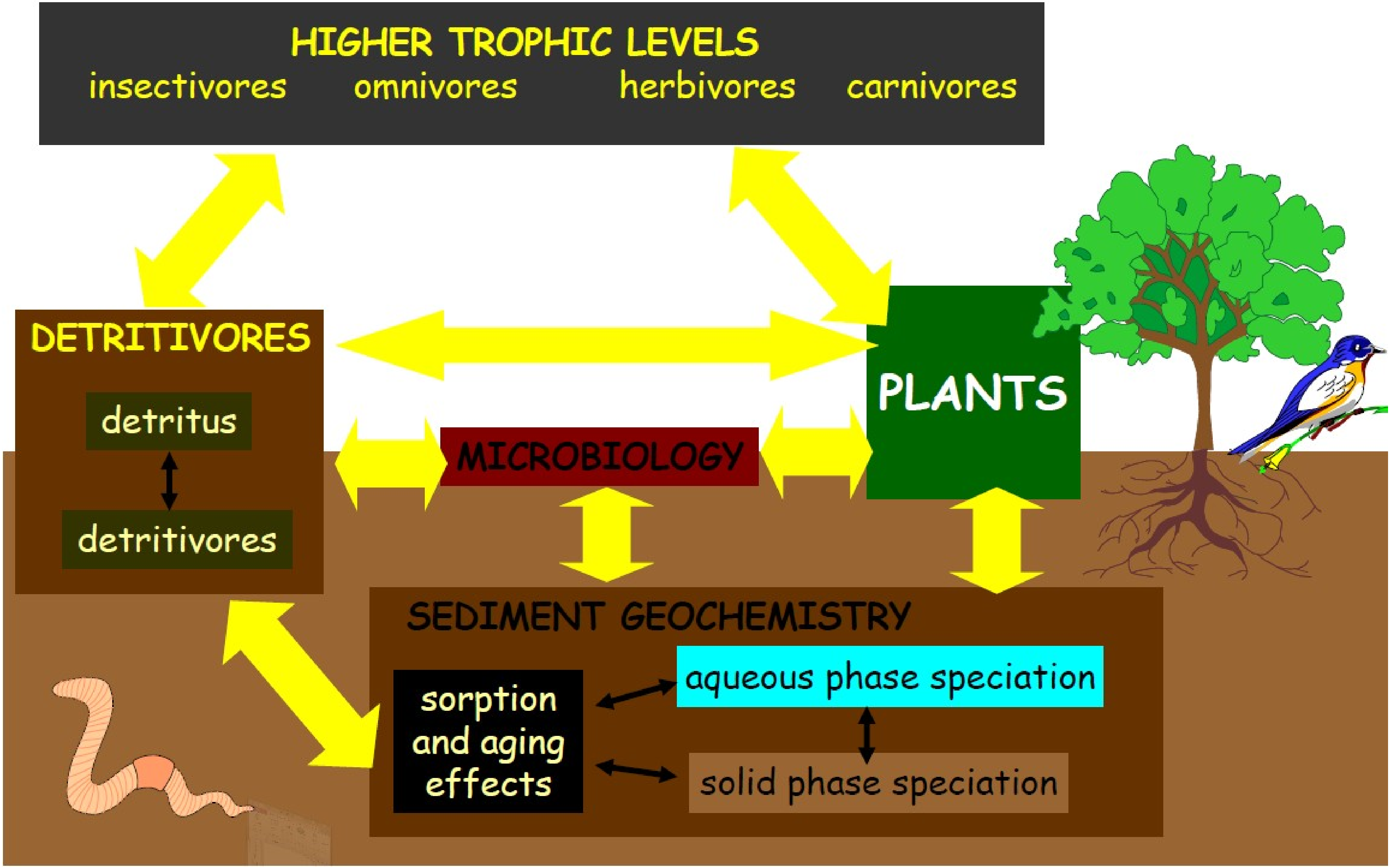


static.wikidoc.org/a/a9/XrayRicket
sLegssmall.jpg

Fate, transport, and, effects of manufactured nanoparticles in the environment



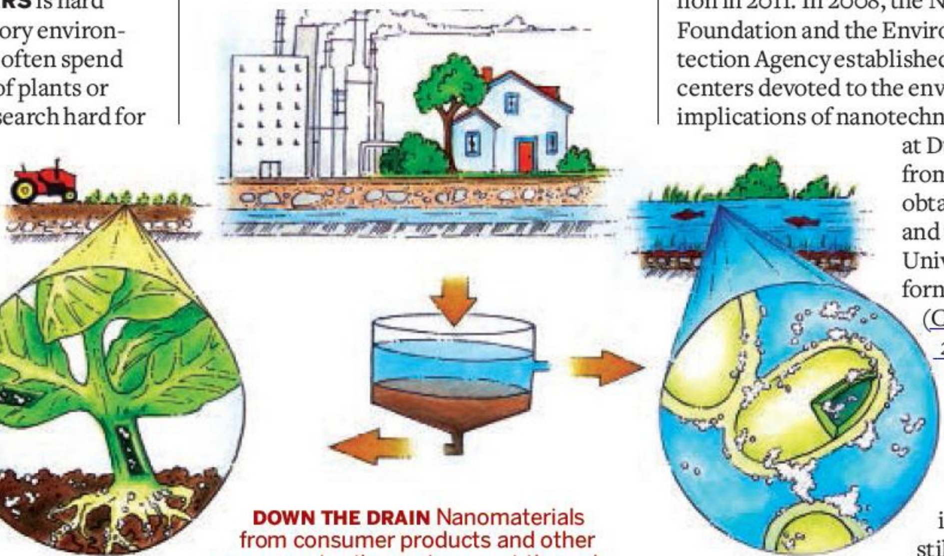
MOVING UP THE FOOD CHAIN

As they transfer to higher organisms in a food web, **NANOMATERIALS** can increase in concentration, new studies show

LAUREN K. WOLF, C&EN WASHINGTON

NURTURING CATERPILLARS is hard work, especially in a laboratory environment. In nature, the insects often spend their larval stage in a stand of plants or trees, so they don't have to search hard for sustenance. But in an artificial enclosure containing a single plant, says Jonathan D. Judy, a third-year graduate student at the University of Kentucky, "you have to keep an eye on them so that they don't get too far away from their food."

During a recent experiment, Judy mothered about 30 tobacco hornworm caterpillars (*Manduca sexta*) on his benchtop, picking them up and gently nudging them back onto their plants when they fell off or wandered away. Like a caring parent, he cleaned their enclosures daily to get rid of feces and



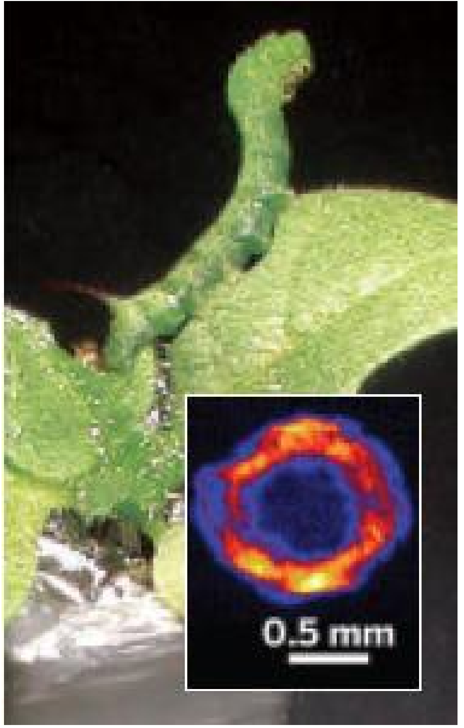
DOWN THE DRAIN Nanomaterials from consumer products and other sources enter the environment through waste streams (top) and get filtered by treatment plants (simplified in this rendering, center). Most materials end up in sludge applied to farmland (left). The rest go back into the water supply (right).

ANTA BARBARA

searchers need to get in front of potential environmental implications so that there's not a big public backlash," Bertsch says. But until now, the reverse has been true: Technology is outpacing nanomaterial-related environmental health and safety research, he says. It will be a struggle for researchers and regulators to catch up.

But they're making valiant efforts. Federal funds allotted for nanotechnology safety research have grown from $34.8 million in fiscal 2005 to a requested $117 million in 2011. In 2008, the National Science Foundation and the Environmental Protection Agency established two research centers devoted to the environmental implications of nanotechnology, one based at Duke University—from which Bertsch obtained funding—and the other at the University of California, Los Angeles (C&EN, Oct. 20, 2008, page 53).

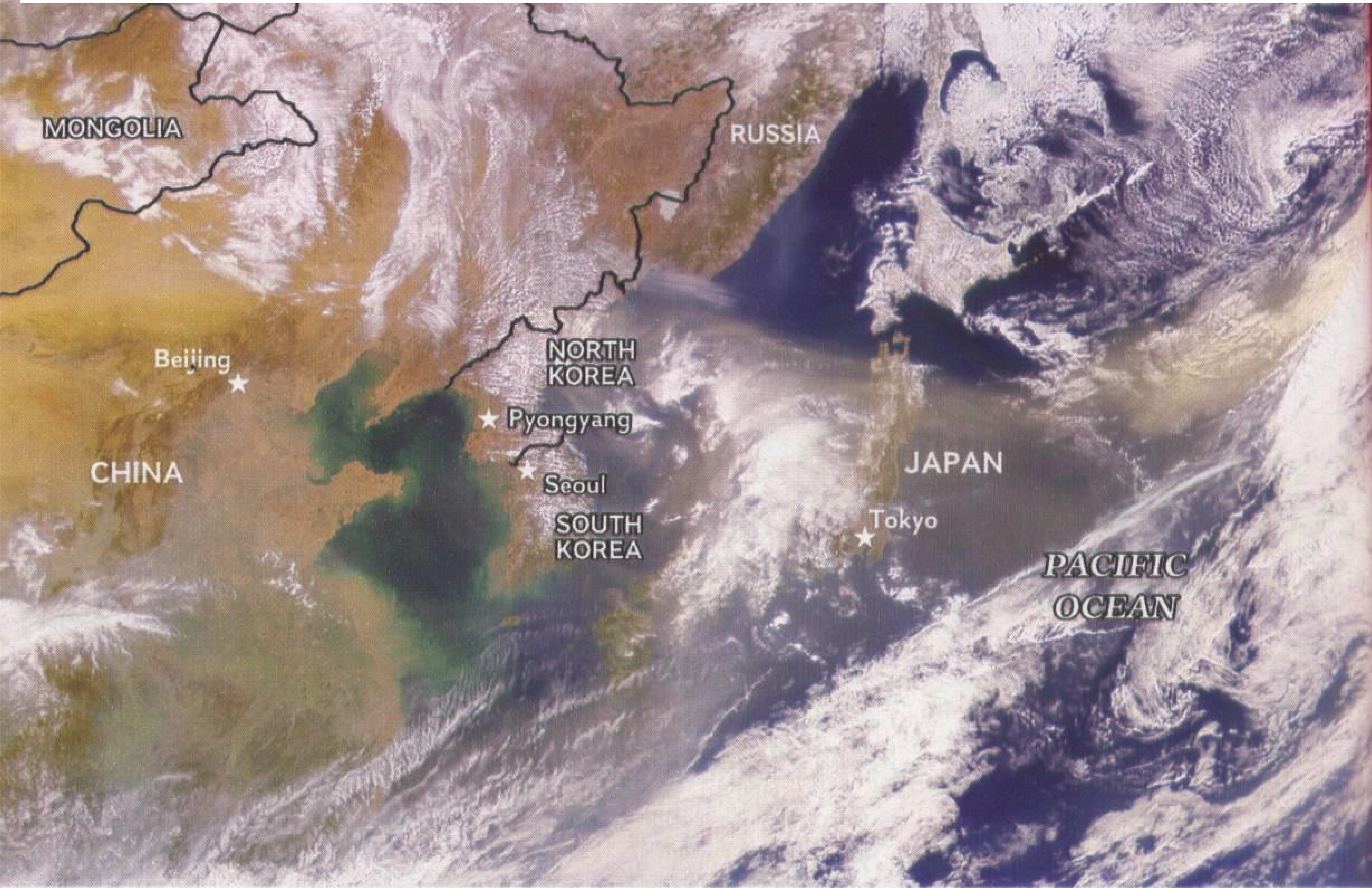
"Research into the potential ecological effects of nanomaterials is important and still new," says Patricia A. Holden, an environmental scientist at UC Santa Barbara. And the investment in these studies could affect nanotechnology's perception and regulation.



A *Manduca sexta* specimen feeds in its lab enclosure. In the inset, an X-ray fluorescence map shows a caterpillar cross section with gold nanoparticles collected in the tissue surrounding its gut.

WWW.CEN-ONLINE.ORG MARCH 14, 2011

Airborne nanoparticles of mineral dust contribute to air pollution and affect climate

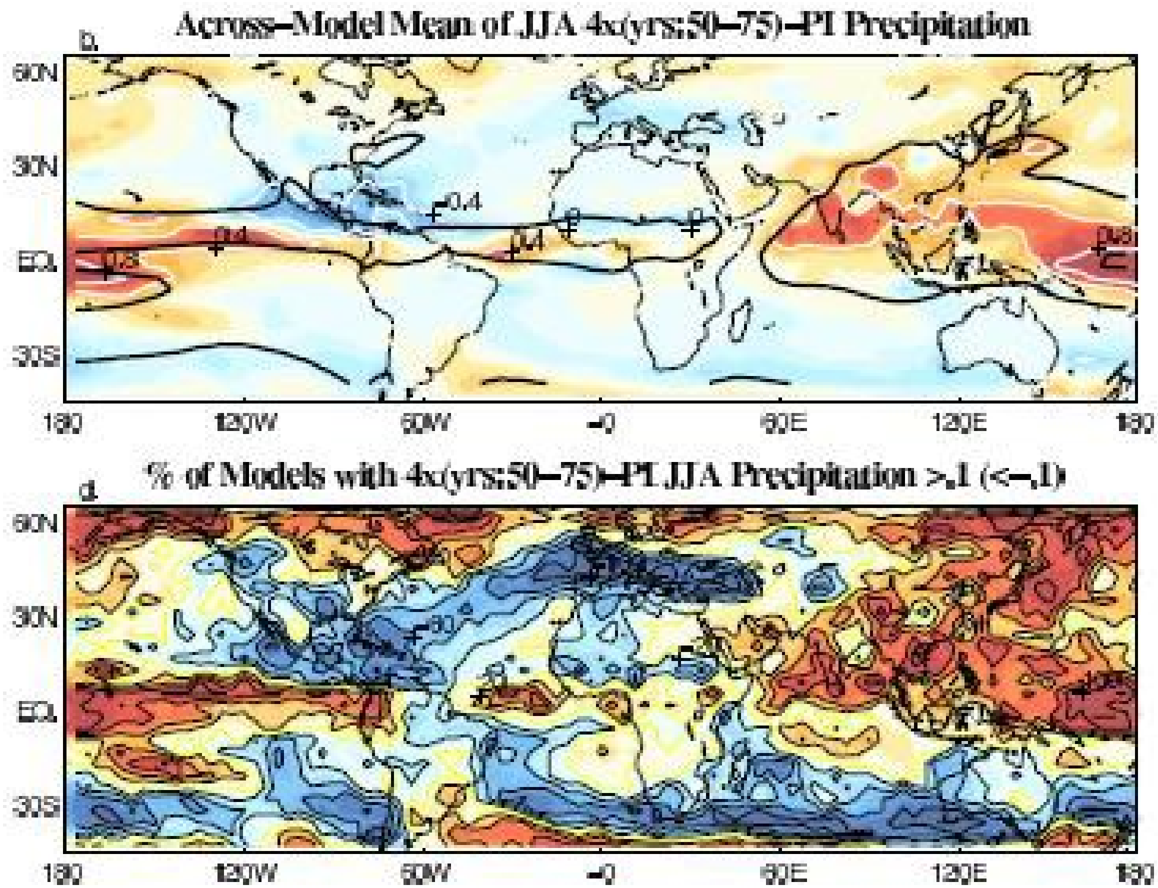


Robust Sahel drying in response to late 20th century forcings

Michela Biasutti[1] and Alessandra Giannini[2]

GEOPHYSICAL RESEARCH LETTERS, VOL. 33, L11706, doi:10.1029/2006GL026067, 2006

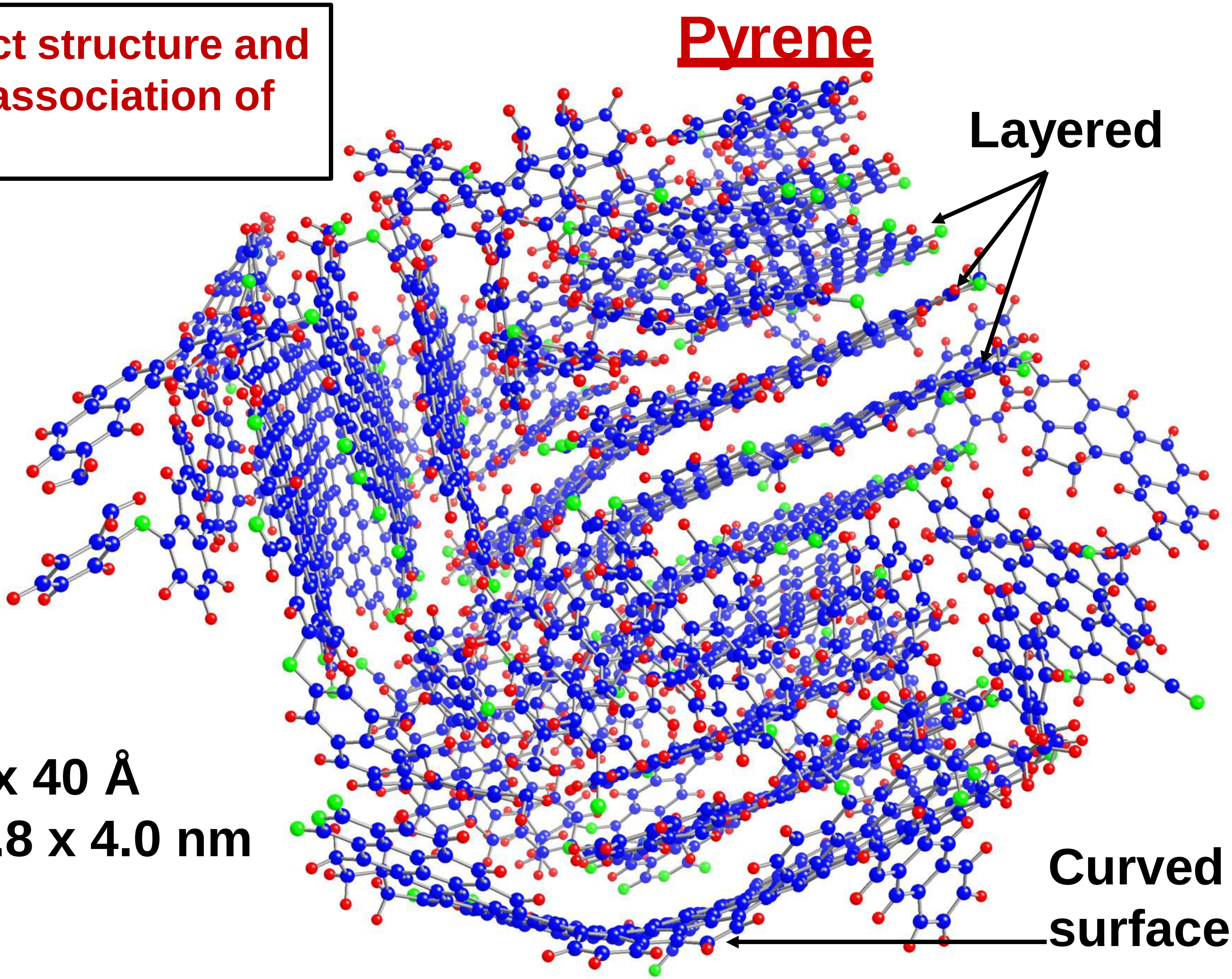
We conclude that late 20^{th} century Sahel climate was significantly dryer than pre-industrial, and at least 30% of the drying was externally forced. Comparison between 20^{th} century runs and runs forced by GHG alone reveals the key role of reflective aerosols: they force a gradient in SST that excites robust drying in the northern edge of the Atlantic Inter-Tropical Convergence Zone (ITCZ) and in the Sahel.



Soot or black carbon produced in fires

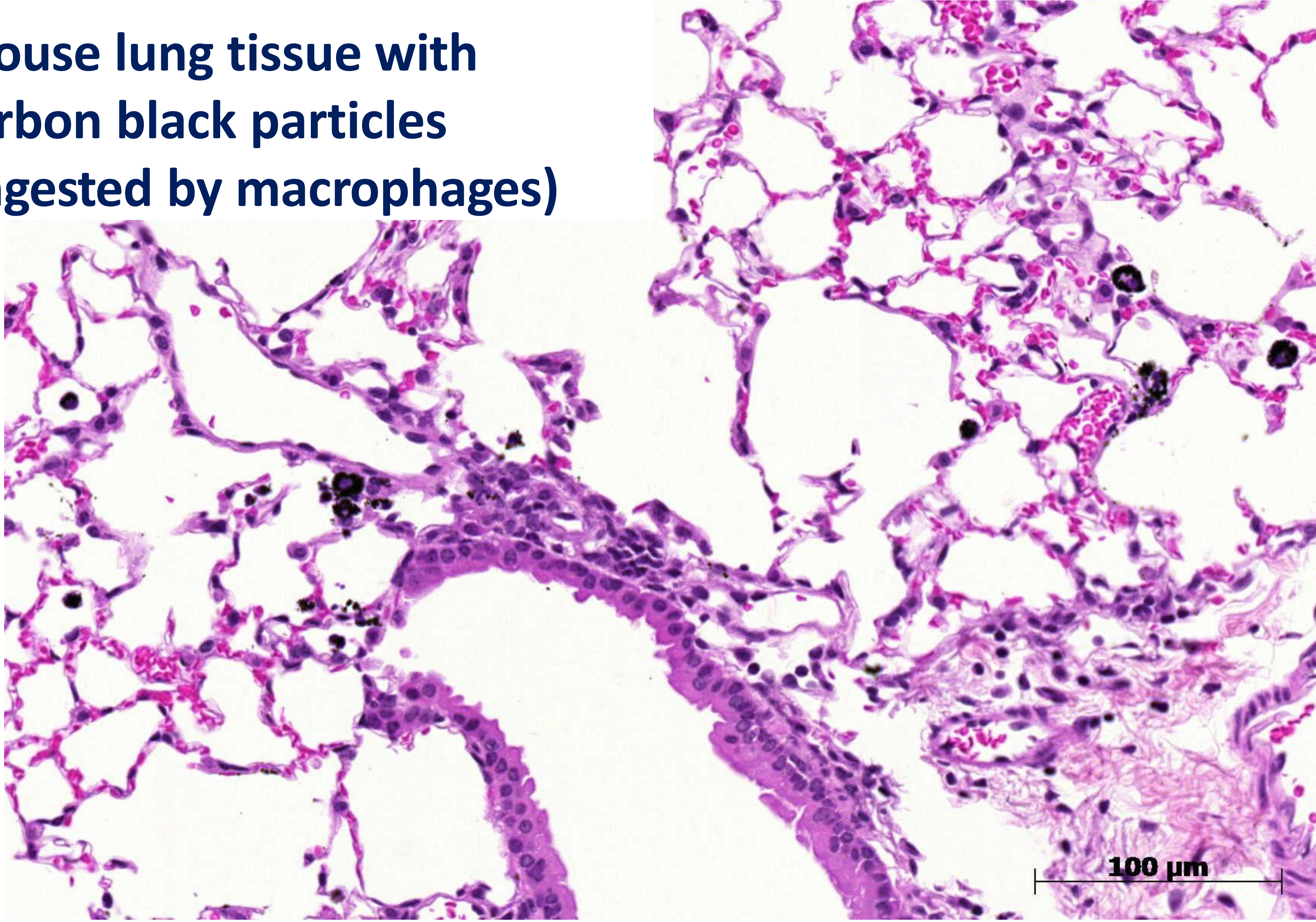
Soot serves as delivery agent for carcinogens to lungs

Compact structure and strong association of pyrene



48 x 40 Å
= 4.8 x 4.0 nm

Mouse lung tissue with carbon black particles (ingested by macrophages)

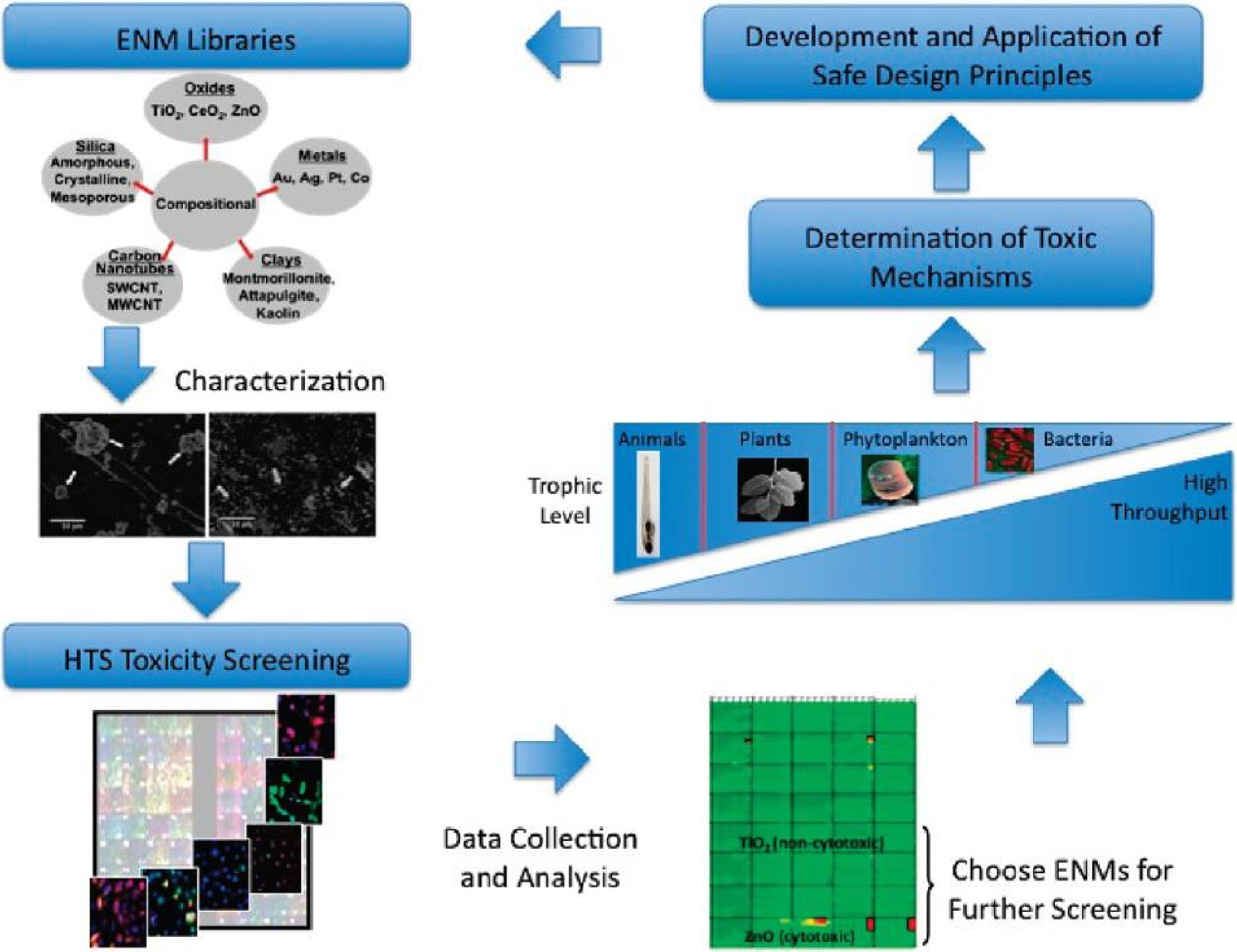


www.item.fraunhofer.de/en/press-media/latest-news/PM_Carbon_Black.html

Miner's lung with silicosis and tuberculosis

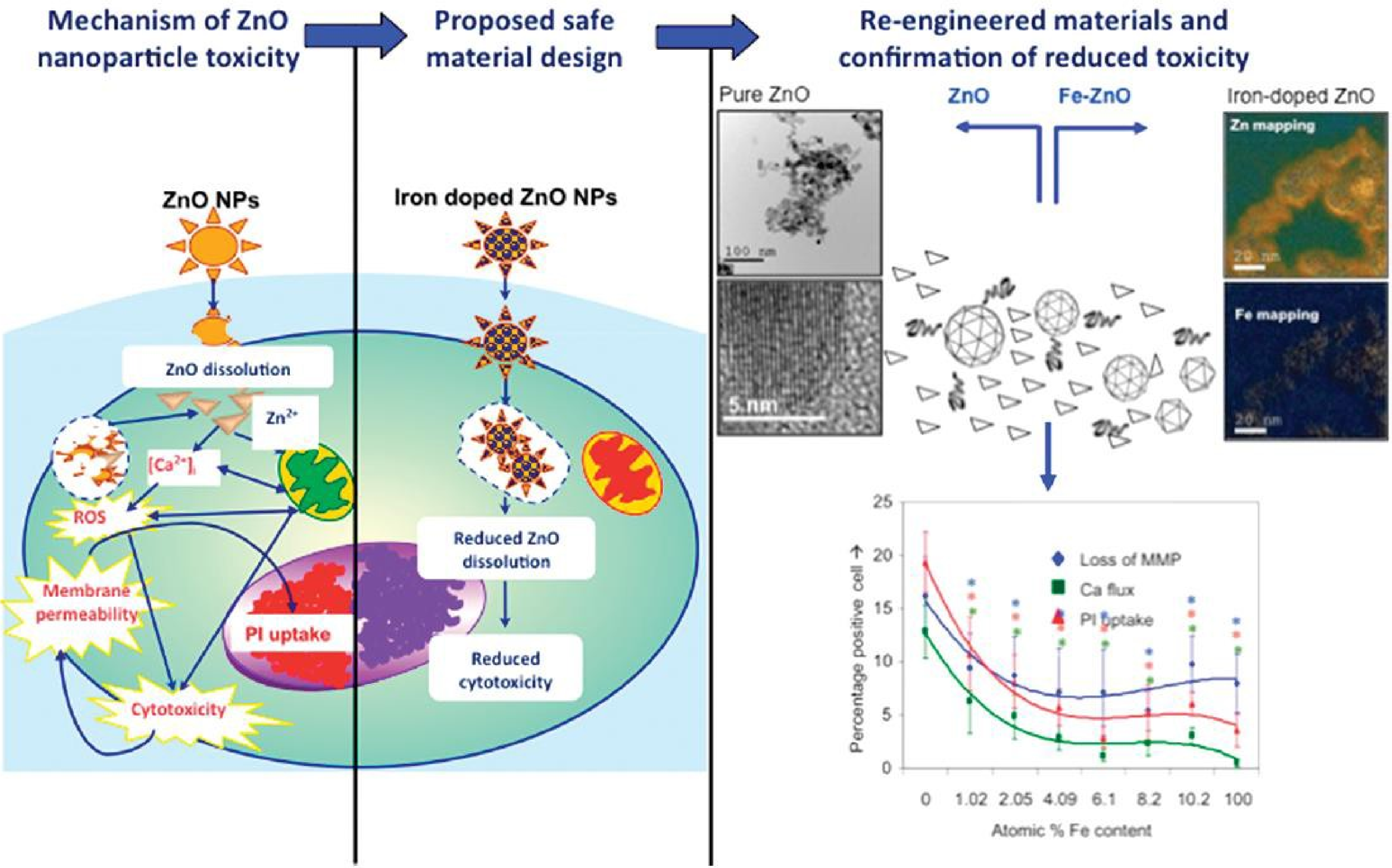
en.wikipedia.org/wiki/Silicosis

Strategy for determining toxicity of nanomaterials



Thomas et al., 2011, ACS Nano, 5, 13–20

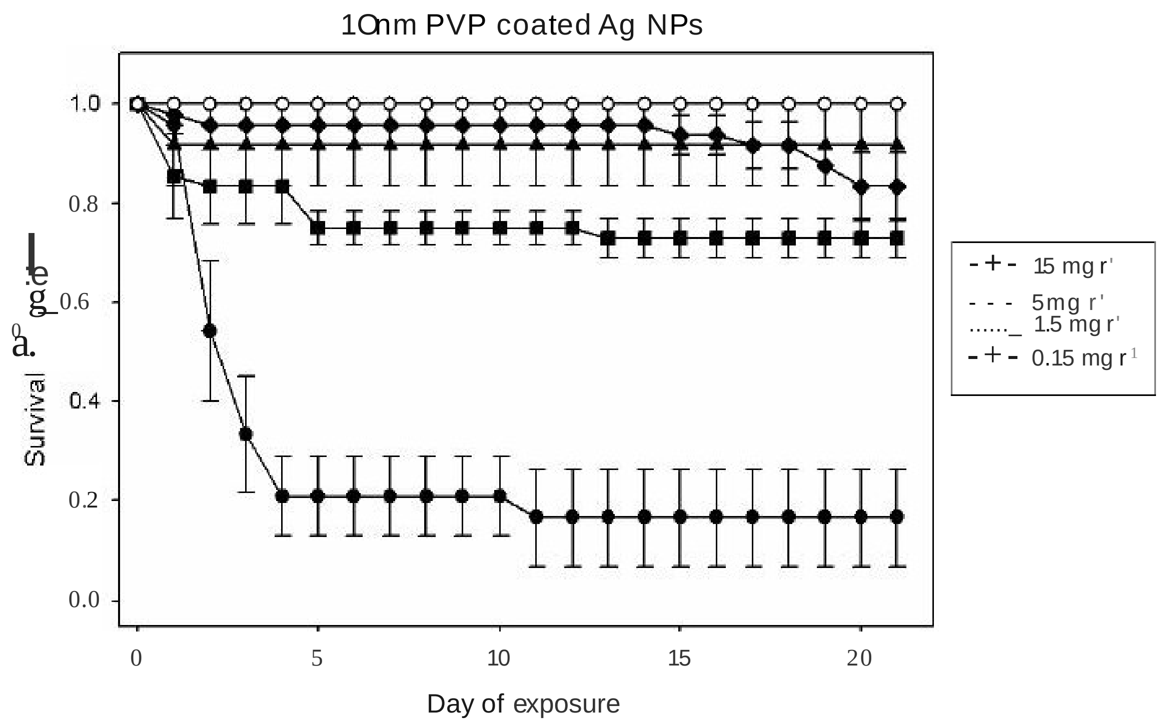
Safer design of environmental nano-materials



Thomas et al., 2011, ACS Nano, 5, 13–20

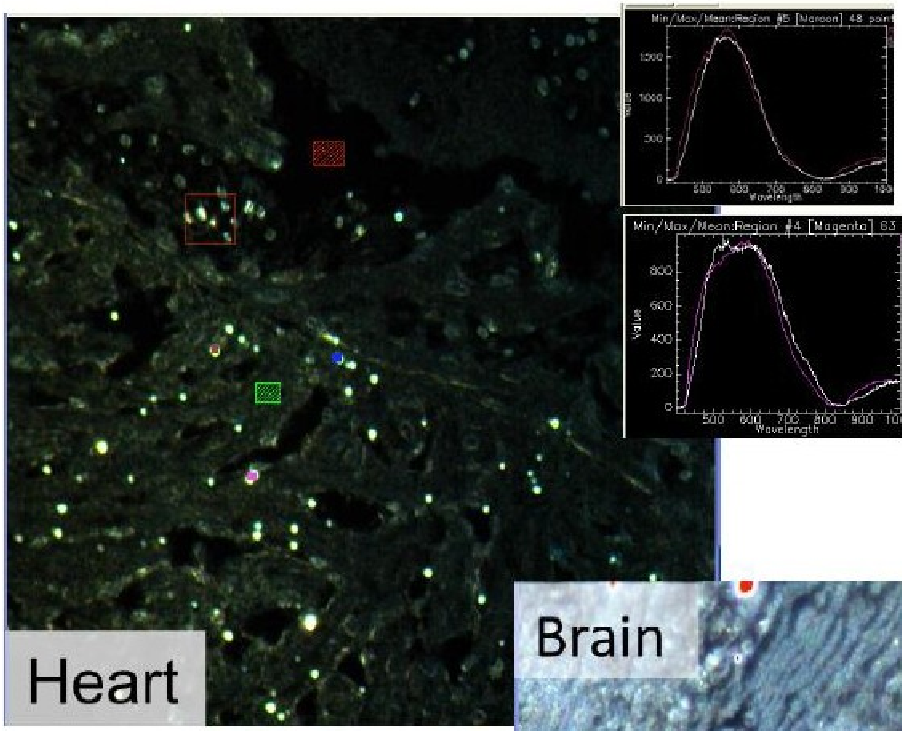
Toxicity of Ag NPs in medaka

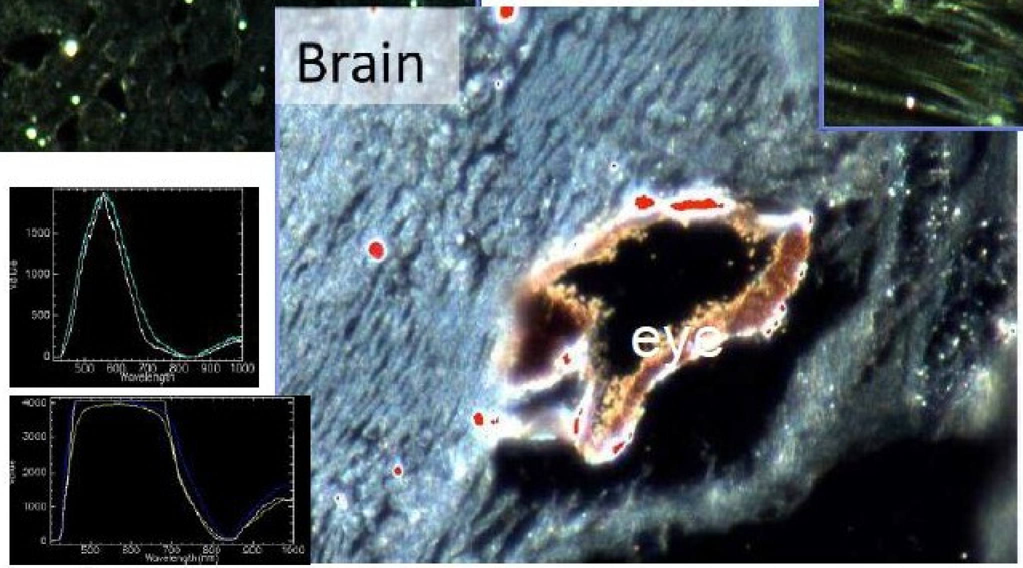
- Silver NP toxicity is coating-dependant
- Causes mortality to medaka larvae at mg l^{-1} levels
- Causes spinal malformation

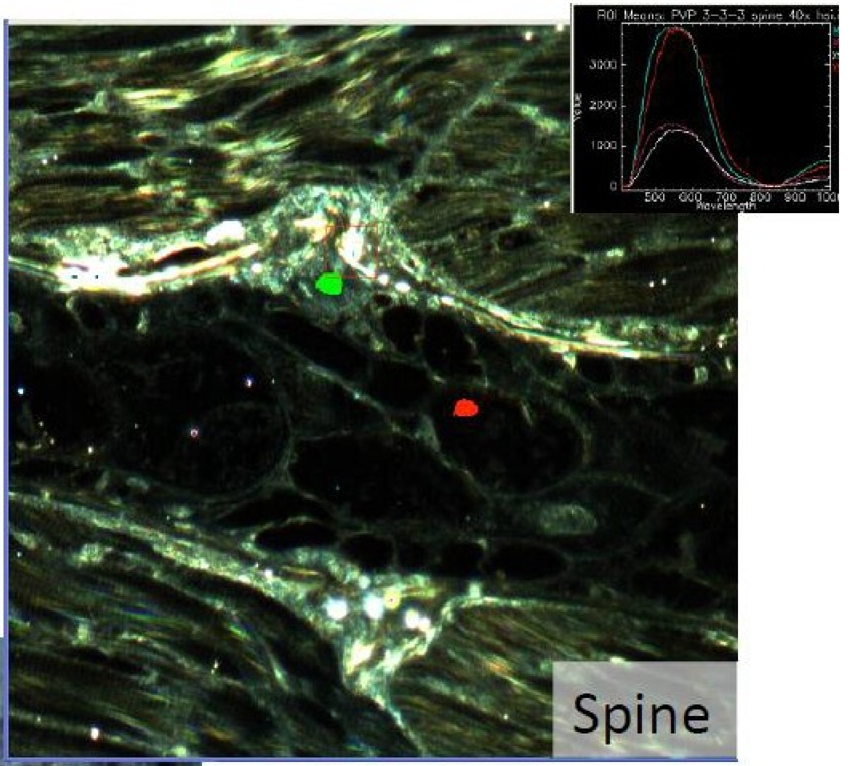


CEINT

Ag NP tissue distribution







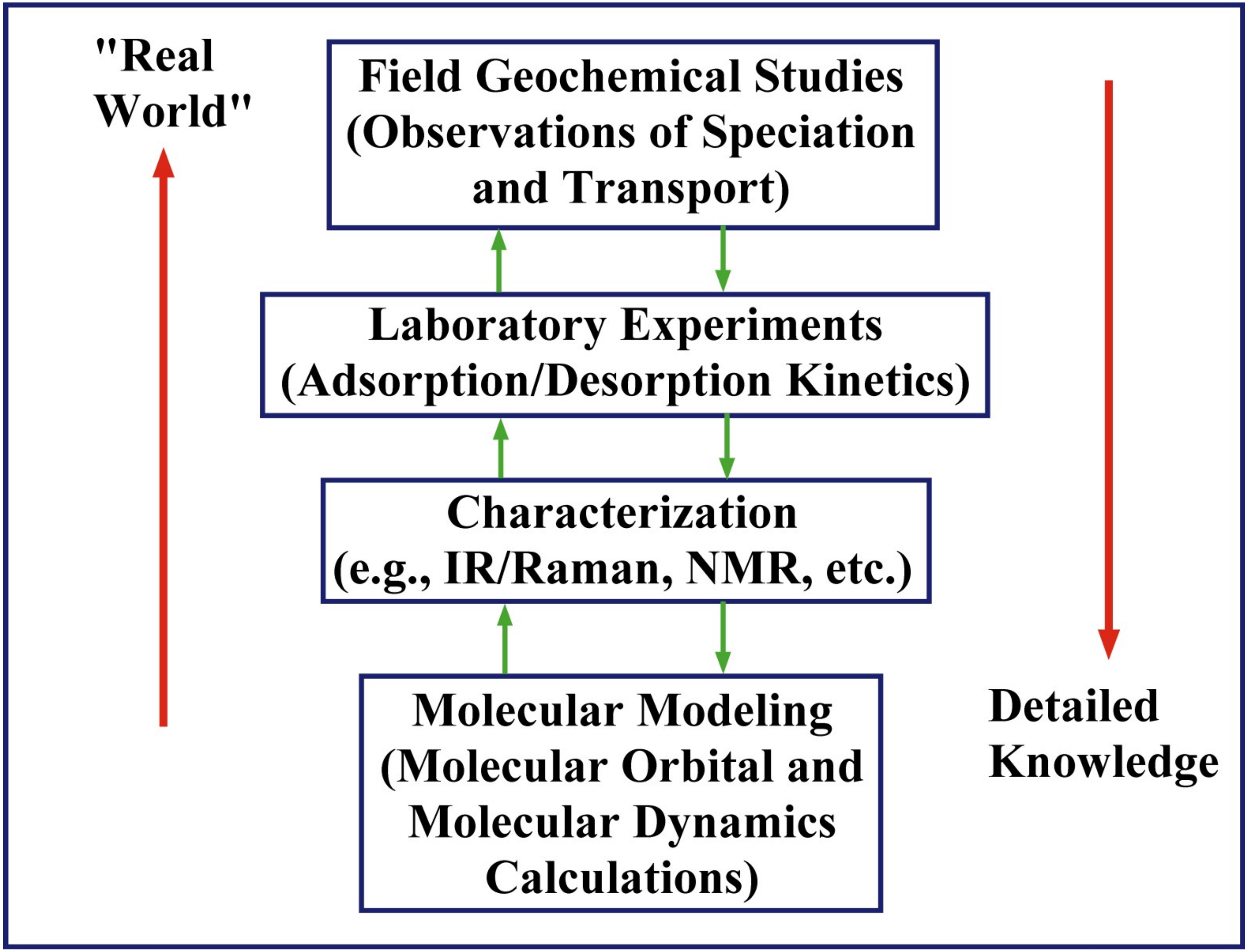
CytoViva

Dark field microscopy

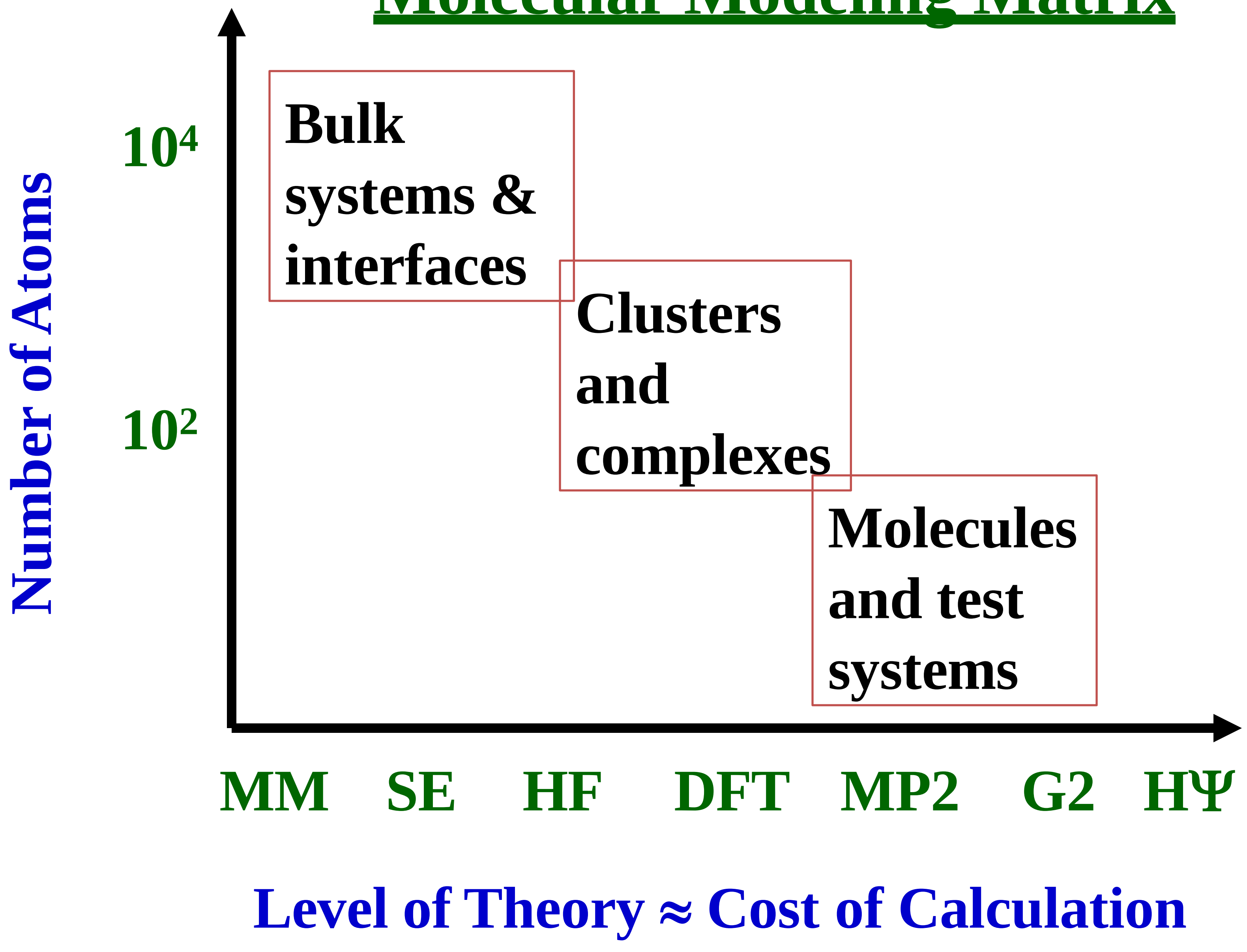
Hyperspectral analysis

CEINT

Where does molecular modeling fit in?

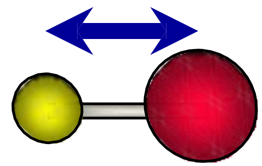


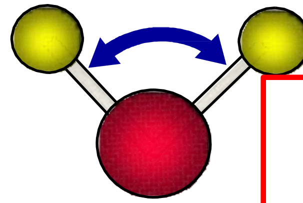
Molecular Modeling Matrix



Molecular Modeling Methods - Classical

$$E = k_2 (r - r_o)^2$$

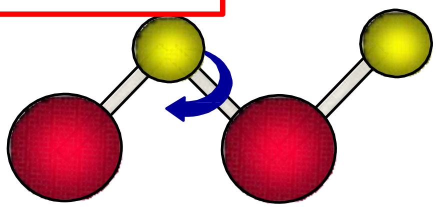


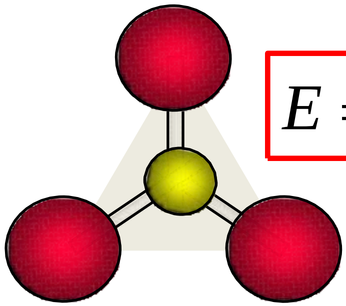


2

Bond Stretch **Angle Bend**

$$E = k(1 + \cos(n\phi - \phi_o))$$

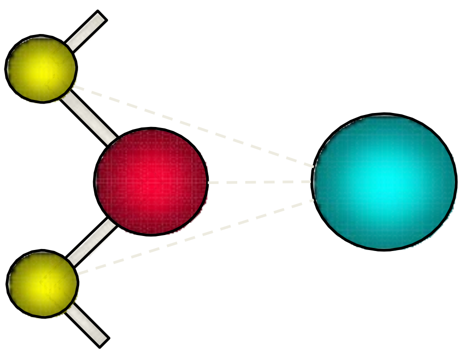




$$E = k(1 + \cos(n\chi - \chi_o))$$

Torsion **Out-of-Plane Stretch**

Non-bonded



$$E_{nonbond} = \sum_{i>j}^{N} \frac{q_i q_j}{r_{ij}} + \sum_{i>j}^{N} \left(\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} \right)$$

Slide courtesy Randy Cygan – Sandia National Laboratories

Molecular Modeling Methods – Quantum

$$H\psi = E\psi \longrightarrow$$

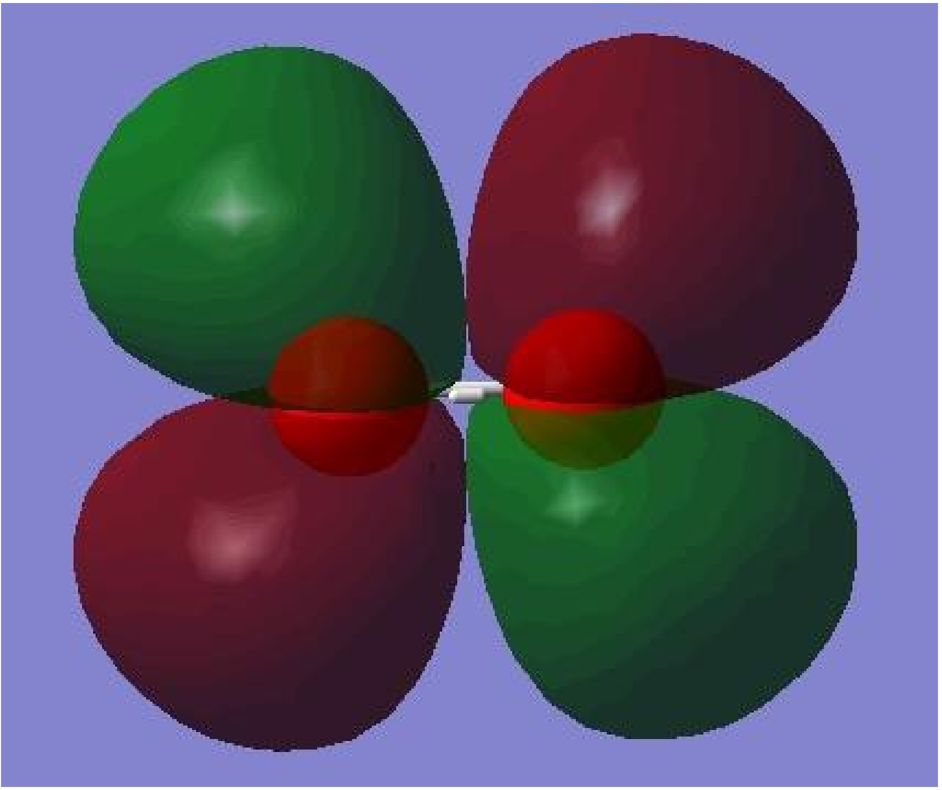
Slater-type orbital

$$\phi = A\exp(-\zeta r)$$

$$\downarrow$$

Gaussian basis function

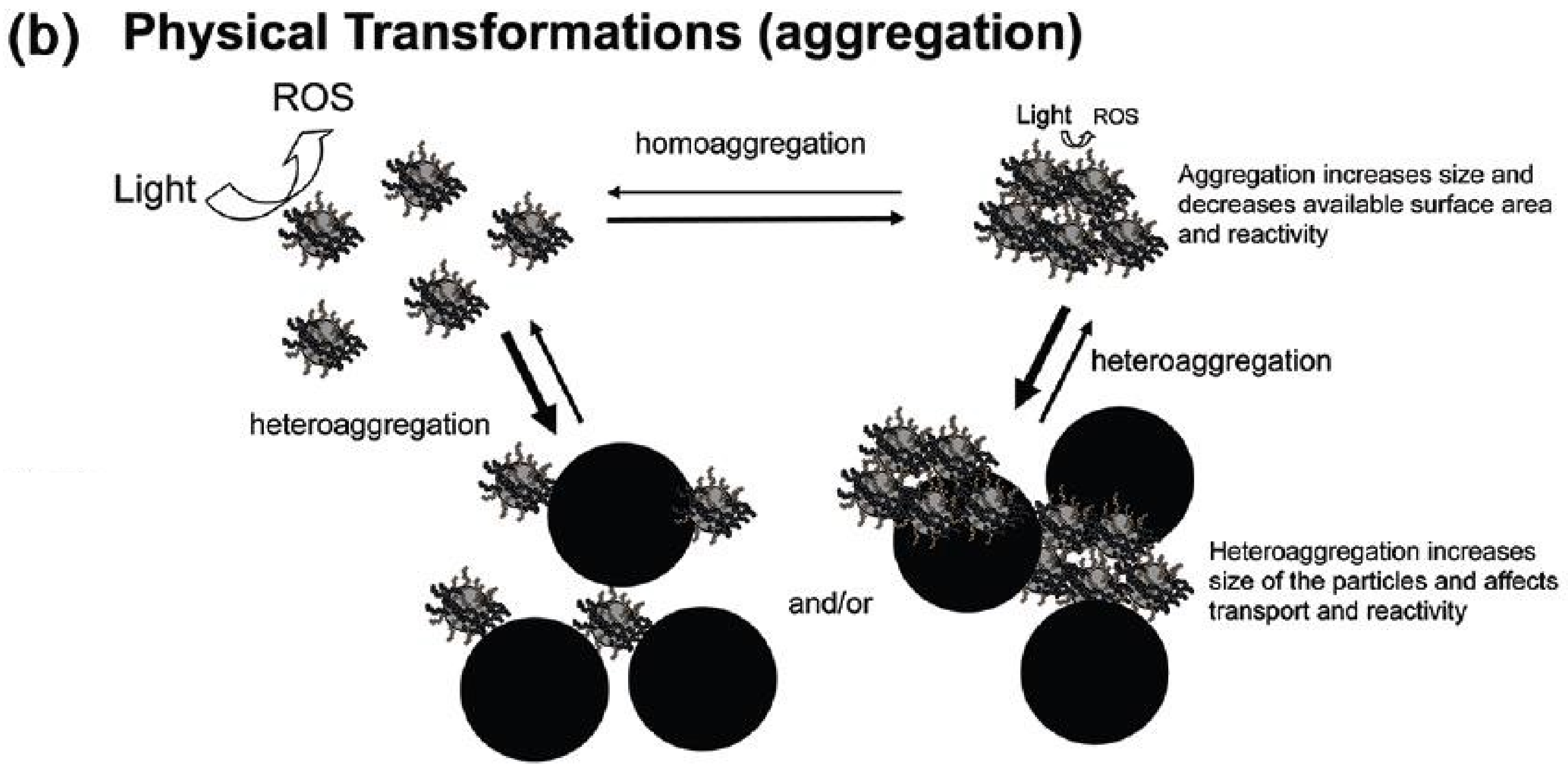
$$\phi = \sum A\exp(-\zeta r^2)$$



Highest Occupied Molecular Orbital for O_2

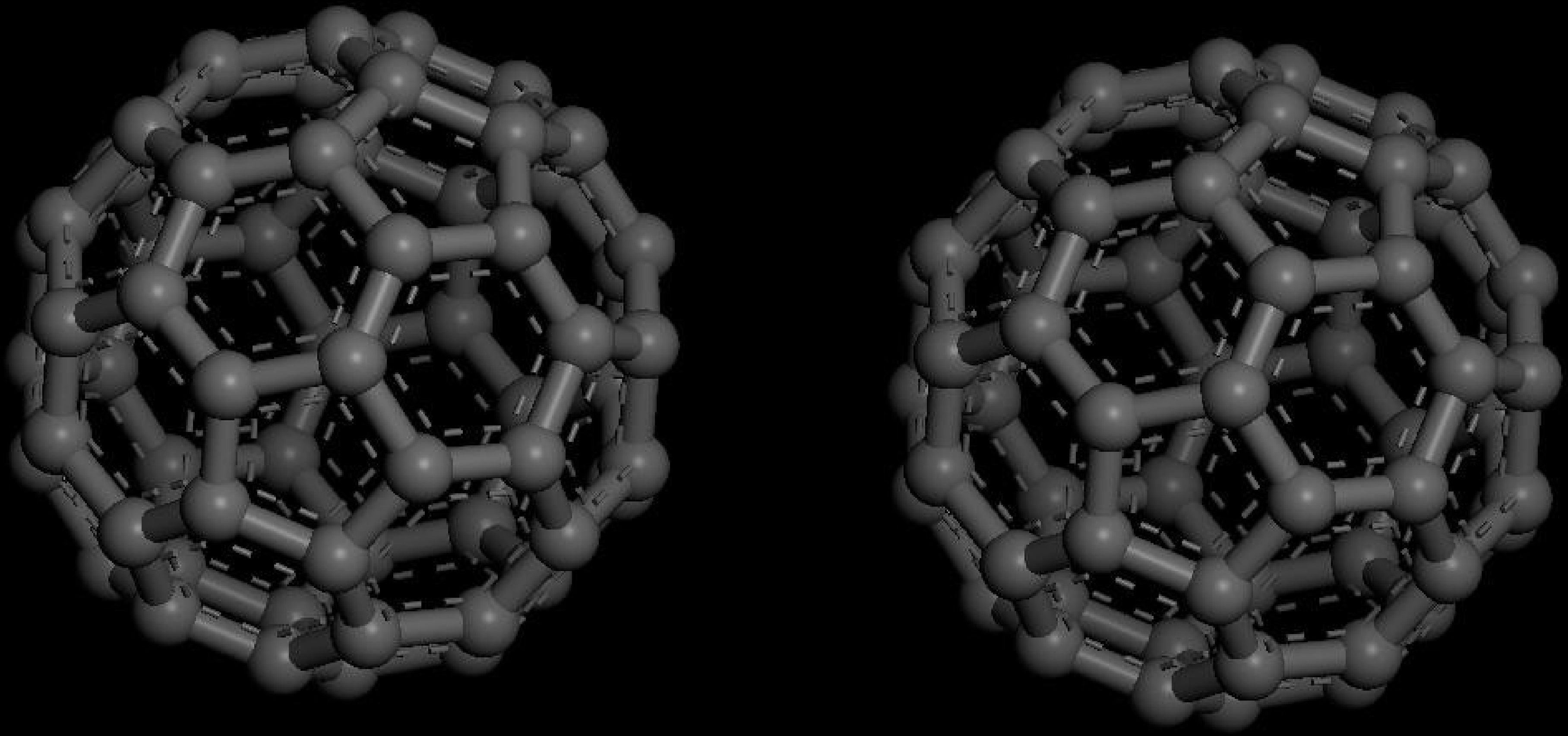
More Gaussians → Higher accuracy & computational expense

Aggregation of nanoparticles affects surface area & reactivity

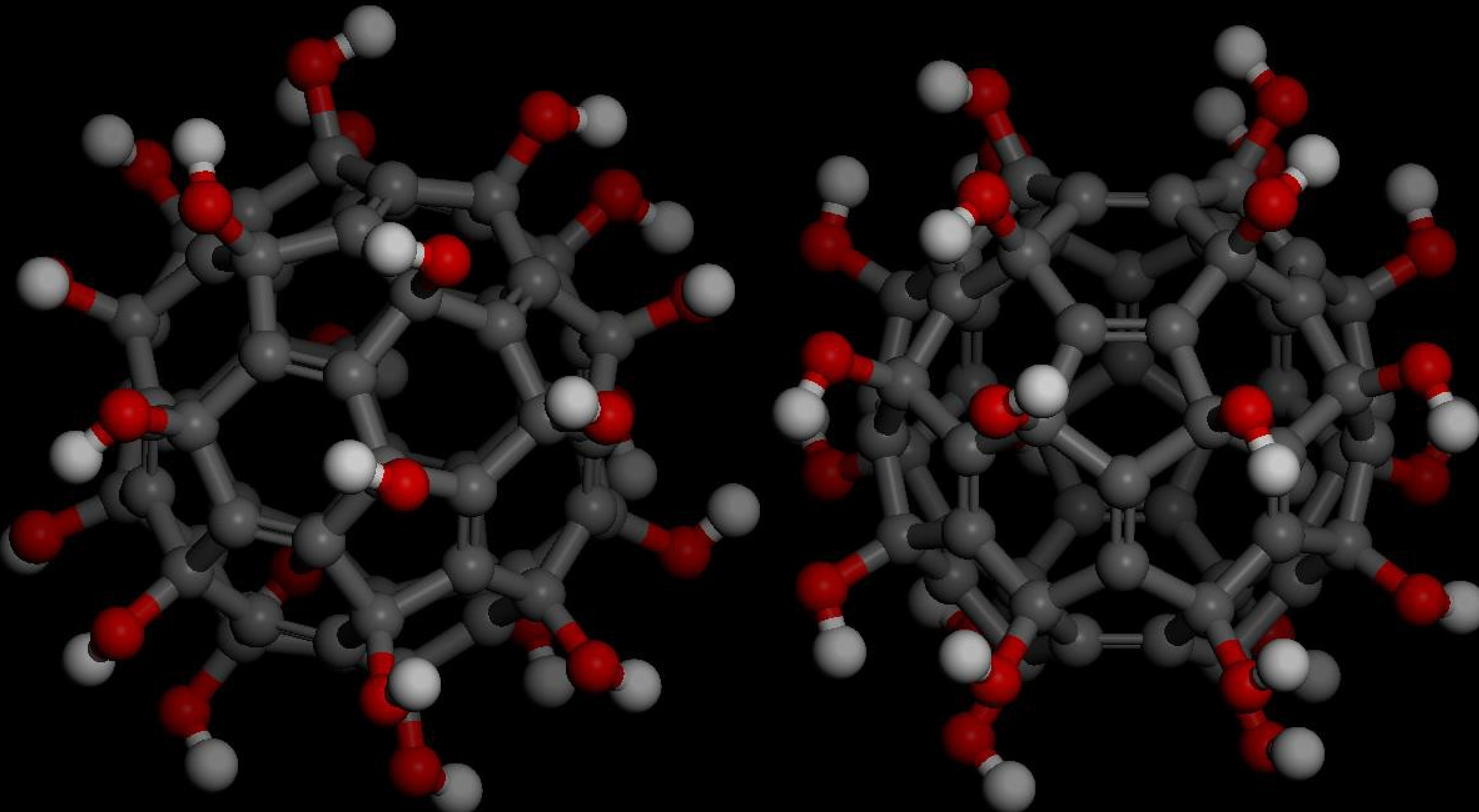


Lowry et al., 2012, Environ. Sci. Technol. 46, 6893–6899

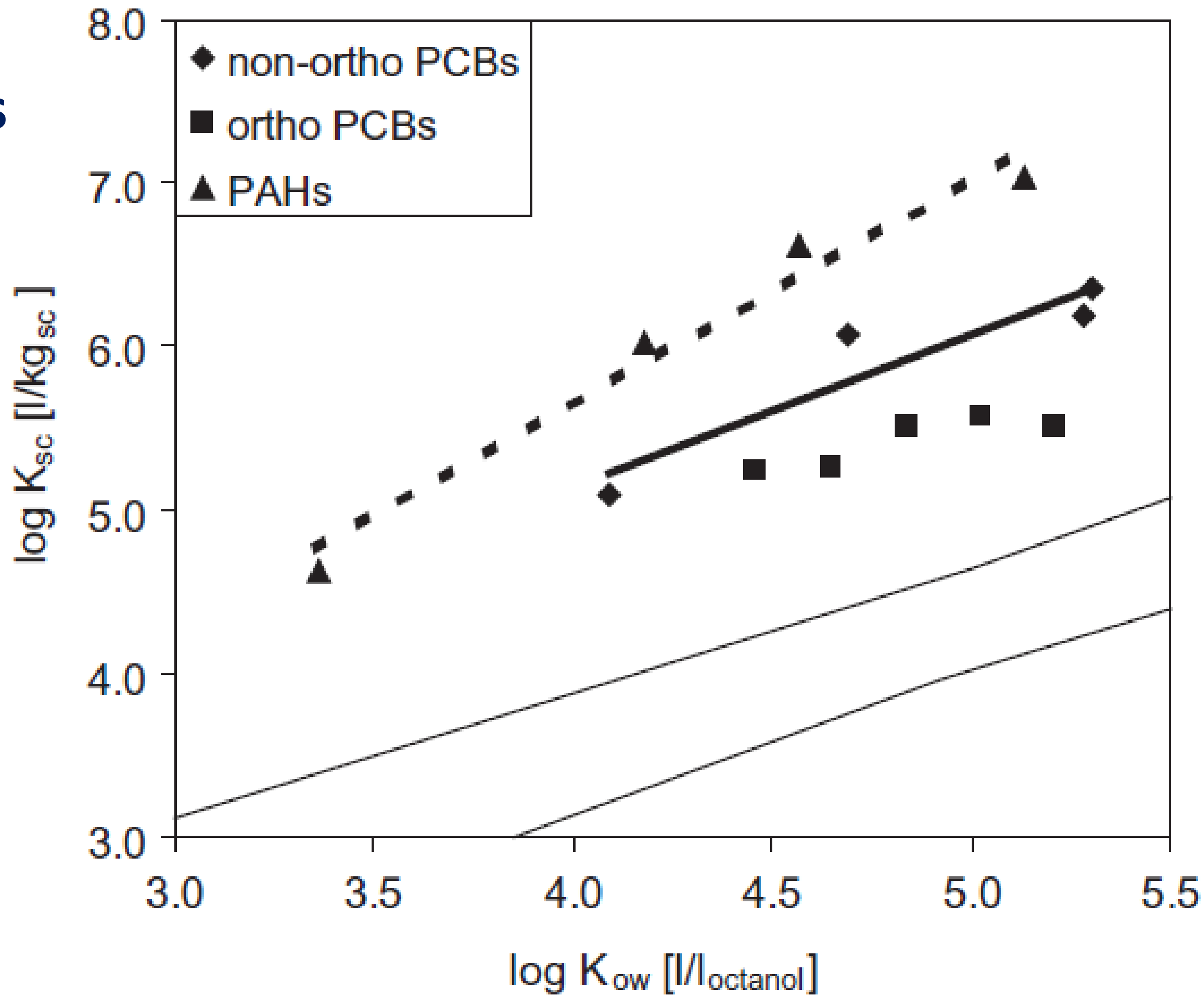
Association of fullerenes (Bucky balls)



Association of fullerenols (partially oxidized Bucky balls)



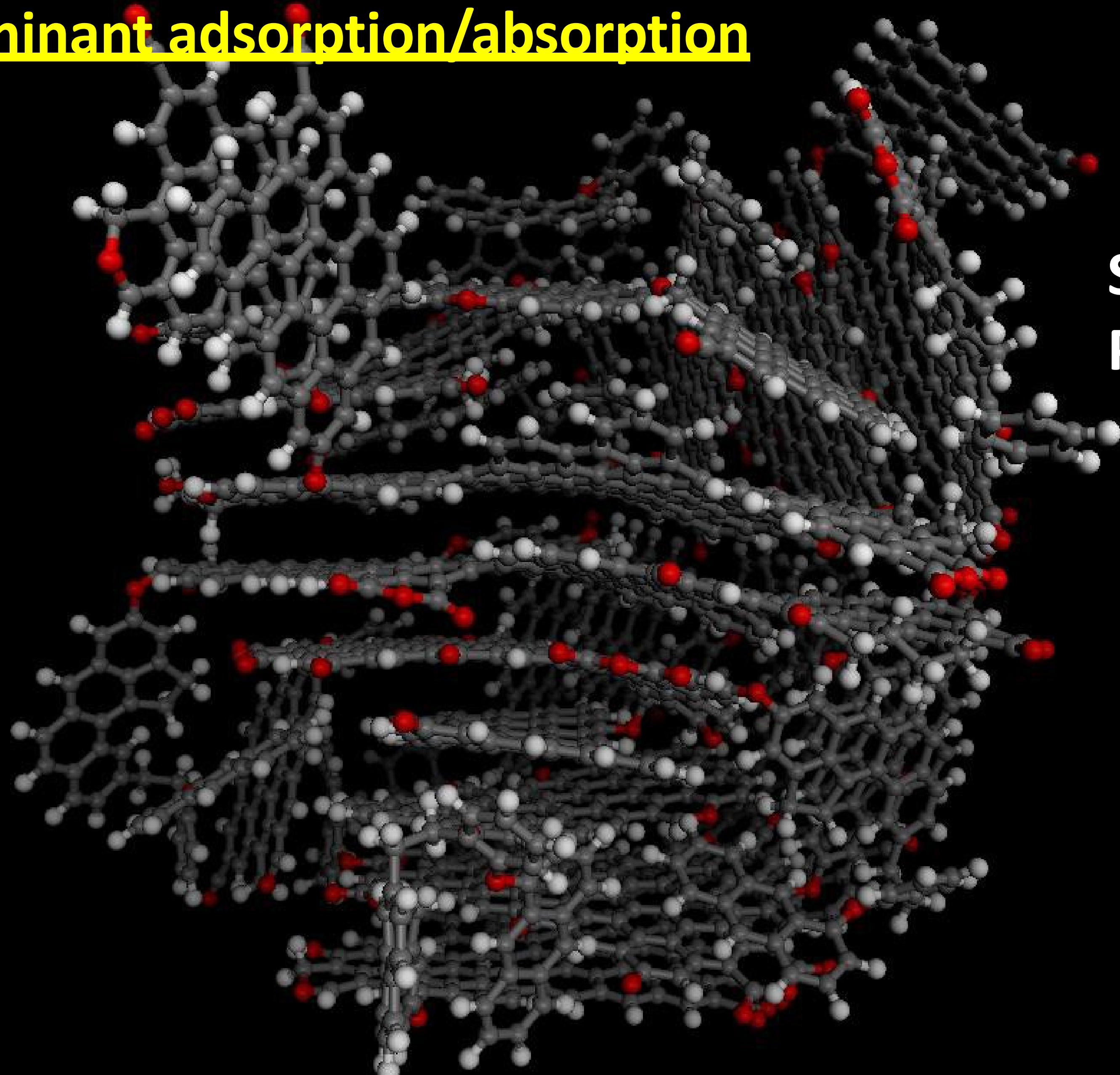
Hydrophobic contaminants (*e.g.*, PCBs) tend to accumulate <u>in soot</u>



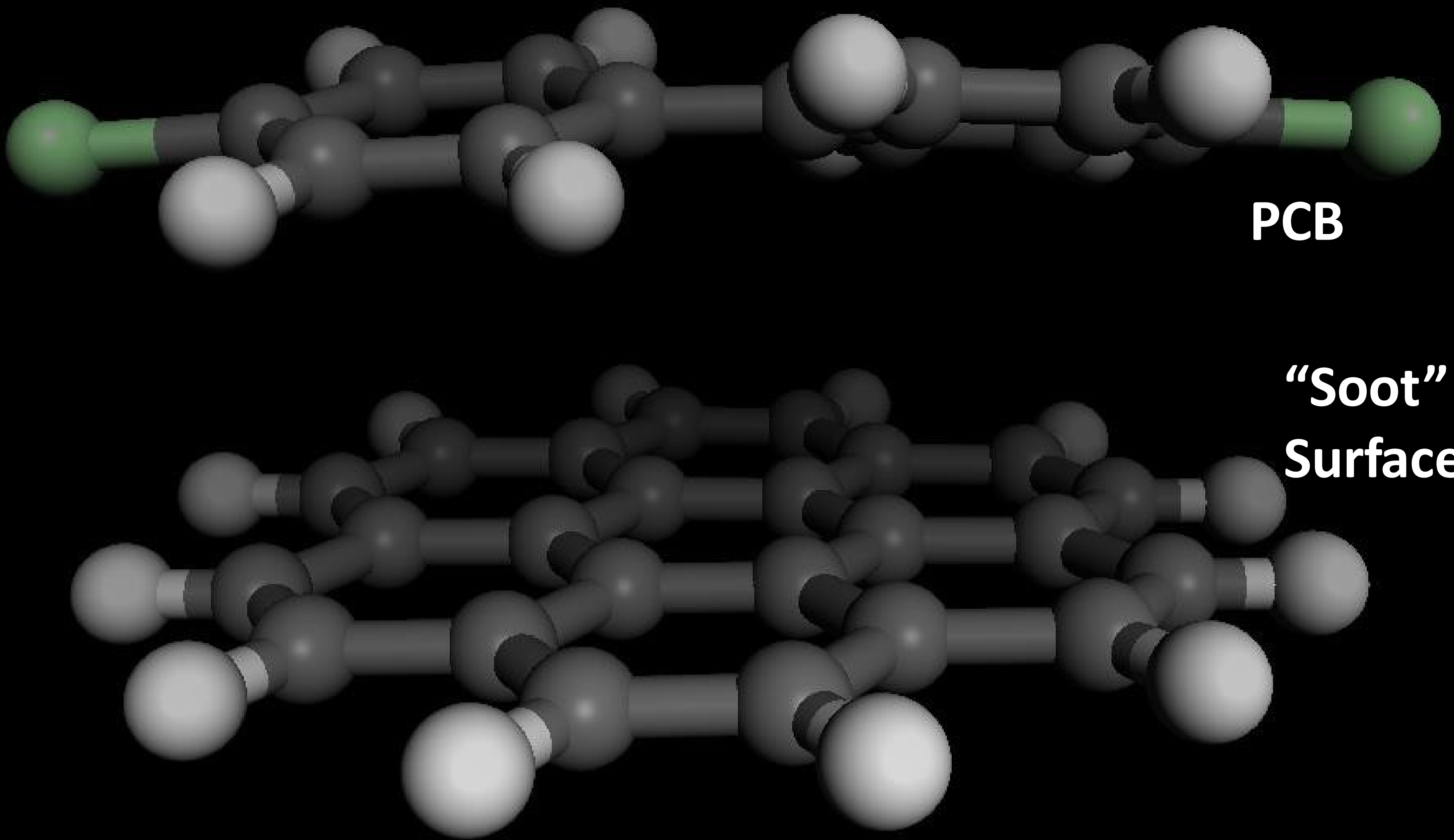
Experimentally determined logK_{sc} values of PCBs

Bucheli and Gustafsson, 2003, Chemosphere 53 (2003) 515–522

Soot surfaces and micropores are ideal sites for contaminant adsorption/absorption



Modeling of interaction energies can predict adsorption and illustrate mechanism



PCB Adsorption onto soot

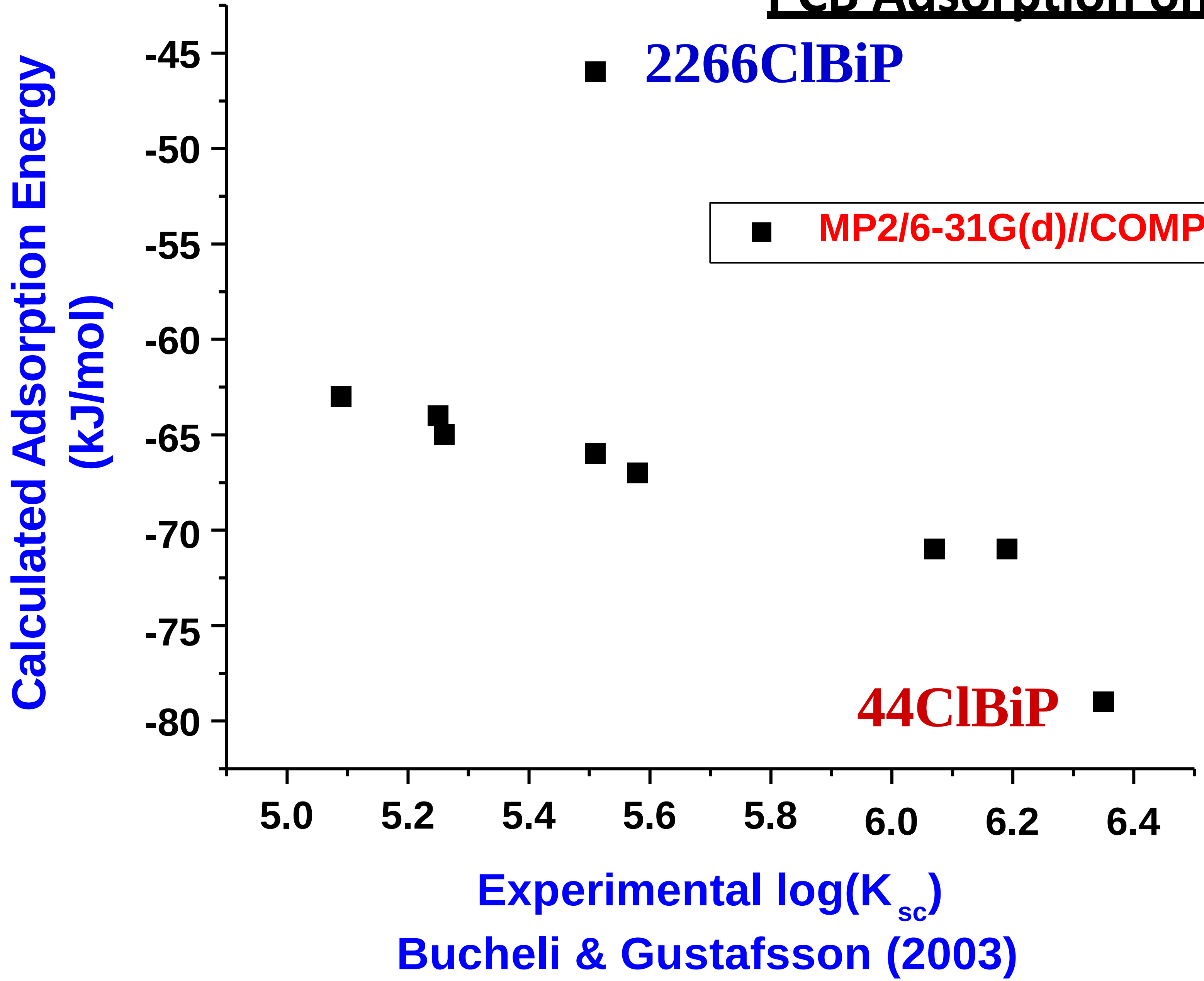
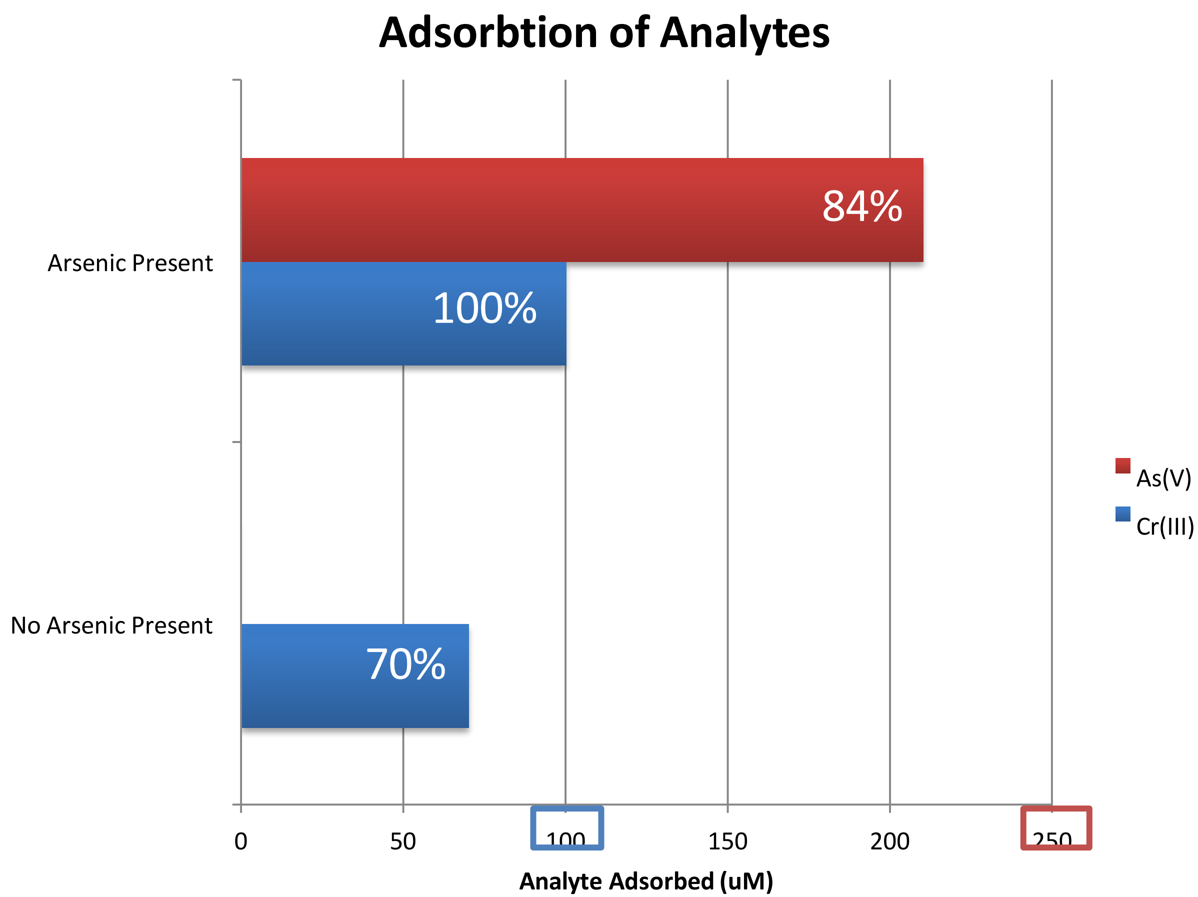


Photo-induced Redox Transformation of Chromate and Arsenite on Iron Oxides

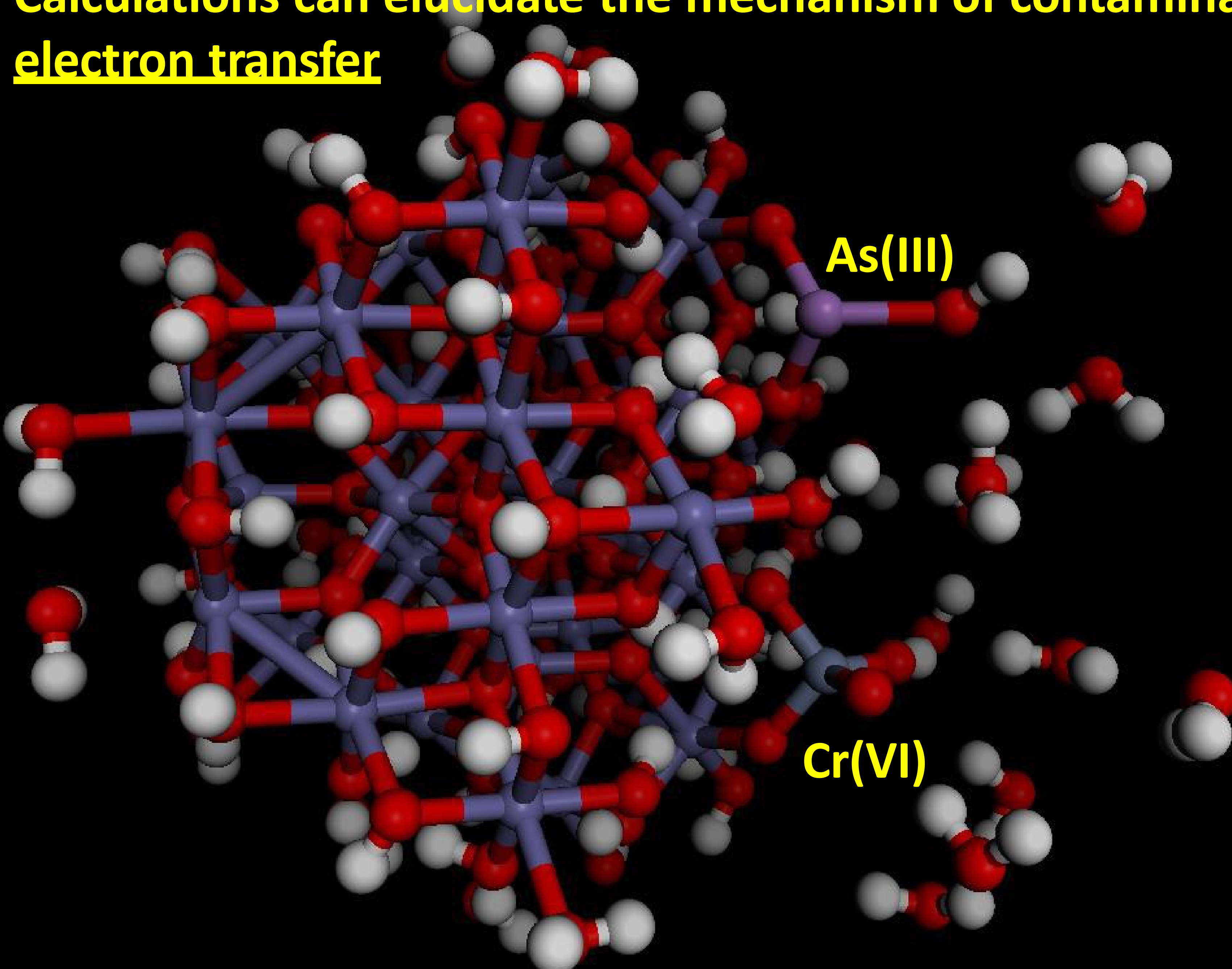
Elizabeth Cerkez, Narayan Bhandari & Daniel Strongin
Temple University



Cr(III) Added **As(V) Added**

- **When Cr(III) is added alone, we see ~70μ M adsorbed.**
- **When both Cr(III) and As(V) are added, we see 210 μ M adsorption of As(V), and ~100 μ M of Cr(III) adsorbed.**
- **Adsorption of As(V) facilitates the adsorption of Cr(III) due to the more negatively charged surface.**

Calculations can elucidate the mechanism of contaminant <u>electron transfer</u>



Conclusions

#1. Nanoparticles, natural and man-made, play a significant role in the environment with both positive and negative effects.

#2. Direct roles of nanoparticles are seen in health impacts on plants and animals and can be magnified up the food chain.

#3. The role of nanoparticles in the atmosphere is one of the biggest uncertainties in predicting future climate change.

#4. Combinations of field observations, laboratory experiments & analyses, and computational chemistry can help reveal critical details of nanoparticle behavior.