Now in the 51st year

Enabling nanotechnology: Future directions for emerging countries

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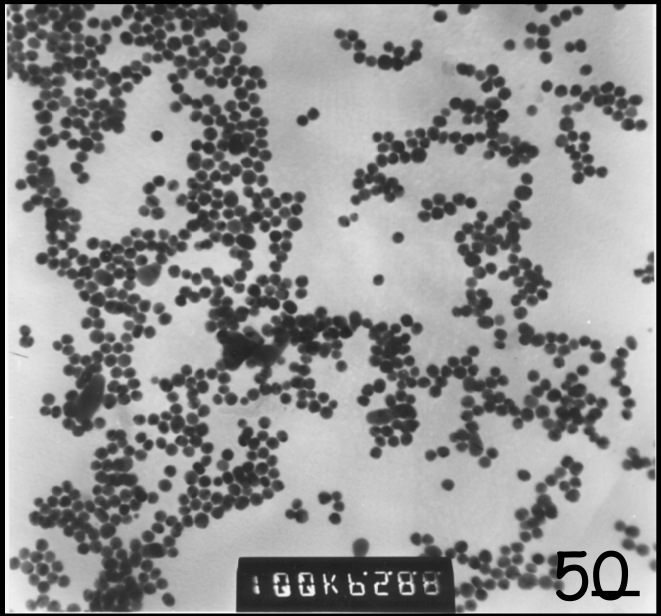
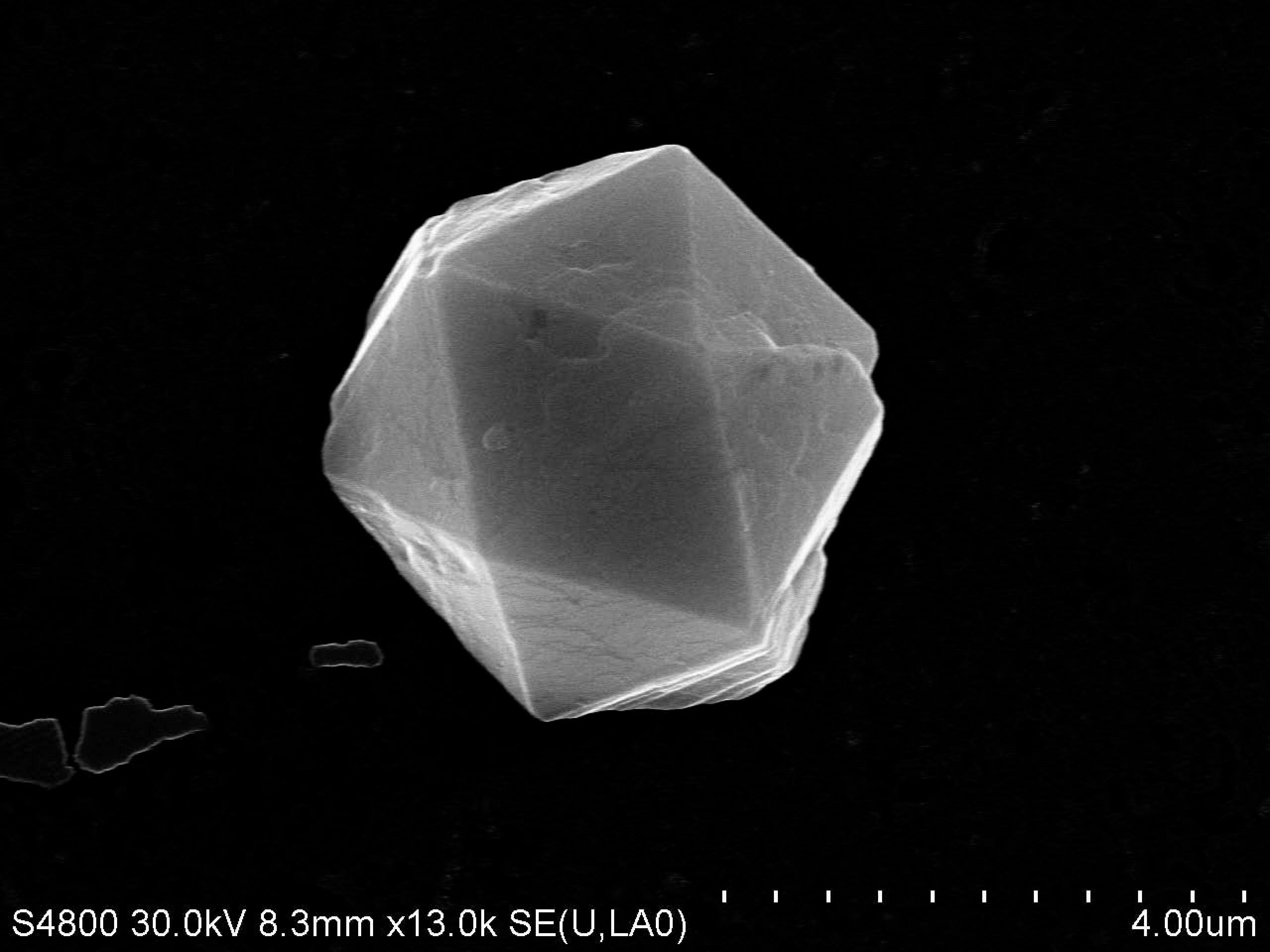
http://www.dstuns.iitm.ac.in/pradeep_research_group.php

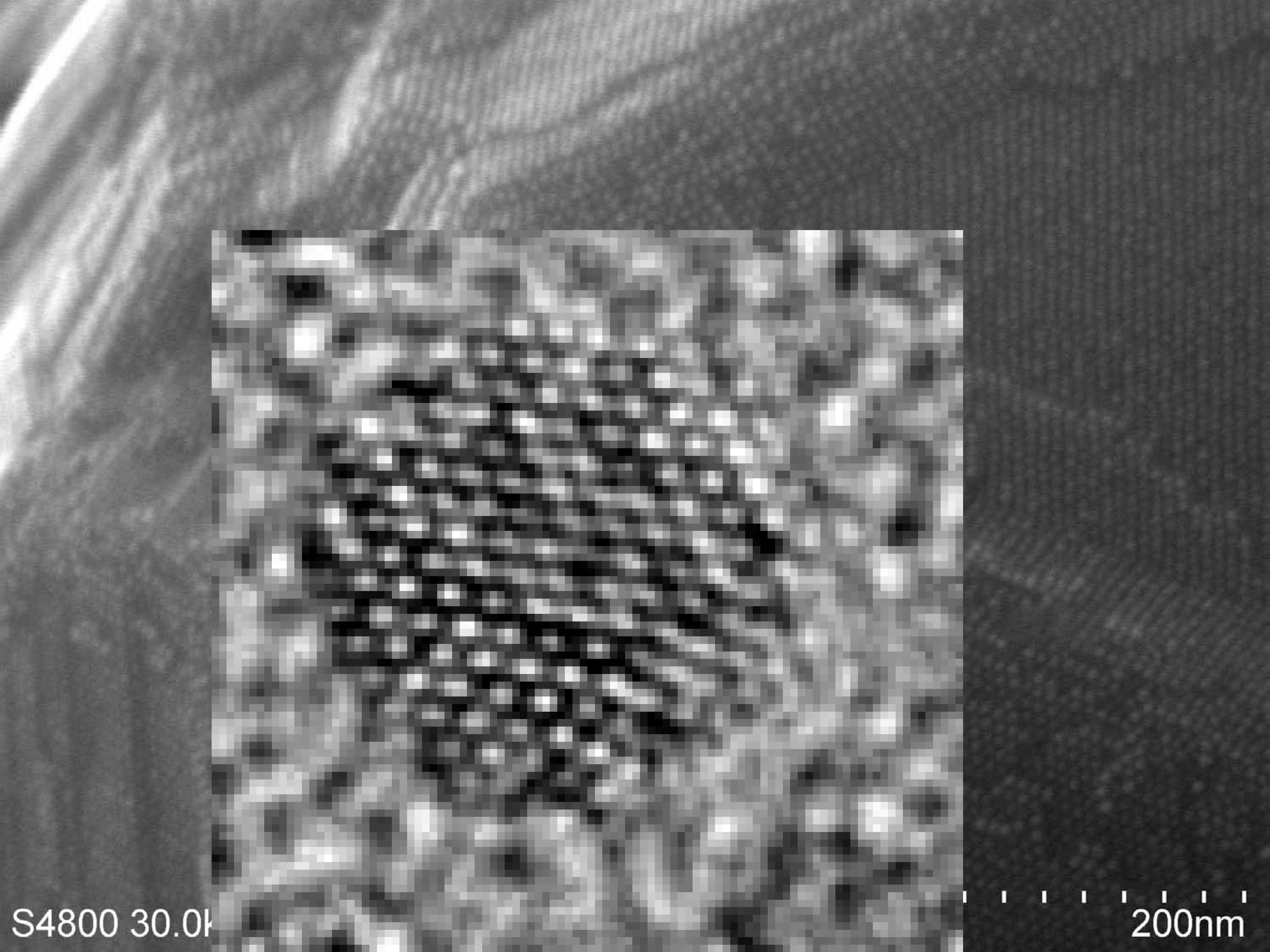
5th Nanotechnology Conclave
New Delhi April 14-15, 2010

New materials

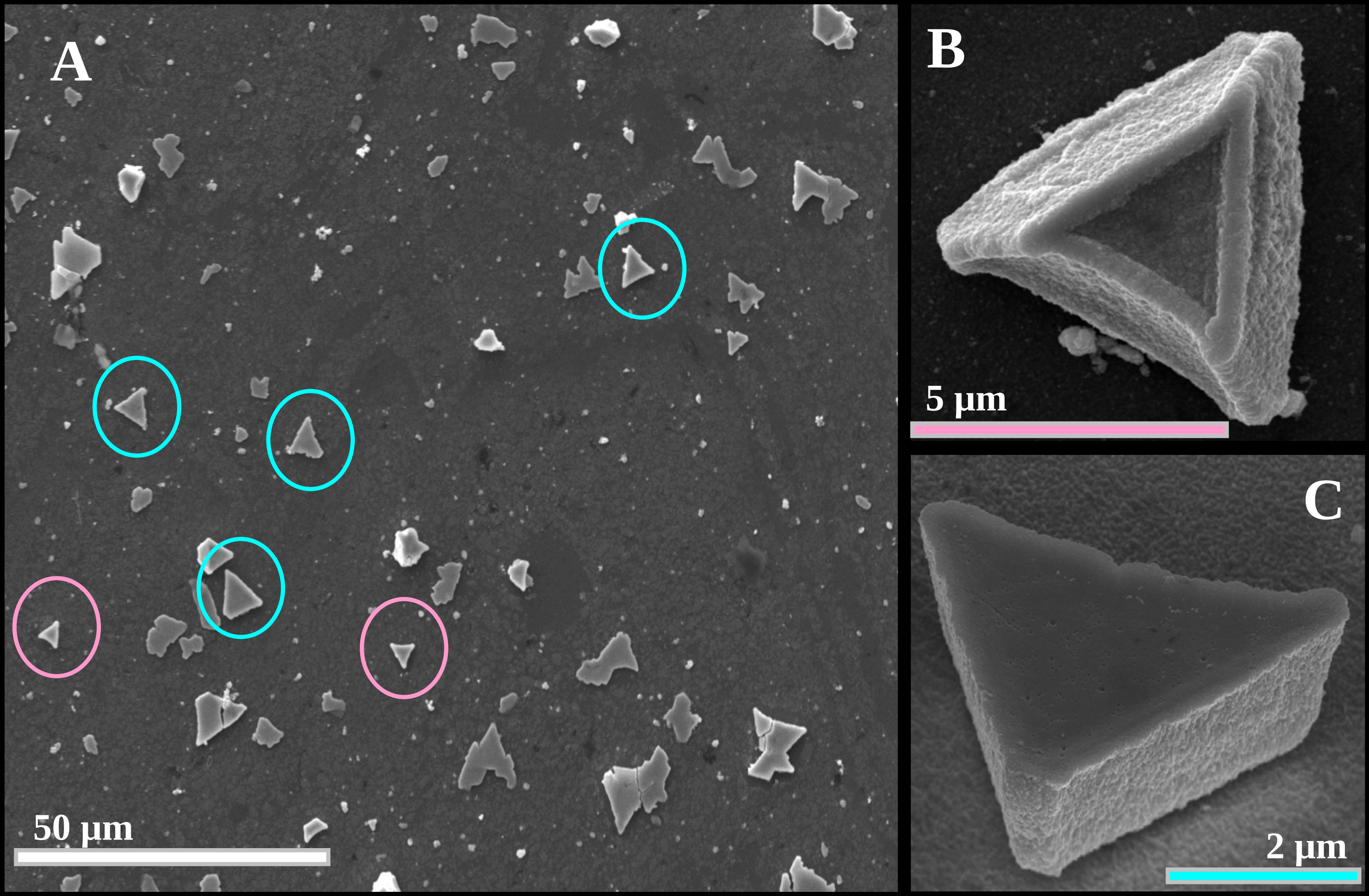


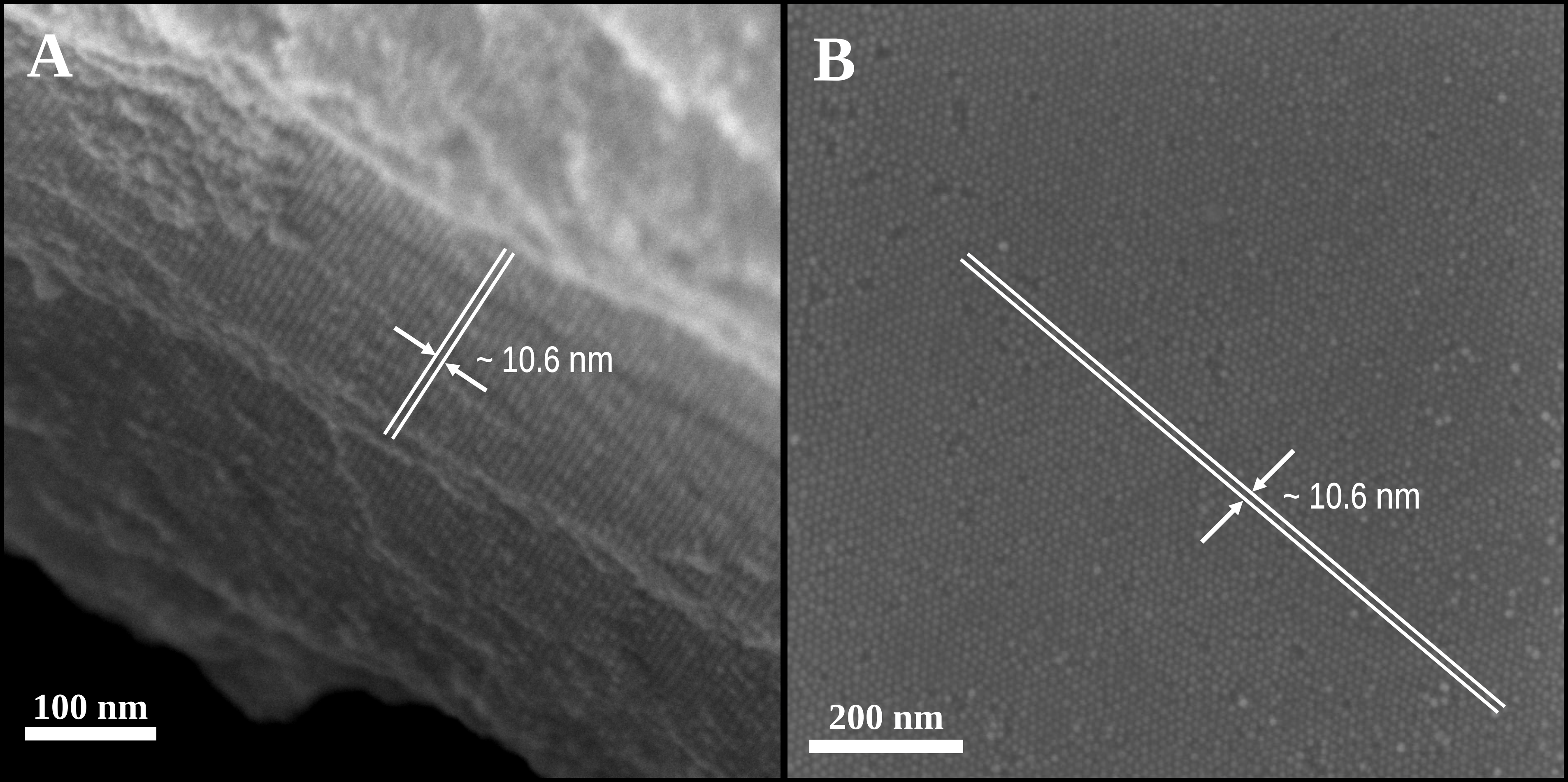
Faraday's gold preserved in Royal Institution. From the site,
http://www.rigb.org/rimain/heritage/faradaypage.jsp

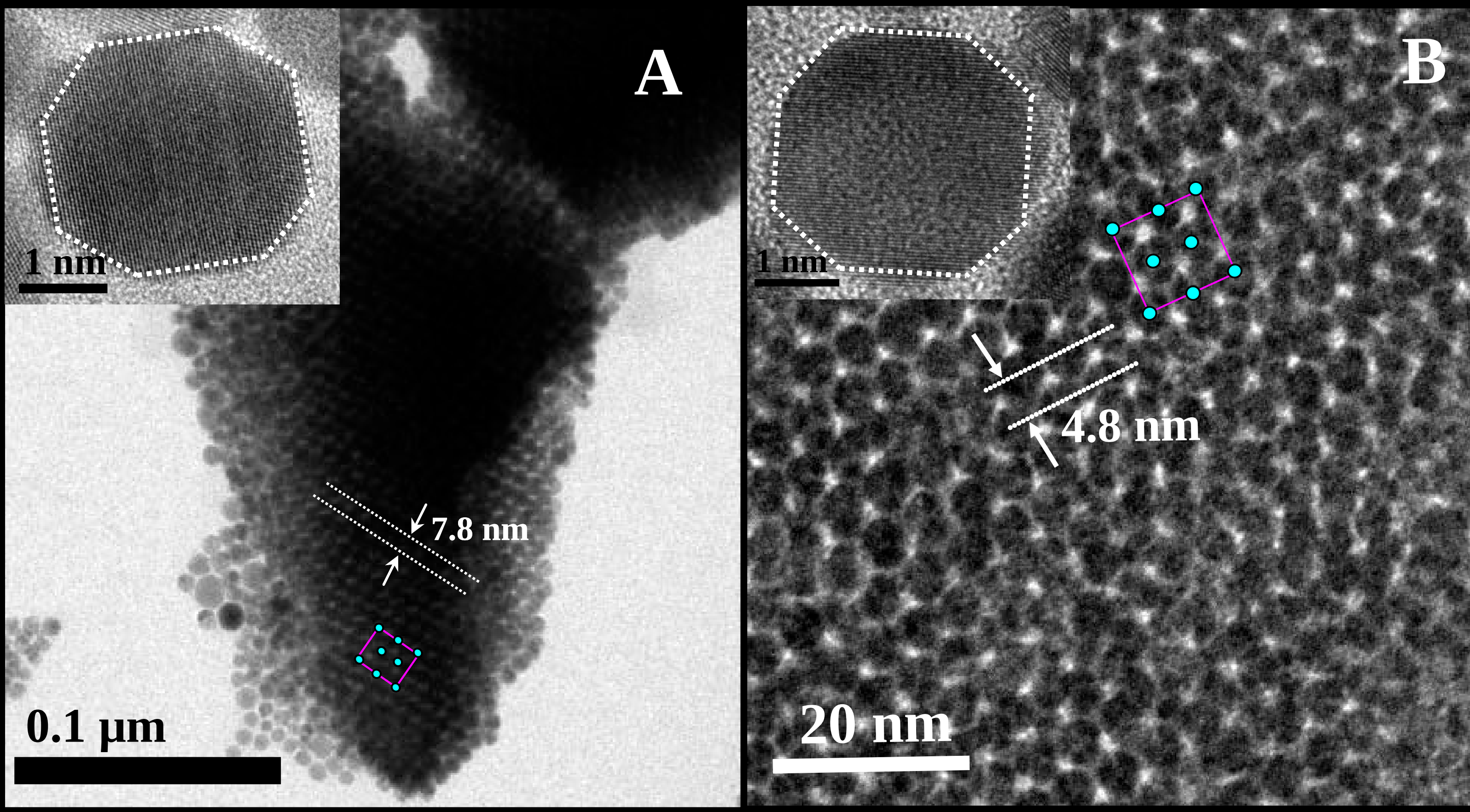

S4800 30.0kV 8.3mm x13.0k SE(U,LA0)
4.00um



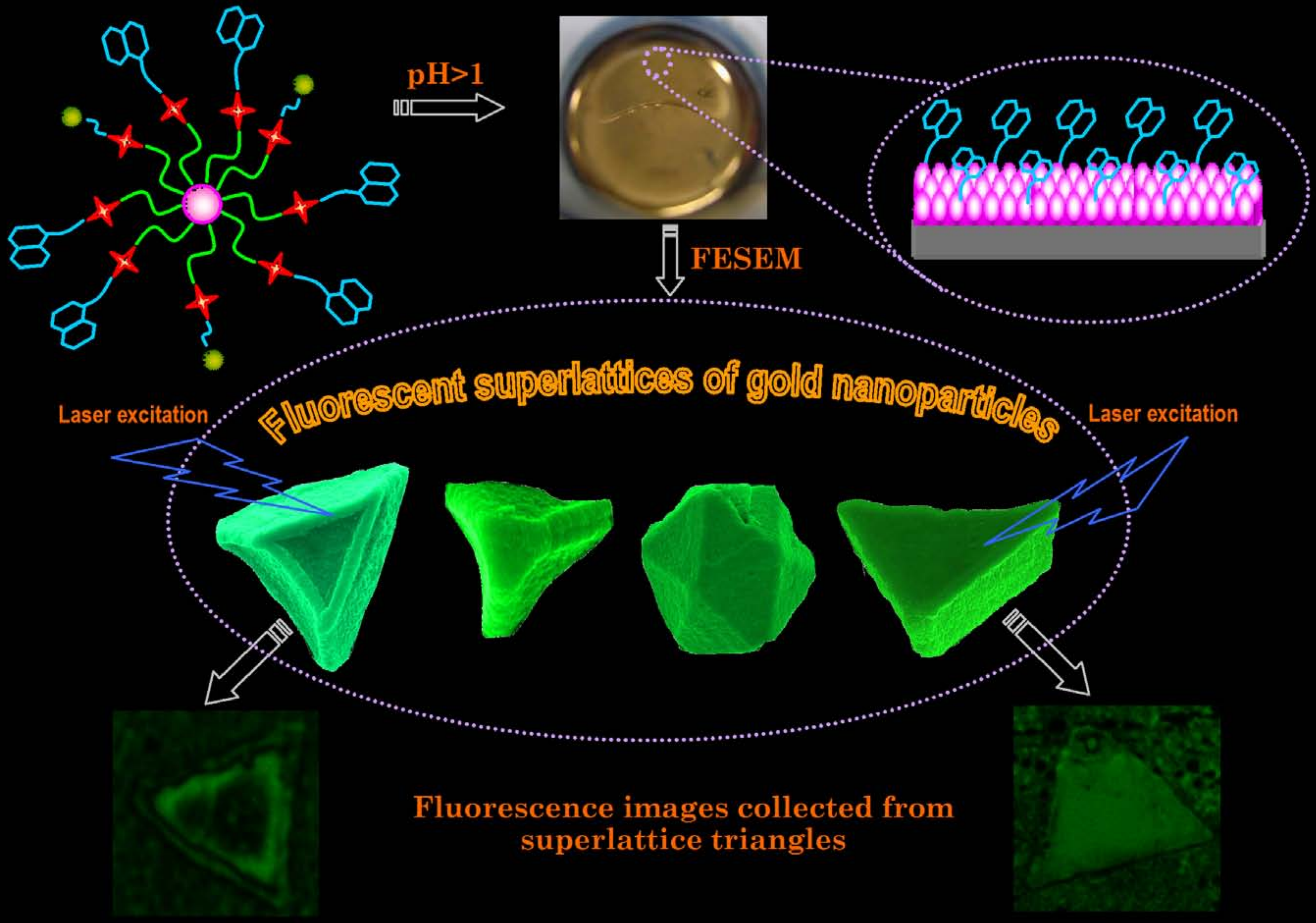
S4800 30.0k
200nm


A
50 µm
B
5 µm
C
2 µm

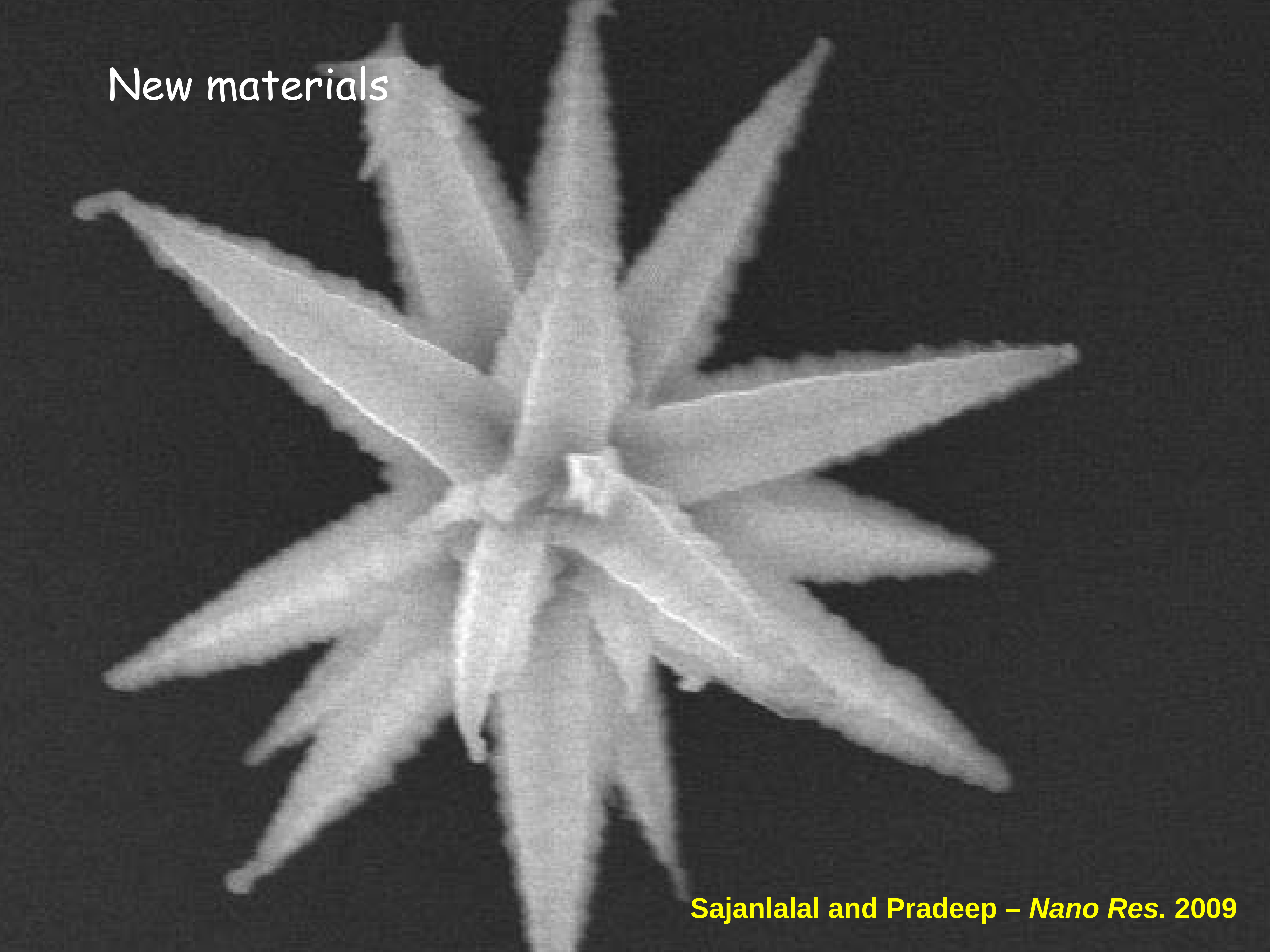

A
~ 10.6 nm
100 nm
B
~ 10.6 nm
200 nm


A
1 nm
7.8 nm
0.1 µm
B
1 nm
4.8 nm
20 nm

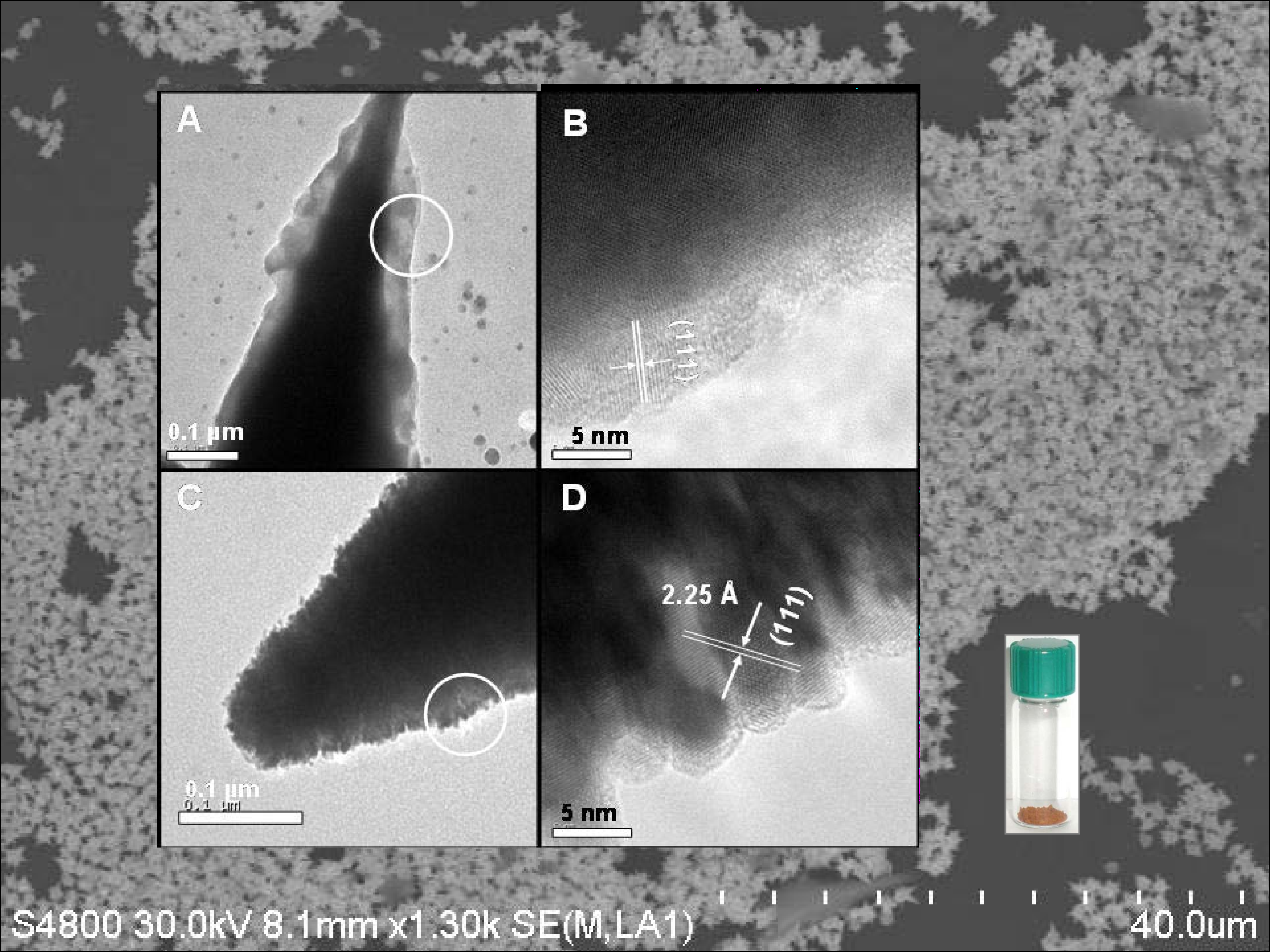
Fluorescent superlattices



New materials



Sajanlalal and Pradeep – *Nano Res.* 2009


A
0.1 μm
B
(111)
5 nm
C
0.1 μm
D
2.25 Å
(111)
5 nm
S4800 30.0kV 8.1mm x1.30k SE(M,LA1)
40.0um

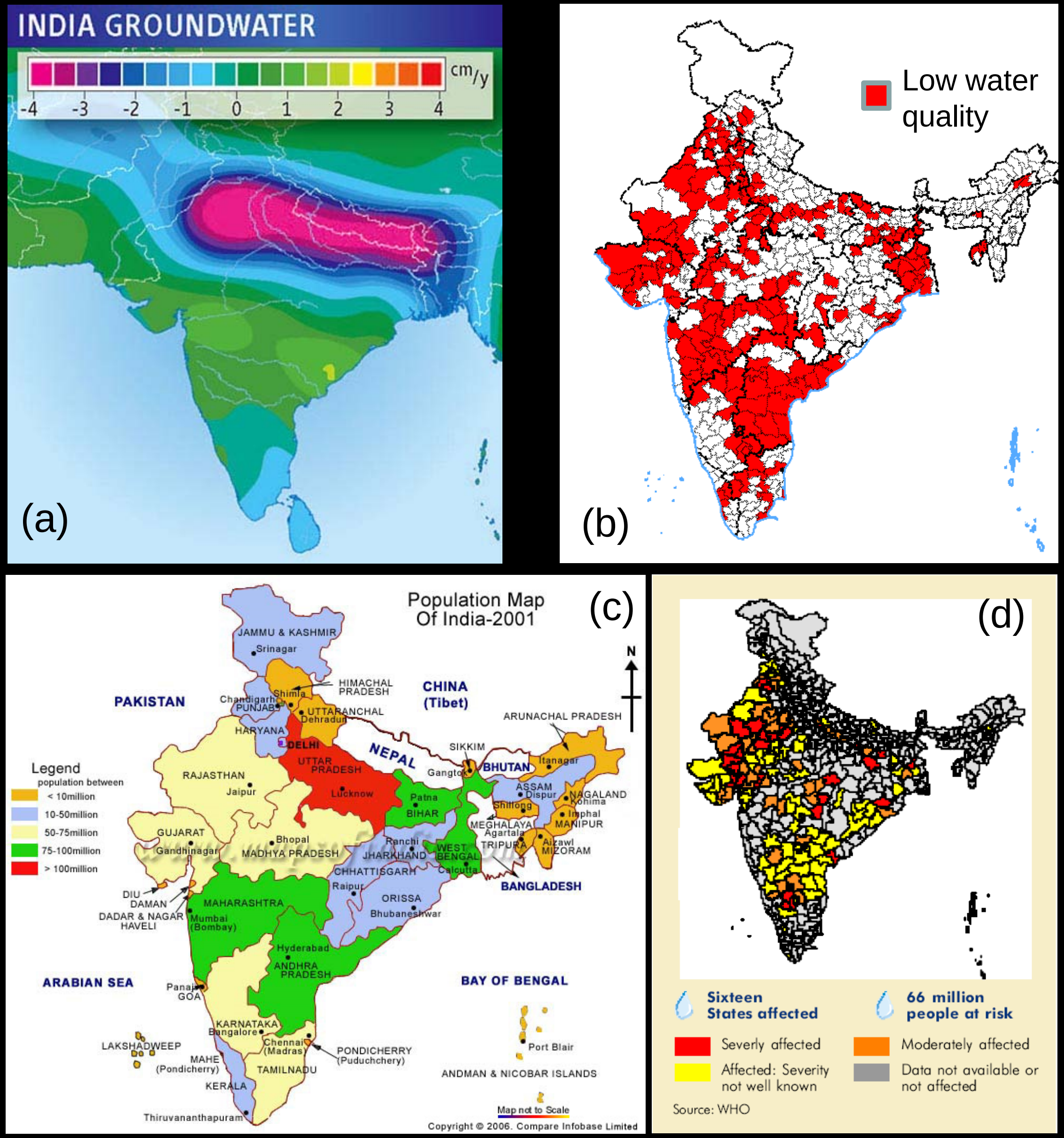
Even for our most pressing needs, nanotechnology offers solutions

There is indeed a need.
Market is ripe.
Solutions exist.

What is the problem then?

One can look at India in many ways

Political map



(a) Satellite-based estimates of groundwater depletion in India, Matthew Rodell, Isabella Velicogna & James S. Famiglietti, Nature 460, 999-1002(20 August 2009)
(b) Environmental Atlas of India, Central Pollution Control Board (http://www.soeatlas.org/PDF_Map%20Gallery/Ground%20Water%20Quality.pdf)
(c) Census 2001
(d) India assessment 2002, Water Supply and Sanitation – A WHO and UNICEF Joint Study.

Lets us take a look at India from the perspective of (a) Ground water availability (b) Water quality (c) Population and (d) water contamination due to fluoride

We have a problem; can nanotechnology help?

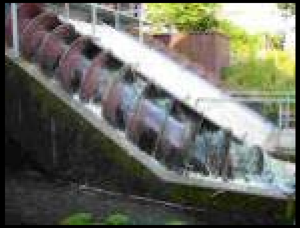
India has a long tradition in clean water

Mohenjodaro - well

http://dspace.rice.edu/bitstream/1911/9176/773/LanMa1890_135_a.jpg

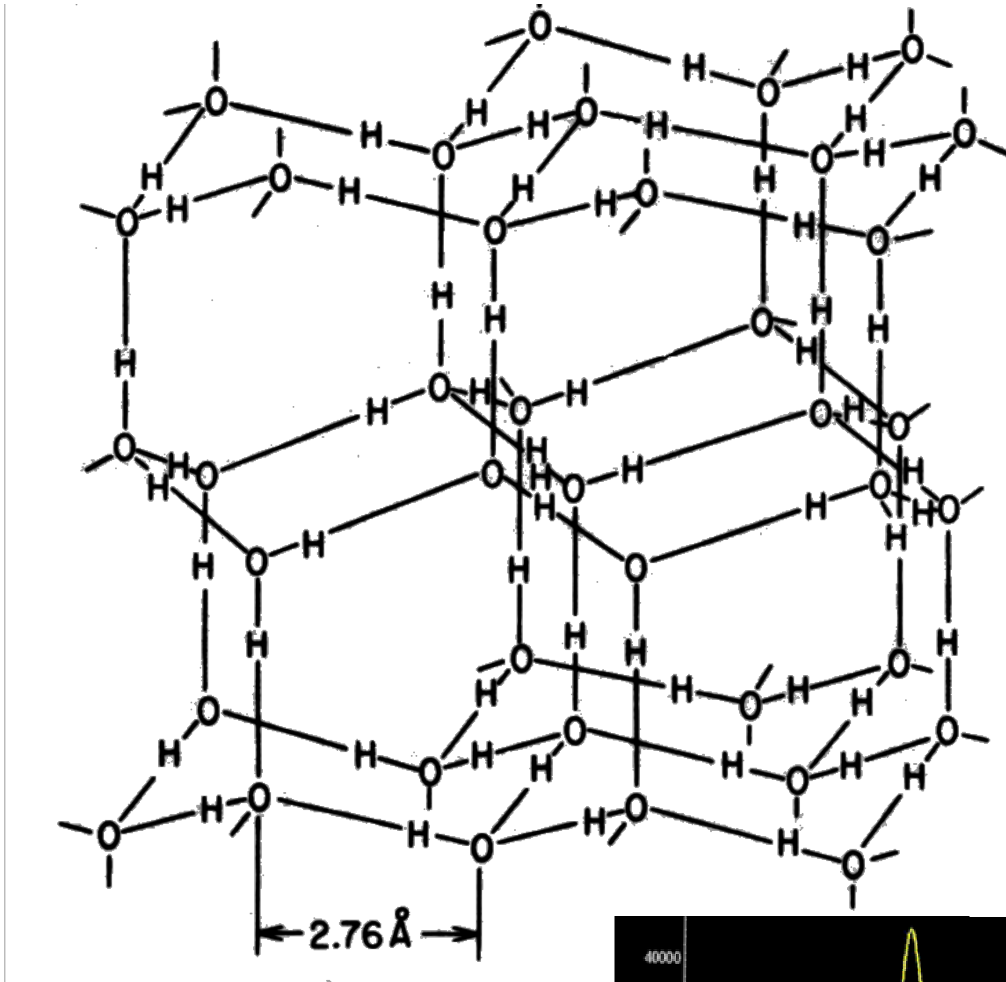
Mohenjodaro – the great bath

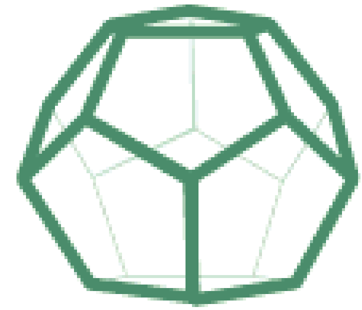
Aqueducts - The Assyrians - the first structure to carry water from one place to another - 7th century BC



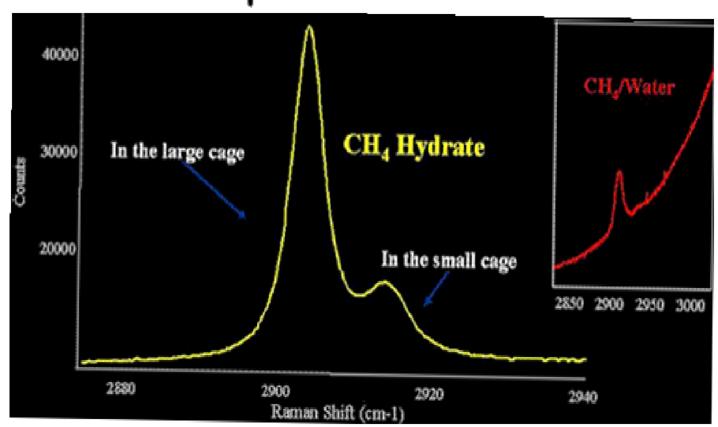
Archimedes' screw - 287 and 212 BC - in the Netherlands Zoetermeer

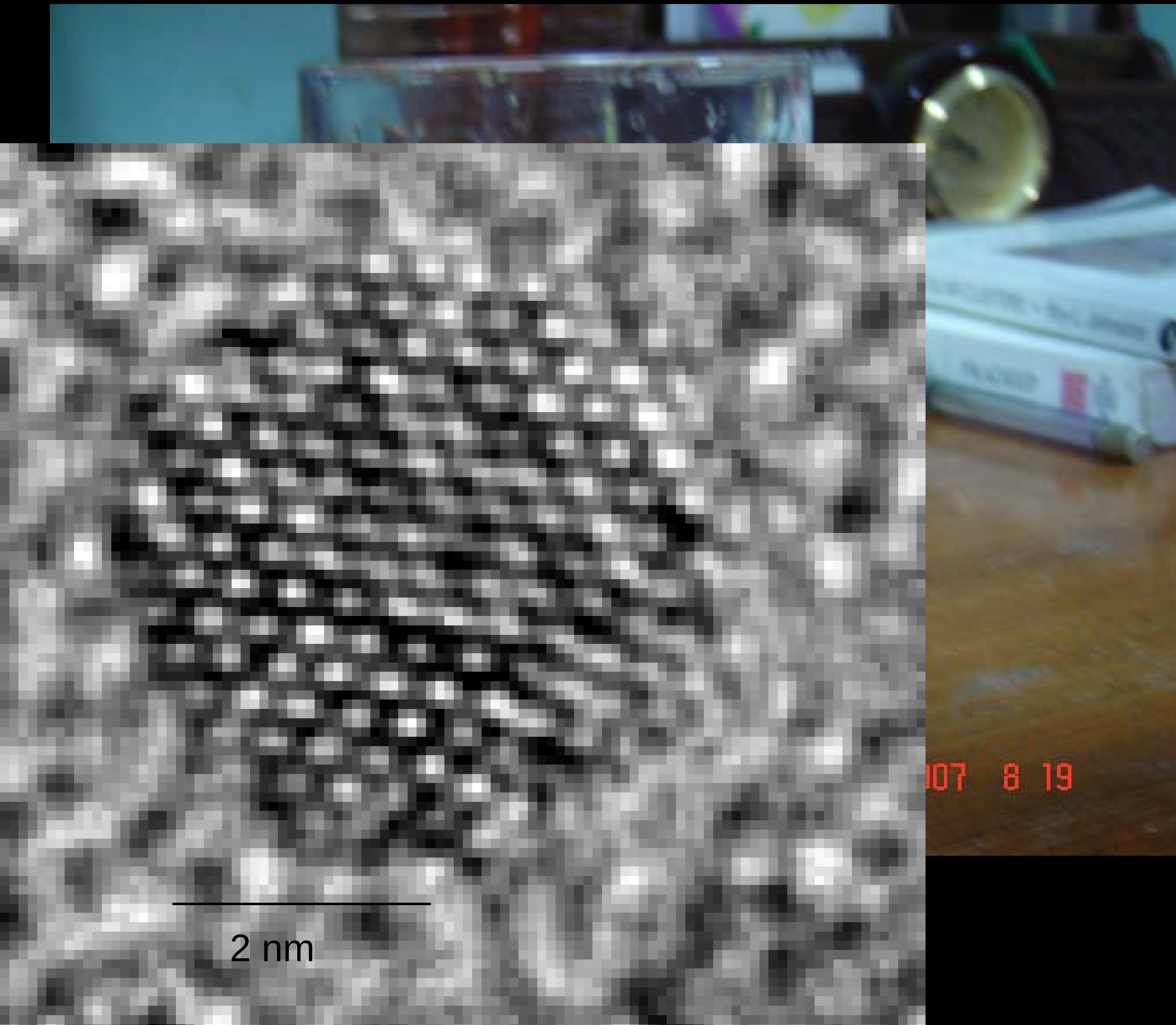
Carbon as a material for water purification



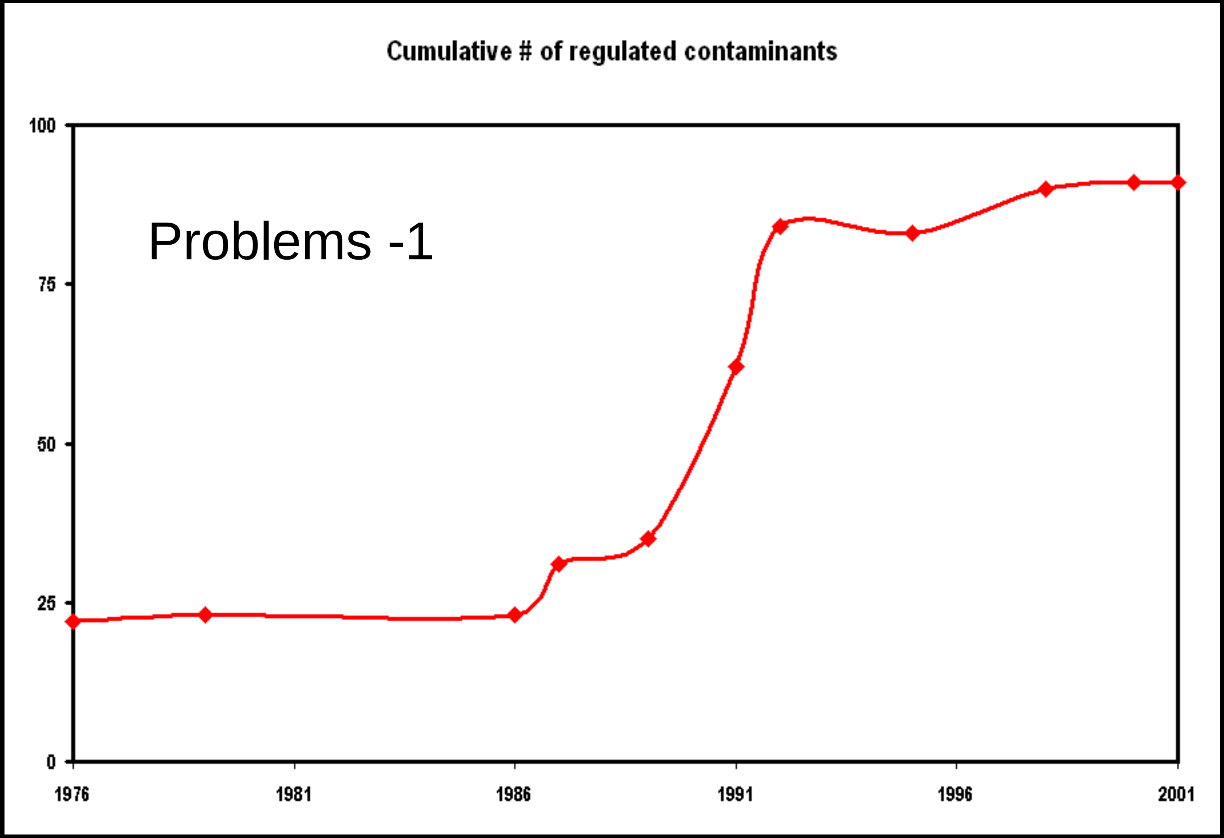


Gas hydrates to ozone chemistry




2 nm

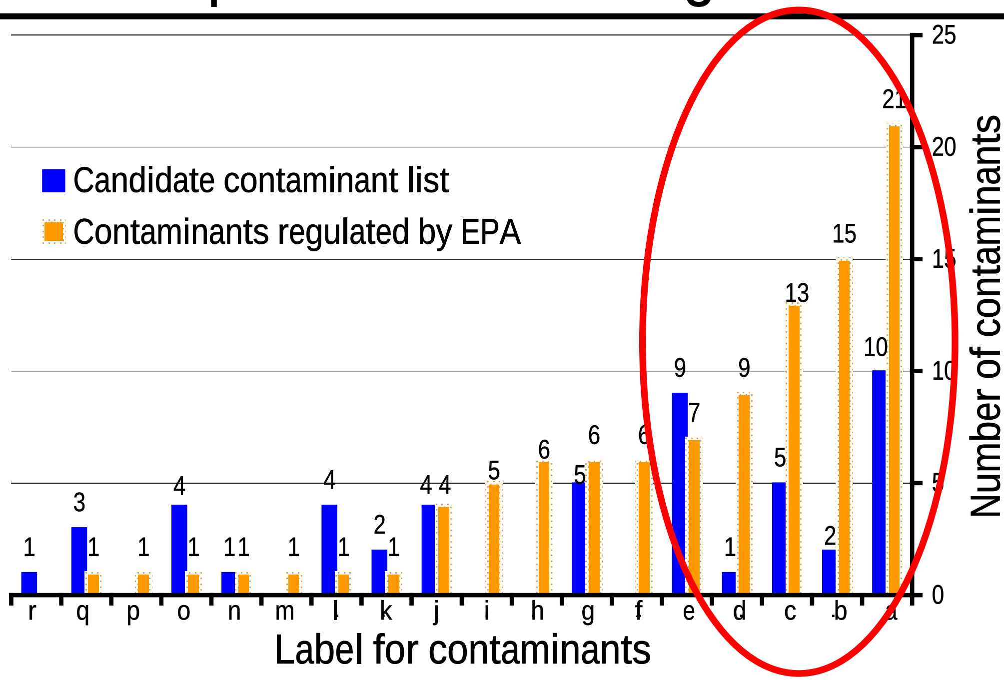
USEPA has played a key role in determining the regulations for many toxic species found in drinking water



Regulatory coverage of USEPA for safe drinking water has increased over 4 times since its inception, with revisions in regulations of many old contaminants

Future of water purification: An enigma with some pointers

Problems -2



(a): Halogenated organic (b): Metal (c): Organochlorine pesticide (d): Inorganic salt (e): Biological contaminant (f): Nuclear (g): Benzo derivative (h): Carbamate pesticide (i): Pesticides (others) (j): Unclassified (k): Triazine derivative pesticide (l): Organophosphorus pesticide (m): Organobromine pesticide (n): Non-metal (o): Nitrophenol derivative, (p): Dioxin, (q): Benzo and halogenated organic (r): Organometallics

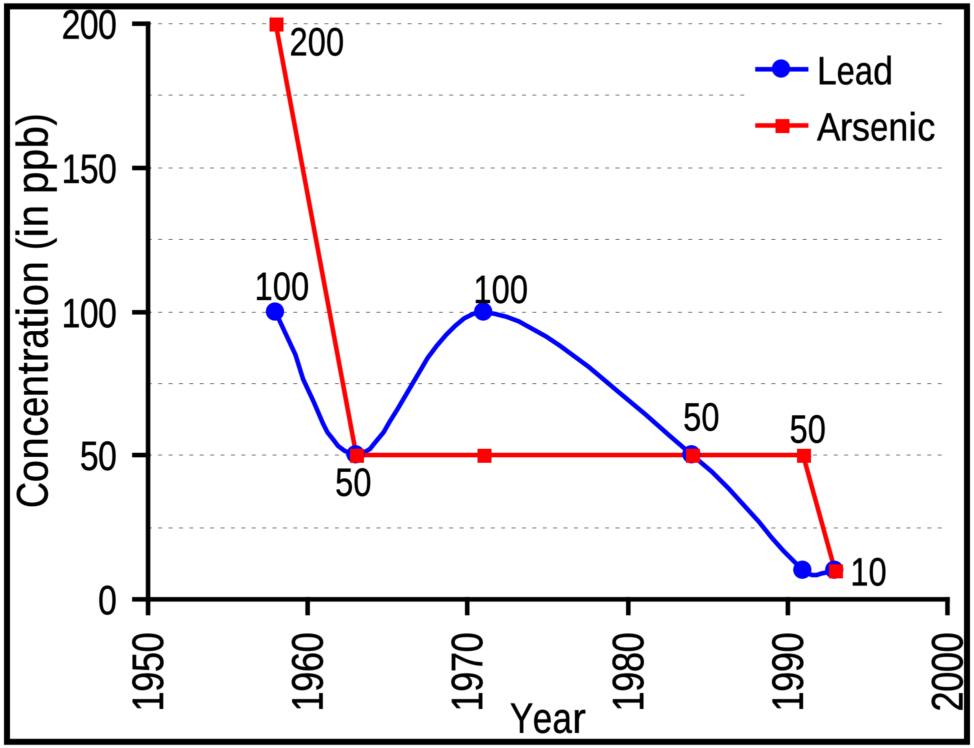
Category-wise distribution of contaminants regulated by USEPA and future contaminants

Continued focus of USEPA regulatory activities on various other halogenated organics found in drinking water. The allowed concentration limits for a number of species may shift to sub-ppb range.

Source: www.epa.org and www.who.int

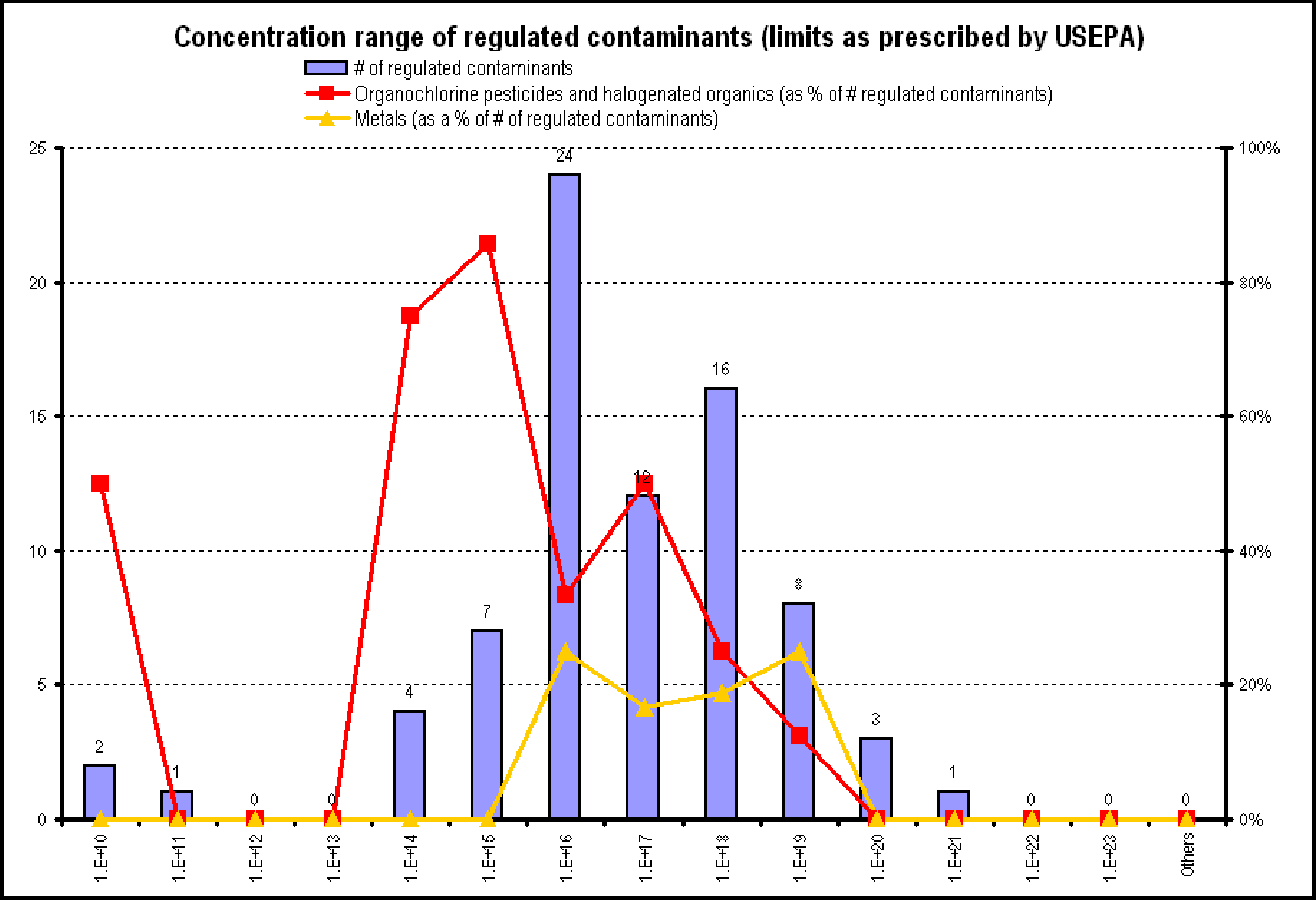
Future of water purification: Shrinking limits for allowed concentration of contaminants in water

Problems - 3



Changes in maximum allowable concentration for lead and arsenic in drinking water, based on WHO advisory

Nanotechnology holds the future for effectively removing many drinking water contaminants



- Number of contaminants present in extremely low concentration range (< 10^{15} molecules per glass of water) are quite significant
- Many of those contaminants contain C-Cl bond or are metallic in nature

Important milestones in the history of water purification (1800-2007)

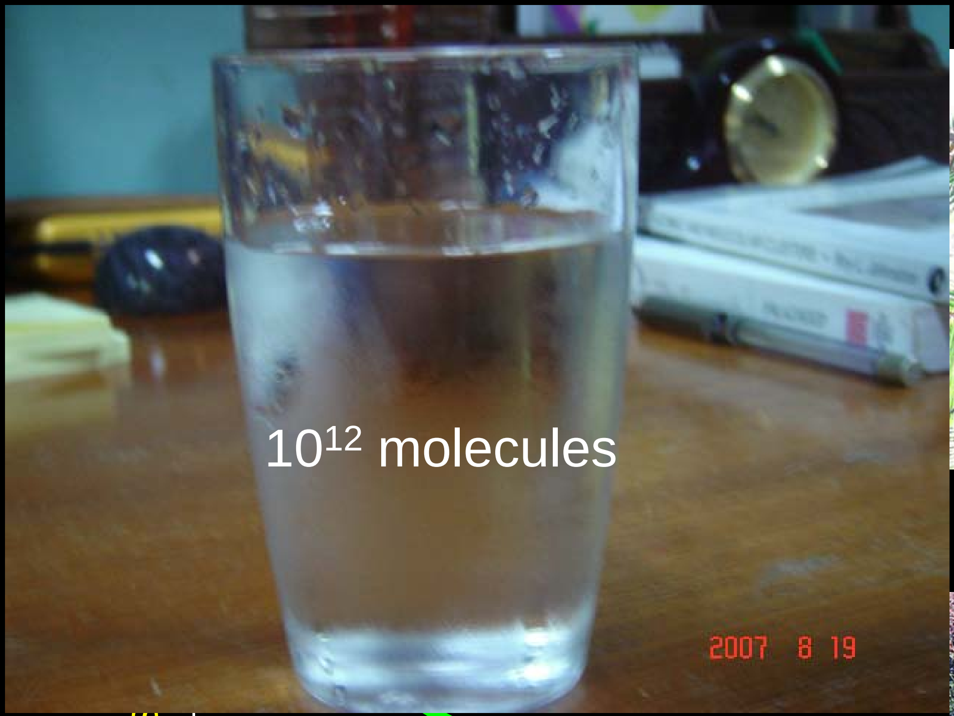
Year	Milestone
1804	Setup of world's first city-wide municipal water treatment plant (Scotland, sand-filter technology)
1810	Discovery of chlorine as a disinfectant (Humphrey Davy)
1852	Formulation of Metropolis Water Act (England)
1879	Formulation of Germ Theory (Louis Pasteur)
1902	Use of Chlorine as disinfectant in drinking water supply (calcium hypo chlorite, Belgium)
1906	Use of ozone as disinfectant (France)
1908	Use of Chlorine as disinfectant in municipal supply, New Jersey
1914	Federal regulation of drinking water quality (USPHS)
1916	Use of UV treatment in municipal supplies
1935	Discovery of synthetic ion exchange resin (Adams, Holmes)
1948	Nobel Prize to Paul Hermann Müller (insecticidal properties of DDT)
1959	Discovery of synthetic reverse osmosis membrane (Yuster, Loeb, Sourirajan)
1962	Publishing of *Silent Spring*, first report on harmful effects of DDT (Rachel Carson)
1965	World's first commercial RO plant launched
1974	Reports on carcinogenic by-products of disinfection with chlorine
	Formulation of Safe Drinking Water Act (USEPA)
1975	Development of carbon block for drinking water purification
1994	Report on use Zerovalent Iron for degradation of halogenated organics (Gillham, Hannesin)
1997	Report on use Zerovalent Iron nanoparticles for degradation of halogenated organics (Wang, Zhang)
1998	Drinking Water Directive applied in EU
2000	Adoption of Millennium Declaration during the UN Millennium Summit (UN Millennium Development Goals)
2003	Report on use Noble metal nanoparticles for degradation of pesticides (Nair, Tom, Pradeep)
2004	Stockholm Convention, banning the use of persistent organic pollutants
2007	Launch of world's first nanotechnology based domestic water purifier (Pradeep, Eureka Forbes Limited)

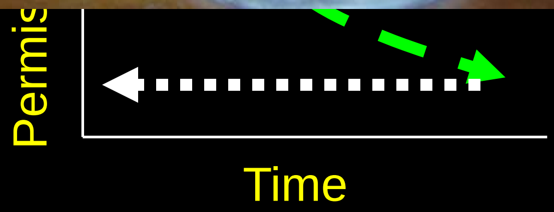
Last globally big invention in water purification

There is a gap and technology is waiting

Credits to several governments, organizations and individuals, we have moved ahead. The journey of "*pure water for all*" calls for next big innovation.

Source: Multiple sources from internet

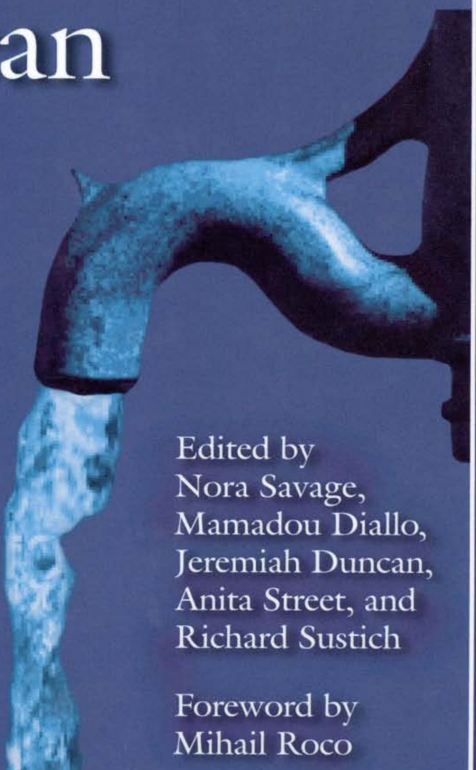




Permissible contamination reaches limits of detection

MICRO & NANO TECHNOLOGIES

Nanotechnology Applications for Clean Water



Chapter by T. Pradeep and Anshup

Edited by
Nora Savage,
Mamadou Diallo,
Jeremiah Duncan,
Anita Street, and
Richard Sustich

Foreword by
Mihail Roco

William Andrew

Nanotechnology Applications for Clean Water

This landmark reference details nanotechnology breakthroughs, cutting edge technologies, and future trends that point to widespread applications for nanotechnologies employed in water remediation and pollution prevention.

A full range of treatment and remediation topics using nanotechnologies are covered, including a case study in detecting and extracting pesticides from drinking water. The U.S./Israel Workshop on Nanotechnology for Water Purification is outlined. Societal implications that may threaten the adoption of these new technologies are also addressed.

KEY FEATURES

- Covers drinking water purification, treatment, and desalination; microbial disinfection; nanofiltration applications; and commercialization of nanotechnology for the removal of heavy metals
- Balanced analysis of nanotechnology-enabled disinfection and microbial control; the principles and applications behind Dendrimer-enhanced filtration; and possible applications of fullerene nanomaterials and the ion exchange process in treatment and reuse
- Explains biosensors for pesticide and explosive detection, nanosensors for environmental monitoring, and colorimetric / fluorescent sensors
- Exhaustive coverage of remediation topics: contaminated site clean up; physicochemistry to increase stability, mobility, and contaminant specificity of nanoparticles; heterogeneous catalytic approaches in purification; stabilization / destruction of chlorine; reducing leachability; synthesis of particles; etc.

ABOUT THE EDITORS

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William Andrew
Applied Science Publishers
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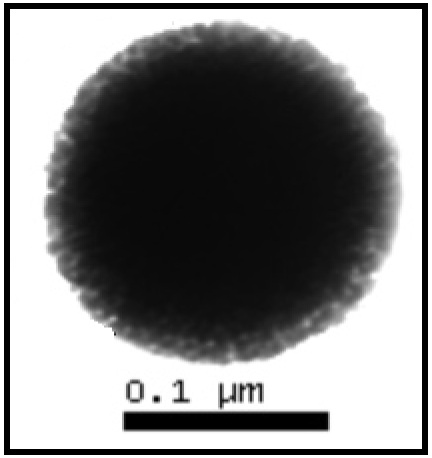
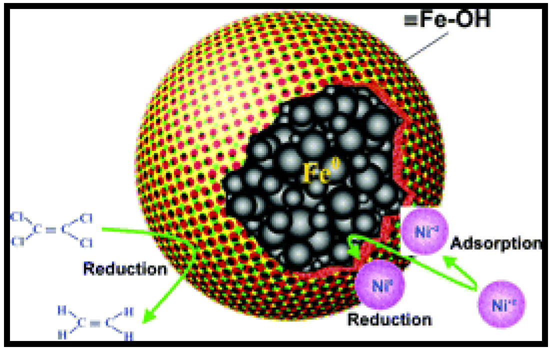
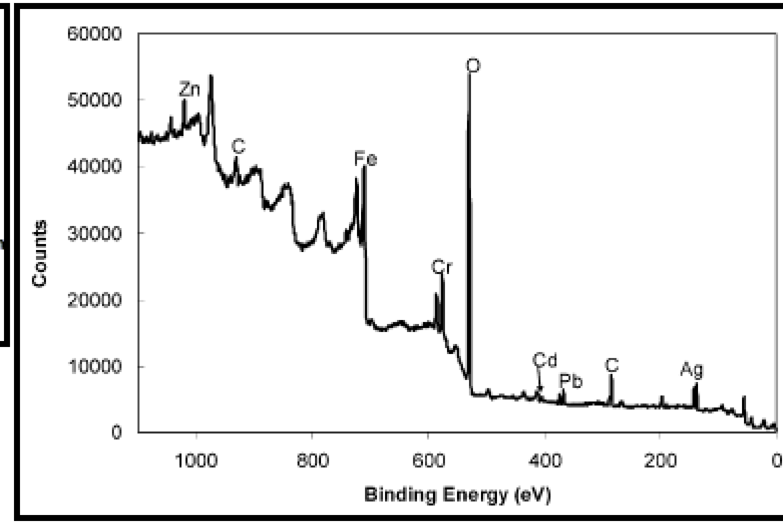
Illustration of metal adsorption on nanoparticle surface (ZVI surface)

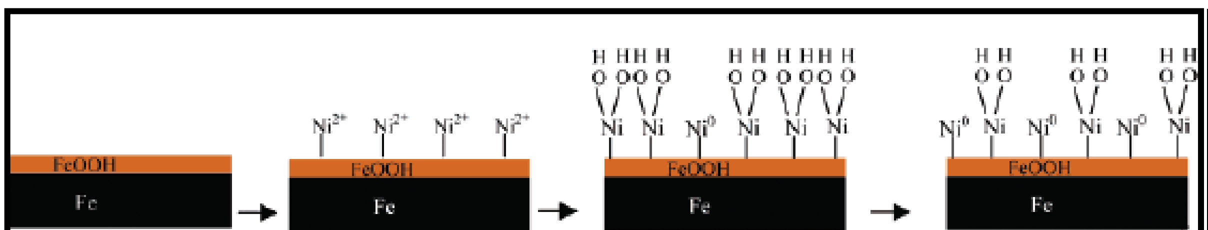




TEM image of Fe nanoparticle and Cartoon representation of chemistry at Fe nanoparticle, *Iron Nanoparticles: the Core-Shell Structure and Unique Properties for Ni(II) Sequestration, Xiao-qin Li and Wei-xian Zhang, Langmuir 2006, 4638-4642*



XPS wide-scan survey of iron nanoparticles after exposure to a metal salt containing solution, *Sequestration of Metal Cations with Zerovalent Iron Nanoparticless A Study with High Resolution X-ray Photoelectron Spectroscopy (HR-XPS), Xiao-qin Li and Wei-xian Zhang, J. Phys. Chem. C 2007, 6939-6946*

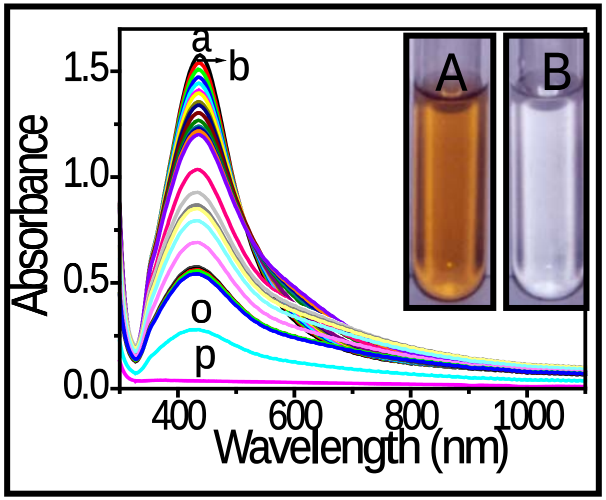


	mg/g	mM/g	mequiv/g	mequiv/mL
nano-Fe−Pb(II)	265	1.27	2.55	12.96
nano-Fe−Ni(II)	130	2.21	4.43	22.46
nano-Fe−Ag(I)	198	3.67	3.67	18.62
clay[25]			0.2−0.5	
zeolite[25]			≤2	
cation exchanger[b]			1.8−4.8	0.8−1.8

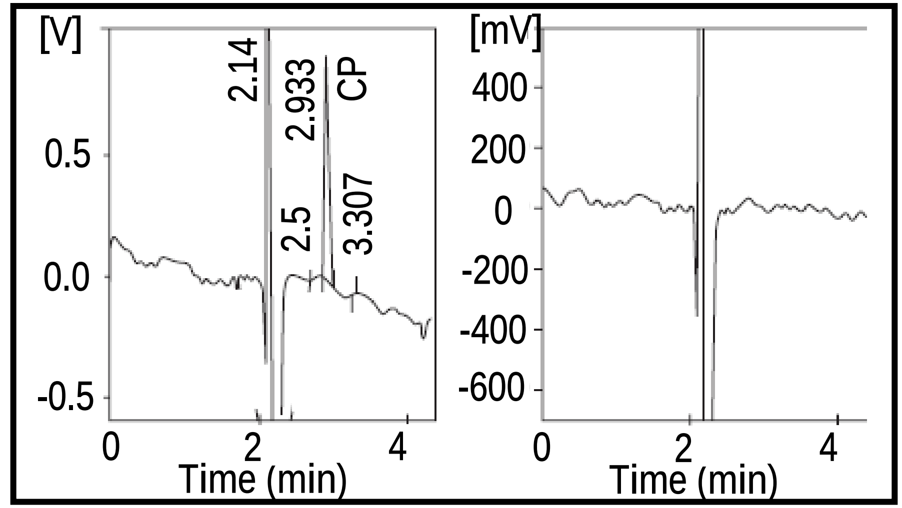
Cartoon representation of chemistry at Fe nanoparticle surface (left) and metal ion removal efficiency for different adsorbents, *Iron Nanoparticles: the Core-Shell Structure and Unique Properties for Ni(II) Sequestration, Xiao-qin Li and Wei-xian Zhang, Langmuir 2006, 4638-4642*

Noble metal nanoparticles: removal of pesticides from water

A.S. Nair, T. Pradeep, Curr. Sci. 84 (2003) 1560



Variation of the UV-visible absorption spectrum of silver nanoparticles upon the addition of CCl_4



Gas chromatogram of chlorpyrifos solution (L) and after treatment with silver nanoparticles (R)

A.S. Nair, R.T. Tom, V.R. Rajeev Kumar, C. Subramaniam, T. Pradeep, Cosmos 3, (2007) 103

Indian patent 2004

June 2007

(L) Silver nanoparticles coated on activated alumina (R) Photograph of a pesticide filter device using supported nanoparticles (WQA certified)

RSC | Advancing the Chemical Sciences

Chemistry World

Pesticide filter debuts in India

20 April 2007

Killugudi Jayaraman/**Bangalore, India**

A domestic water filter that uses metal nanoparticles to remove dissolved pesticide residues is about to enter the Indian market. Its developers at the Indian Institute of Technology (IIT) in Chennai (formerly Madras) believe it is the first product of its kind in the world to be commercialised.

Mumbai-based Eureka Forbes Limited, a company that sells water purification systems, is collaborating with IIT and has tested the device in the field for over six months. Jayachandra Reddy, a technical consultant to the company, expects the first 1000 units to be sold door-to-door from late May.

The pesticide-zapping filter © Thalappil Pradeep

'Our pesticide fiter is an offshoot of basic research on the chemistry of nanoparticles,' Thalappil Pradeep who led the team at IIT Chennai told *Chemistry World*. He and his student Sreekumaran Nair discovered in 2003 that halocarbons such as carbon tetrachloride (CCl4) completely break down into metal halides and amorphous carbon upon reaction with gold and silver nanoparticles[1].

Pradeep said this prompted them to extend their study to include organochlorine and organophosphorous pesticides, whose presence in water is posing a health risk in rural India. In research funded by the Department of Science and Technology in New Delhi, his team found[2,3] that gold and silver nanoparticles loaded on alumina were indeed able to completely remove endosulfan, malathion and chlorpyrifos - three pesticides that have been found at elevated levels in Indian water supplies.

Use and recycle

The mechanism of removal is 'adsorption followed by catalytic destruction', Pradeep explained. 'The chemistry occurs in a wide concentration range of environmental significance.' He added that tests proved silver particles from the filter are not released into the water. The IIT study found that gold particles perform better in the case of endosulfan. However, for cost reasons, the commercialised filters use only silver particles, which range in size from 60 to 80 nanometres at a concentration (on their alumina support) of 33 parts per million.

'Based on consumption patterns of a typical Indian household, the filter is designed to have enough nanomaterials to provide 6000 litres of pesticide-free water for one year,' Pradeep said. 'After that, the company will recycle the filters to recover the silver.'

Use of nanoparticles for environmental remediation is an emerging area of research worldwide.

Nanoscale iron powders had been shown to degrade other pesticides, including DDT and lindane[4], 'and there are reports about the use of nanomaterials for removing arsenic, heavy metals and fluorides,' said Pradeep. 'But ours is the first product to hit the market,' he said.

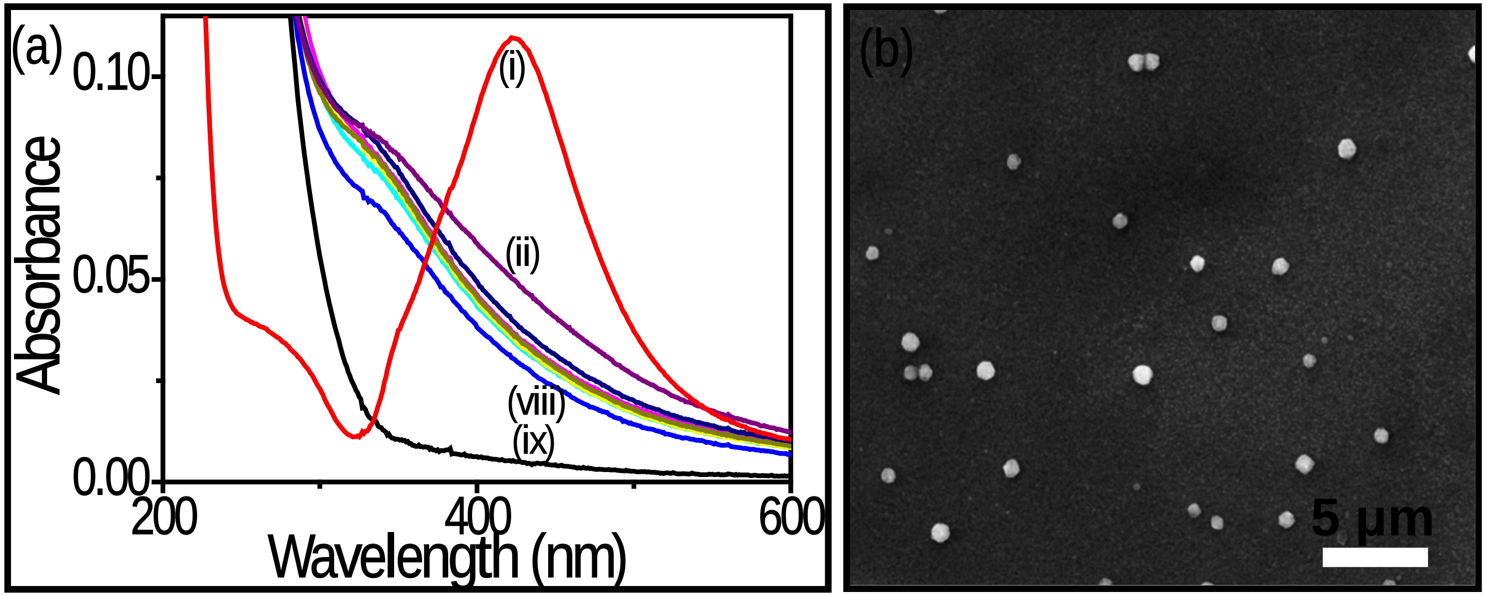
World first

Murali Sastry, chief scientist of TATA Chemicals Innovation Centre in Pune - India's first nanotechnology research centre in the private sector - agrees. 'What Pradeep has done is definitely novel,' Sastry told *Chemistry World*. 'I am not aware of any similar product in the market.'

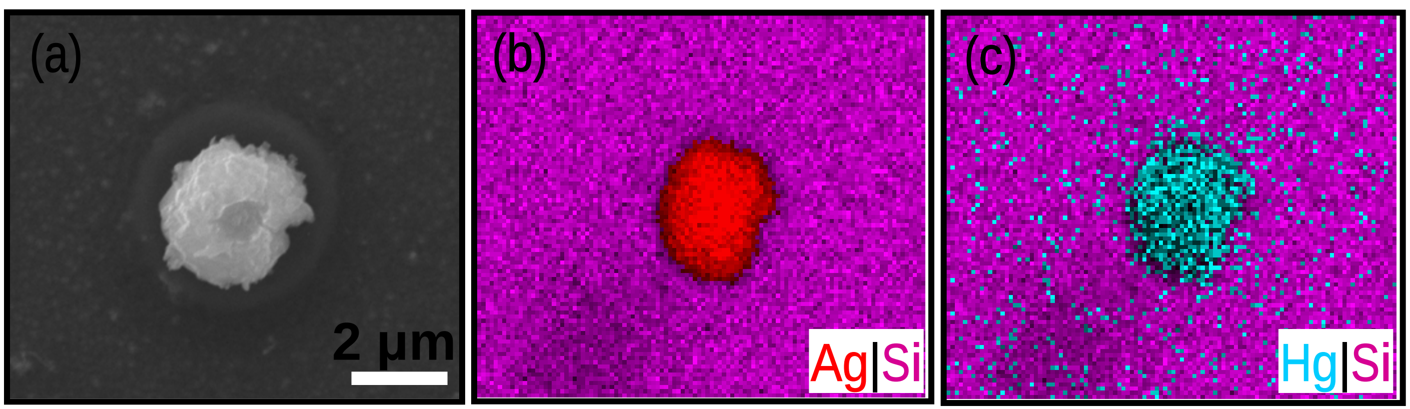
Product is marketed now
Cartridges are recovered after use

A pesticide test kit has been developed > 25 ppb

Noble metal nanoparticles: removal of heavy metals from water



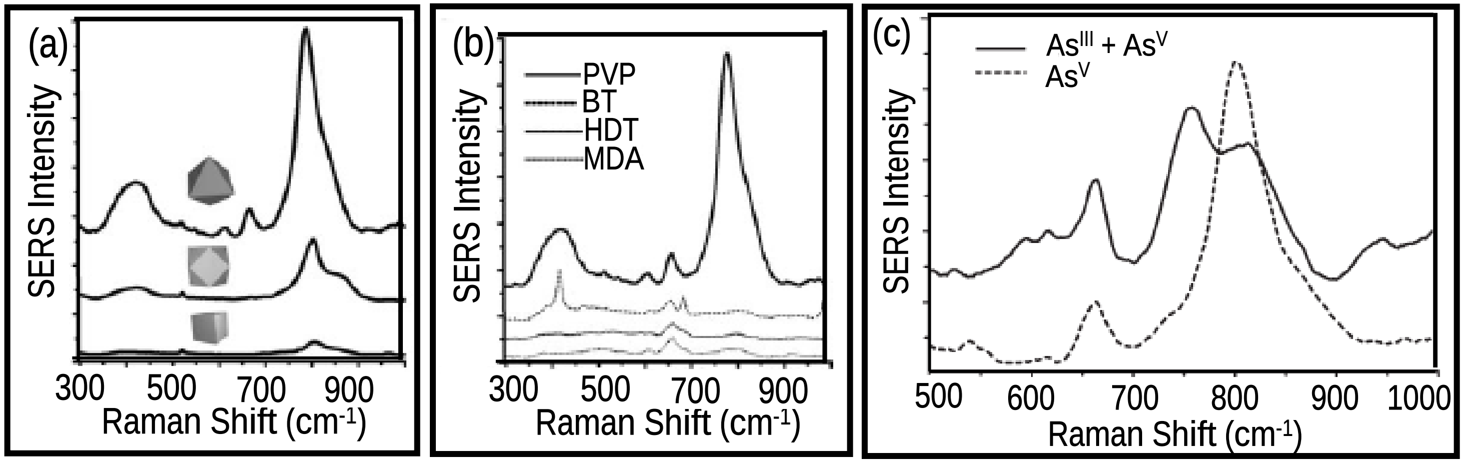
(a) UV-vis absorption spectra of silver nanoparticles (i) before Hg^{2+} treatment (ii-ix) after Hg^{2+} treatment. (b) Large area SEM image of the Ag-Hg bimetallic nanoparticles



(a) SEM image of an Ag-Hg alloy nanoparticle, (b) elemental image of Ag and (c) elemental image of Hg overlaid on Si (Si is from ITO substrate).

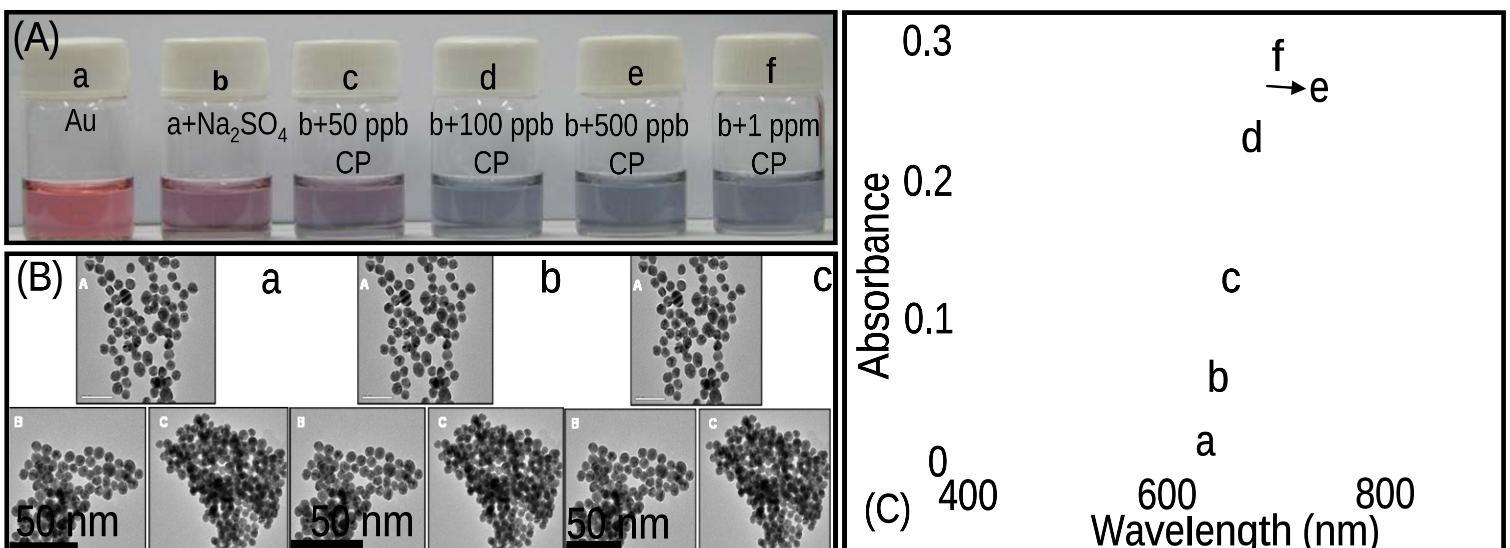
T. Pradeep et al (unpublished)

Noble metal nanomaterials: detection of toxic species



SERS spectra of arsenate ion ($1X10^{-6}$ M) on (a) LB films of silver nanocrystals (b) LB arrays of silver octahedra coated with various organic species. BT: benzenethiol, HDT: hexadecanethiol, MDA: mercaptodecanoic acid. (c) SERS-based speciation of arsenate and arsenite ions (18 ppb)

M. Mulvihill, A. Tao, K. Benjauthrit, J. Arnold, P. Yang, Angew. Chem. Int. Ed. 47 (2008) 6456



Colorimetric detection of chlorpyrifos using the gold nanoparticle-Na_2SO_4 system

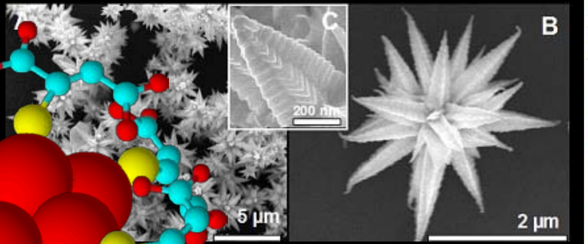
K.P. Lisha, Anshup, T. Pradeep, J. Environ. Sci. Health B. (in press)

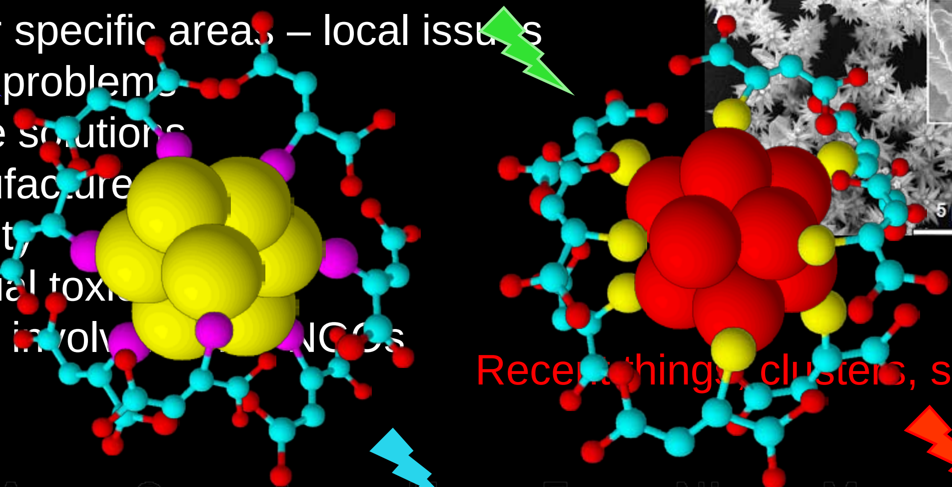
Current dev ents

350 nm

550 nm

- Purifiers for specific areas – local issues – seasonal problems
- All inclusive solutions
- Local manufacture
- Sustainability
- Nanomaterial toxi
- Community involv NGOs

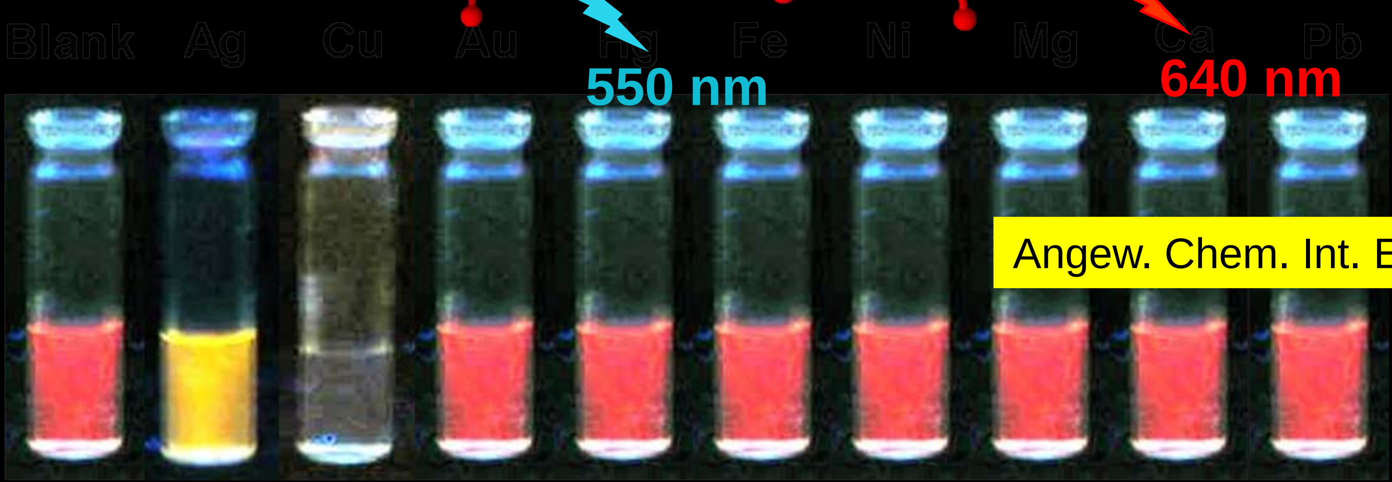


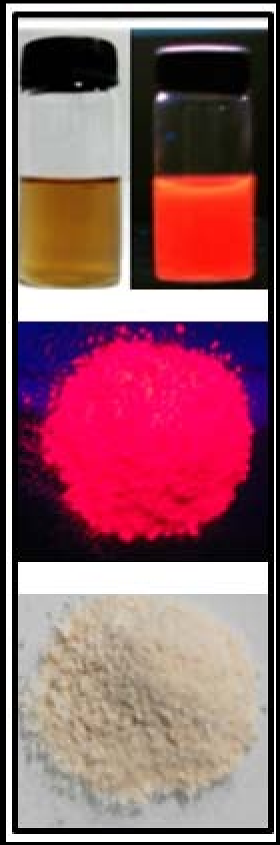


Recent things: clusters, sensing

550 nm

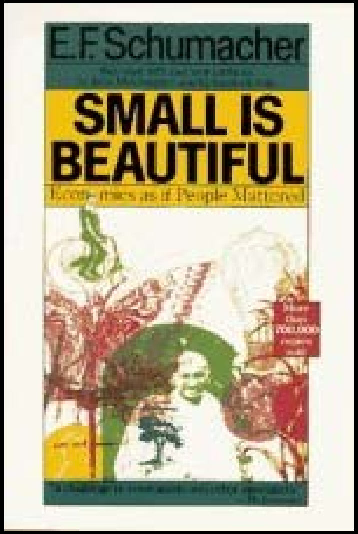
640 nm





Angew. Chem. Int. Ed. 2010 In Press

Several new technologies
Nanotubes
Dendrimers
Magnetic particles
Membranes
Self organised structures
Capacitive deionization



E. F. Schumacher

Pure water can be affordable…..

A technology solution may appear to you in one of these forms

Aquasure
Supreme 1800

Aquasure
Supreme 3000

Aquasure
Royal 3000

Forbes Futura

Aquasure Mobile
Water purifier

Aquasure
Storage 4-in-1

Aquasure
Storage UV


Pureit

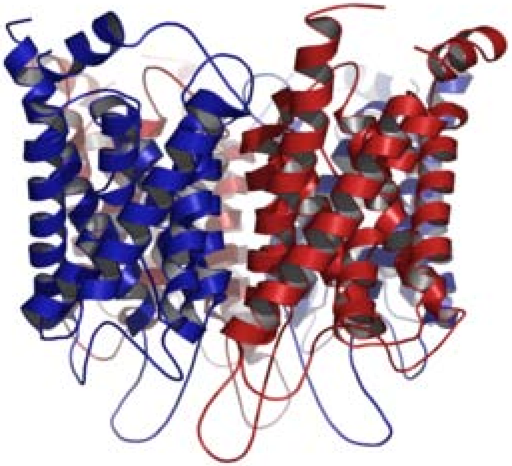

Tata Swach


Genzon
Water

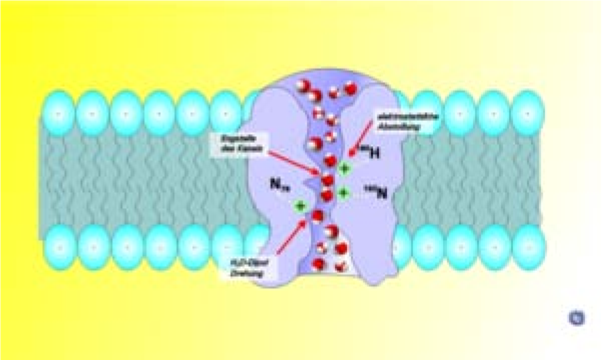
Aquasure Steel


Kenstar

For ultimate nanotechnology solutions, more work is needed



Crystallographic structure of the aquaporin 1 (AQP1) channel



Schematic depiction of water movement through the narrow selectivity filter of the aquaporin channel

Numerous areas: India and the world

Energy
Environment
Health
Water
Housing
-
-
-
-
Magnitude of our problems
Diversity of the country – regional implications
.-
-
Scientific challenges
-
-

Areas of collaboration

Areas of global significance

New sensors for ultralow sensing in water
Visual displays
Sustainable purification technologies; combining solar, membrane and materials
Water harvesting
Aquaporins

Industry oriented exchange programmes

IIT Madras

Nano Mission, Department of Science and Technology
World Gold Council
Well-meaning individuals

Thank you all