Innovations to address groundwater contamination

T. Pradeep

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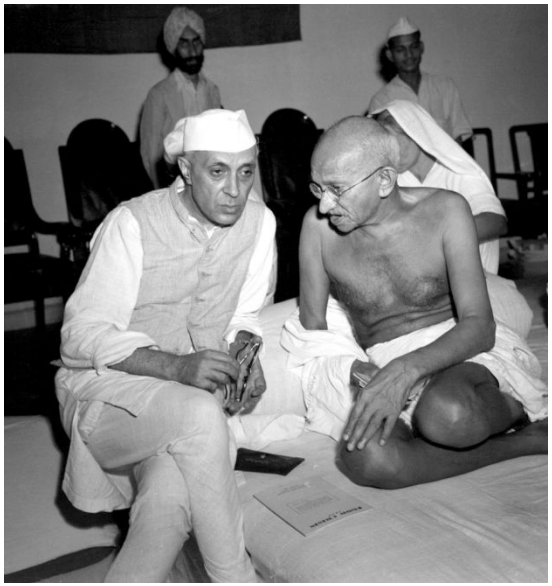
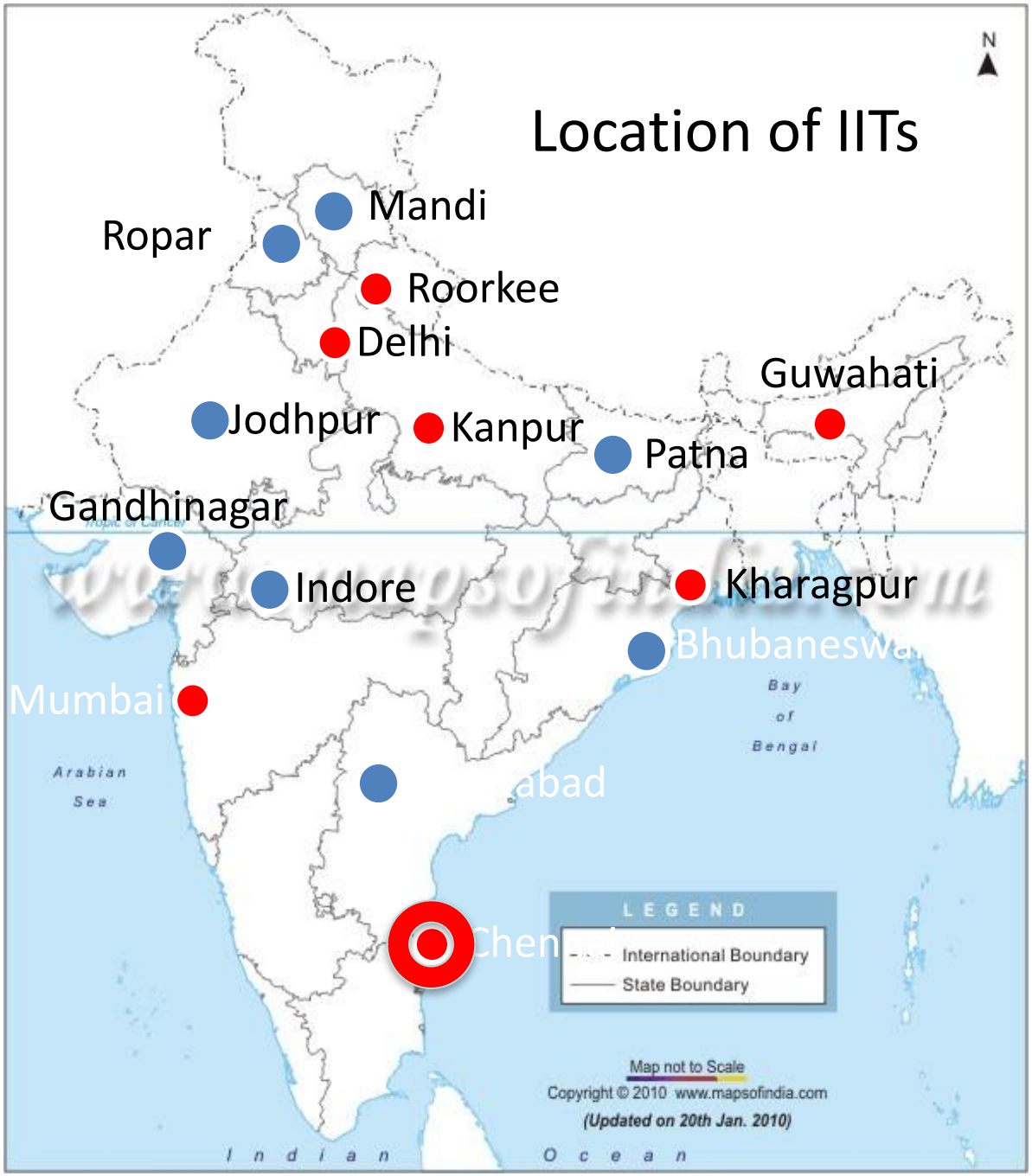
Indian Institute of Technology Madras
Chennai 600 036, India



South Asia Groundwater Forum, Jaipur, June 1-3, 2016


Location of IITs
N
Mandi
Ropar
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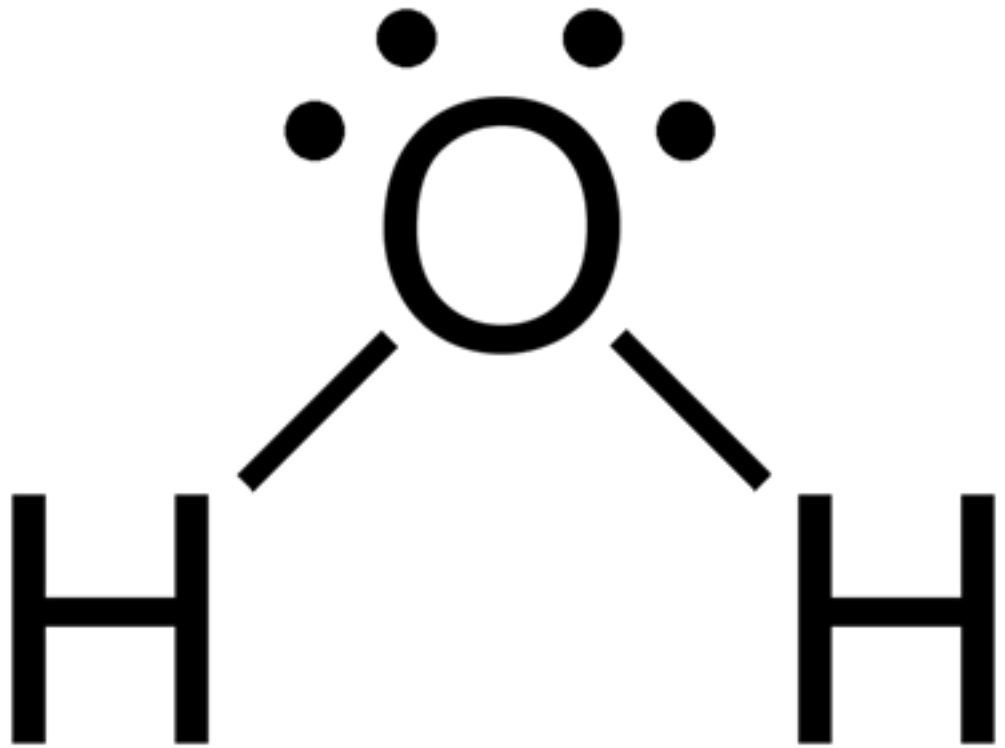
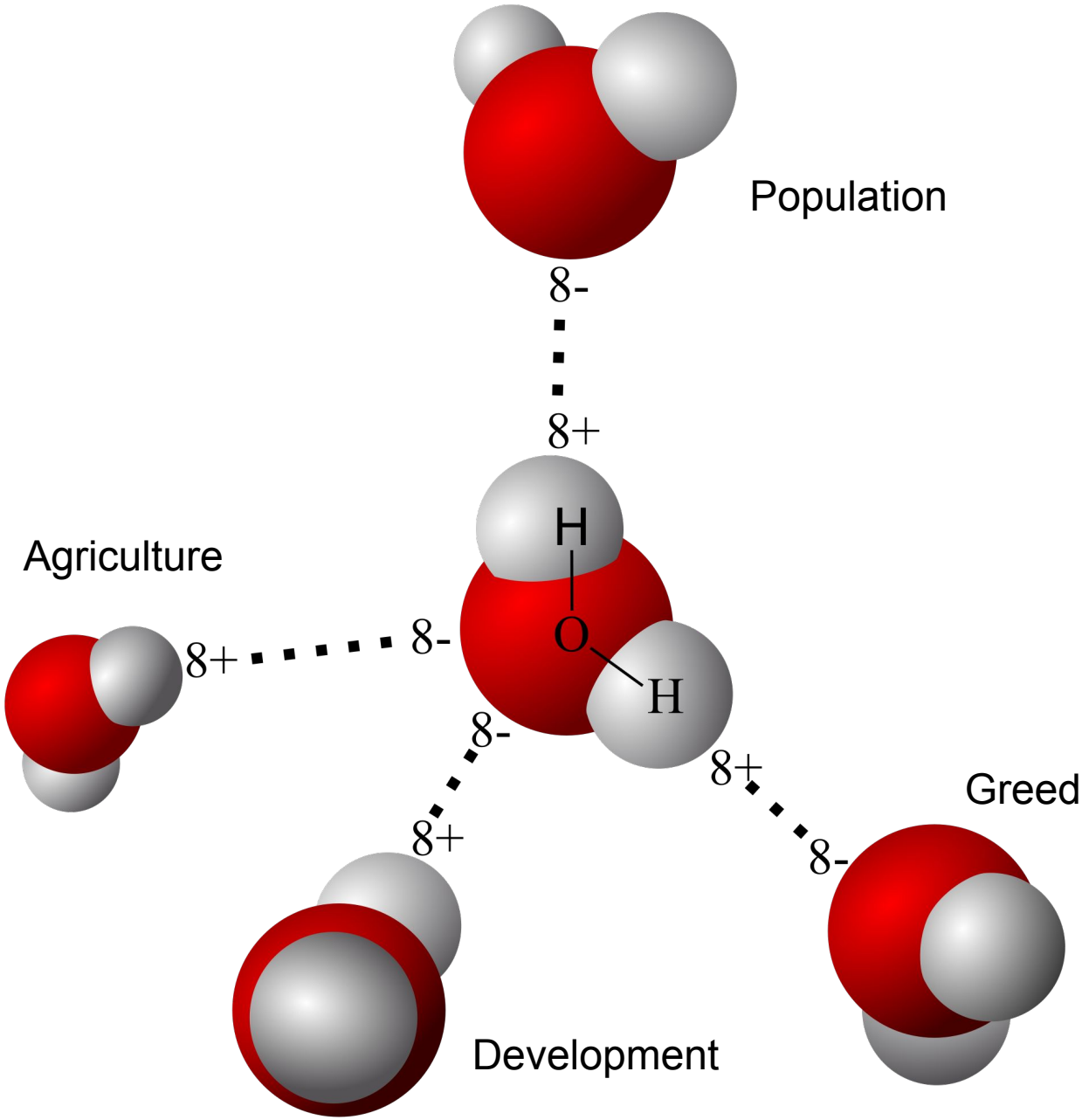
Delhi
Guwahati
Jodhpur
Kanpur
Patna
Gandhinagar
Indore
Kharagpur
Bhubaneswa
Mumbai
Bay
of
Bengal
Arabian
Sea
abad
Chen
LEGEND
International Boundary
State Boundary
Map not to Scale
Copyright © 2010 www.mapsofindia.com
(Updated on 20th Jan. 2010)
I n d i a n
O c e a n



Universal solvent


Population
δ-
δ+
H
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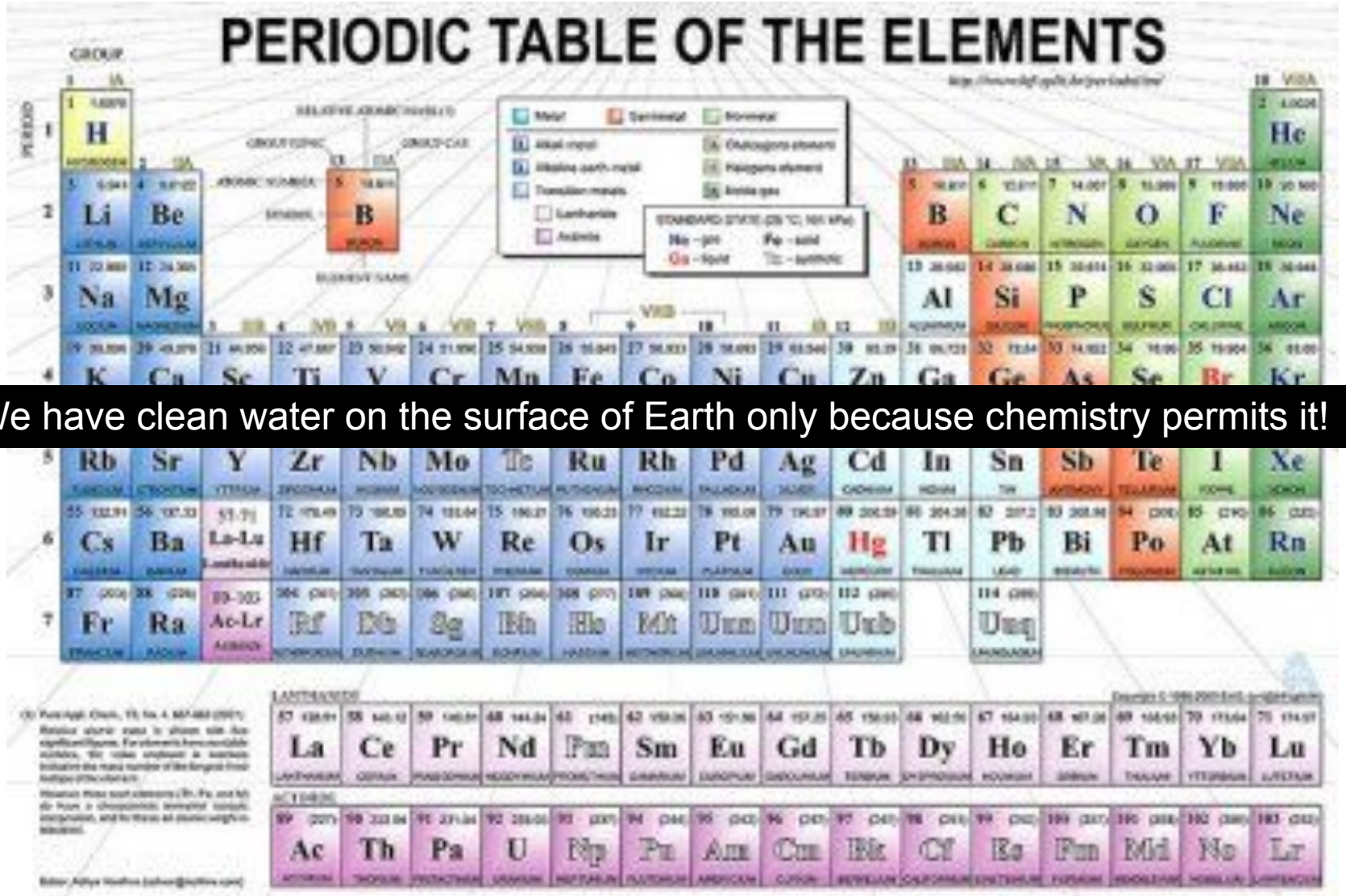
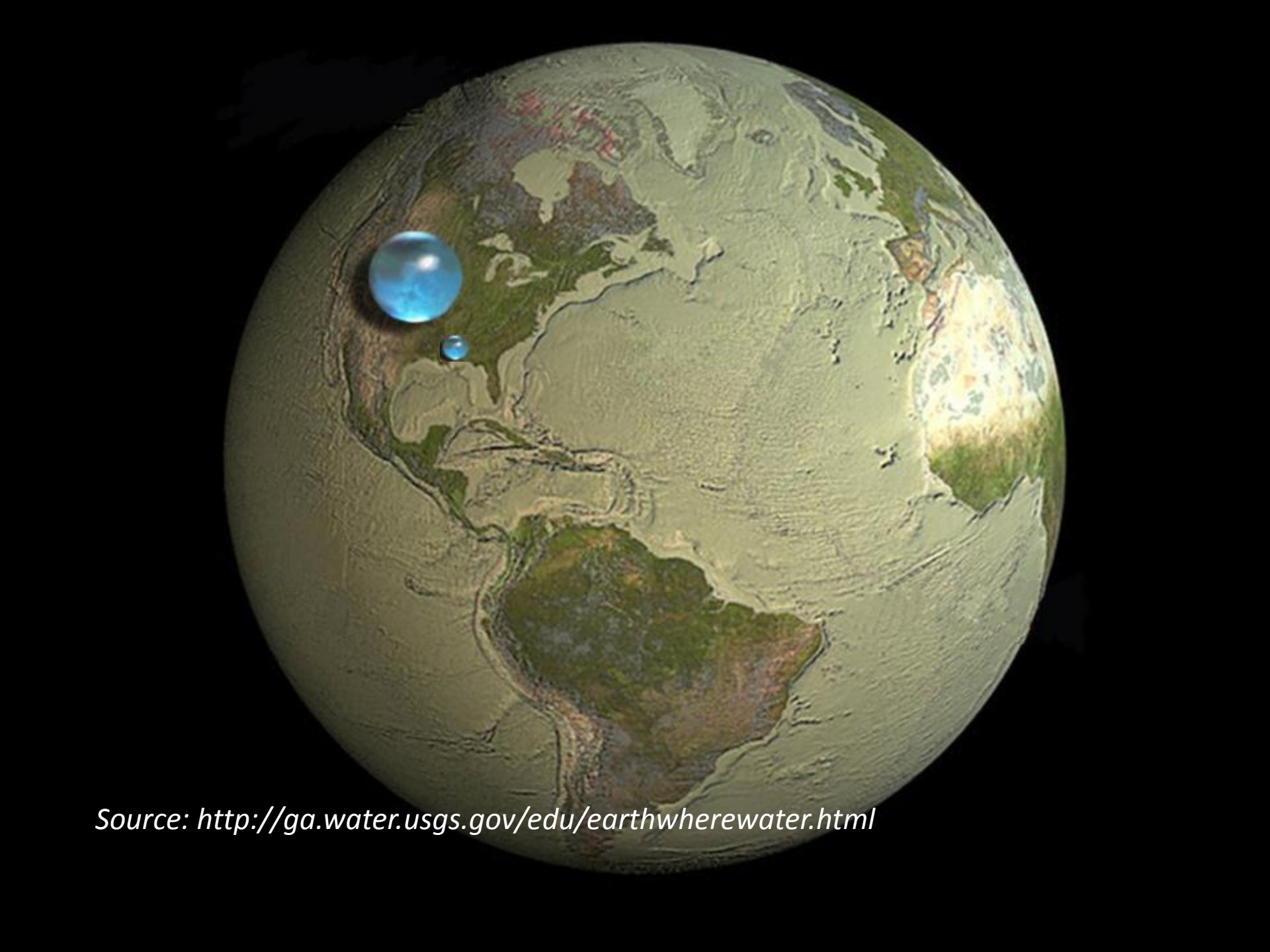
H
Agriculture
δ+
δ-
δ-
δ+
δ+
δ-
Greed
Development


PERIODIC TABLE OF THE ELEMENTS
We have clean water on the surface of Earth only because chemistry permits it!

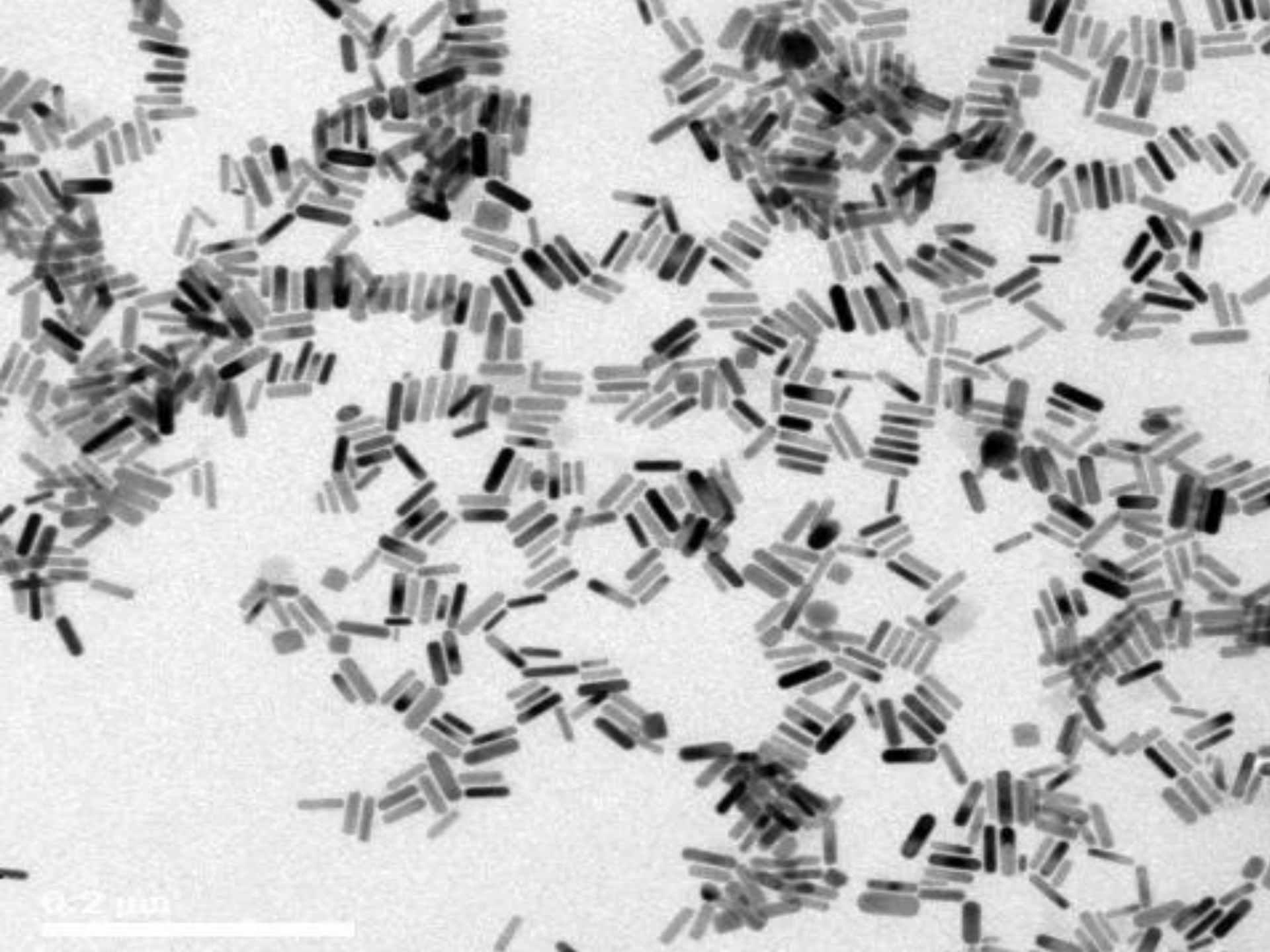


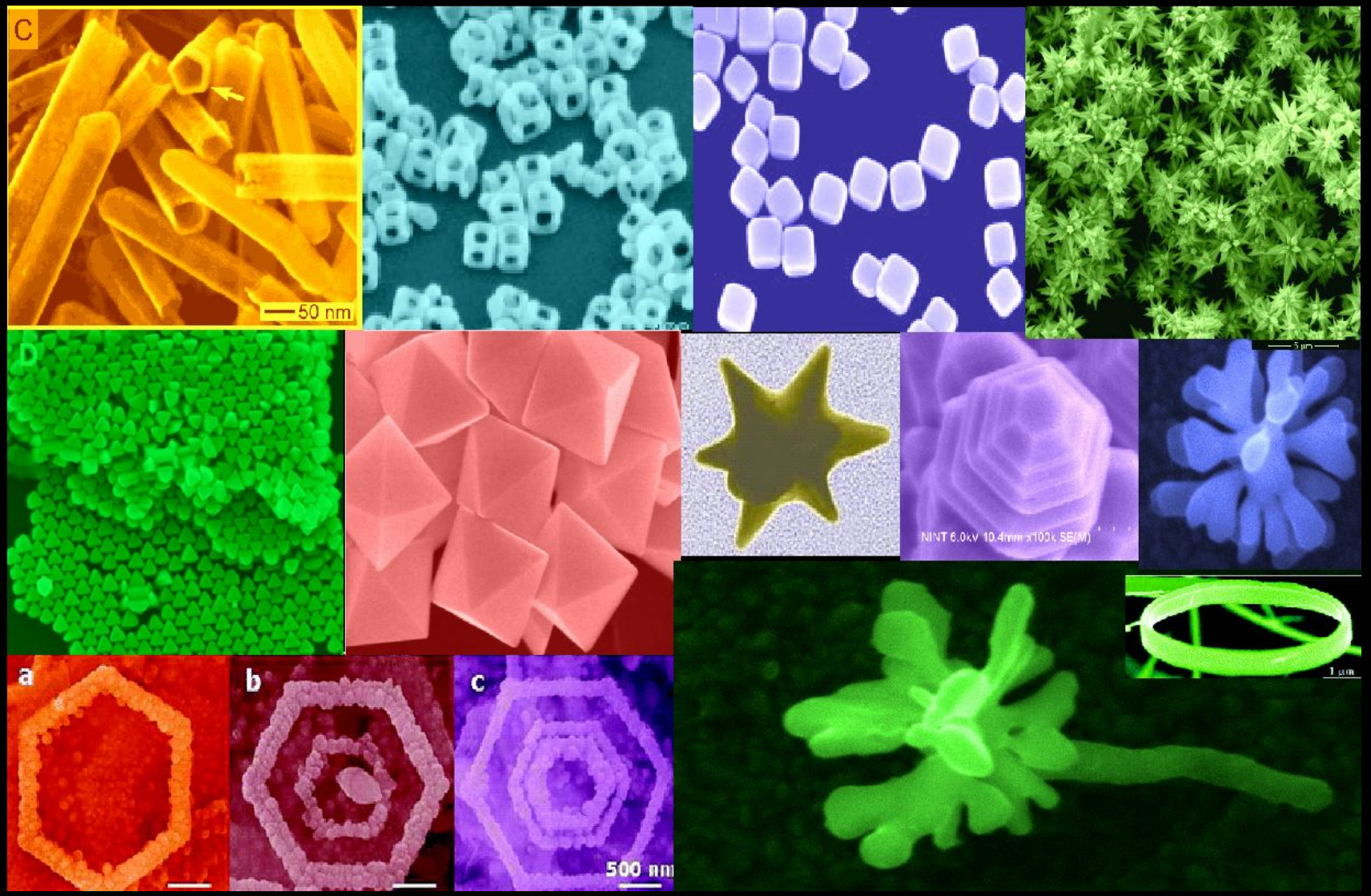
Source: http://ga.water.usgs.gov/edu/earthwherewater.html

Why nanotechnology?

Nano 10^{-9}

Quantum





Sajanlal and Pradeep, Kirk-Othmer Encyclopedia, 2012

www.pubs.acs.org
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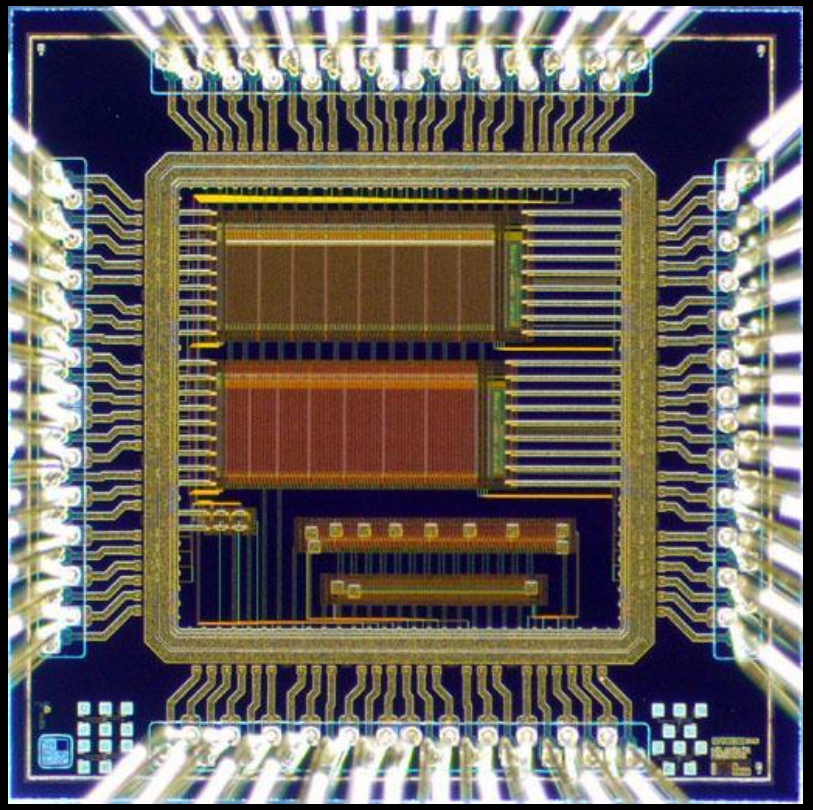
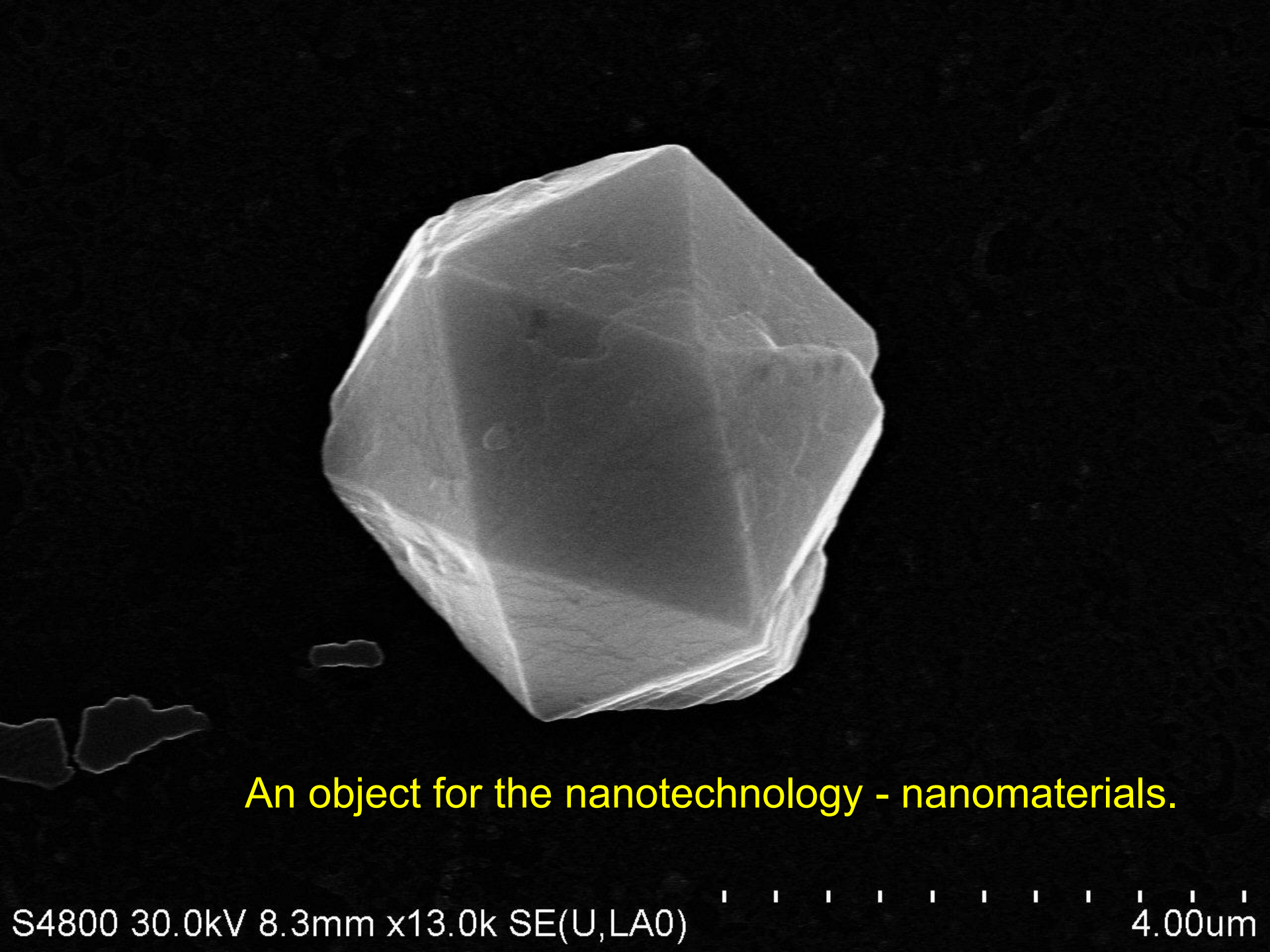
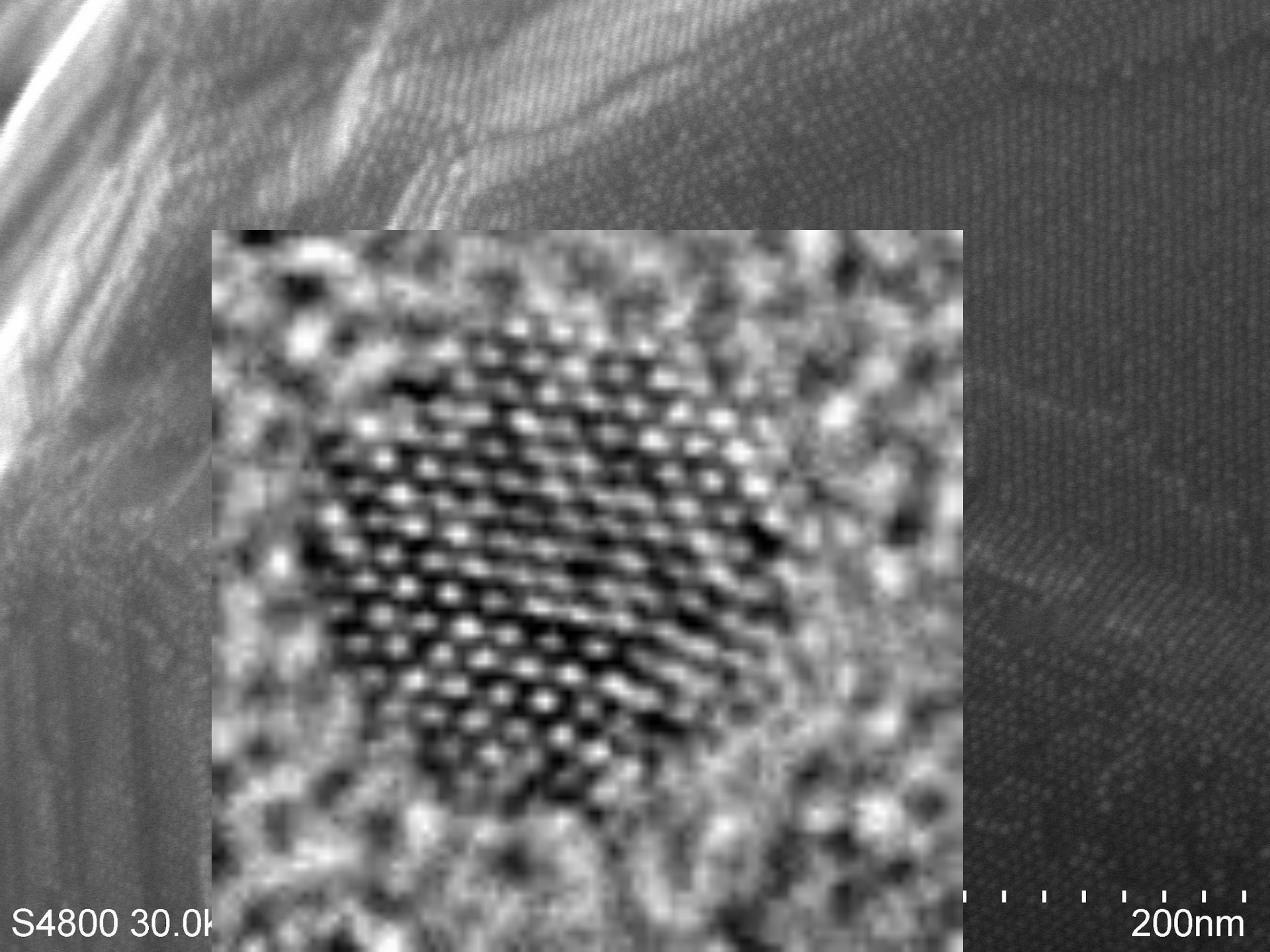
Technology is about manipulating objects

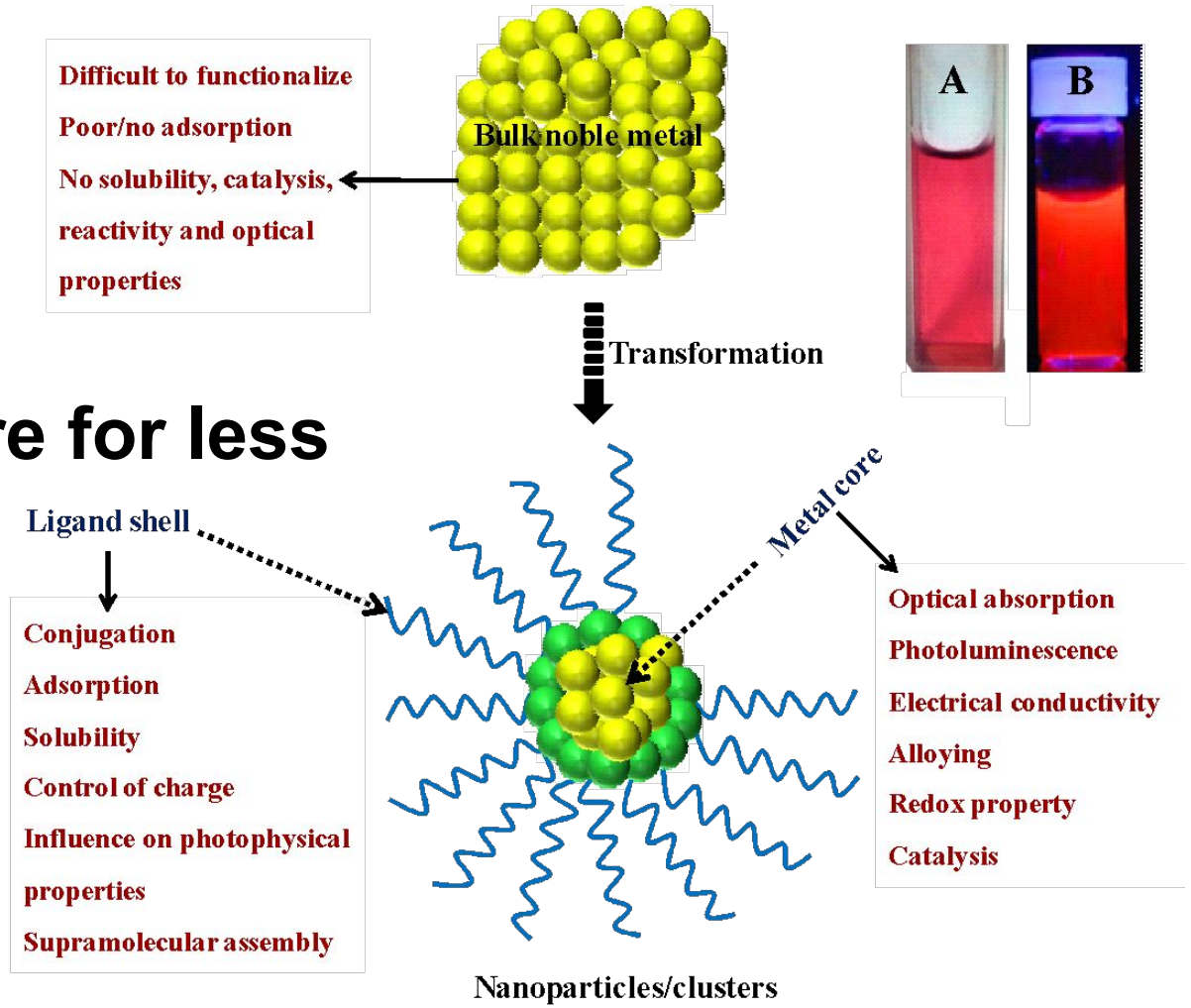


Growth of civilization reduced the size of objects manipulated


An object for the nanotechnology - nanomaterials.
S4800 30.0kV 8.3mm x13.0k SE(U,LA0)
4.00um

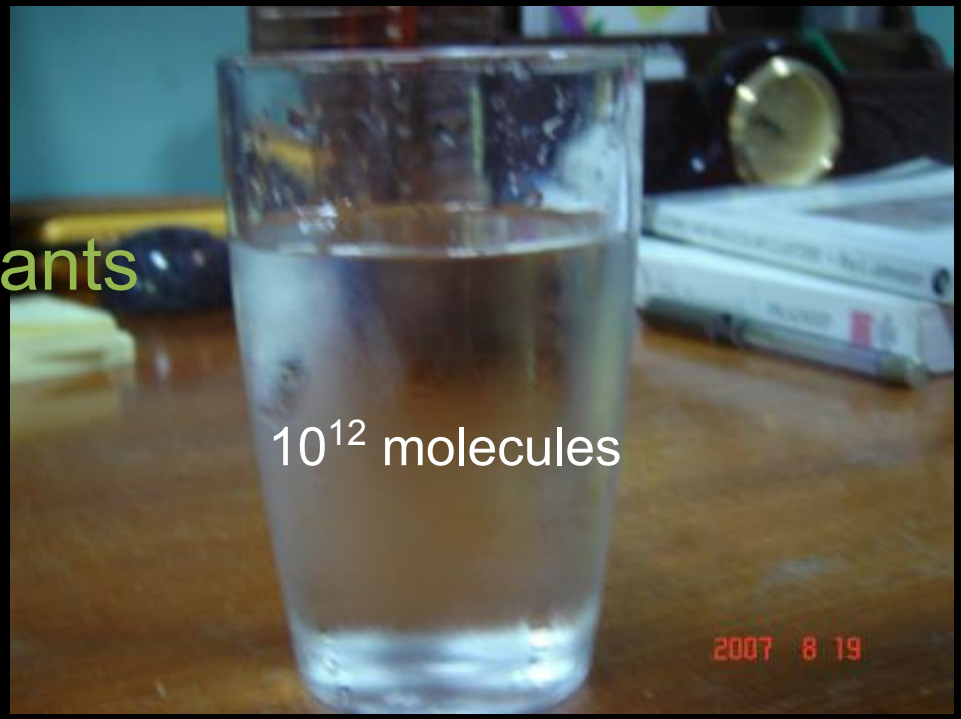

S4800 30.0k
200nm

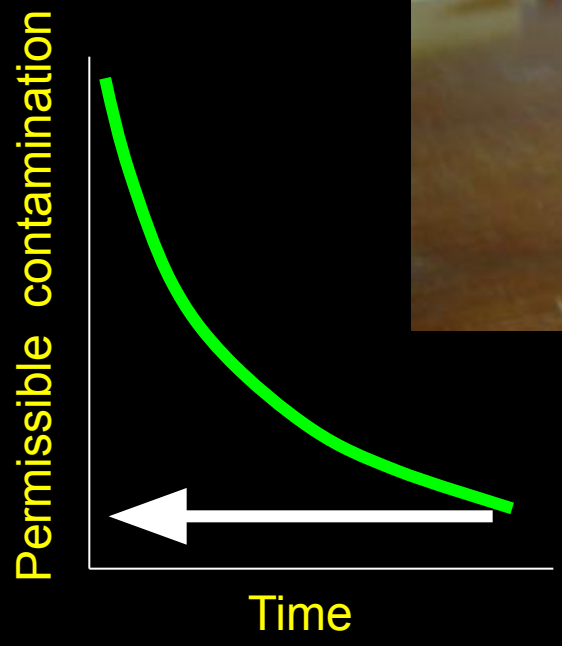
1. More for less



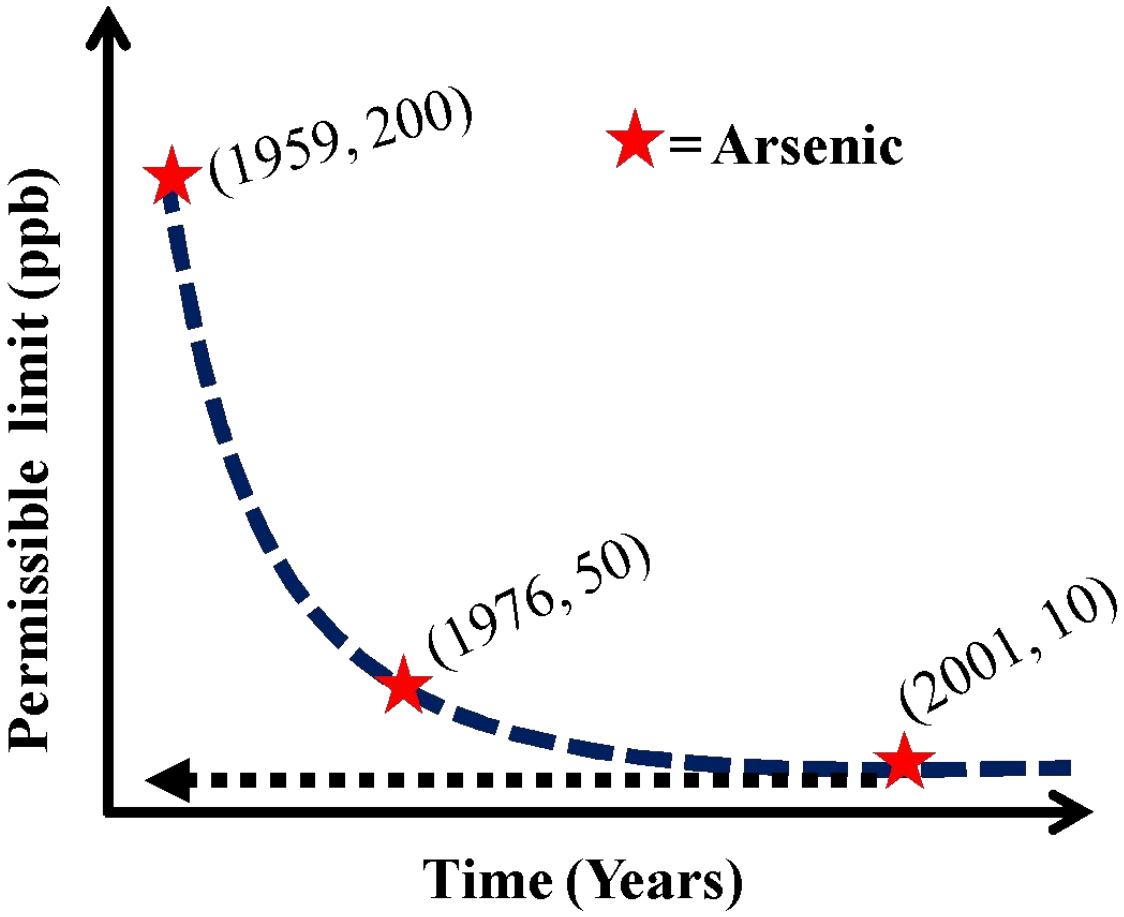
Variation in properties originating from ligand shell and metal core as bulk noble metals transform to nanoparticles/clusters. Sizes are not to scale. New properties such as color and photoluminescence arise in such size regime. Photographs of Au@citrate nanoparticles (inset A) showing intense absorption of visible light and Au@SG (SG corresponds to glutathione thiolate) clusters (inset B) showing intense photoluminescence upon ultraviolet irradiation (from the author's work).

2. Limits of contaminants



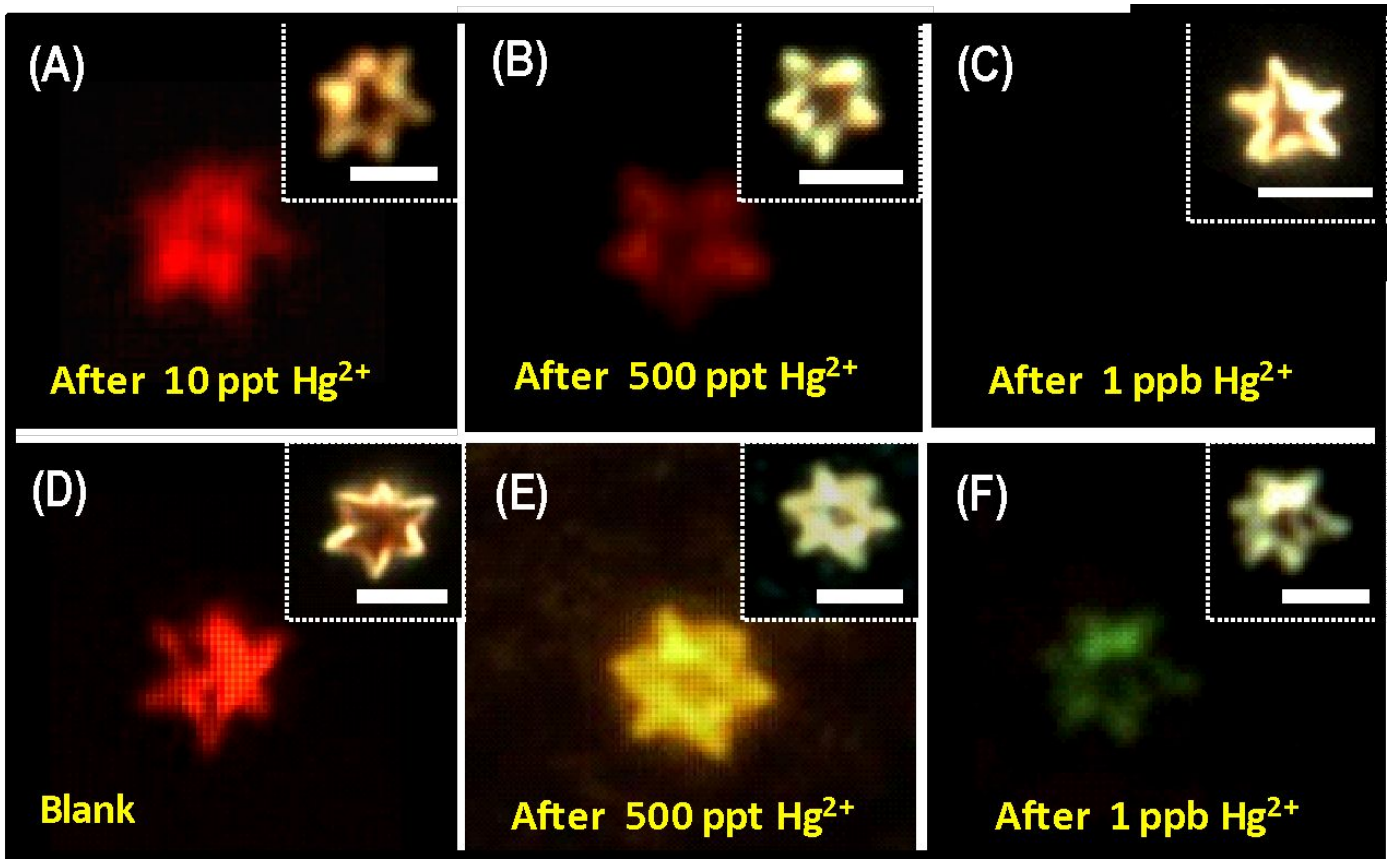


Permissible contamination reaches limits of detection



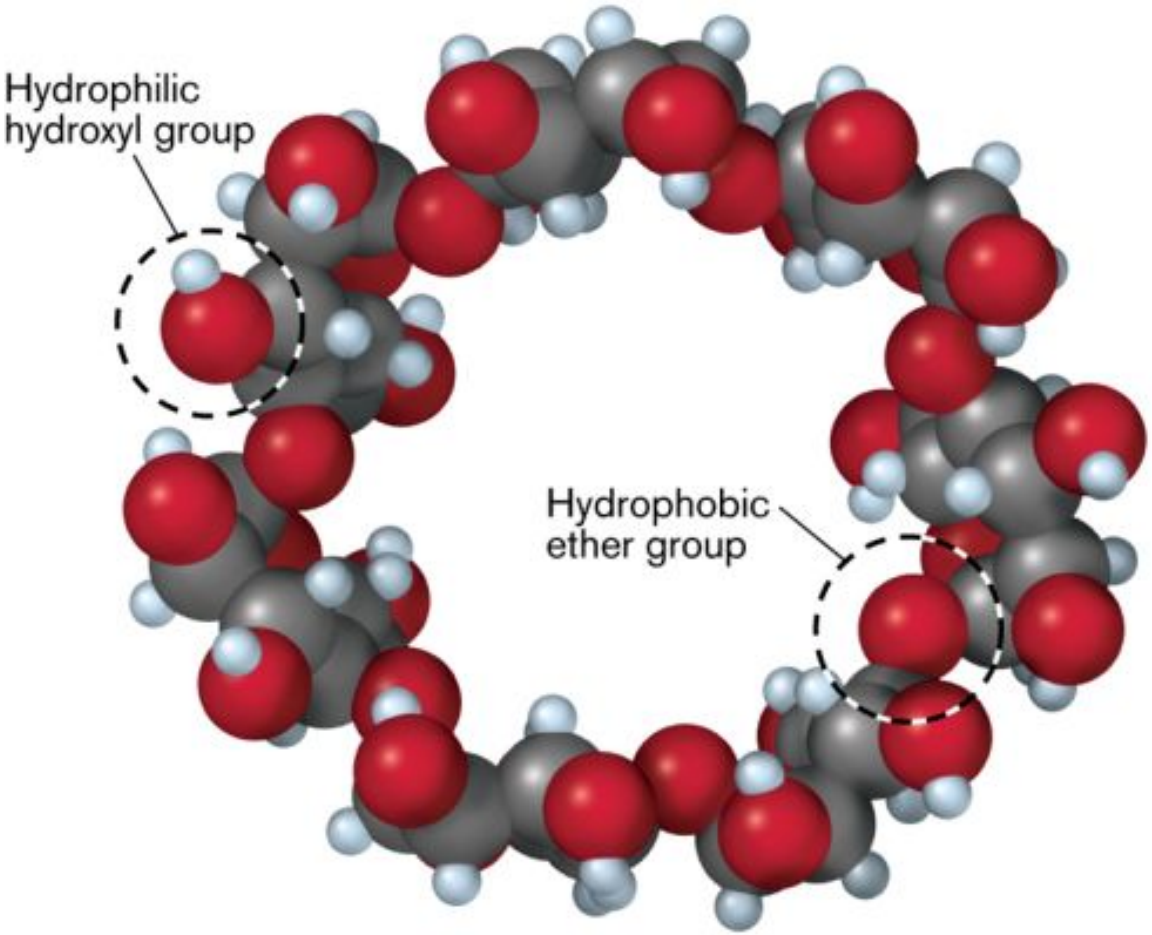
Decrease in the permissible limit of arsenic in drinking water, according to US EPA, with time. The graph indicates a general trend.

3. Can we reach limits?

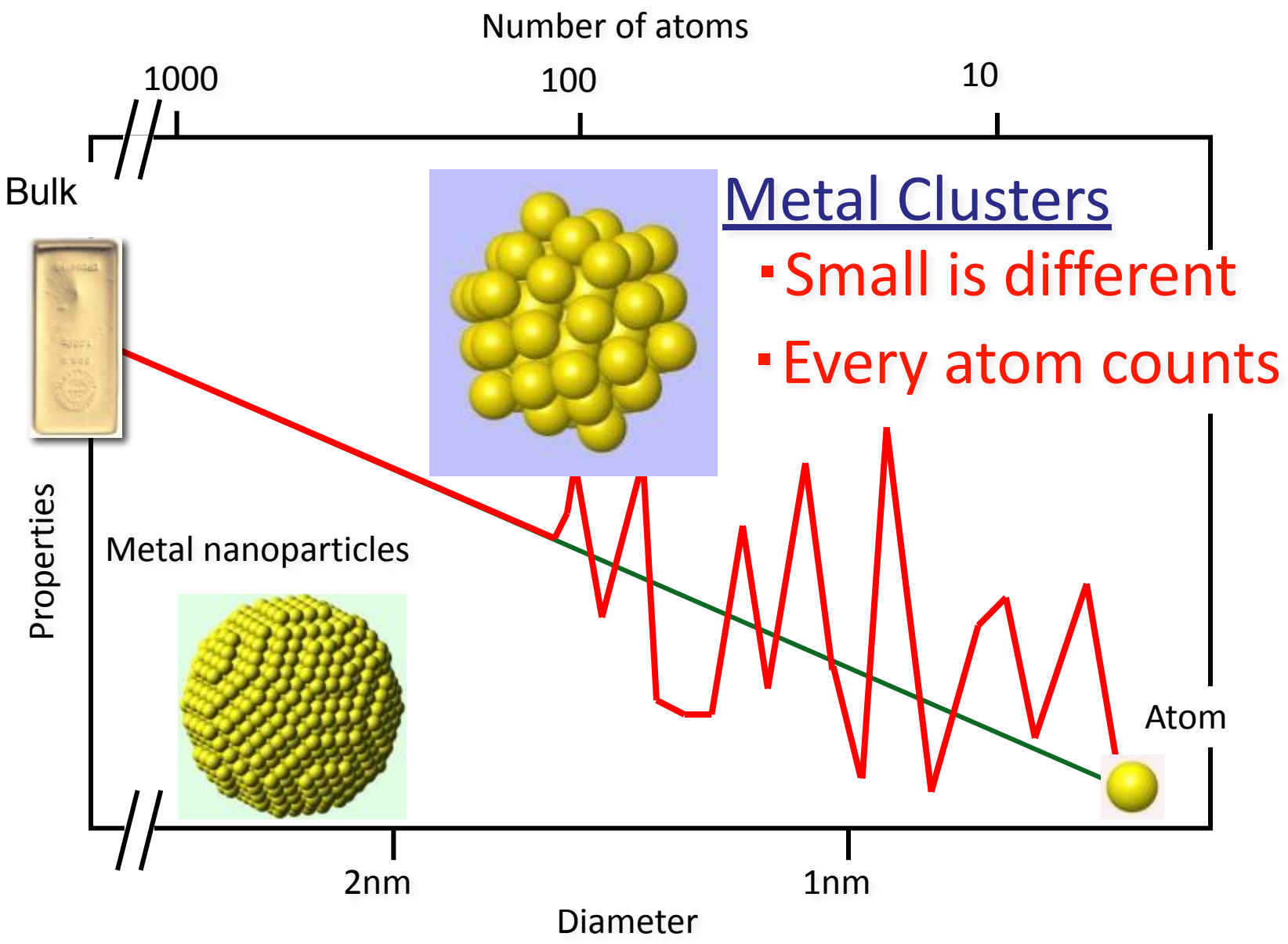


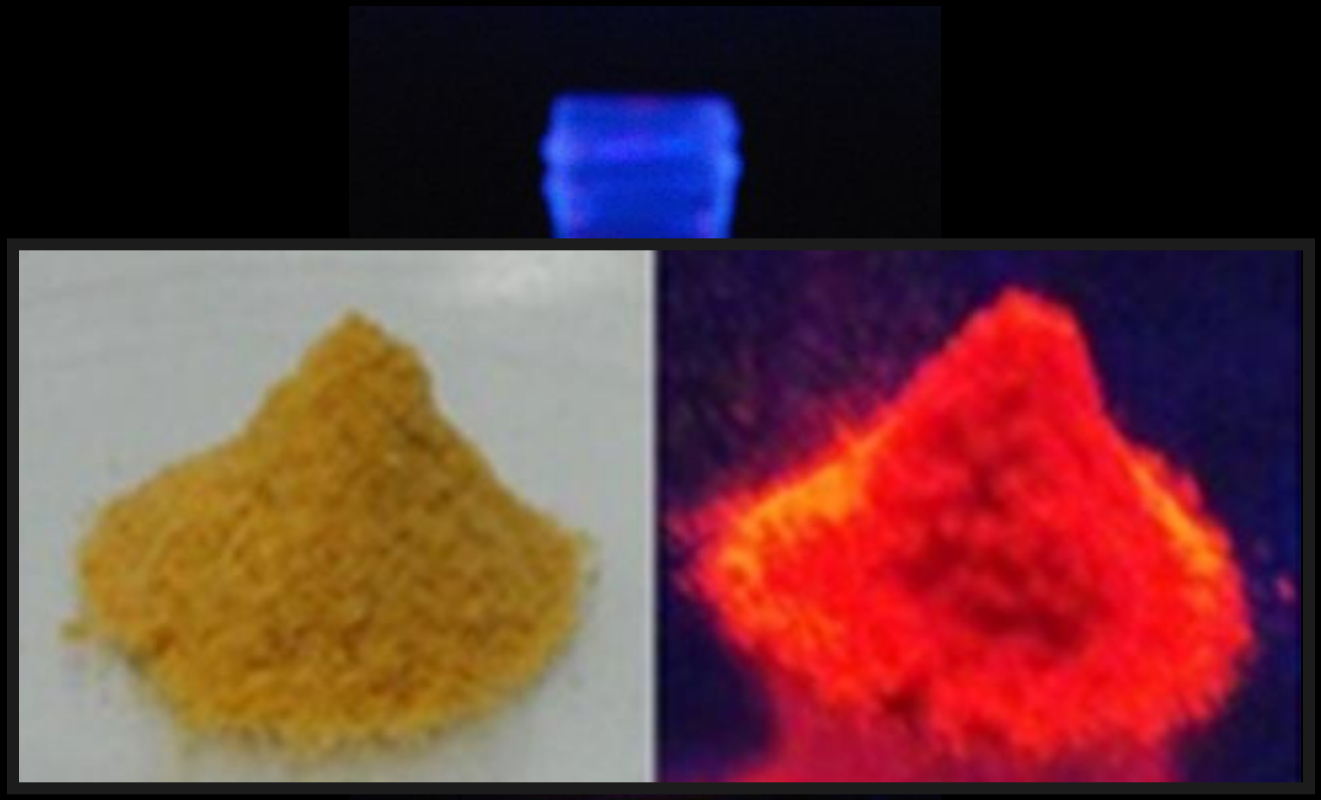
(A)–(C) Dark field fluorescence images of $Au@SiO_2@Ag_{15}$ MFs showing the gradual disappearance of luminescence with increasing Hg^{2+}. (D)–(F) Fluorescence images showing variation in color during the addition of Hg^{2+} of different concentrations to $Au@SiO_2$-FITC$@Ag_{15}$ MFs. Insets in all images show the corresponding optical images of the MFs; scale bars are 3 µm.

Cavities, channels, imprints, assemblies, fibres, …

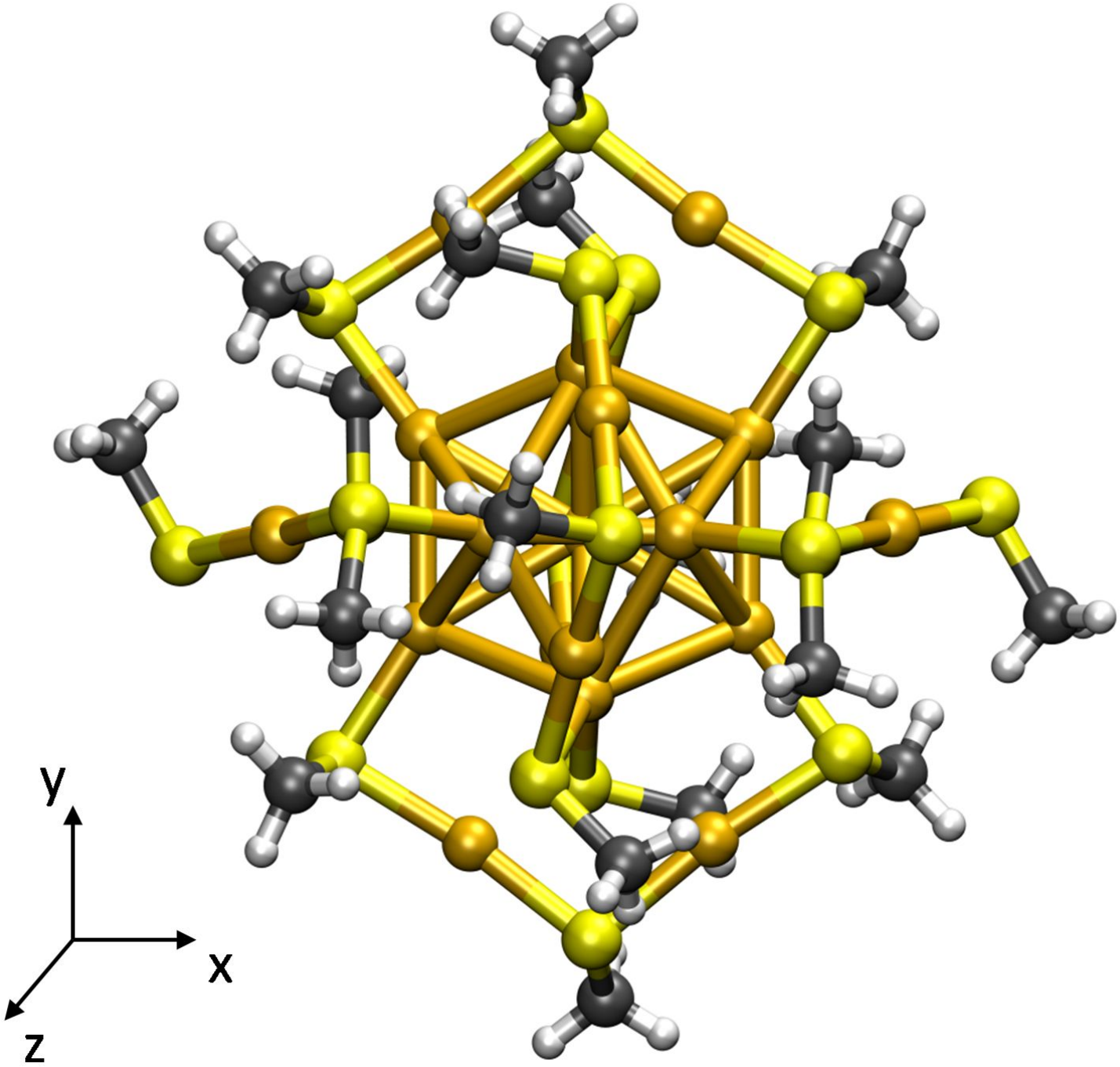


Metal Clusters





Shibhu, Habeeb, Uday, Kamalesh, Lourdu, Ammu, Ananya, Indranath, Atanu, ….


y
x
z

PNAS PNAS PNAS

Biopolymer-re nanocomposit water purifica

Mohan Udhaya Sankar[1], Saha Kamalesh Chaudhari, and Tha

Unit of Nanoscience and Thematic Uni

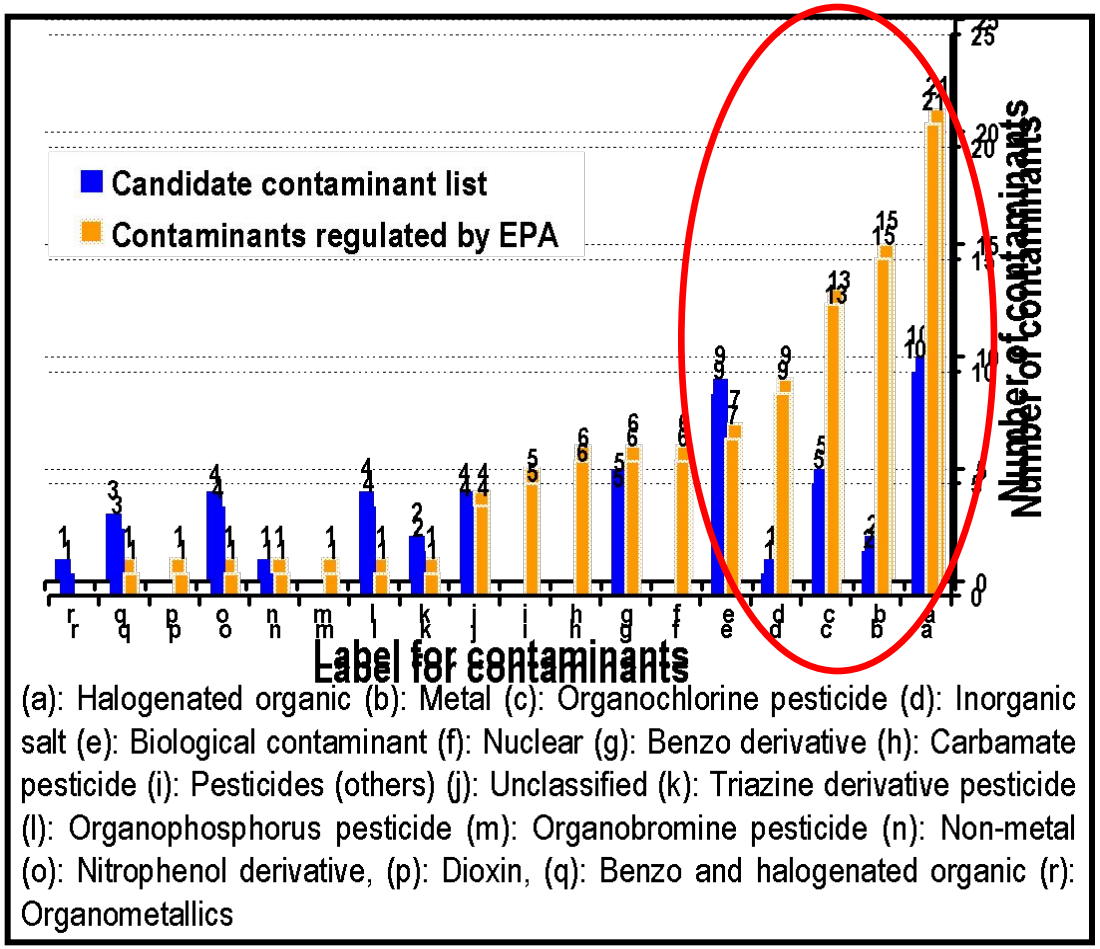
Edited by Eric Hoek, University of Calif

Creation of affordable materials fo water is one of the most promising drinking water for all. Combinin composites to scavenge toxic sp other contaminants along with th affordable, all-inclusive drinking v without electricity. The critical p synthesis of stable materials tha uously in the presence of comp drinking water that deposit and surfaces. Here we show that suc be synthesized in a simple and effe out the use of electrical power. T sand-like properties, such as highe forms. These materials have beer water purifier to deliver clean drin ily. The ability to prepare nanos ambient temperature has wide water purification.

hybrid | green | appropriate technolog

Featured in:
The Guardian, UK
The Hindu, Telegraph, Times of India, etc.
Scientific American
New Scientist
and many others

Future of water purification: An enigma with some pointers



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

Noble metal nanoparticles for water purification: A critical review, T. Pradeep and Anshup, Invited critical review, Thin Solid Films, 517 (2009) 6441-6478 (DOI: 10.1016/j.tsf.2009.03.195).

World's first nanochemistry-based water purifier

RSC | Advancing the Chemical Sciences

Chemistry World

Pesticide filter debuts in India

20 April 2007

Kilugudi 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.

'Our pesticide filter 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 (CCl_4) 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 [illegible] water supplies.

Use and recycle

The resid[illegible] Pra[illegible]

Mum[illegible] nanotech[illegible] novel,' Sastry

Chemistry world

First ever nanotechnology product for clean water

A plant to make supported nanomaterials for water purification; with capacity of 4.5 tons per month, 2007

1. Patents: A method of preparing purified water from water containing pesticides, **Indian patent 200767**
2. Extraction of malatheon and chlorpiryhphos from drinking water by nanoparticles , **US 7,968,493** A method for decontaminating water containing pesticides, **EP 17,15,947**

Product is marketed now by a Eureka Forbes Ltd.

Several new technologies are now available

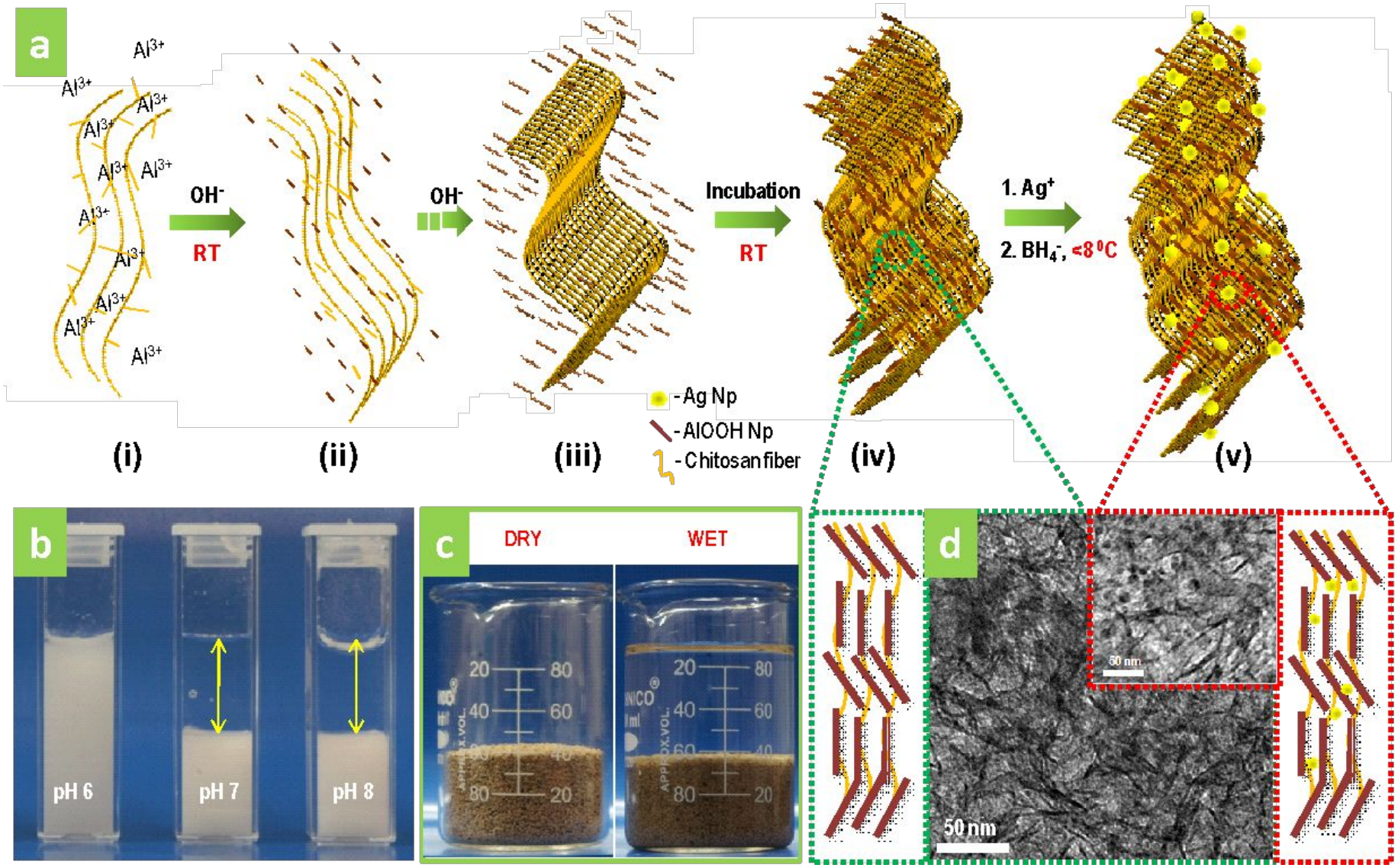
Affordable materials for water purification - Bioinspired

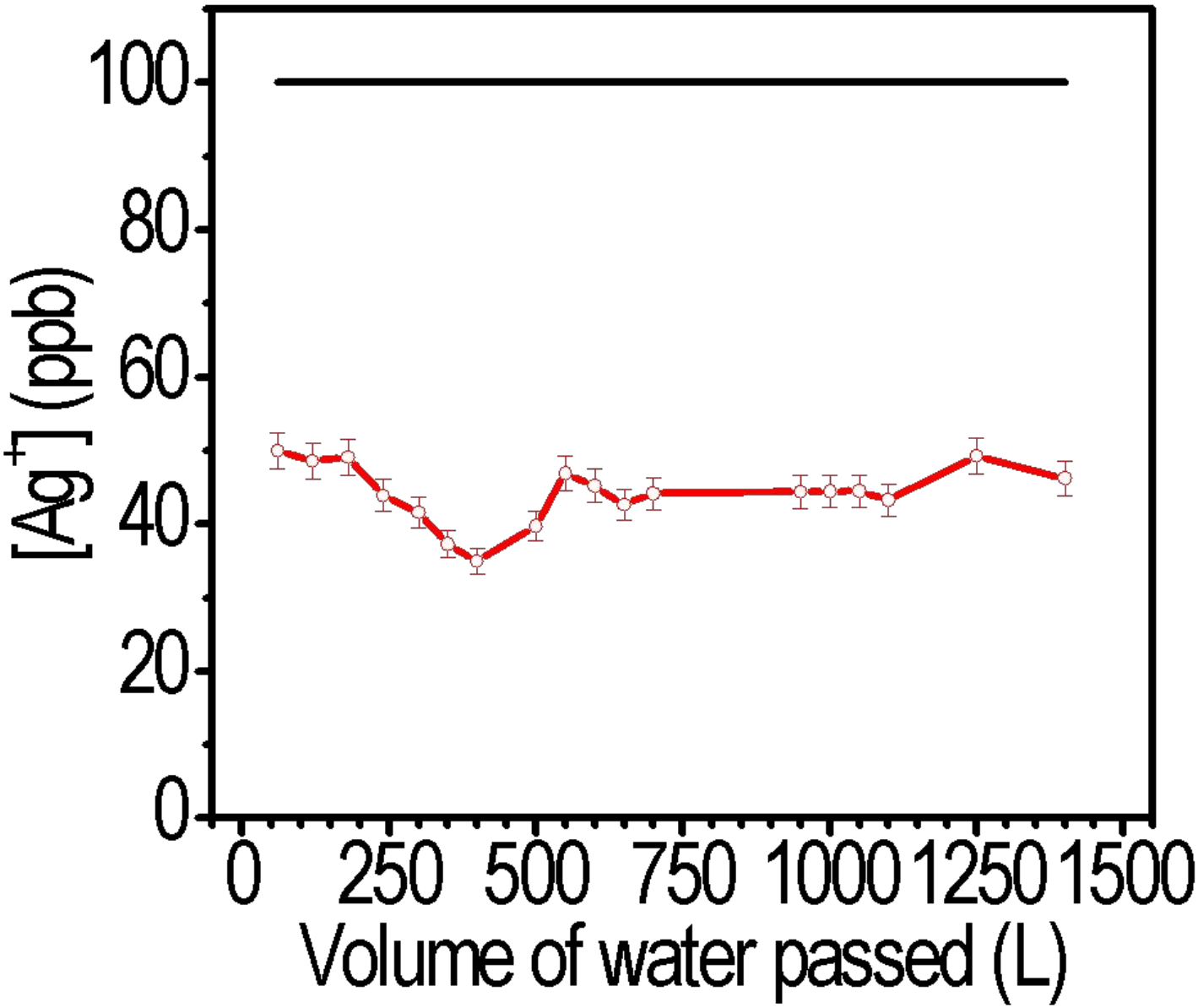
Water positive

Water-based, room temperature, water stable

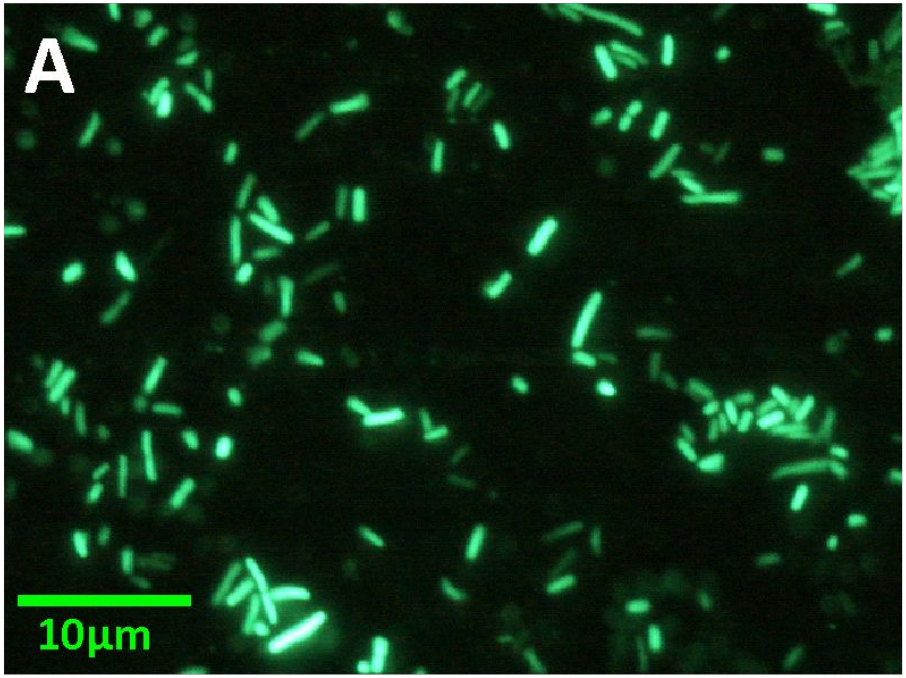
Green

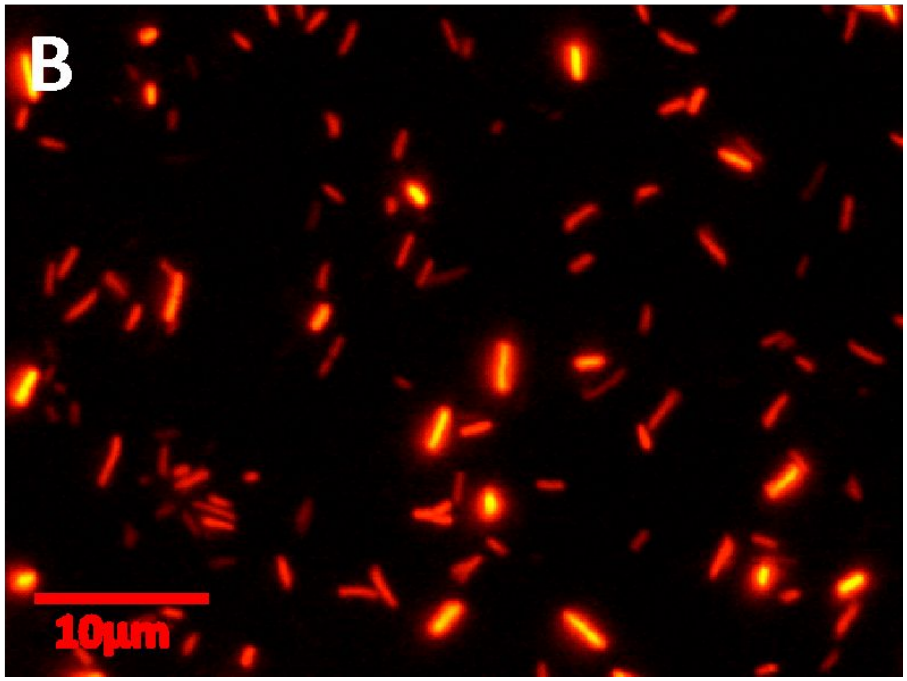
M. U. Sankar et al, PNAS 2013


a
Al3+
OH-
RT
OH-
Incubation
RT
1. Ag+
2. BH4-, ≤8 0C
- Ag Np
- AlOOH Np
- Chitosan fiber
(i)
(ii)
(iii)
(iv)
(v)
b
pH 6
pH 7
pH 8
c
DRY
WET
d
50 nm
50 nm

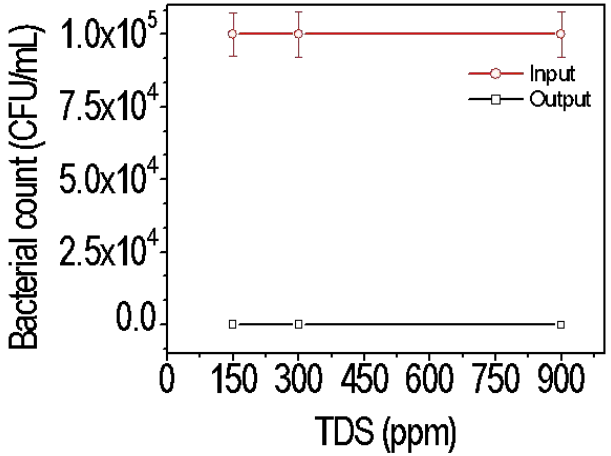

100
80
60
40
20
0
[Ag+] (ppb)
0
250
500
750
1000
1250
1500
Volume of water passed (L)

Live/dead staining experiments



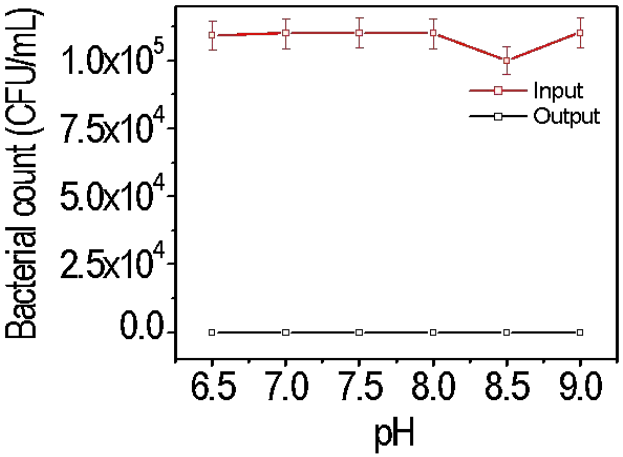


A



TDS

B

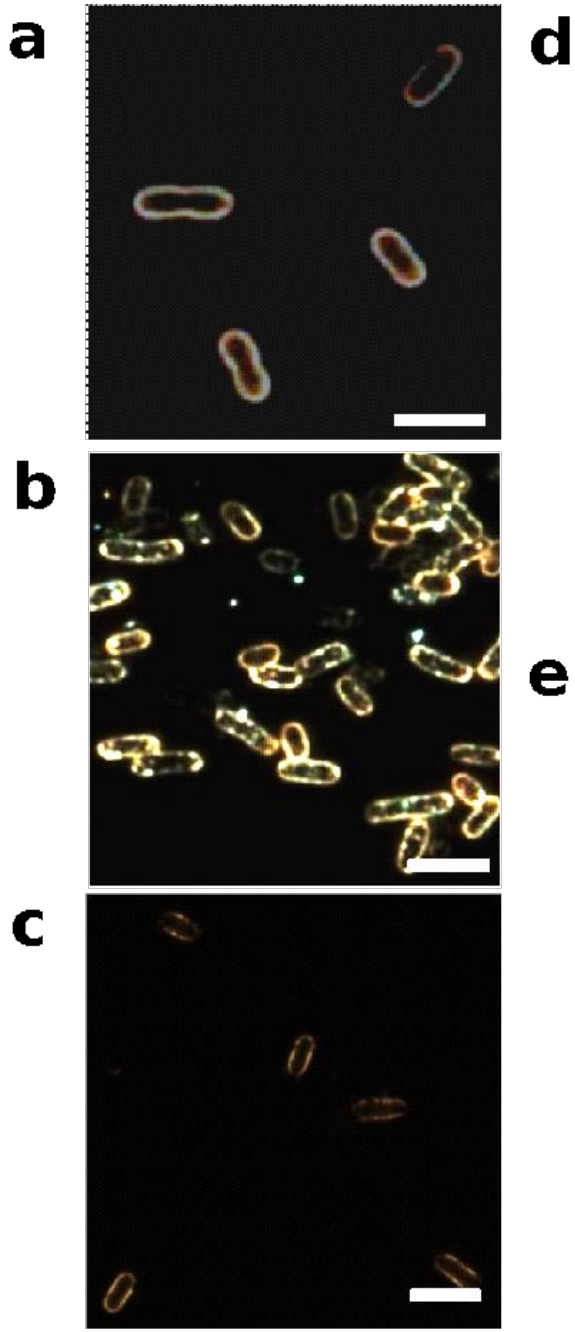


pH

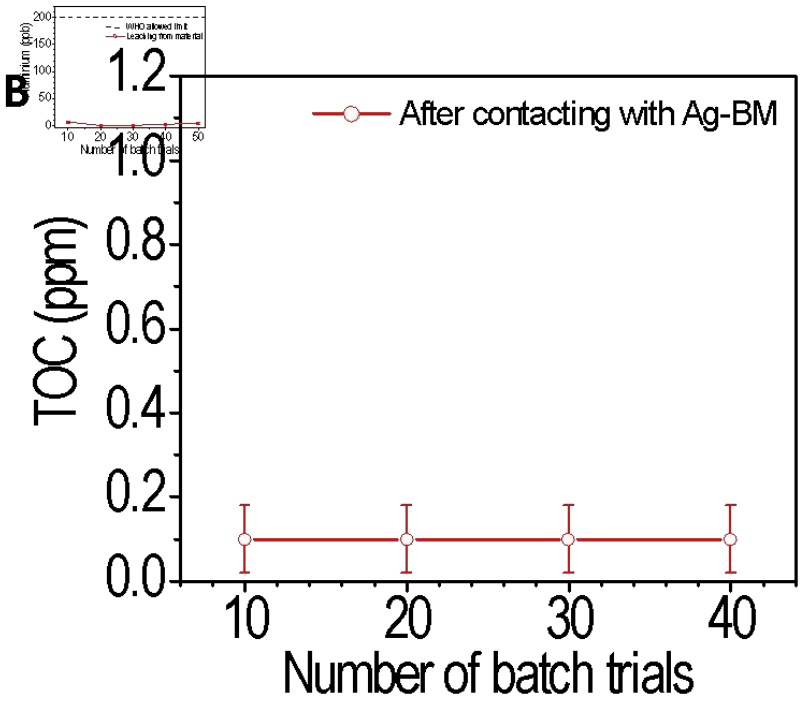
Real water experiments

C

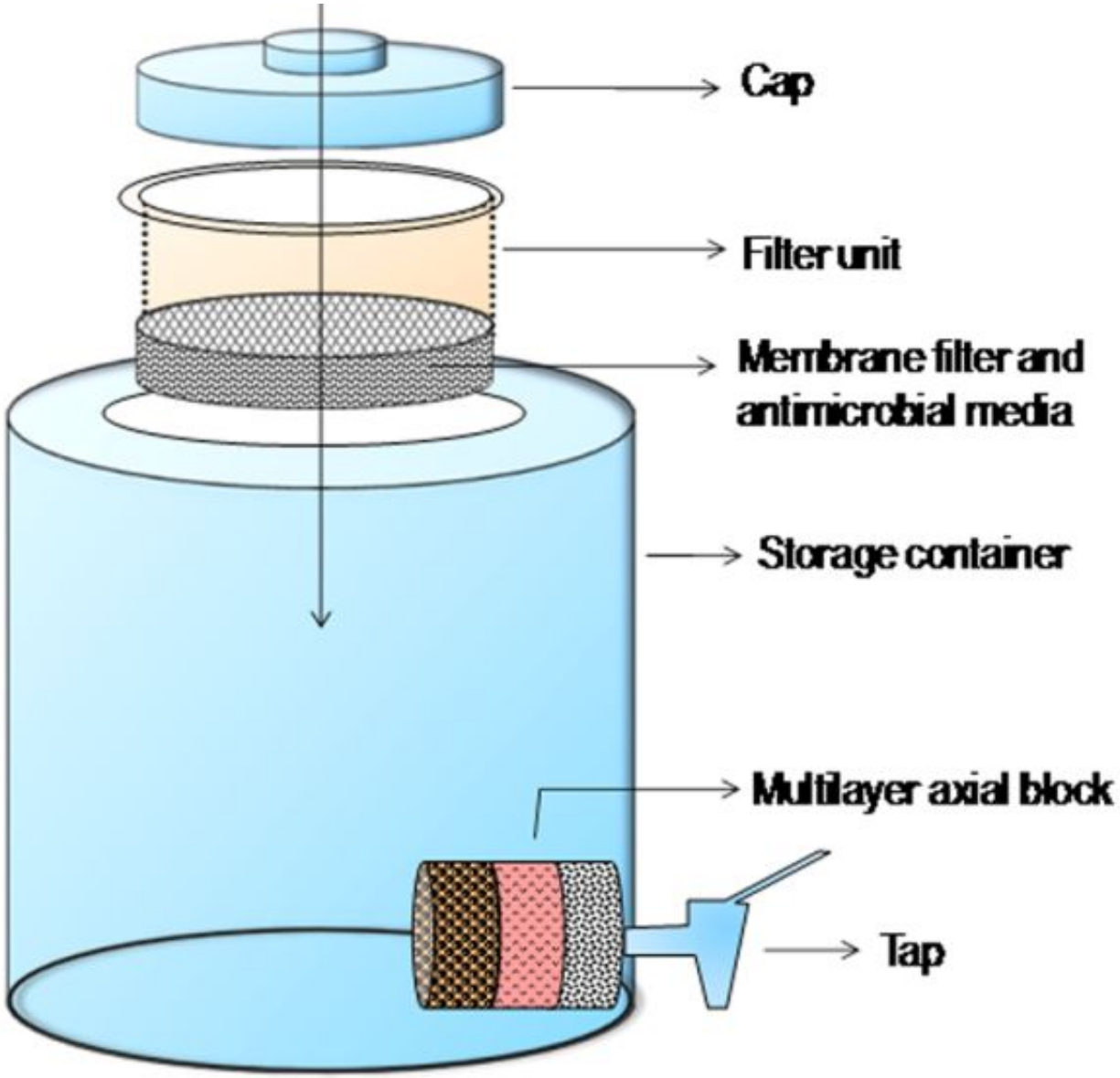
TOC – Humic acid


a
b
c
d
e
Scatte
400
60
Wa

A



Leaching experiments


Cap
Filter unit
Membrane filter and antimicrobial media
Storage container
Multilayer axial block
Tap

Physicochemical characteristics of influent natural drinking water

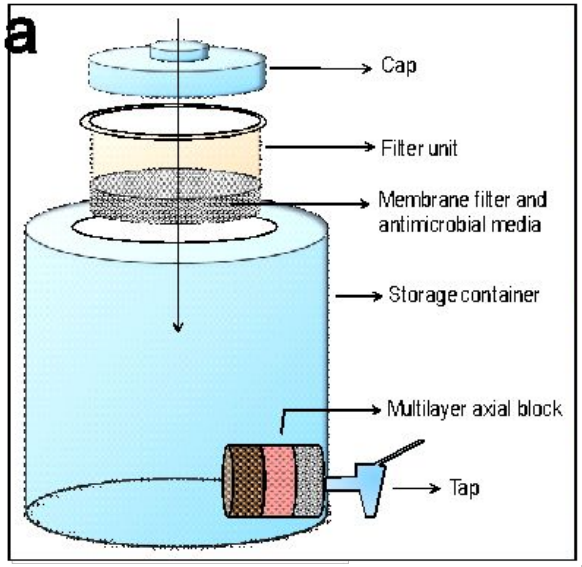
(Note: All parameters are expressed in mg L^{-1}, except for pH and conductivity)

ND-not detected

Natural drinking water (without treatment so that there is a residual bacterial count in it) was used for testing to ensure that that the material functions in the field.

Parameters	Value
Total coliforms (CFU/mL)	1-2 x 10^3
p H @25°C	7.8
Conductivity (µS/cm)	640.000
Fluoride	0.573
Chloride	86.340
Nitrate	1.837
Sulphate	32.410
Silicate	15.870
Lithium	ND
Sodium	53.740
Ammonium	ND
Potassium	2.330
Magnesium	14.340
Calcium	28.720

a


Cap
Filter unit
Membrane filter and antimicrobial media
Storage container
Multilayer axial block
Tap

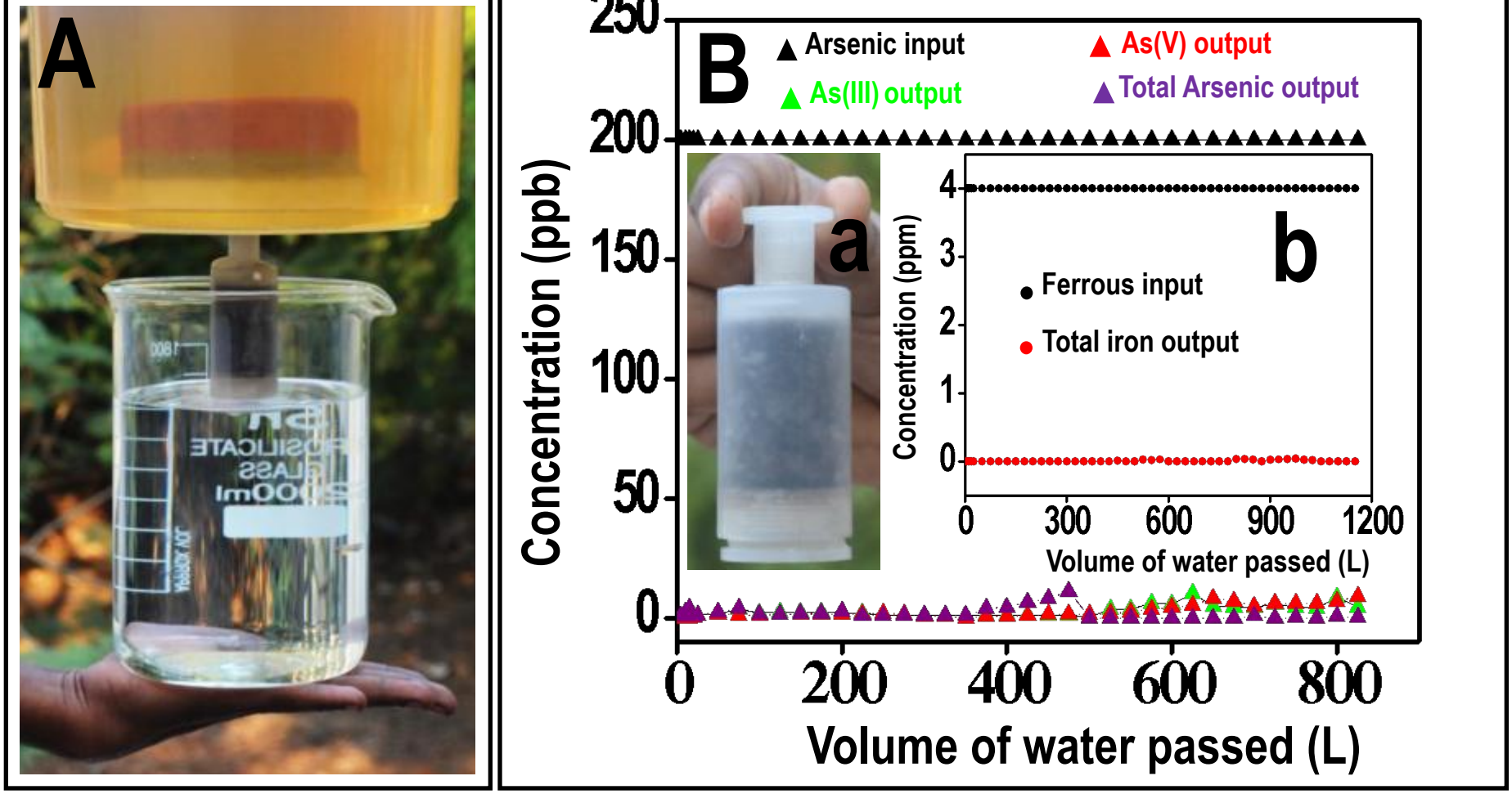
b

c

d

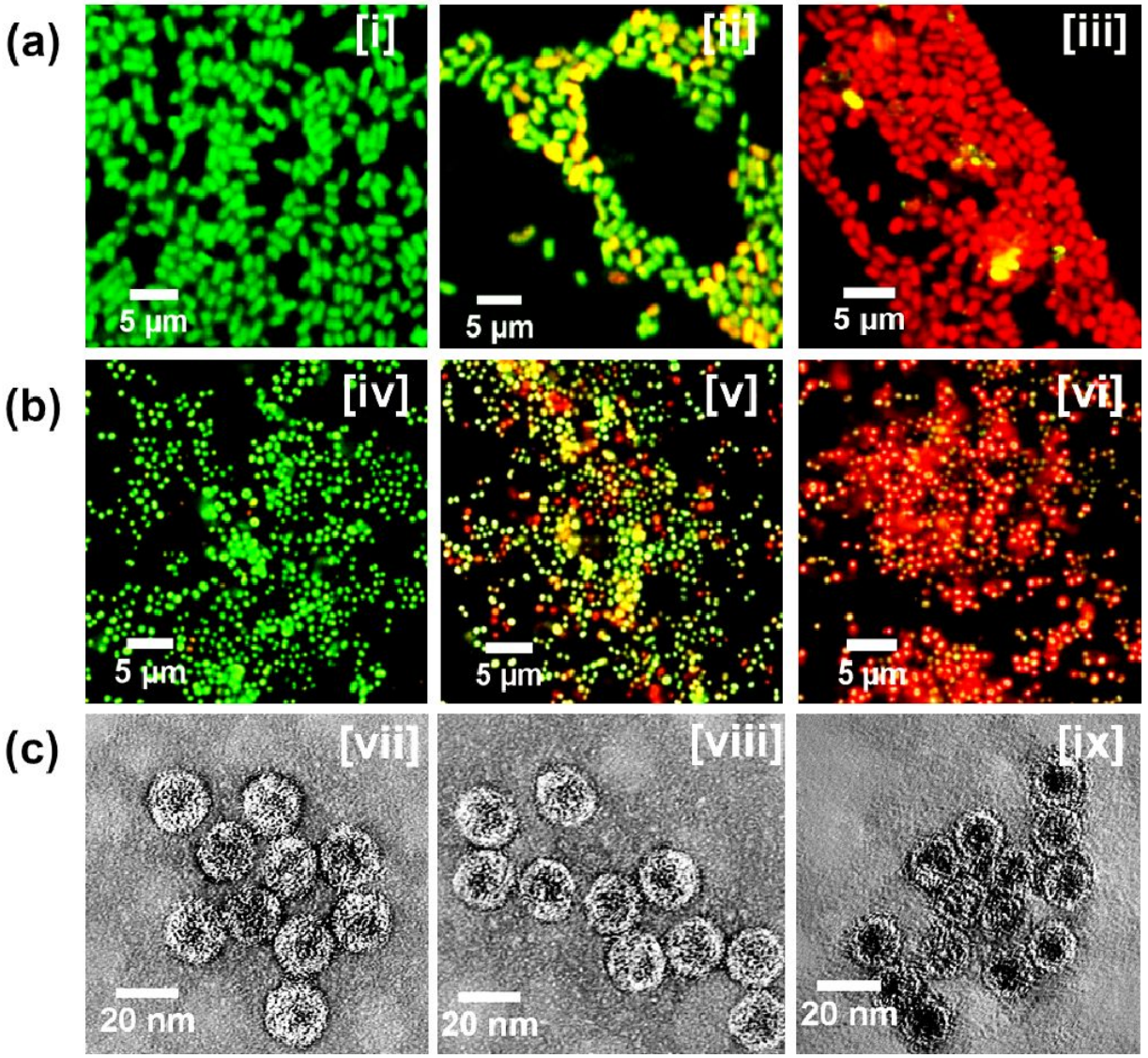
e

f



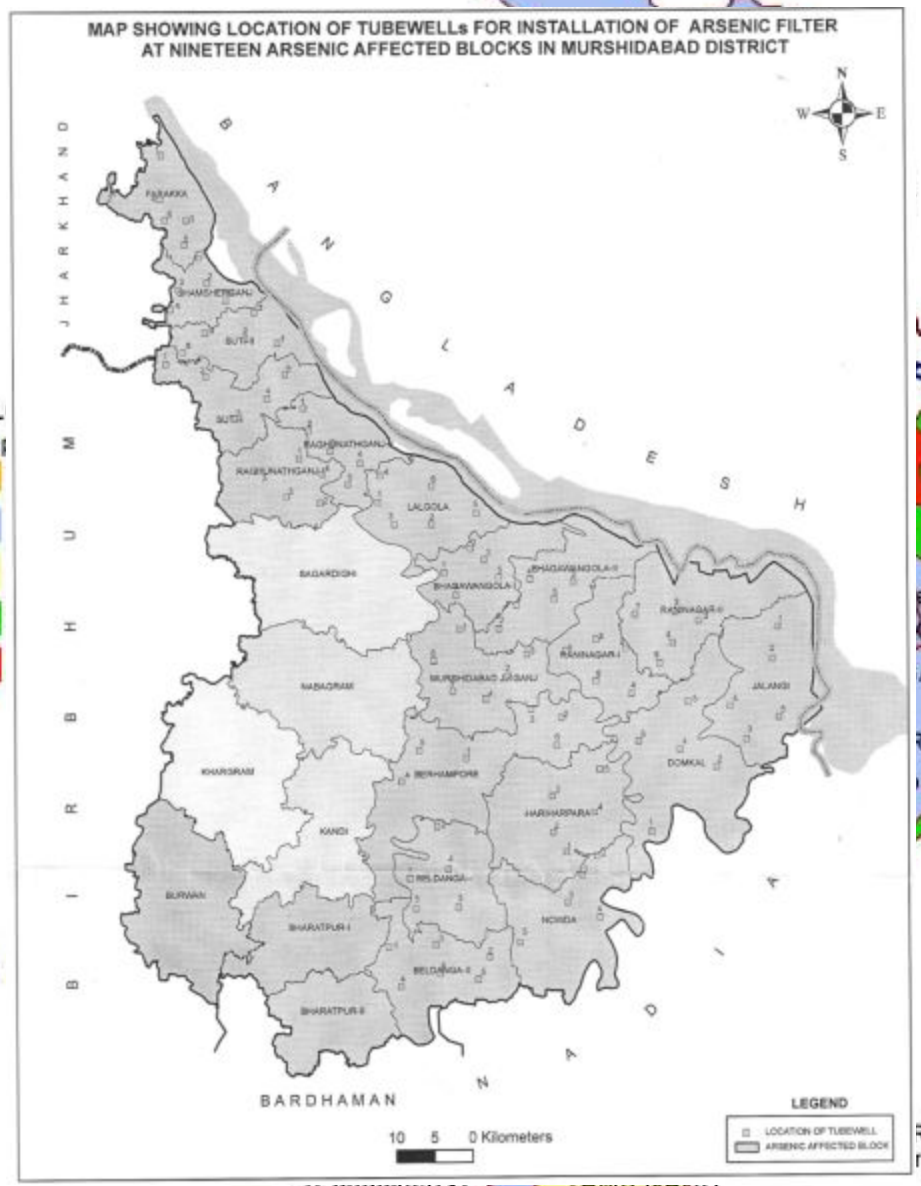
A simple set-up which has been used for arsenic testing study: arsenic containing water is turned into arsenic free clean drinking water using a simple cartridge having the arsenic adsorbent (A), and a cartridge having about 20 g of the adsorbent (a). Arsenic experiment which was conducted using a 60 g cartridge, under natural water conditions (B), and the ferrous experiment which was conducted with combination of arsenic experiment (b).

Anion effect



R. Swathy, et al. Scientific Reports, 2014


AMRIT
DRINKING WATER
ARSENIC & METAL REMOVAL BY INDIAN TECHNOLOGY
INDIAN INSTITUTE OF TECHNOLOGY MADRAS


MAP SHOWING LOCATION OF TUBEWELLs FOR INSTALLATION OF ARSENIC FILTER
AT NINETEEN ARSENIC AFFECTED BLOCKS IN MURSHIDABAD DISTRICT
N
W
E
S
JHARKHAND
BIRBHUM
BARDHAMAN
LEGEND
LOCATION OF TUBEWELL
ARSENIC AFFECTED BLOCK
10 5 0 Kilometers


Population Map
Of India-2001
CHINA
(Tibet)
ARUNACHAL PRADESH
SIKKIM
Gangtok
BHUTAN
Itanagar
ASSAM
Dispur
NAGALAND
Kohima
Patna
BIHAR
Shillong
Imphal
MANIPUR
MEGHALAYA
Agartala
TRIPURA
Aizawl
MIZORAM
WEST
BENGAL
Calcutta
BANGLADESH
BAY OF BENGAL
Port Blair
ANDMAN & NICOBAR ISLANDS
KERALA
Thiruvananthapuram
Map not to Scale
Copyright © 2006, Compare Infobase Limit

Imagining how new adsorbents are changing the dynamics at ground level

- Existing unit for iron and arsenic removal – 20 m^3/h
- Uses activated alumina and iron oxide (old generation of adsorbents)

- Existing unit for iron and arsenic removal – 18 m^3/h
- Uses iron oxyhydroxide (new generation of adsorbents)
- Input arsenic concentration: 168 ppb
- Output arsenic concentration: 2 ppb

Performance data from Murshidabad (continued)

S. No.	Sample Name	Input arsenic (ppb)	Output arsenic (ppb)	Number of days running
23.	Babaltali Jumma Masjid, Raninagar – II	10.7	0	180 days
24.	Sargachhi Paschimpara Jumma Masjid, Beldanga – I	1.26	0.04	180 days
25.	Pratappur Jumma Masjid, Hariharpara	27.19	0.13	180 days
26.	Fakirabad Jumma Masjid, Domkal	24.67	0	180 days
27.	Shialmari Jumma Masjid, Raninagar – II	287.5	0.09	240 days
28.	Bhabta Ahelahadis Jumma Masjid, Beldanga	8.6	5.7	240 days

A glimpse of performance data for installations in Nadia

S. No.	Sample Name	Input arsenic (ppb)	Output arsenic (ppb)	Number of days running
1.	Dhapadia Junior Madrasah	46.5	2.15	30 days
2.	Khidirpur Shishu Shiksha Kendra	14.99	0	260 days
3.	Junior Madrasah	12.7	0	60 days
4.	Dhapana Board High School	14.96	0.6	45 days
5.	Birpur Primary School	19.56	0	90 days
6.	Bethuaduari JCM High School	4.56	0	45 days
7.	Jugnuthala Primary School	23.36	0	60 days
8.	Dahakula Primary High School	36.6	0	60 days
9.	Bargachi Primary School Nagadi	9.56	0	90 days
10.	Dahakula Primary School	22.7	0	60 days
11.	BJ Kumari Primary School	5.9	0	100 days
12.	Arijnagar Primary School	0.13	-	60 days
13	Patikpari Girls Primary School	9.6	0	60 days
14	Bawanipur Primary School Nagadi	0.49	0	60 days

Work was featured in several journals

Nature Nanotechnology, July 2014 issue

A glimpse of performance data for installations in Murshidabad

S.No	Sample Name	Input arsenic (ppb)	Output arsenic (ppb)	Number of days running
1.	Topidanga Jumma Masjid, Bhagwangola-II	31	0	30 days
2.	Bhandahara Jumma Masjid, Bhagwangola-II	20.7	0.4	30 days
3.	Horirampur Jumma Masjid, Bhagwangola-II	37	0	45 days
4.	Dihipara Jumma Masjid, Bhagwangola-II	4.8	1.8	30 days
5.	Bahadurpur High School, Bhagwangola-I	9.4	0.2	30 days
6.	Charlabangola Higher Sec School, Bhagwangola-I	28.2	0.1	245 days
7.	Mahisasthali Girls' High School, Bhagwangola-I	0	0	30 days
8.	Orahar Girls' High School, Bhagwangola-I	0.53	0	10 days
9.	Rabindratola BN Pandey High School, Bhagwangola-I	84.3	0	245 days
10.	Karbalajamam Masjid, Berhampore	6.8	0	150 days
11.	PHED office, Berhampore	32	0	10 days
12.	Nabipur Bazar Jumma Masjid, Raninagar-II	1.3	0	60 days
13.	Rukunpur Jumma Masjid, Hariharpara	25.6	2.2	60 days
14.	Klyanpur Jumma Masjid, Domkal	64.7	0	200 days
15.	Benadaha Mondalpara Hanafi Jamat, Beldanga-I	9.04	0	180 days
16.	Maniknagar Jumma Masjid, Domkal	1	0.04	60 days
17.	South Hariharpura Jumma Masjid, Hariharpara	5.47	0	60 days
18.	Lochan Mati Danga Para Jumma Masjid, Hariharpara	14.6	0	150 days
19.	Paschim Malipara Jumma Masjid, Raninagar – II	3.3	0.13	90 days
20.	Khalilabad Jumma Masjid, Hariharpara	179.0	0	270 days
21.	Bhatu Komnagar Masjid, Raninagar –II	67.89	0.22	360 days

Plan for immediate future

In-line arsenic sensor and remote data management – indicates when filtration systems require maintenance. **IMPROVED FILTER SUSTAINABILITY**

ARSENIC TOXIC WATER

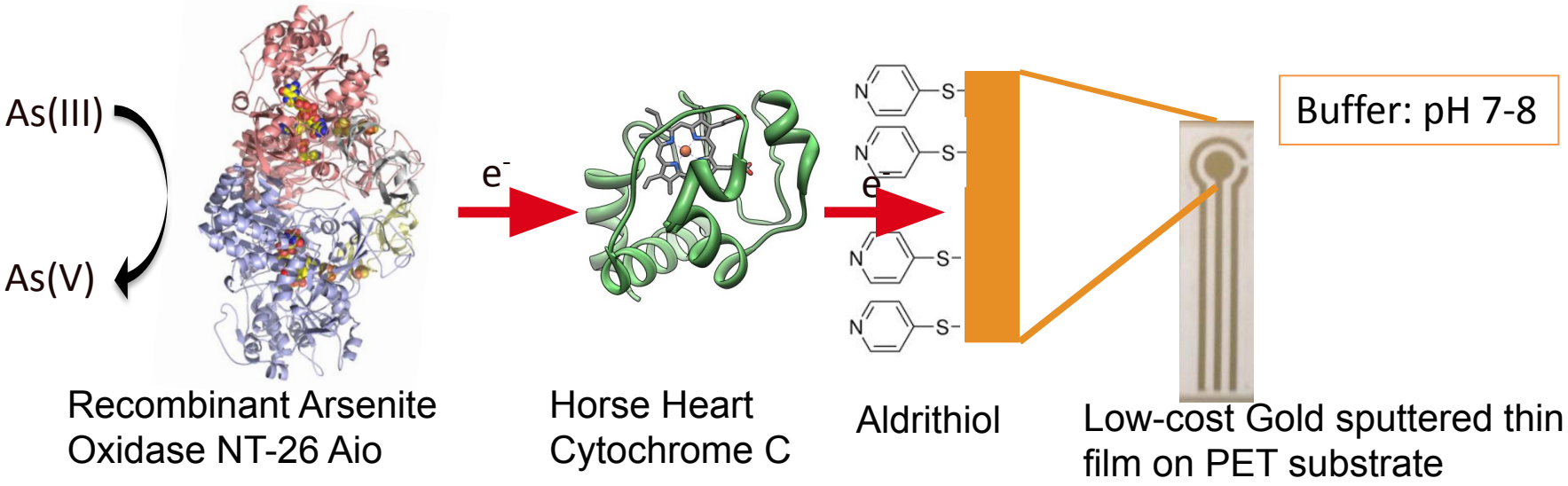
India Mark II hand water pump – most common water pump used globally

InnoNano Research's in-line arsenic removal filtration system

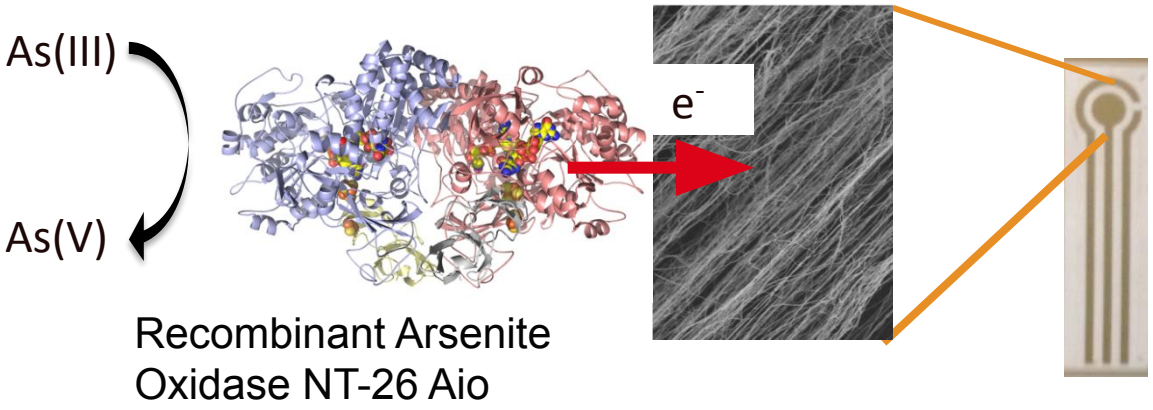
SUSTAINABLE SOURCE OF ARSENIC FREE SAFE DRINKING WATER

Biosensor Design

1st Generation Design (Mediated Electrochemistry)



2nd Generation Design (Direct Electron Transfer)



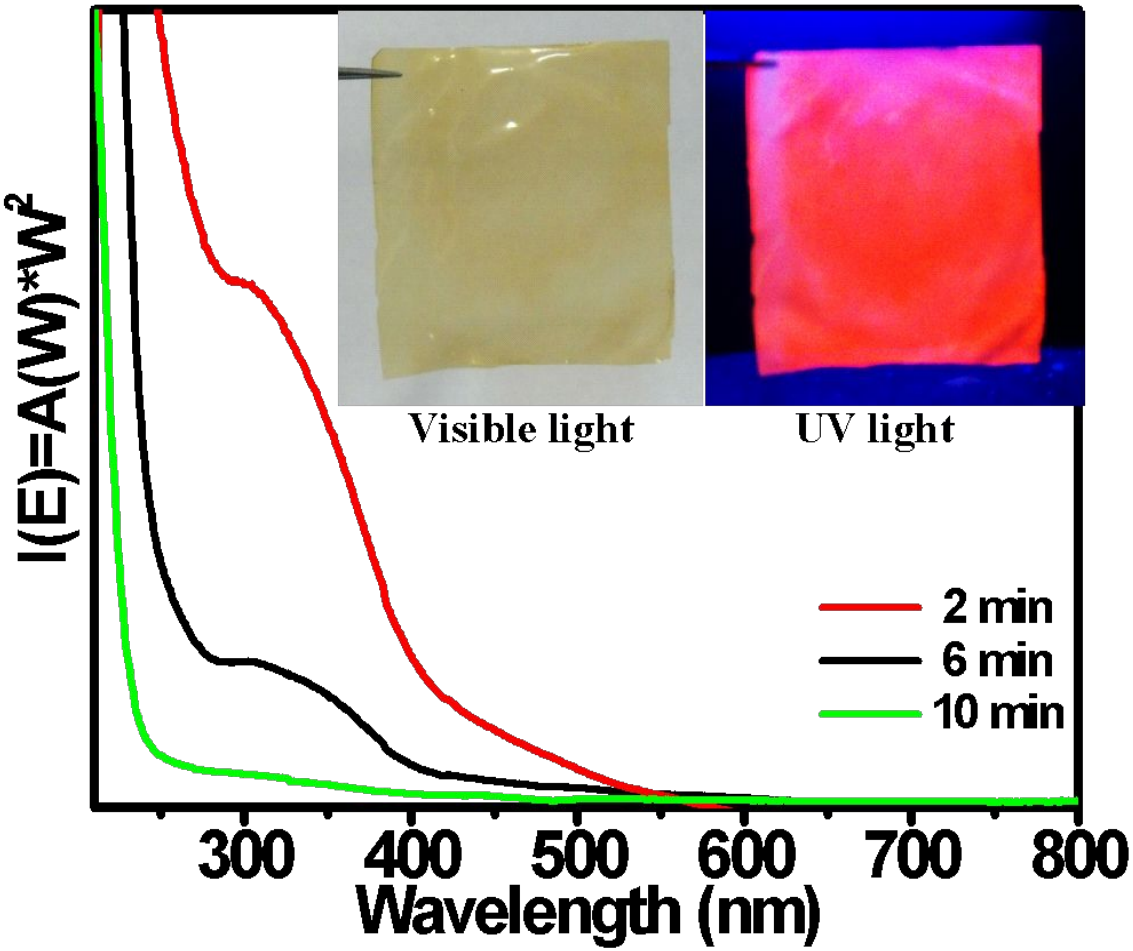
Integrate Arsenic *monitor* and Arsenic *filter* into in-line filtration/monitoring unit to improve management of Arsenic problem

- Easy-to-use
- Quantitative
- Fast < 3 minutes
- Low cost
- Non-toxic
- Automatic recording of test results with well GPS position

+

- Proprietary nano materials
- Manufactured in India
- Filters arsenic & iron
- Integrated to Mark II hand pumps

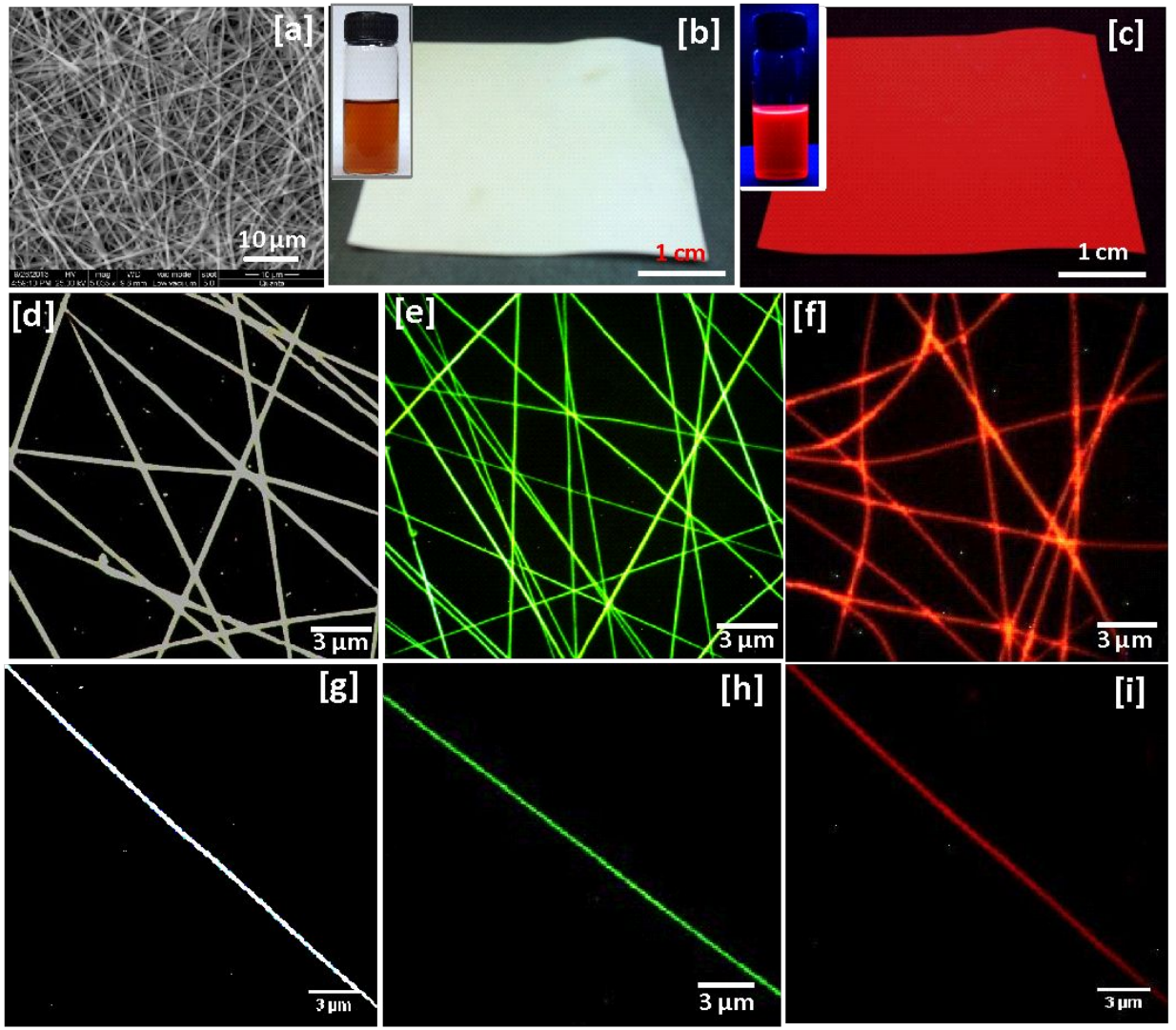
Quantum cluster based metal ion sensing paper
Large area uniform illumination using quantum cluster



Decrease in the absorption of Au_{15} as a biofilm is dipped into the cluster solution. Inset: Free standing quantum cluster loaded film in visible light and UV light.

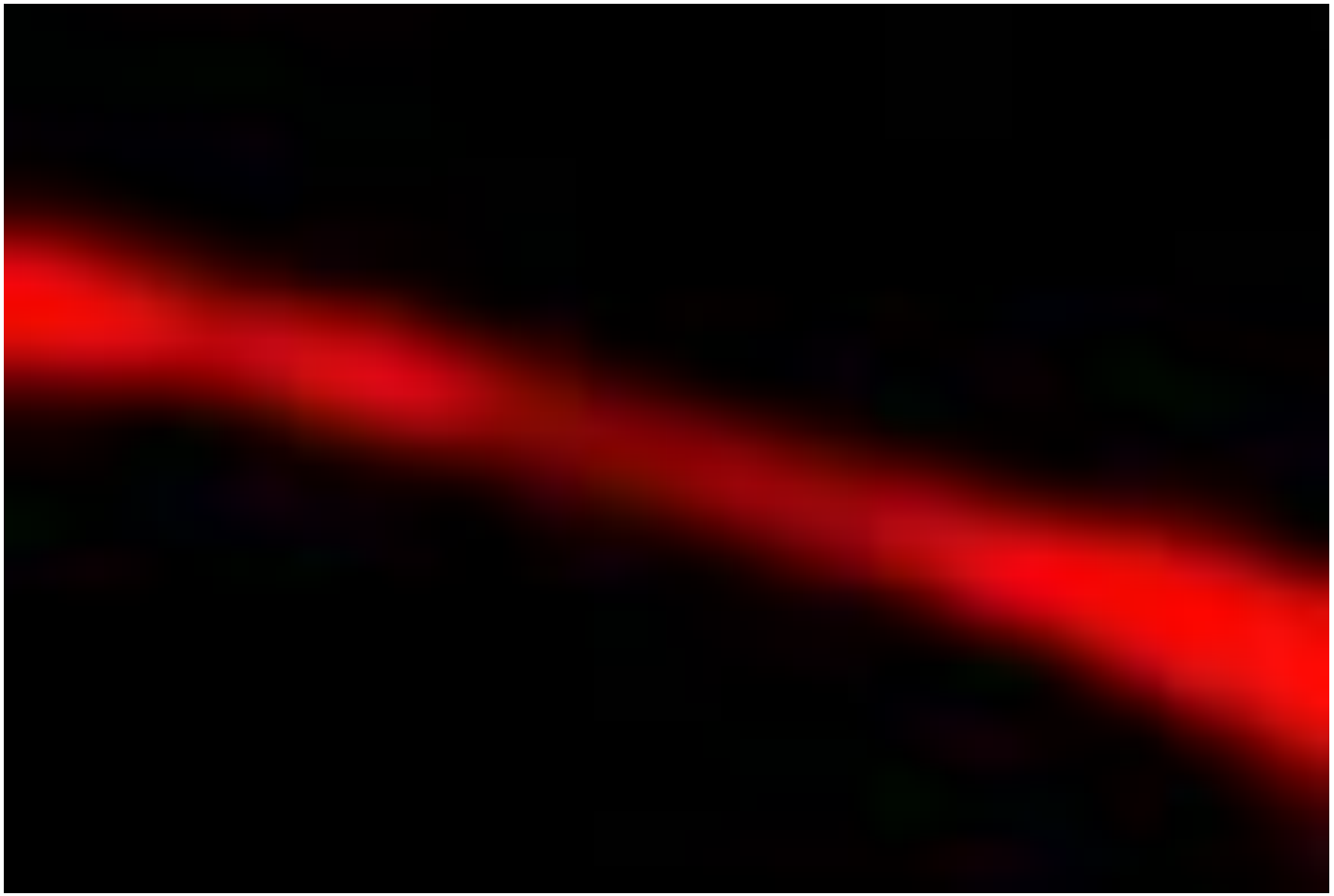
Anu George et al. *ACS Applied Materials & Interfaces*, 2012

Approaching detection limits of tens of Hg^{2+}

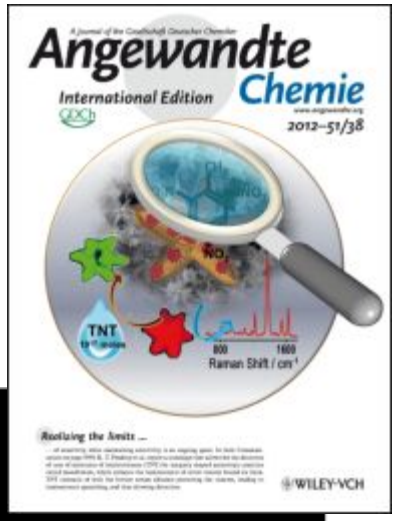


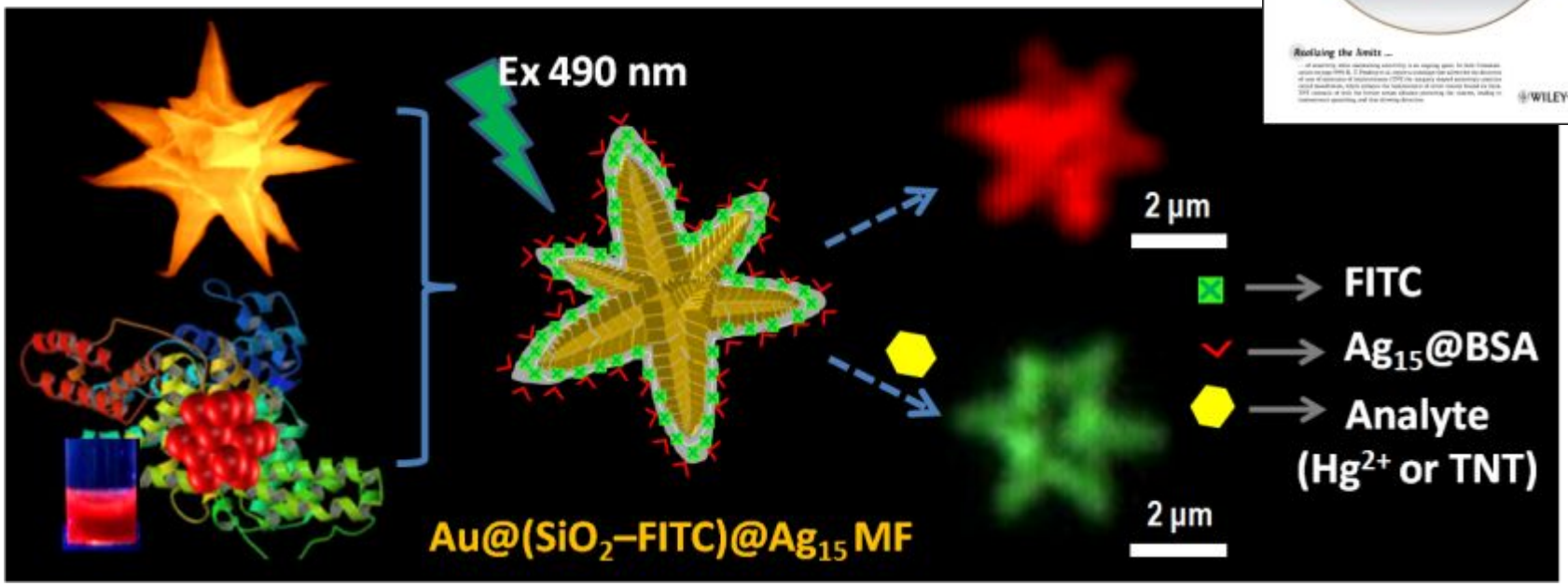
Atanu Ghosh et al. Anal. Chem.2014.

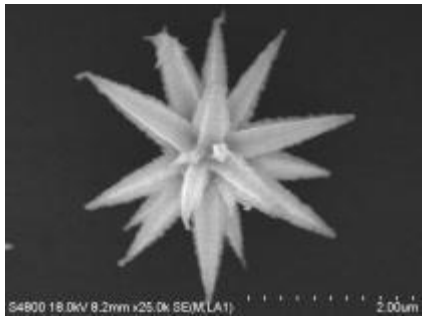
Video of mercury quenching experiment using the nanofiber



Sub-zeptomolar detection







Featured in:
The Hindu, Telegraph, Times of India, etc.
C&E News
and many others

Ammu Mathew, et al. Angew. Chem. Int. Ed. 2012

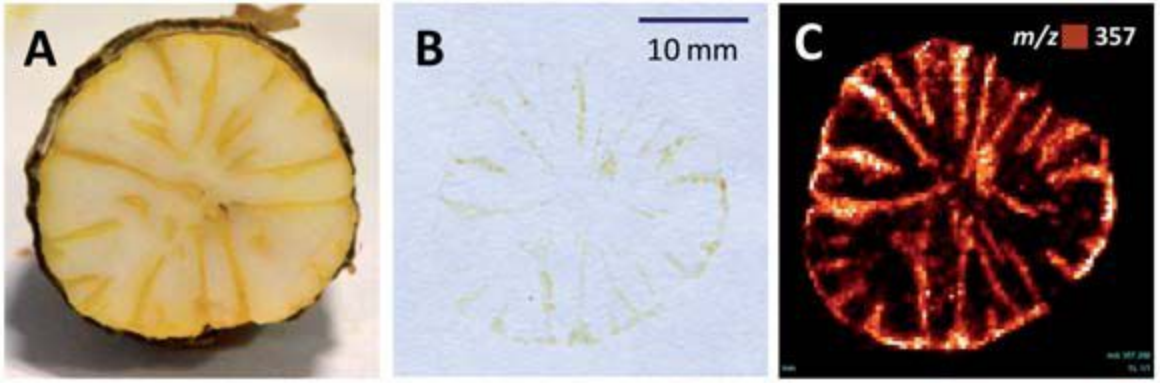
Cheap Nanotech Filter Clears Hazardous Microbes and Chemicals from Drinking Water

A $16 device could provide a family of five with clean water for an entire year

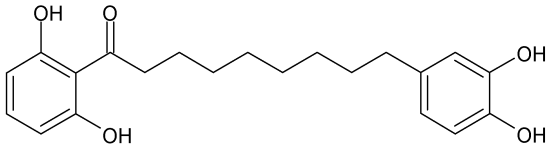
By Luciana Gravotta

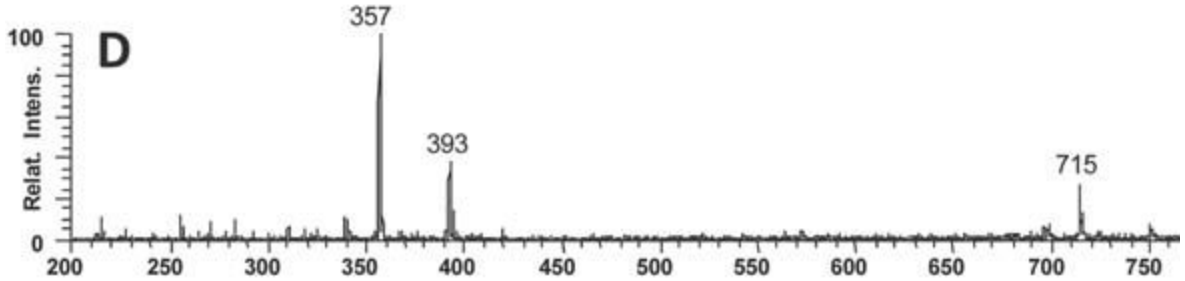
About 780 million people—a tenth of the world's population—do not have access to clean drinking water. Water laced with contaminants such as bacteria, viruses, lead and arsenic claims millions of lives each year. But an inexpensive device that effectively clears such contaminants from

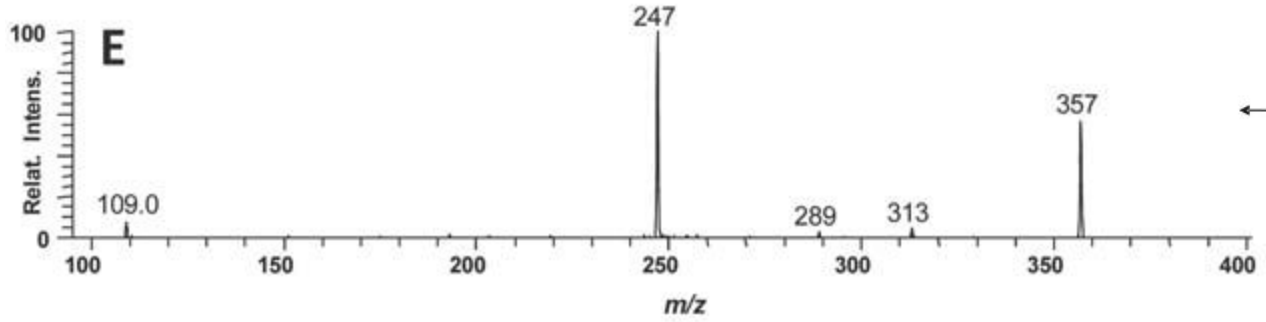
Imaging of seed section using DESI

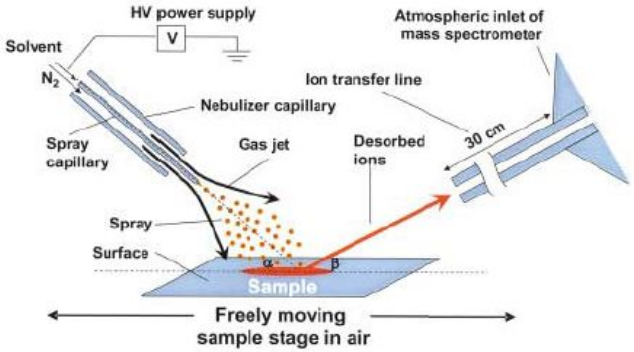


Myristica malabarica seed
Malabaricone C (*m/z* 357)

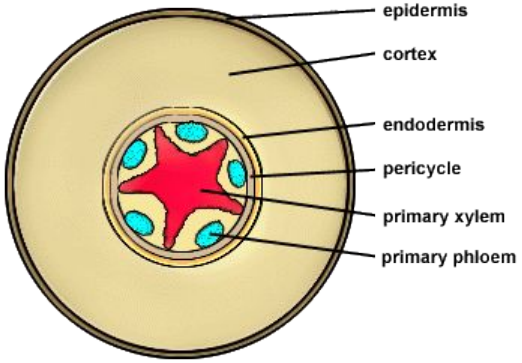


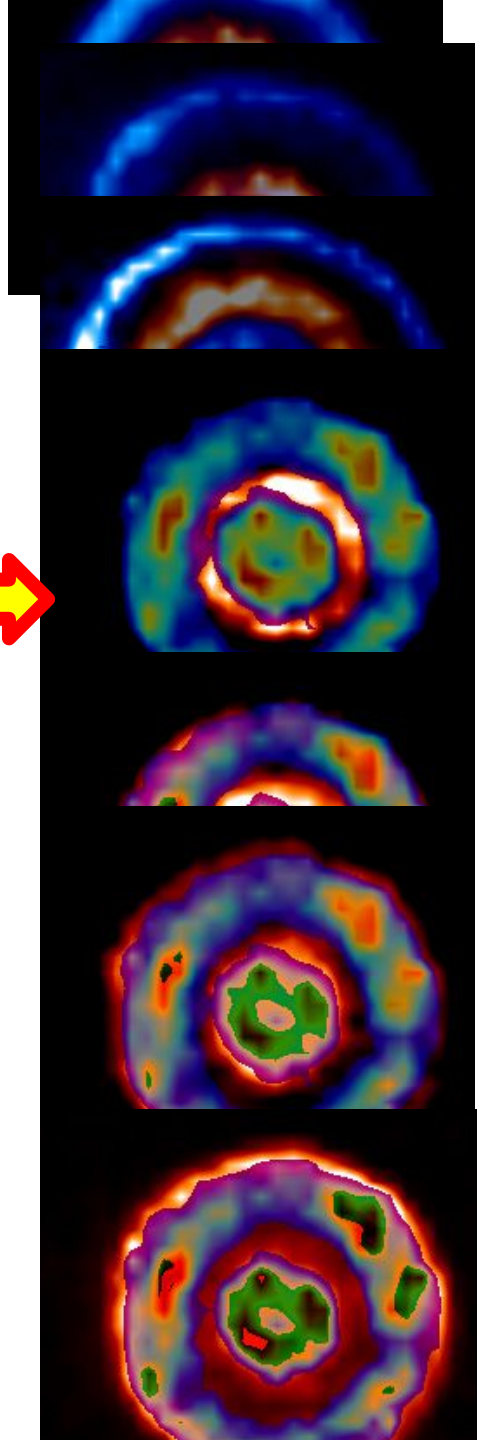






Ifa, D. R.; Srimany, A.; Eberlin, L. S.; Naik, H. R.; Bhat, V.; Cooks, R. G.; Pradeep, T. *Anal. Methods* **2011**, *3*, 1910-1912.





m/z 174.1
*m/z*490.5;468.5;600.0;772.4

m/z 155.1
m/z 490.5:468.5:600.0:772.4

m/z 365.3
m/z 174.1:610.3:915.5

m/z 306.25
m/z 490.5;468.5;600.0;772.4

m/z 306.25
m/z 365.33

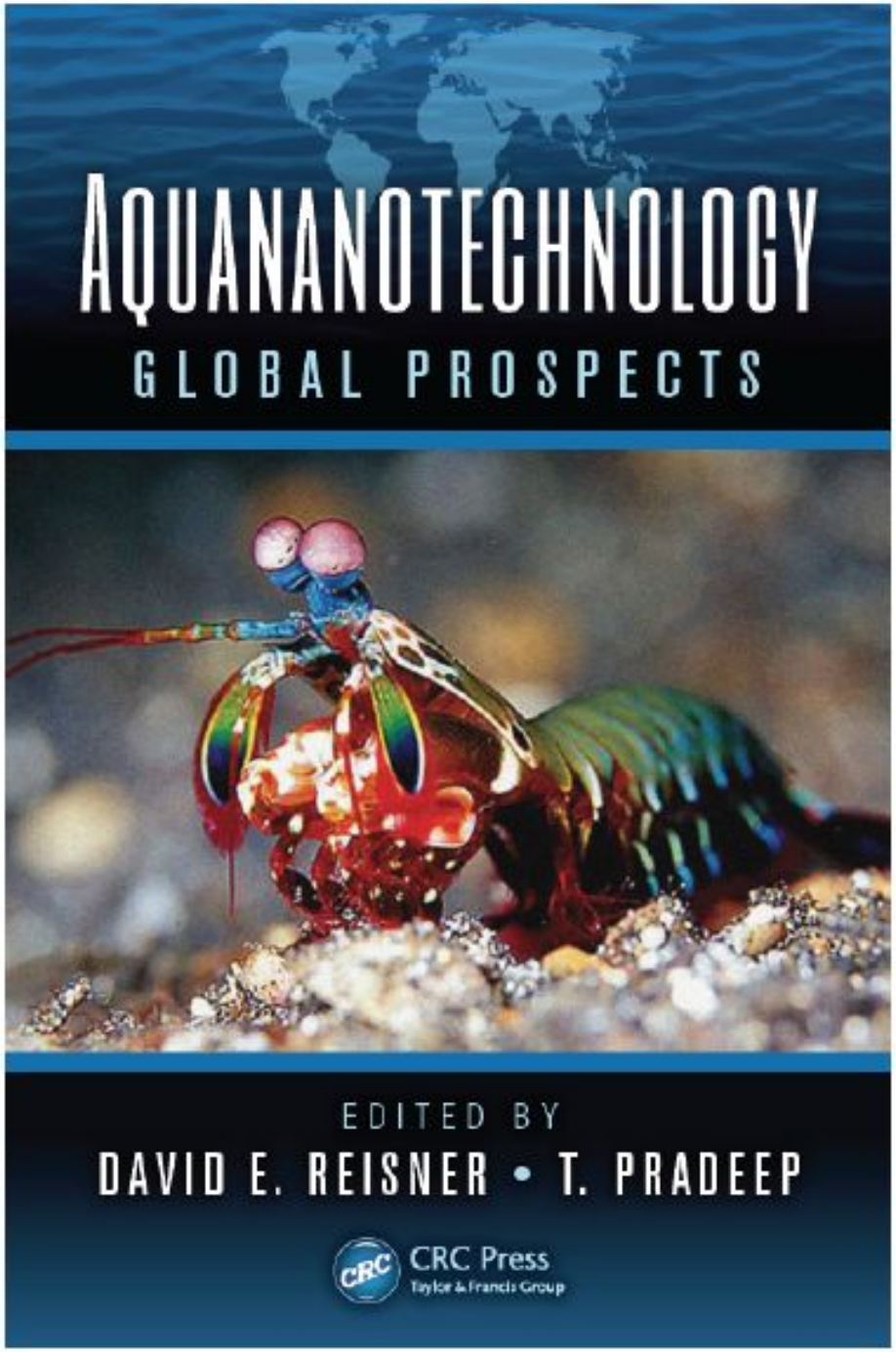
m/z 306.25
m/z 198.25

m/z 306.25
m/z 348.25

m/z 306.25
m/z 633.25

m/z 306.25
m/z 328.25

New Book


AQUANANOTECHNOLOGY
GLOBAL PROSPECTS
EDITED BY
DAVID E. REISNER • T. PRADEEP
CRC Press
Taylor & Francis Group

Tiny particles offer a number of solutions

What more?

Affordable sensors
Solutions for many known and unknown species
Unknown and poorly understood health effects
Impact of our water existing technologies
Effect of agrochemicals on environment and health
Smart sensors and smart purifiers
Sustainable chemistry
Biology
Poetry

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सत्यमेव जयते

Thank you