



Now in the 58th year

Clean water using advanced materials: Science, incubation and industry

T. Pradeep

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Founder
InnoNano Research Pvt. Ltd.
An IIT Madras Incubated Company

Co-founder
InnoDI Water Technologies Pvt. Ltd.
An IIT Madras Incubated Company



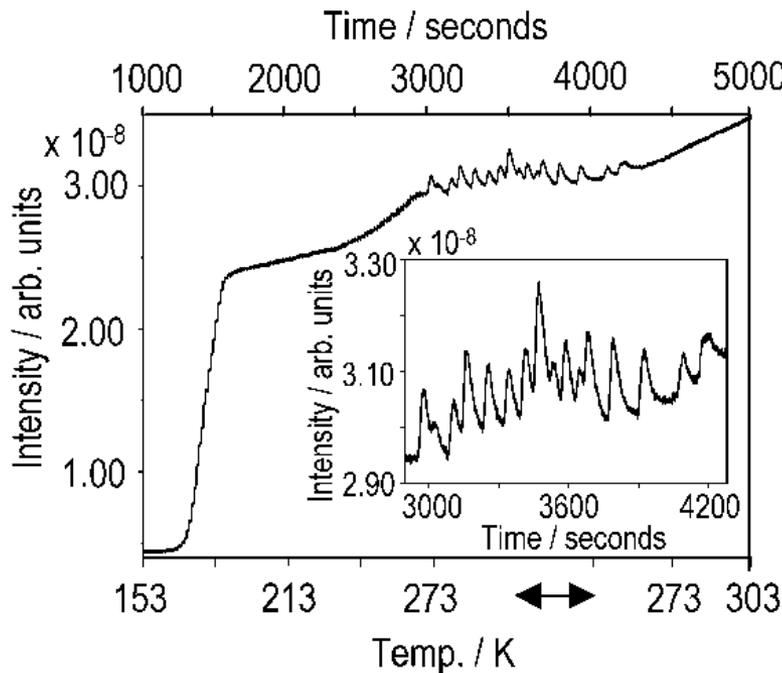
Prof. Amrutur V. Anilkumar
Prof. Uttama Lahiri



Associate Editor
ACS
Sustainable
Chemistry & Engineering



Concentration of CO₂ over Melting Ice Oscillates



¹ M. S. Gopinathan,¹ and T. Pradeep^{1,2,*}

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(Received 10 October 2003; published 23 July 2004)

CO₂ concentration over melting ice oscillates as long as water and ice coexist. A mechanism for CO₂ containing ice leading to its release, readsorption of CO₂ is proposed. Thermokinetics of these processes lead to non-Fickian behavior. Oscillations are also observed over impure ice contaminated with CO₂. Similar oscillations have been observed in several other solute or ice-

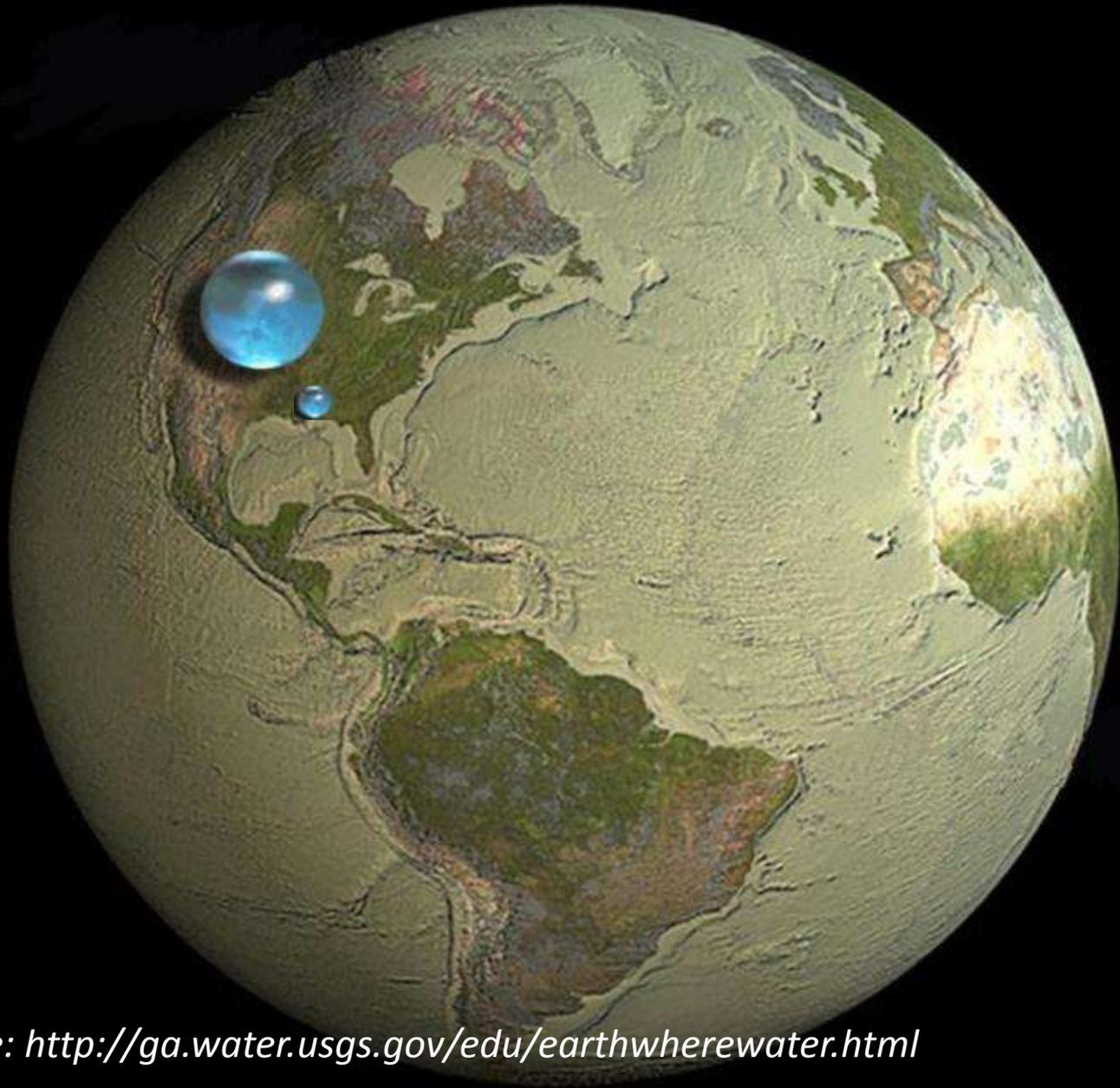
PACS numbers: 82.20.-w, 68.35.Ja, 82.40.Bj, 82.80.Ms

My greetings to Professor Roddam Narasimha



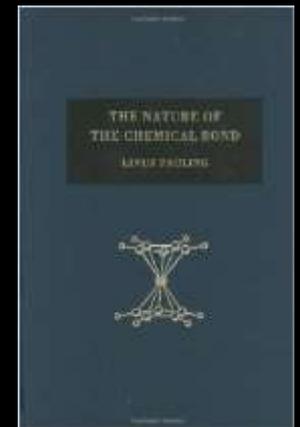
Our blue planet

12.6×10^{20} litres, 42×10^{45} molecules



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

Water is probably the most researched subject, yet not fully understood.



Challenges and opportunities

- About 780 million people live without clean drinking water.
- More than two billion people worldwide rely on wells for their water.
- By 2025, an estimated 1.8 billion people will live in areas plagued by water scarcity.
- Half of the global population lives in countries where water tables are rapidly falling - Ogallala Aquifer in the United States
- Over the past 40 years the world's population has doubled and use of water has quadrupled.
- Agriculture accounts for ~70% of global freshwater withdrawals and up to 90% in some fast-growing economies.

- By 2035, energy consumption will increase by 35 percent, increasing water use by 15 percent.
- In the US, thermoelectric power plants account for nearly 50% of all freshwater withdrawals.
- 46% of the globe's (terrestrial) surface is covered by transboundary river basins which can lead to future conflicts over water.
- The global middle class will surge from 1.8 to 4.9 billion by 2030, which will result in a significant increase in freshwater consumption.

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PERIODIC TABLE OF THE ELEMENTS

<http://www.ck12.org/periodic-table/>

We have clean water on the surface of Earth only because chemistry permits it!

LANTHANIDES

57 138.91 La	58 140.12 Ce	59 140.91 Pr	60 144.24 Nd	61 144.91 Pm	62 150.36 Sm	63 151.96 Eu	64 157.25 Gd	65 158.93 Tb	66 162.50 Dy	67 164.93 Ho	68 167.26 Er	69 174.97 Tm	70 178.49 Yb	71 174.97 Lu
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ACTINIDES

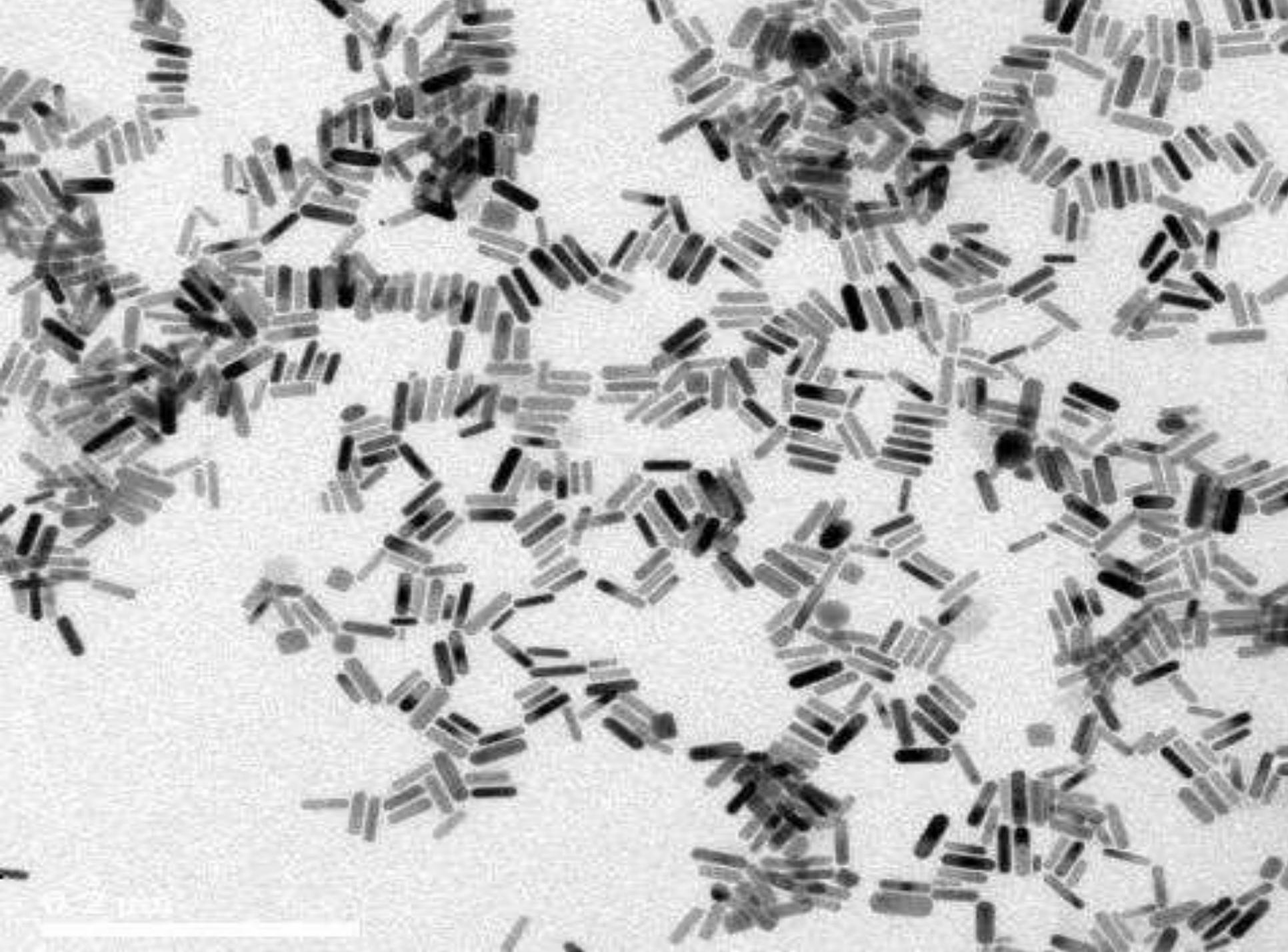
89 227.03 Ac	90 232.04 Th	91 231.04 Pa	92 238.03 U	93 237.05 Np	94 244.06 Pu	95 247.07 Am	96 251.08 Cm	97 252.08 Bk	98 259.10 Cf	99 264.10 Es	100 267.10 Fm	101 272.10 Md	102 285.10 No	103 289.10 Lr
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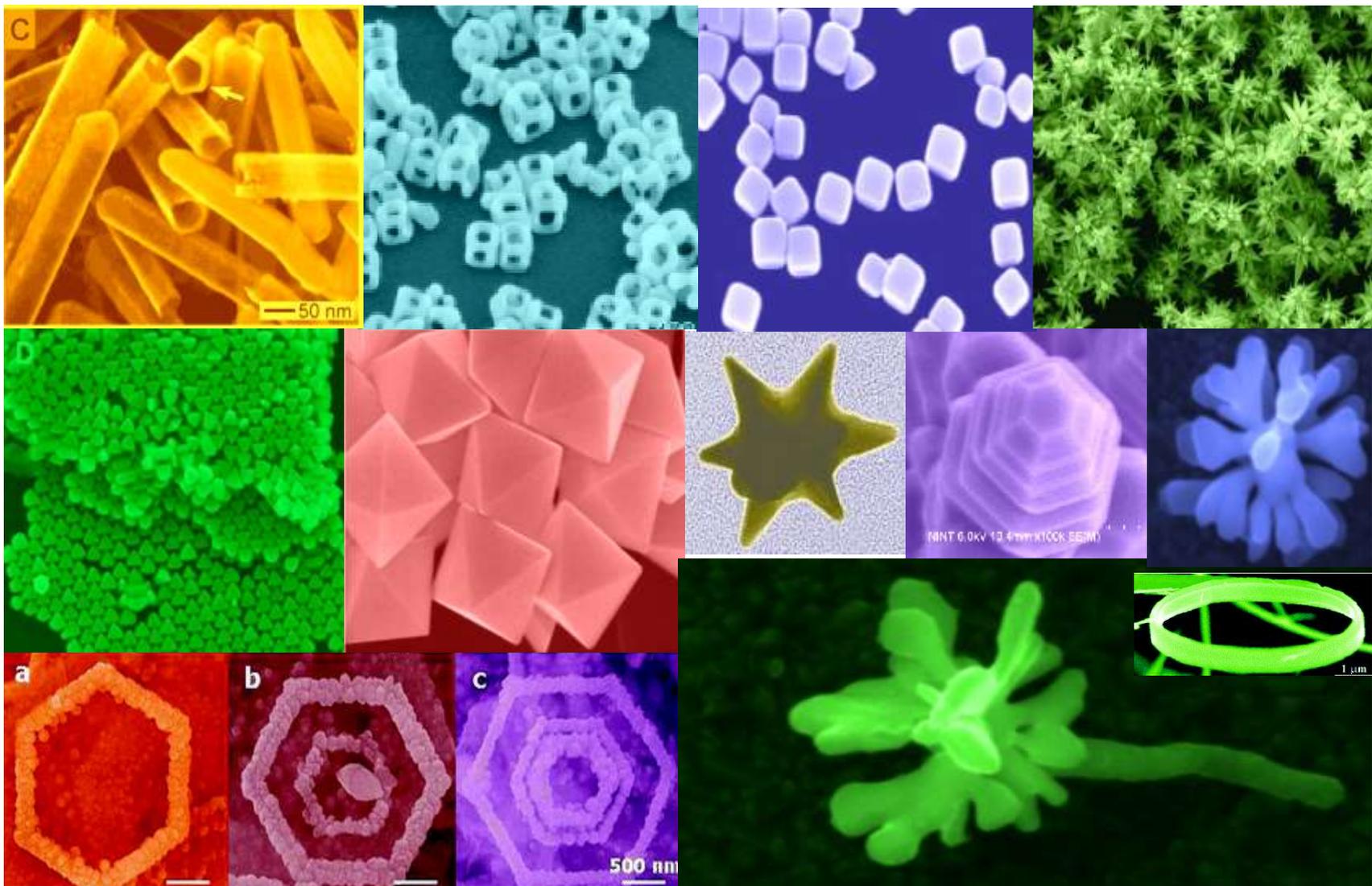
Source: <http://www.ck12.org/periodic-table/>

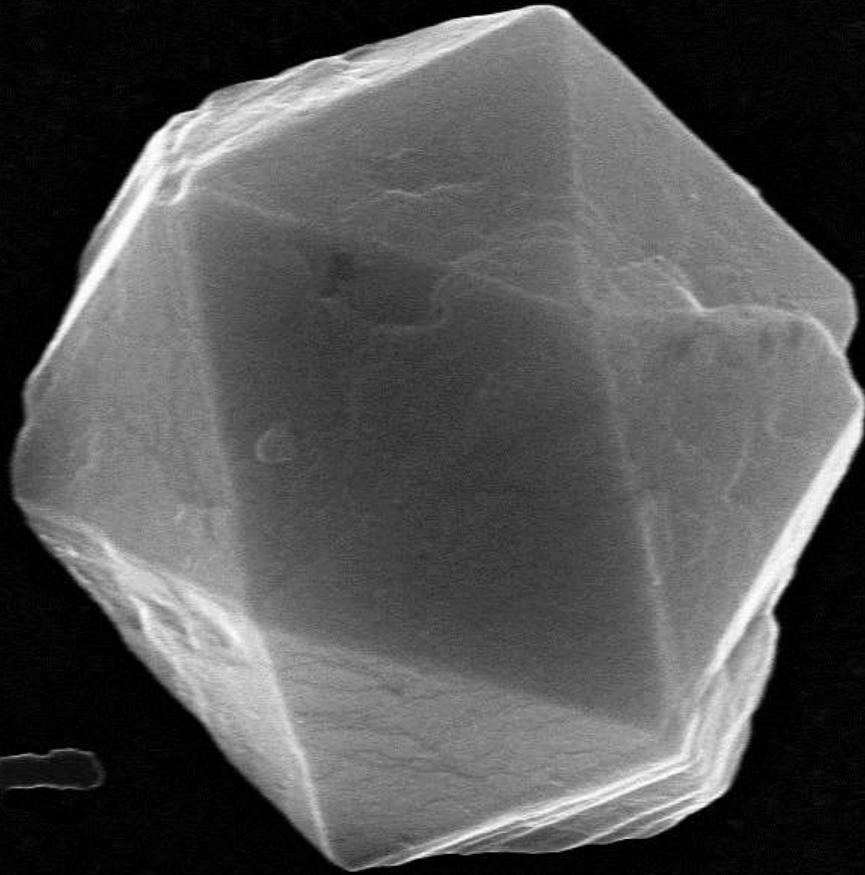
Why nanotechnology?

Nano 10^{-9}

Quantum



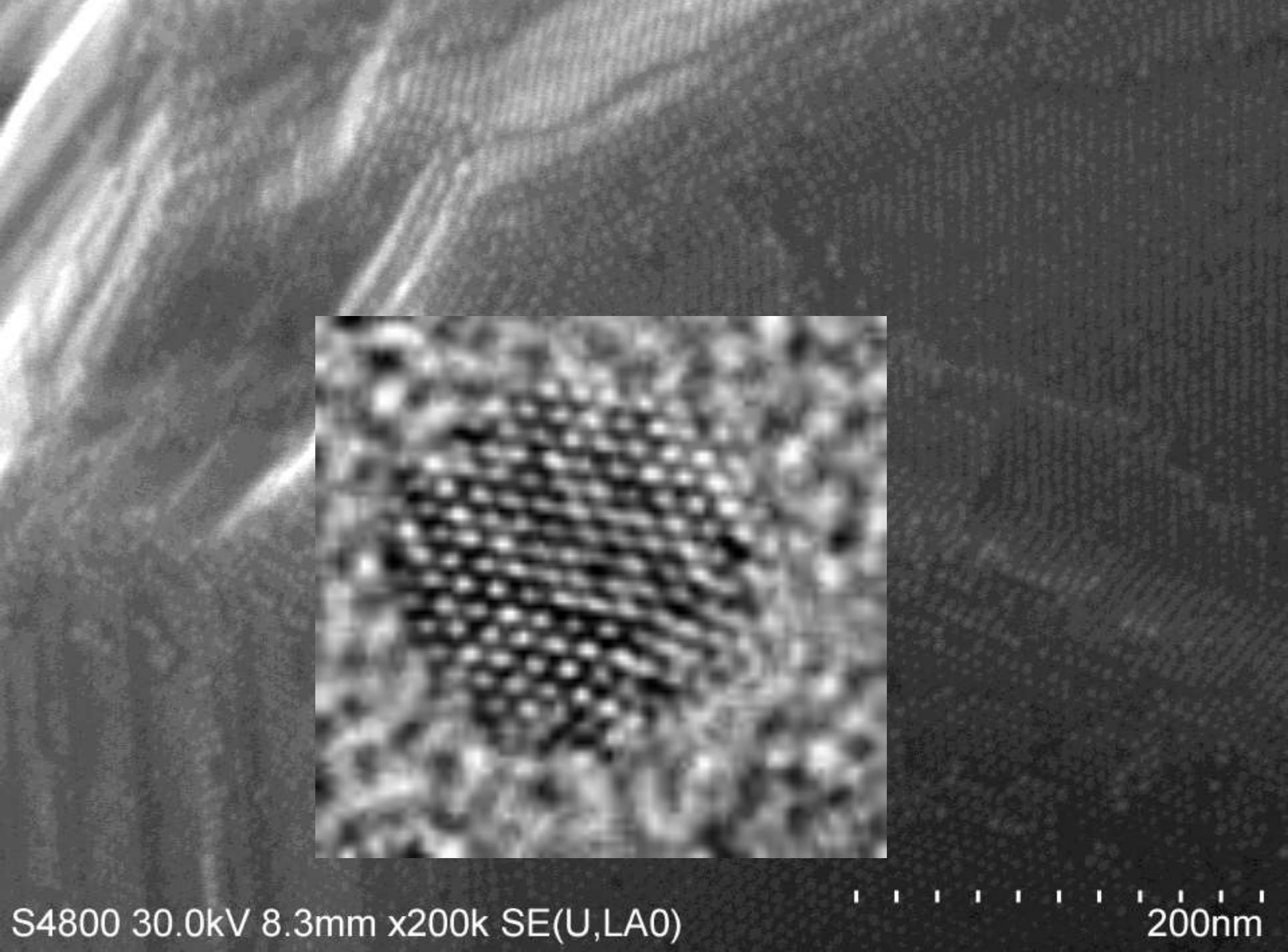




An object for the nanotechnology - nanomaterials.

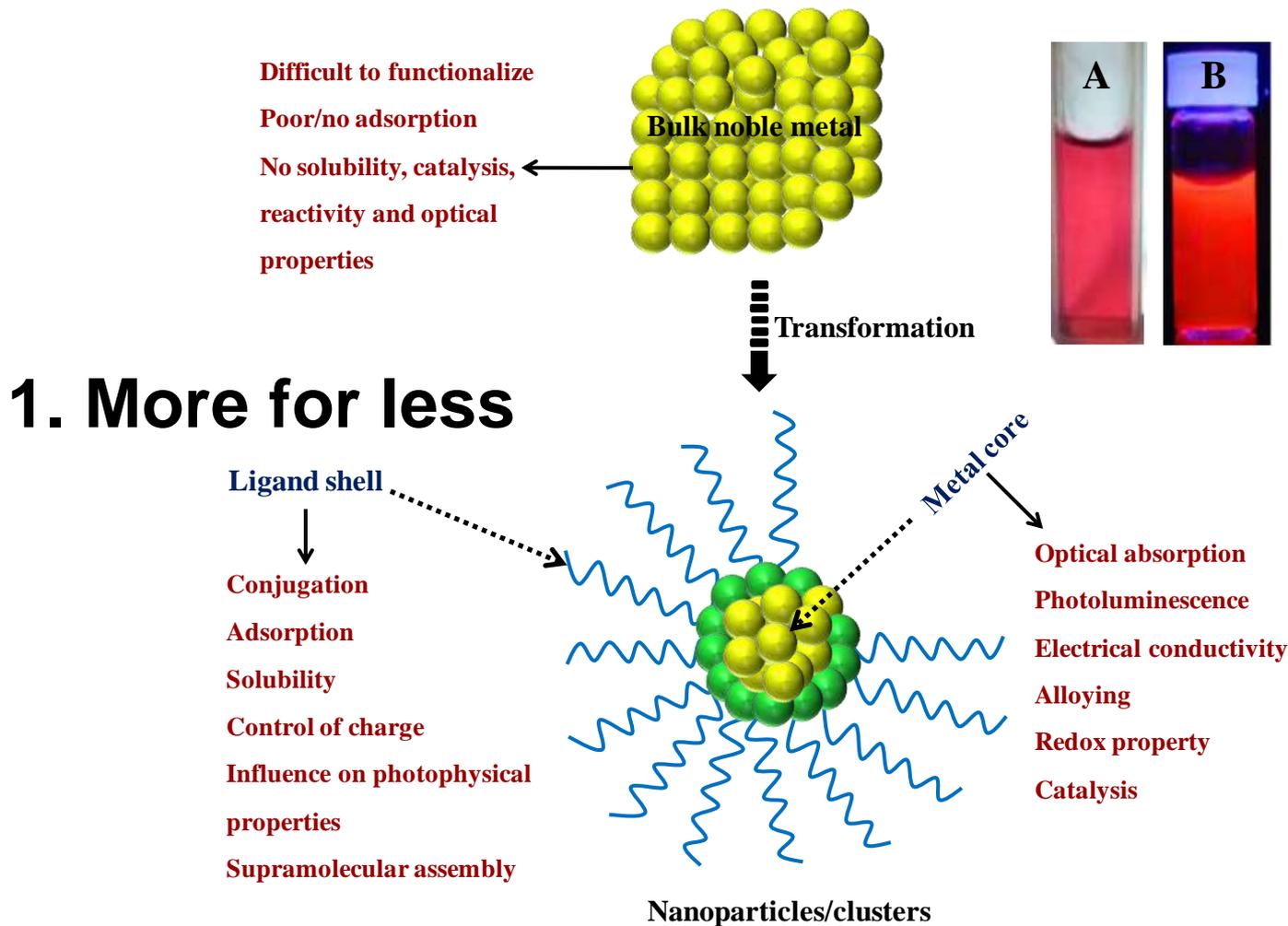
S4800 30.0kV 8.3mm x13.0k SE(U,LA0)

4.00um



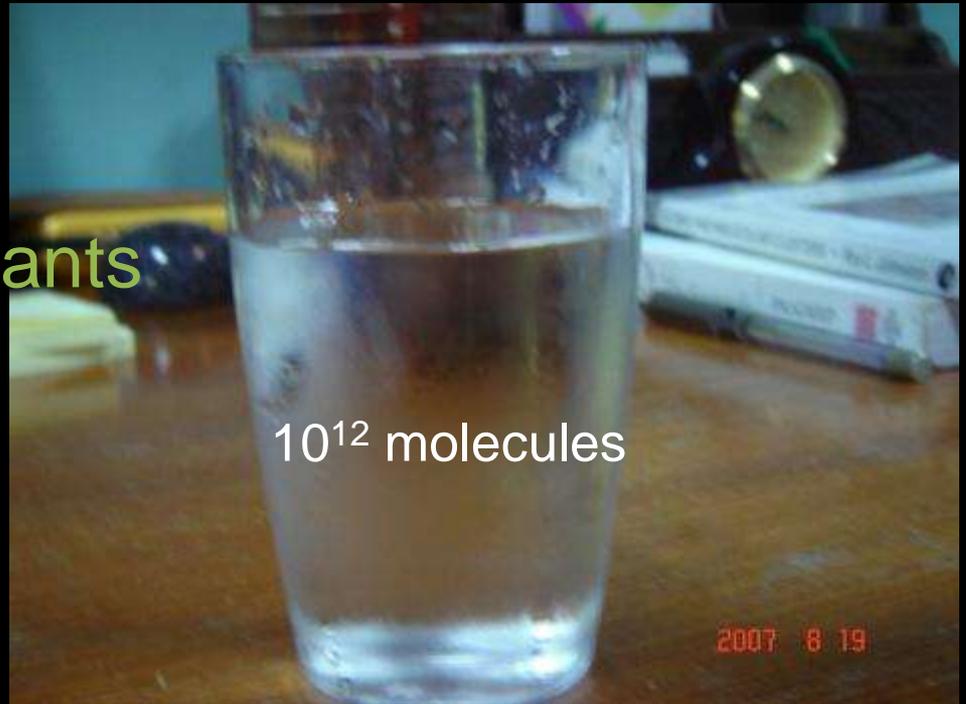
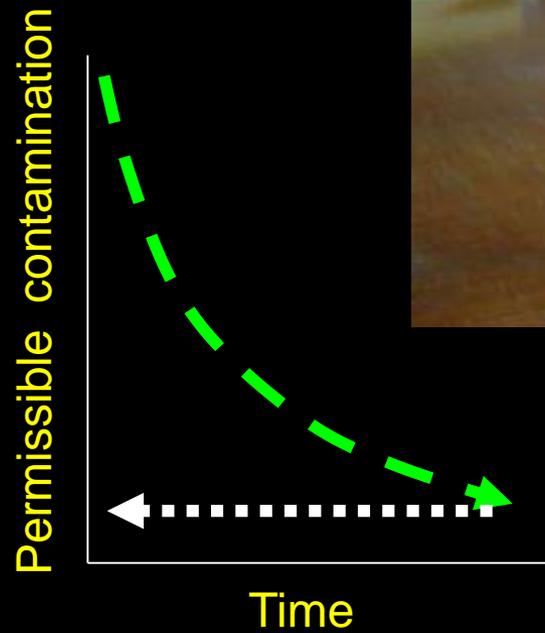
S4800 30.0kV 8.3mm x200k SE(U,LA0)

200nm

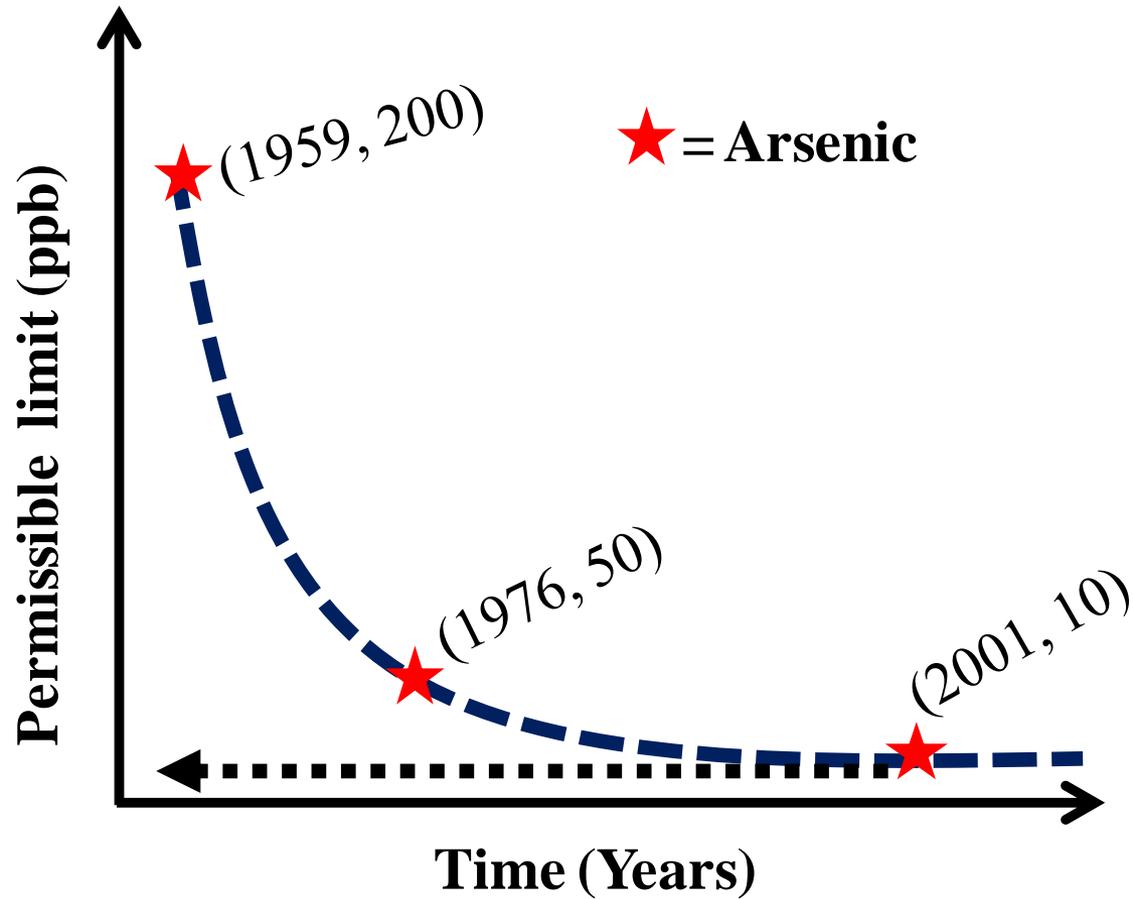


Variation in properties originating from ligand shell and metal core as bulk noble metals transform to nanoparticles/clusters. Sizes are not to scale. New properties such as color and photoluminescence arise in such size regime. Photographs of Au@citrate nanoparticles (inset A) showing intense absorption 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

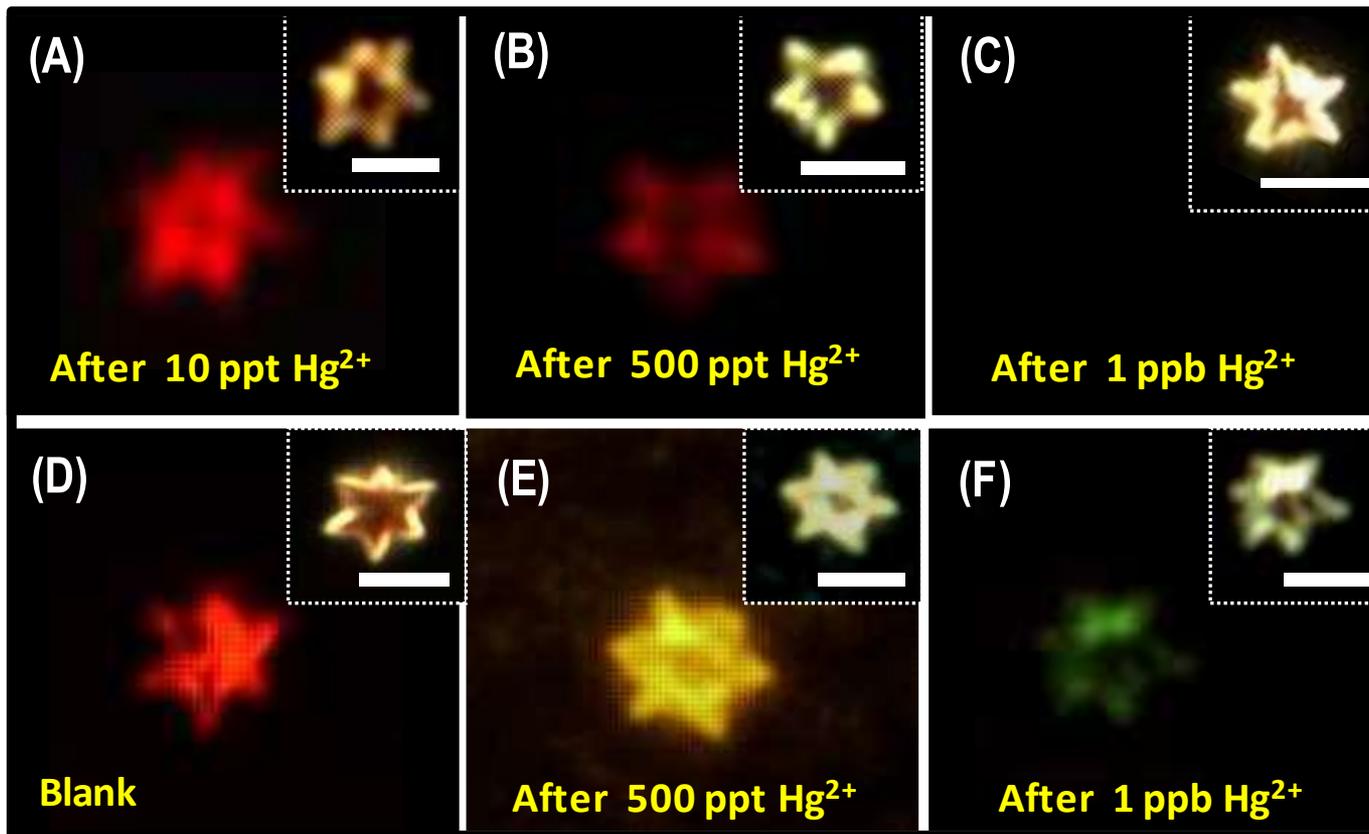


Permissible contamination reaches limits of detection



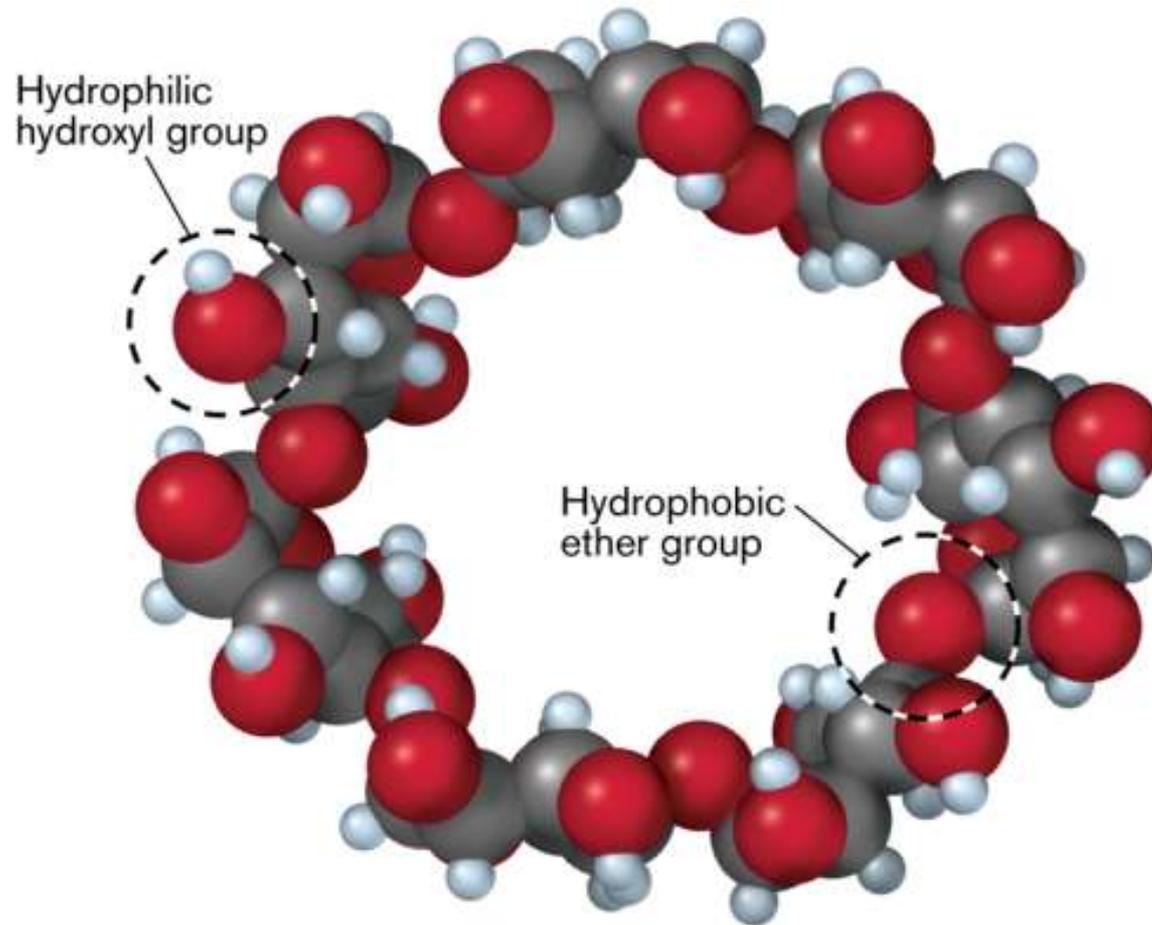
Decrease in the permissible limit of arsenic in drinking water, according to US EPA, with time. The graph indicates a general trend.

3. Can we reach limits?

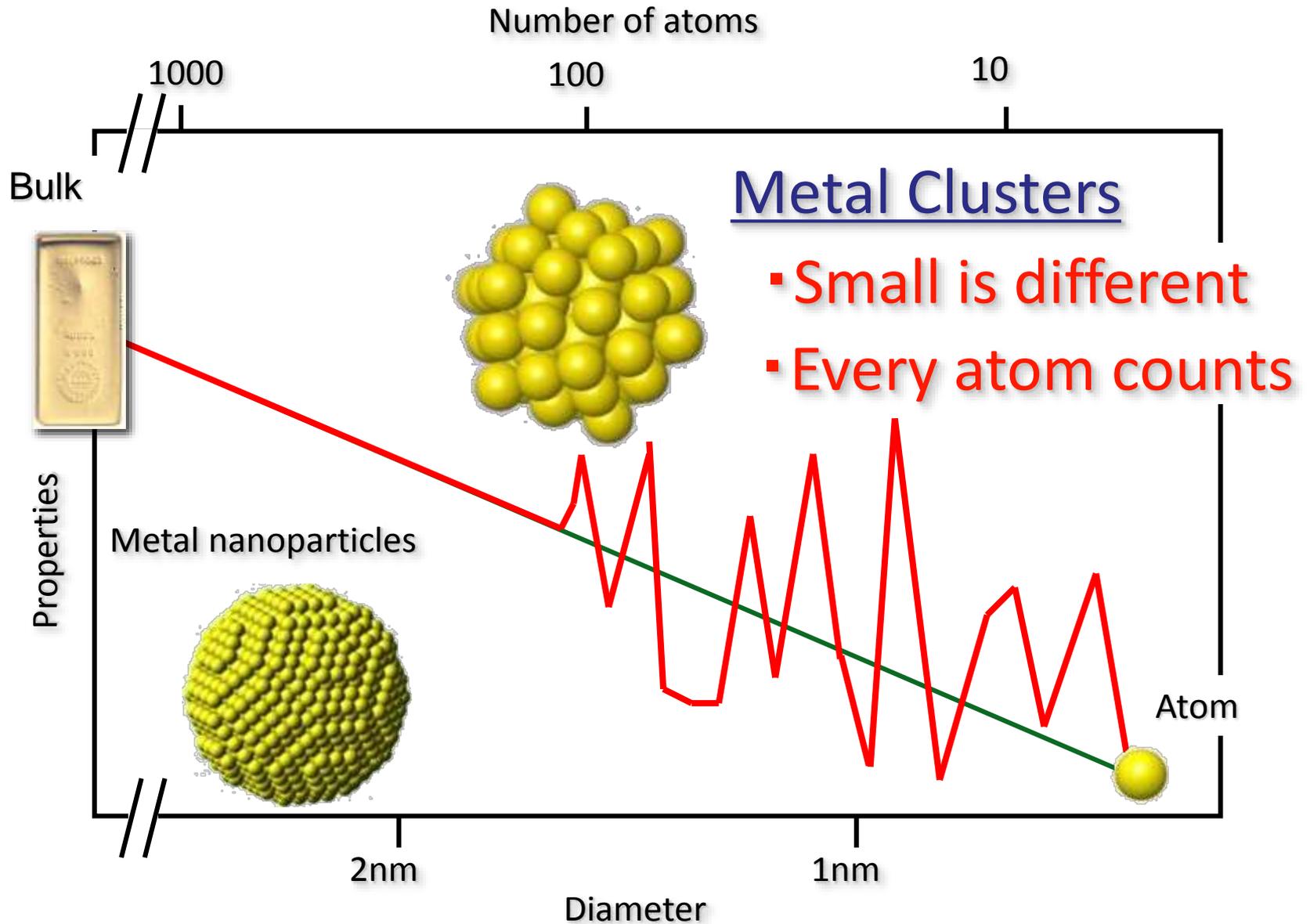


(A)–(C) Dark field fluorescence images of Au@SiO₂@Ag₁₅ MFs showing the gradual disappearance of luminescence with increasing Hg²⁺. (D)–(F) Fluorescence images showing variation in color during the addition of Hg²⁺ of different concentrations to Au@SiO₂-FITC@Ag₁₅ MFs. Insets in all images show the corresponding optical images of the MFs; scale bars are 3 μm .

Cavities, channels, imprints, assemblies, fibres, ...



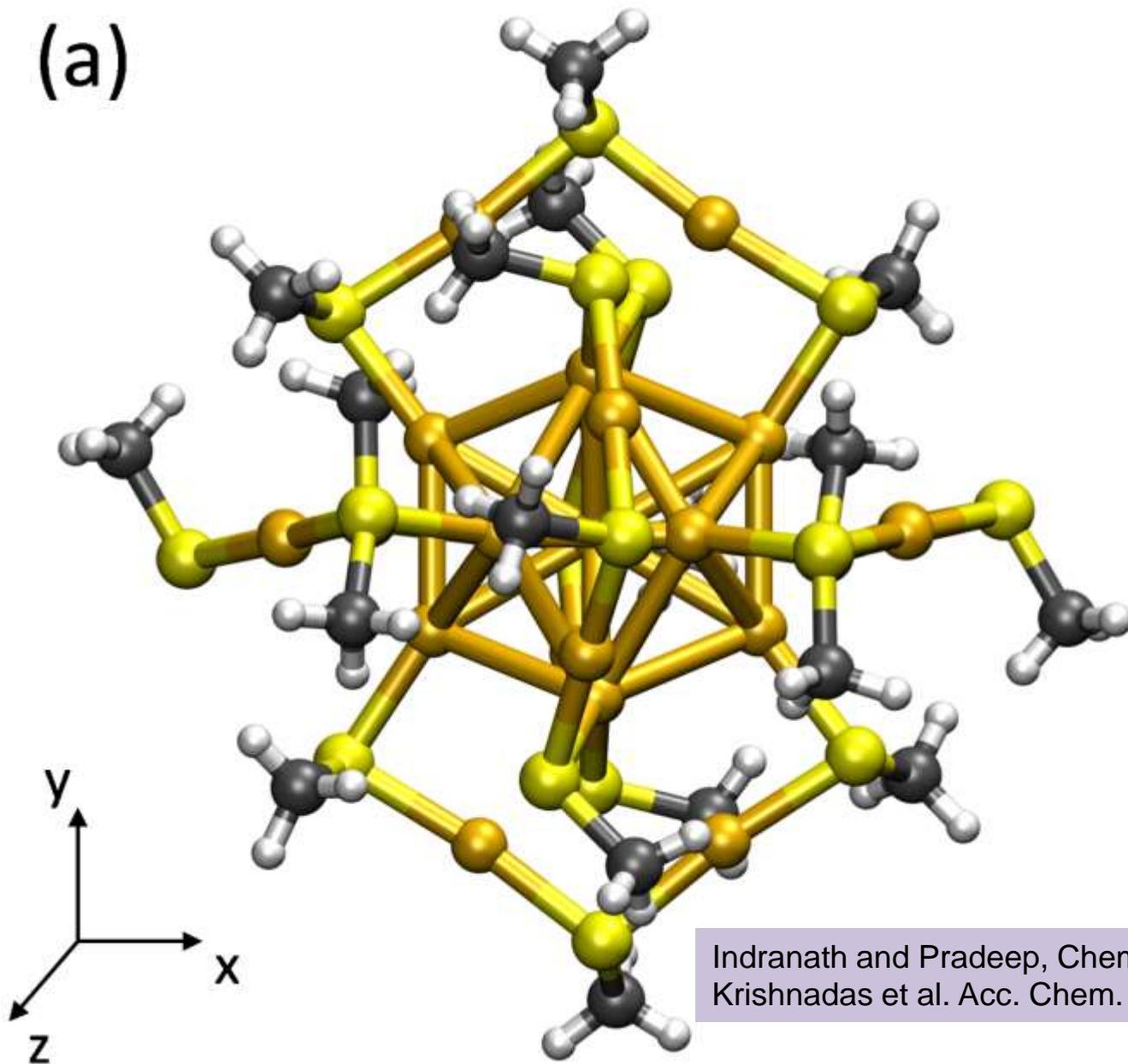
Metal Clusters





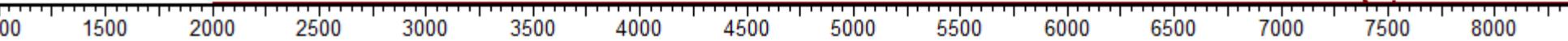
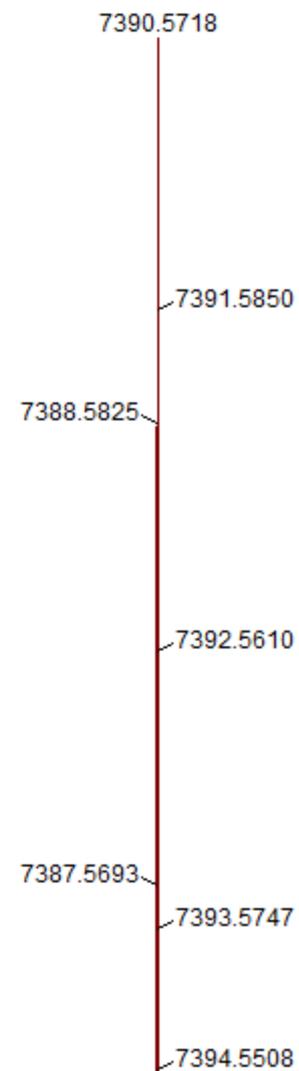
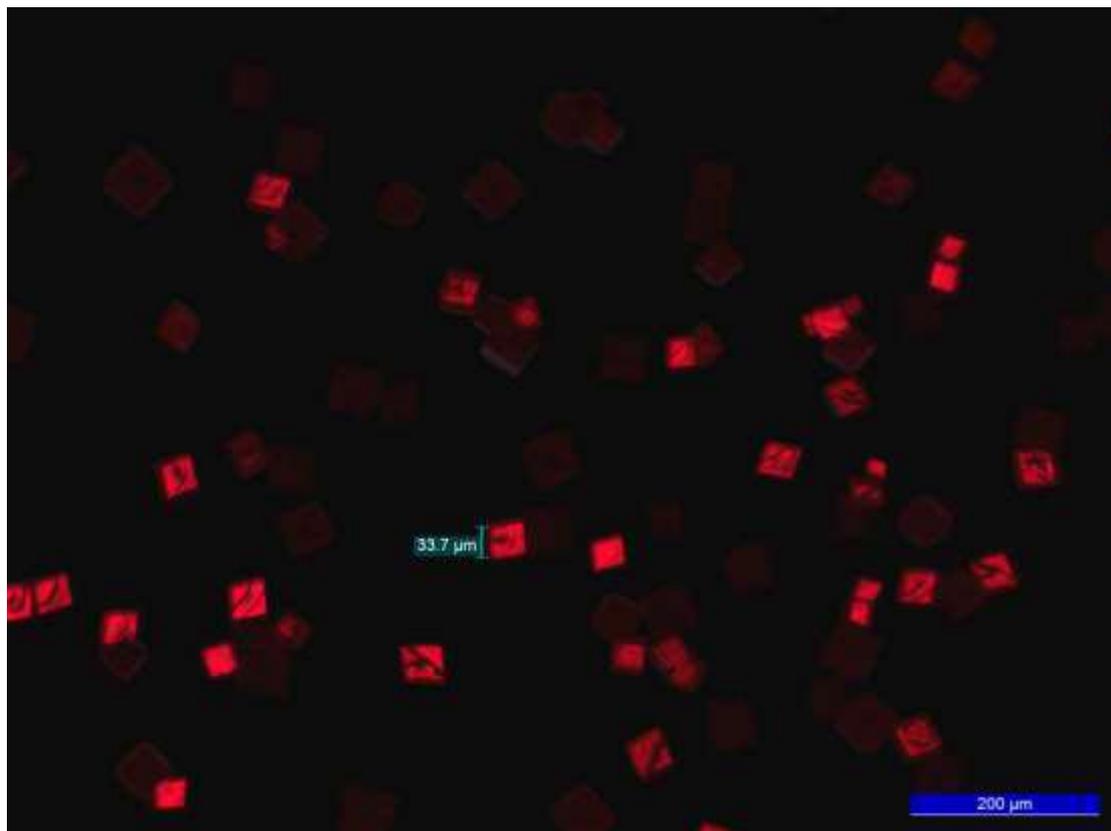
Shibhu, Habeeb, Uday, Kamalesh, Lourdu, Ammu, Ananya, Indranath, Atanu, Krishnadas, Shridevi, Papri,

(a)

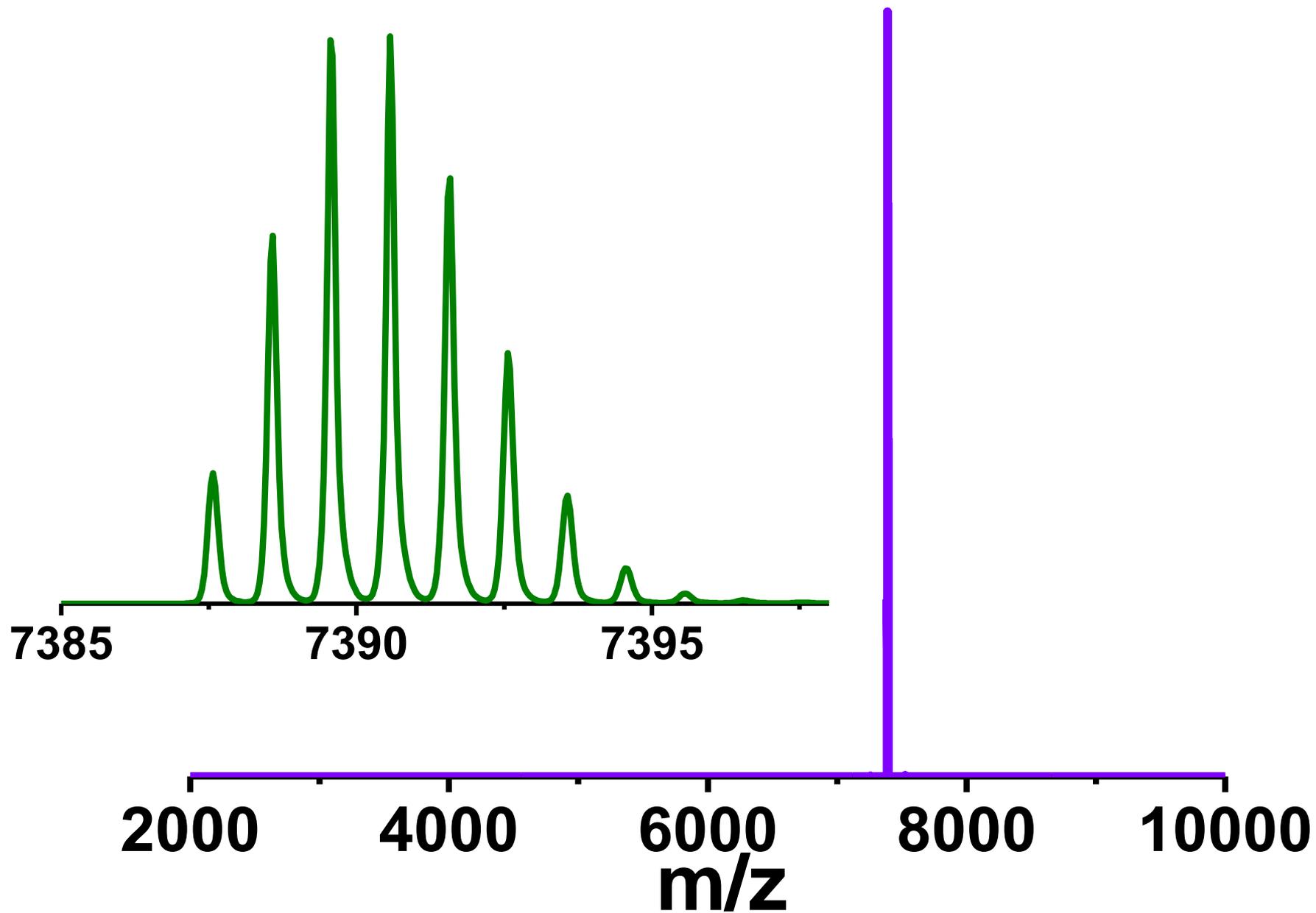


Indranath and Pradeep, Chem. Rev. 2017
Krishnadas et al. Acc. Chem. Res. 2017 (to appear)

Au₂₅PET₁₈



$\text{Au}_{25}(\text{PET})_{18}^-$



Biopolymer-re nanocomposit water purifica

Mohan Udhaya Sankar¹, 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
without electricity. The critical p
synthesis of stable materials tha
uously in the presence of com
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 high
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

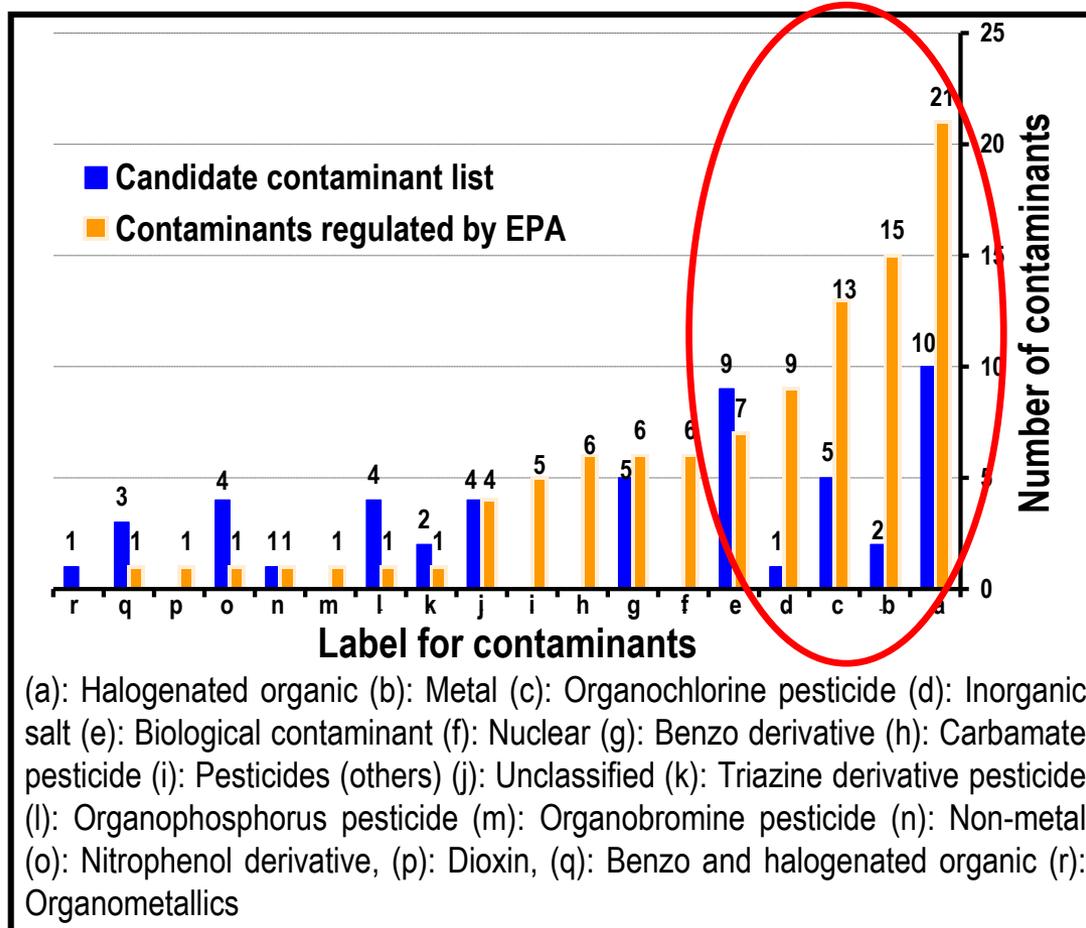
The Hindu, Telegraph, Times of India, etc.

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. Trailappi Pradeep, who led the team at IIT Chennai, told Chemistry World. He and his student Snehasuman Fair discovered in 2003 that heteroatoms such as carbon tetrachloride (CCl₄) completely break down into metal halides and amorphous carbon upon reaction with gold and silver nanoparticles.

Pradeep said this prompted them to extend their study to include organochlorine and organophosphorus 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 that gold and silver nanoparticles loaded on alumina were indeed able to completely remove endosulfan, malathion and chlorpyrifos – three pesticides that are common in rural water supplies.

Use and recycle

The next

Pradeep



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

Chemistry world
First ever
nanotechnology
product for clean
water

1. Patents: A method of preparing purified water from water containing pesticides, **Indian patent 200767**
 2. Extraction of malathion and chlorpyrifos 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



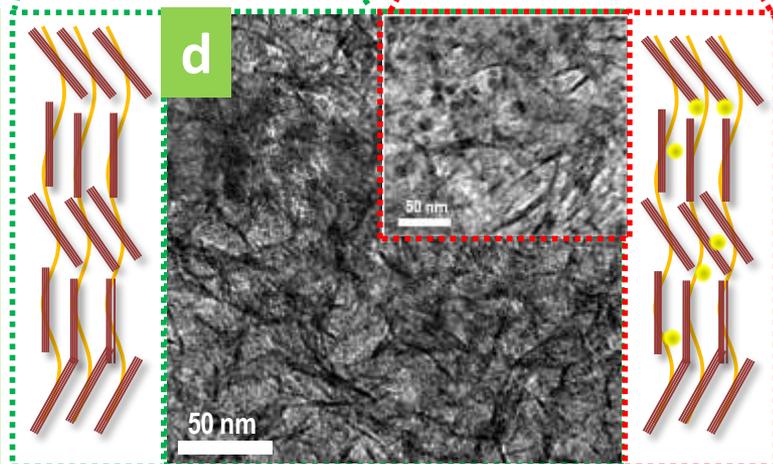
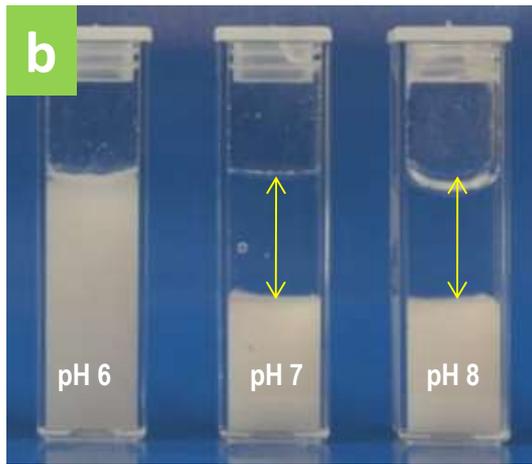
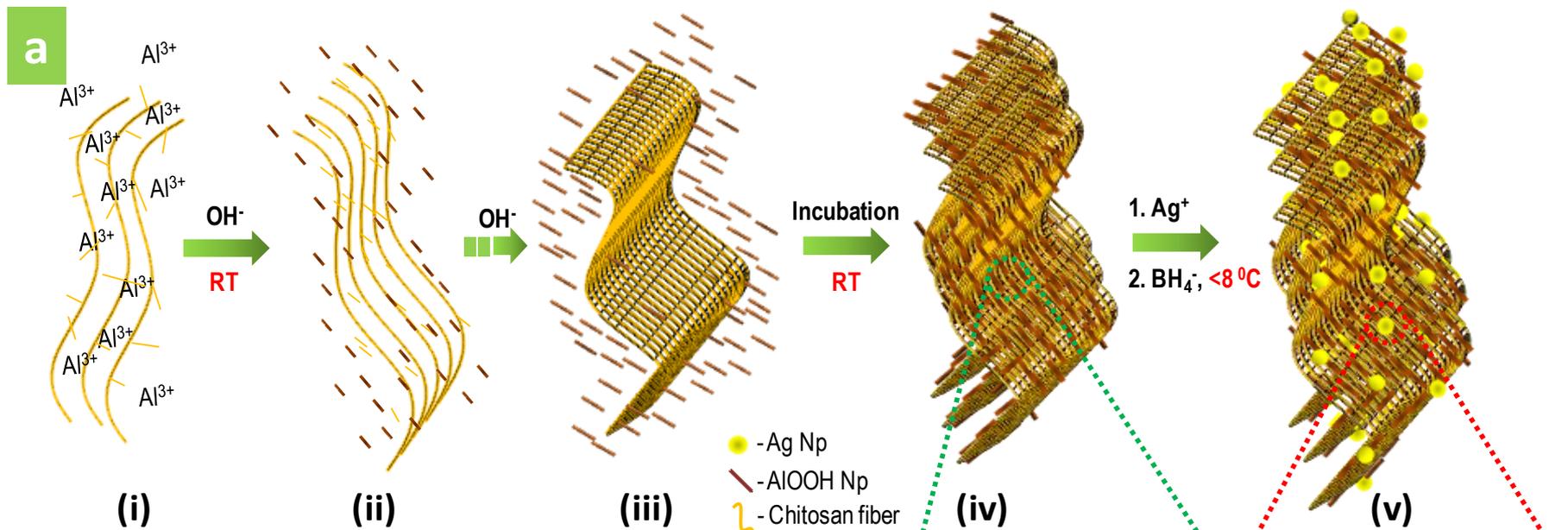
Affordable materials for water purification - Bioinspired

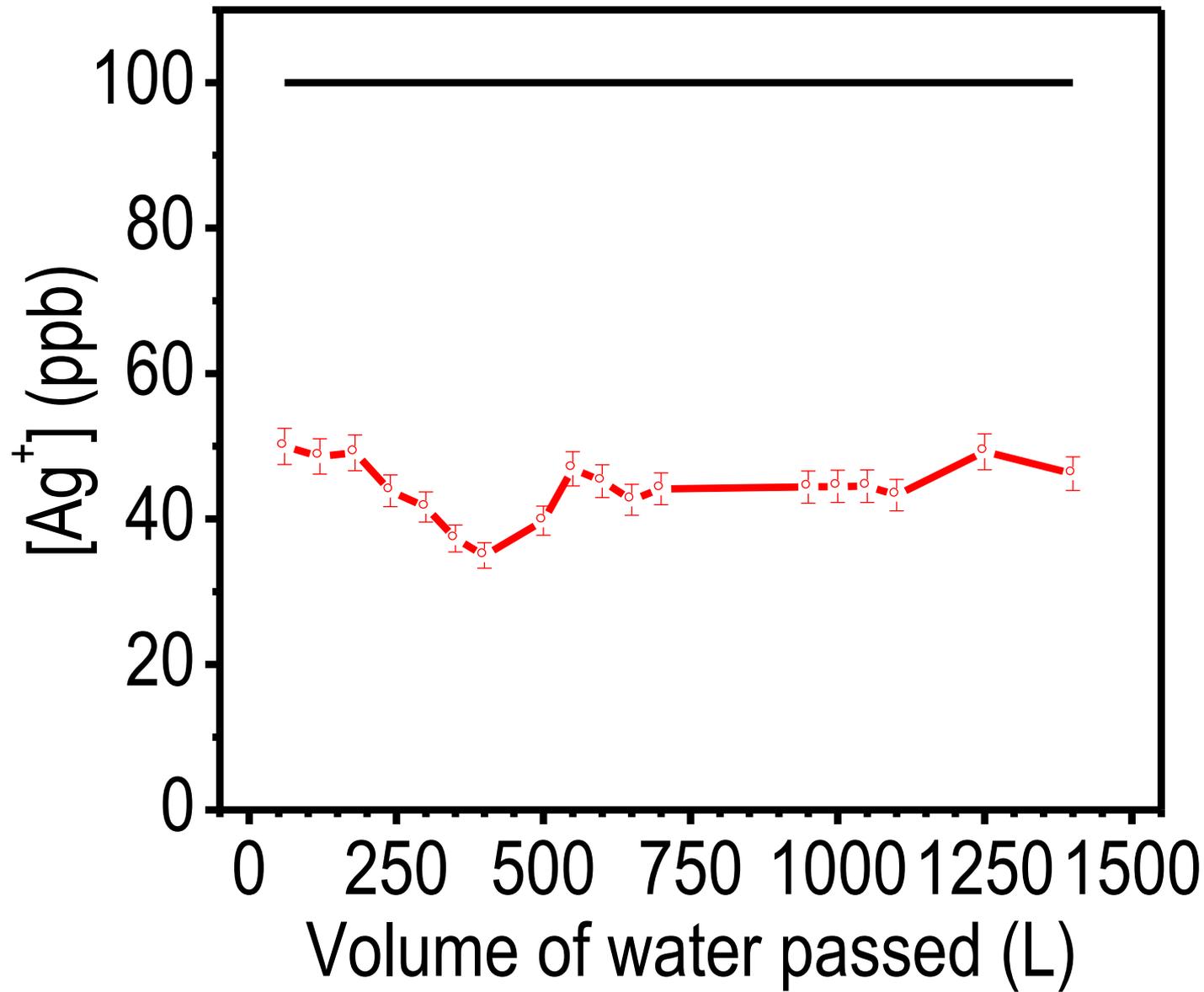
Water positive

Water-based, room temperature, water stable

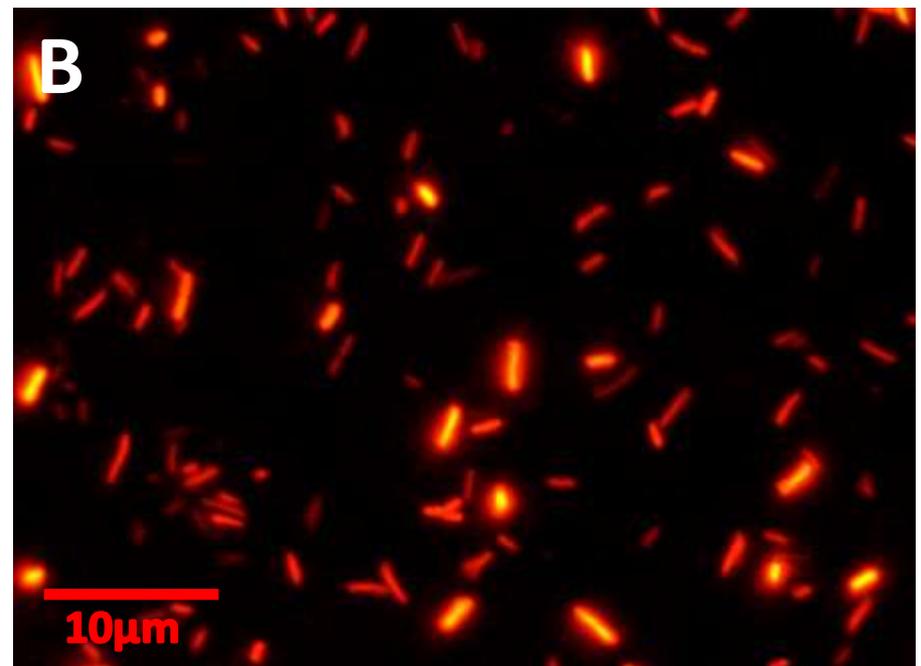
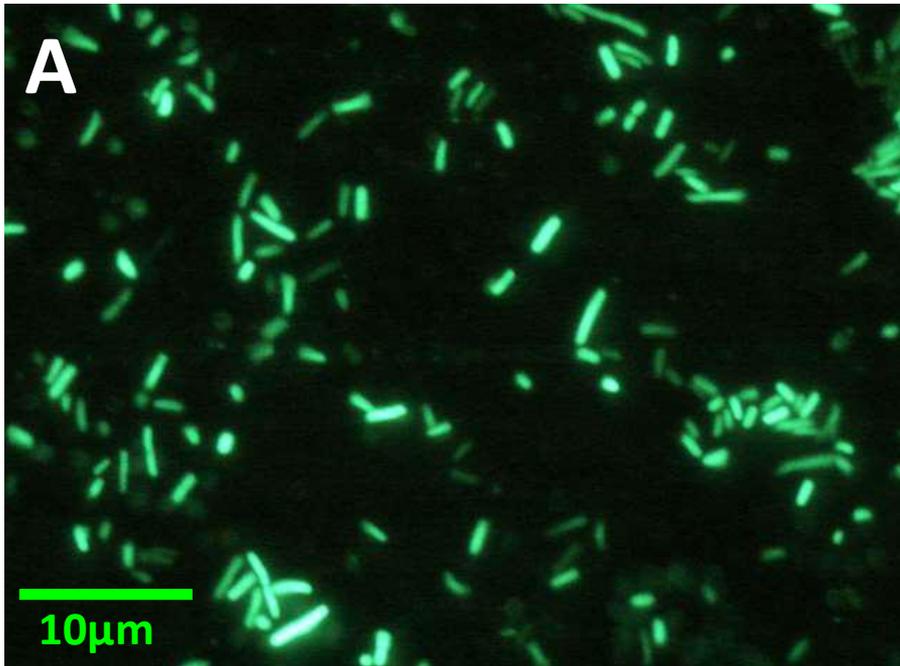
Green

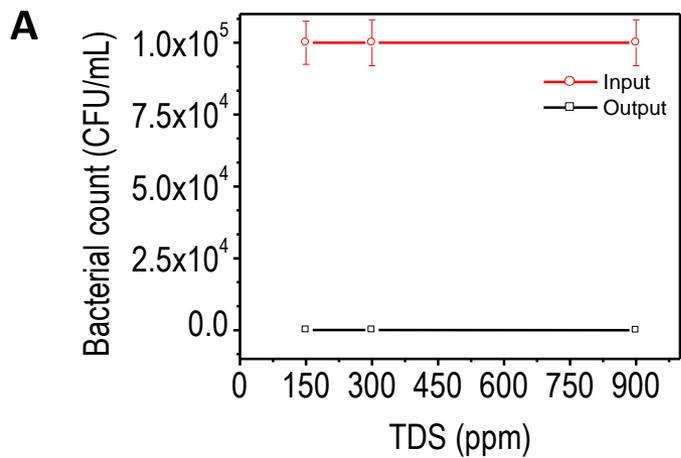
M. U. Sankar et al, PNAS 2013



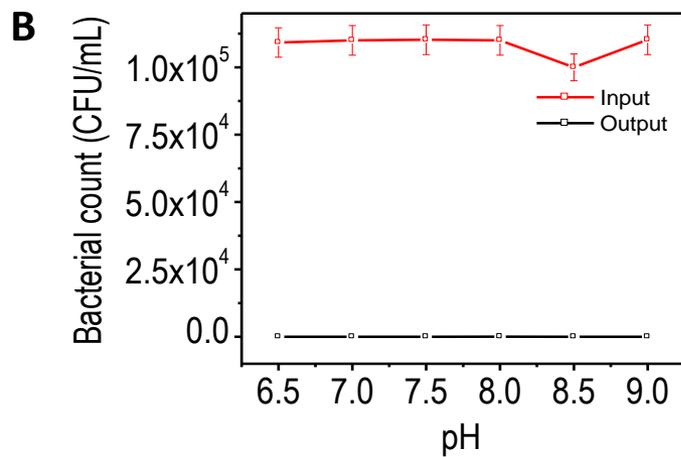


Live/dead staining experiments



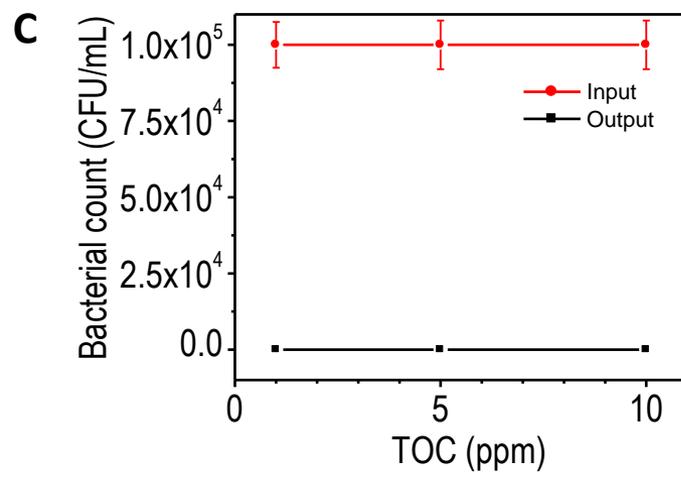


TDS

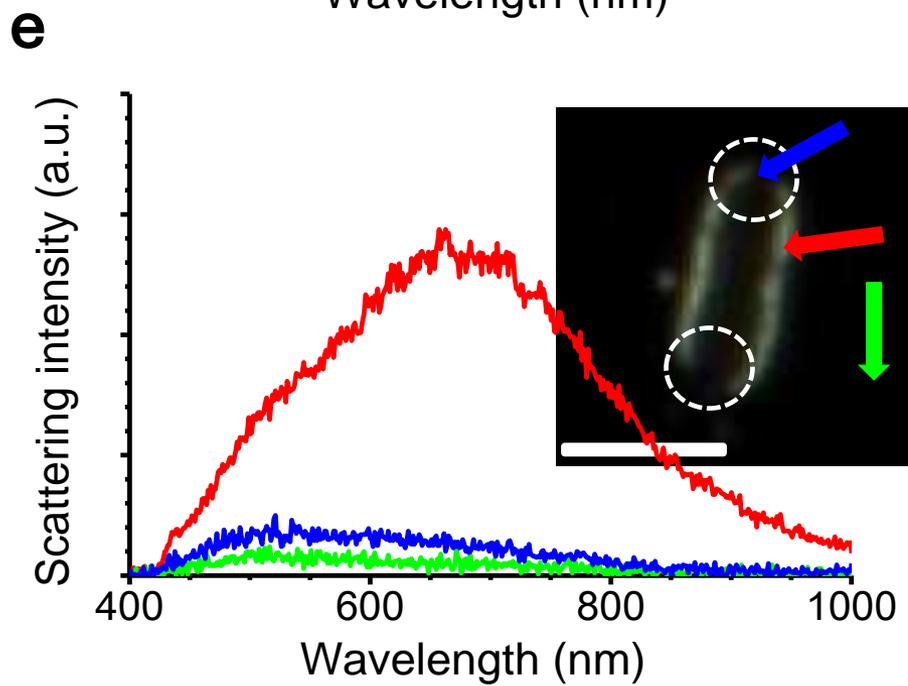
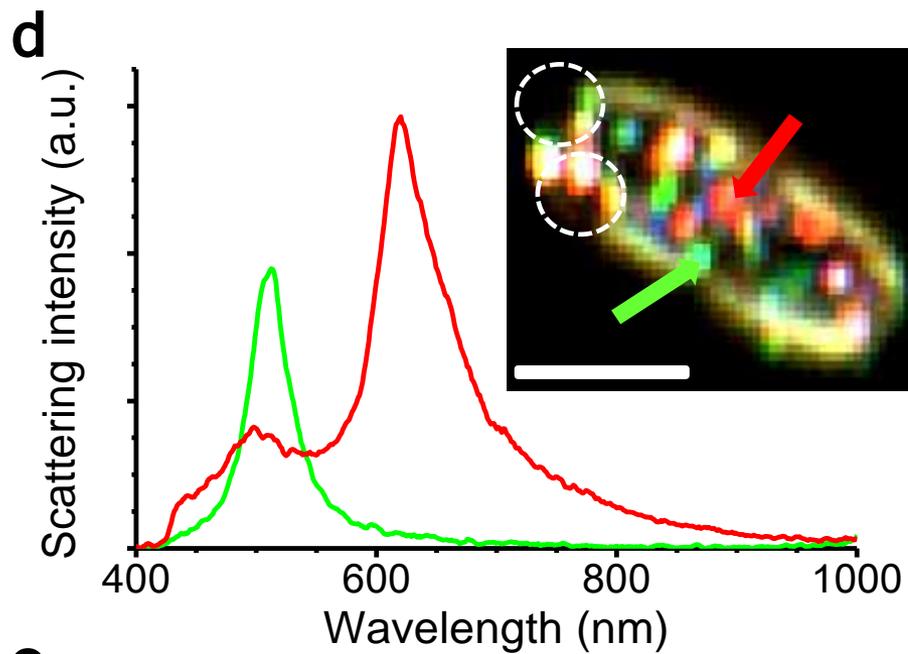
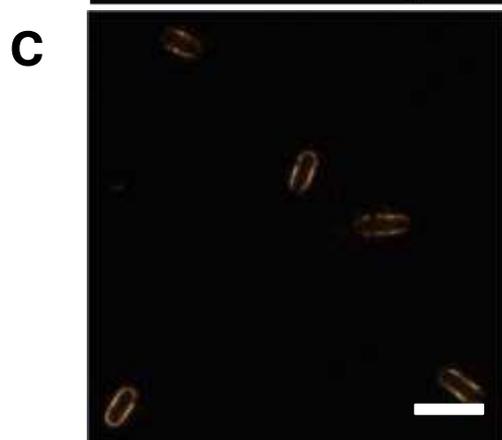
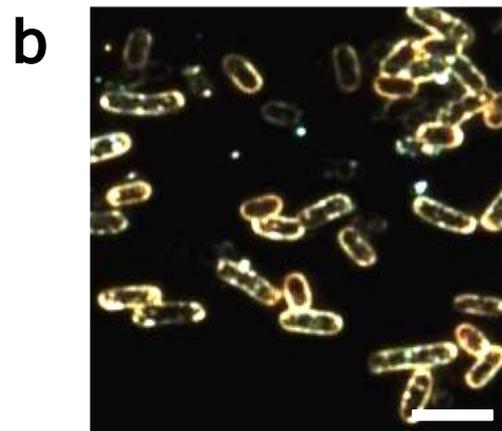
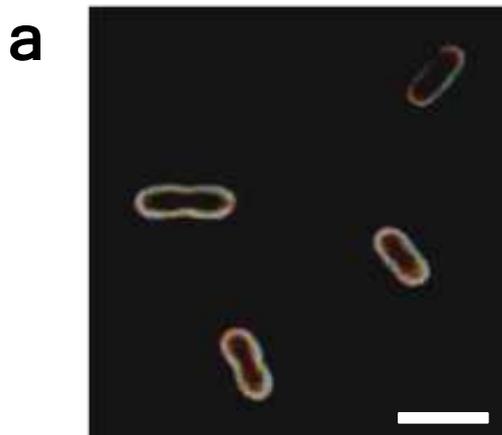


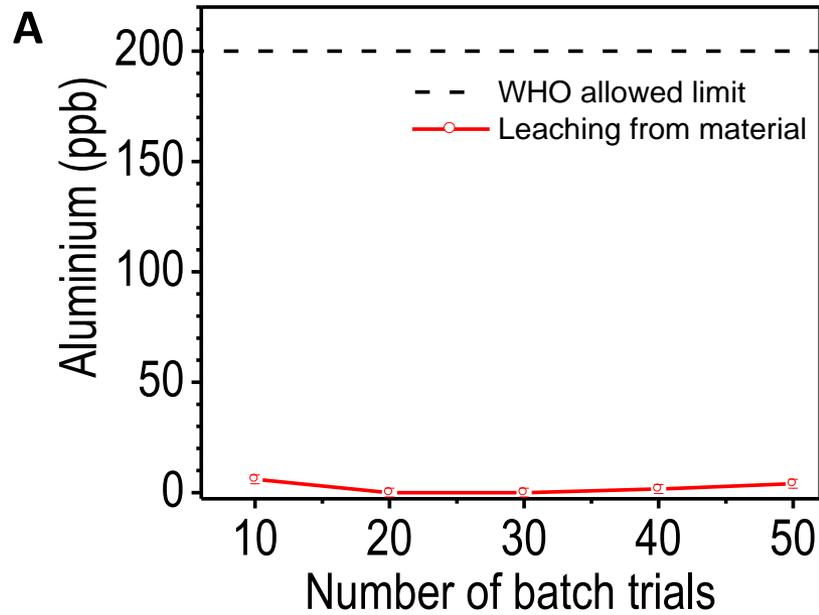
pH

Real water experiments

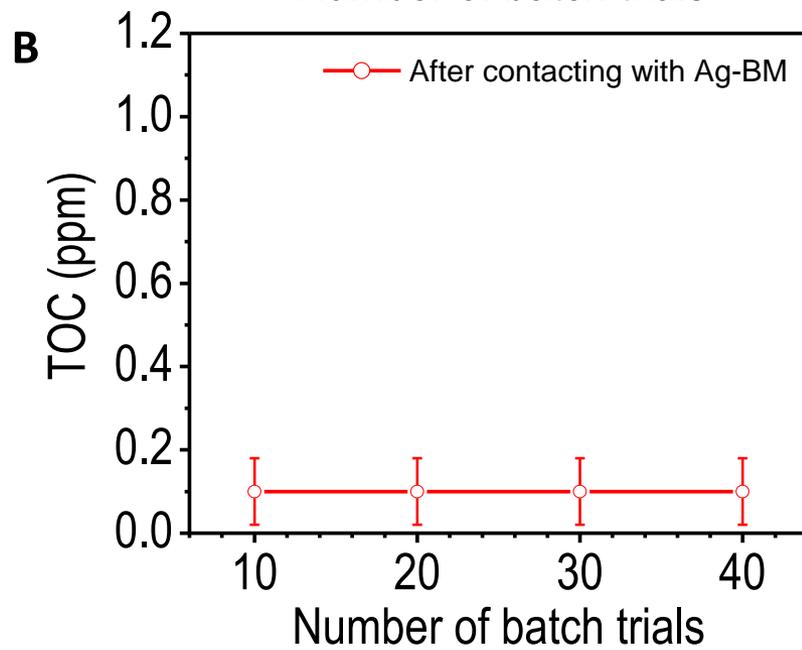


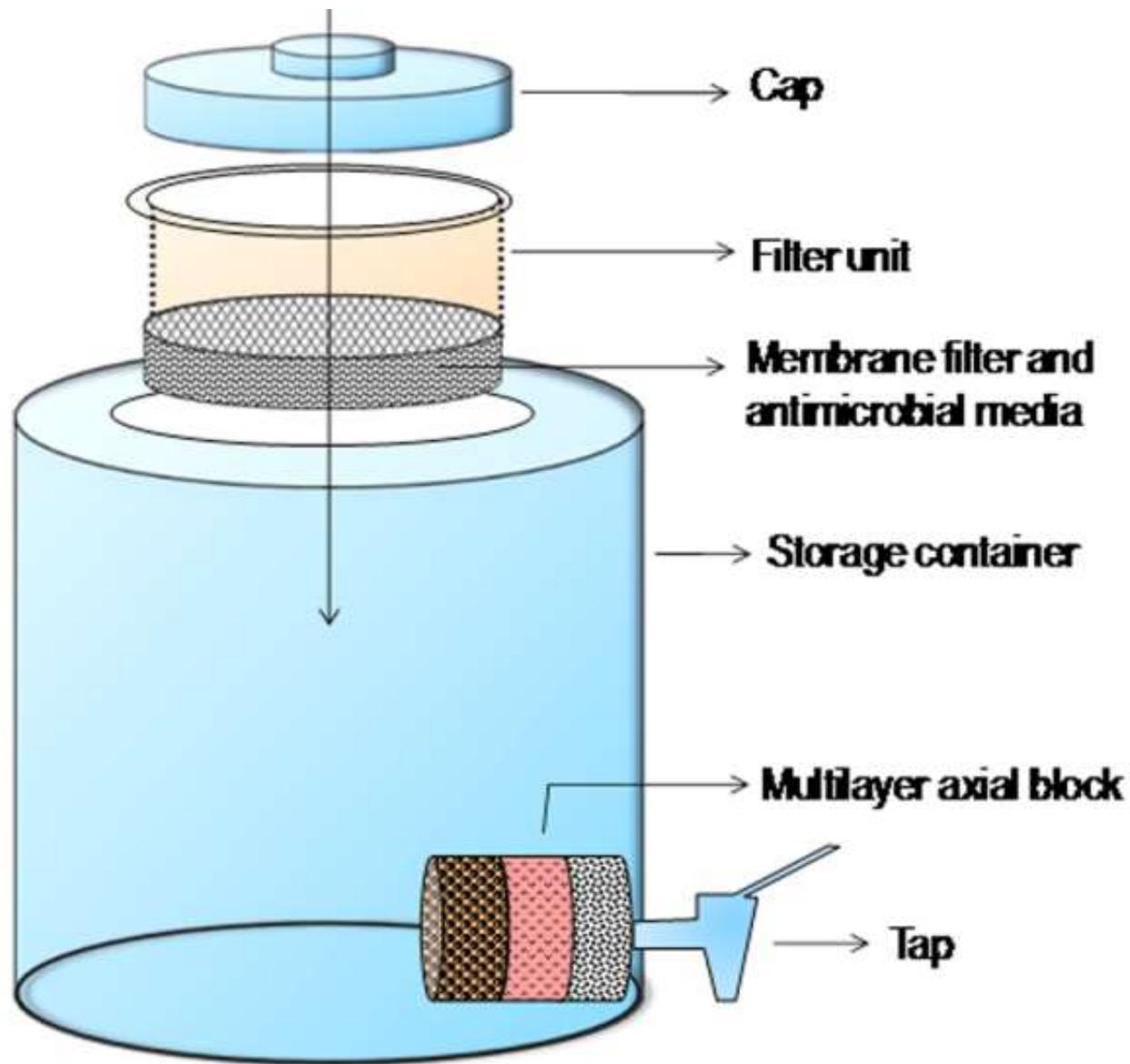
TOC – Humic acid





Leaching experiments





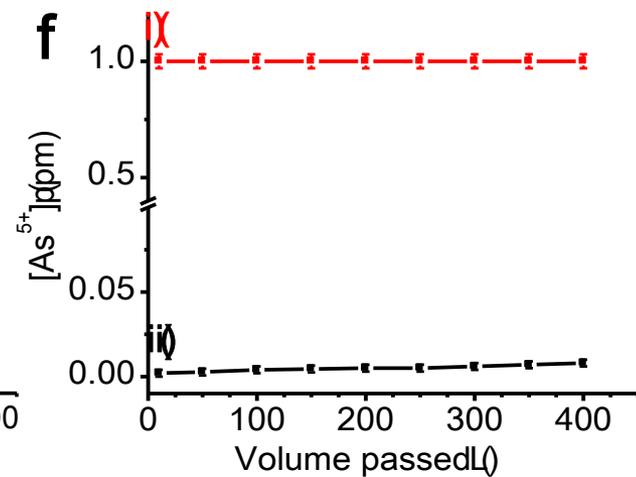
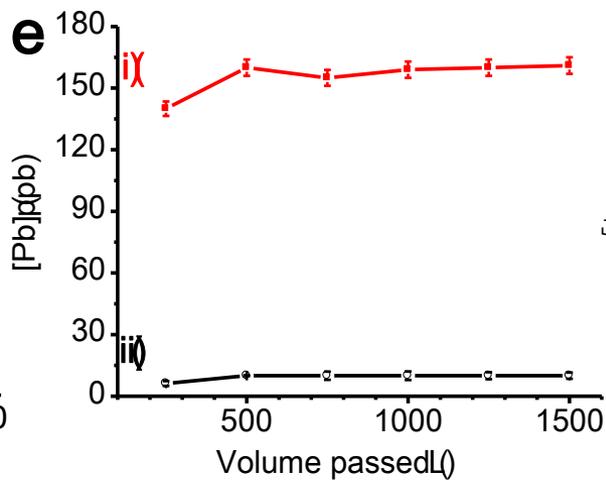
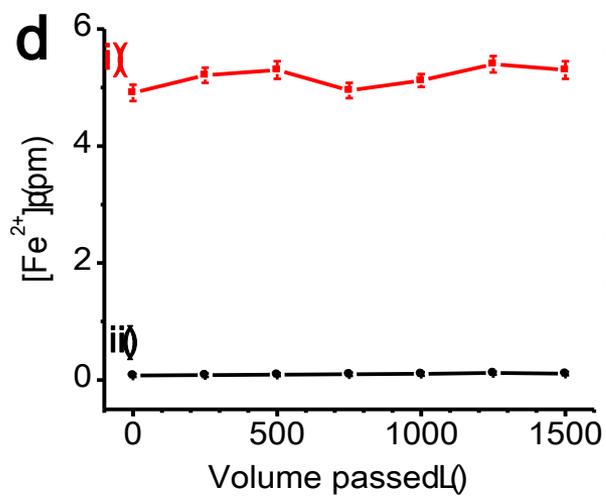
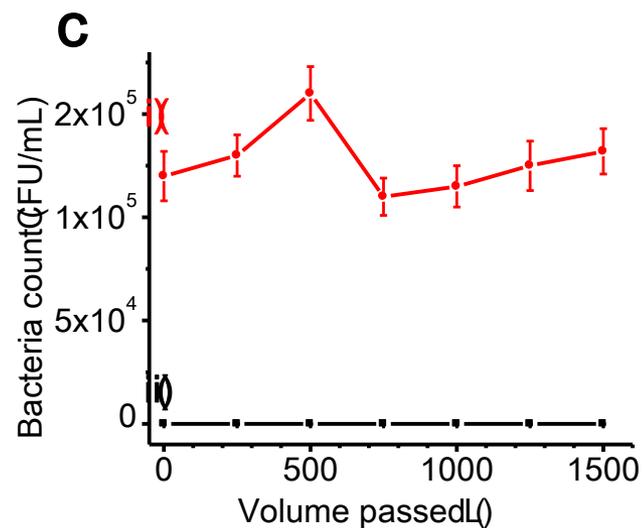
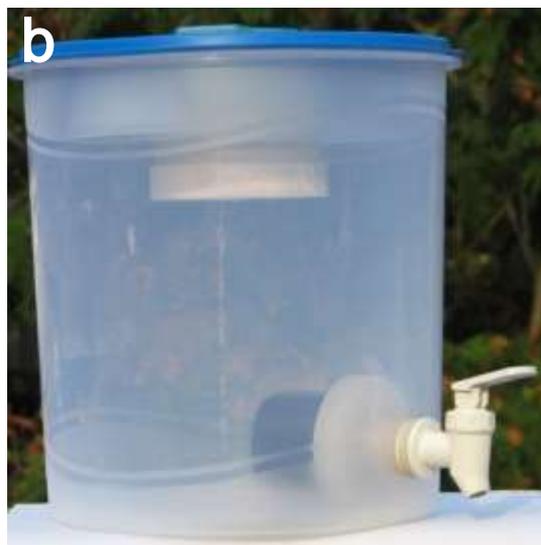
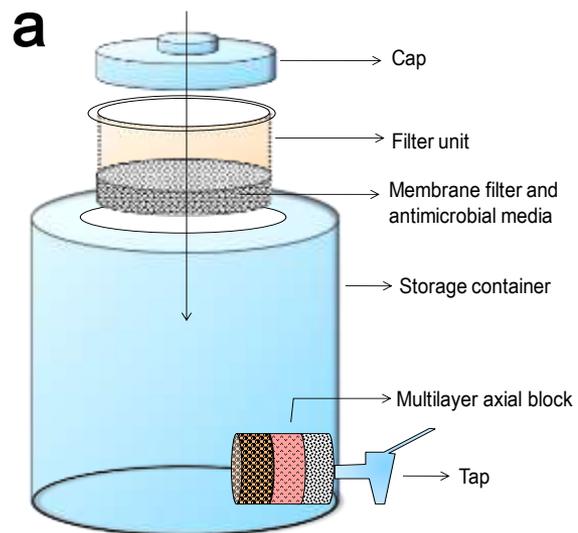
Physicochemical characteristics of influent natural drinking water

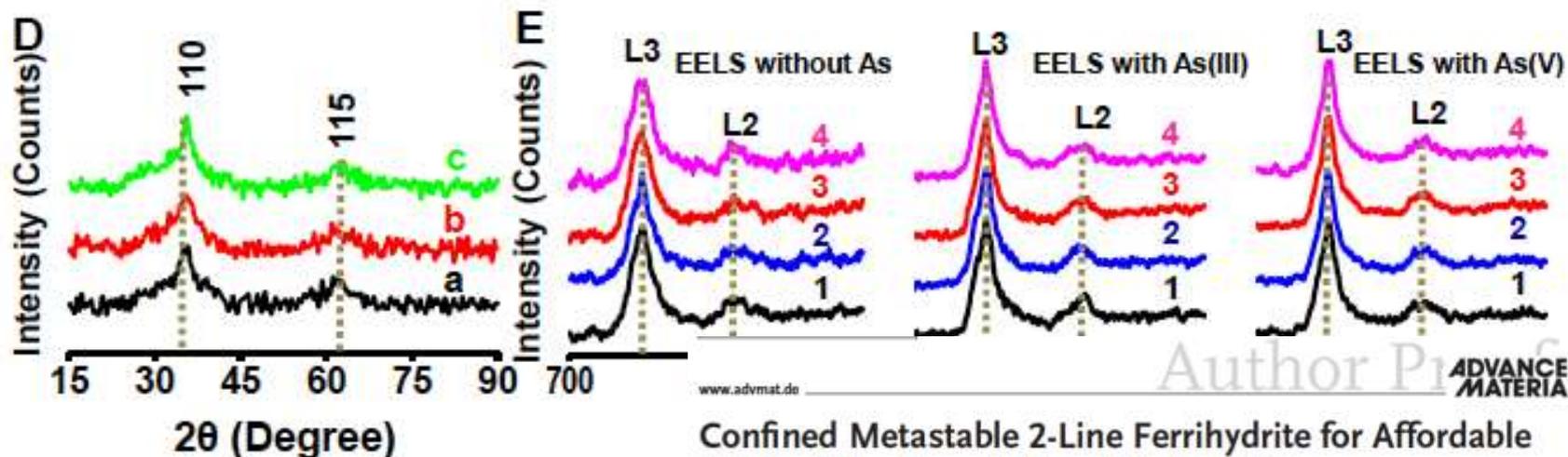
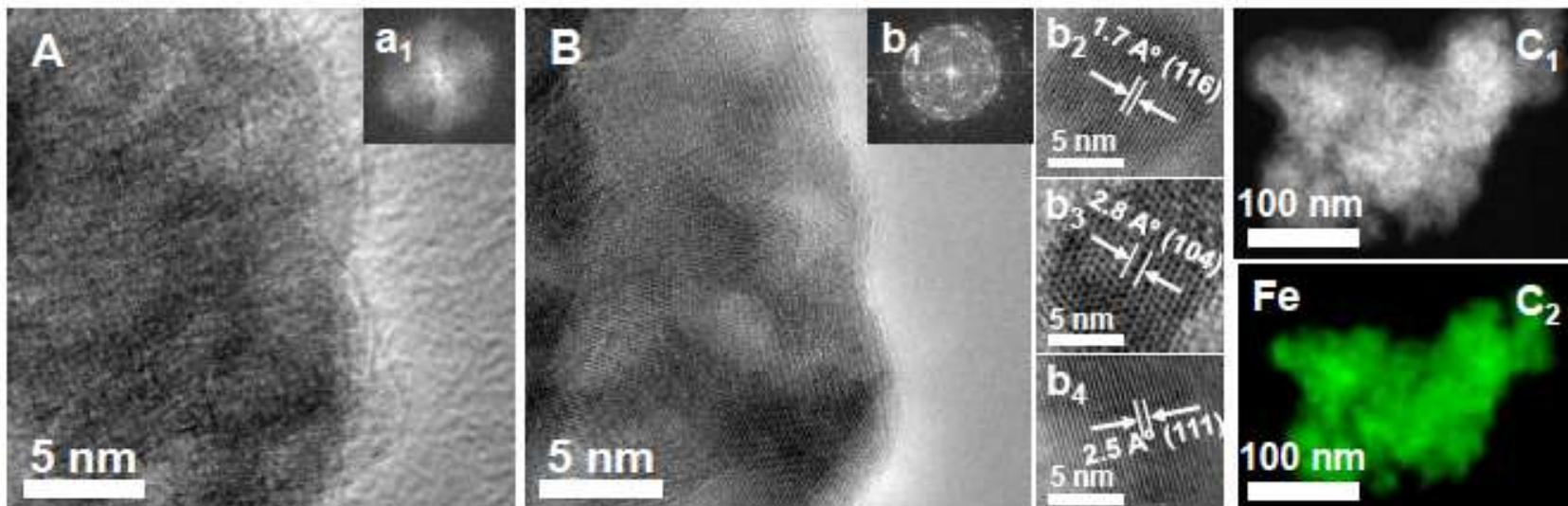
(Note: All parameters are expressed in mg L⁻¹, except for pH and conductivity)

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



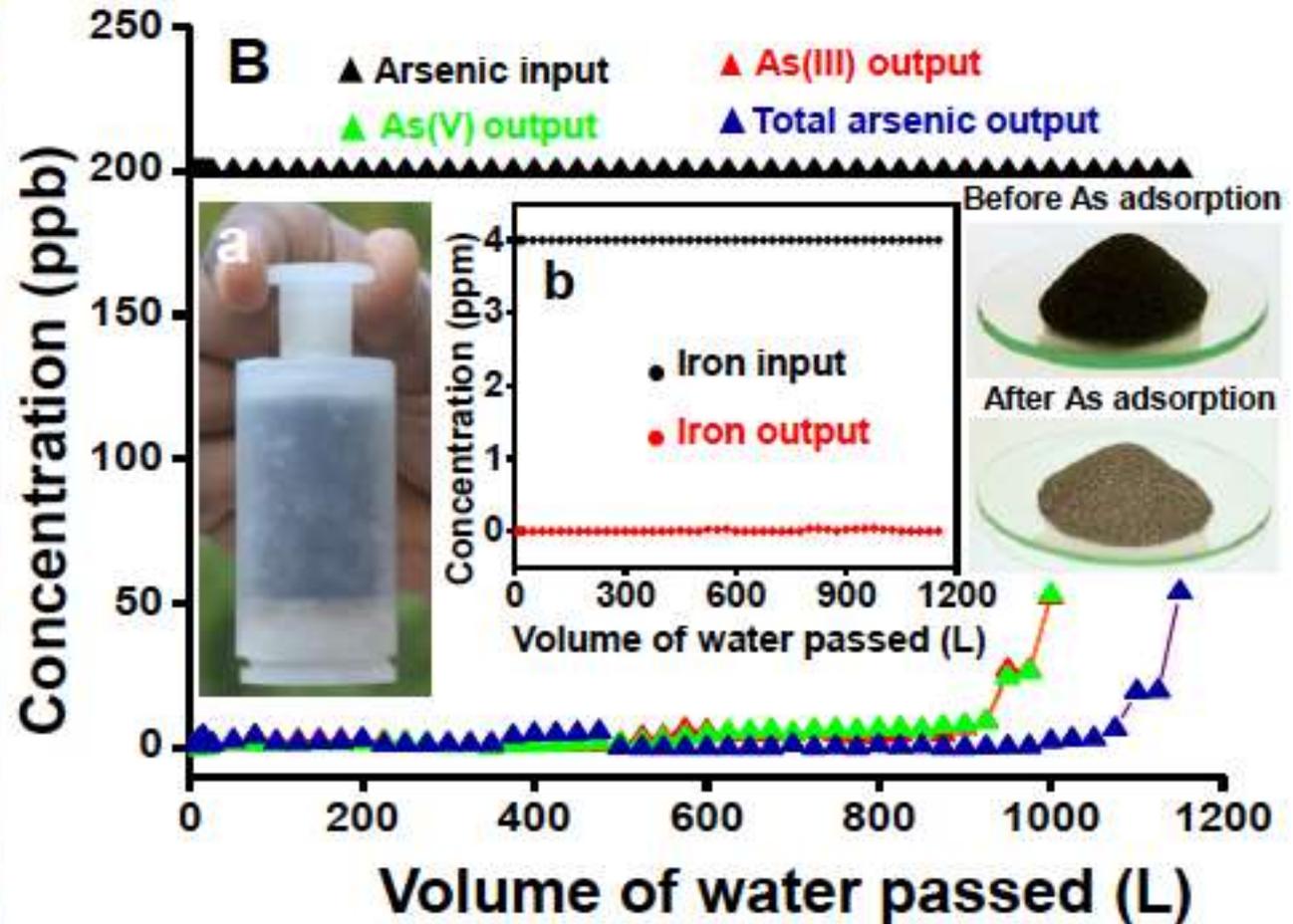


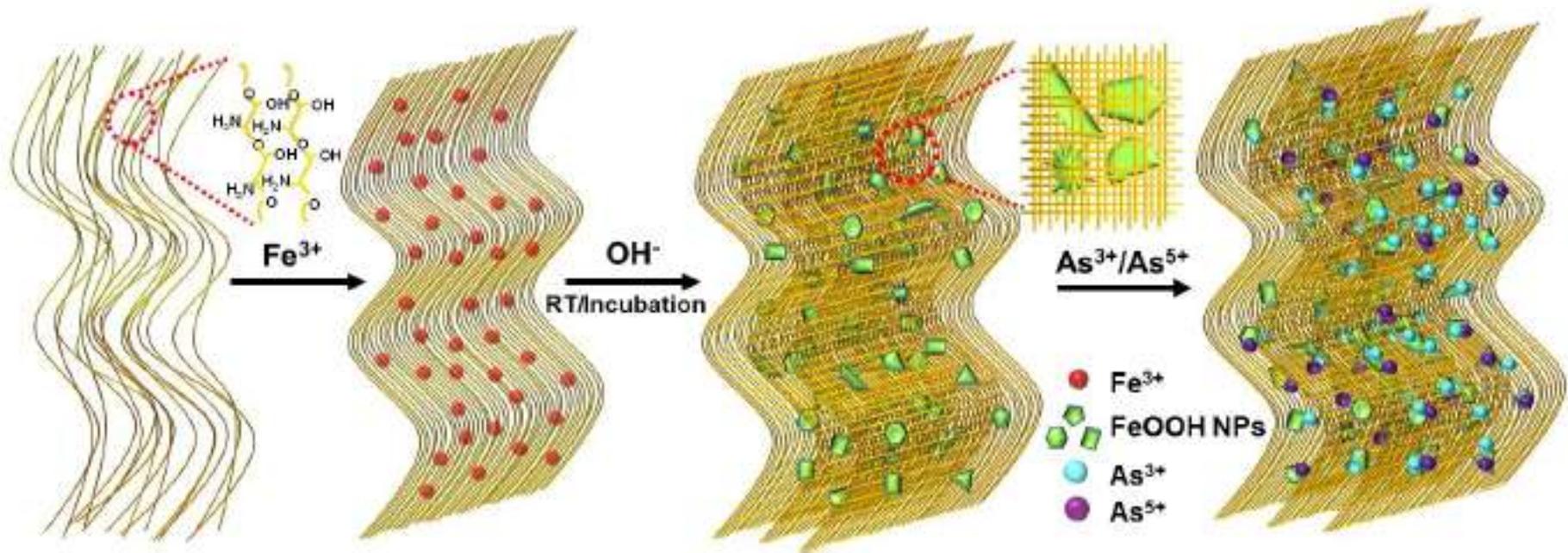
www.advmat.de

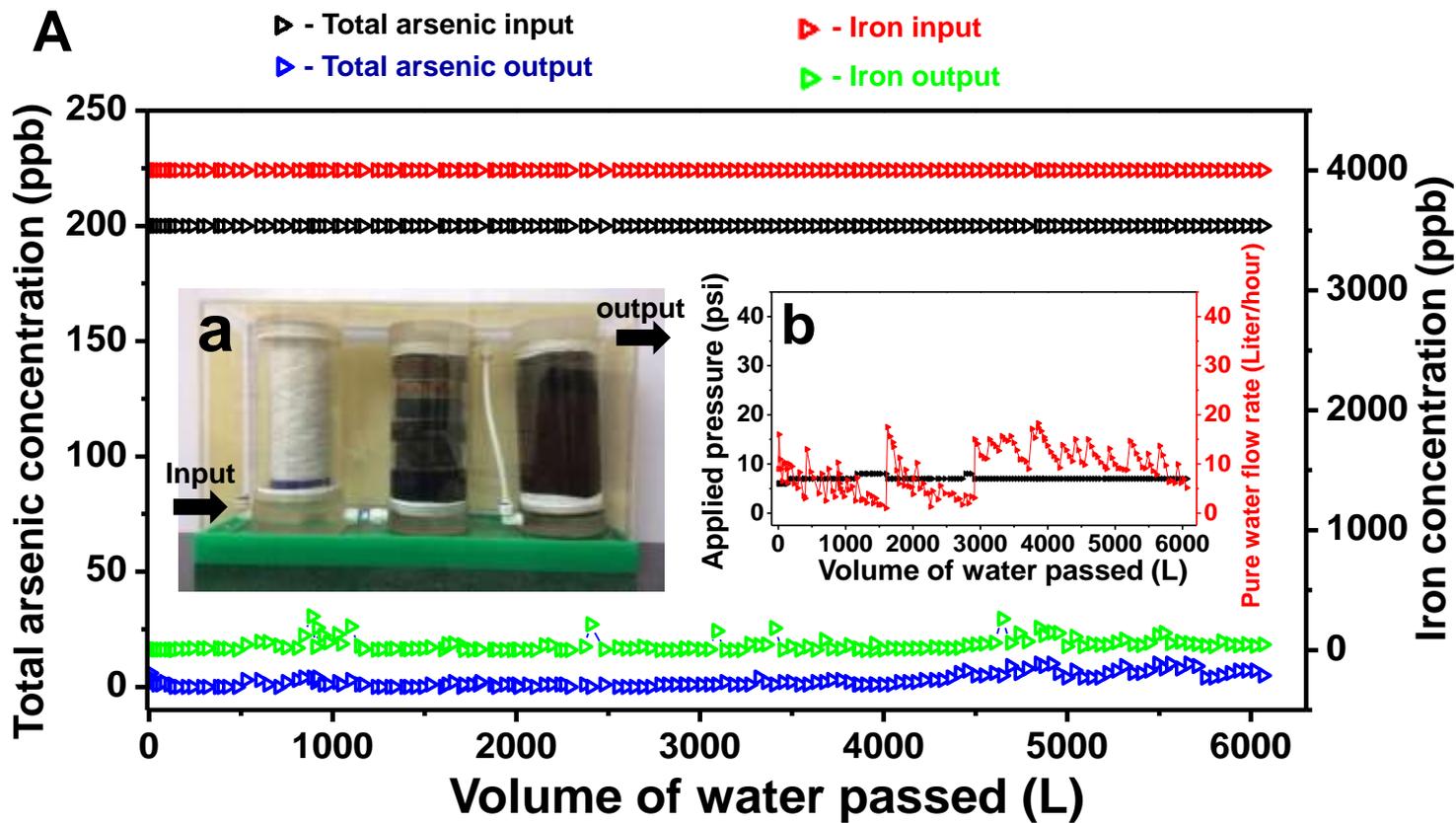
Author PAPER ADVANCED MATERIALS

Confined Metastable 2-Line Ferrihydrite for Affordable Point-of-Use Arsenic Free Drinking Water

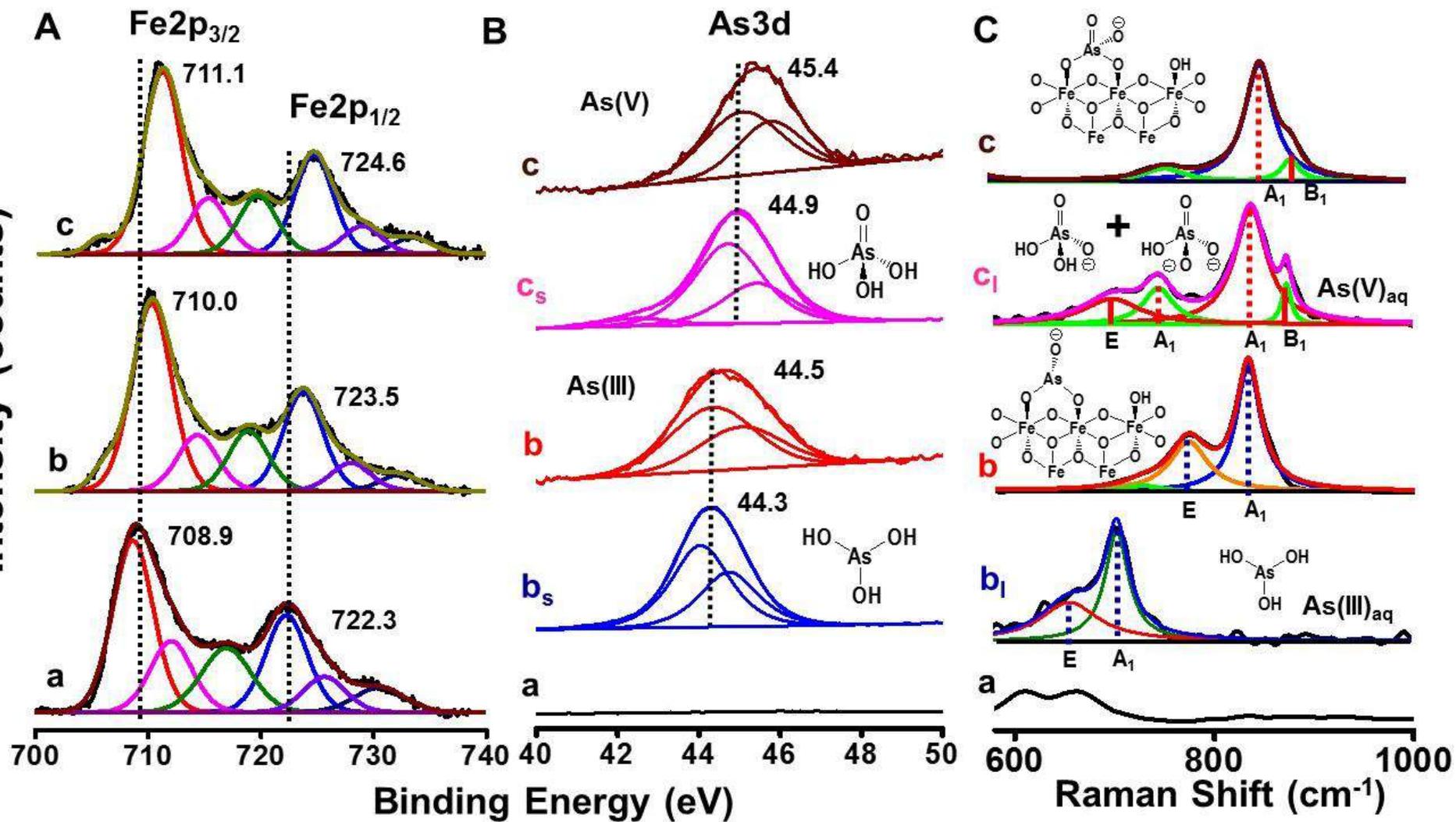
By Avula Anil Kumar, Anirban Som, Paolo Longo, Chennu Sudhakar, Radha Gobinda Bhuin, Soujit Sen Gupta, Anshup, Mohan Udhaya Sankar, Amrita Chaudhary, Ramesh Kumar, and T. Pradeep*



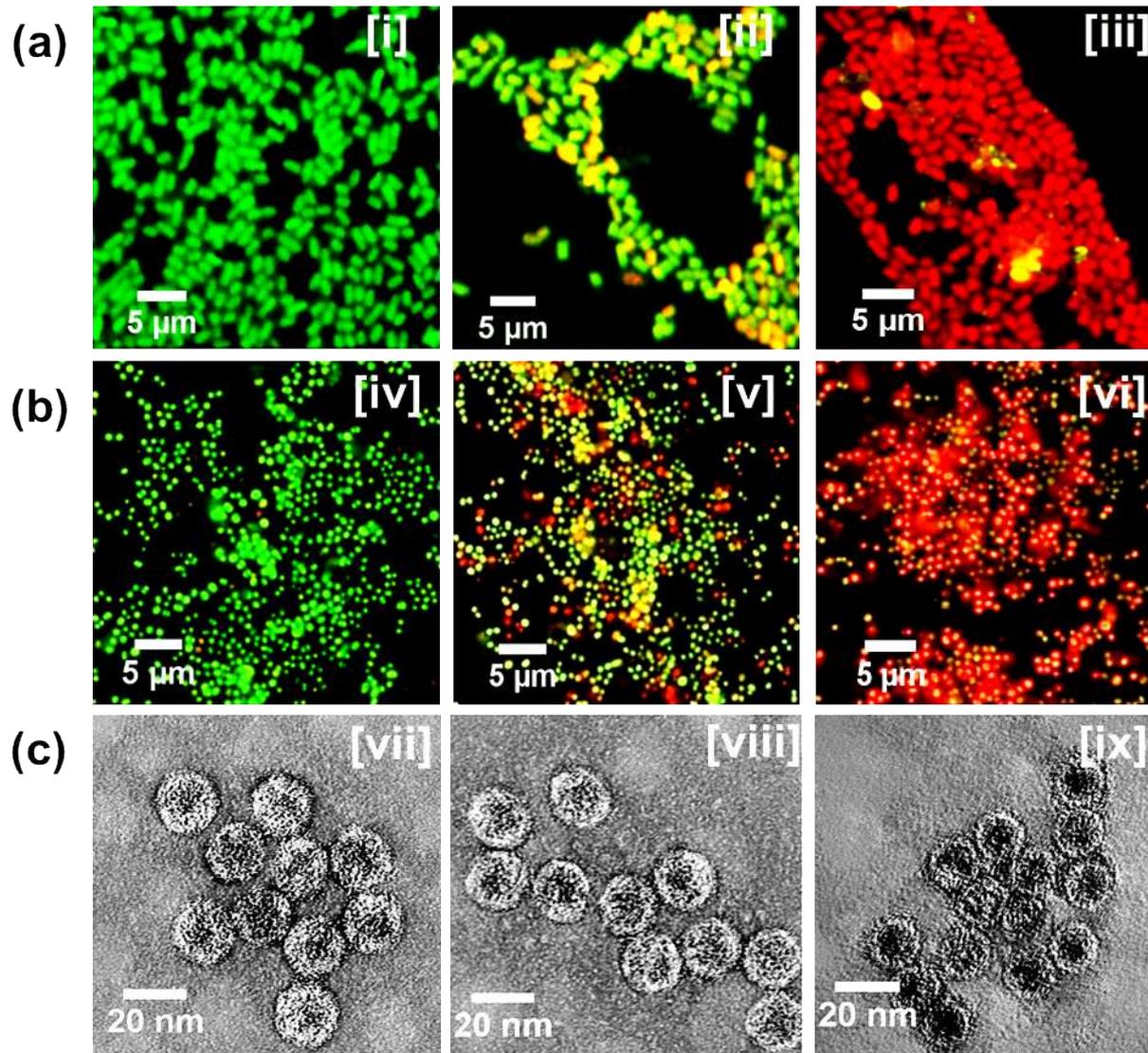




Intensity (counts)

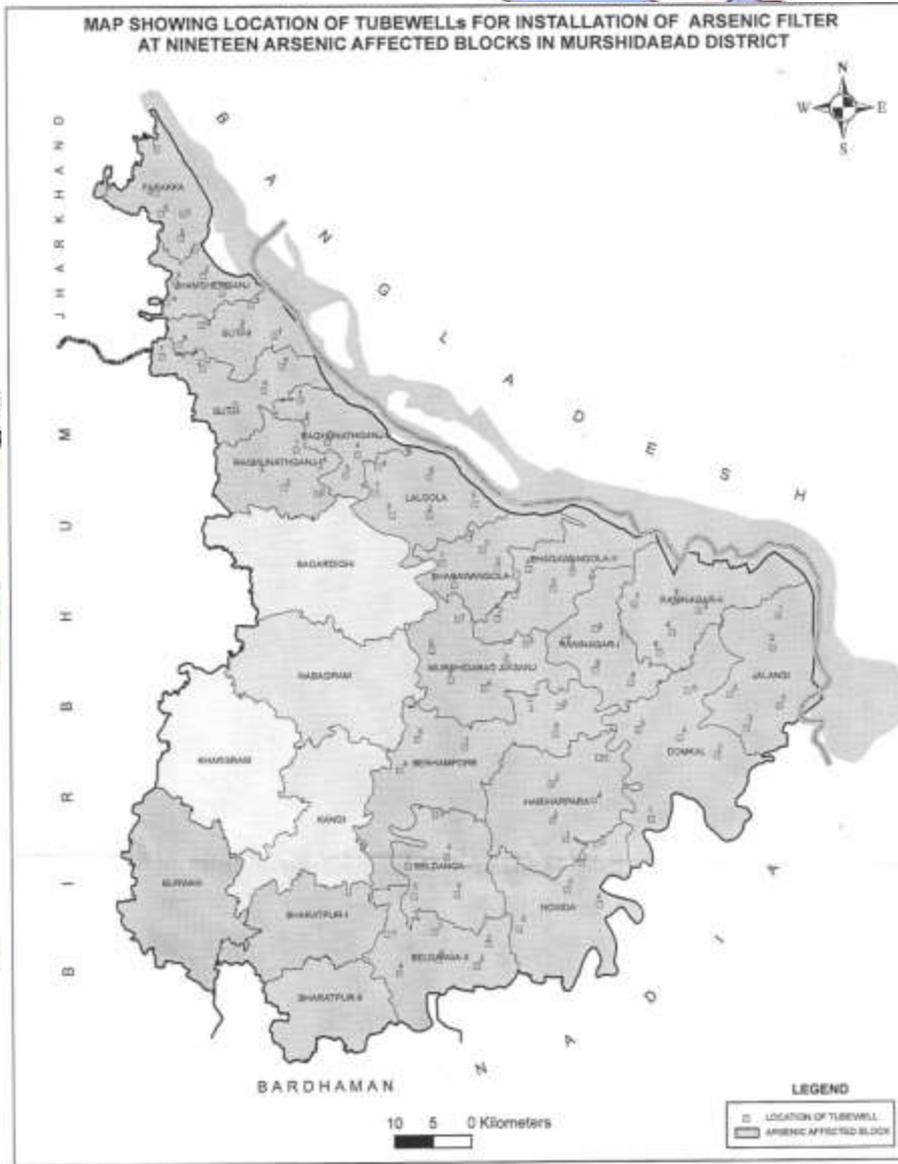


Anion effect





Population Map Of India-2001



Imagining how new adsorbents are changing the dynamics at ground level



- Existing unit for iron and arsenic removal – 20 m³/h
- Uses activated alumina and iron oxide (old generation of adsorbents)



- Existing unit for iron and arsenic removal – 18 m³/h
- Uses iron oxyhydroxide (new generation of adsorbents)
- Input arsenic concentration: 168 ppb
- Output arsenic concentration: 2 ppb

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.	Dhipara 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.	Rabindratala 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 Hariharpara 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

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

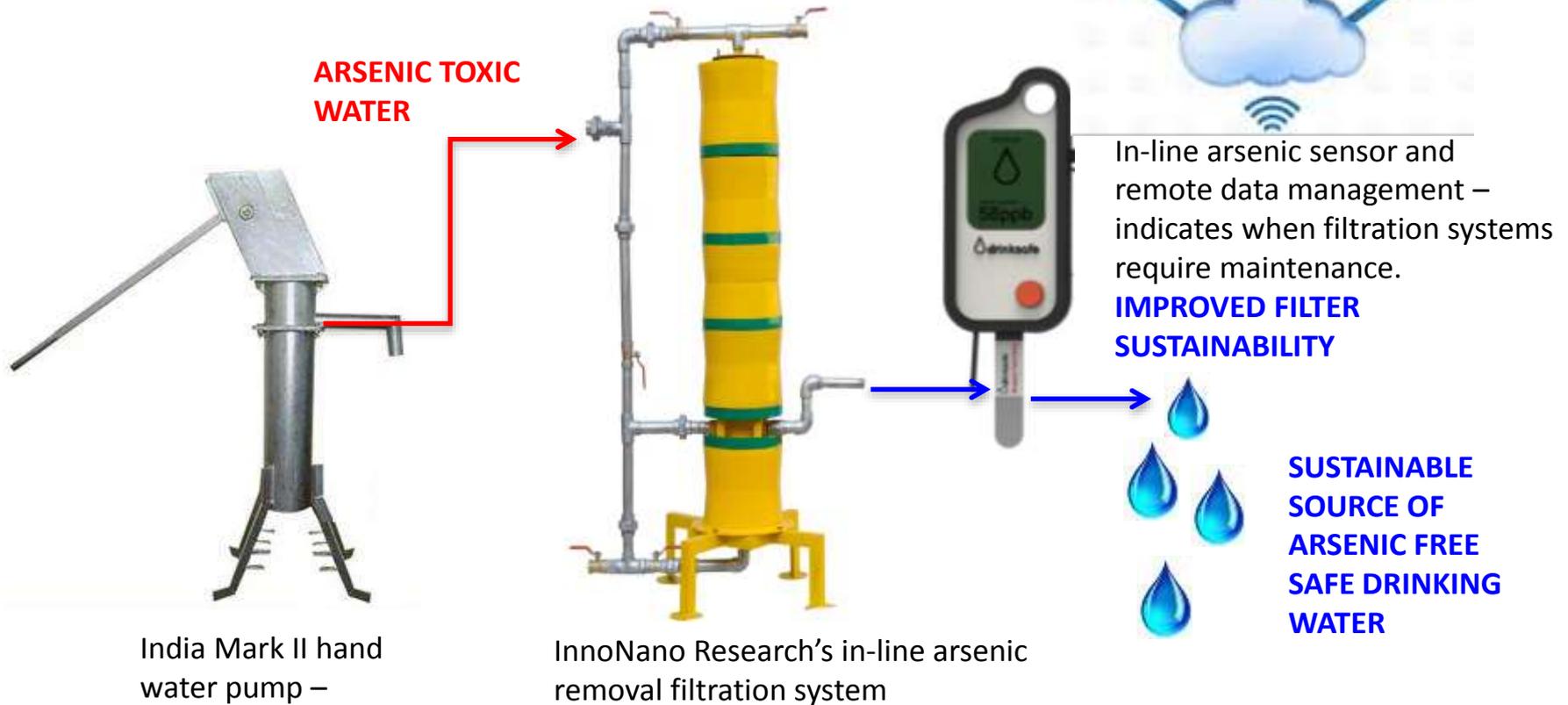
S. No.	Sample Name	Input arsenic (ppb)	Output arsenic (ppb)	Number of days running
1.	Dhapadia Junior Madrasah	46.5	2.15	30 days
2.	Khidirpur Shishu Shiksha Kendra	14.99	0	260 days
3.	Junior Madrasah	12.7	0	60 days
4.	Dhapana Board High School	14.96	0.6	45 days
5.	Birpur Primary School	19.56	0	90 days
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



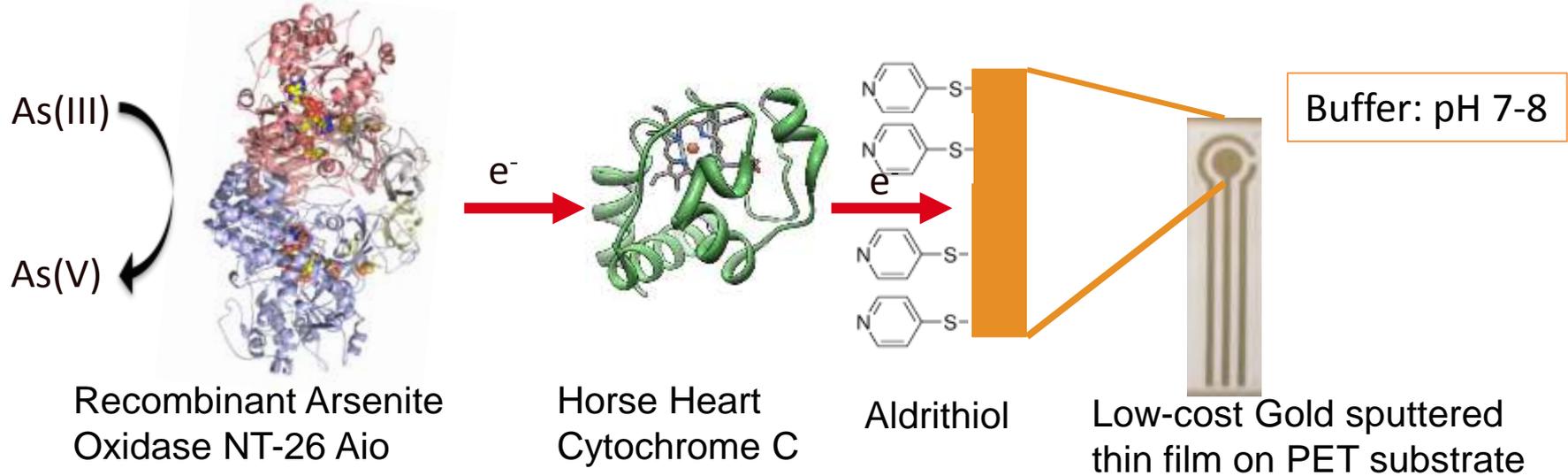
Nature Nanotechnology, July 2014 issue

Plan for immediate future

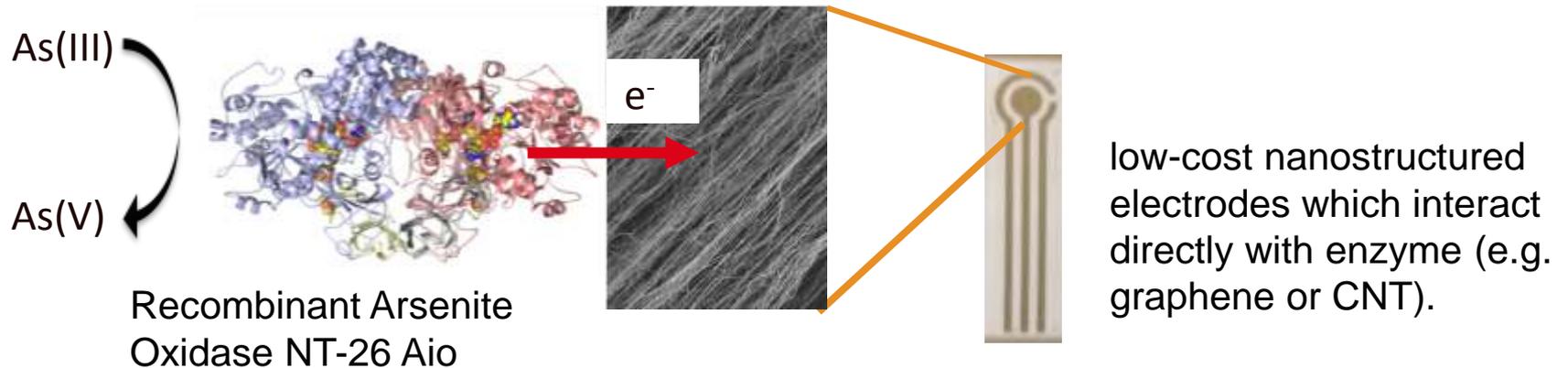


Biosensor Design

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

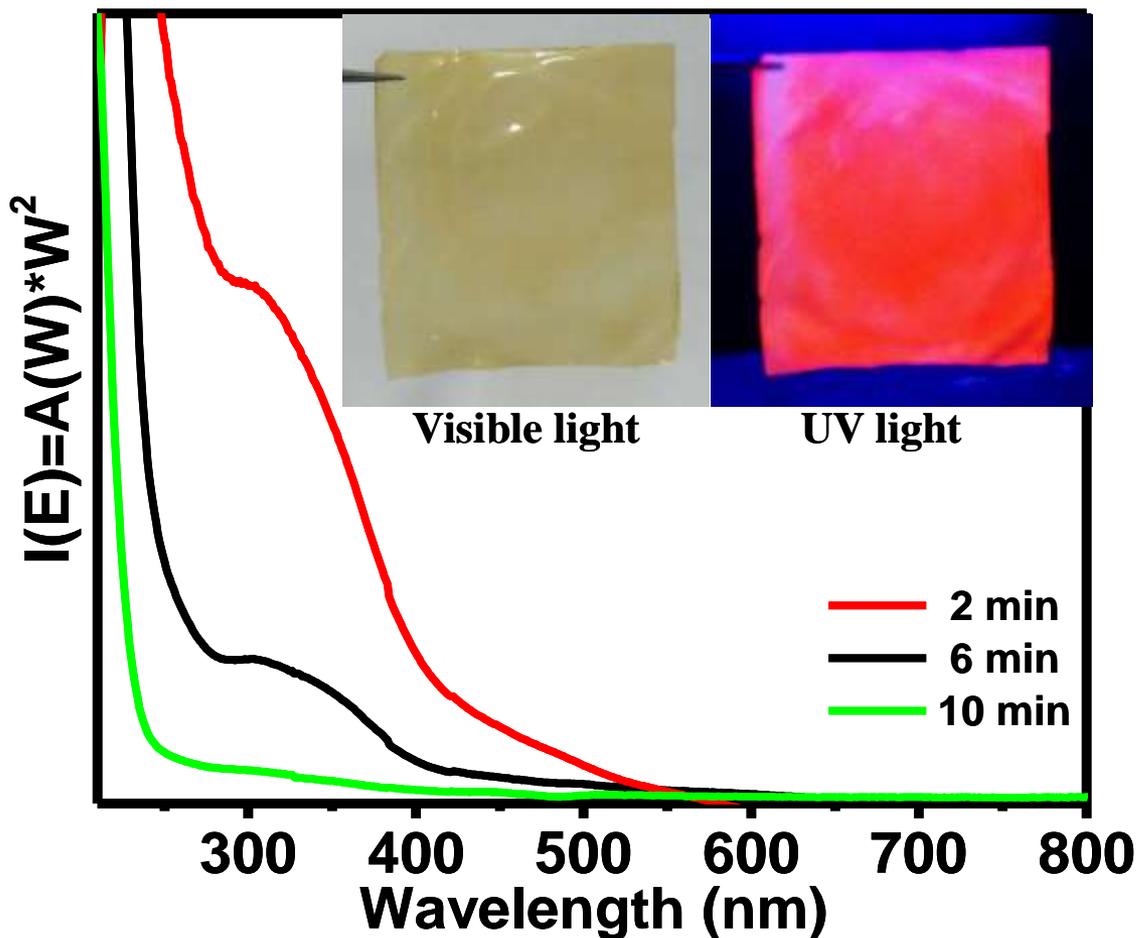


- ✓ Easy-to-use
- ✓ Quantitative
- ✓ Fast < 3 minutes
- ✓ Low cost
- ✓ Non-toxic
- ✓ Automatic recording of test results with well GPS position

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

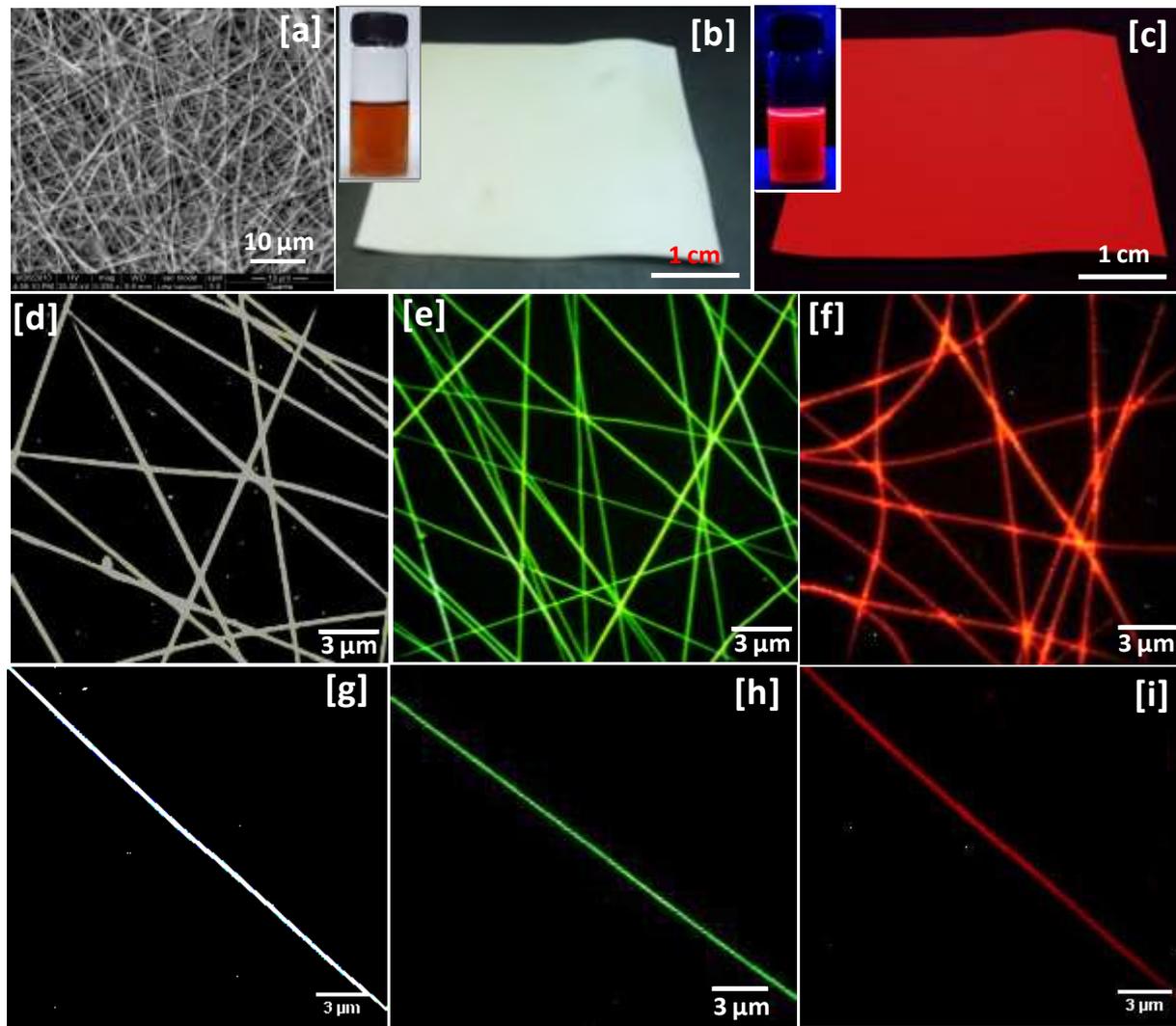
Quantum cluster based metal ion sensing paper

Large area uniform illumination using quantum cluster



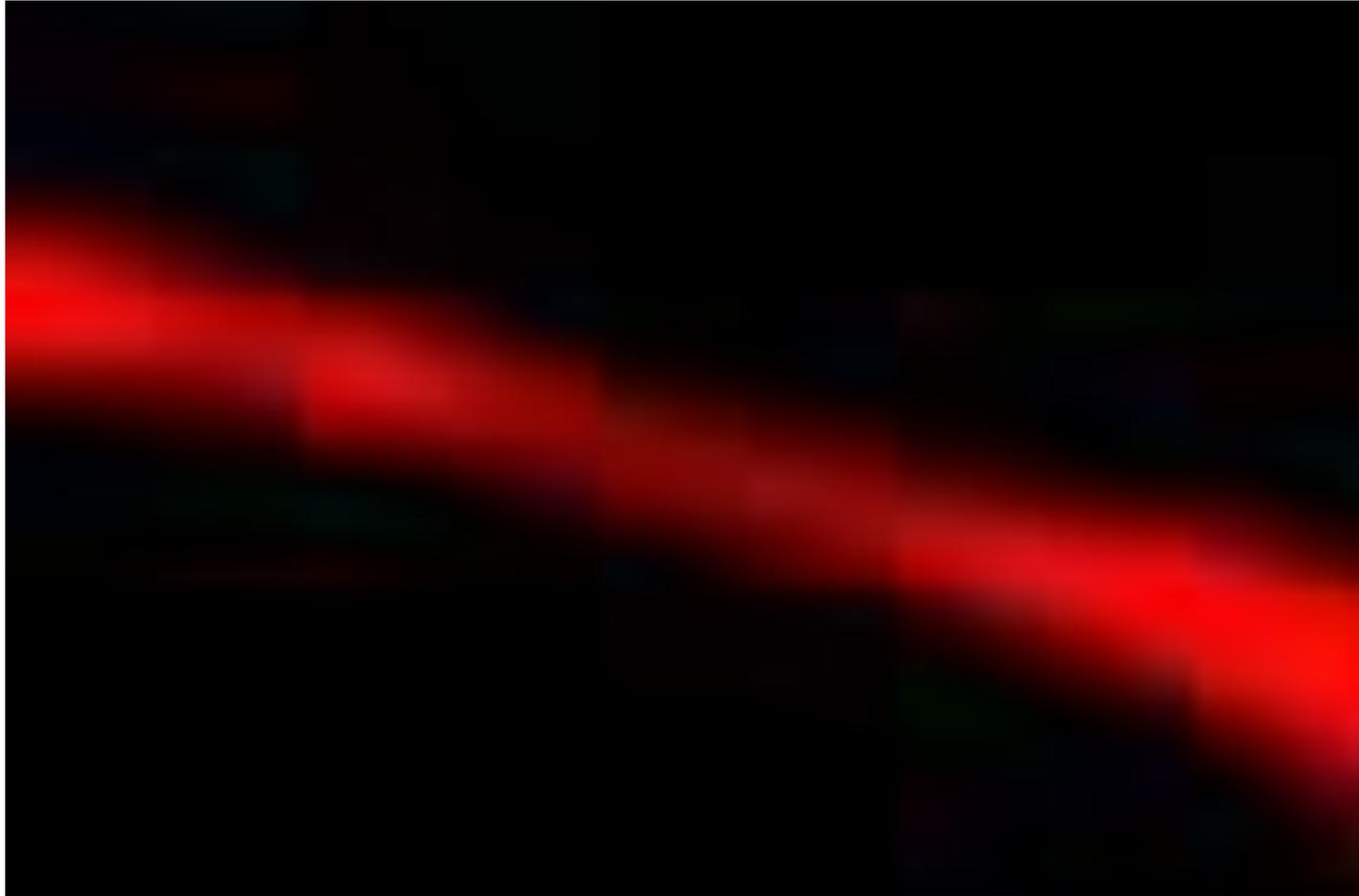
Decrease in the absorption of Au_{15} as a biofilm is dipped into the cluster solution. Inset: Free standing quantum cluster loaded film in visible light and UV light.

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

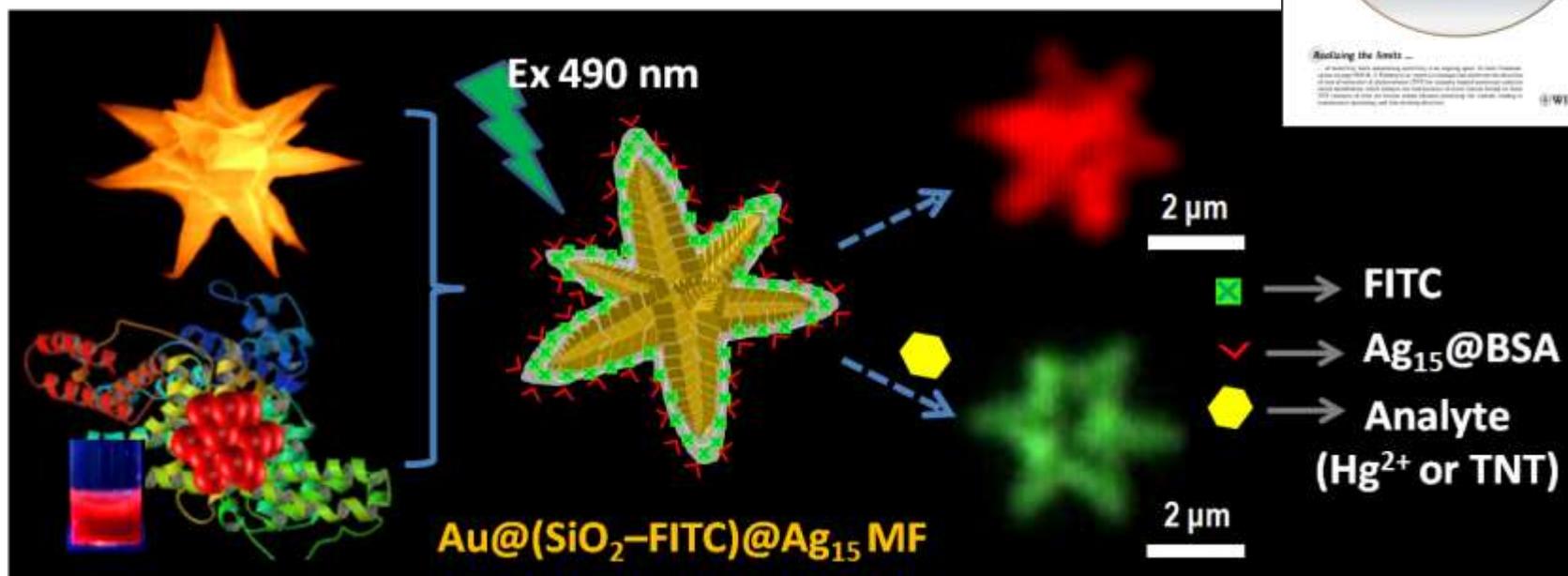
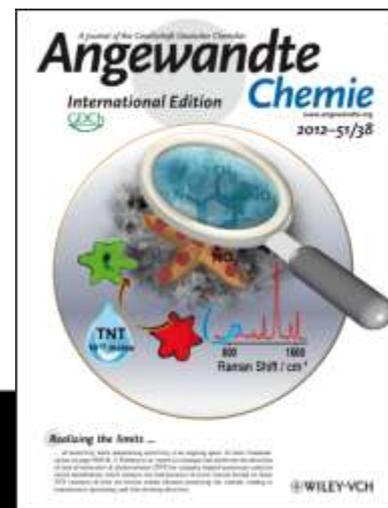


Atanu Ghosh et al. Anal. Chem. 2014.

Video of mercury quenching experiment using the nanofiber

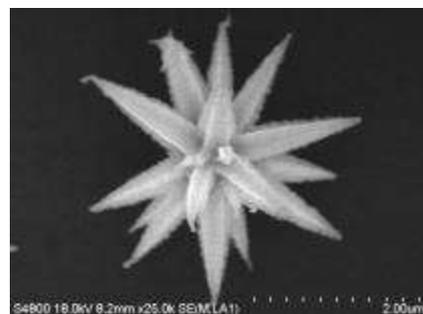


Sub-zeptomolar detection



Featured in:

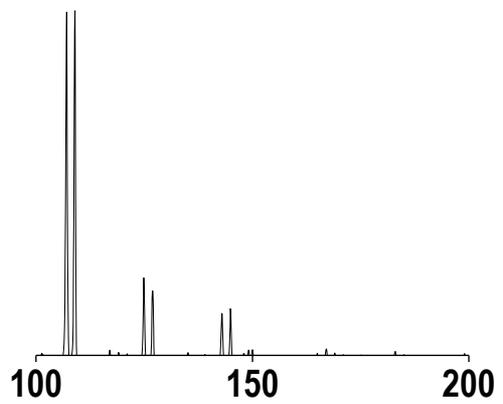
The Hindu, Telegraph, Times of India, etc.
C&E News
and many others



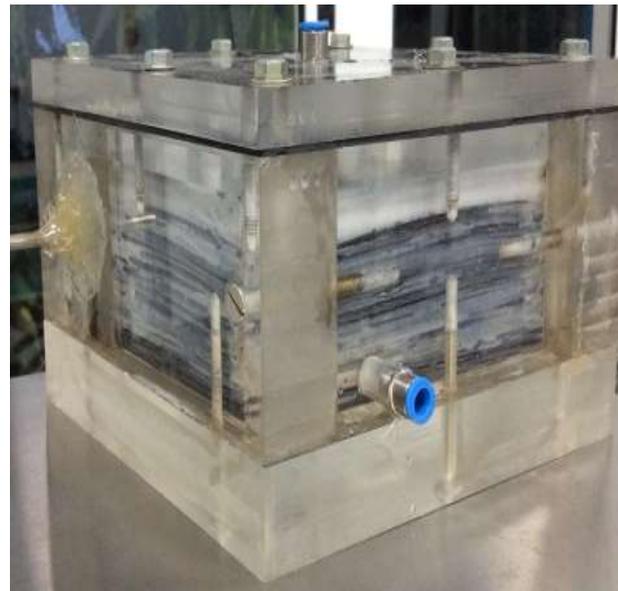
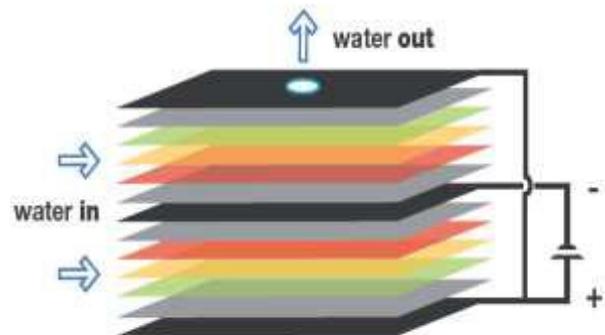
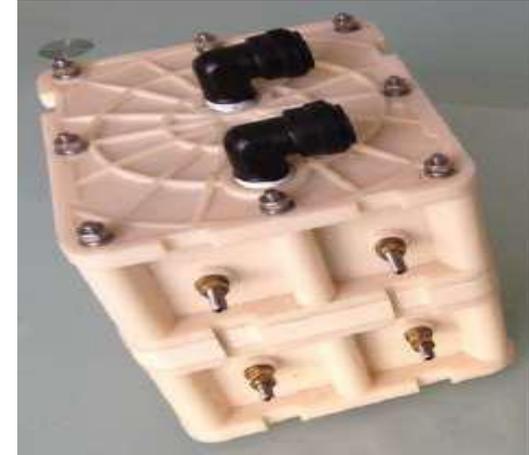
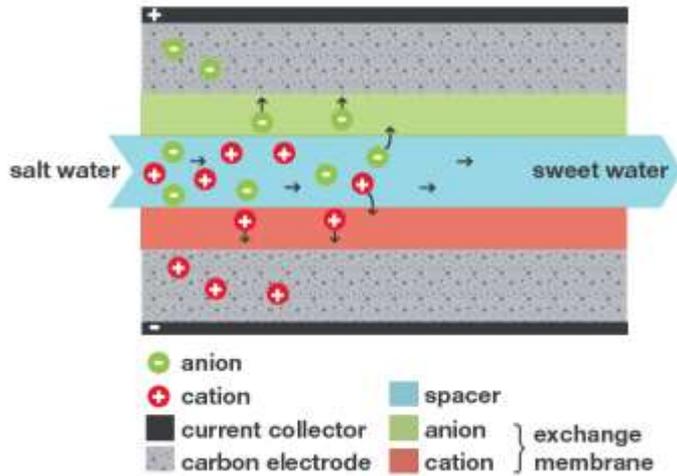
Ammu Mathew, et al. Angew. Chem. Int. Ed. 2012



D. Sarkar, et. al. Adv. Mater. 2016



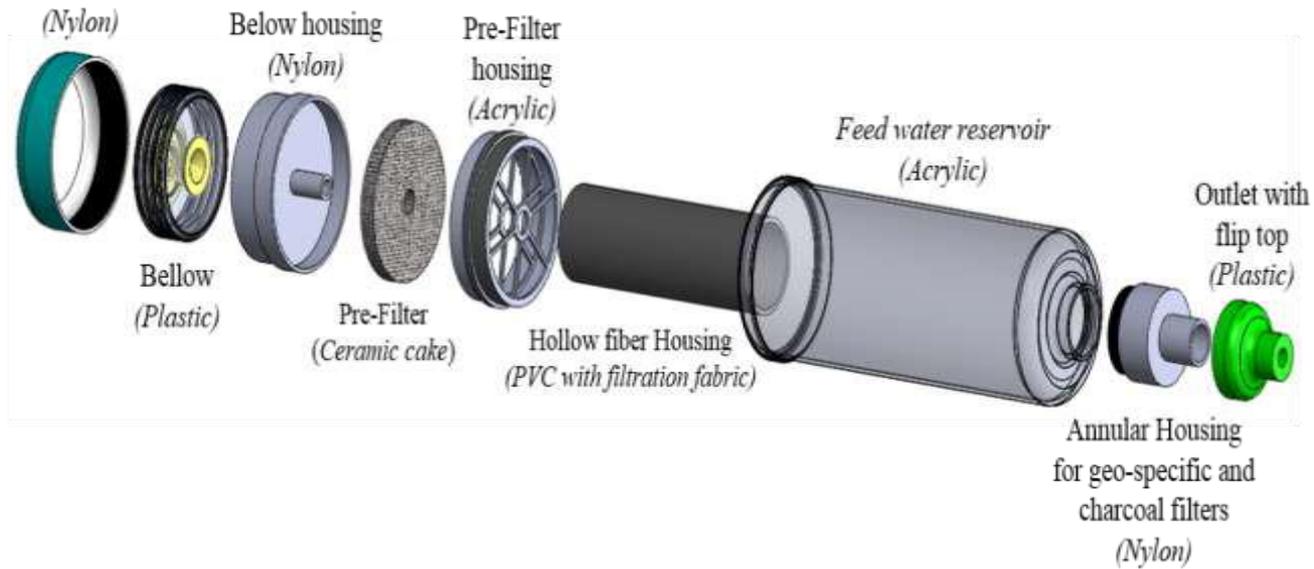
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Geo-specific water purifier bottle

Design



Prototype







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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



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NANOTECH ON TAP

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

GROUNDWATER in the Indian state of 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. The technology has received government support for field-testing as an option for low-cost, point-of-use water treatment.

The granules are nanocomposites made from ferric oxyhydroxide and a biopolymer, chitosan. Iron oxides remove arsenic ions from water by adsorption. The team boosted their metal oxyhydroxide's activity by reducing the particle size to nanoscale, thereby increasing the surface-to-volume ratio, and anchoring the material within a network of chitosan. With this structure, which resembles sand and is made at room temperature, embedded particles don't leach into water, and the captured arsenic stays put. What goes on "in the atomic scale is not completely understood," Pradeep says, but that has not stopped the material's real-world use.

At the Ambattur industrial estate, in a suburb of the Indian city of Chennai, a facility makes about 36 kg of the ferric oxyhydroxide-chitosan nanocomposite per day. Production at the plant—run by InnoNano Research, a start-up founded by the IIT Madras team—is enabling field trials in West Bengal.

With funding from the state government, about 100 community water purifiers using the nanocomposites, typically in 600-L tanks, have been installed in the district of Murshidabad, says an InnoNano cofounder known only as Anshup.

Each one, he estimates, serves 50–100 families and lasts one to two years. In the lab, the composite reduces a 1-ppm arsenic load to less than 10 ppb, the limit set by the World Health Organization (WHO). In field trials, natural arsenic loads of up to 330 ppb, the highest found in the field according to the team, drop to less than 10 ppb.



COURTESY OF THALAPIL PRADEEP

Globally, 137 million people are exposed to arsenic levels greater than the WHO limit. And some 780 million people do not have clean drinking water, according to the Centers for Disease Control & Prevention (CDC). "Every 20 seconds, a child dies from a water-related disease, especially in the developing world," says Emmanuel I. Unuabonah, a researcher from Redeemer's University in Nigeria who also develops water treatment materials.

TO REMOVE MICROBES, the Ambattur plant produces smaller quantities of another material developed by the team, an aluminum oxyhydroxide-chitosan composite (*Proc. Natl. Acad. Sci. USA* 2013, DOI: 10.1073/pnas.1220222110). When impregnated with silver nanoparticles, the material kills microbes by gradually releasing Ag⁺, a microbicide. Team member Udhaya Sankar estimates that 120 g of the composite could continuously provide 10 L of microbe-free drinking water daily for a year.

In the lab, microbial loads of 10⁵ colony-forming units (100 times the amount in natural drinking water) drop to zero. Lab studies also show that together, the Fe and Al composites remove both arsenic and microbes; limited field trials corroborate the lab results, says team member Amrita Chaudhary.

The composites can be made to remove other contaminants, such as lead or mercury, and assembled for specific needs. The antimicrobial material is housed at the roof of a vessel fed with untreated water from the top. The vessel volume can vary from a few liters for a household to hundreds of liters for a small community. A multilayer block of composites for specific contaminants sits behind the water tap.

InnoNano's materials join many water purification techniques, including ultraviolet radiation, chlorine treatment, and various filtration methods. "You need a basket of technologies," Pradeep says, to address the diverse needs around the world.

A powder called the P&G Purifier of Water, developed by CDC and Procter & Gamble, is perhaps the best-known water purification technology for use in impoverished or disaster-stricken areas. The product, which contains ferric sulfate and calcium hypochlorite, costs 3.5 cents per sachet. One sachet treats 10 L of water in about 30 minutes, removing metals, including arsenic, and killing microbes. For a family using 10 L of drinking water per day, treatment would cost \$12.80 per year, a month's earnings for many West Bengalis. InnoNano's

filters would deliver the same amount of drinking water for \$2.00–\$3.00 per year, Chaudhary says.

The nanocomposites stand a good chance of being used on a large scale, Redeemer's Unuabonah says. However, more evidence of their robustness is needed, and the arsenic-scavenging material needs to be tested on higher levels of contamination.

The technology is already popular in Murshidabad. The system works well, says Rajeev Kumar, a former Murshidabad district magistrate, and because community units—such as schools or offices—are responsible for operating the tanks, people have a sense of ownership. In a documentary prepared for IIT Madras, residents ask for installations in their villages. The district has ordered at least 100 more purifiers.

For its part, InnoNano wants not only to provide a purification solution, but also to maintain the installations. "Originally, we were thinking of keeping our role to materials manufacturing," Pradeep says, "but that alone is not enough."—VIRAT MARKANDEYA, special to C&EN







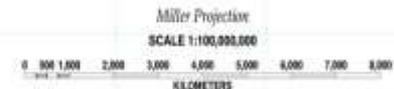
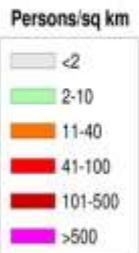


World population density 1994

Parting message

Every problem is dwarfed in front of the giant water crisis looming large on the planet. Water stress – in quantity and quality- is felt most severely by the populous countries. Indian subcontinent is at the centre of action.

Many of the problems of water quality can be handled affordably by new technologies. Arsenic, fluoride, mercury, pesticides,....affordable, accessible and reliable solutions are here in the country.





When we are unable to give clean water to children, the nation loses future.



Department of Science and Technology

Thank you

