

Now in the 58th year

Nanomaterials and Clean Water



THEMATIC UNIT OF EXCELLENCE



International Conference on Biological Applications of Nanoparticles, ICON-BIO 2017, December 4-5, 2017

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 is an example.
- 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.
- 67% of Indian agriculture is based on ground 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.



SUSTAINABLE GOALS

17 GOALS TO TRANSFORM OUR WORLD



http://www.un.org/sustainabledevelopment/blog/2015/12/sustainable-development-goals-kick-off-with-start-of-new-year/#prettyPhoto

Indian realities

- Over xx million suffer due to arsenic
- Over xx million suffer due to fluoride
- Cr, Mn, Pb, U, and many more are found in water
- uCKD and others are around
- Endocrine disrupting chemicals are plenty

GHI was released a month ago

Should we continue to be where we are?

.....Long-term exposure to arsenic from drinking-water and food can cause cancer and skin lesions. It has also been associated with developmental effects, cardiovascular disease, neurotoxicity and diabetes. <u>http://www.who.int/mediacentre/factsheets/fs372/en/</u> Where is Liberty, Equality, Fraternity?

T. Pradeep

Email: pradeep@iitm.ac.in Phone: 044-2257-4208

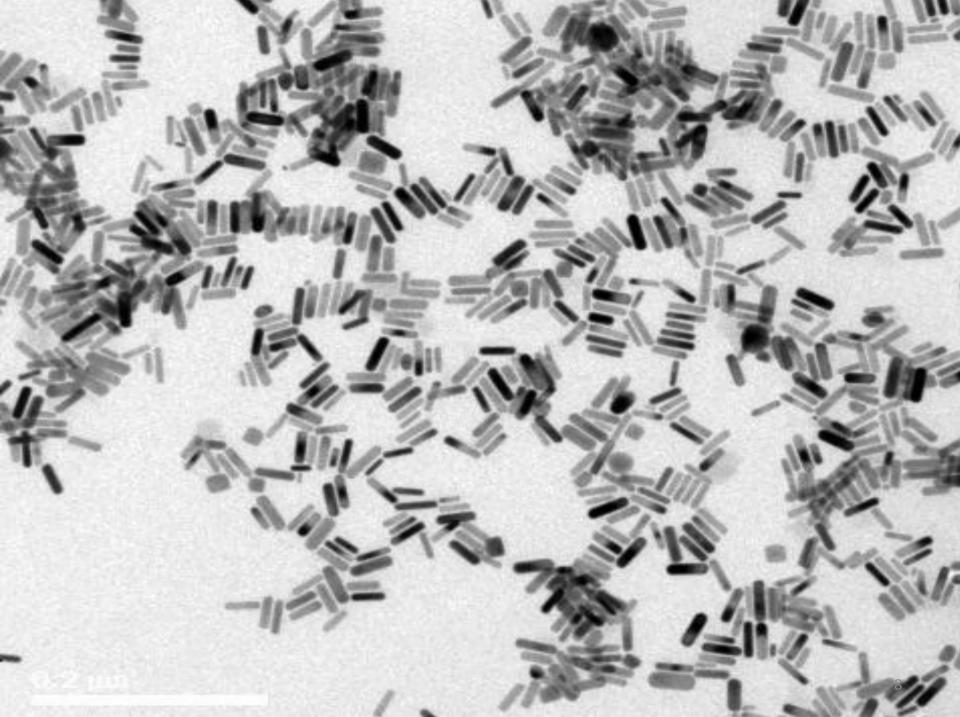


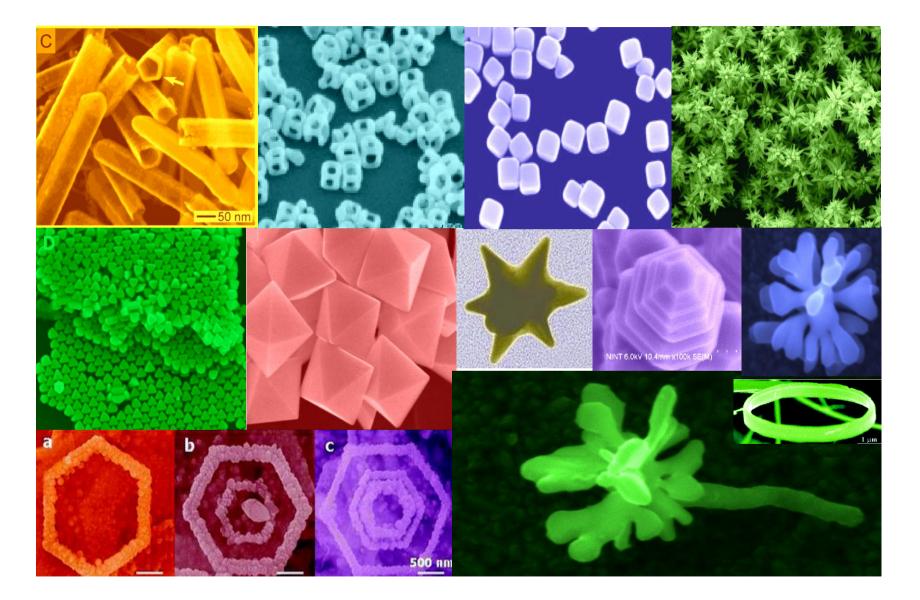
Founder InnoNano Research Pvt. Ltd. An IIT Madras Incubated Compan



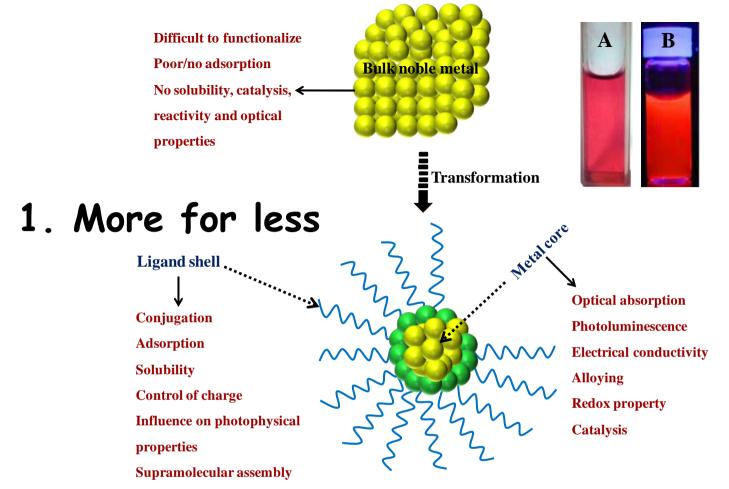


Nano 10-9



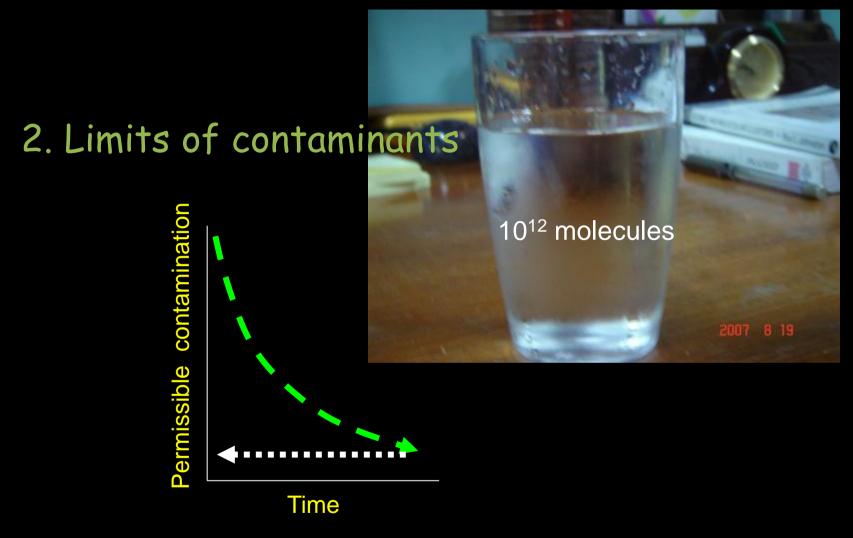


Sajanlal and Pradeep, Kirk-Othmer Encyclopedia, 2012

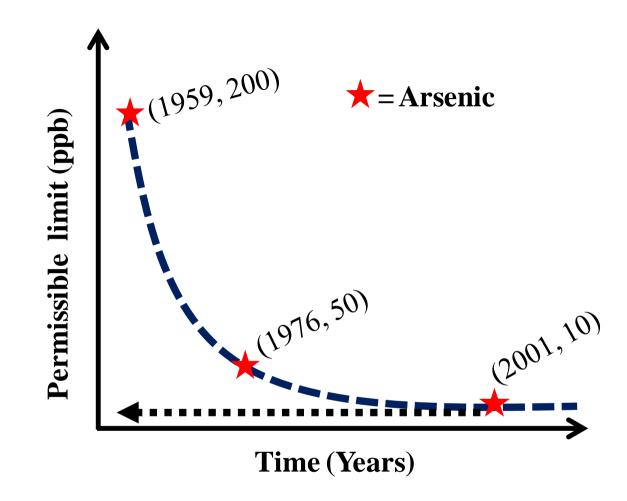


Nanoparticles/clusters

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).

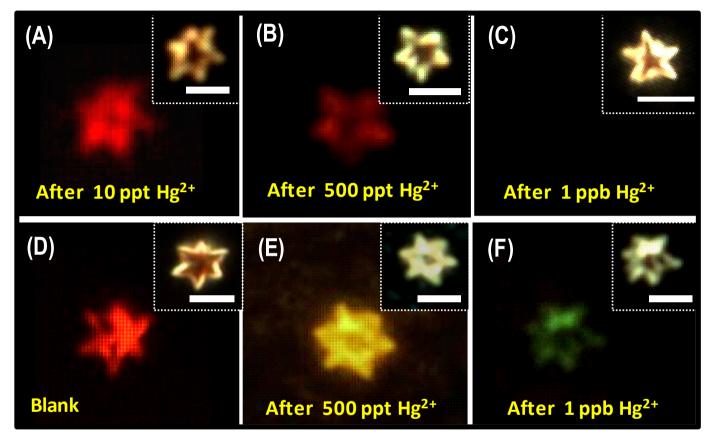


Permissible contamination reaches limits of detection



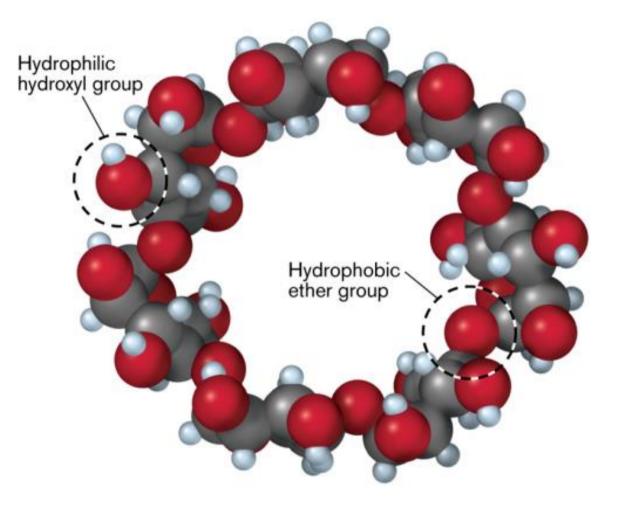
Decrease in the permissible limit of arsenic in drinking water, according to US EPA, with time. The graph indicates a general trend.

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 μ m.

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



Nanotechnology research in clean water

New adsorbents

Nanoparticles, nanotubes, graphene, polymers, 2D materials

New sensors

Colorimetric, fluorescence, FRET, DNA, assembly, biosensors

New catalysts

Emerging toxins, heterojunctions

Novel phenomena

Graphenic analogues, nanopores, aquaporins

New devices

CDI, atmospheric water capture, novel membranes

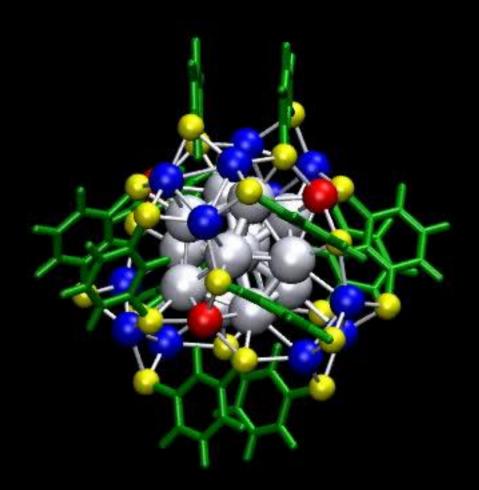




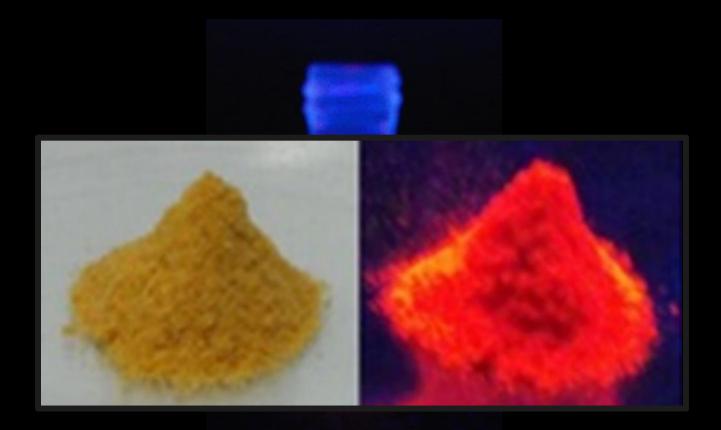
EDITED BY DAVID E. REISNER • T. PRADEEP Contents

Inquisitive science Technology Translation What next? VideoMach unregistered

Clusters



Science of nanomaterials has advanced tremendously in the recent past. 17



Shibhu, Habeeb, Uday, Kamalesh, Lourdu, Ammu, Ananya, Indranath, Atanu, Krishnadas, Shridevi, Papri, Esma, Debasmita, Abhijit, Amrita, Jyoti, Sugi, Bodi, Paulami,



Review

Atomically Precise Clusters of Noble Metals: Emerging Link between Atoms and Nanoparticles

Indranath Chakraborty[†][®] and Thalappil Pradeep^{*®}

DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

Supporting Information

ABSTRACT: Atomically precise pieces of matter of nanometer dimensions composed of noble metals are new categories of materials with many unusual properties. Over 100 molecules of this kind with formulas such as $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, and $Au_{102}(SR)_{44}$ as well as $Ag_{25}(SR)_{18}$, $Ag_{29}(S_2R)_{12}$, and $Ag_{44}(SR)_{30}$ (often with a few counterions to compensate charges) are known now. They can be made reproducibly with robust synthetic protocols, resulting in colored solutions, yielding powders or diffractable crystals. They are distinctly different from nanoparticles in their spectroscopic properties such as optical absorption and emission, showing well-defined features, just like molecules. They show isotopically resolved molecular ion peaks in mass spectra and provide diverse information when examined through multiple instrumental methods. Most important of these properties is luminescence, often in the visible–near-infrared window, useful in biological applications. Luminescence in the visible region, especially by clusters protected with proteins, with a large Stokes shift, has been used for various sensing applications,



down to a few tens of molecules/ions, in air and water. Catalytic properties of clusters, especially oxidation of organic substrates, have been examined. Materials science of these systems presents numerous possibilities and is fast evolving. Computational insights have given reasons for their stability and unusual properties. The molecular nature of these materials is unequivocally manifested in a few recent studies such as intercluster reactions forming precise clusters. These systems manifest properties of the core, of the ligand shell, as well as that of the integrated system. They are better described as protected molecules or *aspicules*, where *aspis* means shield and *cules* refers to molecules, implying that they are "shielded molecules". In order to understand their diverse properties, a nomenclature has been introduced with which it is possible to draw their structures with positional labels on paper, with some training. Research in this area is captured here, based on the publications available up to December 2016.

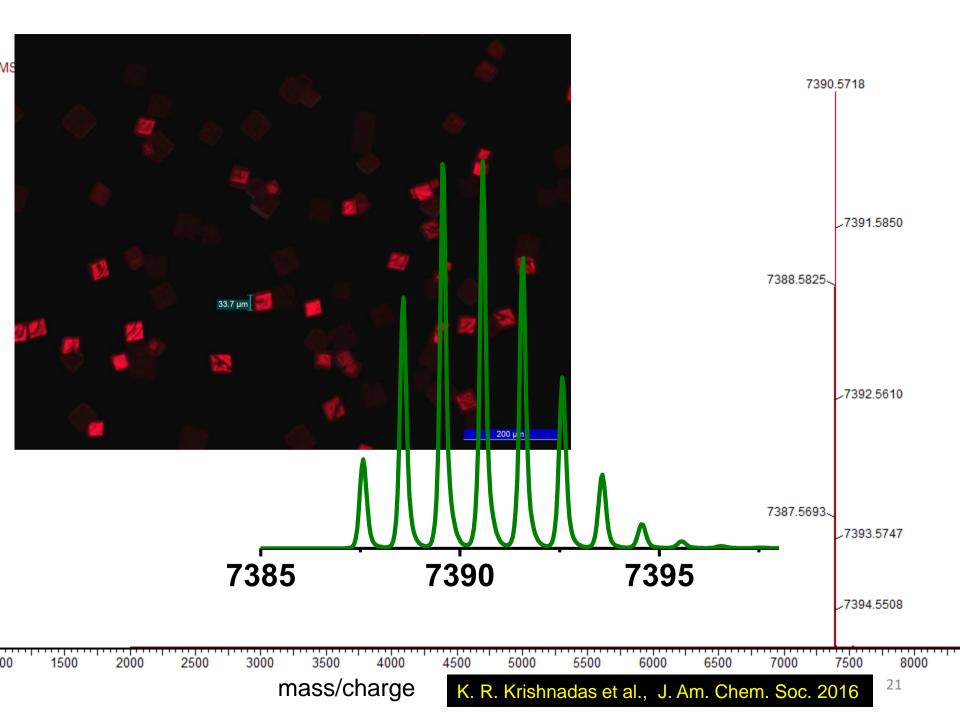
Also the pioneering work of R. W. Murray, Robert L. Whetten, Uzi Landman, Tatuya Tsukuda, Yuichi Negishi, Hannu Hakkinen, R. Jin, Nanfeng Zheng, Terry Bigioni, Osman Bakr, Kornberg, Jianping Xie, C. M. Aikens, Thomas Buergi, Amala Dass, A. W. Castleman Jr., H. Schmidbauer, ...

Indranath and Pradeep, Chem. Rev. 2017 Krishnadas et al. Acc. Chem. Res. 2017

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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

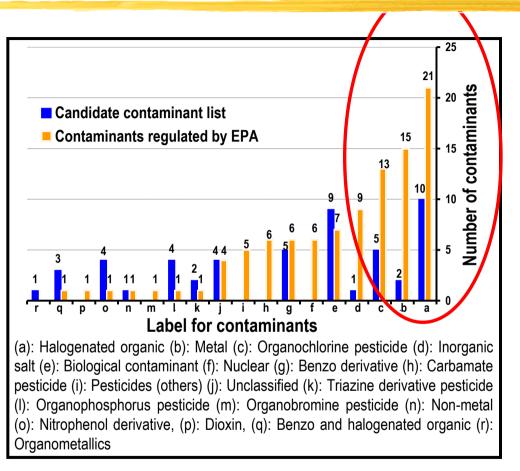
Creation of affordable materials fo water is one of the most promising drinking water for all. Combinin composites to scavenge toxic sp other contaminants along with the affordable, all-inclusive drinking v without electricity. The critical p synthesis of stable materials that uously in the presence 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. 1 sand-like properties, such as highe forms. These materials have been water purifier to deliver clean drin ily. The ability to prepare nanos ambient temperature has wide i 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 23

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 Advencing the

Chemistry World

Pesticide filter debuts in India

20 April 2007

Kilugudi Jayaraman/Bangalore, India

A domestic water filter that uses metal nanoparticles to remove disactined perticitie metalasis is about to enter the indian nanout, its developers at the indian institute of Technology (I/T) in Chennal (formerly Madasa) belaws it is the first product of fis kind in the world to commercialised.

Munital-based Euroka Forbes Limited, a company that sells water purification systems, is collaborating with IT and has tested the device in the field for over sile months. Jugatemath Reddy, a bedrinkal domainant to the company, expects the first 1000 units to be solid door-to-door from late May.

'Our pesticide Riler is an offshoot of basic research on the chemistry of nanoparticles.' Thatappi Praceap who ind the seam at IT Chemai told Chemistry (Vond. He and his staket Seawmanan Net alcovered in 2020) that halocarbona such as carbon technohoride (CCH) completely break down litto metal halides and

amorphous carbon upon reaction with gold and silver nanoparticles¹.

Practeep said this prompted them to extend their study to include organochiorine and organophrophropus particides, whose presence in vater is posing a health risk in rural incia, 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 endosuitan, malathion and chiorpyritics - three pesticides that have a loaded by the second se

Chemistry world First ever nanotechnology product for clean water





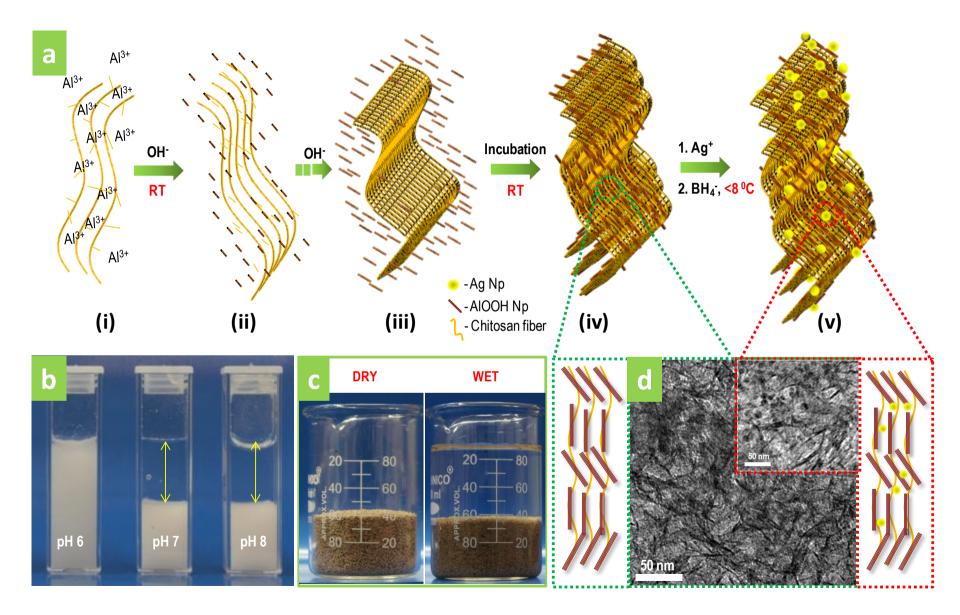
A plant to make supported nanomaterials for water purification; with capacity of 4.5 tons per month, 2007

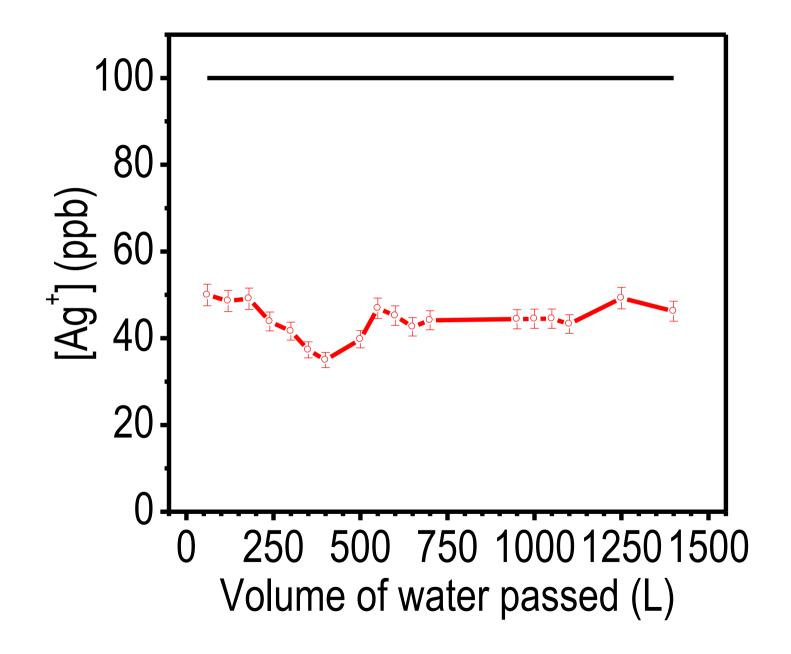
 Patents: A method of preparing purified water from water containing pesticides, Indian patent 200767
 Extraction of malatheon and chlorpiryhphos from drinking water by nanoparticles , US 7,968,493 A method for decontaminating water containing pesticides, EP 17,15,947
 Product is marketed now by a Eureka Forbes Ltd.
 Several new technologies are now available

A. Sreekumaran Nair et al. 2003

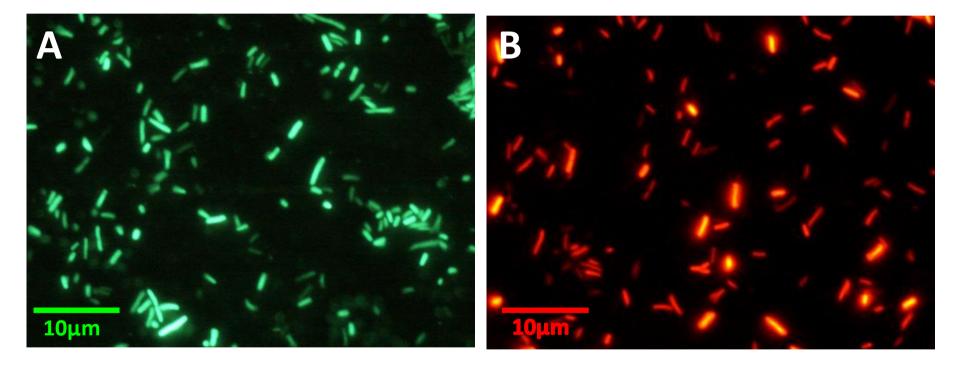
Affordable materials for water purification - Bioinspired Water positive Water-based, room temperature, water stable Green

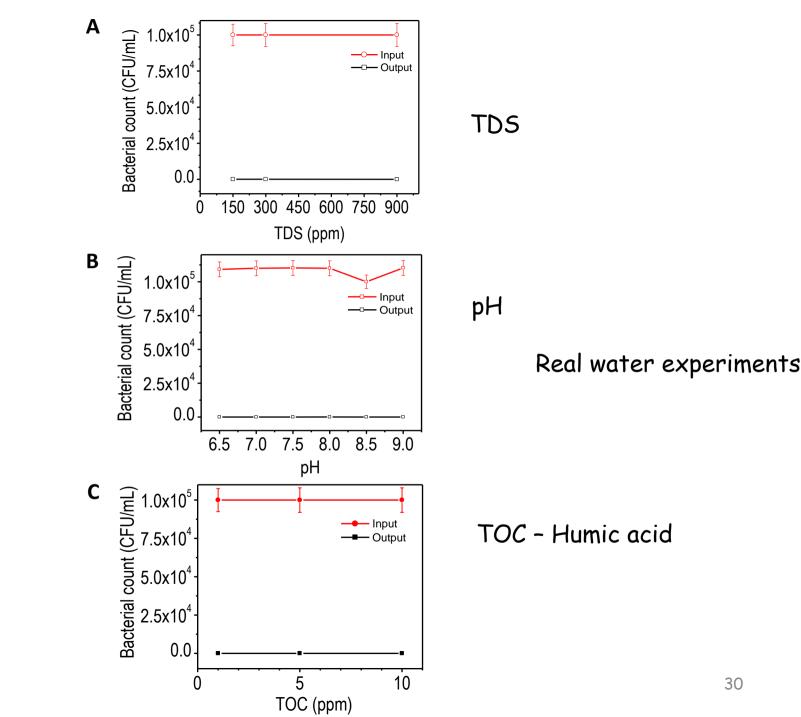
M. U. Sankar et al, PNAS 2013

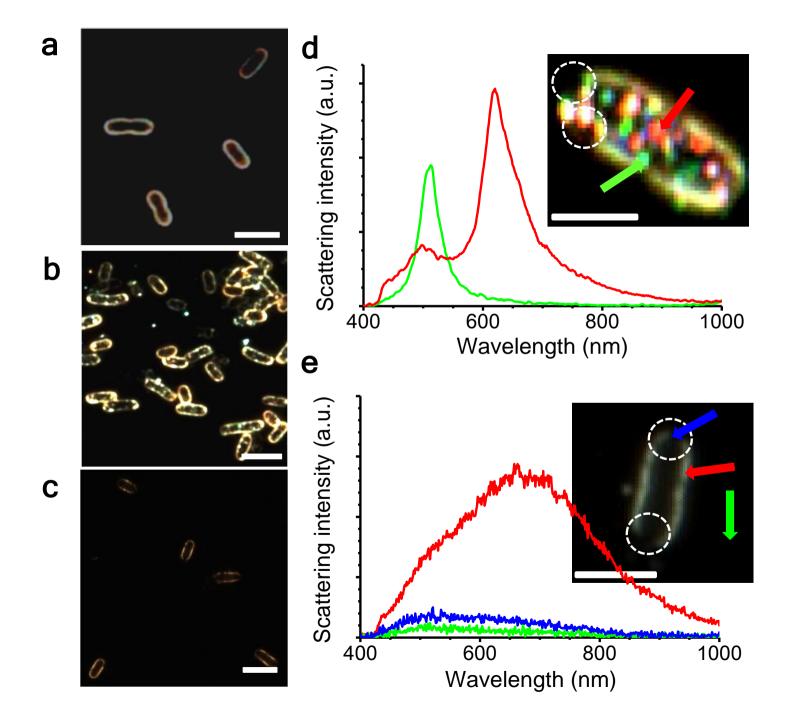


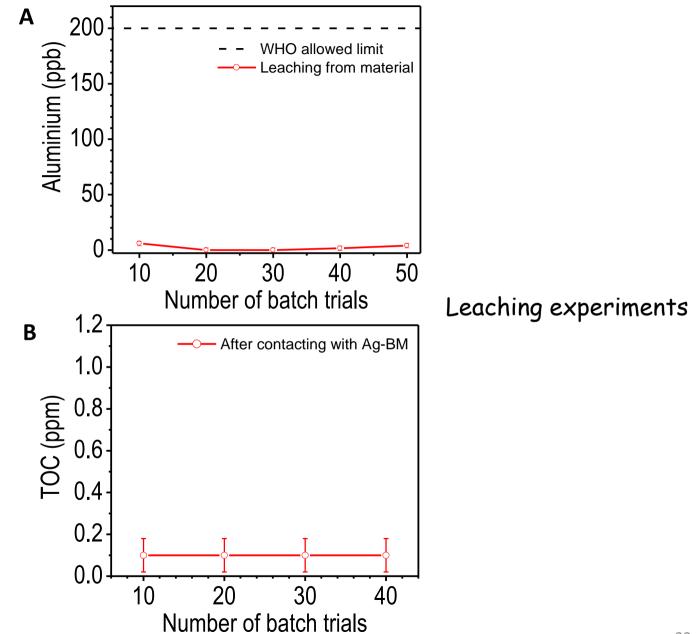


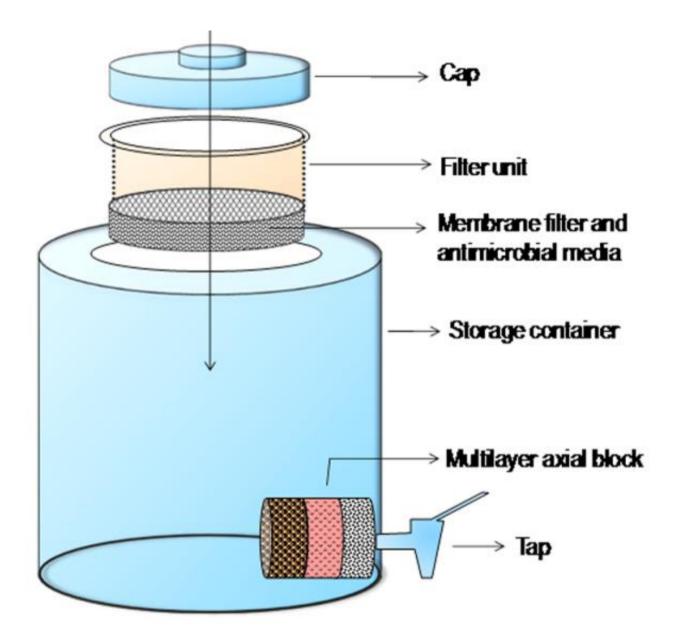
Live/dead staining experiments









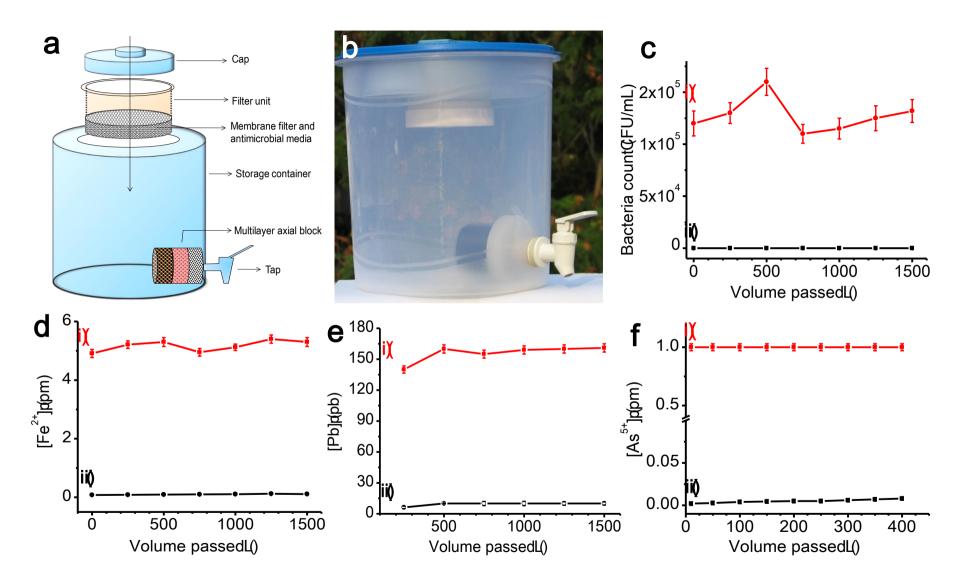


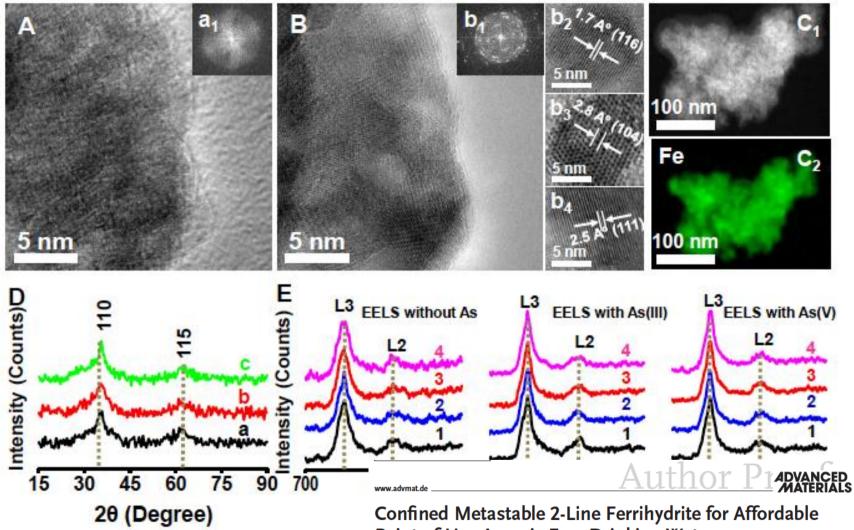
Physicochemical characteristics of influent natural drinking water

(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.

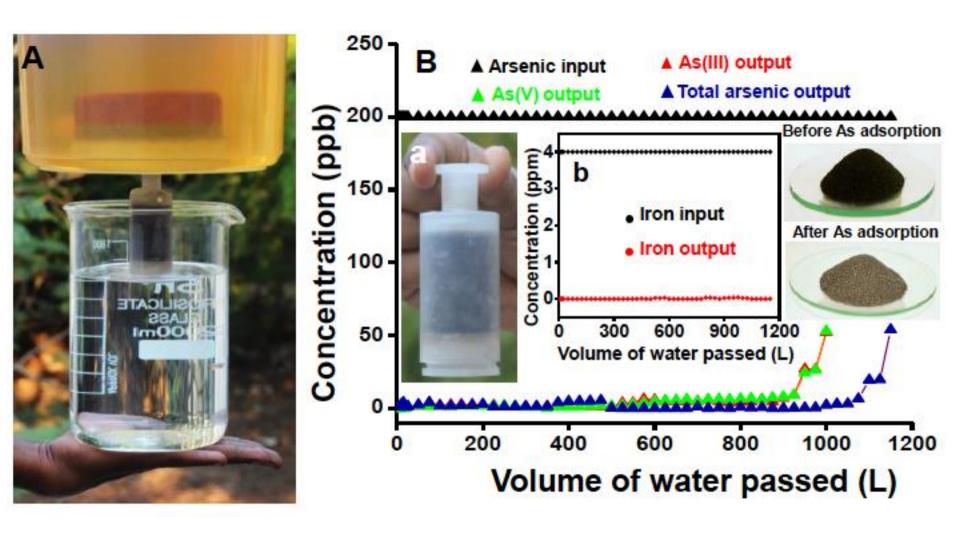
Parameters	Value
Total coliforms (CFU/mL)	1-2 x 10 ³
p H @25°C	7.8
Conductivity (µS/cm)	640.000
Fluoride	0.573
Chloride	86.340
Nitrate	1.837
Sulphate	32.410
Silicate	15.870
Lithium	ND
Sodium	53.740
Ammonium	ND
Potassium	2.330
Magnesium	14.340
Calcium	28.720



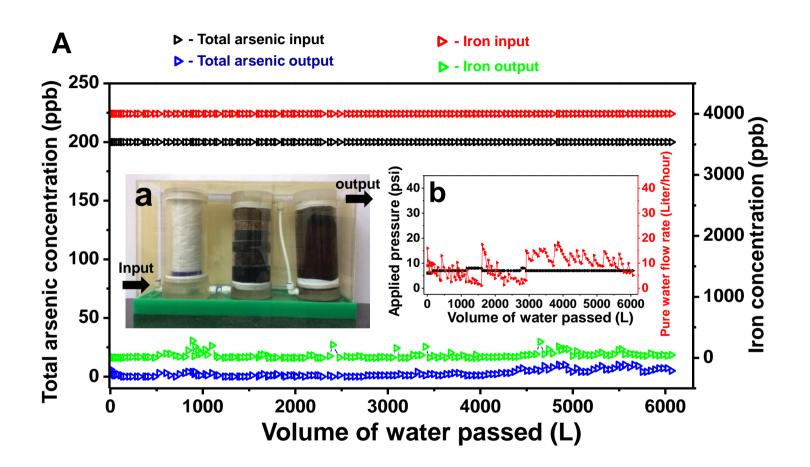


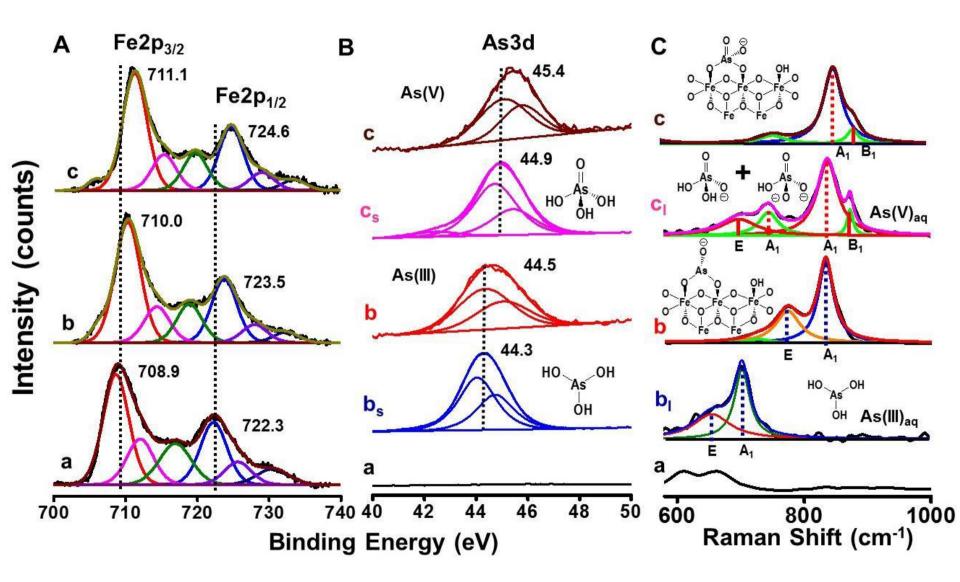
Point-of-Use Arsenic Free Drinking Water

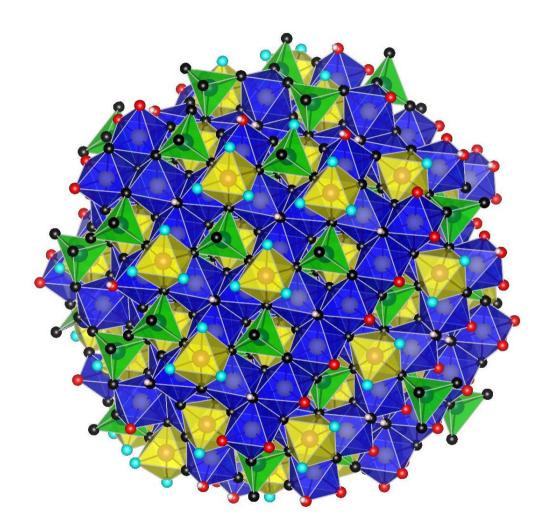
By Avula Anil Kumar, Anirban Som, Paolo Longo, Chennu Sudhakar, Radha Gobinda Bhuin, Soujit Sen Gupta, Anshup, Mohan Udhaya Sankar, Amrita Chaudhary, Ramesh Kumar, and T. Pradeep*



A. Anil Kumar, et al. Adv. Mat. 2016

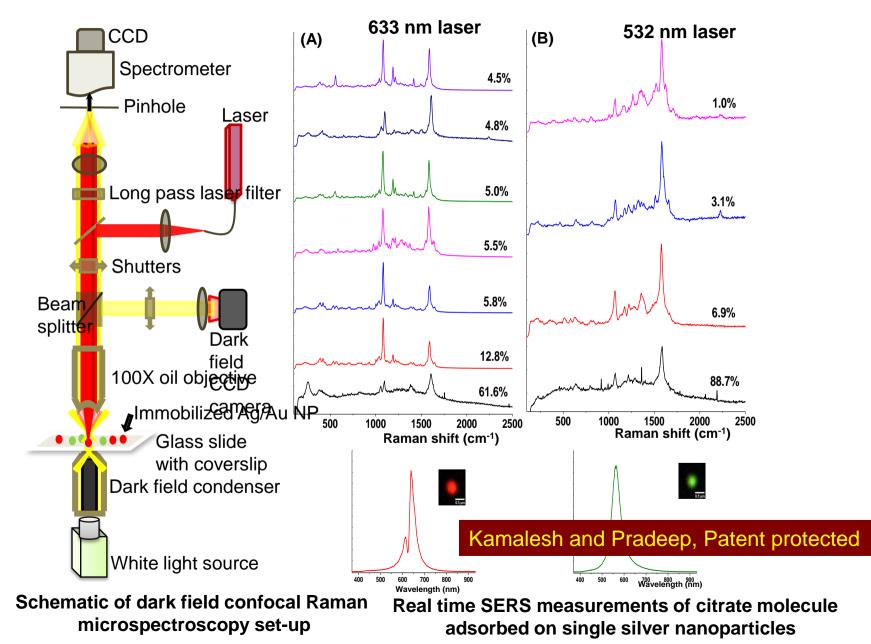






Chennu Sudhakar et al. Unpublished

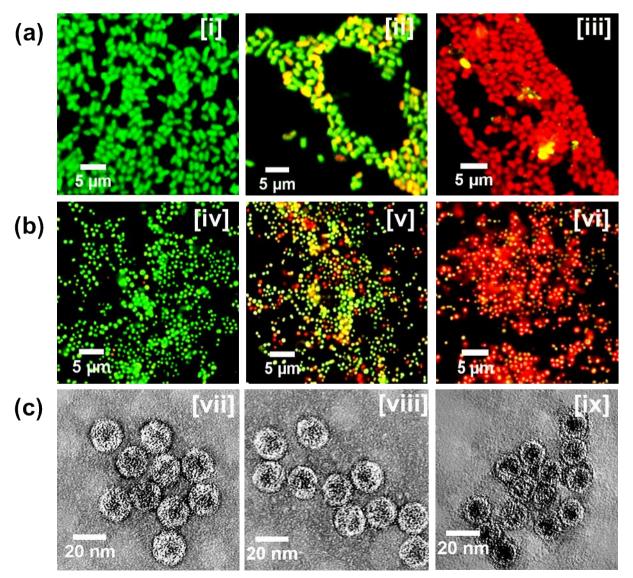
Vibrational Tomography of Citrate Adsorbed on Single Isolated Silver Nanoparticles by Real Time Raman Spectroscopy



erent orientations of citrate molecules

Tripti Ahuja, Kamalesh Chaudhari, et al. Unpublished

Anion effect

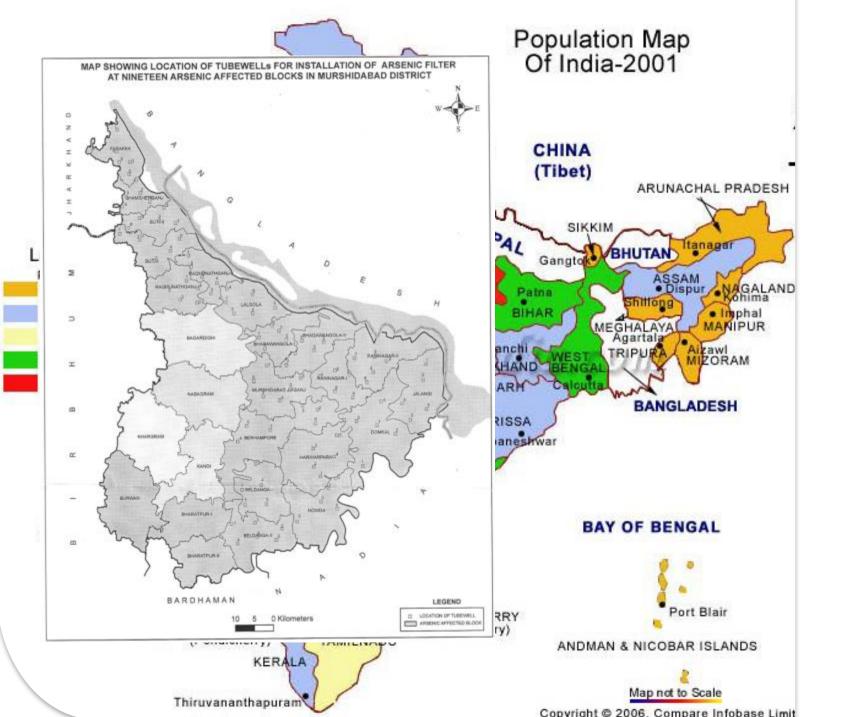


R. Swathy, et al. Scientific Reports, 2014 43

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Inquisitive science Technology Translation What next?





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 47

Performance data from Murshidabad (continued)

Sample Name	Input arsenic (ppb)	Output arsenic (ppb)	Number of days running
Babaltali Jumma Masjid, Raninagar – II	10.7	0	180 days
Sargachhi Paschimpara Jumma Masjid, Beldanga – I	1.26	0.04	180 days
Pratappur Jumma Masjid, Hariharpara	27.19	0.13	180 days
Fakirabad Jumma Masjid, Domkal	24.67	0	180 days
Shialmari Jumma Masjid, Raninagar – II	287.5	0.09	240 days
Bhabta Ahelahadis Jumma Masjid, Beldanga	8.6	5.7	240 days
		(699)	
Dhapadia Junior Madrasah	46.5	2.15	30 days
Khidirpur Shishu Shiksha Kendra	14.99	0	260 days
Junior Madrasah	12.7	0	60 days
Dhapana Board High School	14.96	0.6	45 days
Birpur Primary School	19.56	0	90 days
Bethuaduari JCM High School	4.56	0	45 days
Jugnuthala Primary School	23.36	0	60 days
Dahakula Primary High School	36.6	0	60 days
Bargachi Primary School Nagadi	9.56	0	90 days
Dahakula Primary School	22.7	0	60 days
BJ Kumari Primary School	5.9	0	100 days
Arijnagar Primary School	0.13	-	60 days
Patikpari Girls Primary School	9.6	0	60 days 48
	 Babaltali Jumma Masjid, Raninagar – II Sargachhi Paschimpara Jumma Masjid, Beldanga – I Pratappur Jumma Masjid, Hariharpara Fakirabad Jumma Masjid, Domkal Shialmari Jumma Masjid, Raninagar – II Bhabta Ahelahadis Jumma Masjid, Beldanga Dhapadia Junior Madrasah Khidirpur Shishu Shiksha Kendra Junior Madrasah Dhapana Board High School Birpur Primary School Bethuaduari JCM High School Jugnuthala Primary School Bargachi Primary School Bargachi Primary School BJ Kumari Primary School BJ Kumari Primary School BJ Kumari Primary School Arijnagar Primary School 	Babaltali Jumma Masjid, Raninagar – II10.7Sargachhi Paschimpara Jumma Masjid, Beldanga – I1.26Pratappur Jumma Masjid, Hariharpara27.19Fakirabad Jumma Masjid, Domkal24.67Shialmari Jumma Masjid, Raninagar – II287.5Bhabta Ahelahadis Jumma Masjid, Beldanga8.6Dhapadia Junior Madrasah46.5Khidirpur Shishu Shiksha Kendra14.99Junior Madrasah12.7Dhapana Board High School14.96Birpur Primary School19.56Bethuaduari JCM High School36.6Bargachi Primary School36.6Bargachi Primary School356Dahakula Primary School22.7BJ Kumari Primary School5.9Ontagar Primary School5.9Orthagar Primary School0.13	Babaltali Jumma Masjid, Raninagar – II10.70Sargachhi Paschimpara Jumma Masjid, Beldanga – I1.260.04Pratappur Jumma Masjid, Hariharpara27.190.13Fakirabad Jumma Masjid, Hariharpara24.670Shialmari Jumma Masjid, Raninagar – II287.50.09Bhabta Ahelahadis Jumma Masjid, Beldanga8.65.7Dhapadia Junior Madrasah46.52.15Khidirpur Shishu Shiksha Kendra14.990Junior Madrasah12.70Dhapana Board High School14.960.6Birpur Primary School9.560Dahakula Primary School36.60Bargachi Primary School22.70Bargachi Primary School5.90Antura Primary School5.90Antura Primary School5.90

Now in Punjab

InnoNano Research Pvt. Ltd.

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Problems in the field

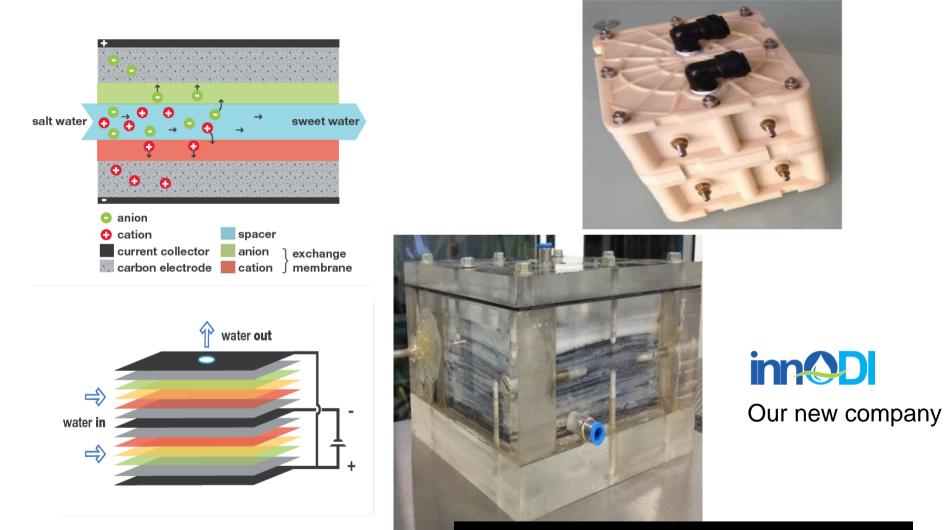
Diverse water quality Spent media Sludge management Reactivation Cost Weather conditions, accessibility

Work was featured in several journals

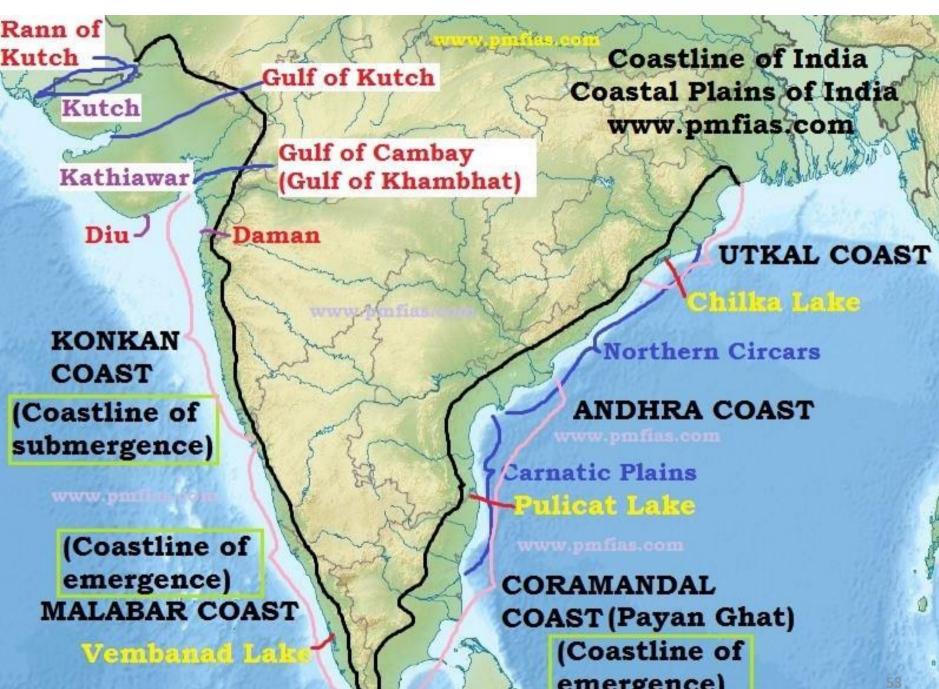


Nature Nanotechnology, July 2014 issue

Capacitive Desalination (CDI)



Soujit Sengupta, Rabiul Islam and others



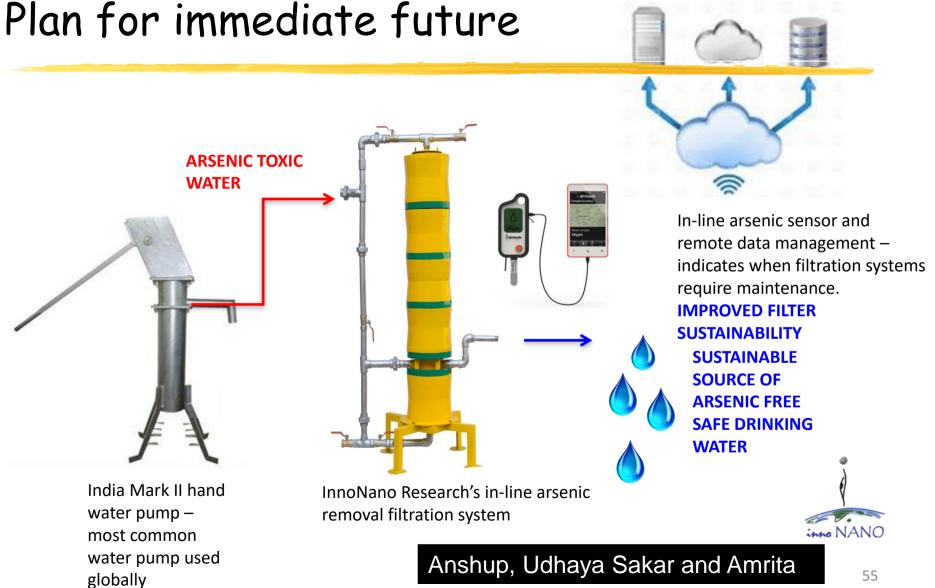
https://www.pmfias.com/wp-content/pleads/2016/01/Coastline-of-India---Indian-Coastline.jpg





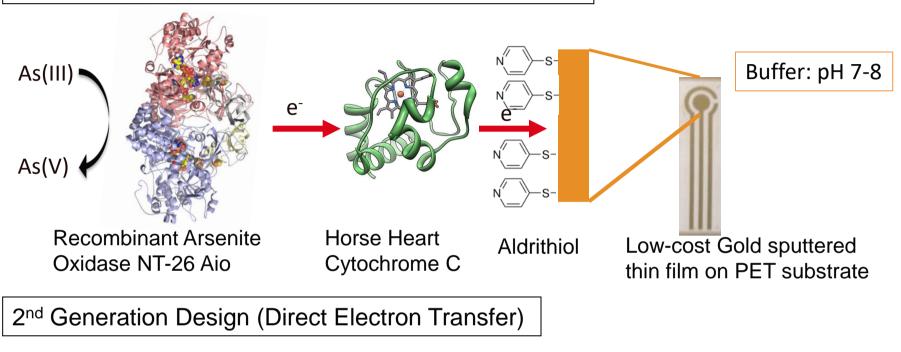
Products under implementation

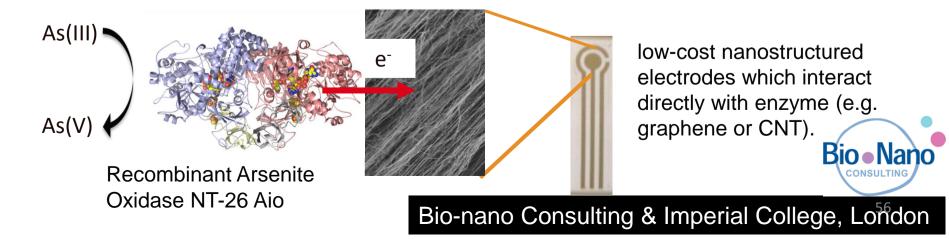
Vijay Sampath, Tullio Servida



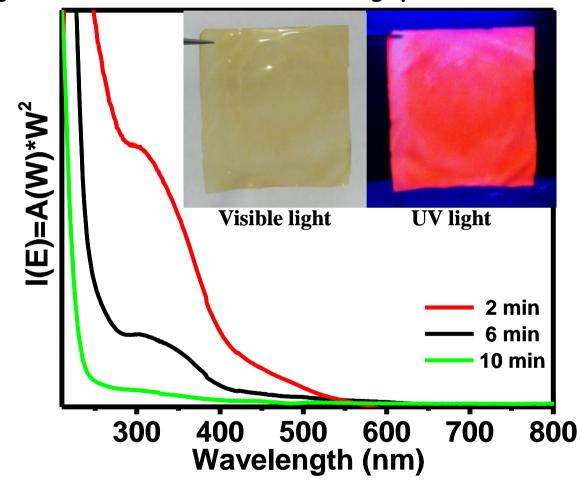
Biosensor Design

1st Generation Design (Mediated Electrochemistry)



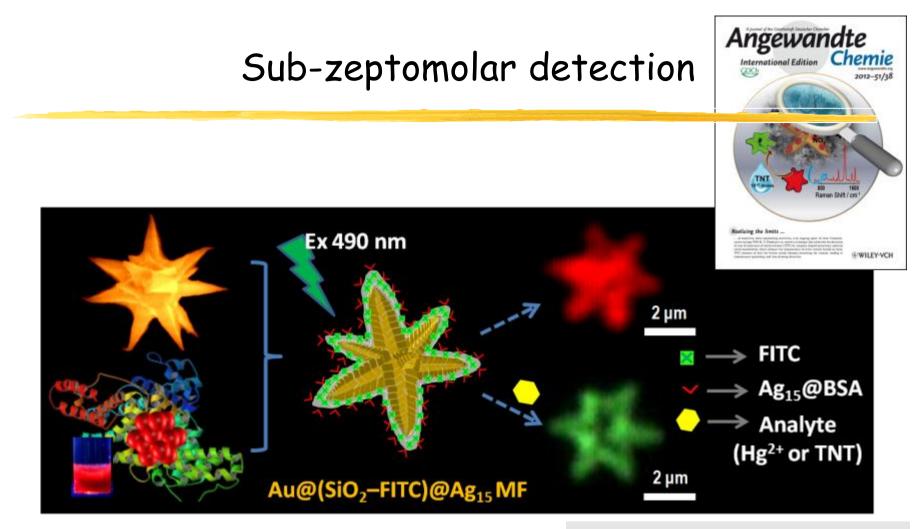


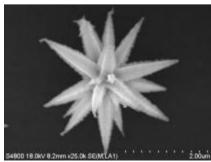
Quantum cluster based metal ion sensing paper Large area uniform illumination using quantum cluster



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





Featured in:

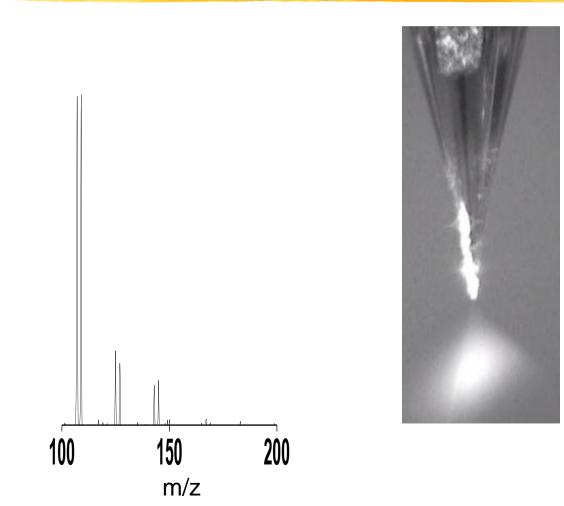
The Hindu, Telegraph, Times of India, etc. C&E News and many others

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

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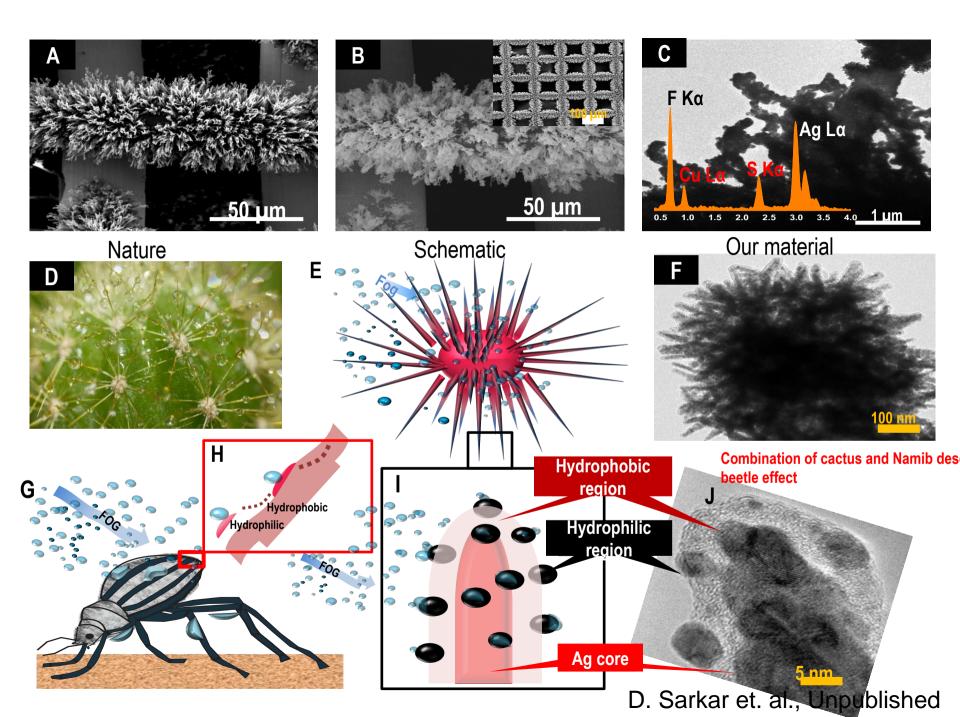
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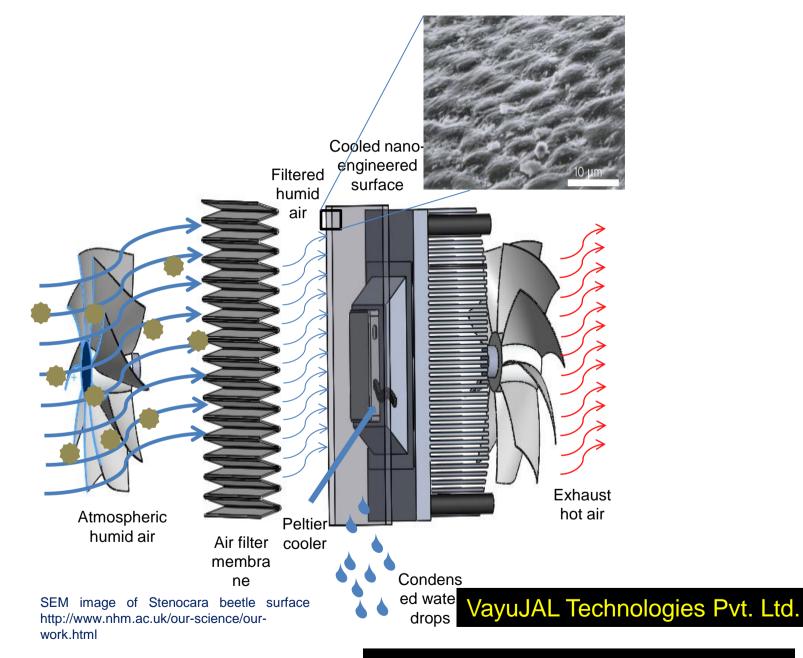
Atmospheric water harvesting



New harvesters

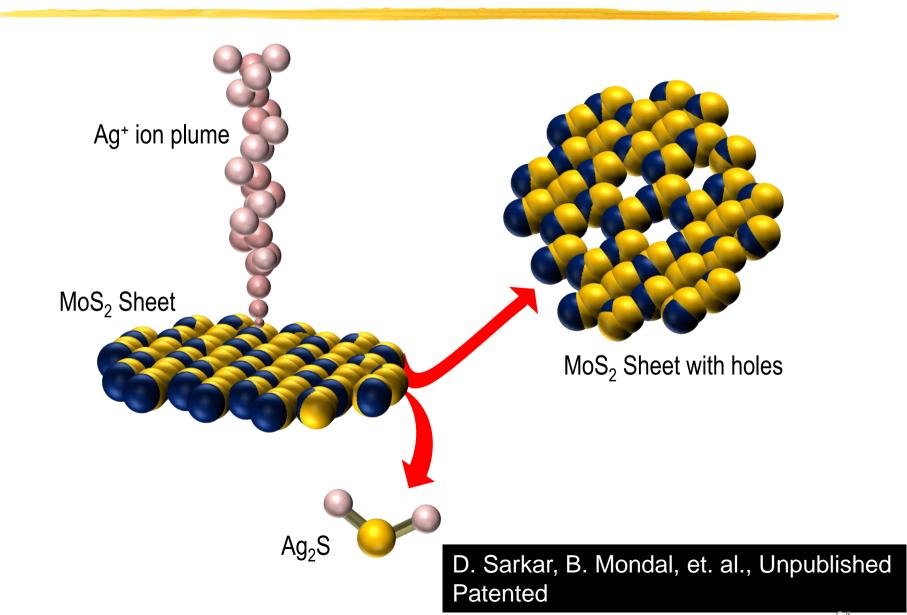
D. Sarkar, et. al. Adv. Mater. 2016

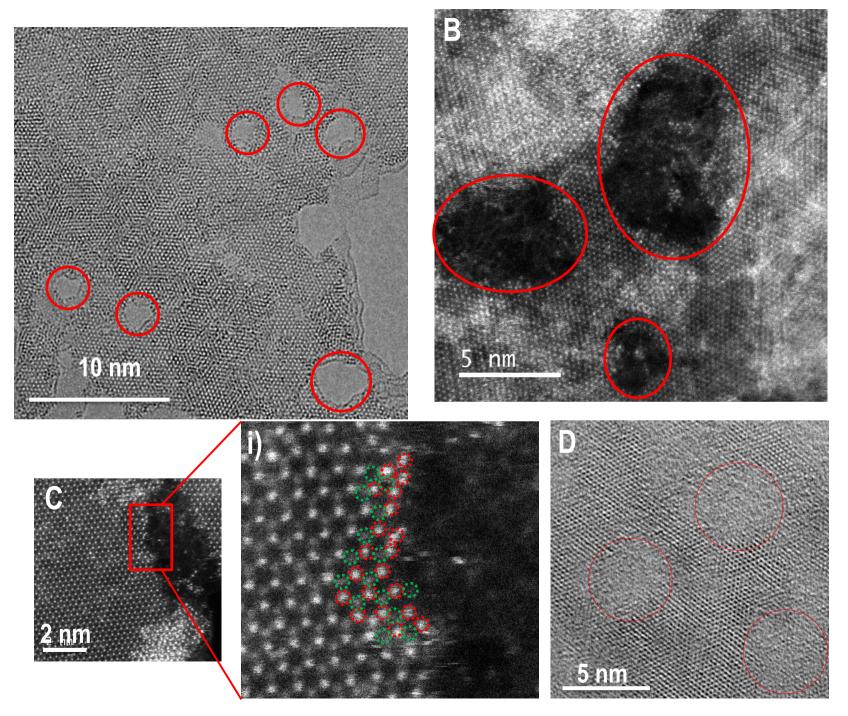


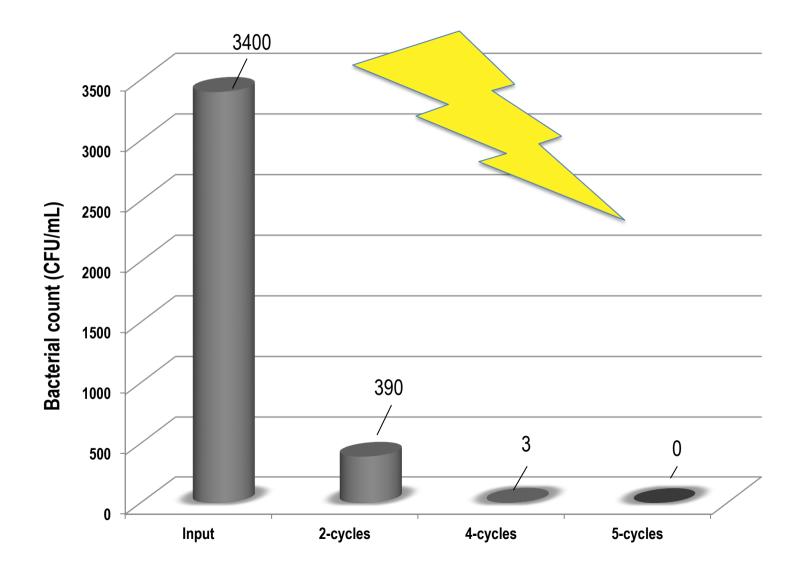


Ankit Nagar and Ramesh Kumar Soni

Atomically precise holes







Road ahead

We can solve ALL the DRINKING WATER problems affordably.

Better mechanisms of monitoring are needed to ensure that the nation stays healthy.

Affordable and sustainable solutions for water harvesting are needed.

We need to create mechanisms of delivery.

Expanding to clean air, sustainable and healthy water, food

Global efforts

International centre for clean water

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 contre of action.

Many of the problems of water quality can be bandled affordably by new technologies.

More solutions are needed with international participation. Available technologies have to reach other parts of the world.

Aller Projection Miller Projection SCALE 1:100,000,000 Solution Miller Projection SCALE 1:100,000,000 Solution NUMETERS NUMETERS https://commons.wikimedia.org/wiki/File:World_population_density_1994.png















Thank you

Where there is clean water, there is hope.