



# Innovations to address groundwater contamination



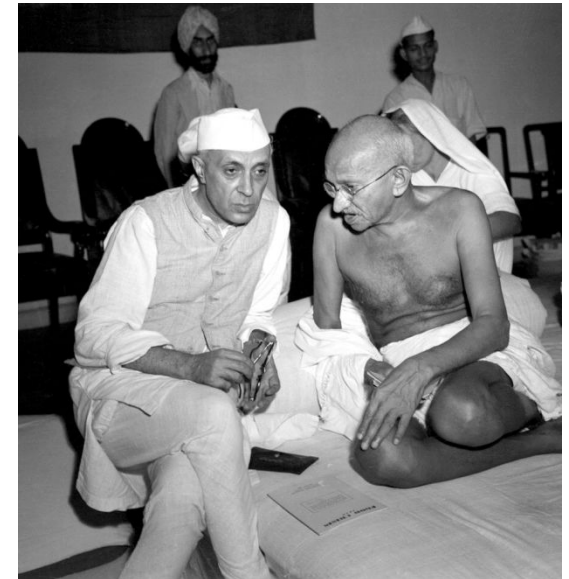
**T. Pradeep**

*Institute Professor and Institute Chair Professor*

*Professor of Chemistry*

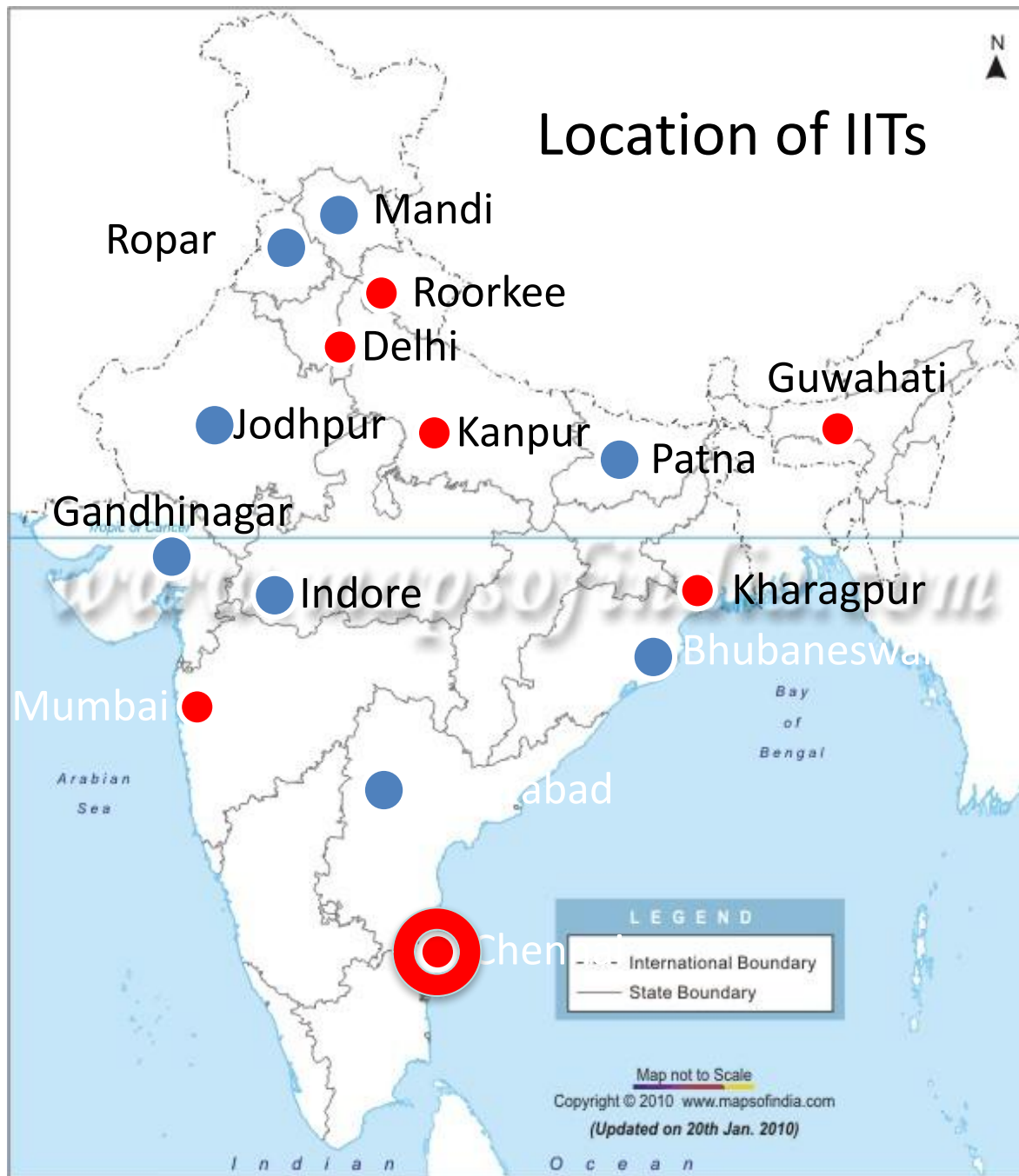
*Indian Institute of Technology Madras*

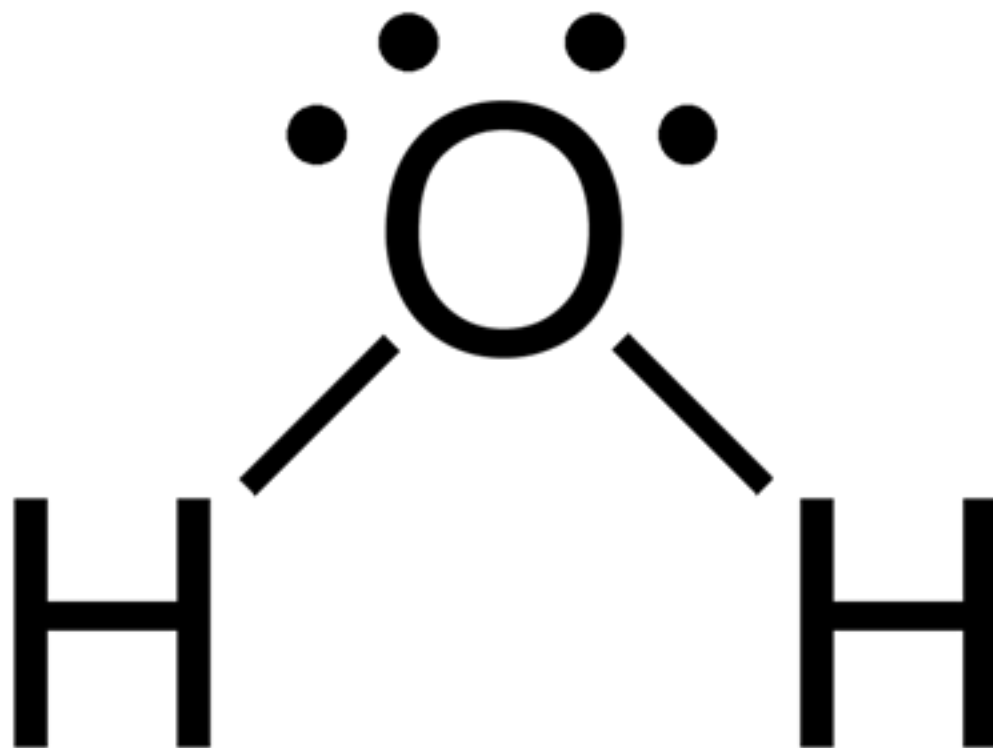
*Chennai 600 036, India*



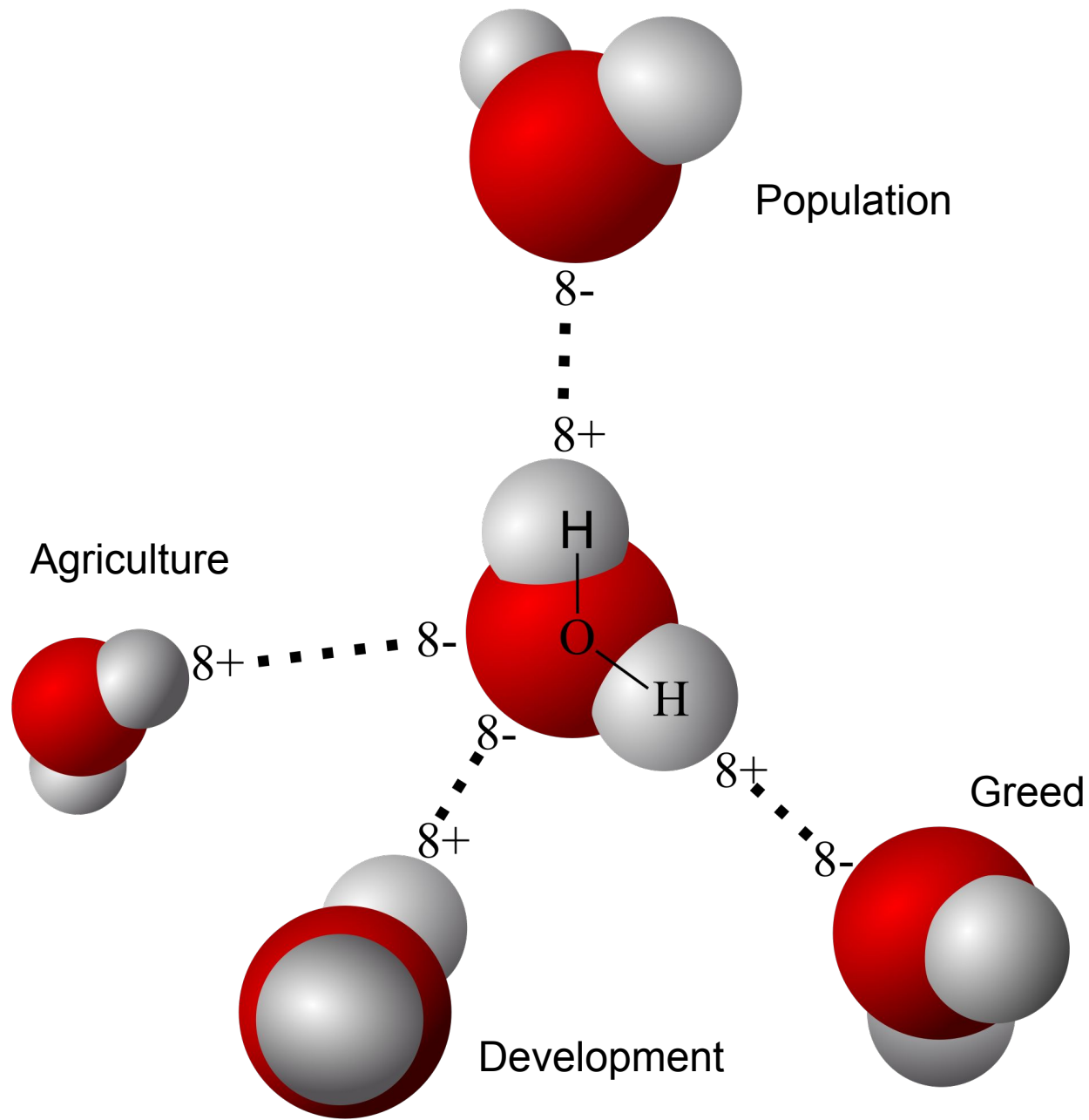
South Asia Groundwater Forum, Jaipur, June 1-3, 2016

# Location of IITs





Universal solvent



# PERIODIC TABLE OF THE ELEMENTS

GROUP 1 1A 2 10 18 8A

PERIOD 1 2 3 4

RELATIVE ATOMIC WEIGHT

GROUP 13C 14 15 16 17 18

ATOMIC NUMBER

SYMBOL

ELEMENT NAME

Metals: Alkali metal, Alkaline earth metal, Transition metals, Lanthanide, Actinide

Nonmetals: Chalcogens element, Halogens element, Noble gas

STANDARD STATE (25 °C, 101 kPa)

He - gas, Fe - solid, O<sub>2</sub> - liquid, Zn - synthetic

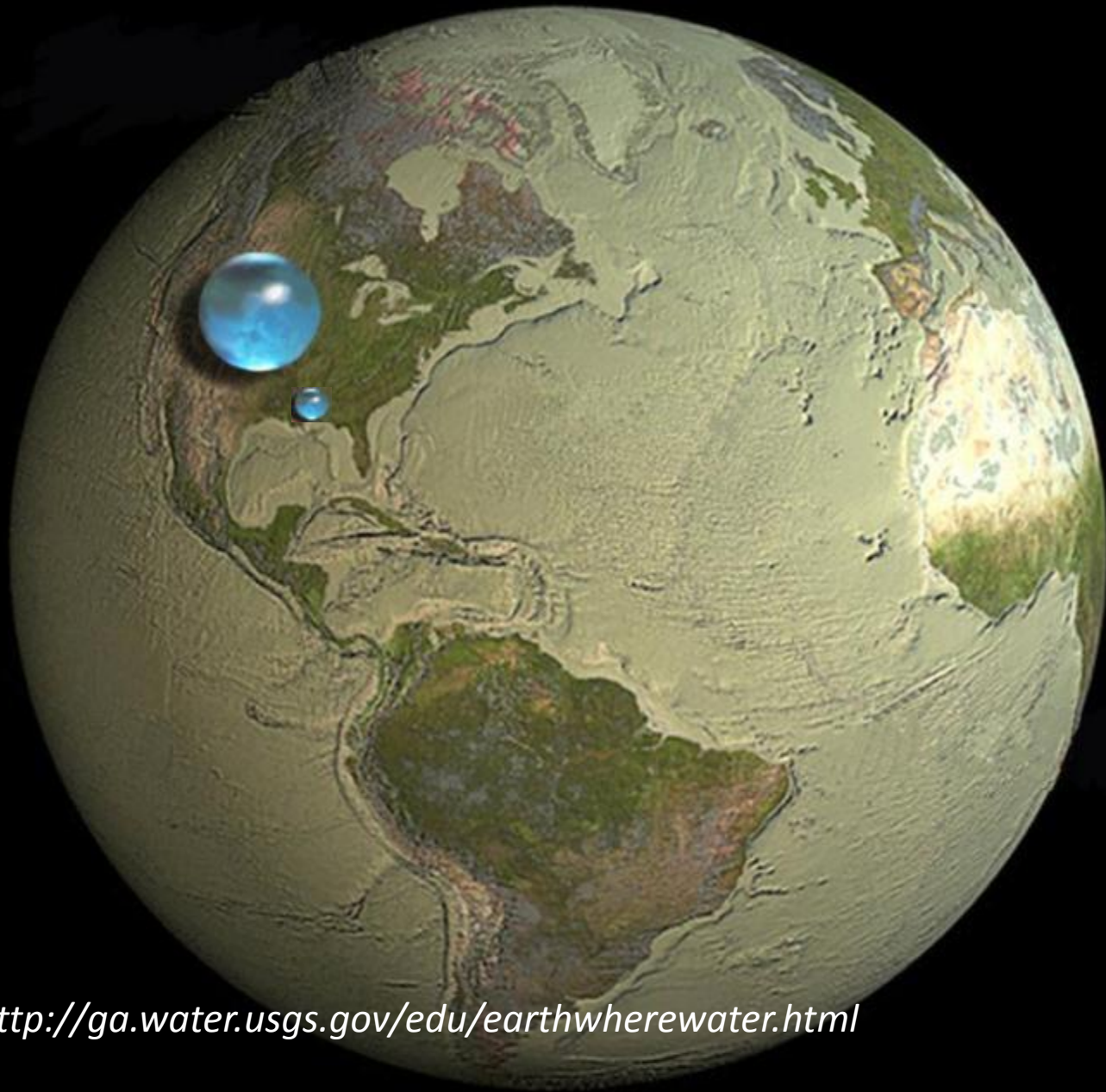
|    |    |    |    |   |    |    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|---|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 1  | 2  | 3  | 4  | 5 | 6  | 7  | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
| H  | He |    |    |   |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Li | Be |    |    | B | C  | N  | O  | F  | Ne |    |    |    |    |    |    |    |    |
| Na | Mg |    |    |   |    |    |    |    |    |    |    | Al | Si | P  | S  | Cl | Ar |
| K  | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |

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

|   |            |            |        |            |             |            |             |             |             |            |            |            |            |           |            |           |            |           |
|---|------------|------------|--------|------------|-------------|------------|-------------|-------------|-------------|------------|------------|------------|------------|-----------|------------|-----------|------------|-----------|
| 5 | Rb         | Sr         | Y      | Zr         | Nb          | Mo         | Tc          | Ru          | Rh          | Pd         | Ag         | Cd         | In         | Sn        | Sb         | Te        | I          | Xe        |
|   | 55 132.91  | 56 137.33  | 57-71  | 72 91.224  | 73 92.906   | 74 95.94   | 75 98.906   | 76 101.07   | 77 101.07   | 78 106.36  | 79 106.90  | 80 112.411 | 81 114.818 | 82 207.2  | 83 121.757 | 84 127.60 | 85 126.905 | 86 131.29 |
| 6 | Cs         | Ba         | La-Lu  | Hf         | Ta          | W          | Re          | Os          | Ir          | Pt         | Au         | Hg         | Tl         | Pb        | Bi         | Po        | At         | Rn        |
|   | 87 132.905 | 88 137.327 | 89-103 | 104 178.49 | 105 180.948 | 106 183.84 | 107 186.207 | 108 188.906 | 109 188.906 | 110 200.59 | 111 200.59 | 112 200.59 | 113 204.38 | 114 207.2 | 115 208.98 | 116 209   | 117 210    | 118 222   |
| 7 | Fr         | Ra         | Ac-Lr  | Rf         | Db          | Sg         | Bh          | Hs          | Mt          | Uun        | Uun        | Uub        |            |           |            |           |            |           |
|   | 87 223     | 88 226     | 89-103 | 104 261    | 105 262     | 106 266    | 107 264     | 108 269     | 109 268     | 110 277    | 111 277    | 112 277    |            |           |            |           |            |           |

|             |  |  |  |  |  |  |  |  |  |  |  |  |  |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   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| LANTHANIDES |  |  |  |  |  |  |  |  |  |  |  |  |  | Periods 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 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612, 613, 614, 615, 616, 617, 618, 619, 620, 621, 622, 623, 624, 625, 626, 627, 628, 629, 630, 631, 632, 633, 634, 635, 636, 637, 638, 639, 640, 641, 642, 643, 644, 645, 646, 647, 648, 649, 650, 651, 652, 653, 654, 655, 656, 657, 658, 659, 660, 661, 662, 663, 664, 665, 666, 667, 668, 669, 670, 671, 672, 673, 674, 675, 676, 677, 678, 679, 680, 681, 682, 683, 684, 685, 686, 687, 688, 689, 690, 691, 692, 693, 694, 695, 696, 697, 698, 699, 700, 701, 702, 703, 704, 705, 706, 707, 708, 709, 710, 711, 712, 713, 714, 715, 716, 717, 718, 719, 720, 721, 722, 723, 724, 725, 726, 727, 728, 729, 730, 731, 732, 733, 734, 735, 736, 737, 738, 739, 740, 741, 742, 743, 744, 745, 746, 747, 748, 749, 750, 751, 752, 753, 754, 755, 756, 757, 758, 759, 760, 761, 762, 763, 764, 765, 766, 767, 768, 769, 770, 771, 772, 773, 774, 775, 776, 777, 778, 779, 780, 781, 782, 783, 784, 785, 786, 787, 788, 789, 790, 791, 792, 793, 794, 795, 796, 797, 798, 799, 800, 801, 802, 803, 804, 805, 806, 807, 808, 809, 810, 811, 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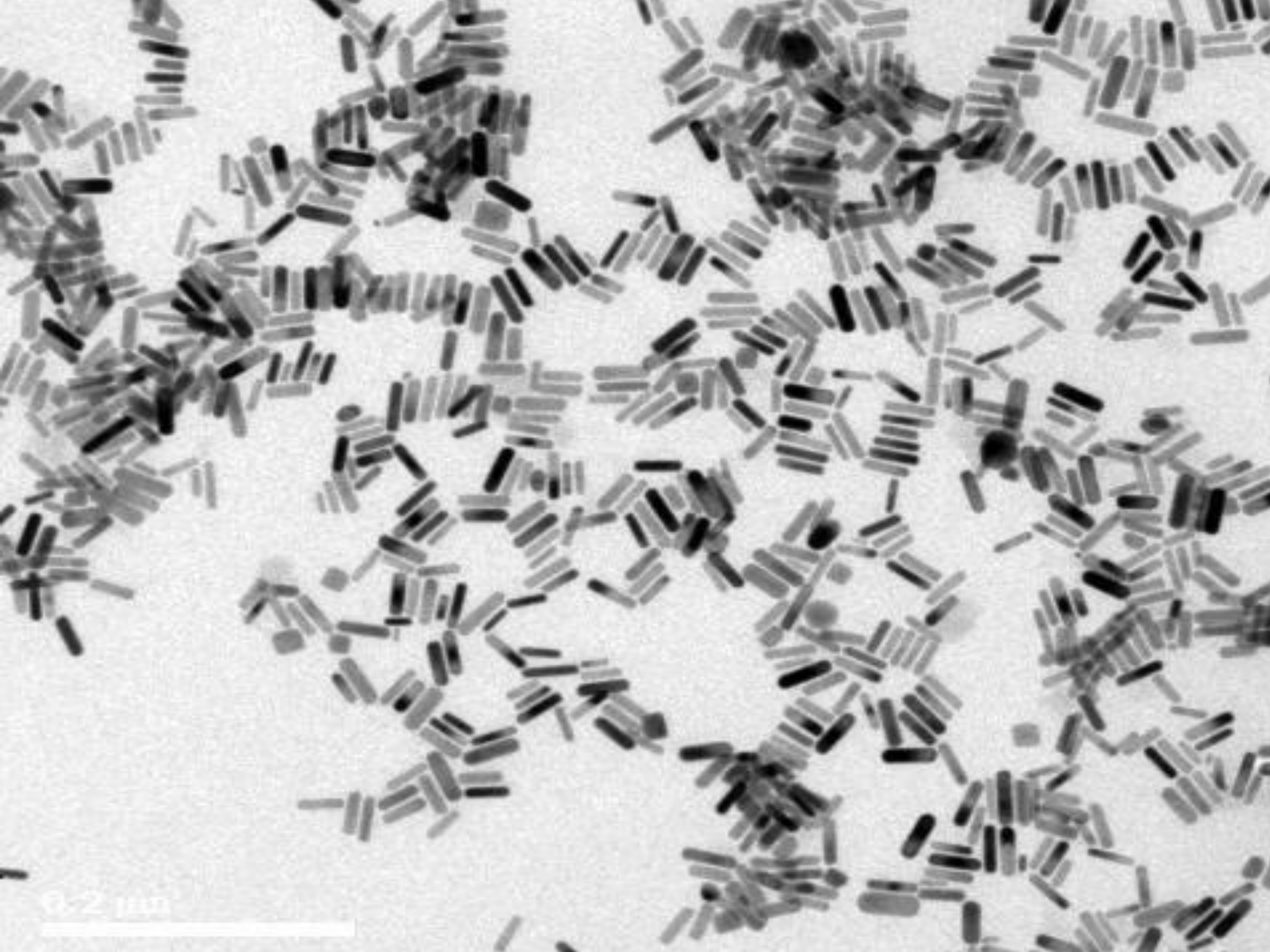
Source: <http://ga.water.usgs.gov/edu/earthwherewater.html>

Why nanotechnology?

Nano  $10^{-9}$

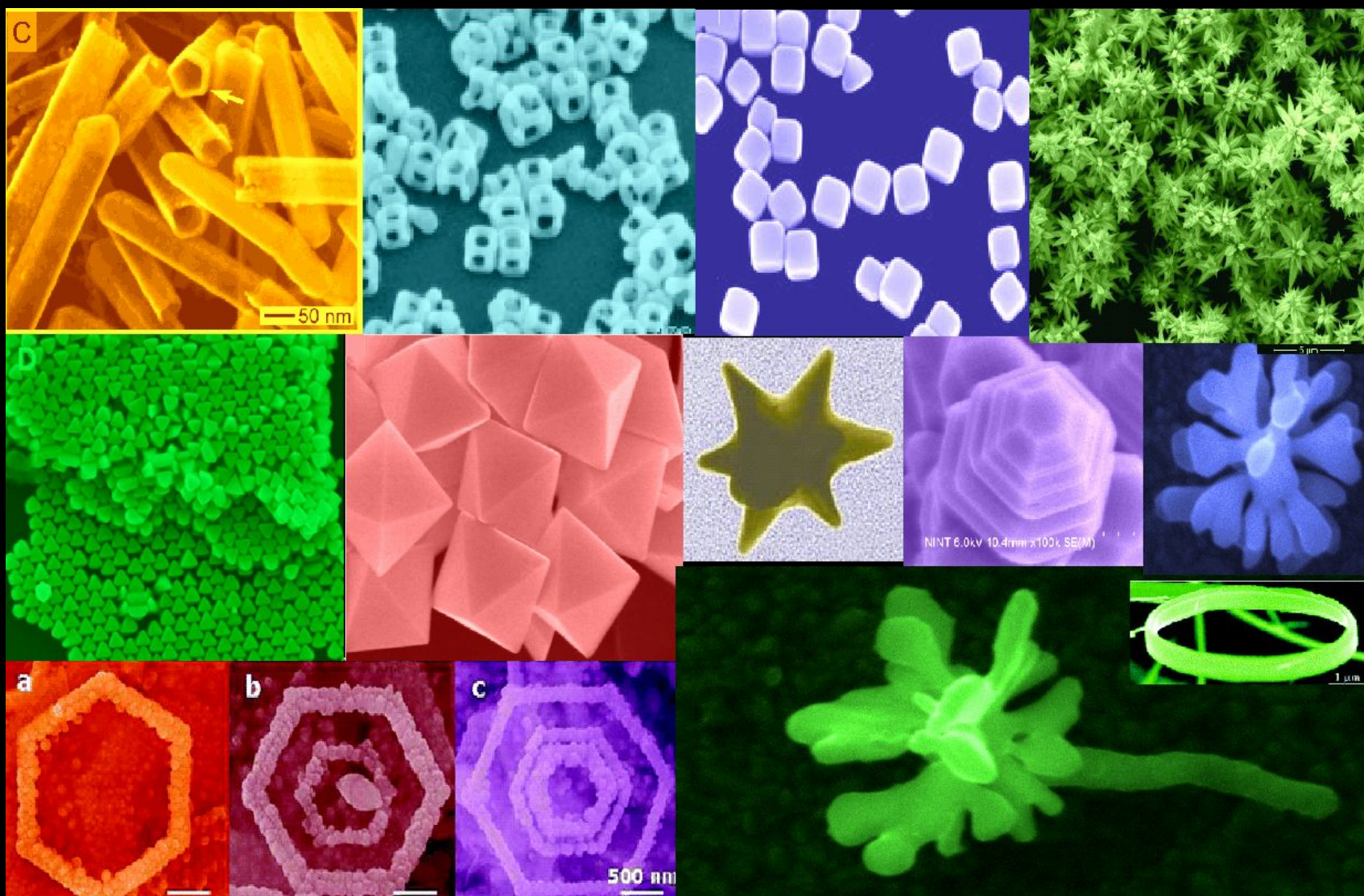


Quantum



0.2  $\mu\text{m}$

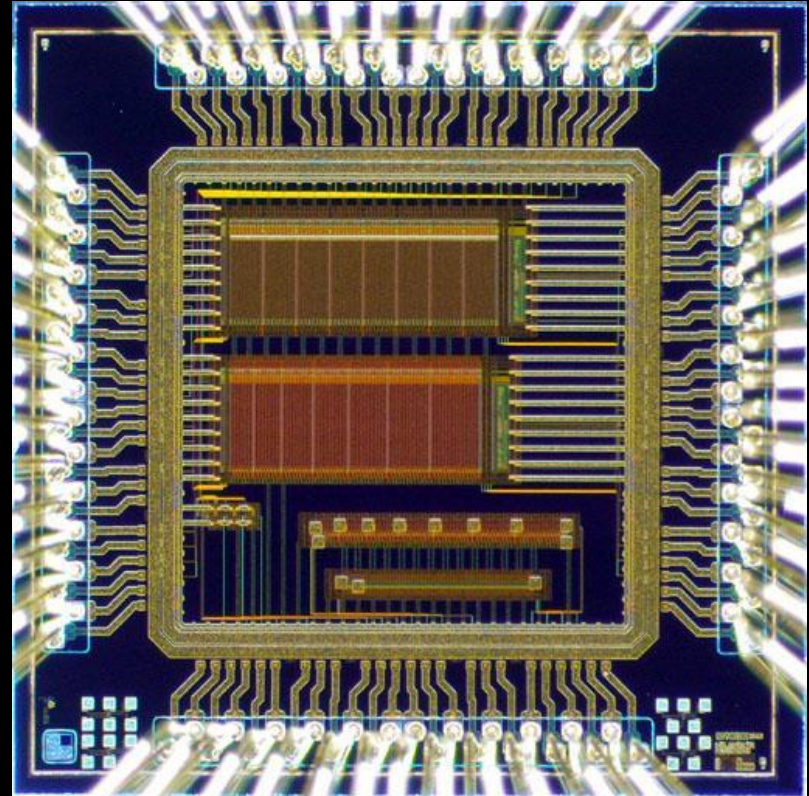




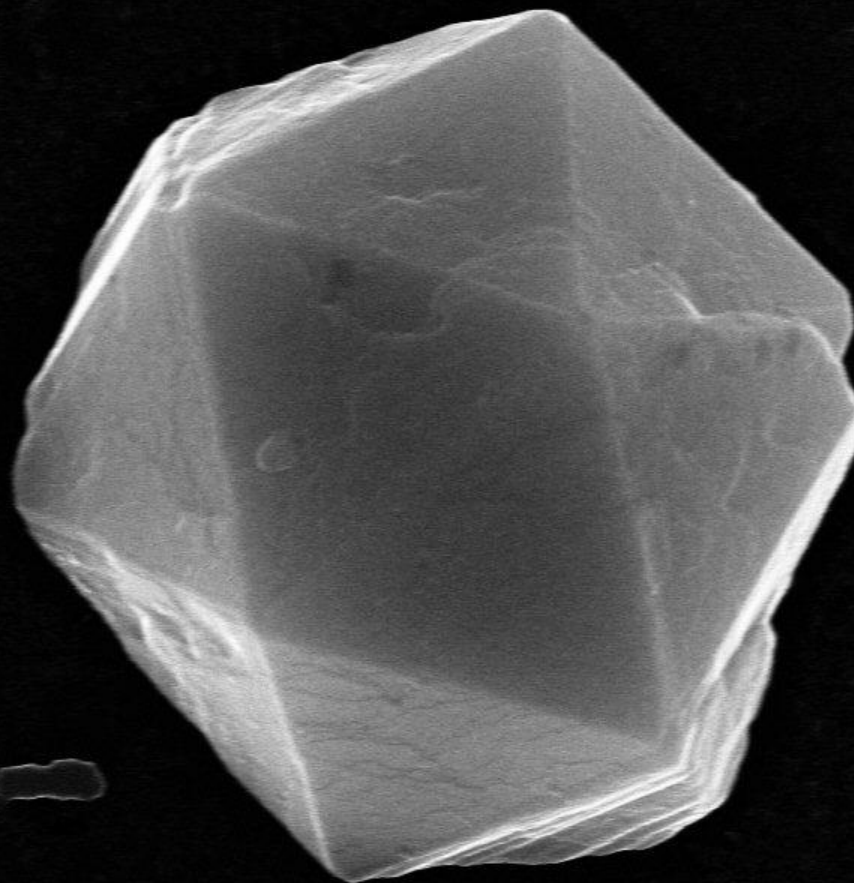
Sajanlal and Pradeep, Kirk-Othmer Encyclopedia, 2012



Technology is about manipulating objects



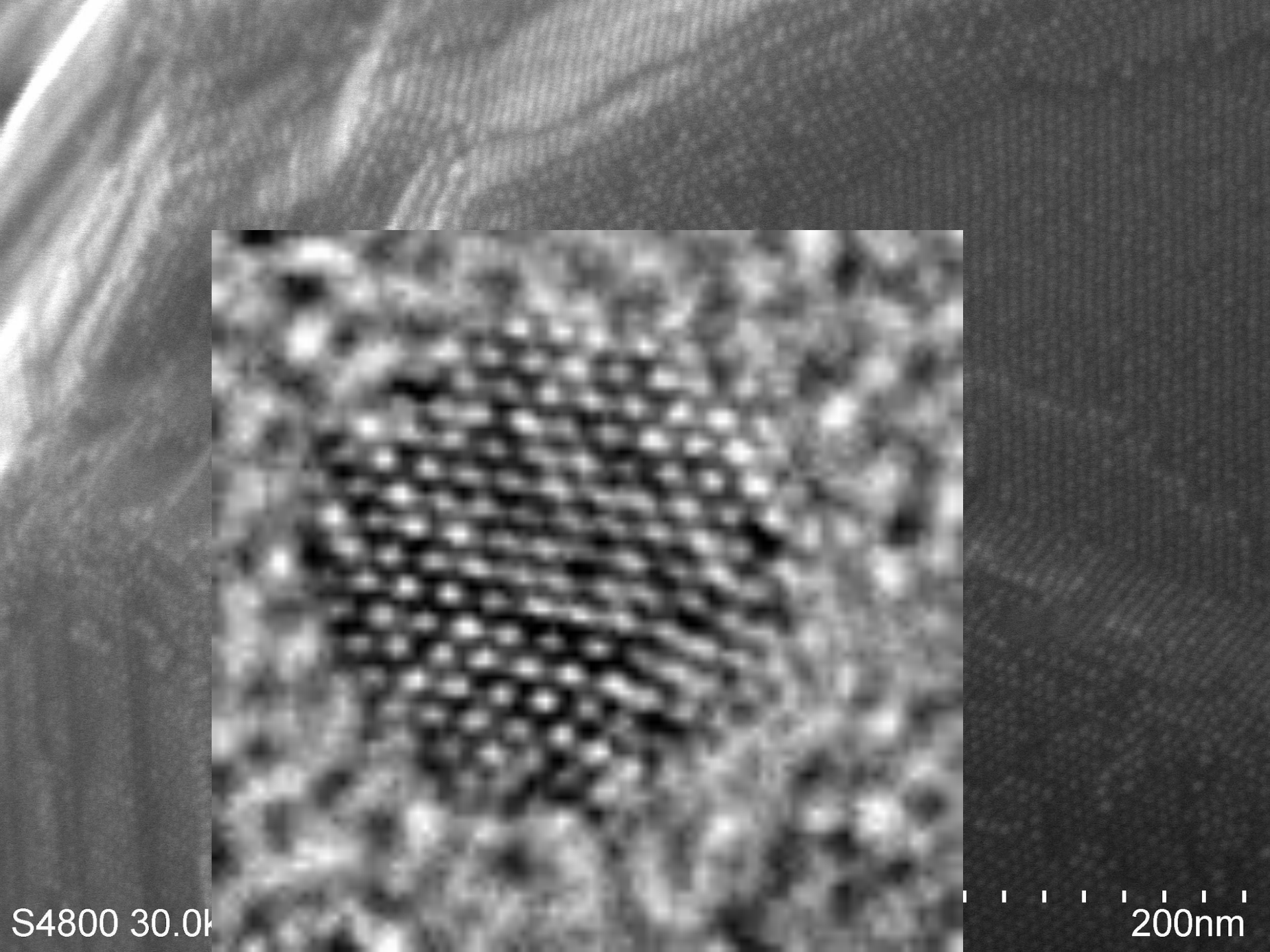
Growth of civilization reduced the size of objects manipulated



An object for the nanotechnology - nanomaterials.

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

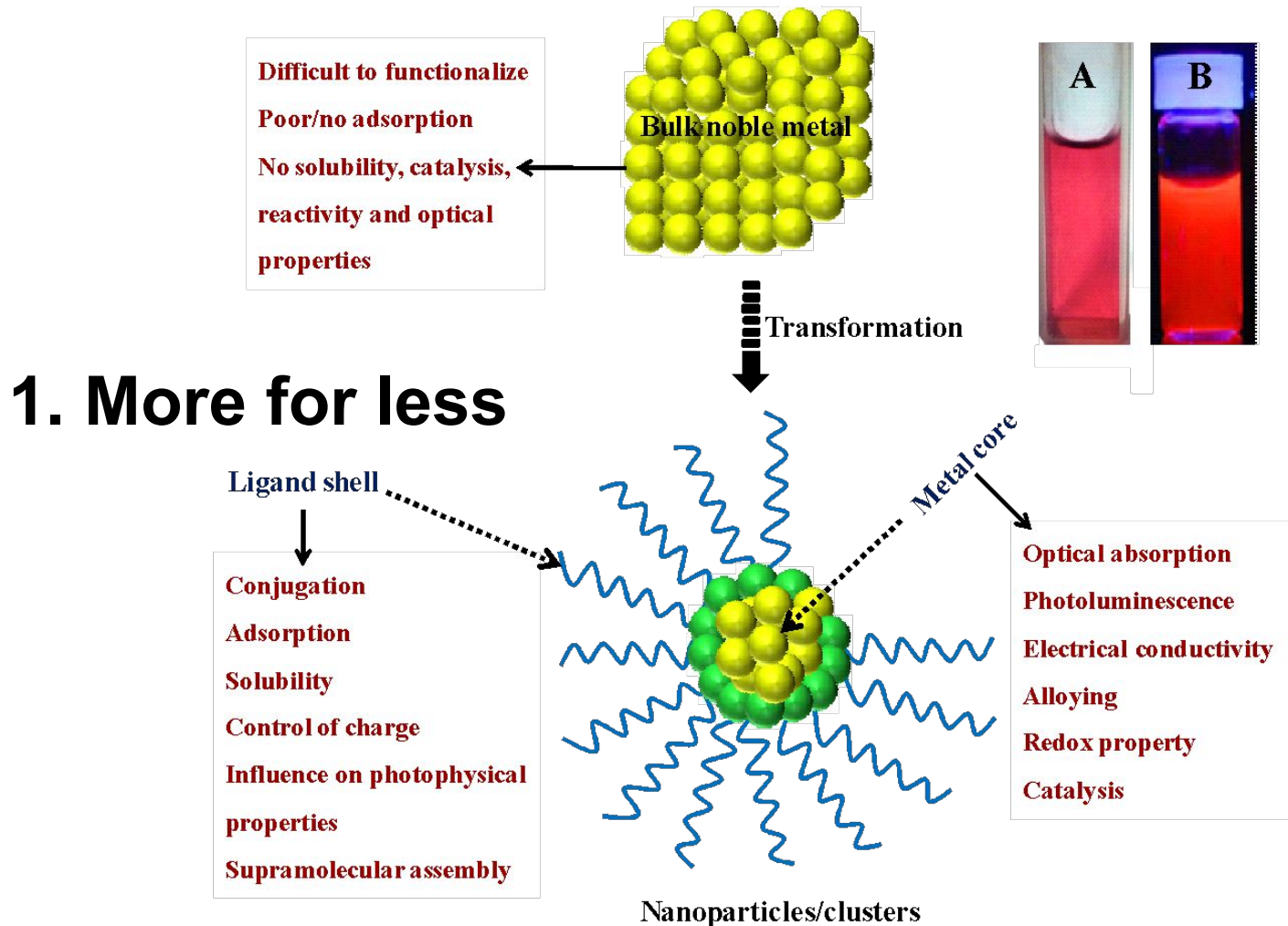
4.00um



S4800 30.0kV

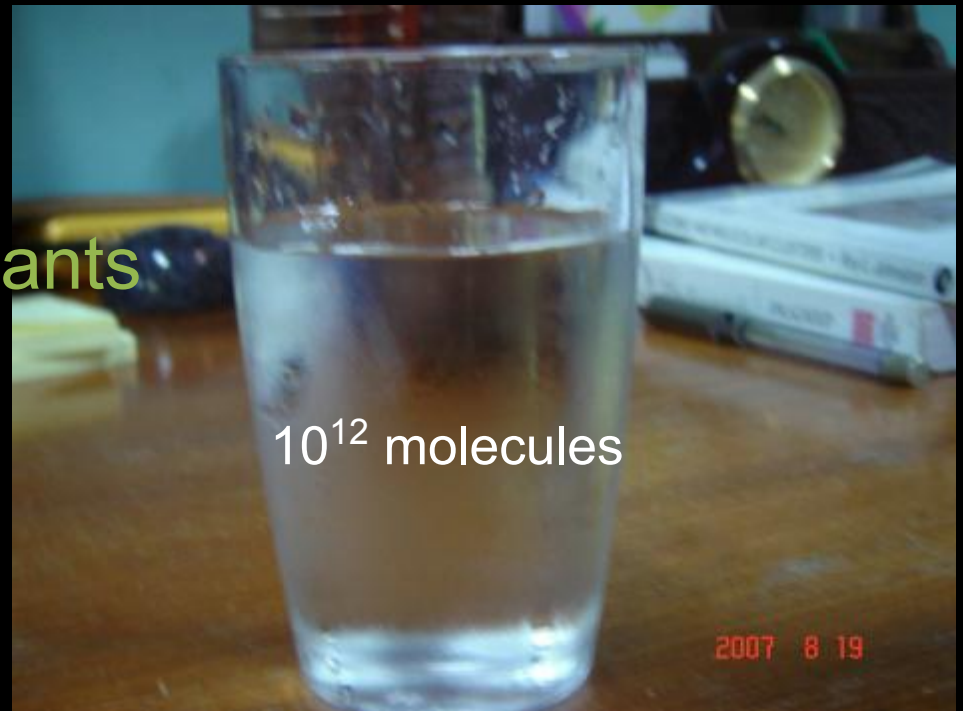
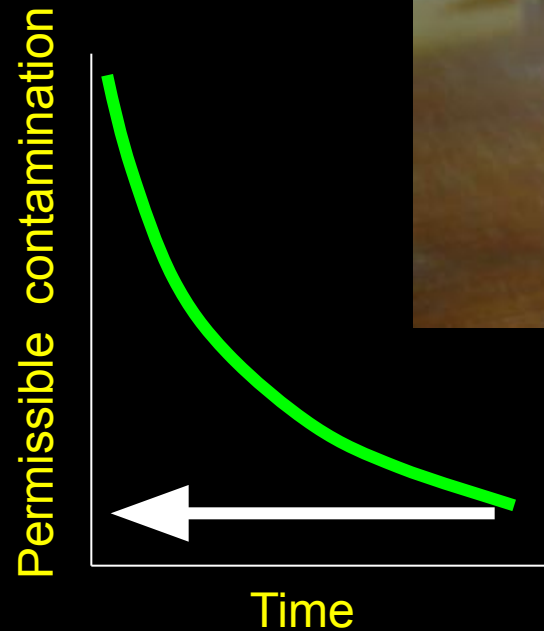
200nm



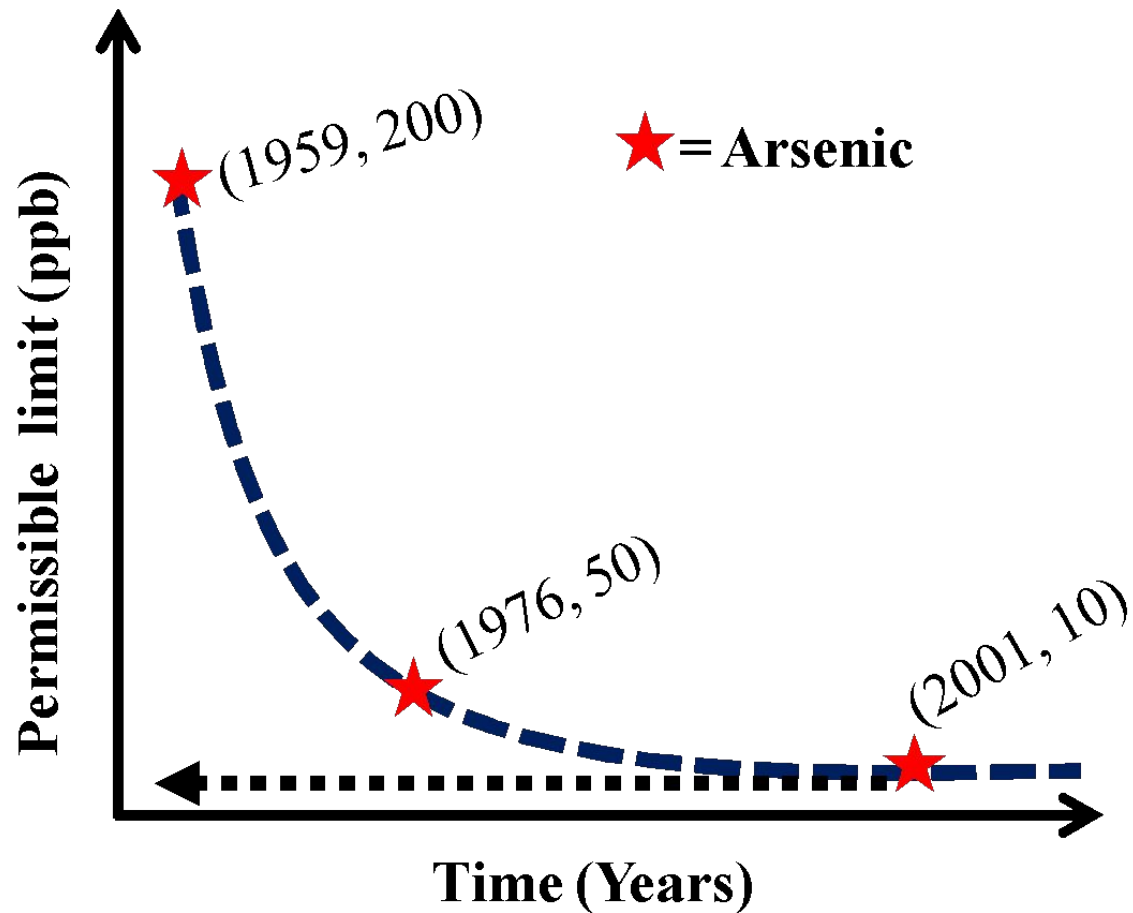


Variation in properties originating from ligand shell and metal core as bulk noble metals transform to nanoparticles/clusters. Sizes are not to scale. New properties such as color and photoluminescence arise in such size regime. Photographs of Au@citrate nanoparticles (inset A) showing intense absorption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

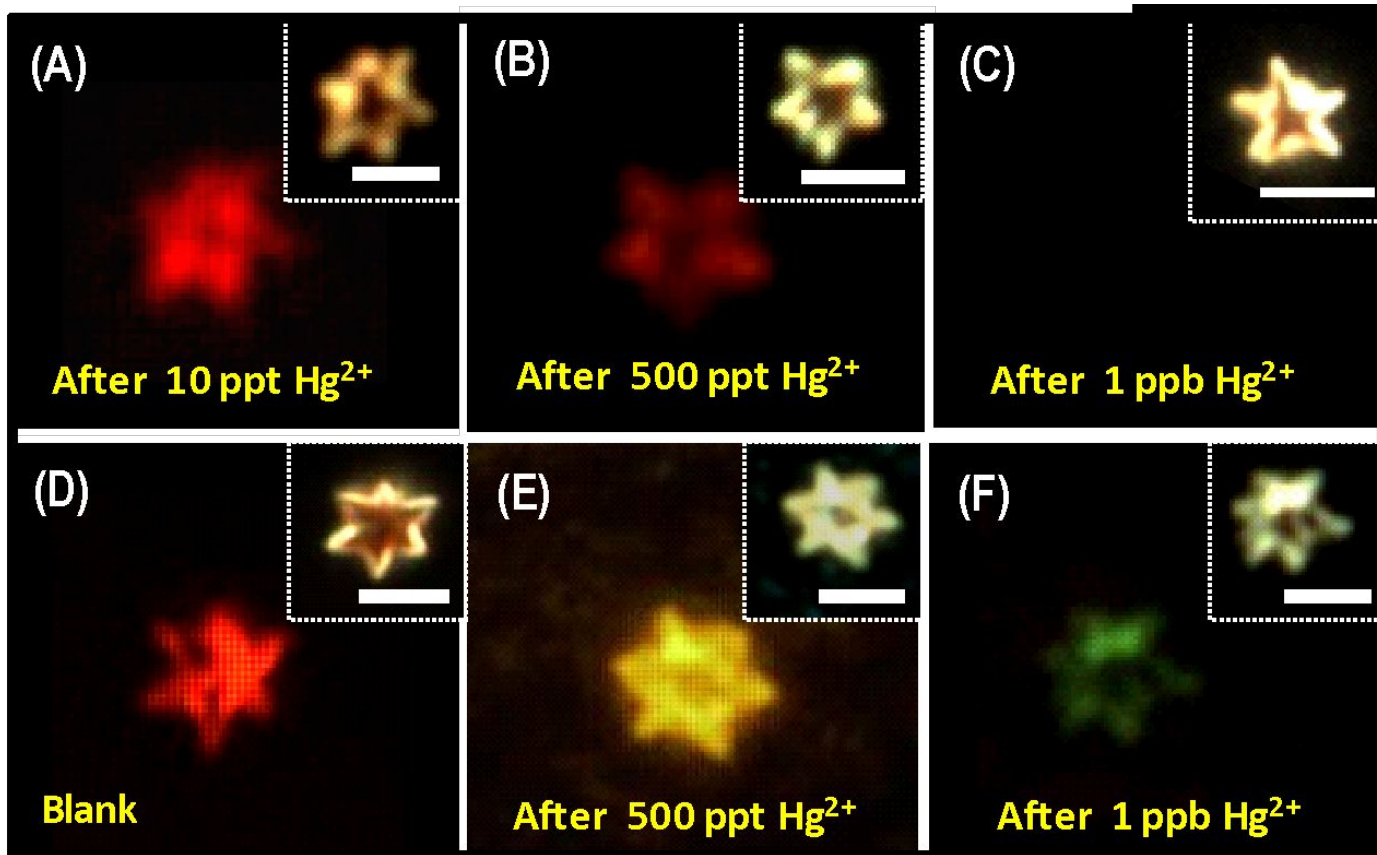


Permissible contamination reaches limits of detection



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

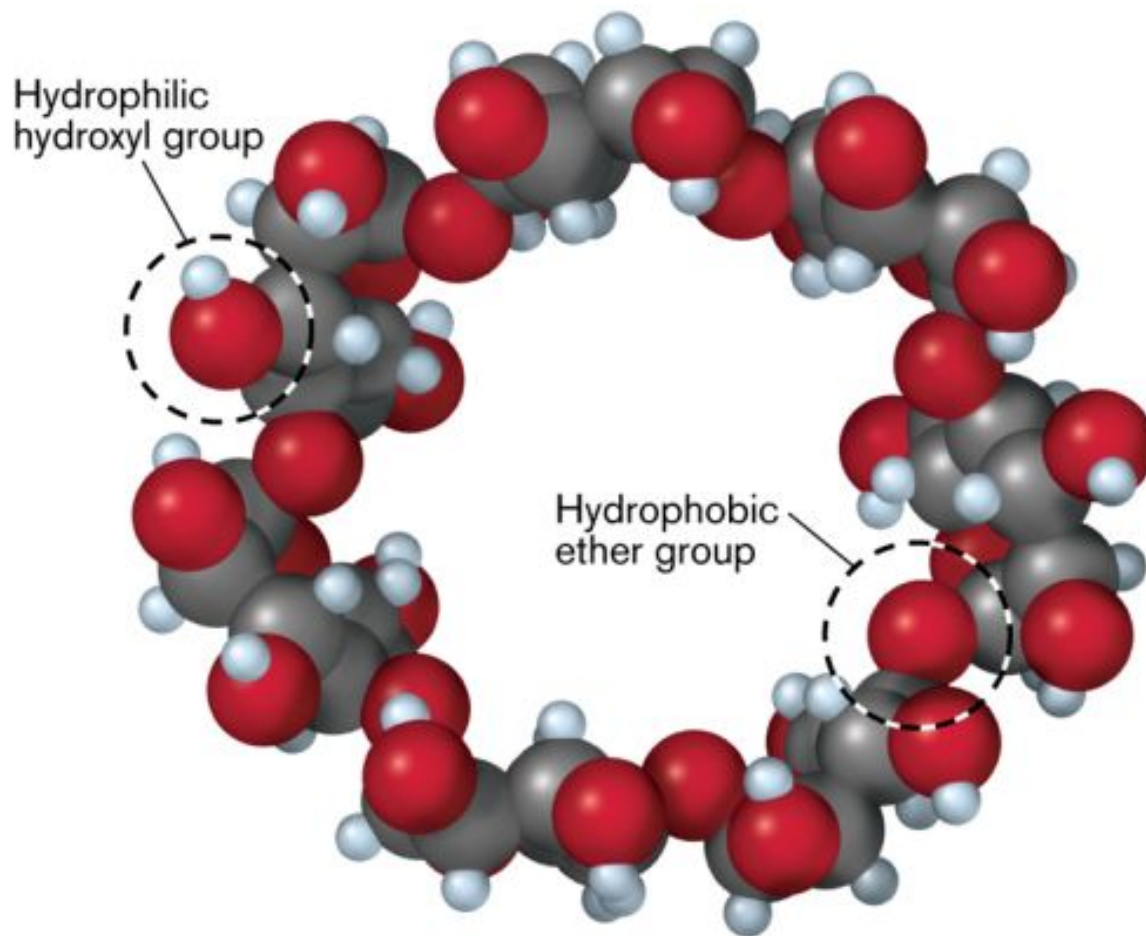
### 3. Can we reach limits?



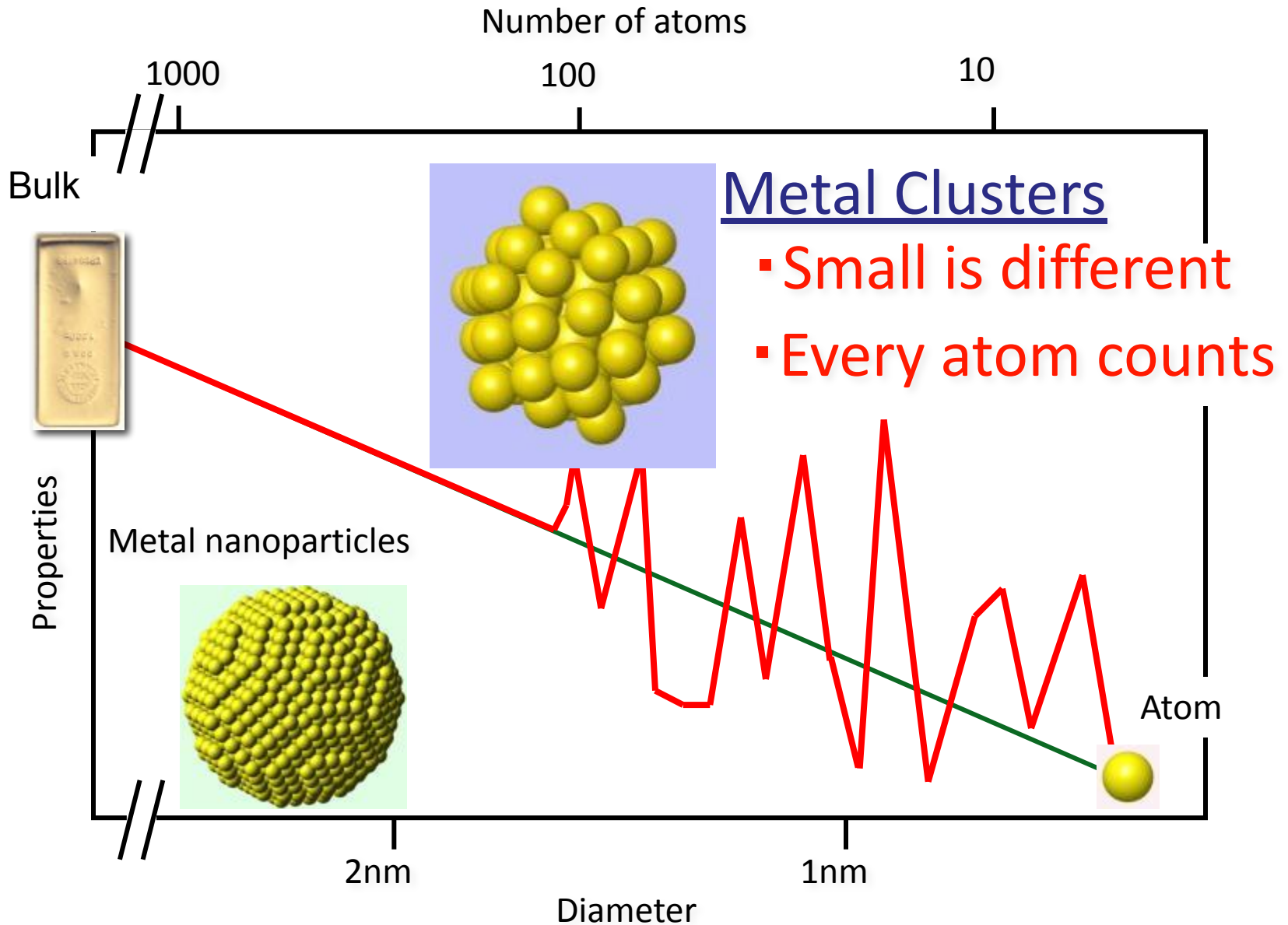
(A)–(C) Dark field fluorescence images of  $\text{Au@SiO}_2\text{@Ag}_{15}$  MFs showing the gradual disappearance of luminescence with increasing  $\text{Hg}^{2+}$ . (D)–(F) Fluorescence images showing variation in color during the addition of  $\text{Hg}^{2+}$  of different concentrations to  $\text{Au@SiO}_2\text{-FITC@Ag}_{15}$  MFs. Insets in all images show the corresponding optical images of the MFs; scale bars are 3  $\mu\text{m}$ .

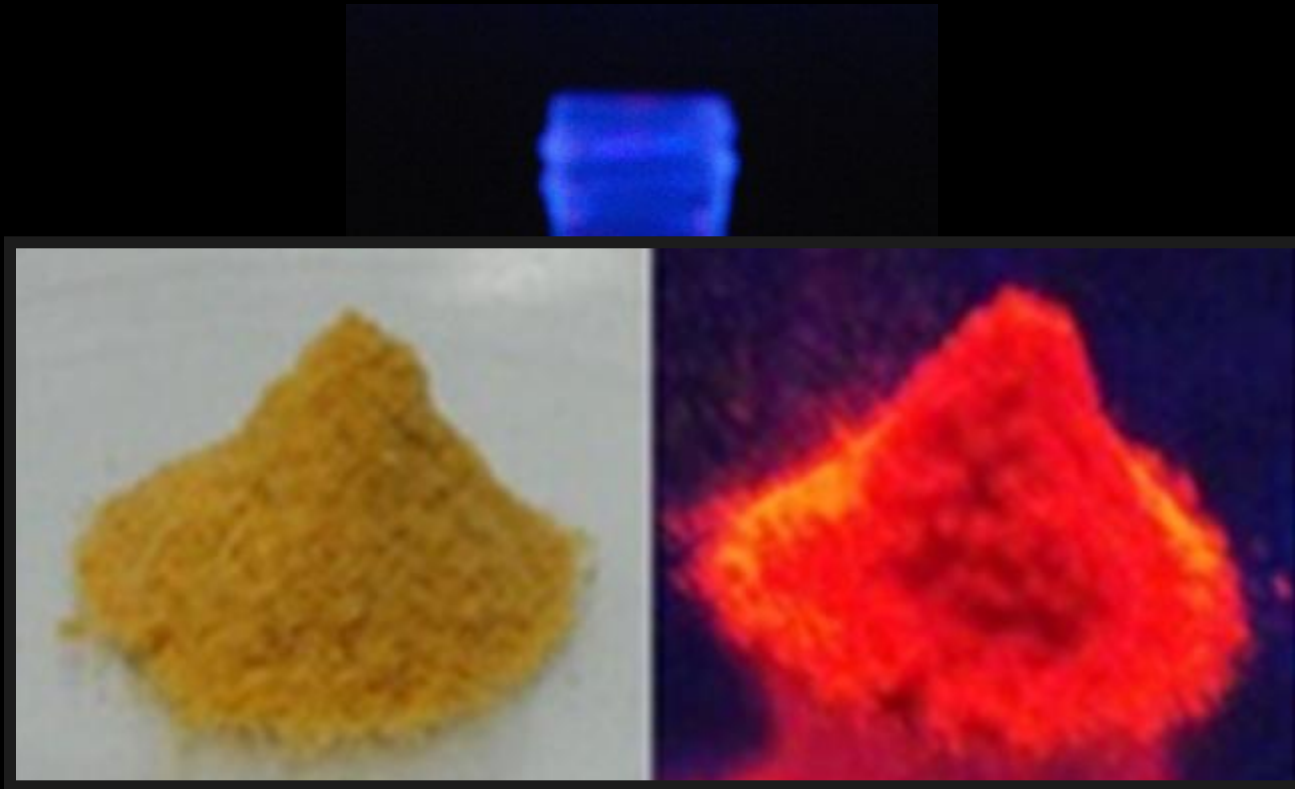


Cavities, channels, imprints, assemblies, fibres, ...

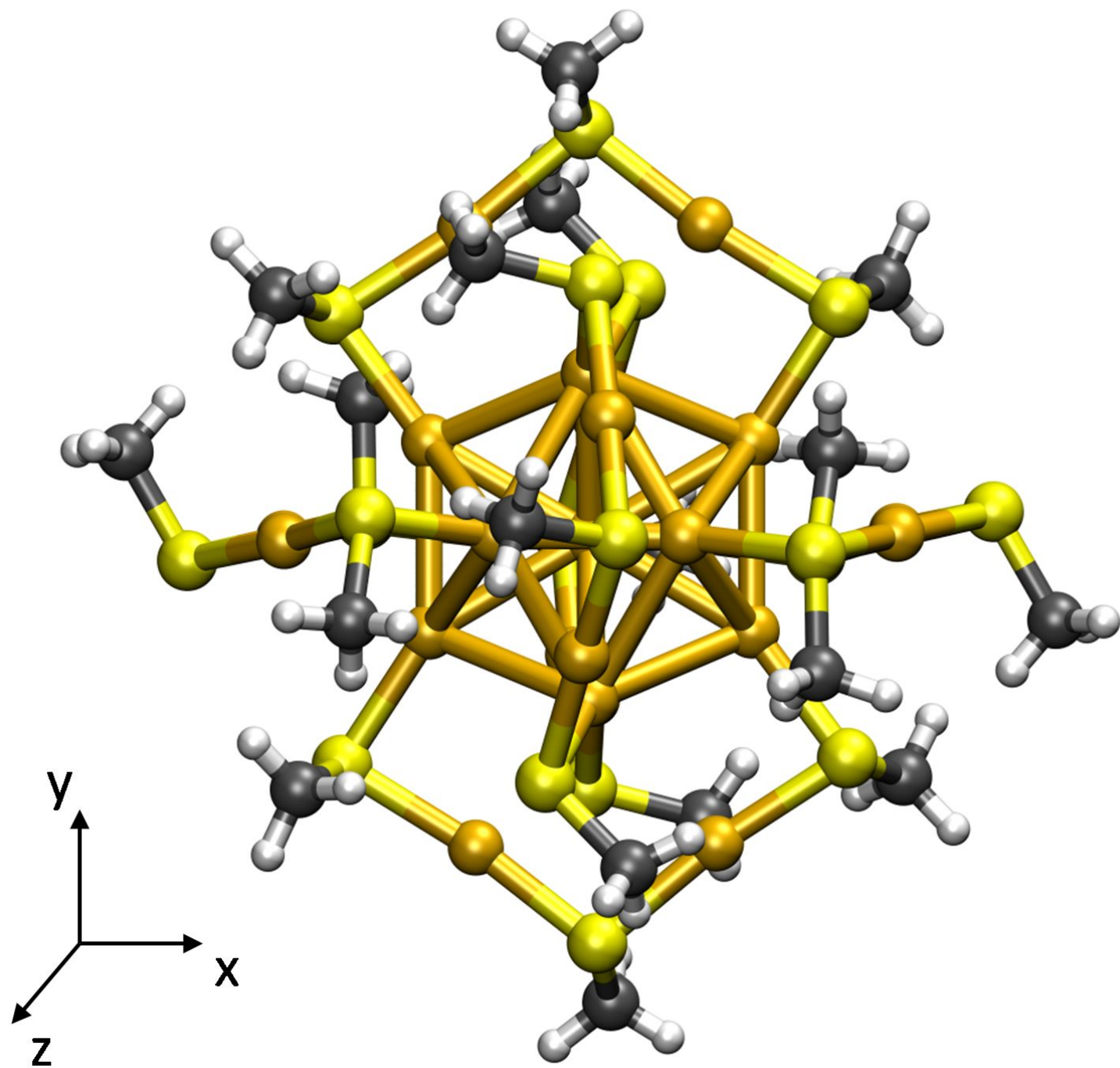


# Metal Clusters





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





# Biopolymer-reinforced nanocomposite for water purification

Mohan Udhaya Sankar<sup>1</sup>, Saha Kamalesh Chaudhari, and Thangavelu Sankar

Unit of Nanoscience and Thematic Unit of Nanoscience

Edited by Eric Hoek, University of California, San Diego

Creation of affordable materials for water purification is one of the most promising drinking water for all. Combining nanocomposites to scavenge toxic species and other contaminants along with the use of affordable, all-inclusive drinking water without electricity. The critical property is the synthesis of stable materials that can be used in the presence of complex contaminants in drinking water that deposit and form on surfaces. Here we show that such materials can be synthesized in a simple and effective way without the use of electrical power. The materials have sand-like properties, such as high mechanical strength and stable forms. These materials have been used as a water purifier to deliver clean drinking water. The ability to prepare nanocomposites at ambient temperature has wide implications for water purification.

hybrid | green | appropriate technology



**Featured in:**

The Guardian, UK

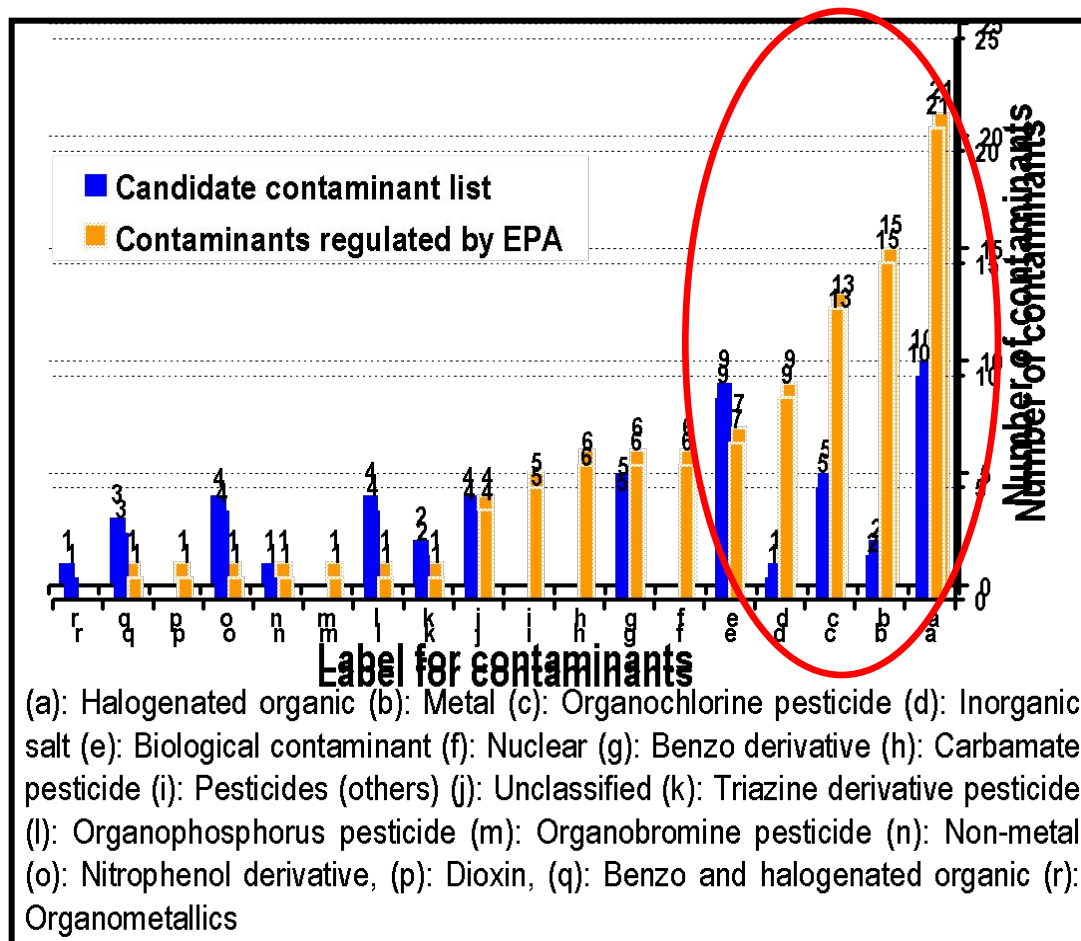
The Hindu, Telegraph, Times of India, etc.

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. Jayachandran Nadey, 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.' Thirupathi Pradeep who led the team at IIT Chennai told Chemistry World. He and his student Sheekumar Nair discovered in 2003 that nanocarbons such as carbon tetrachloride (CCl<sub>4</sub>) completely break down into metal halides and amorphous carbon upon reaction with gold and silver nanoparticles<sup>1</sup>.

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<sup>2,3</sup> that gold and silver nanoparticles loaded on alumina were indeed able to completely remove endosulfan, malathion and chlorpyrifos - three pesticides that are common in drinking water supplies.

Use and recycle  
The method  
Pradeep

Chemistry world

First ever  
nanotechnology  
product for clean  
water

Mumbai  
nanotechnology  
novel. Gauri



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 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**

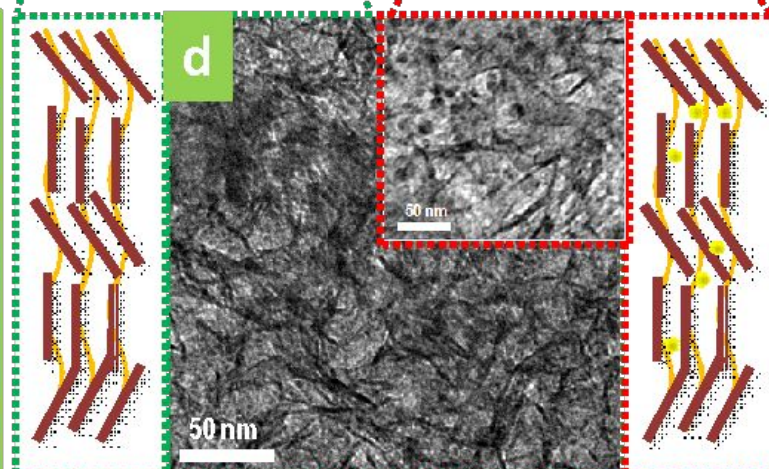
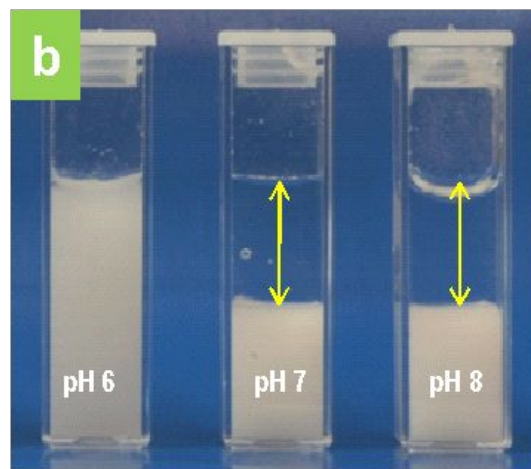
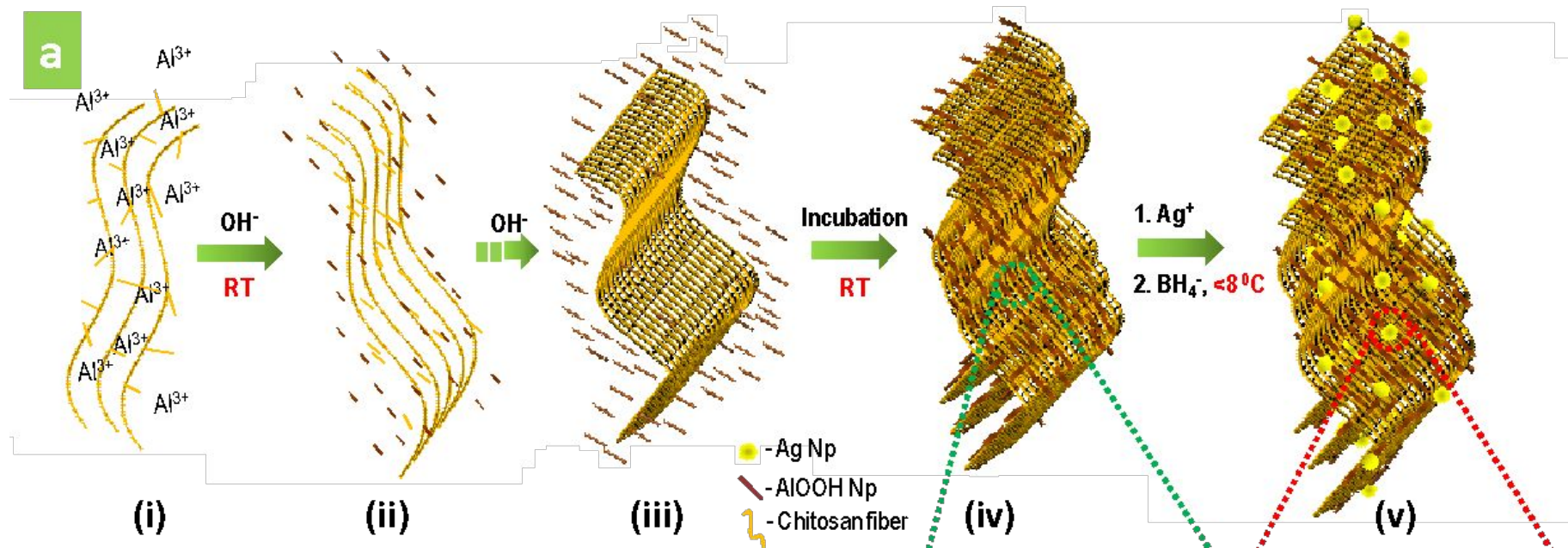
**Water positive**

**Water-based, room temperature, water stable**

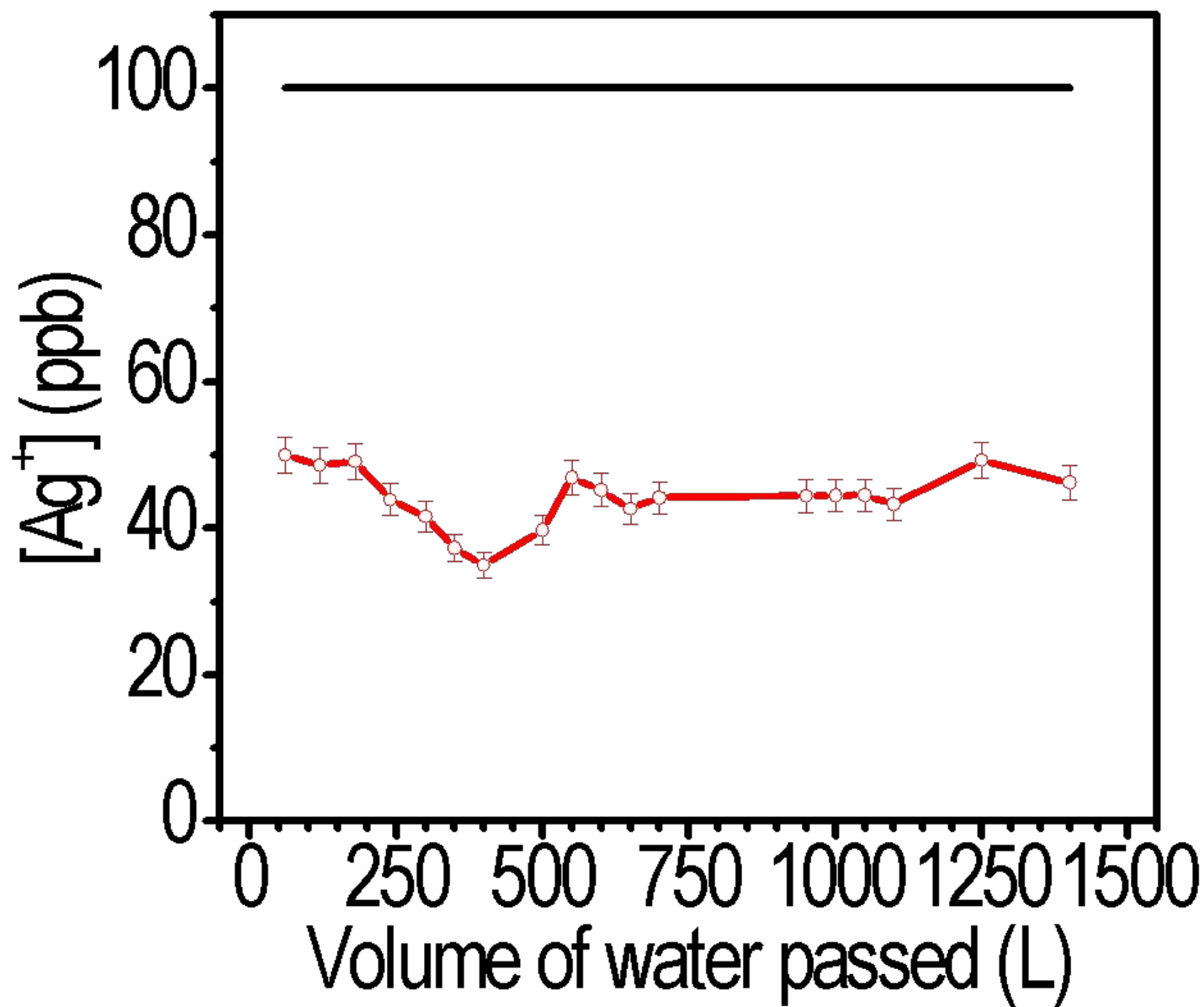
**Green**

**M. U. Sankar et al, PNAS 2013**

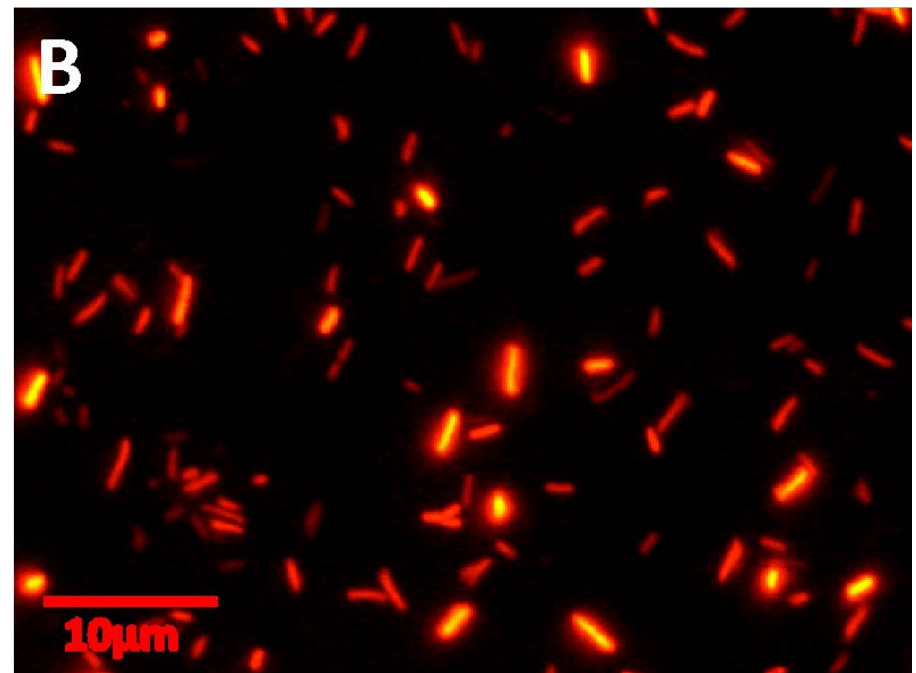
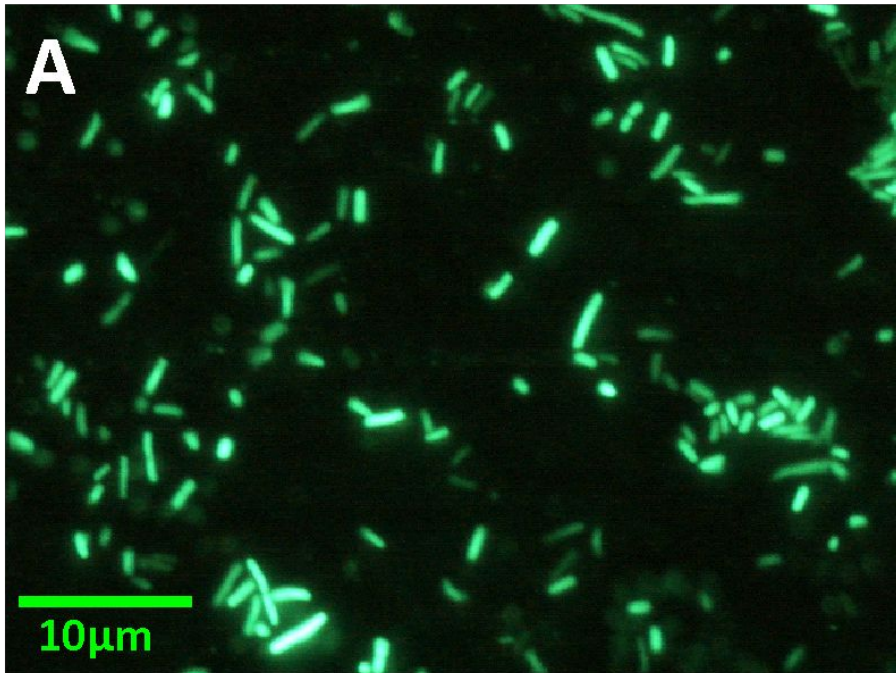


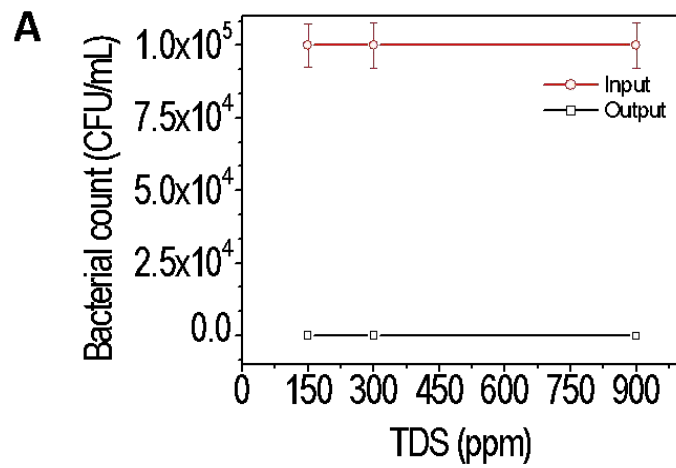




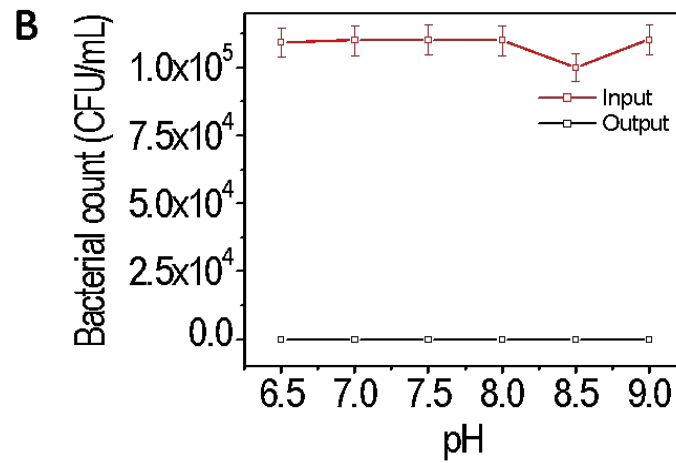


## Live/dead staining experiments





TDS

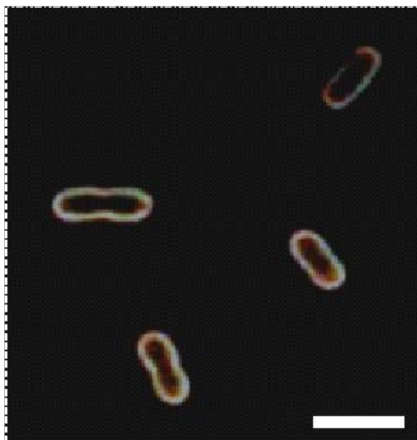
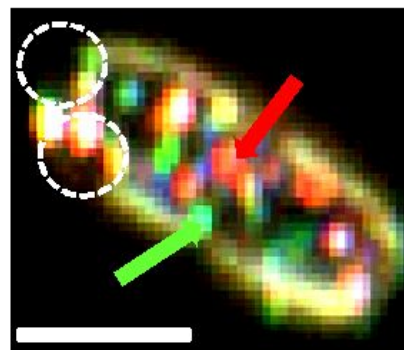
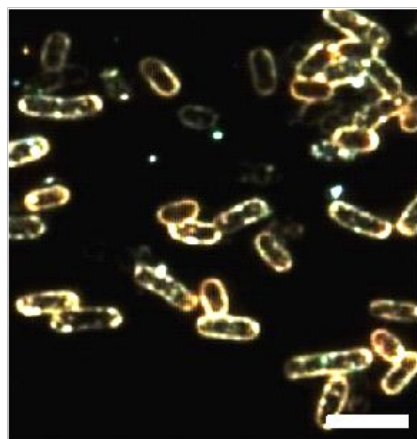
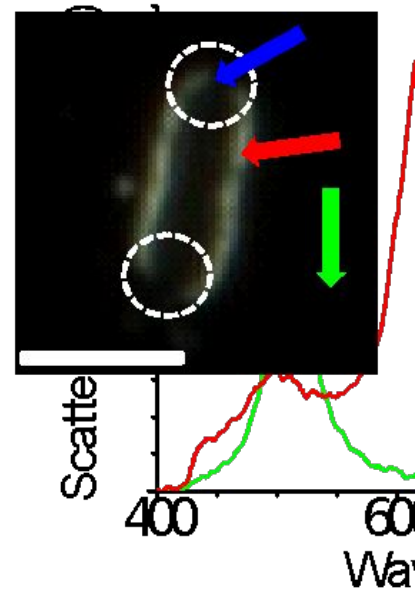
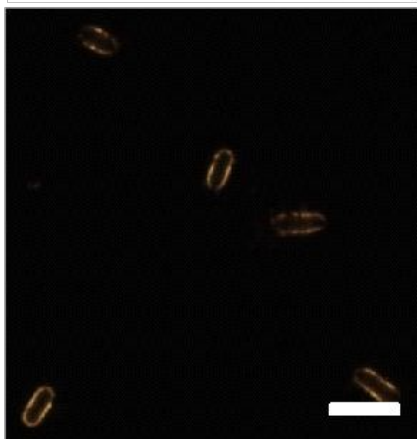


pH

Real water experiments

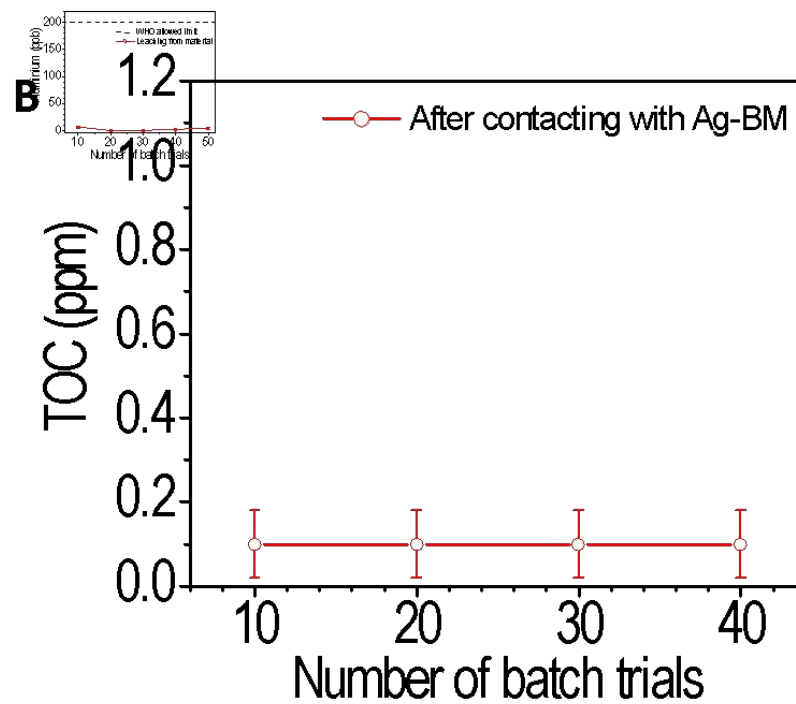
**C**

TOC – Humic acid

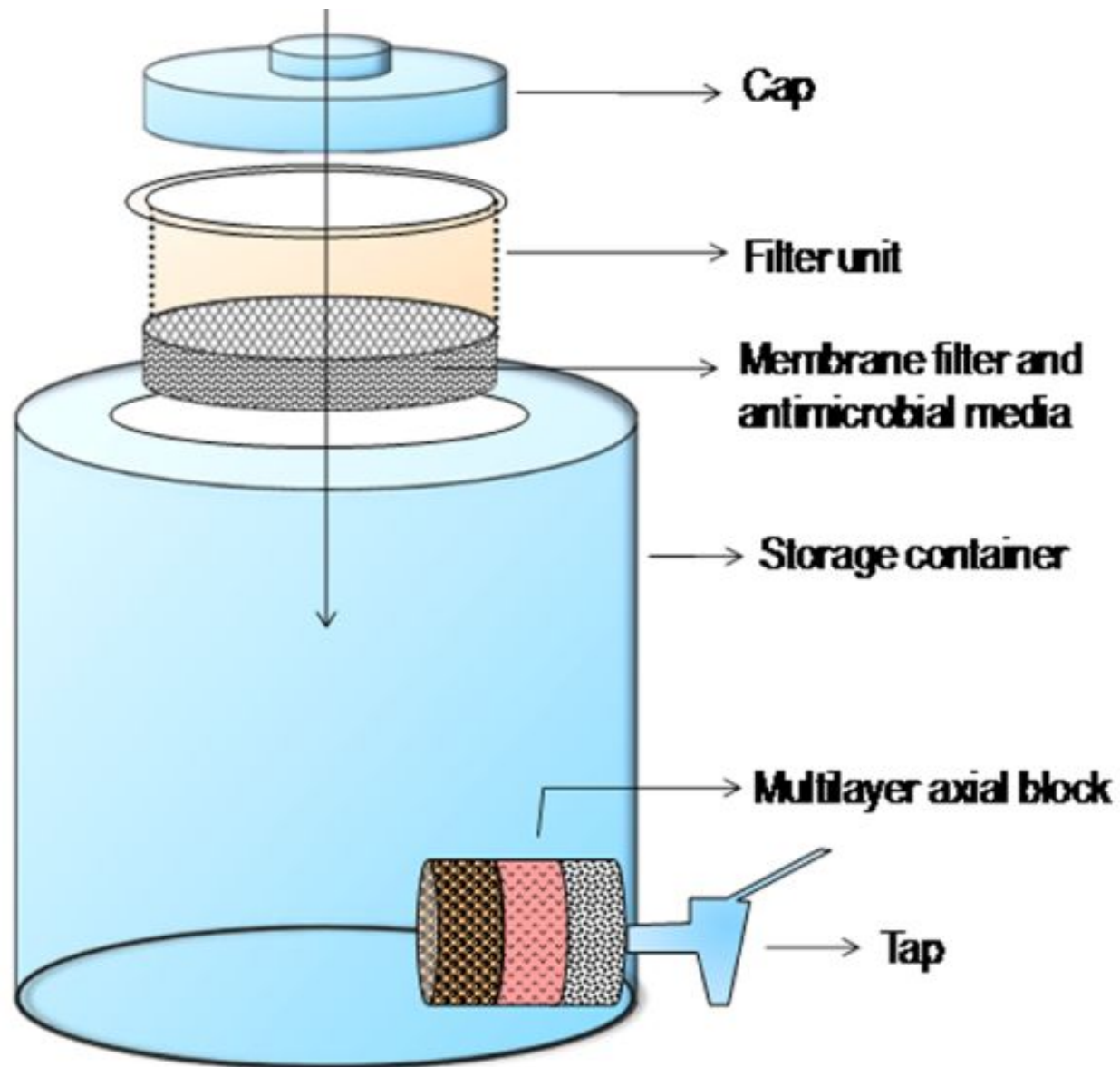
**a****d****b****e****c**



A



Leaching experiments



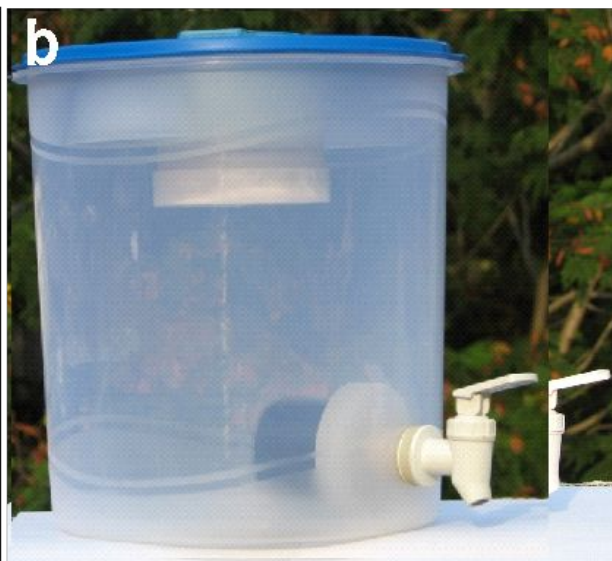
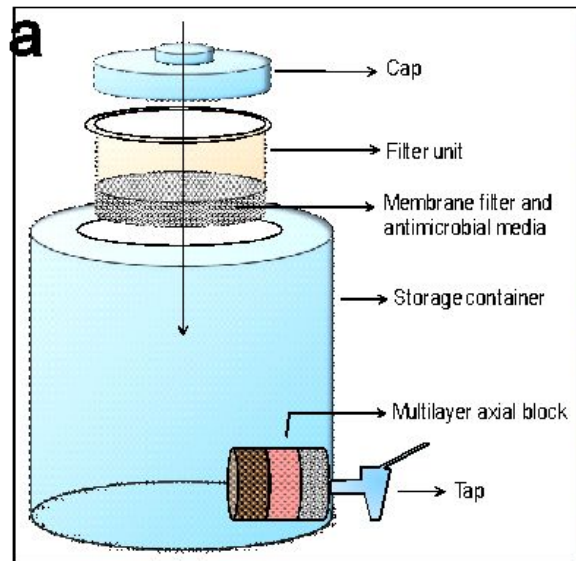
## Physicochemical characteristics of influent natural drinking water

(Note: All parameters are expressed in mg L<sup>-1</sup>, 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.

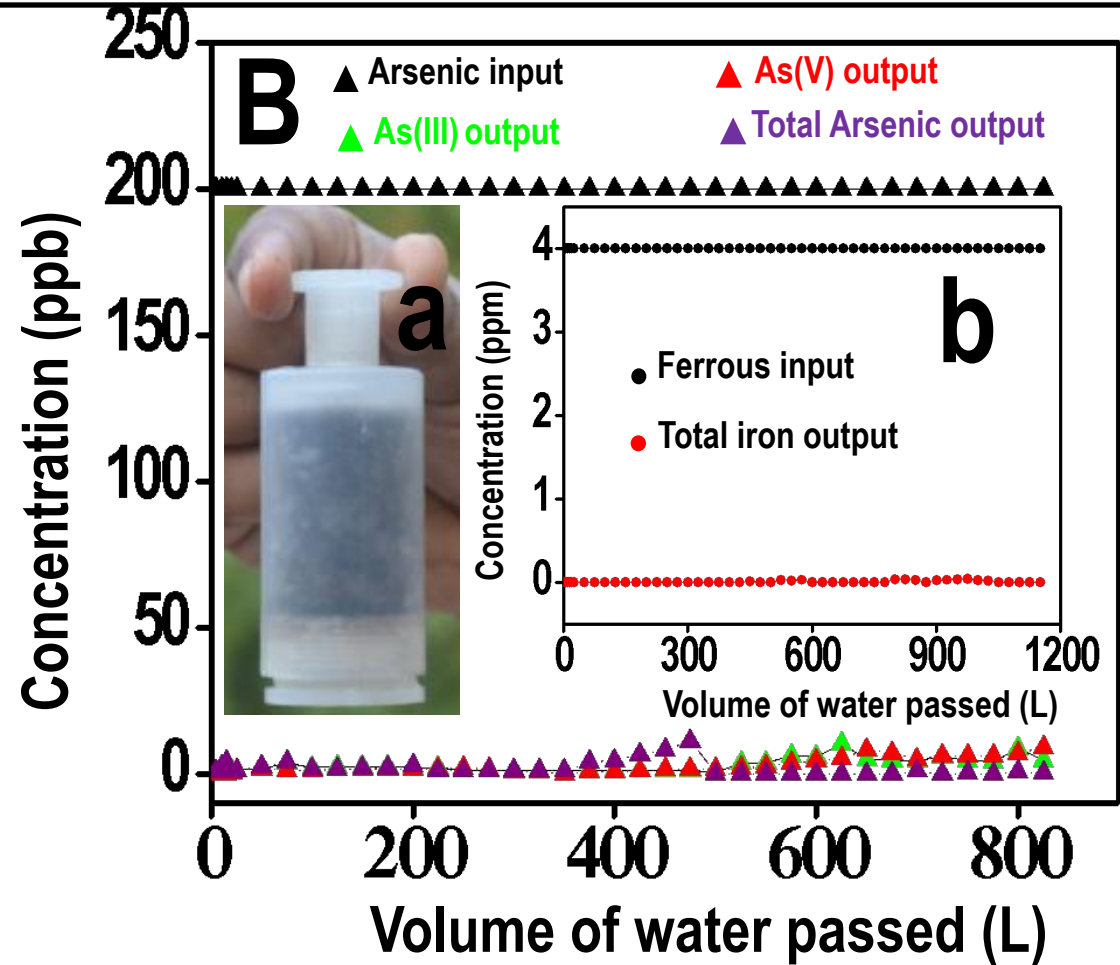
| Parameters               | Value                 |
|--------------------------|-----------------------|
| Total coliforms (CFU/mL) | 1-2 x 10 <sup>3</sup> |
| p H @25°C                | 7.8                   |
| Conductivity (µS/cm)     | 640.000               |
| Fluoride                 | 0.573                 |
| 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                |



**d**

**e**

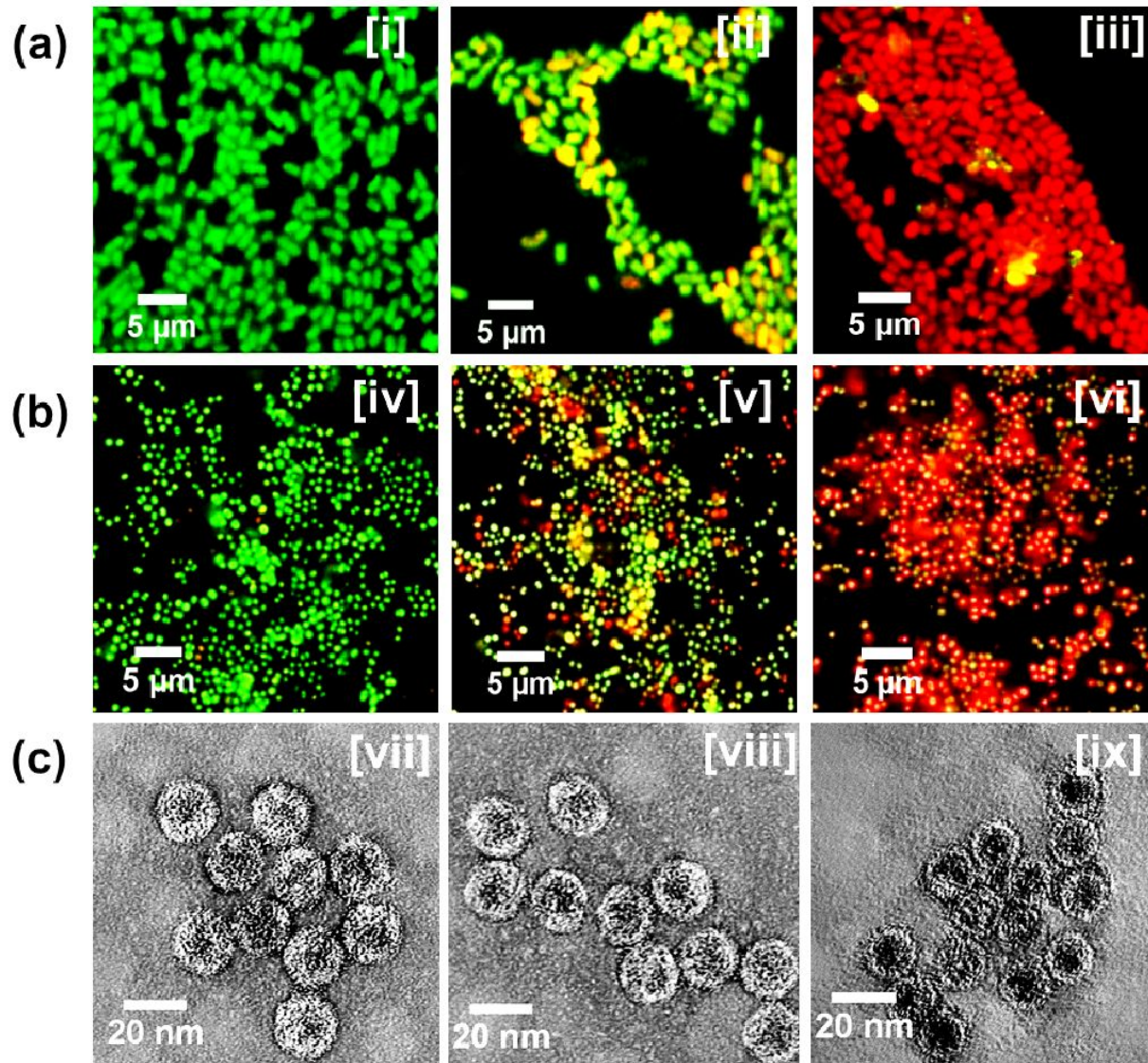
**f**



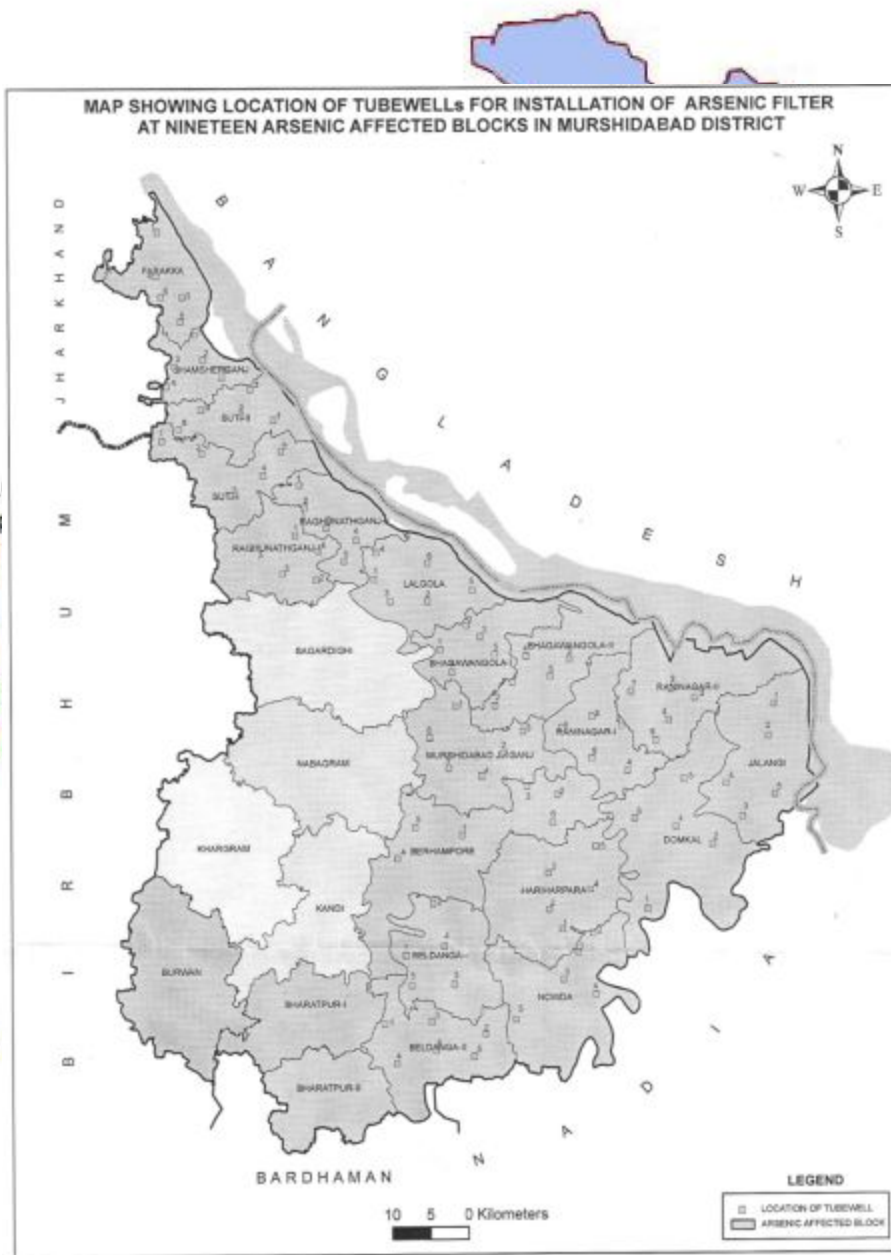
A simple set-up which has been used for arsenic testing study: arsenic containing water is turned into arsenic free clean drinking water using a simple cartridge having the arsenic adsorbent (A), and a cartridge having about 20 g of the adsorbent (a). Arsenic experiment which was conducted using a 60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



# Anion effect







## Population Map Of India-2001





# Imagining how new adsorbents are changing the dynamics at ground level



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



- Existing unit for iron and arsenic removal – 18 m<sup>3</sup>/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

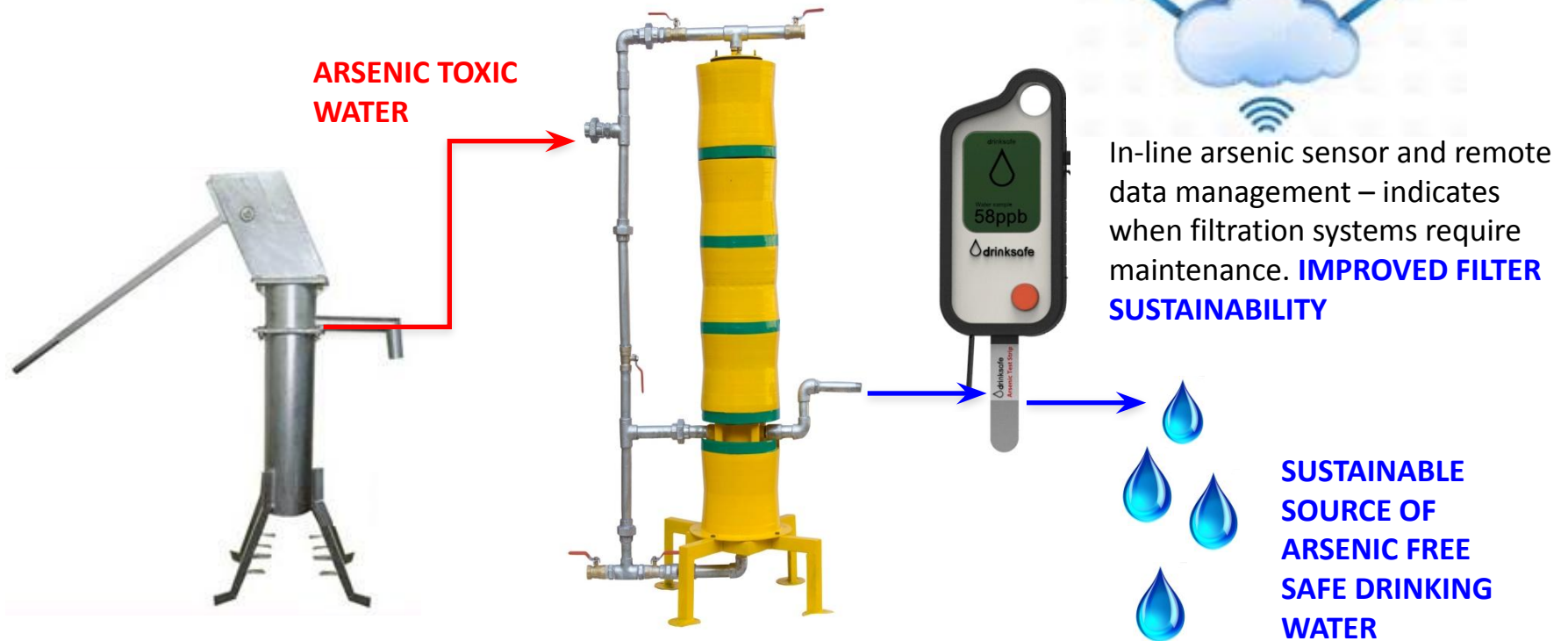


Nature Nanotechnology, July 2014 issue

# 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.   | 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.   | 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

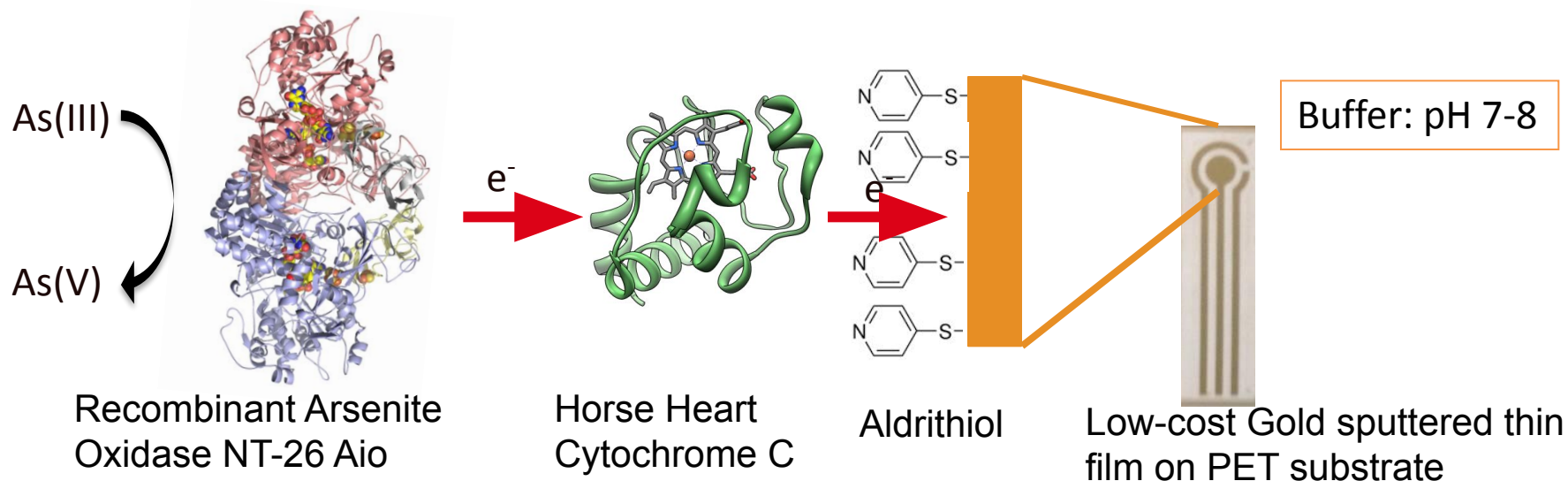


India Mark II hand water pump – most common water pump used globally

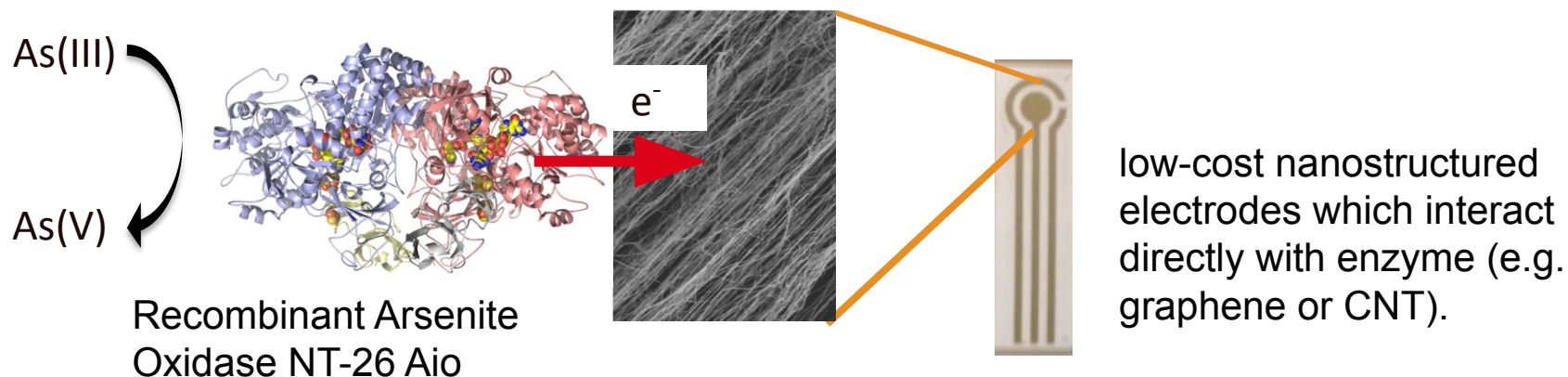
InnoNano Research's in-line arsenic removal filtration system

# Biosensor Design

## 1<sup>st</sup> Generation Design (Mediated Electrochemistry)



## 2<sup>nd</sup> Generation Design (Direct Electron Transfer)



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



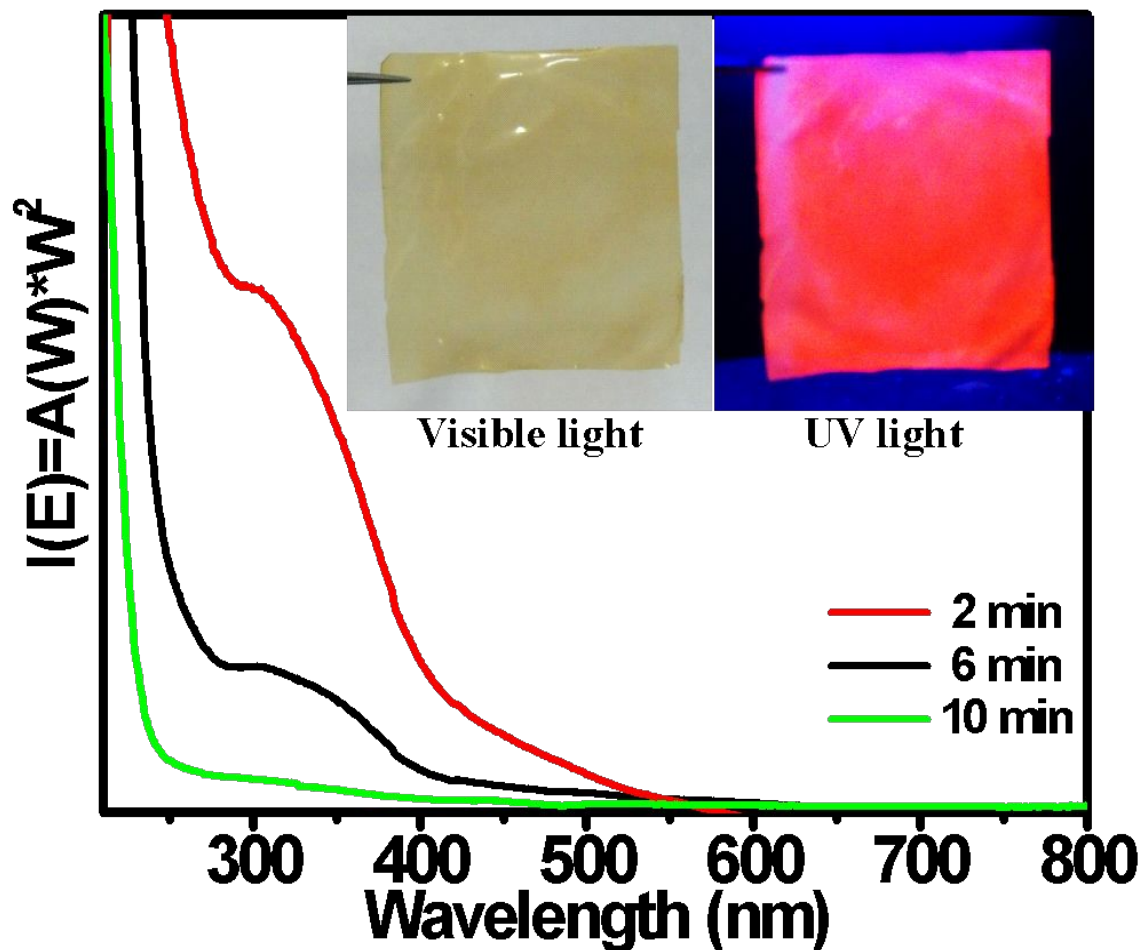
- ✓ Easy-to-use
- ✓ Quantitative
- ✓ Fast < 3 minutes
- ✓ Low cost
- ✓ Non-toxic

Automatic recording of test  
results with well GPS position

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

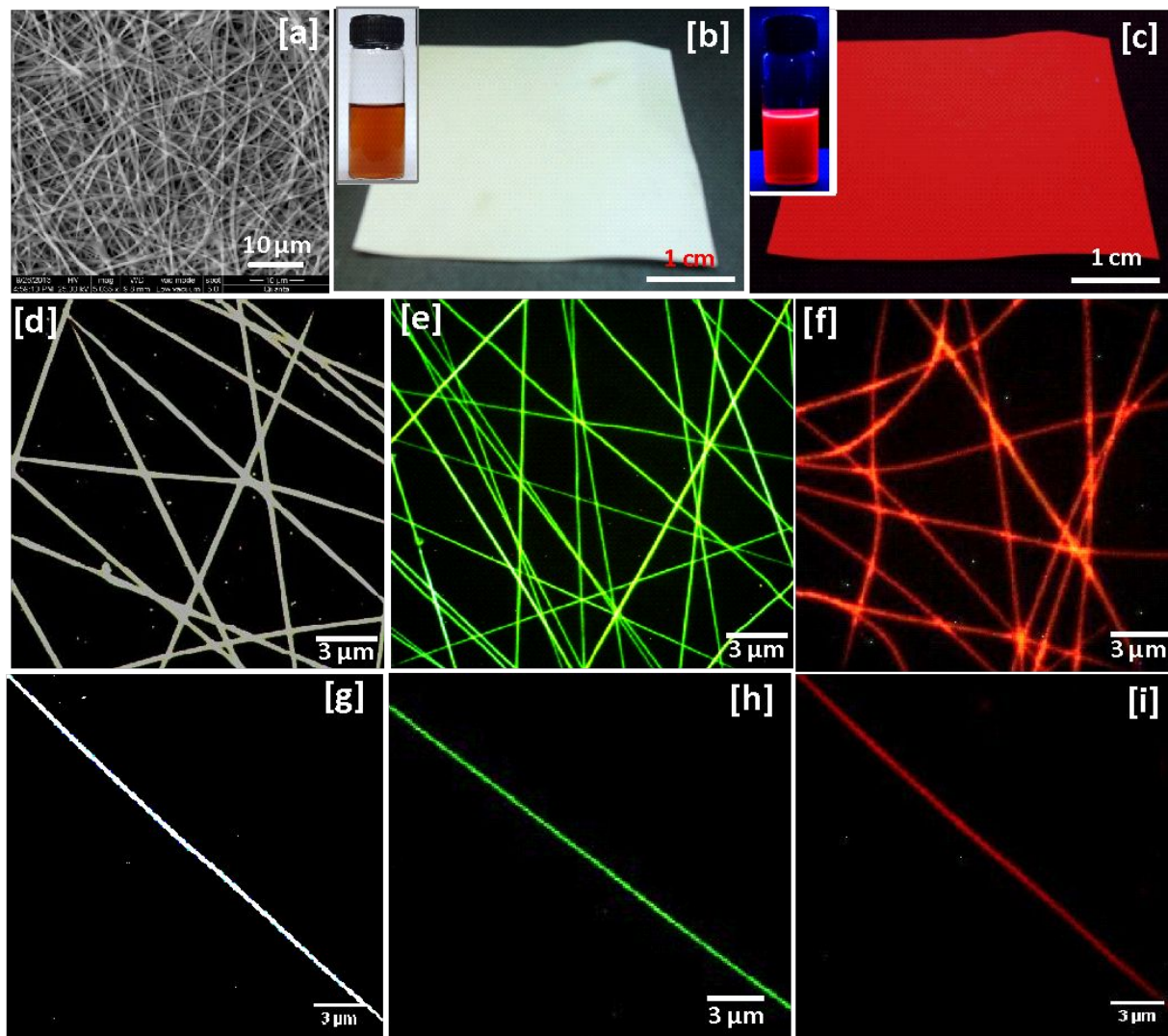


Quantum cluster based metal ion sensing paper  
Large area uniform illumination using quantum cluster



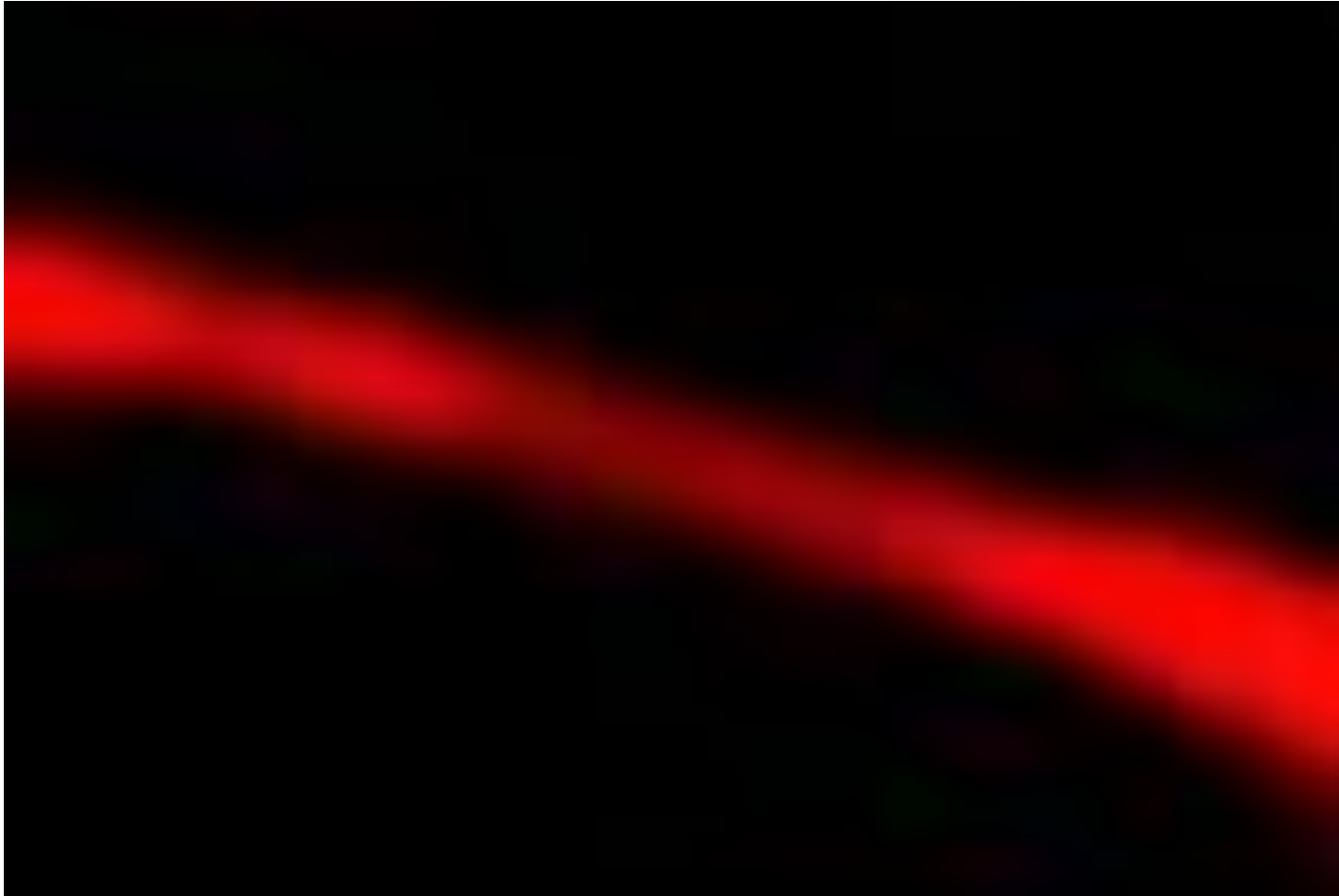
Decrease in the absorption of  $Au_{15}$  as a biofilm is dipped into the cluster solution. Inset: Free standing quantum cluster loaded film in visible light and UV light.

# Approaching detection limits of tens of $\text{Hg}^{2+}$

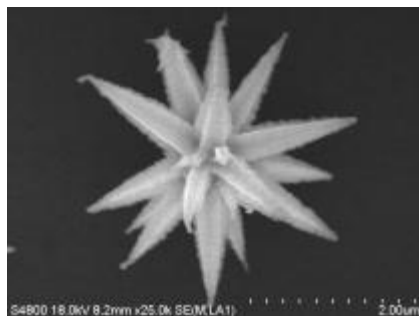
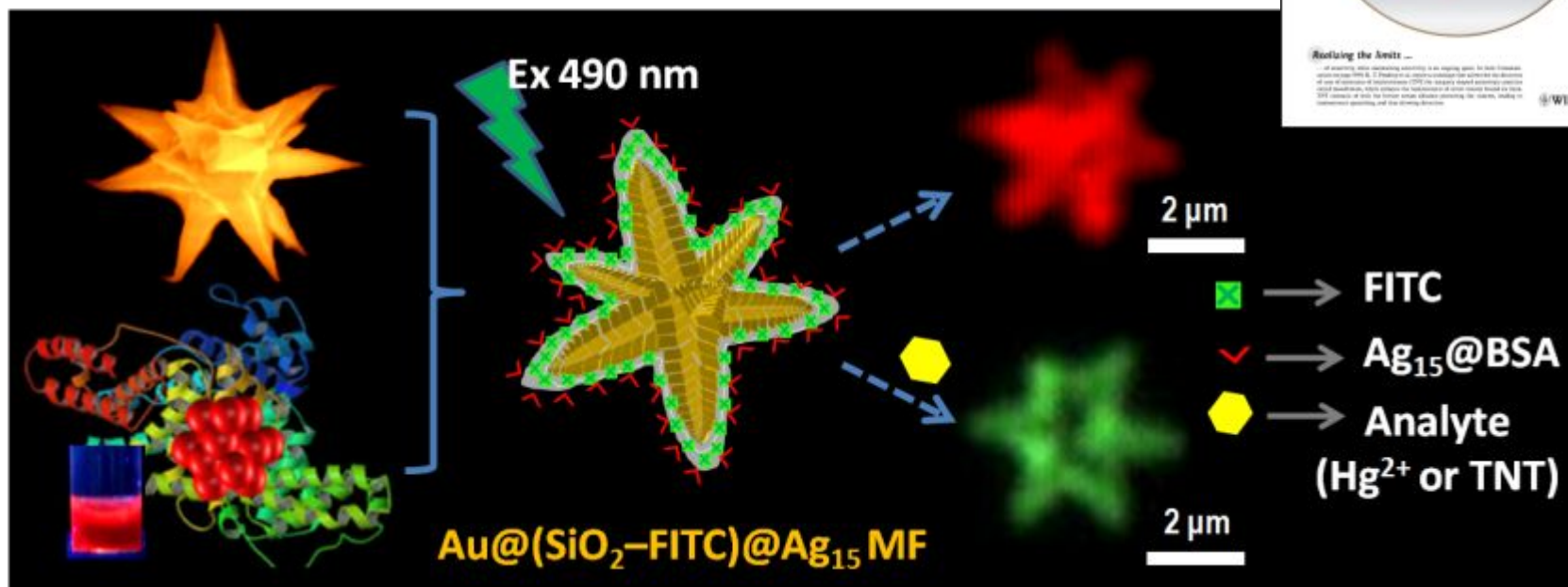
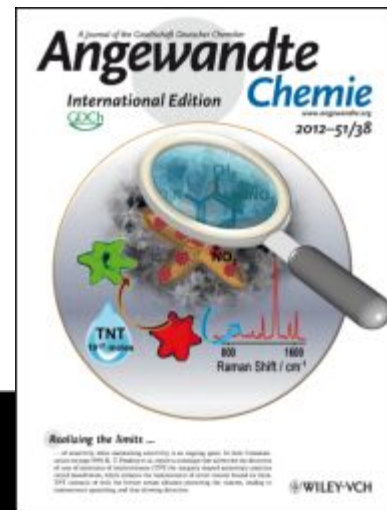


Atanu Ghosh et al. Anal. Chem. 2014.

## 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



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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

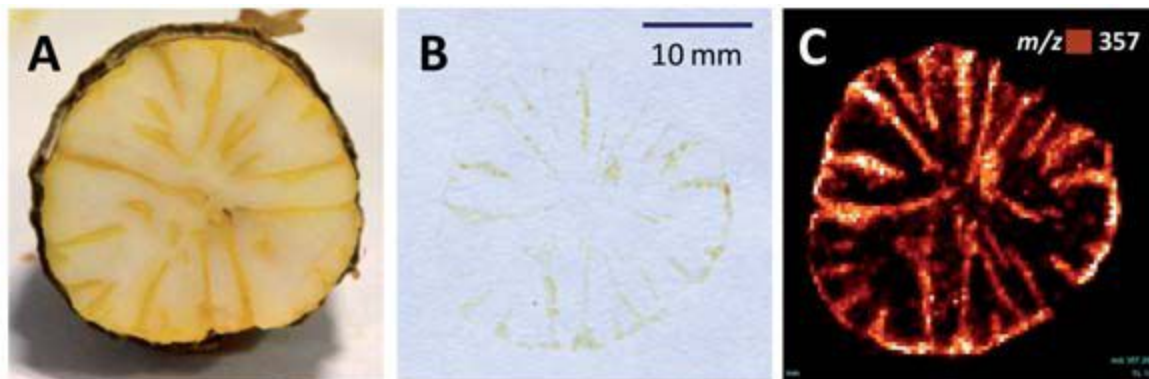


More from Scientific American

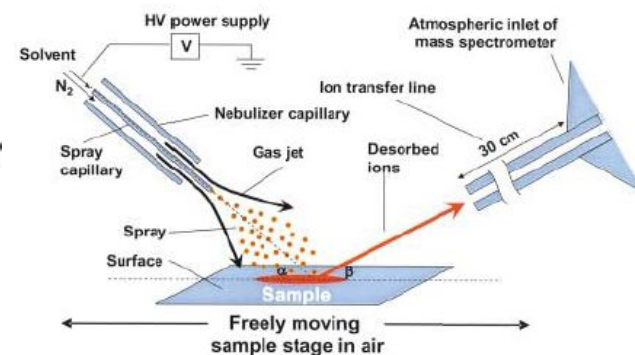
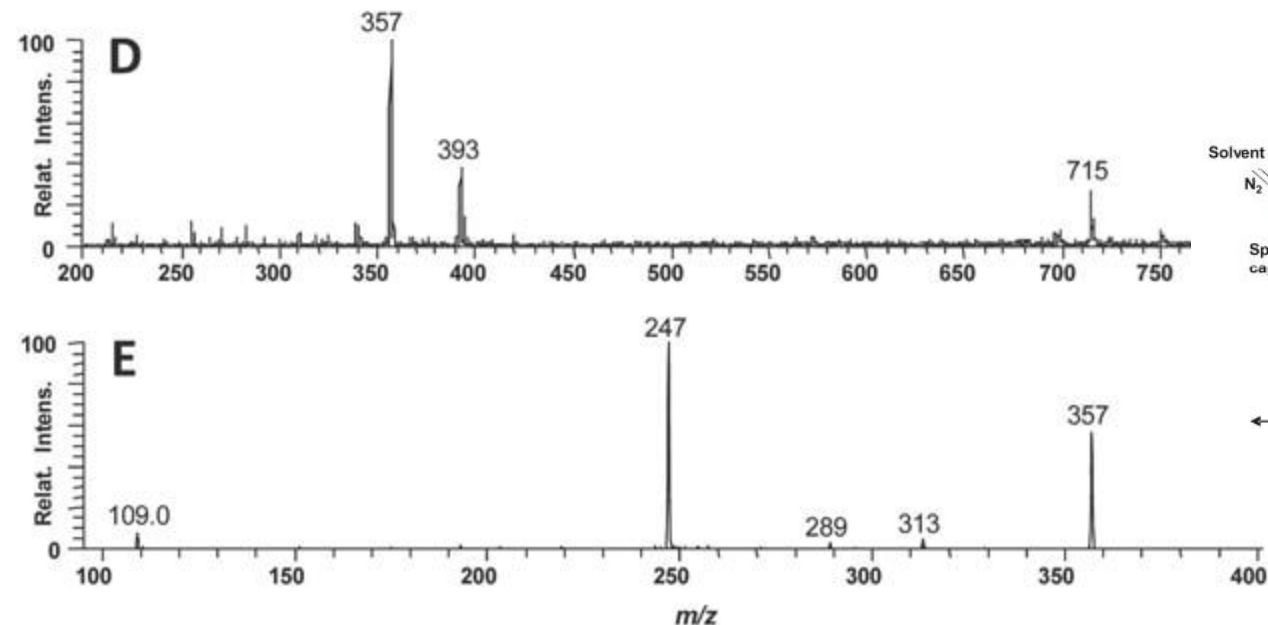
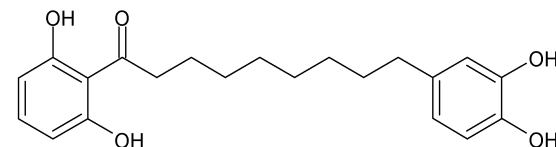




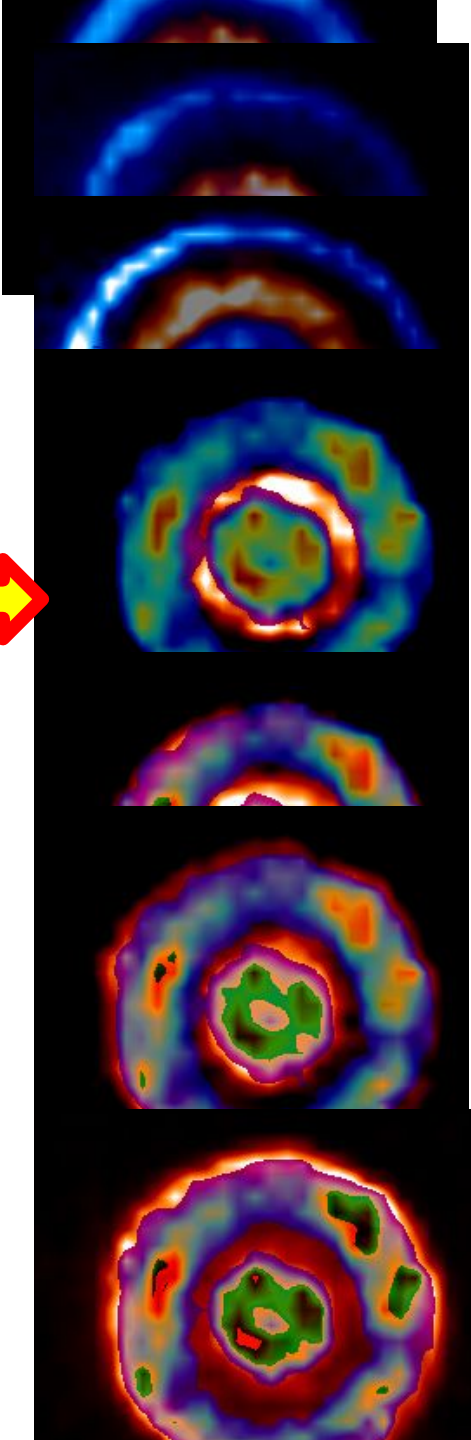
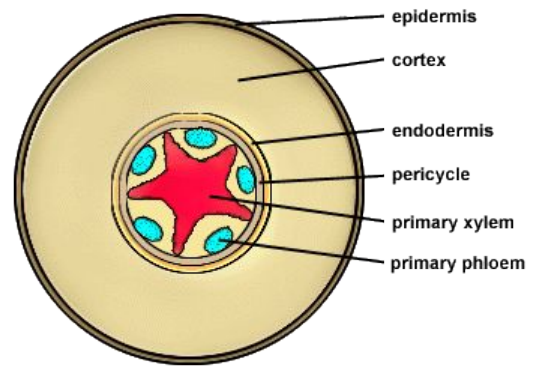
# Imaging of seed section using DESI



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

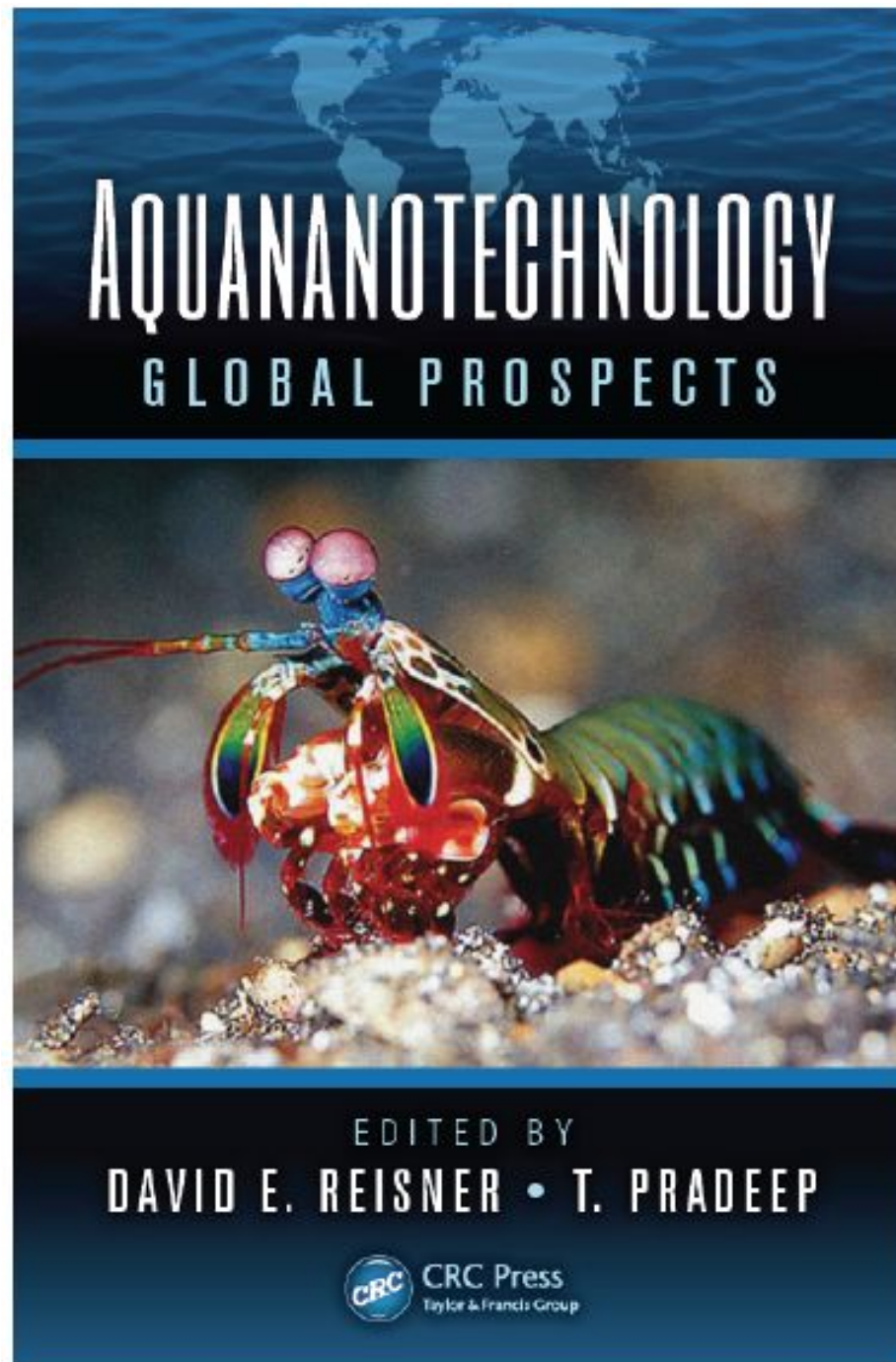


Ifa, D. R.; Srimany, A.; Eberlin, L. S.; Naik, H. R.; Bhat, V.; Cooks, R. G.; Pradeep, T. *Anal. Methods* **2011**, 3, 1910-1912.



-   $m/z$  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





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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**Thank you**