Since 1959

Treatment Methods for Arsenic

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International Centre for Clean Water

Associate Editor
ACS Sustainable Resource Management

JJM Assam Lecture, June 20, 2024, IITM

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Manual...

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MINISTRY OF HOUSING AND URBAN AFFAIRS

MANUAL ON WATER SUPPLY AND TREATMENT SYSTEMS (DRINK FROM TAP)

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MARCH 2024

RESEARCH ARTICLE

WATER RESOURCES

Global threat of arsenic in groundwater

Joel Podgorski[1,2*] and Michael Berg[1,3*]

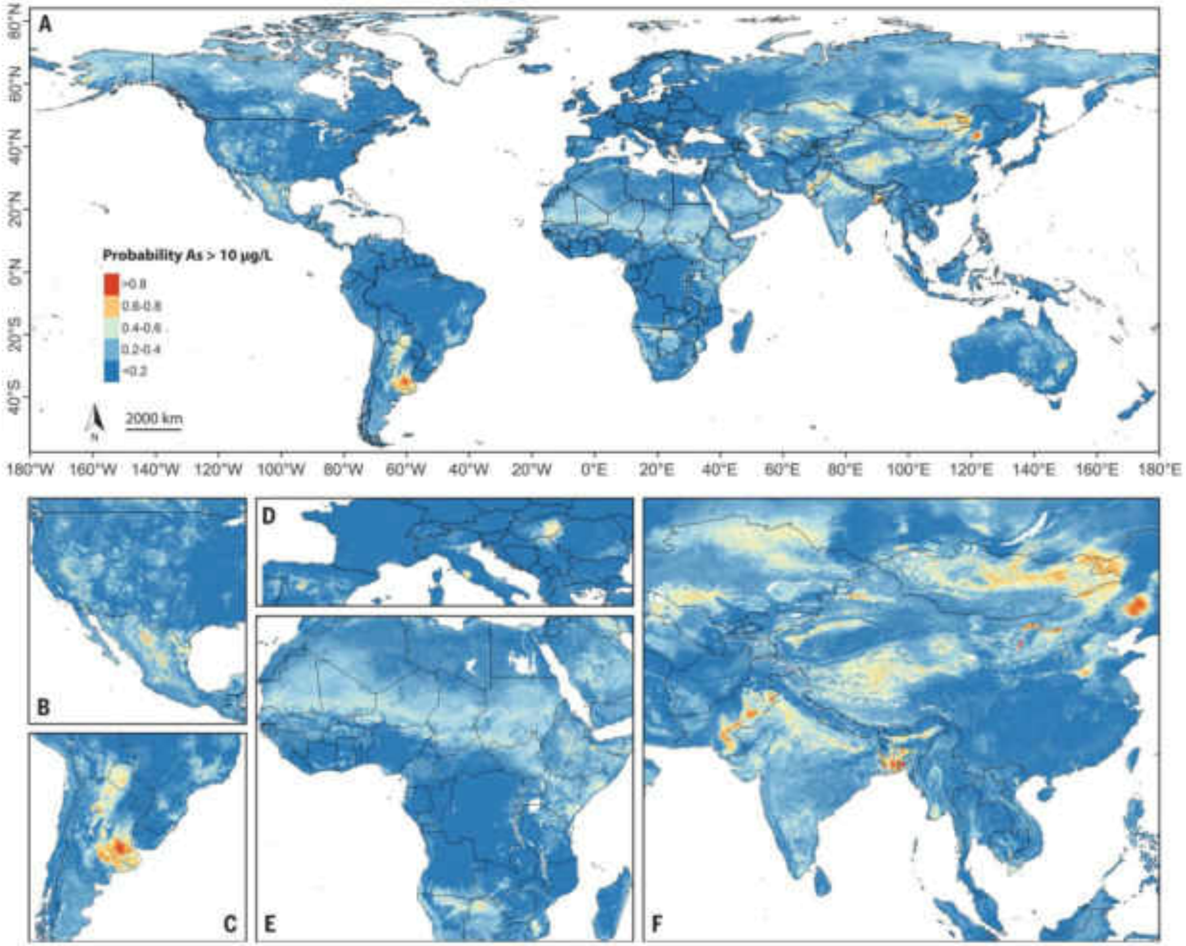


Fig. 2. Global prediction of groundwater arsenic. (A to F) Modeled probability of arsenic concentration in groundwater exceeding 10 mg/liter for the entire globe (A) along with zoomed-in sections of the main more densely populated affected areas (B) to (F). The model is based on the arsenic data points in Fig. 1 and the predictor variables in table S2. Figs. S2 to S8 provide more detailed views of the prediction map.

Podgorski et al., Science 368, 845–850 (2020) 22 May 2020

Analysis based on machine learning models

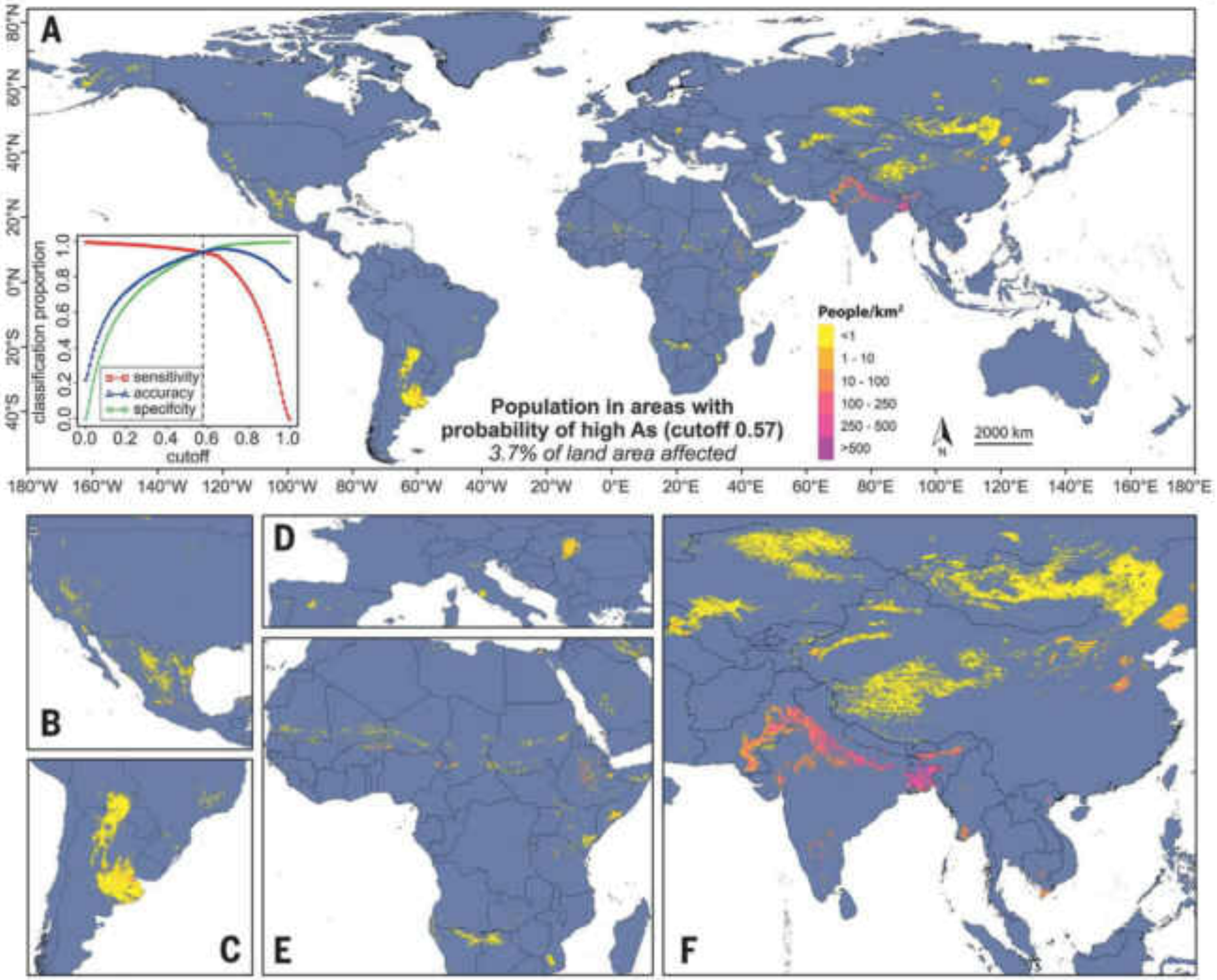


Fig. 4. Estimated population at risk. (A to L) Population in risk areas potentially containing aquifers with arsenic concentrations >10 mg/ liter using probability cutoffs of 0.57 (A), at which sensitivity and specificity are equal [inset in (A)] as applied to the full (training and test) dataset, and 0.72 (G), at which PPV and NPV are equal [inset in (G)] using the full dataset. The detailed areas of Fig. 2 are also repeated here for both models (B) to (F) and (H) to (L).

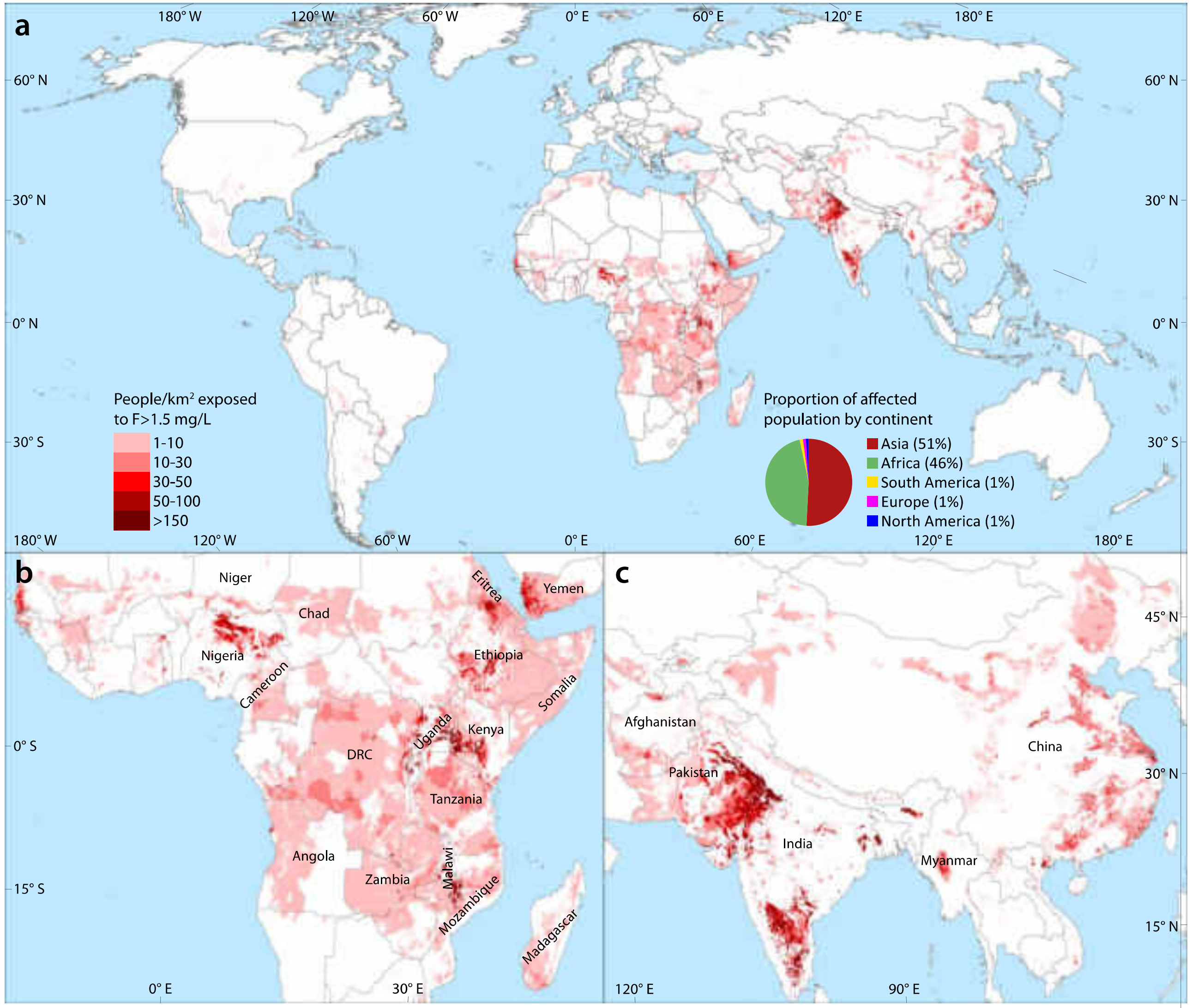


Fig. 4 Estimated population potentially exposed to fluoride concentrations in drinking water greater than 1.5 mg/L. a Global map and break-down by continent. Detailed views of **b** sub-Saharan Africa and southern Arabian peninsula and **c** south and east Asia with the most strongly affected countries indicated. The population was calculated with the hybrid approach (see text) for areas with a greater than 25% probability of incurring high fluoride in groundwater (Fig. 1) by multiplying the total population by the hazard percentage and the proportion of domestic water usage coming from untreated groundwater[51].

ARTICLE
https://doi.org/10.1038/s41467-022-31940-x OPEN

Global analysis and prediction of fluoride in groundwater

Joel Podgorski [1✉] & Michael Berg [1✉]

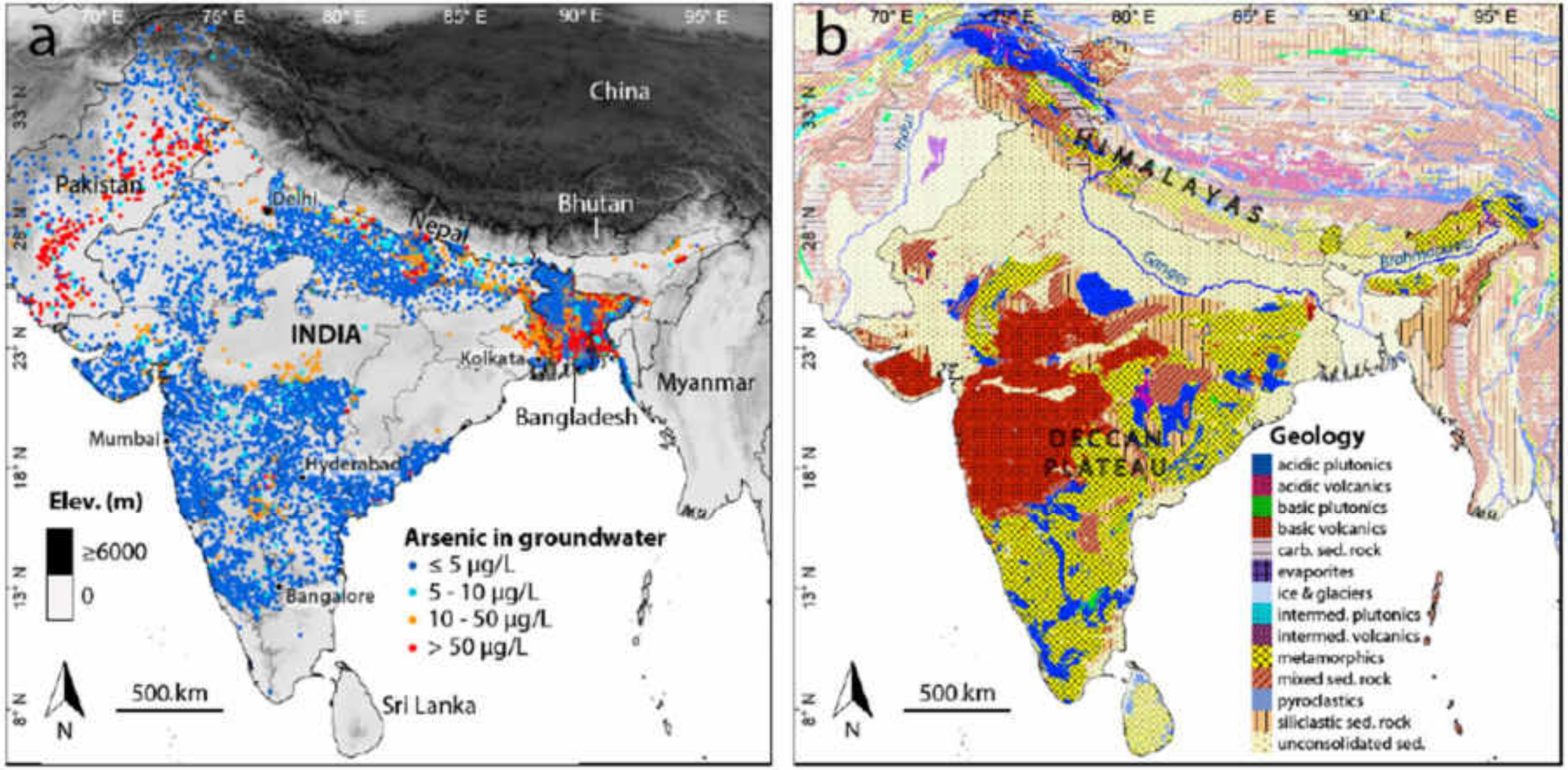


Figure 1. Arsenic concentration in Indian groundwater (**a**) topographical representation of averaged arsenic data points in Indian groundwater (**b**) Indian lithology [25].

Review

Arsenic Contamination in Indian Groundwater: From Origin to Mitigation Approaches for a Sustainable Future

Water **2023**, *15*, 4125. https://doi.org/10.3390/w15234125

Deepali Marghade [1,*], Girish Mehta [2], Sagar Shelare [2], Ganesh Jadhav [3] and Keval Chandrakant Nikam [3]

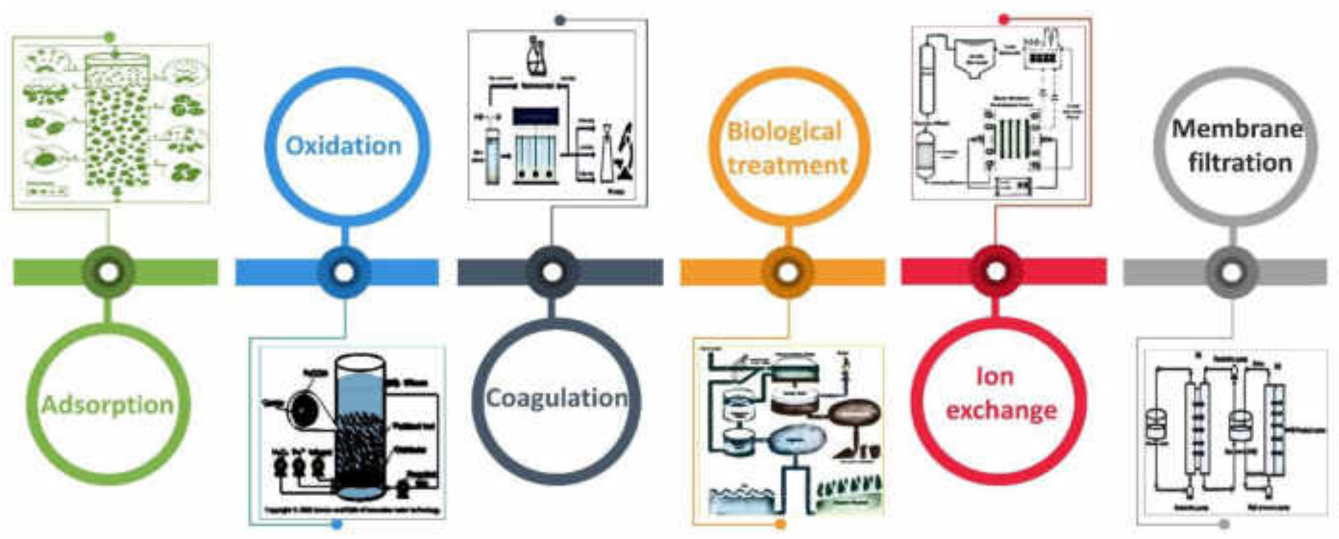
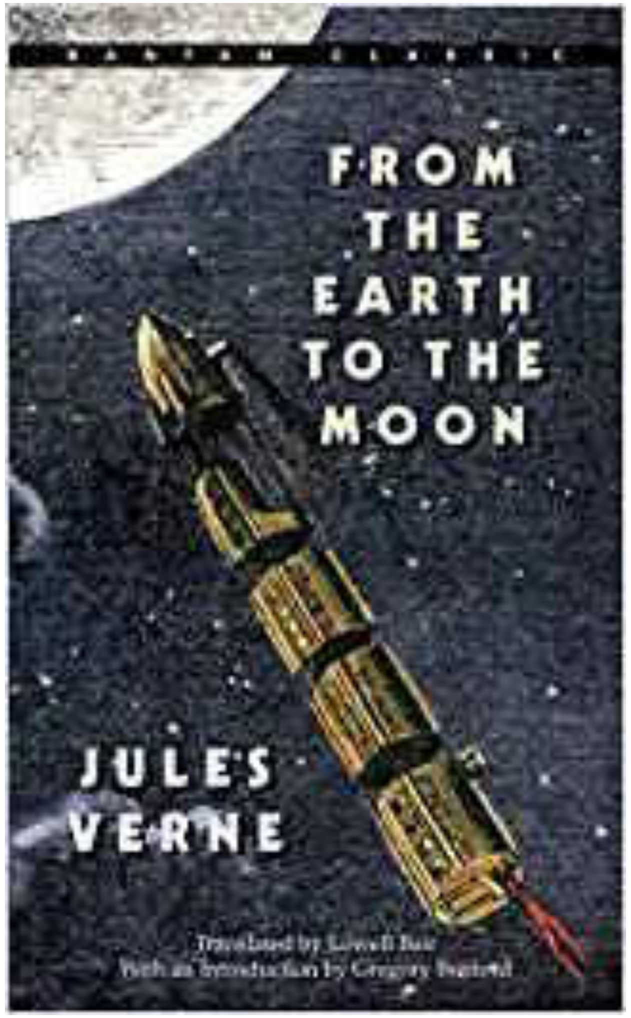
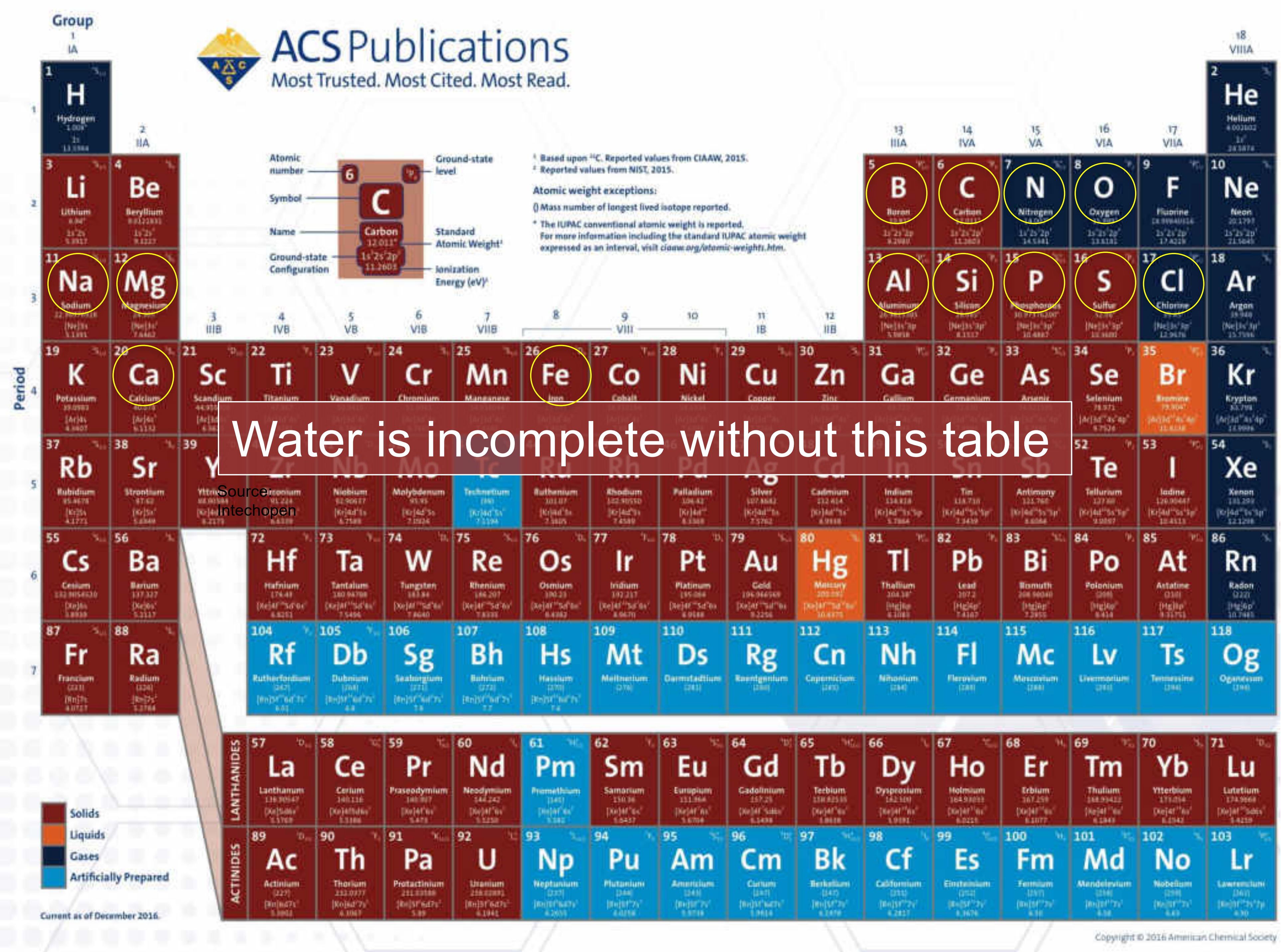


Figure 5. Various Mitigation Methods for Arsenic Contamination.

Our dreams become reality with materials



Water is incomplete without this table



Source Intechopen

AB(s) = A+(aq) + B-(aq)

Ksp = [A+][B-]

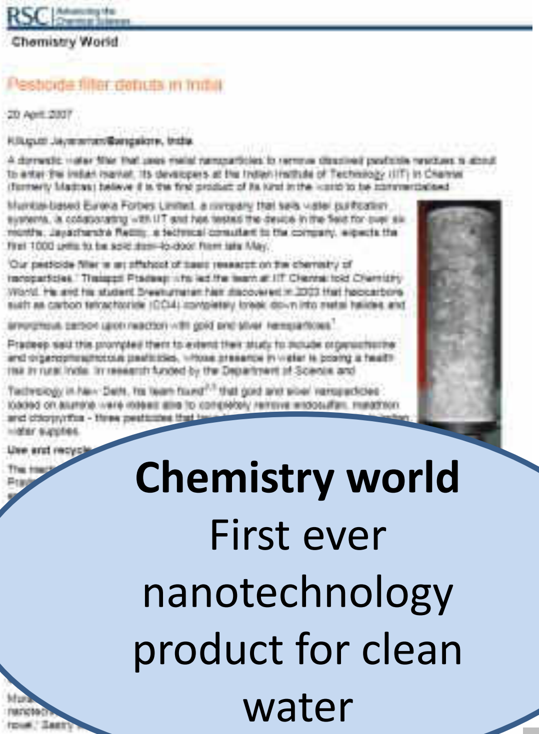
Table 5-7

Solubility-Product Constants, K_{sp}, at 25 °C

Fluorides	
BaF_2	2.4×10^{-5}
MgF_2	8×10^{-8}
PbF_2	4×10^{-8}
SrF_2	7.9×10^{-10}
CaF_2	3.9×10^{-11}
Chlorides	
$PbCl_2$	1.6×10^{-5}
$AgCl$	1.7×10^{-10}
Hg_2Cl_2[a]	1.1×10^{-18}
Bromides	
$PbBr_2$	4.6×10^{-6}
$AgBr$	5.0×10^{-13}
Hg_2Br_2[a]	1.3×10^{-22}
Iodides	
PbI_2	8.3×10^{-9}
AgI	8.5×10^{-17}
Hg_2I_2[a]	4.5×10^{-29}
Sulfates	
$CaSO_4$	2.4×10^{-5}
Ag_2SO_4	1.2×10^{-5}
$SrSO_4$	7.6×10^{-7}
$PbSO_4$	1.3×10^{-8}
$BaSO_4$	1.5×10^{-9}
Chromates	
$SrCrO_4$	3.6×10^{-5}
Hg_2CrO_4[a]	2×10^{-9}
$BaCrO_4$	8.5×10^{-11}
Chromates (*cont.*)	
Ag_2CrO_4	1.9×10^{-12}
$PbCrO_4$	2×10^{-16}
Carbonates	
$NiCO_3$	1.4×10^{-7}
$CaCO_3$	4.7×10^{-9}
$BaCO_3$	1.6×10^{-9}
$SrCO_3$	7×10^{-10}
$CuCO_3$	2.5×10^{-10}
$ZnCO_3$	2×10^{-10}
$MnCO_3$	8.8×10^{-11}
$FeCO_3$	2.1×10^{-11}
Ag_2CO_3	8.2×10^{-12}
$CdCO_3$	5.2×10^{-12}
$PbCO_3$	1.5×10^{-15}
$MgCO_3$	1×10^{-15}
Hg_2CO_3[a]	9.0×10^{-15}
Hydroxides	
$Ba(OH)_2$	5.0×10^{-3}
$Sr(OH)_2$	3.2×10^{-4}
$Ca(OH)_2$	1.3×10^{-6}
$AgOH$	2.0×10^{-8}
$Mg(OH)_2$	8.9×10^{-12}
$Mn(OH)_2$	2×10^{-13}
$Cd(OH)_2$	2.0×10^{-14}
$Pb(OH)_2$	4.2×10^{-15}
$Fe(OH)_2$	1.8×10^{-15}
$Co(OH)_2$	2.5×10^{-16}
Hydroxides (*cont.*)	
$Ni(OH)_2$	1.6×10^{-16}
$Zn(OH)_2$	4.5×10^{-17}
$Cu(OH)_2$	1.6×10^{-19}
$Hg(OH)_2$	3×10^{-26}
$Sn(OH)_2$	3×10^{-27}
$Cr(OH)_3$	6.7×10^{-31}
$Al(OH)_3$	5×10^{-33}
$Fe(OH)_3$	6×10^{-38}
$Co(OH)_3$	2.5×10^{-43}
Sulfides	
MnS	7×10^{-16}
FeS	4×10^{-19}
NiS	3×10^{-21}
CoS	5×10^{-22}
ZnS	2.5×10^{-22}
SnS	1×10^{-26}
CdS	1.0×10^{-28}
PbS	7×10^{-29}
CuS	8×10^{-37}
Ag_2S	5.5×10^{-51}
HgS	1.6×10^{-54}
Bi_2S_3	1.6×10^{-72}
Phosphates	
Ag_3PO_4	1.8×10^{-18}
$Sr_3(PO_4)_2$	1×10^{-31}
$Ca_3(PO_4)_2$	1.3×10^{-32}
$Ba_3(PO_4)_2$	6×10^{-39}
$Pb_3(PO_4)_2$	1×10^{-54}

[a] As Hg_2^{2+} ion. $K_{sp} = [Hg_2^{2+}][X^-]^2$

World's first nanochemistry-based water purifier



RSC

Chemistry World

Pesticide filter debuts in India

20 April 2007

Killugudi Jayaraman/Bangalore, India

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

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

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

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

Use and recycle

Chemistry world
First ever nanotechnology product for clean water

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

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

Product is marketed now by a Eureka Forbes Ltd.

Several new technologies are now available

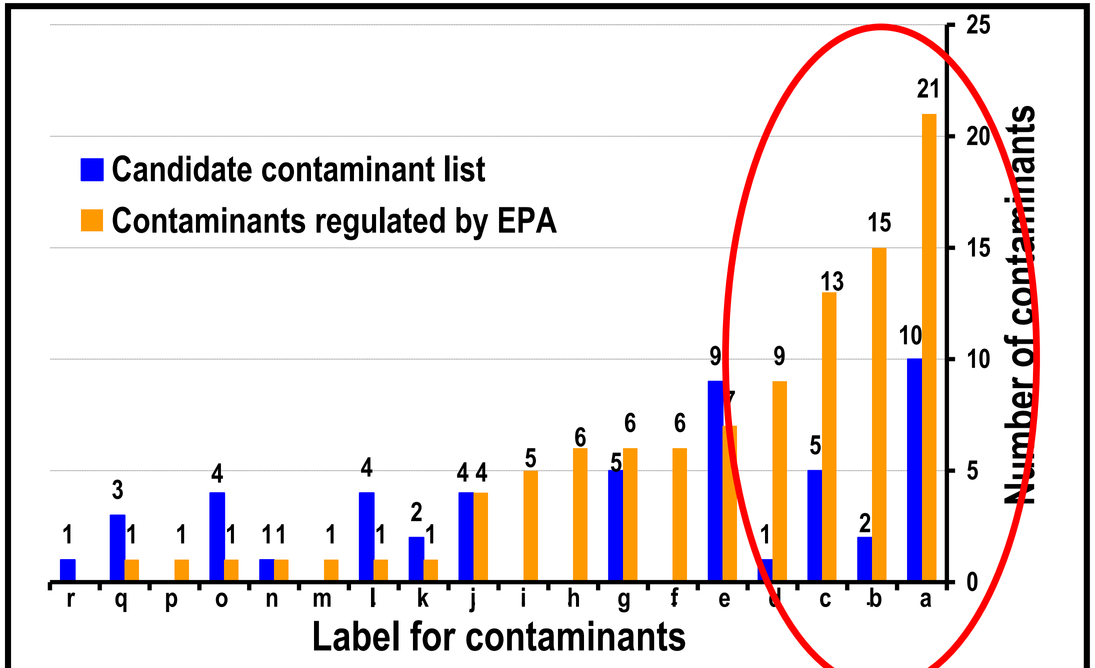
Water purification, history

Important milestones in the history of water purification (1800–2007) from the perspective of noble metal nanoparticles in water treatment (compiled from multiple sources on the World Wide Web).

Year	Milestone
1804	Setup of world's first city-wide municipal water treatment plant (Scotland, sand-filter technology)
1810	Discovery of chlorine as a disinfectant (H. Davy)
1852	Formulation of Metropolis Water Act (England)
1879	Formulation of Germ Theory (L. Pasteur)
1902	Use of chlorine as a disinfectant in drinking water supply (calcium hypochlorite, Belgium)
1906	Use of ozone as a disinfectant (France)
1908	Use of chlorine as a disinfectant in municipal supply, New Jersey
1914	Federal regulation of drinking water quality (USPHS)
1916	Use of UV treatment in municipal supplies
1935	Discovery of synthetic ion exchange resin (B. A. Adams, E. L. Holmes)
1948	Nobel Prize to Paul Hermann Muller (insecticidal properties of DDT)
1959	Discovery of synthetic reverse osmosis membrane (S. Yuster, S. Loeb, S. Sourirajan)
1962	*Silent Spring* published, first report on harmful effects of DDT (R. Carson)
1965	World's first commercial RO plant launched
1974	Reports on carcinogenic by-products of disinfection with chlorine Formulation of Safe Drinking Water Act (USEPA)
1975	Development of carbon block for drinking water purification
1994	Report on use of zerovalent iron for degradation of halogenated organics (R. W. Gillham, S. F. O'Hannesin)
1997	Report on use of zerovalent iron nanoparticles for degradation of halogenated organics (C-B. Wang, W.-X. Zhang)
1998	Drinking Water Directive applied in EU
2000	Adoption of Millennium Declaration during the UN Millennium Summit (UN Millennium Development Goals)
2003	Report on use of noble metal nanoparticles for the degradation of pesticides (A.S. Nair, R. T. Tom, T. Pradeep)
2004	Stockholm Convention, banning the use of persistent organic pollutants
2007	Launch of noble metal nanoparticle-based domestic water purifier (T. Pradeep, A. S. Nair, Eureka Forbes Limited)

T. Pradeep and Anshup, *Thin Solid Films*, 2009

Future of water purification: An enigma with some pointers

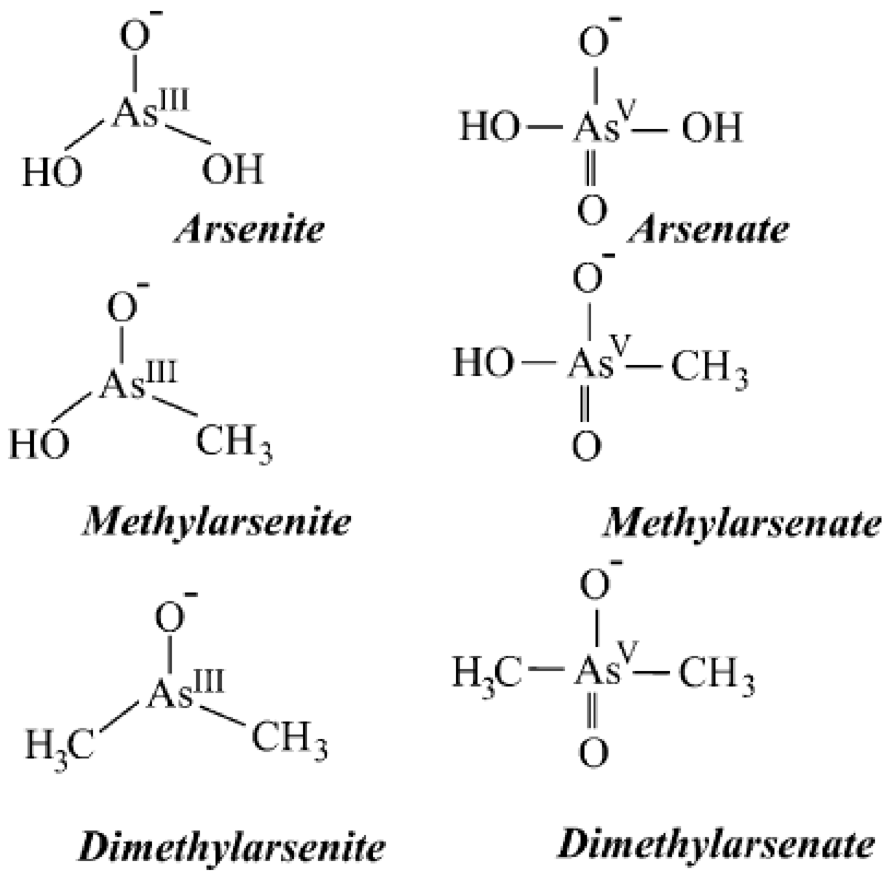


(a): Halogenated organic (b): Metal (c): Organochlorine pesticide (d): Inorganic salt (e): Biological contaminant (f): Nuclear (g): Benzo derivative (h): Carbamate pesticide (i): Pesticides (others) (j): Unclassified (k): Triazine derivative pesticide (l): Organophosphorus pesticide (m): Organobromine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

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

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).

Arsenic species of relevance



Scheme 1. Arsenic species found in water.

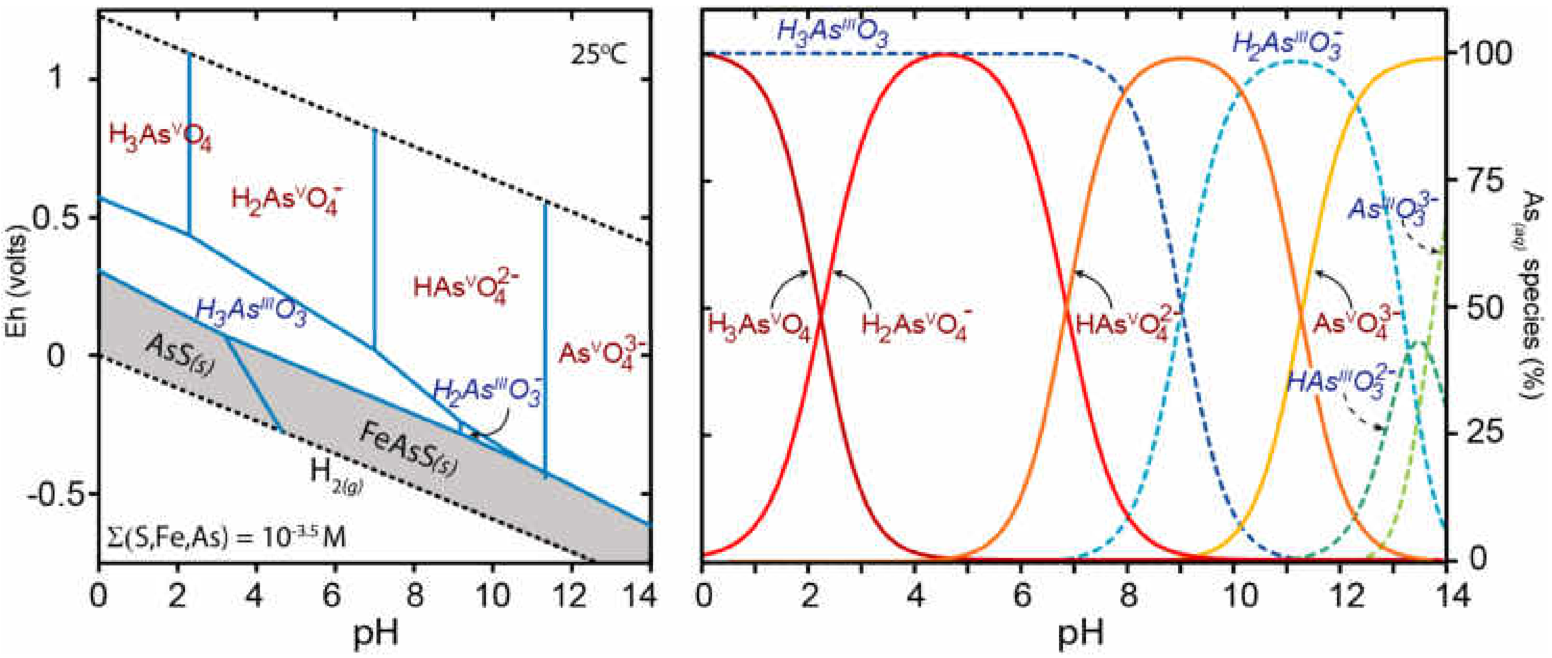


Figure 1. Eh-pH activity diagram of arsenic species at 25 °C, 1 bar, (S, Fe, As) = 10^{-3} M (**left**). Dashed lines bound the stability field of water, arsenate (As^{V}) species are shown in red, arsenite (As^{III}) species are shown in blue italics, solid phases are shown with a darkened background. The distribution of pH-dependent dissolved arsenic species are shown (**right**) with arsenate as red solid lines and red text and arsenite in dashed blue lines with blue italic text. Dissolved arsenic species become protonated at low pH and the charge on the oxyanion decreases. Under environmental conditions (pH ≈ 5–9), arsenate generally exists as $H_2AsO_4{}^{-}$ and $HAsO_4{}^{2-}$, while arsenite is the uncharged molecule $H_3AsO_3{}^{0}$. Under highly reducing conditions and in the presence of high sulfur activity, solid-phase arsenic sulfides (e.g., AsS) are stable.

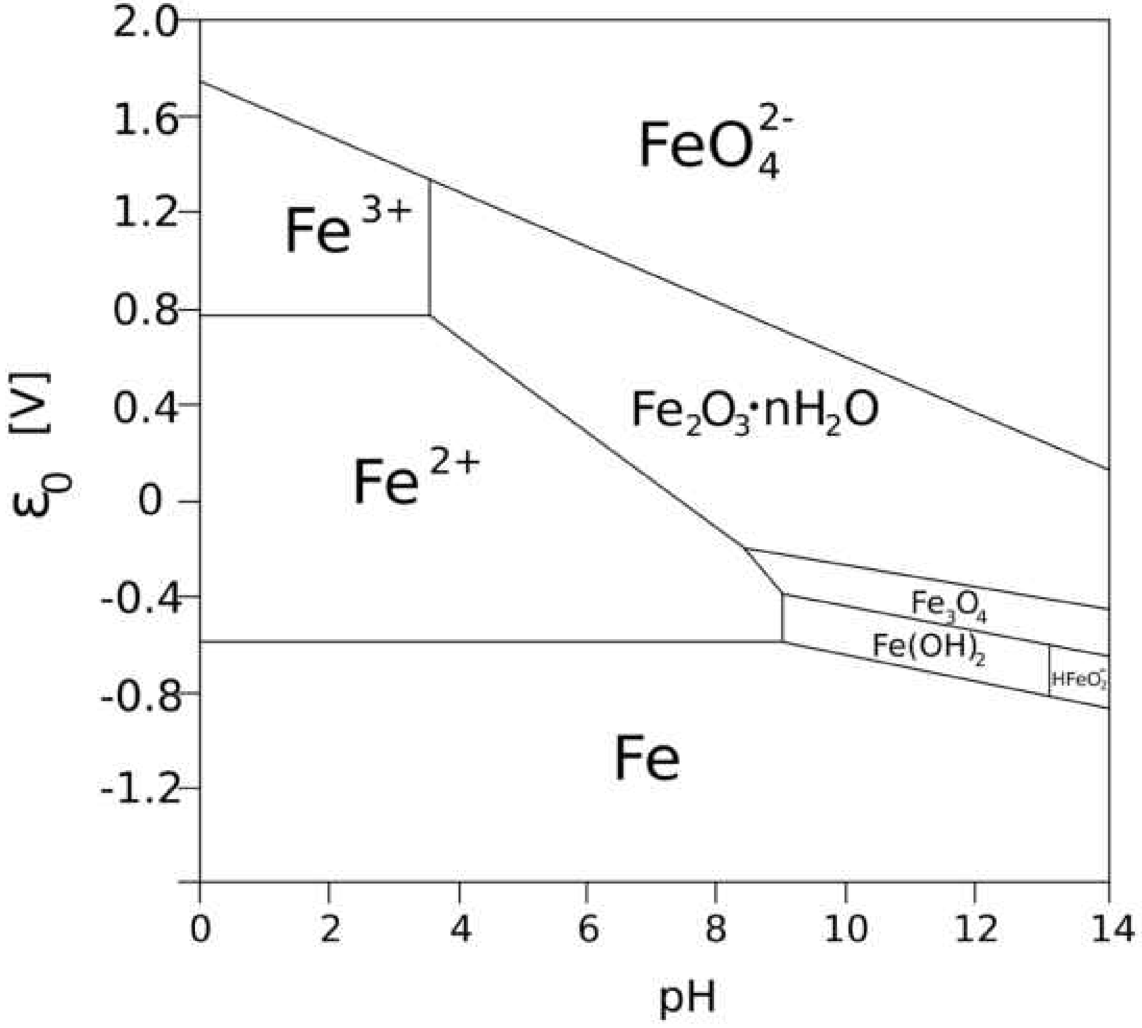
water MDPI

Review

Arsenic in Drinking Water and Diabetes

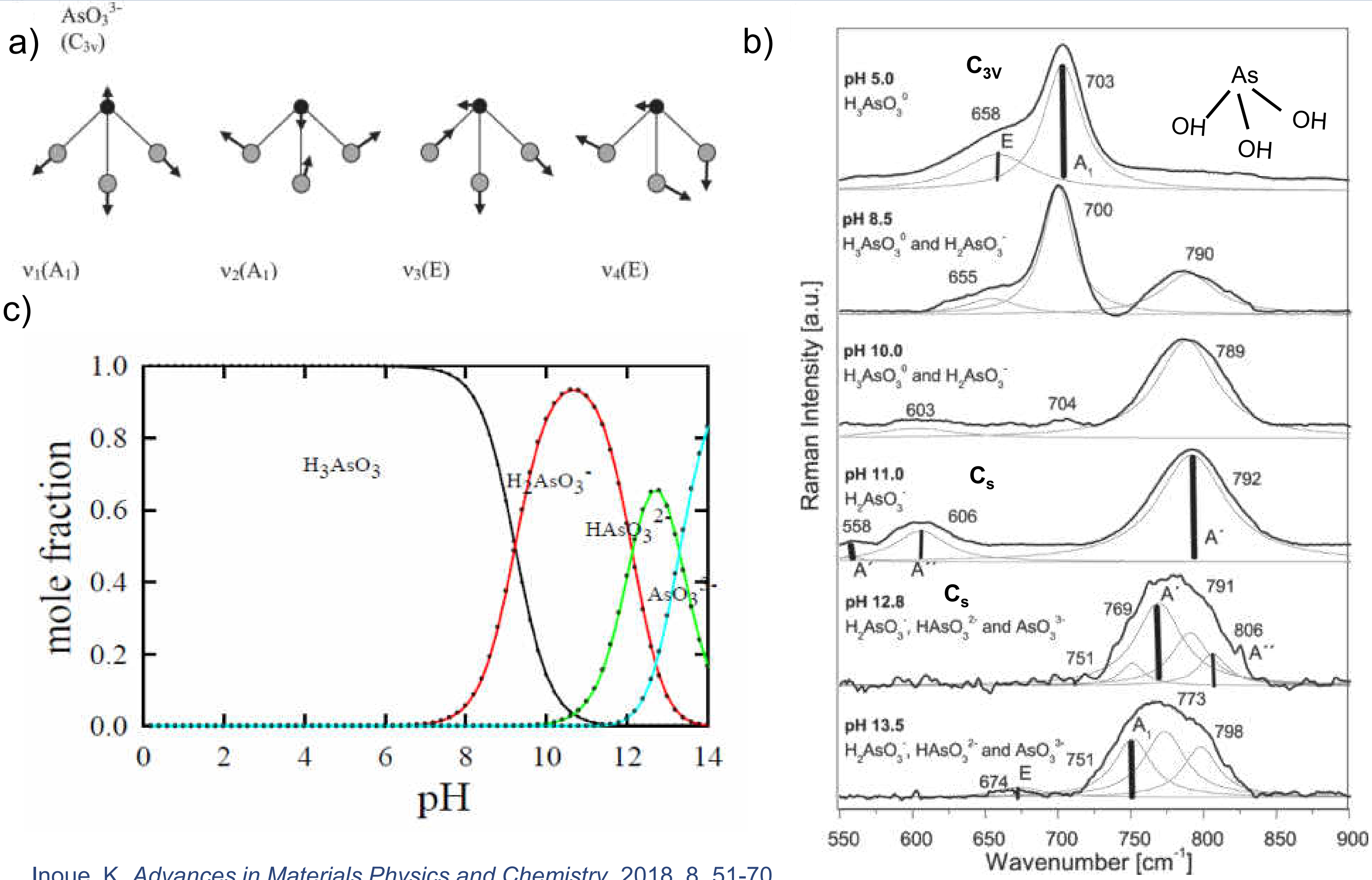
Aryatara Shakya [1], Matthew Dodson [1], Janick F. Artiola [2], Monica Ramirez-Andreotta [2], Robert A. Root [2], Xinxin Ding [1], Jon Chorover [2] and Raina M. Maier [2,*]

1 Department Pharmacology & Toxicology, University of Arizona, Tucson, AZ 85721, USA; aryatarashakya@arizona.edu (A.S.); dodson@pharmacy.arizona.edu (M.D.); xding@pharmacy.arizona.edu (X.D.)
2 Department Environmental Science, University of Arizona, Tucson, AZ 85721, USA; artiola@gmail.com (J.F.A.); mdramire@arizona.edu (M.R.-A.); robroot.az@gmail.com (R.A.R.); chorover@arizona.edu (J.C.)
* Correspondence: rmaier@ag.arizona.edu



Pourbaix diagram of iron.

Distribution of arsenite species

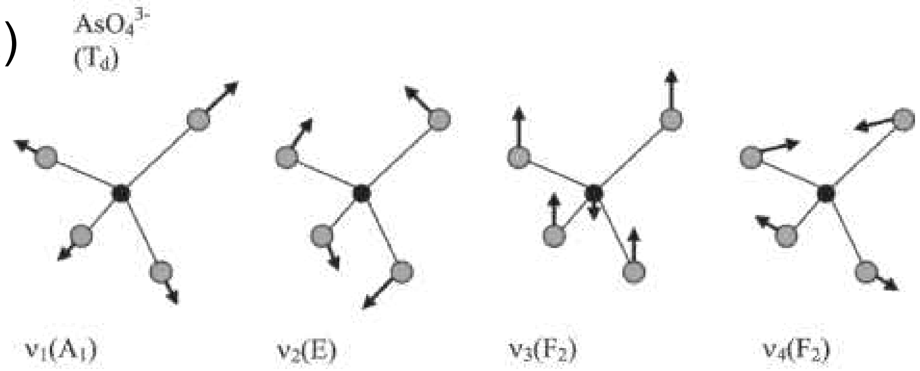


Inoue, K. *Advances in Materials Physics and Chemistry*, 2018, 8, 51-70.

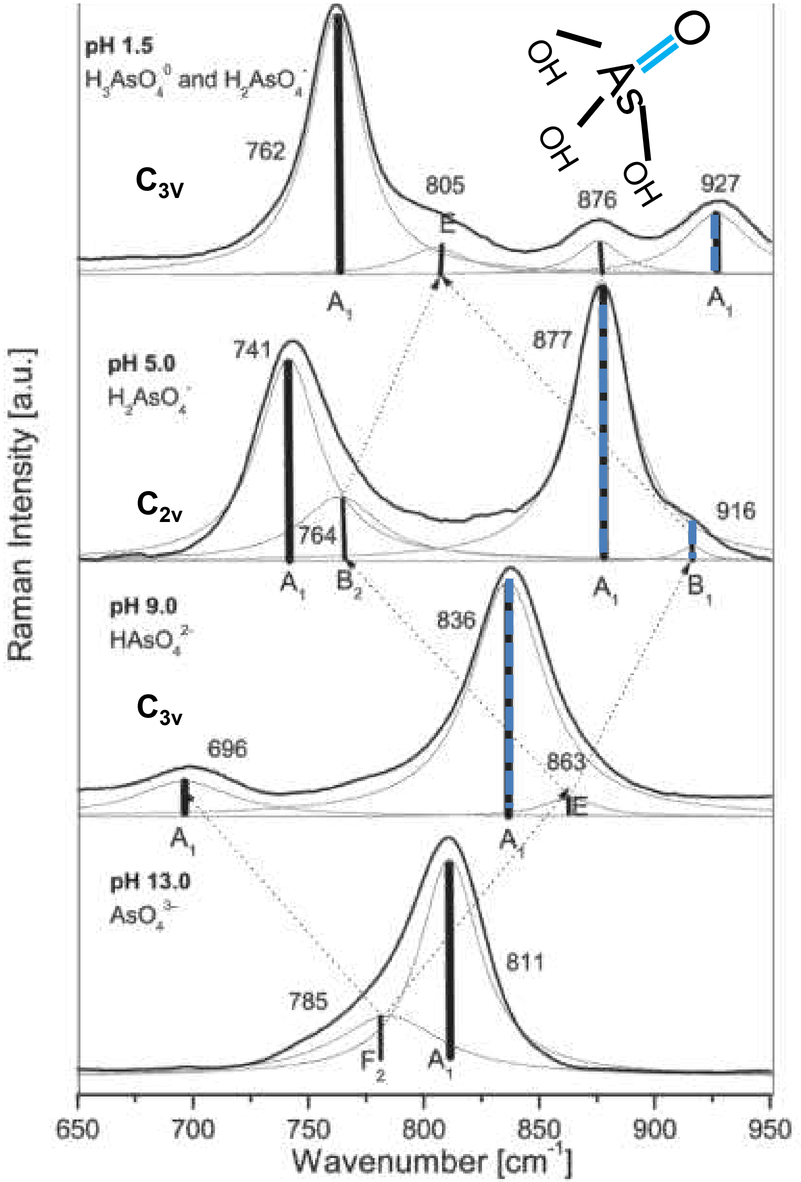
Müller, K. et al. *Water research*, 2010, *44*, 5660 - 5667.

Distribution of arsenate species

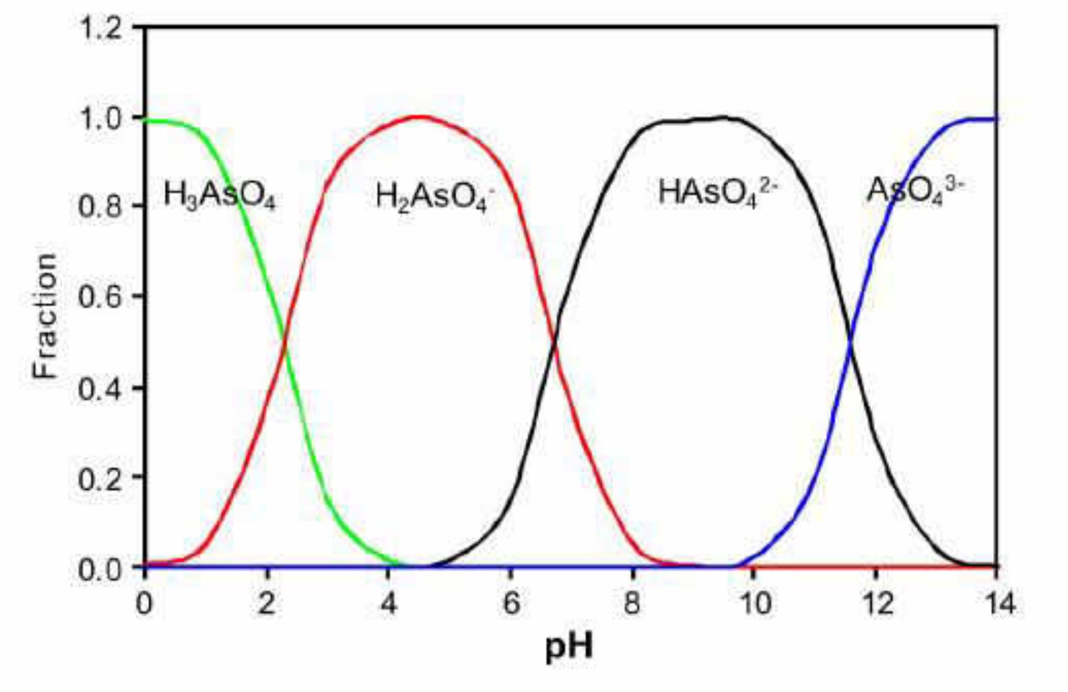
a)



b)



c)



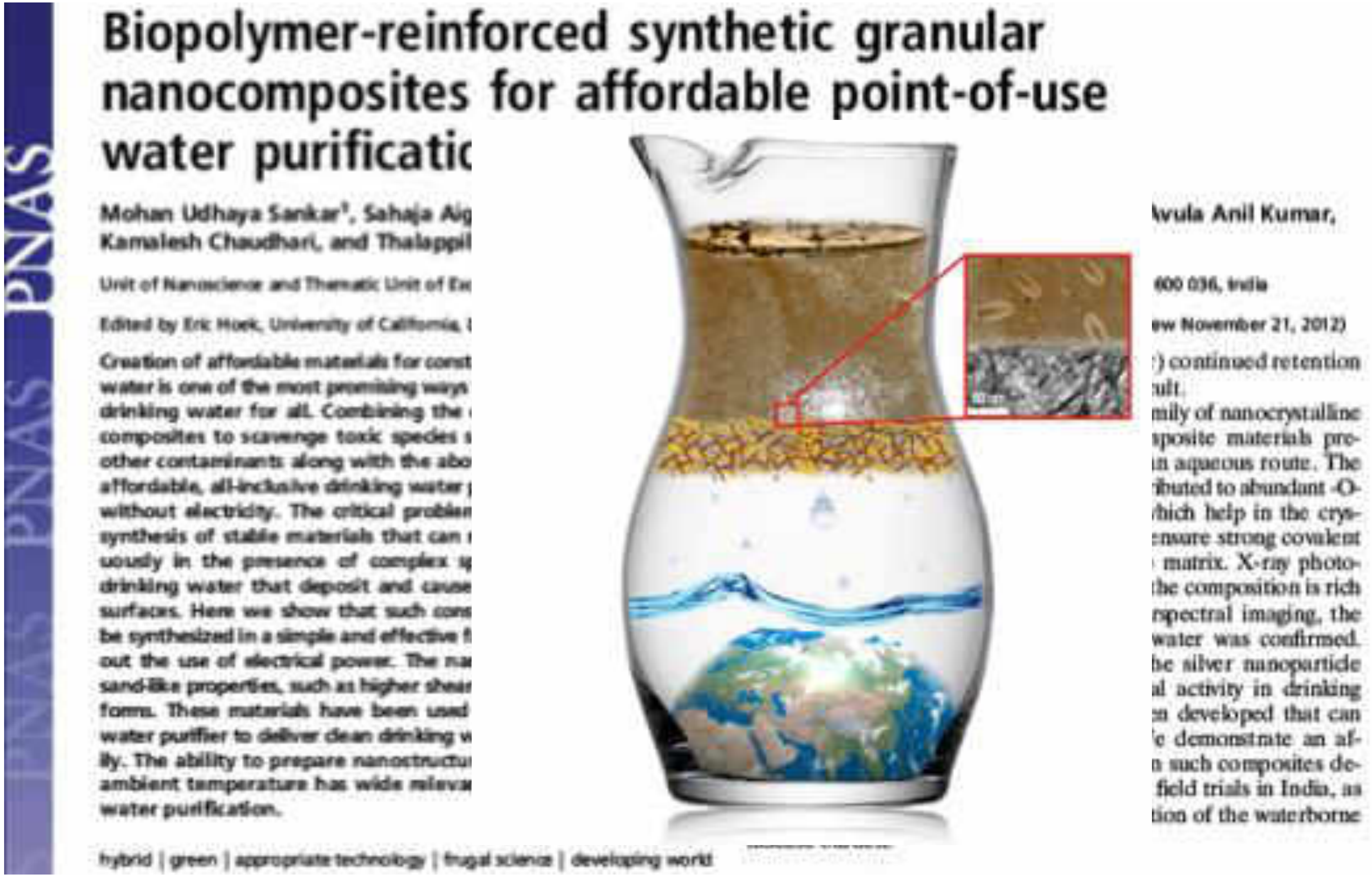
Sisi Q. et al. J. Environ. Eng., 2013, 139, 368-374

Müller, K. et al. *Water research*, 2010, *44,* 5660 -5667

Clean water for everyone

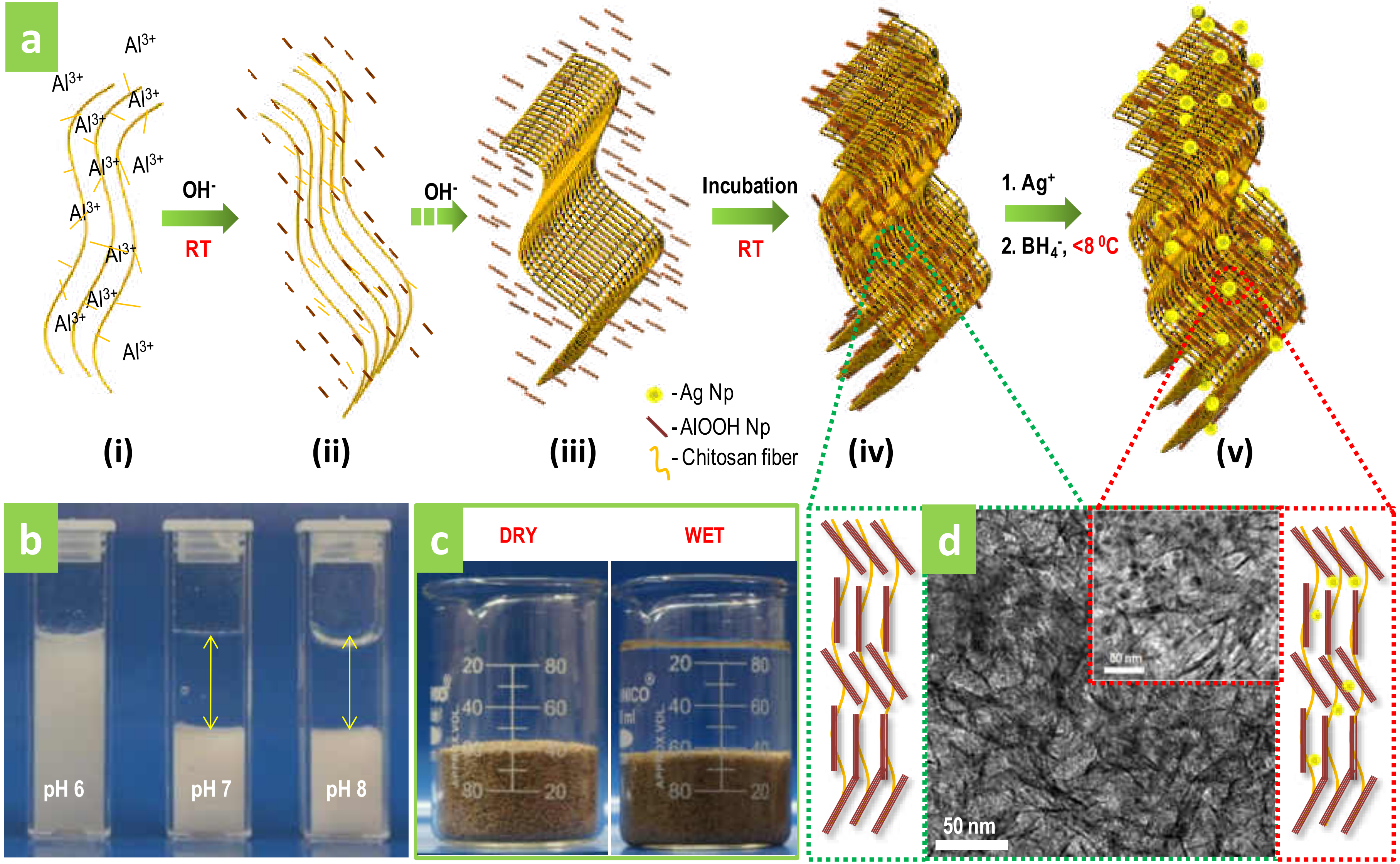
ACS Sustainable Chemistry & Engineering Editorial, December 2016

Water positive materials



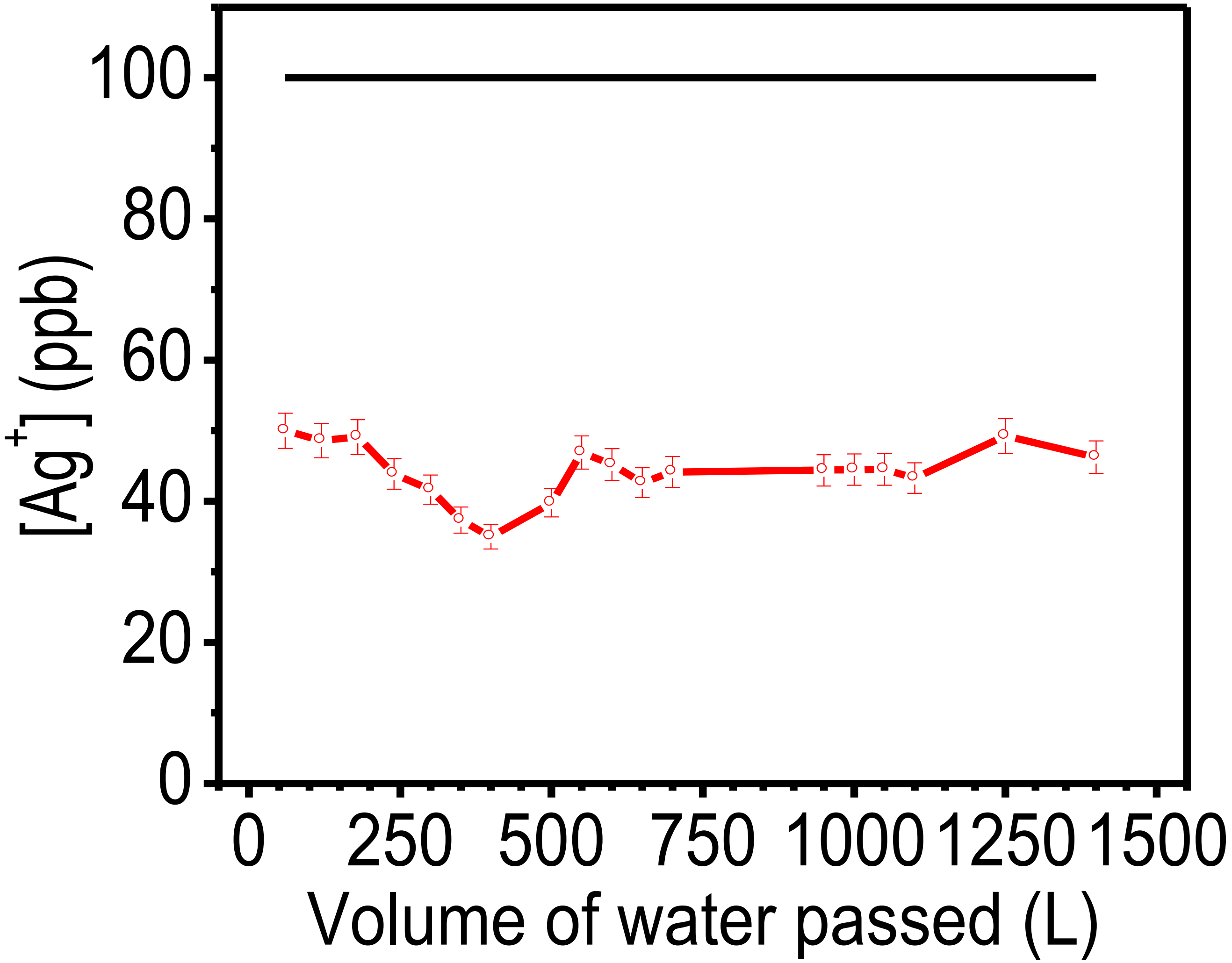
M. Udhaya Sankar, et. al. *Proc. Natl. Acad. Sci.,* 110 (2013) 8459-8464.

How to make?

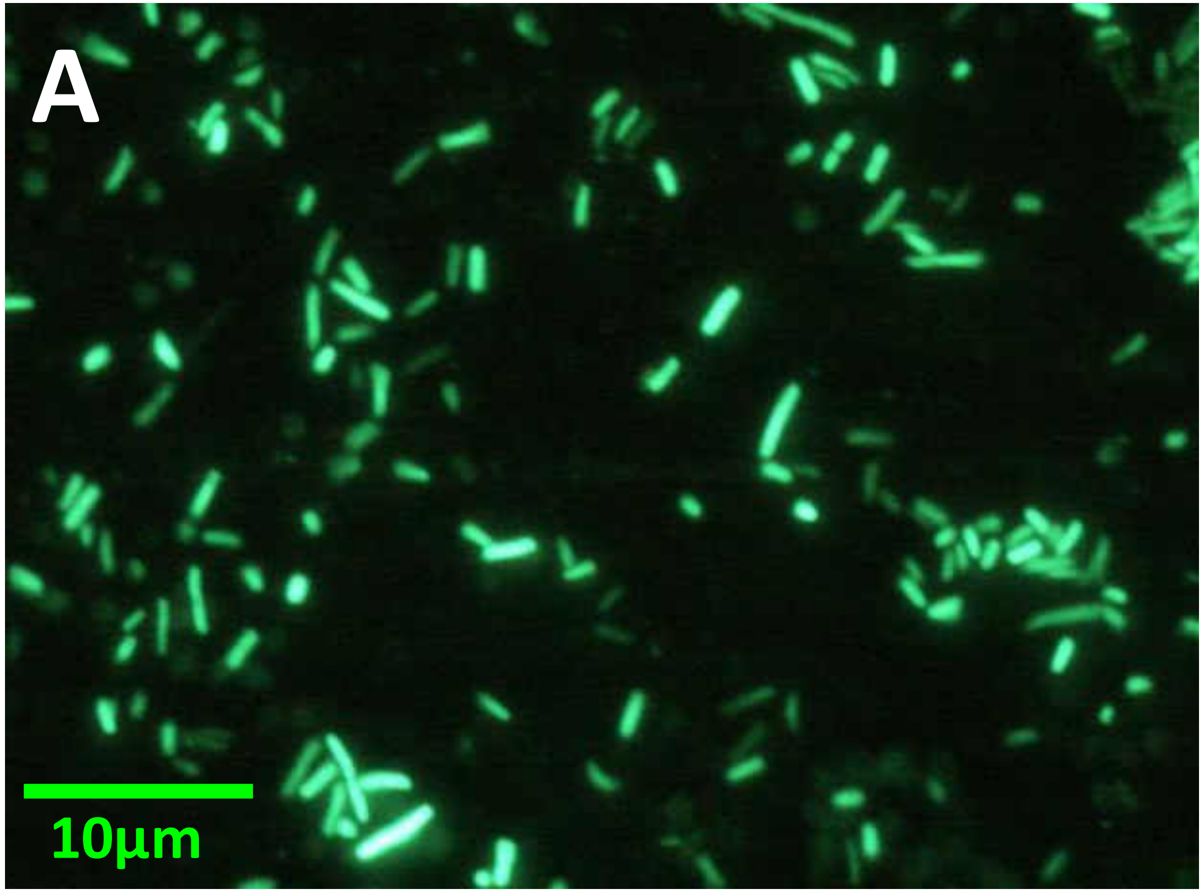


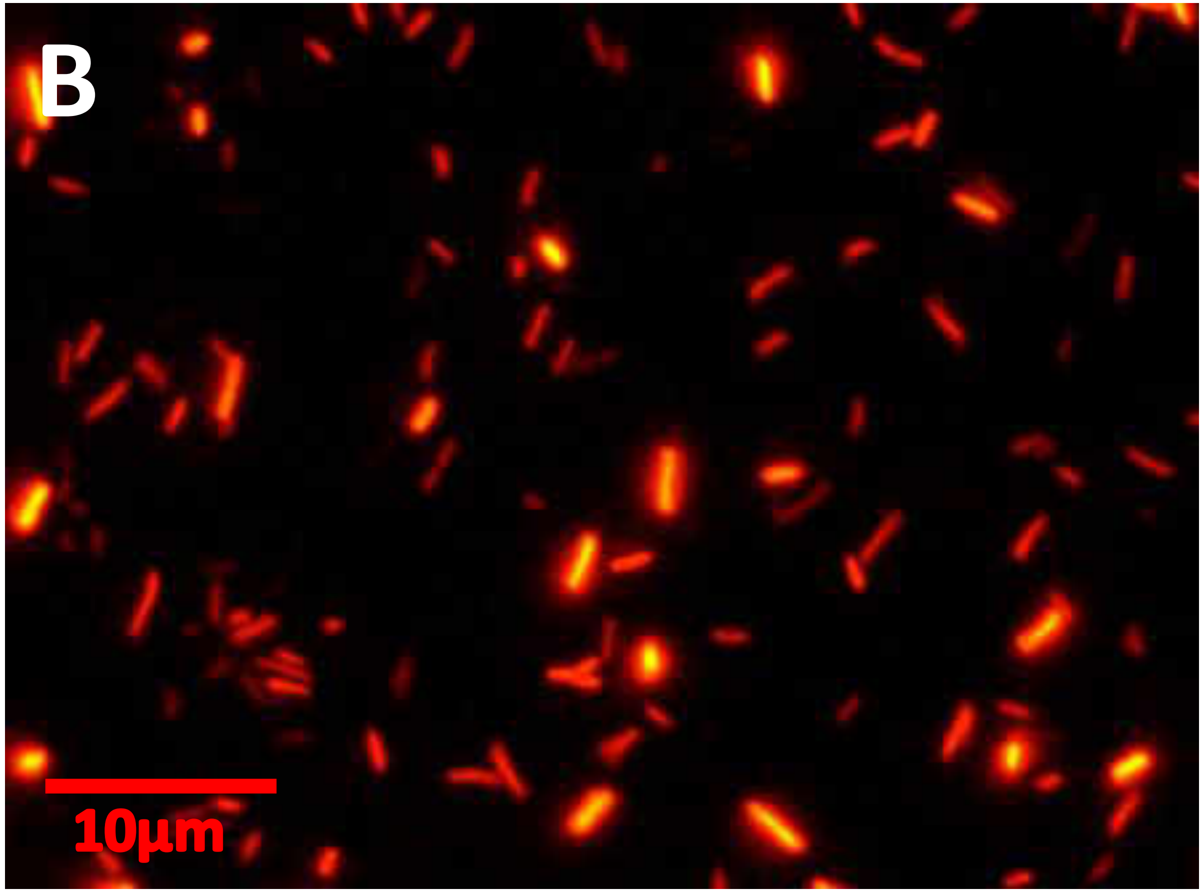
a
Al3+
OH-
RT
OH-
Incubation
RT
1. Ag+
2. BH4-, <8 0C
-Ag Np
-AlOOH Np
-Chitosan fiber
(i)
(ii)
(iii)
(iv)
(v)
b
pH 6
pH 7
pH 8
c
DRY
WET
d
50 nm

What is special?

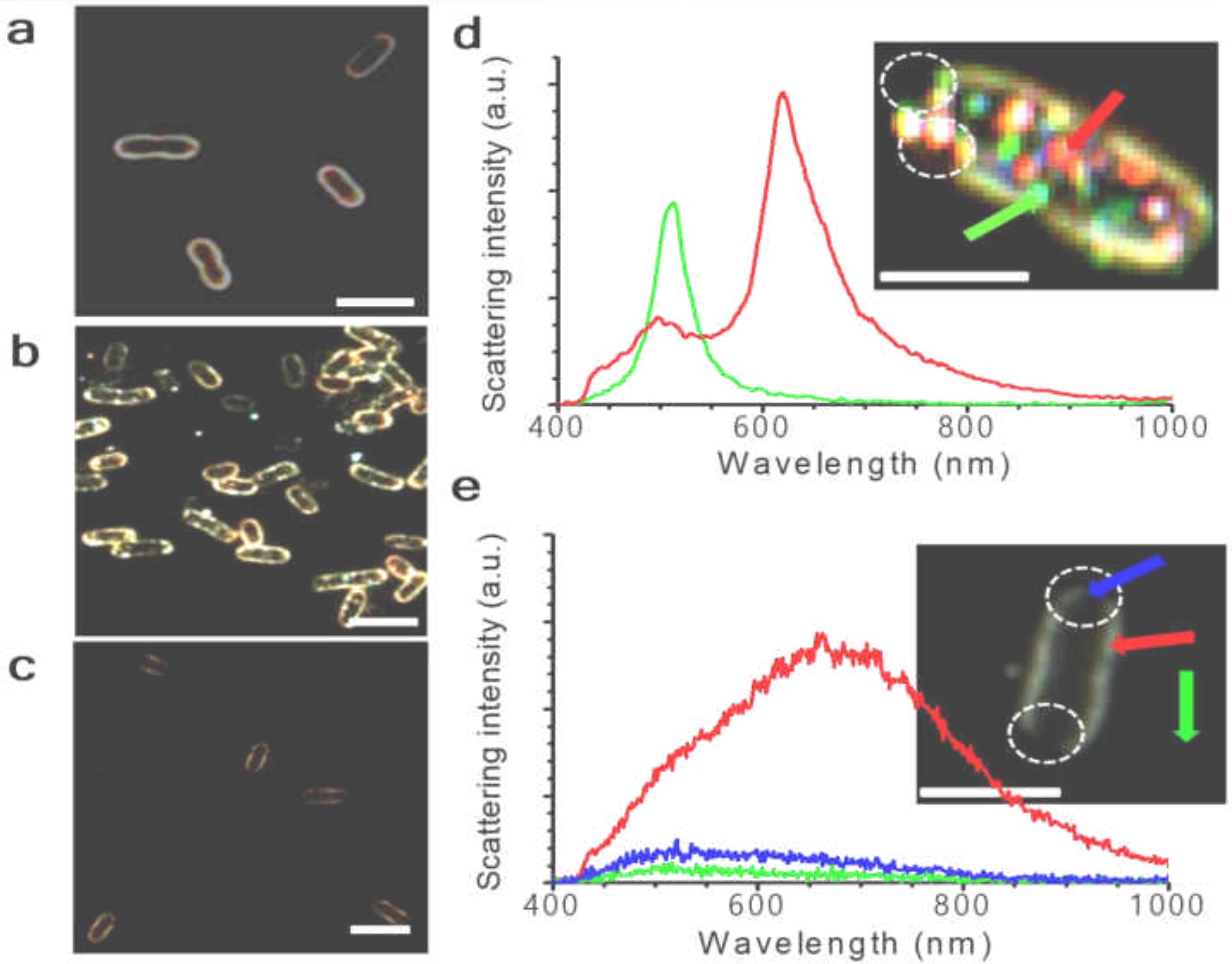


Live/dead staining experiments

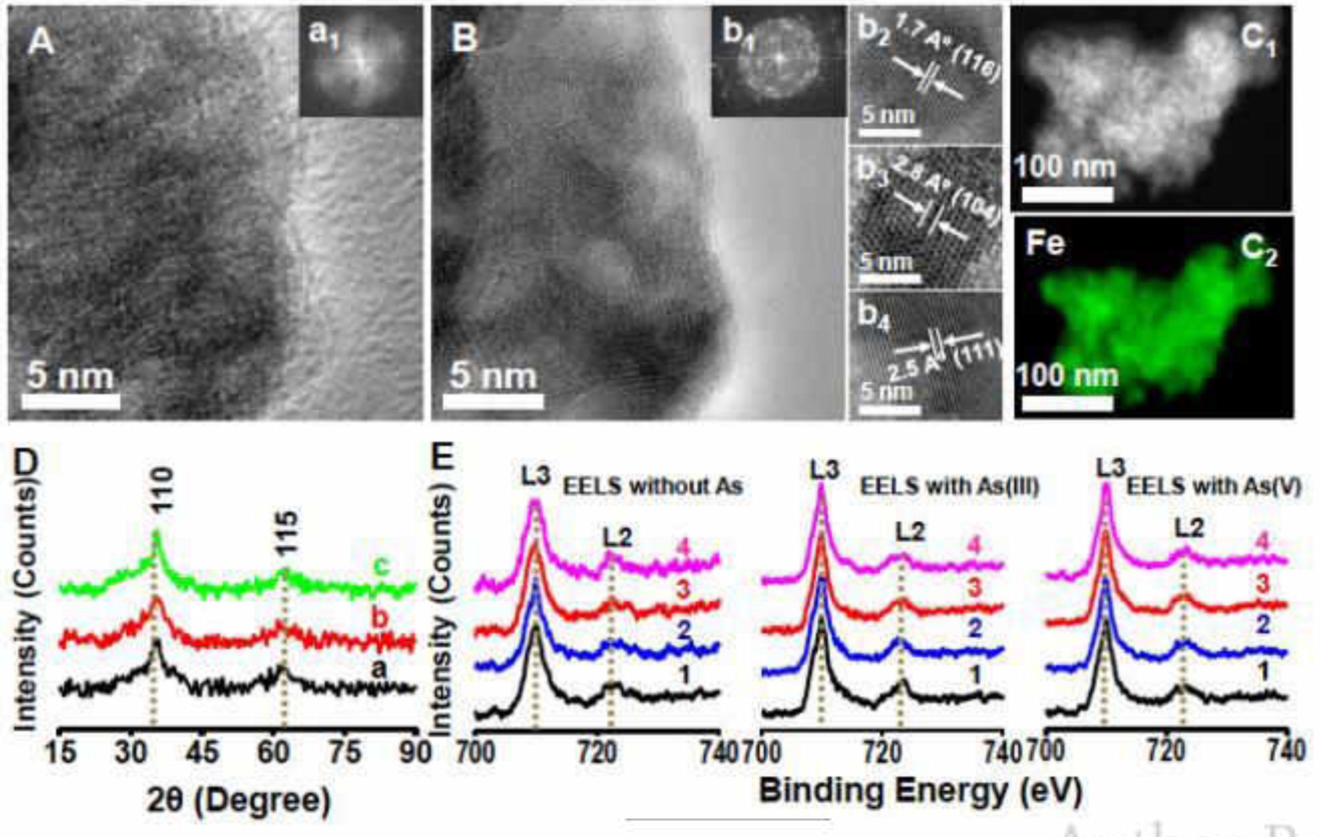


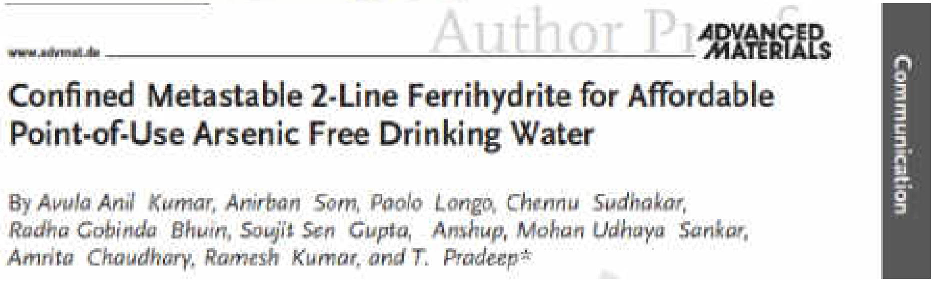


No nanotoxicity



Variety of materials





www.advmat.de

Author Proof

ADVANCED MATERIALS

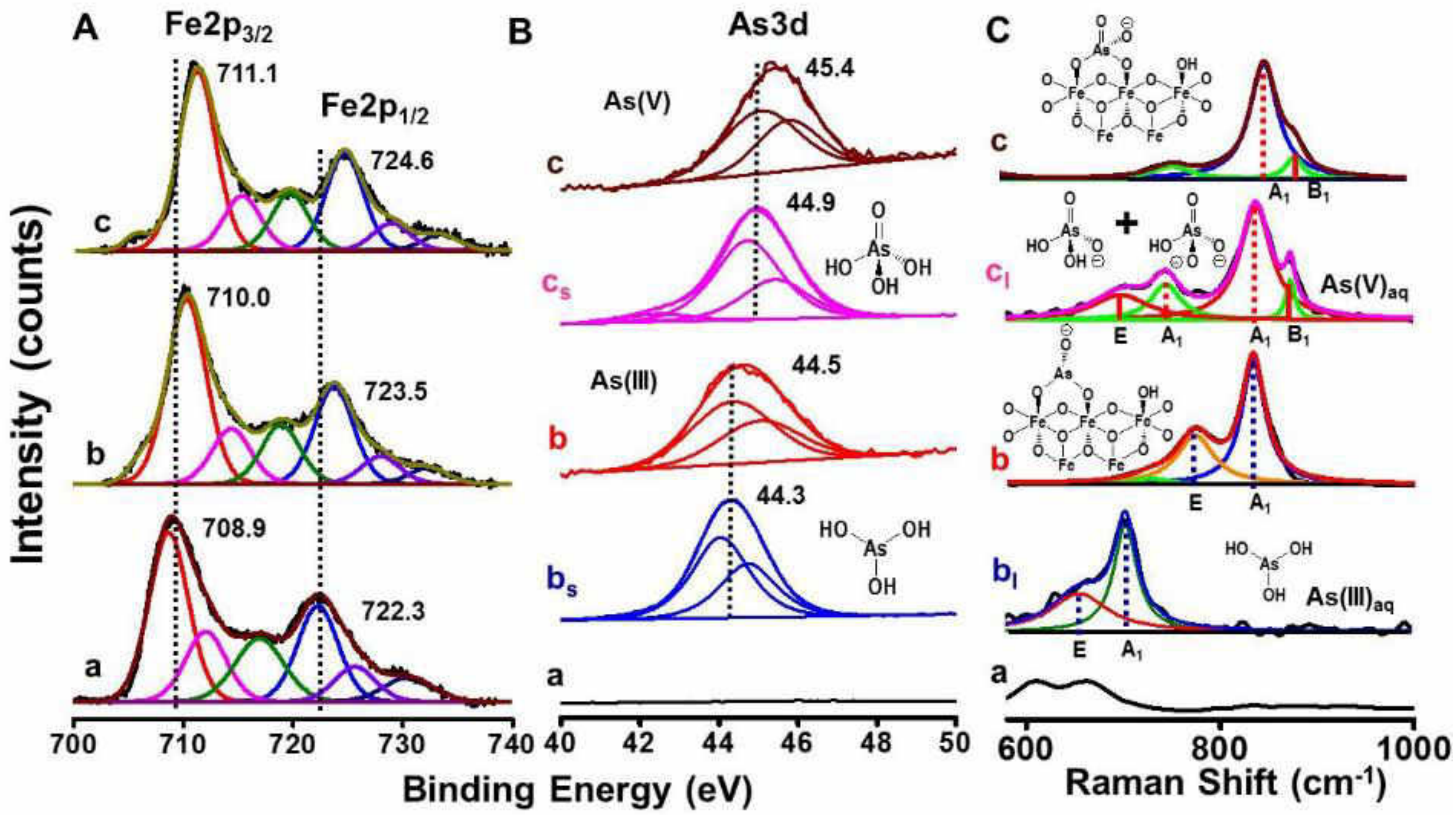
Communication

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*

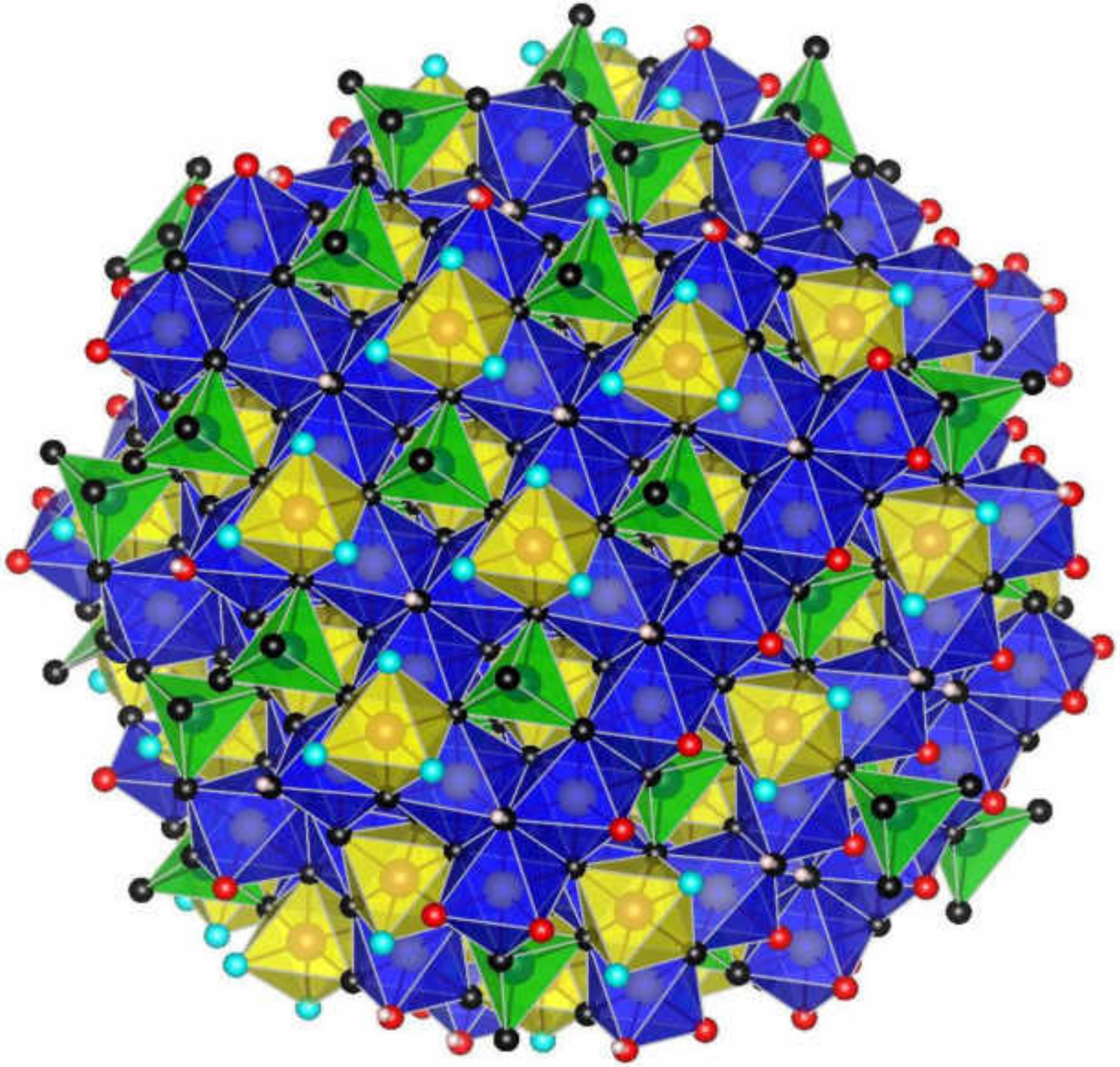
A. Anil Kumar, et. al. *Adv. Mater.*, 29 (2016) 1604260.

Mechanism



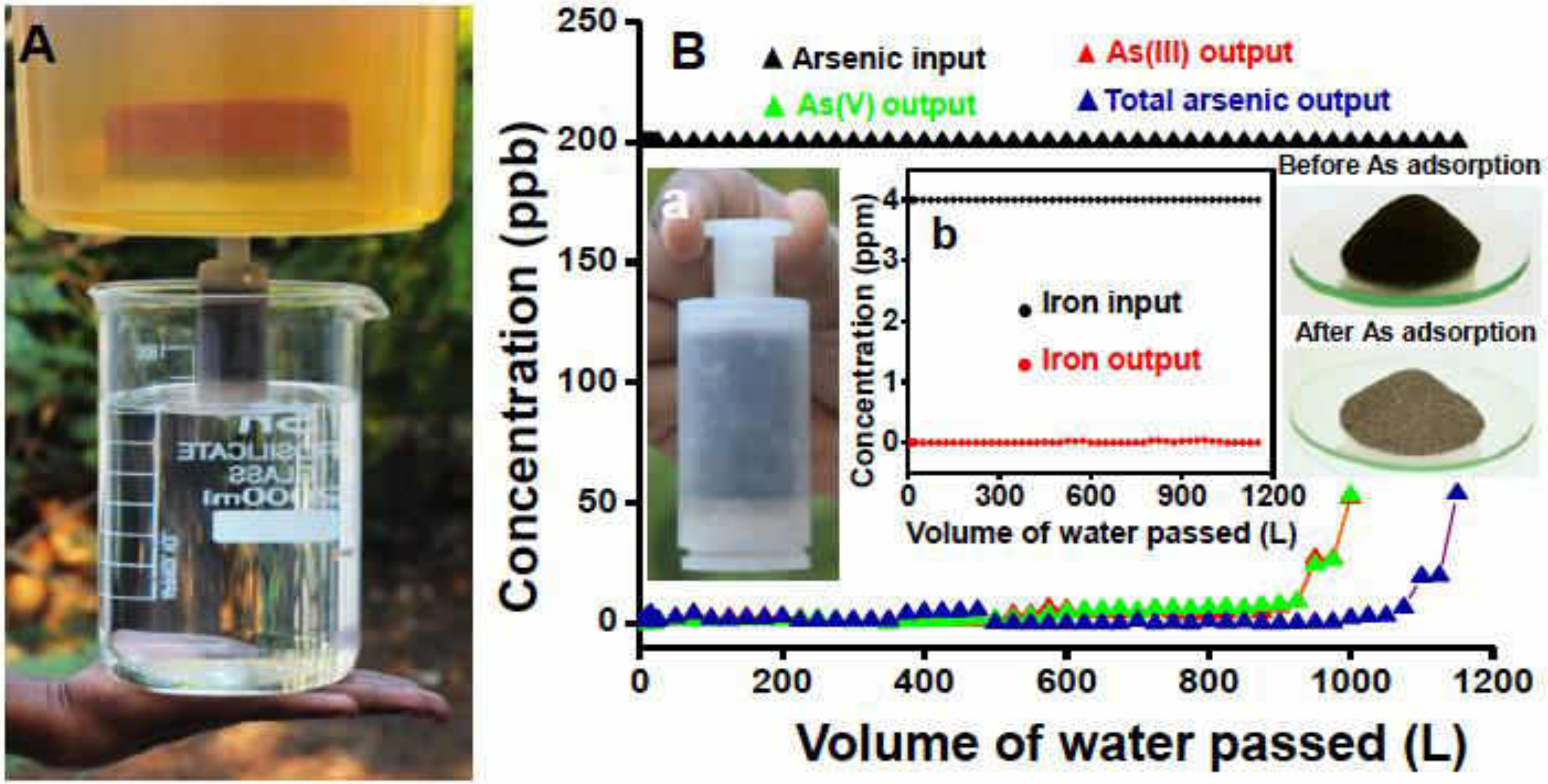
A
Fe2p3/2
711.1
Fe2p1/2
724.6
c
710.0
723.5
b
708.9
722.3
a
Intensity (counts)
700
710
720
730
740
B
As3d
45.4
As(V)
c
44.9
cs
As(III)
44.5
b
44.3
bs
a
40
42
44
46
48
50
Binding Energy (eV)
C
c
A1
B1
cl
As(V)aq
E
A1
A1
B1
b
E
A1
bl
As(III)aq
E
A1
a
600
800
1000
Raman Shift (cm-1)

Modeling surfaces



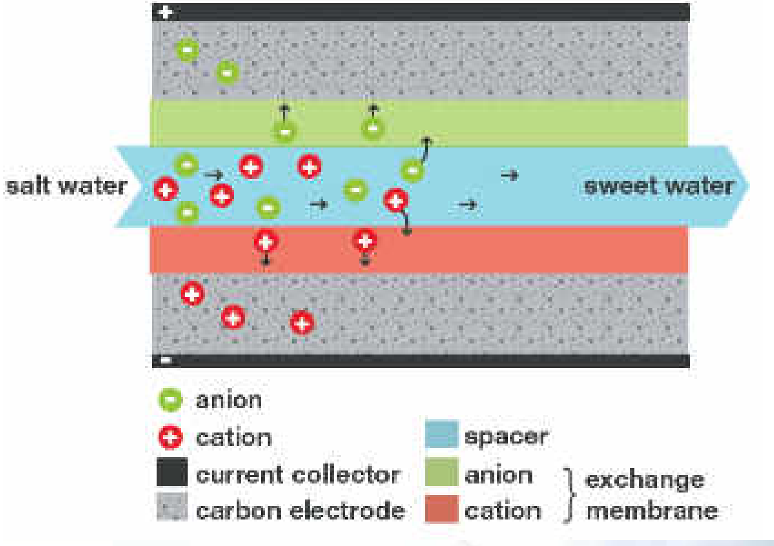
Chennu Sudhakar, et al. *ACS Sustainable Chemistry & Engineering*, 6 (2018) 9990-10000.

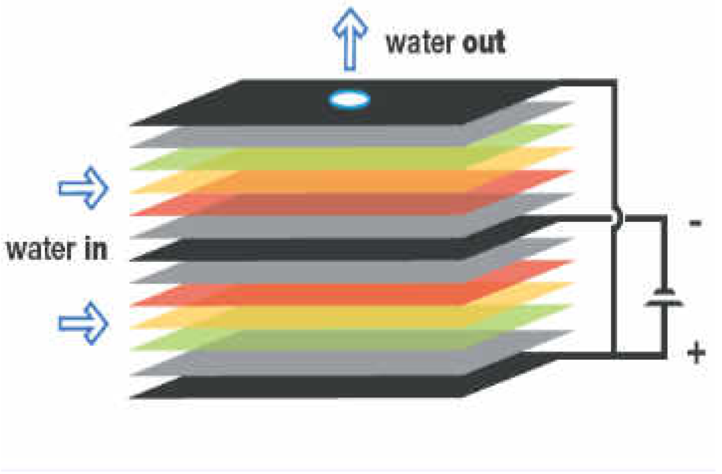
Lab studies

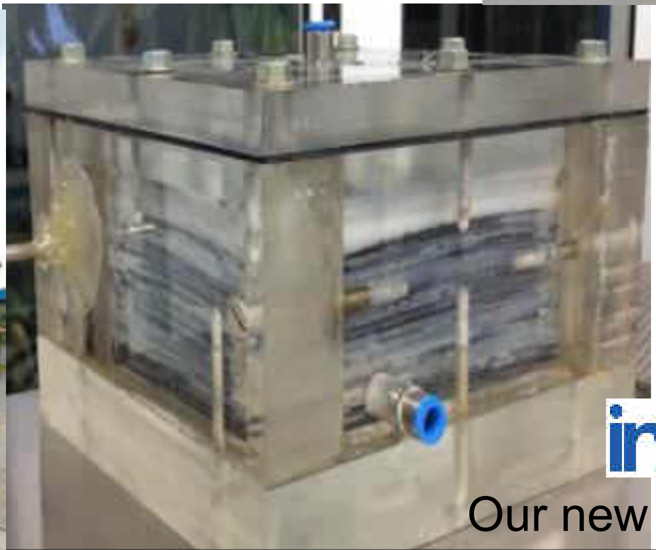


A. Anil Kumar, et. al. *Adv. Mater.*, 29 (2016) 1604260.

Capacitive Desalination (CDI)



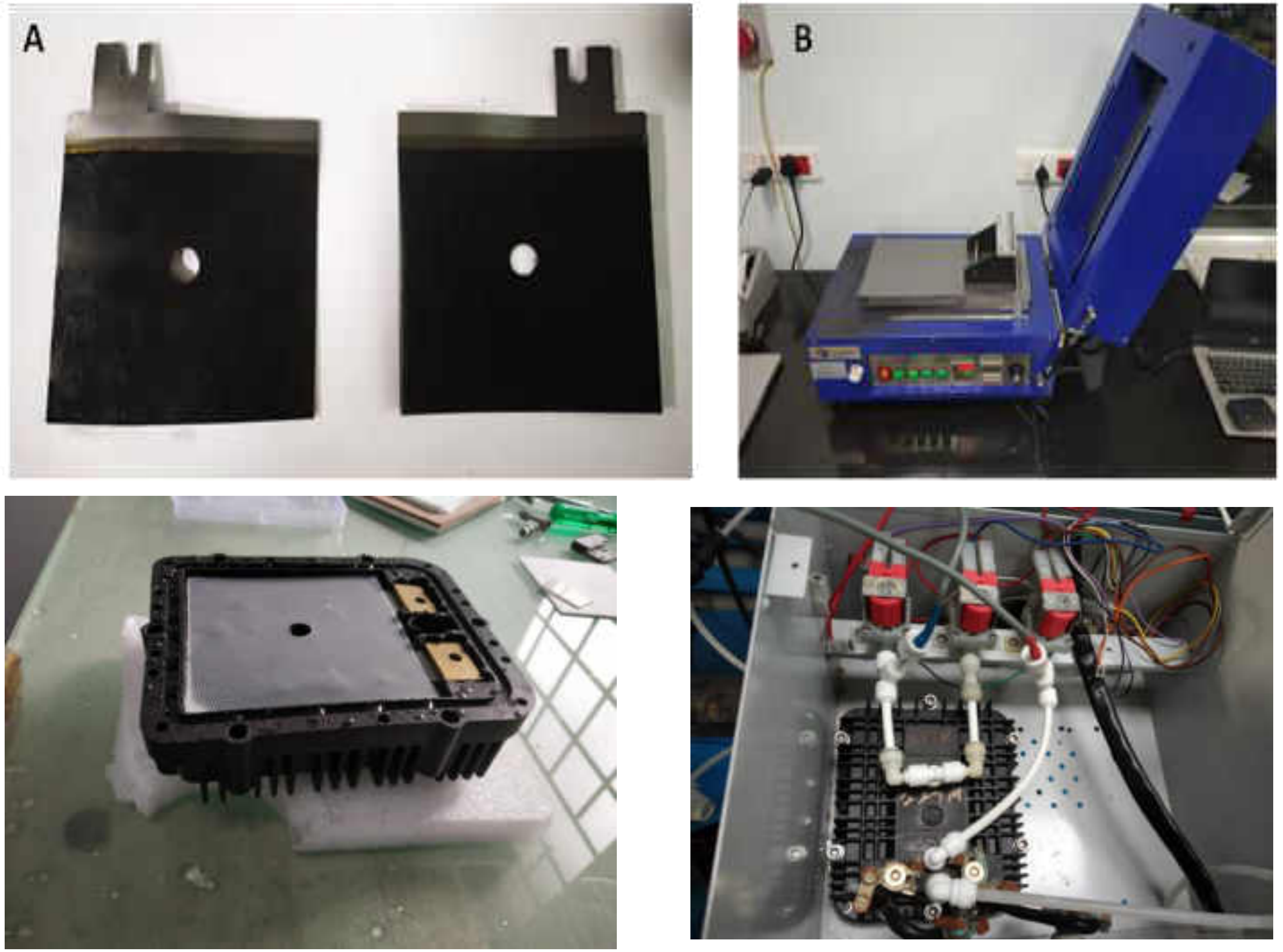




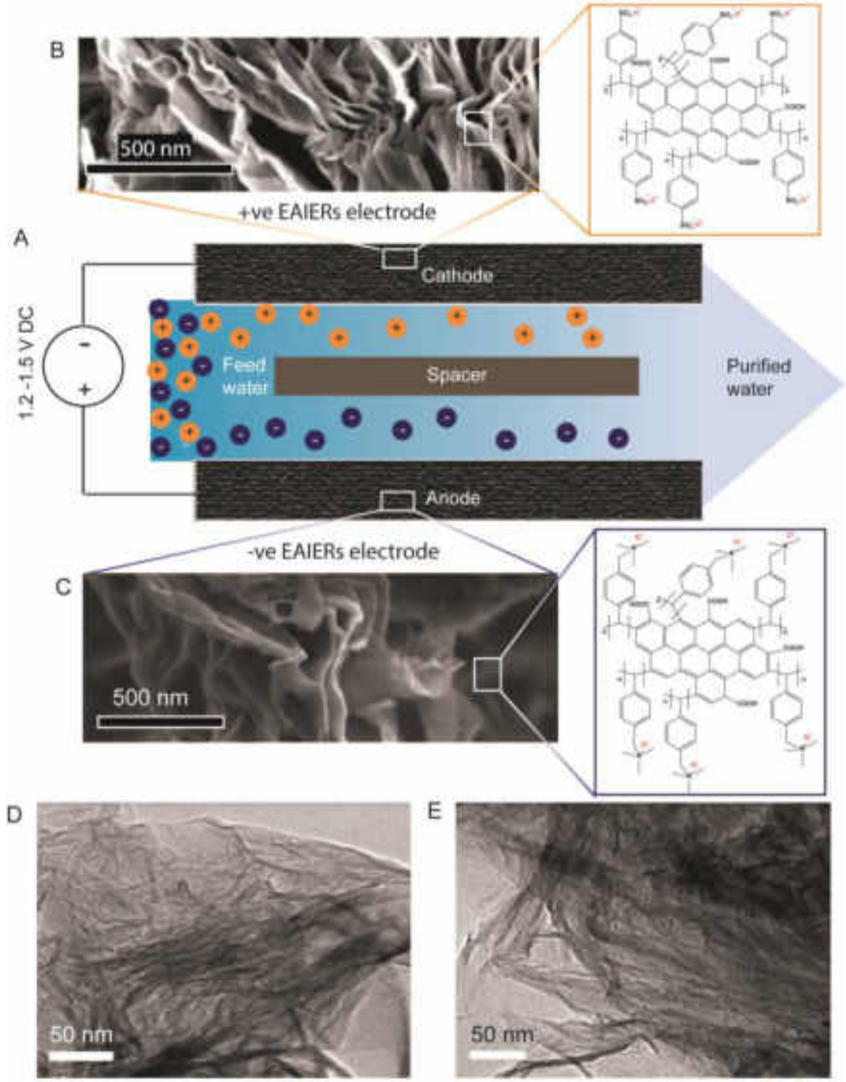
Our new company

Soujit Sengupta, Rabiul Islam and others

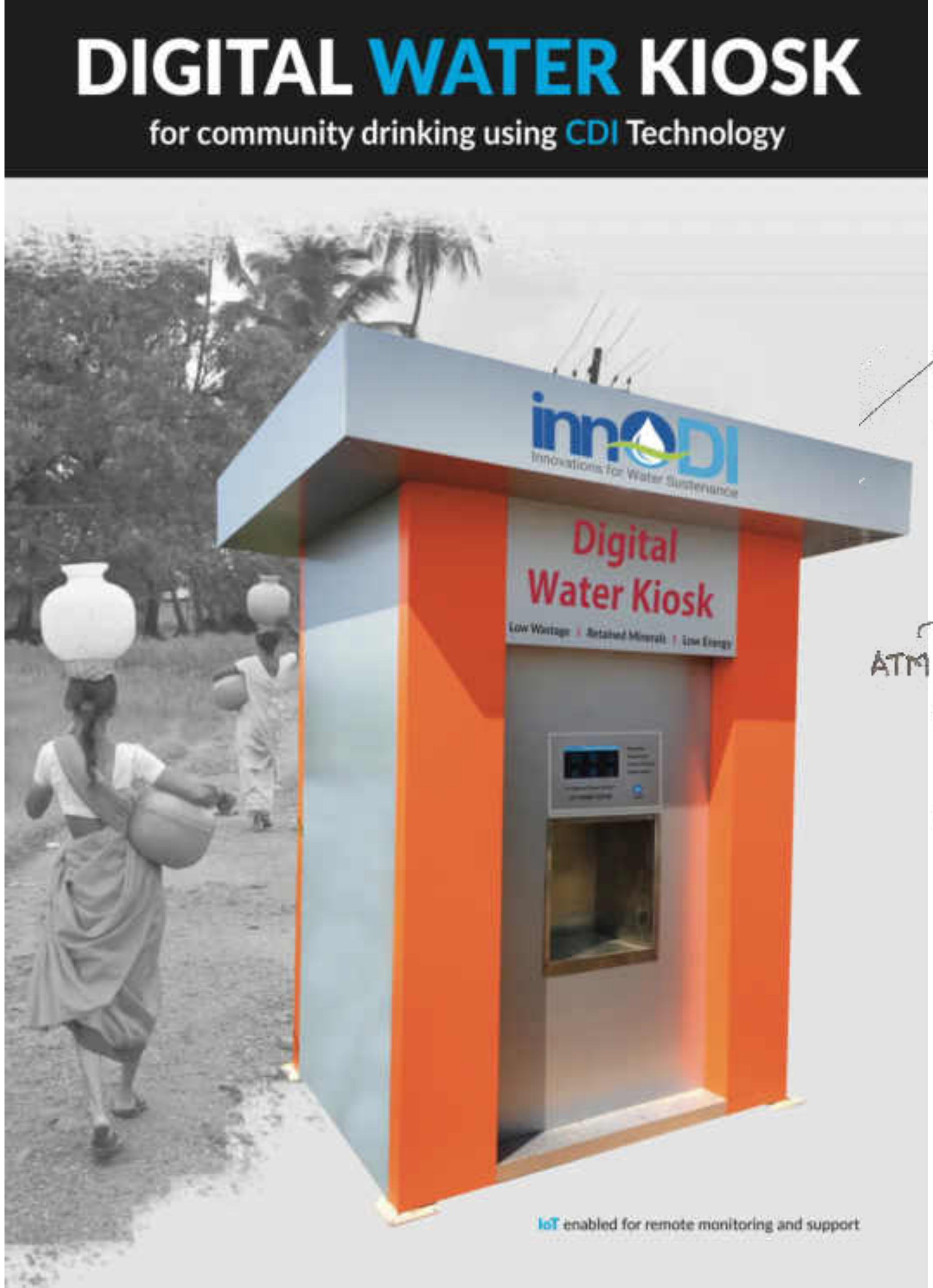
Various stages of electrode preparation

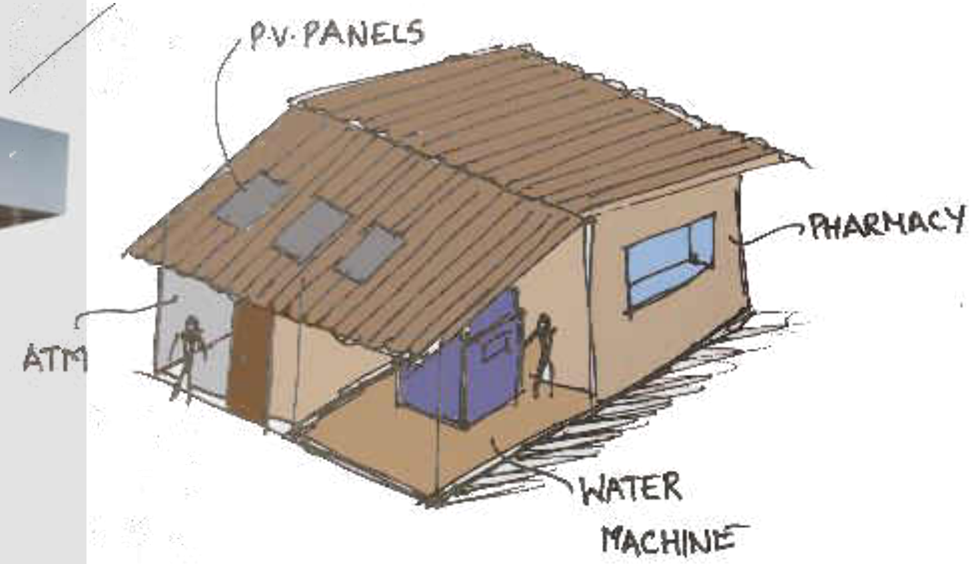


A Covalently Integrated Reduced Graphene Oxide -Ion Exchange Resin Electrode for Efficient CDI



Rabiul *et al., Adv. Mater. Interfaces* **2021**, *8,* 2001998

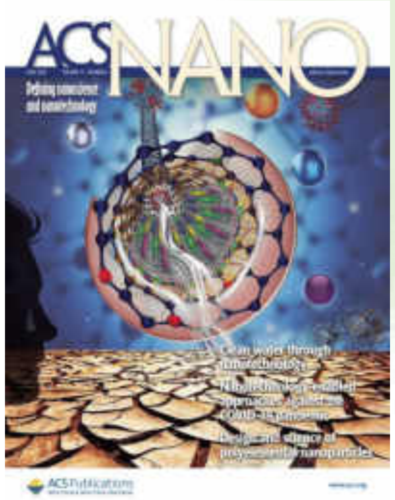


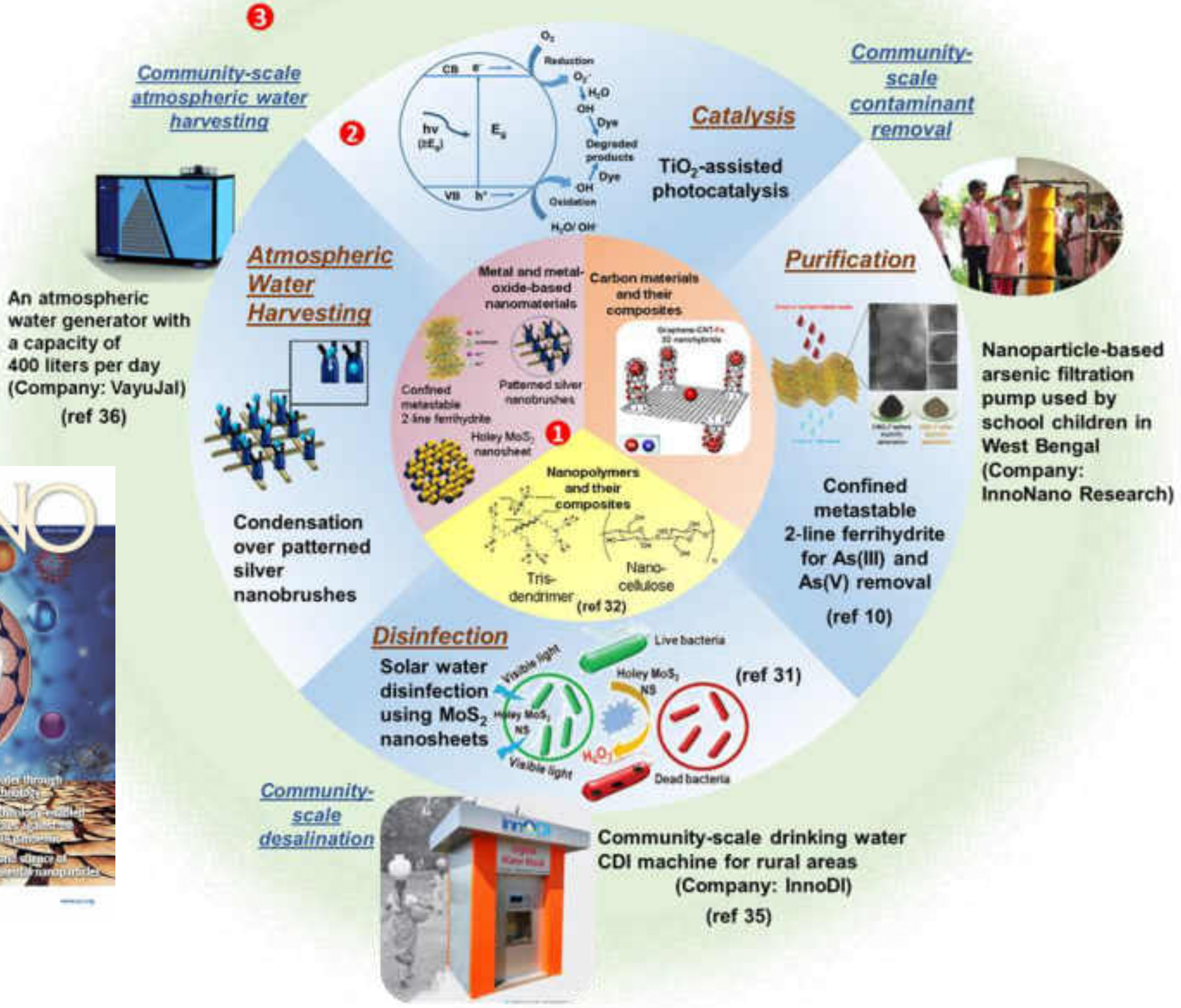


Products under implementation

Vijay Sampath and Tullio Servida

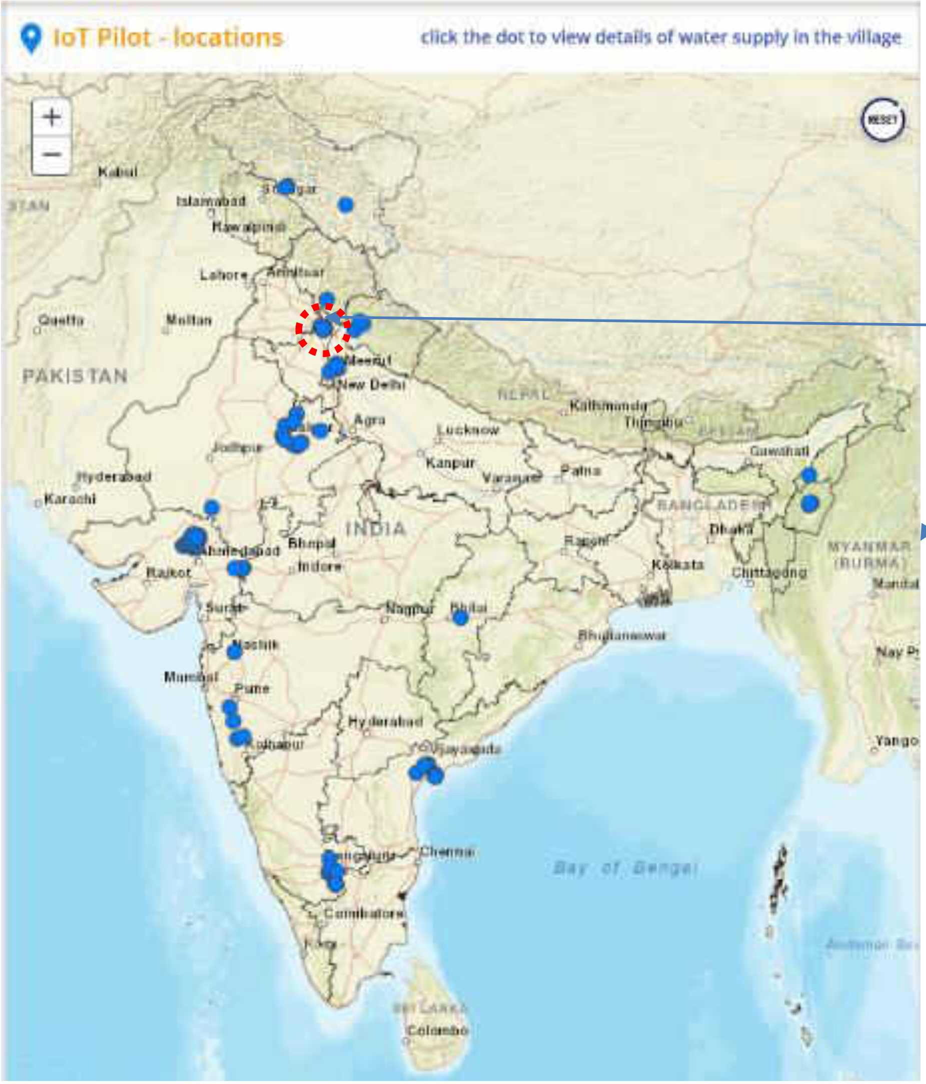
Evolution of materials to products





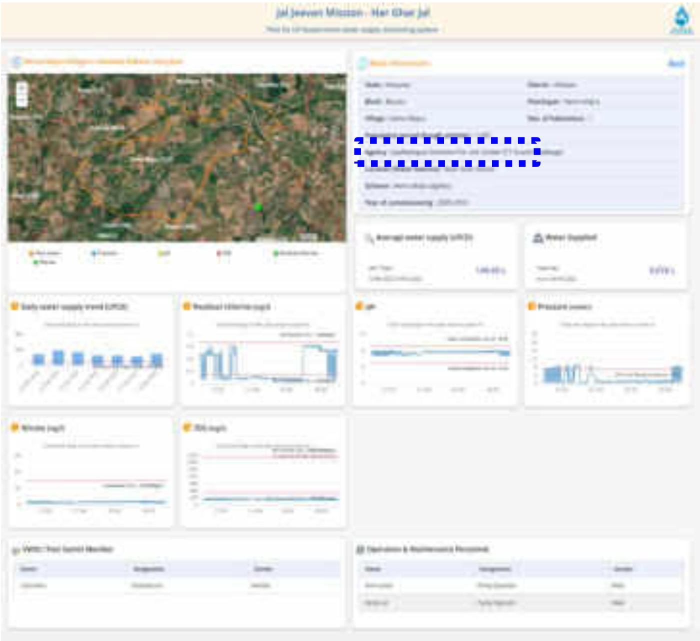
Ankit Nagar and T. Pradeep, *ACS Nano* 14 (2020) 6420-6435.

India’s water is being monitored



IITM/IISc

Installations made by four companies



https://www.youtube.com/watch?v=fiJyptbXBtM

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Manswita Mandal for help with the slides