Since 1959

Materials for Water

Thalappil Pradeep

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pradeep@iitm.ac.in

https://pradeepresearch.org

Co-founder

InnoNano Research Pvt. Ltd.
InnoDI Water Technologies Pvt. Ltd.
VayuJAL Technologies Pvt. Ltd.
Aqueasy Innovations Pvt. Ltd.
Hydromaterials Pvt. Ltd.
EyeNetAqua Solutions Pvt. Ltd.
DeepSpectrum Innovations Pvt. Ltd.

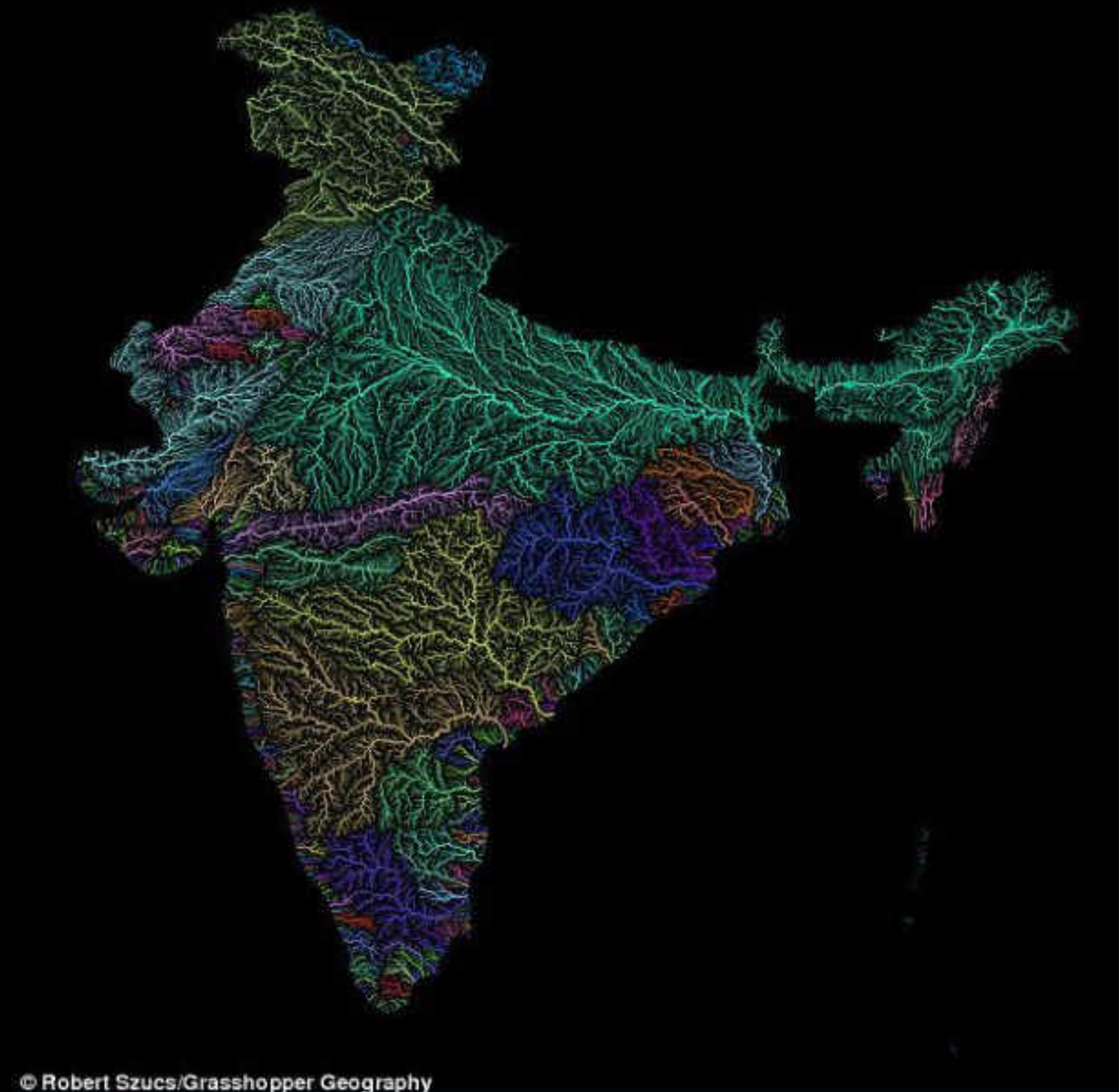
Associate Editor

ACS Sustainable Chemistry & Engineering

Professor-in-charge

ICCW

International Centre for Clean Water



From S. Vishwanath

Water purification, history

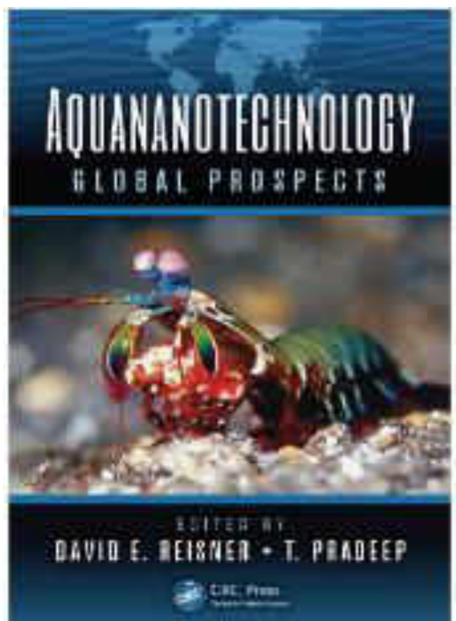
Important milestones in the history of water purification (1800–2007) from the perspective of noble metal nanoparticles in water treatment (compiled from multiple sources on the World Wide Web).

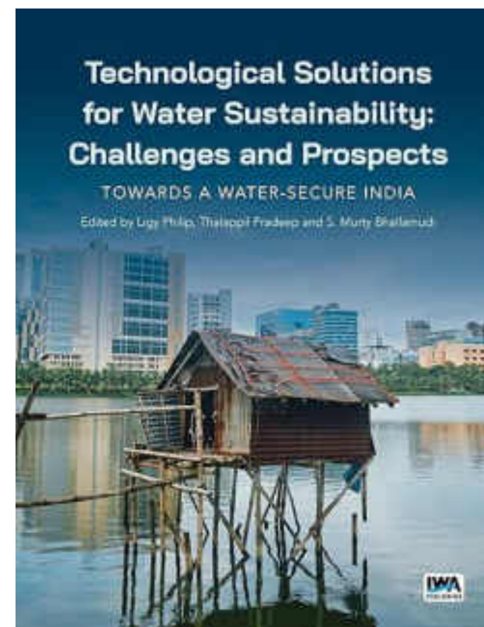
Year	Milestone
1804	Setup of world's first city-wide municipal water treatment plant (Scotland, sand-filter technology)
1810	Discovery of chlorine as a disinfectant (H. Davy)
1852	Formulation of Metropolis Water Act (England)
1879	Formulation of Germ Theory (L. Pasteur)
1902	Use of chlorine as a disinfectant 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

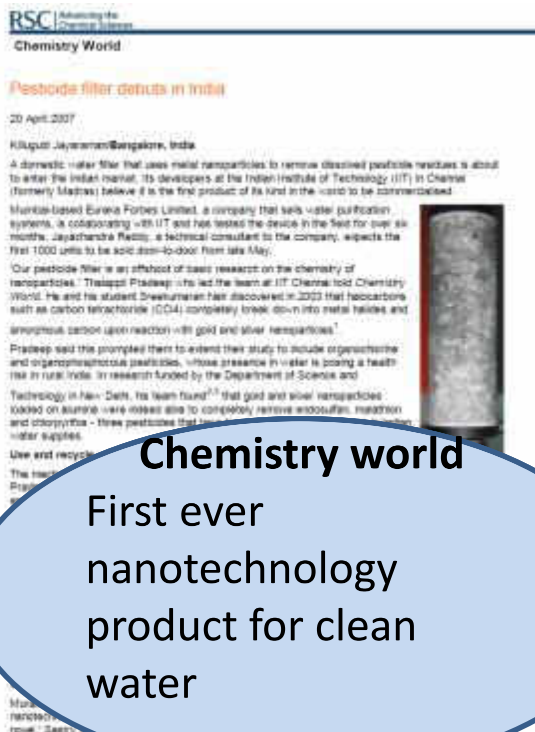
Affordable clean water is a problem of advanced materials

New adsorbents
New sensors
New catalysts
Novel phenomena
New devices





World's first nanochemistry-based water purifier



RSC | Advancing the Chemical Sciences

Chemistry World

Pesticide filter debuts in India

20 April 2007

K.S. 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 ...

water supplies.

Use and recycle

The ...

Chemistry world

First ever nanotechnology product for clean water

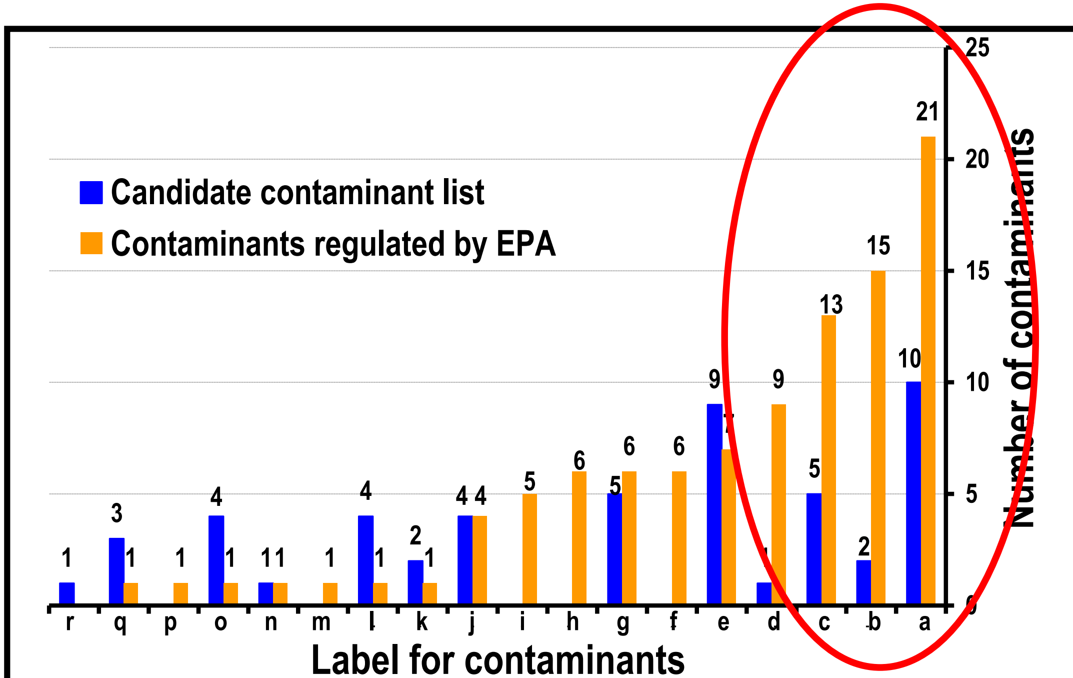
A plant to make supported nanomaterials for water purification; with capacity of 4.5 tons per month, 2007

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

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).

Clean water for everyone

ACS Sustainable Chemistry & Engineering Editorial, December 2016

Water positive materials

PNAS PNAS PNAS PNAS

Biopolymer-reinforced synthetic granular nanocomposites for affordable point-of-use water purification

Mohan Udhaya Sankar[1], Sahaja Aigal[1], Shihabudheen M. Maliyekkal[1], Amrita Chaudhary, Anshup, Avula Anil Kumar, Kamalesh Chaudhari, and Thalappil Pradeep[2]

Unit of Nanoscience and Thematic Unit of Excellen… …n, Chennai 600 036, India

Edited by Eric Hoek, University of California, Los A… …ved for review November 21, 2012)

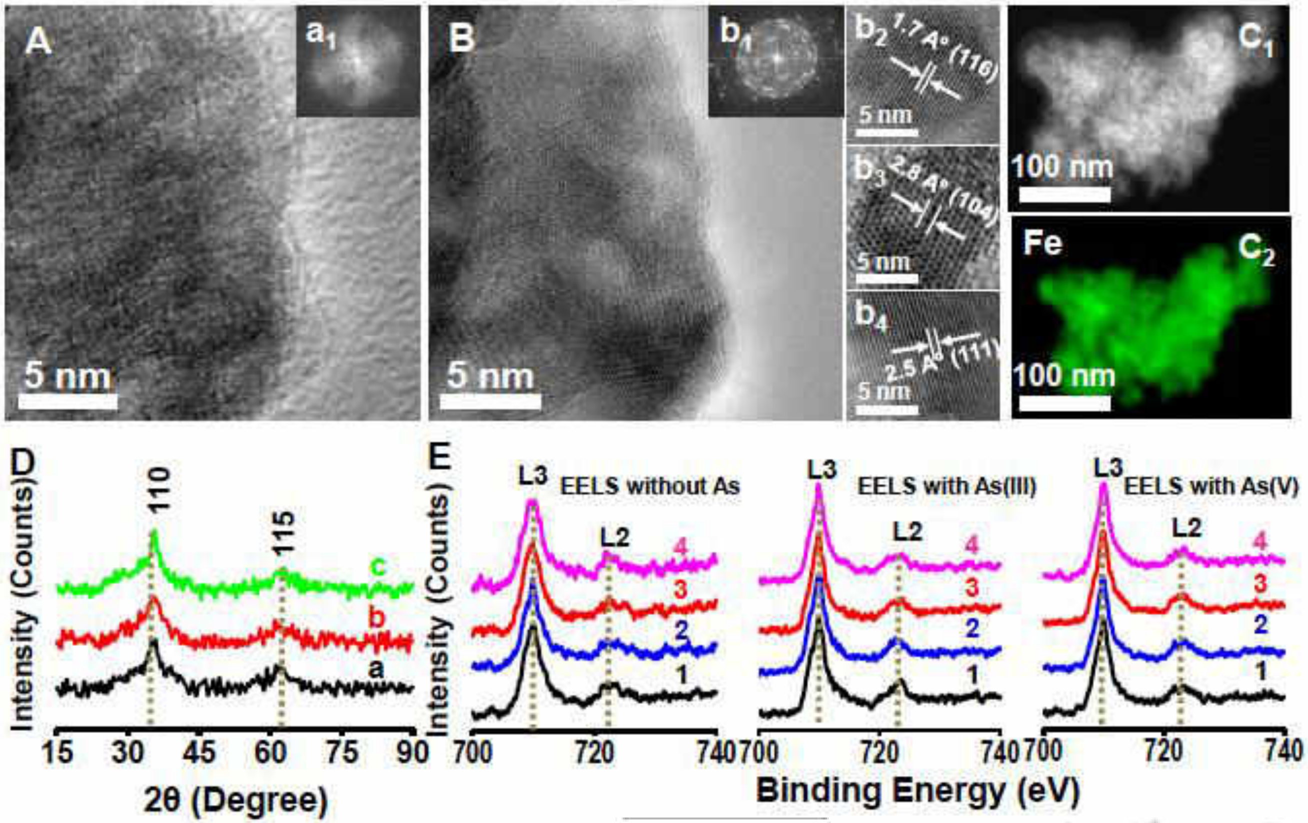
Creation of affordable materials for constant r…
water is one of the most promising ways to pr…
drinking water for all. Combining the capa…
composites to scavenge toxic species such…
other contaminants along with the above ca…
affordable, all-inclusive drinking water purif…
without electricity. The critical problem in…
synthesis of stable materials that can relea…
uously in the presence of complex specie…
drinking water that deposit and cause scal…
surfaces. Here we show that such constant…
be synthesized in a simple and effective fashio…
out the use of electrical power. The nanocon…
sand-like properties, such as higher shear stre…
forms. These materials have been used to d…
water purifier to deliver clean drinking water…
ily. The ability to prepare nanostructured c…
ambient temperature has wide relevance f…
water purification.

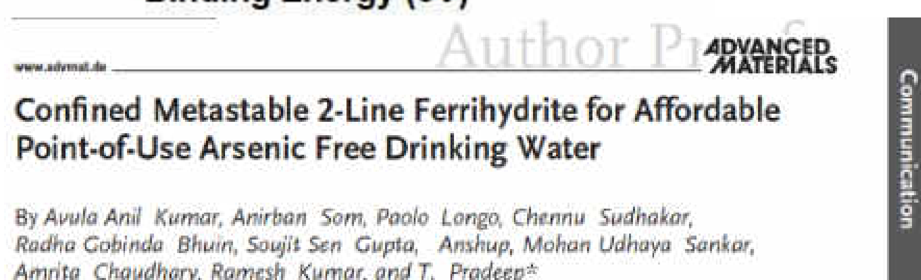
…ble; and (c) continued retention
…ix is difficult.
…unique family of nanocrystalline
…nular composite materials pre-
…through an aqueous route. The
…ition is attributed to abundant -O-
…hitosan, which help in the crys-
…and also ensure strong covalent
…ace to the matrix. X-ray photo-
…firms that the composition is rich
…sing hyperspectral imaging, the
…g in the water was confirmed.
…activate the silver nanoparticle
…timicrobial activity in drinking
…have been developed that can
…water. We demonstrate an af-
…e based on such composites de-
…ndergoing field trials in India, as
…d eradication of the waterborne
…disease burden.

hybrid | green | appropriate technology | frugal science | developing world

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

Variety of materials





www.advmat.de ADVANCED MATERIALS

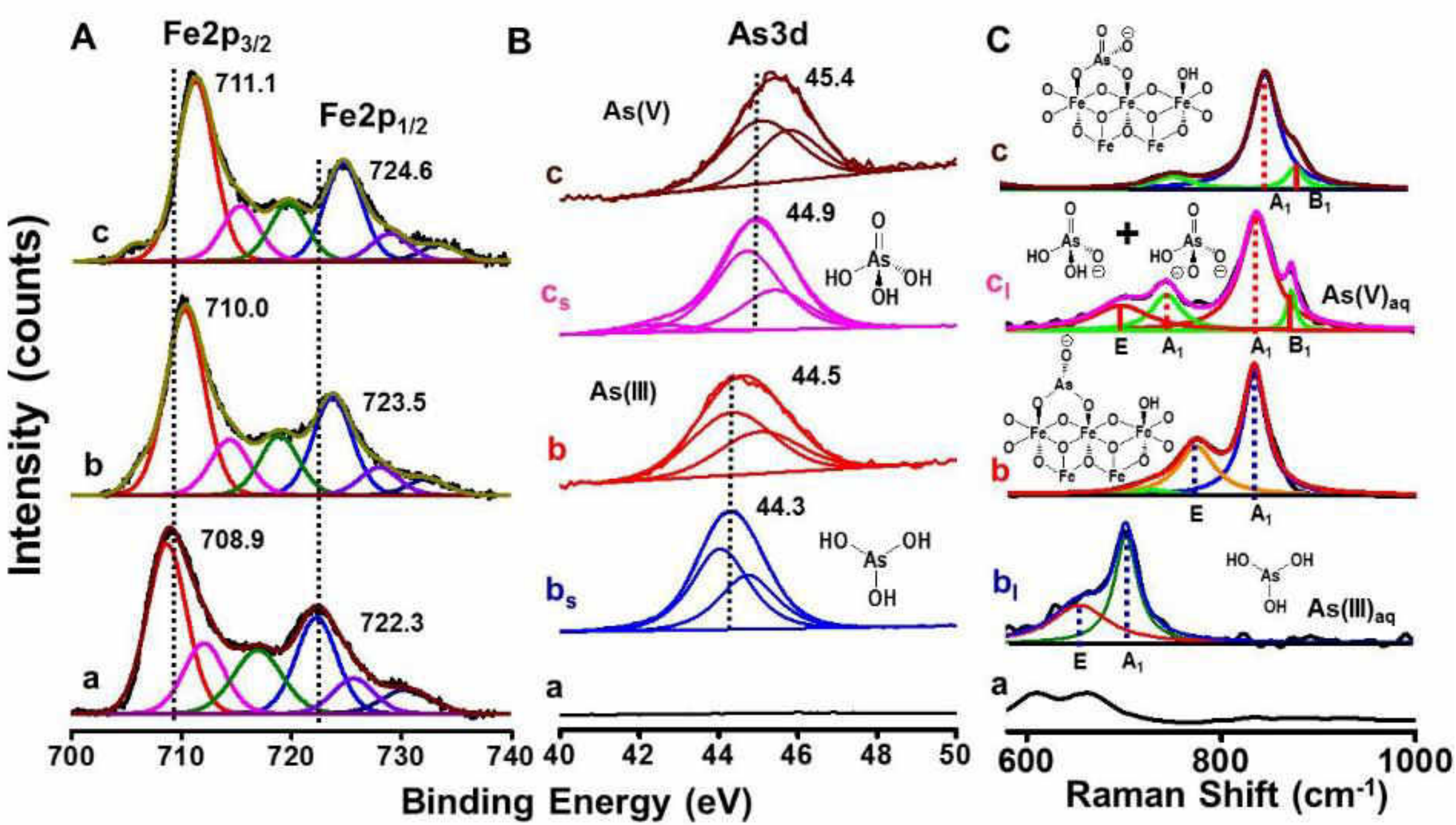
Confined Metastable 2-Line Ferrihydrite for Affordable Point-of-Use Arsenic Free Drinking Water

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*

Communication

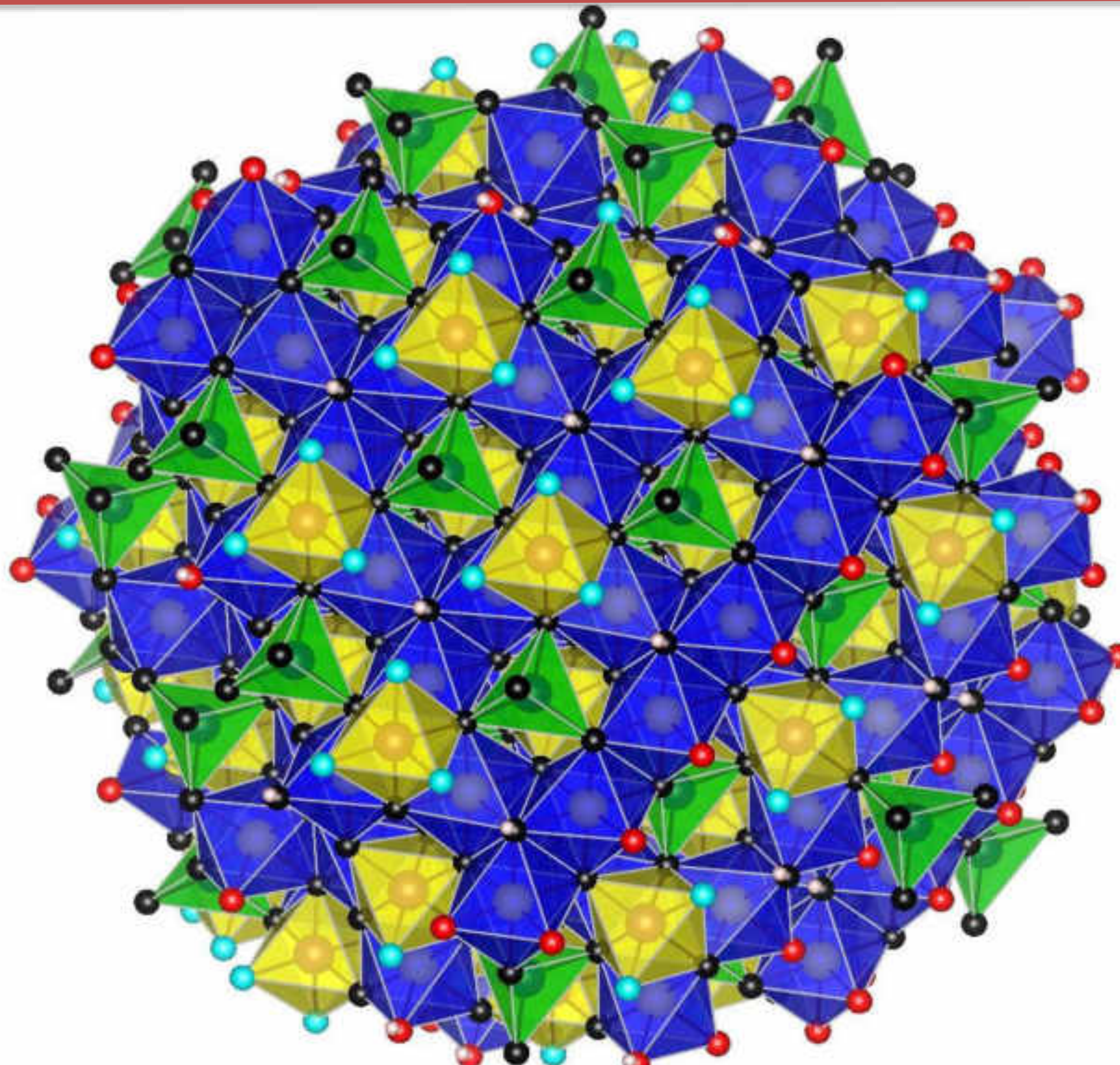
A. Anil Kumar, et. al. *Adv. Mater.*, 29 (2016) 1604260.

Mechanism



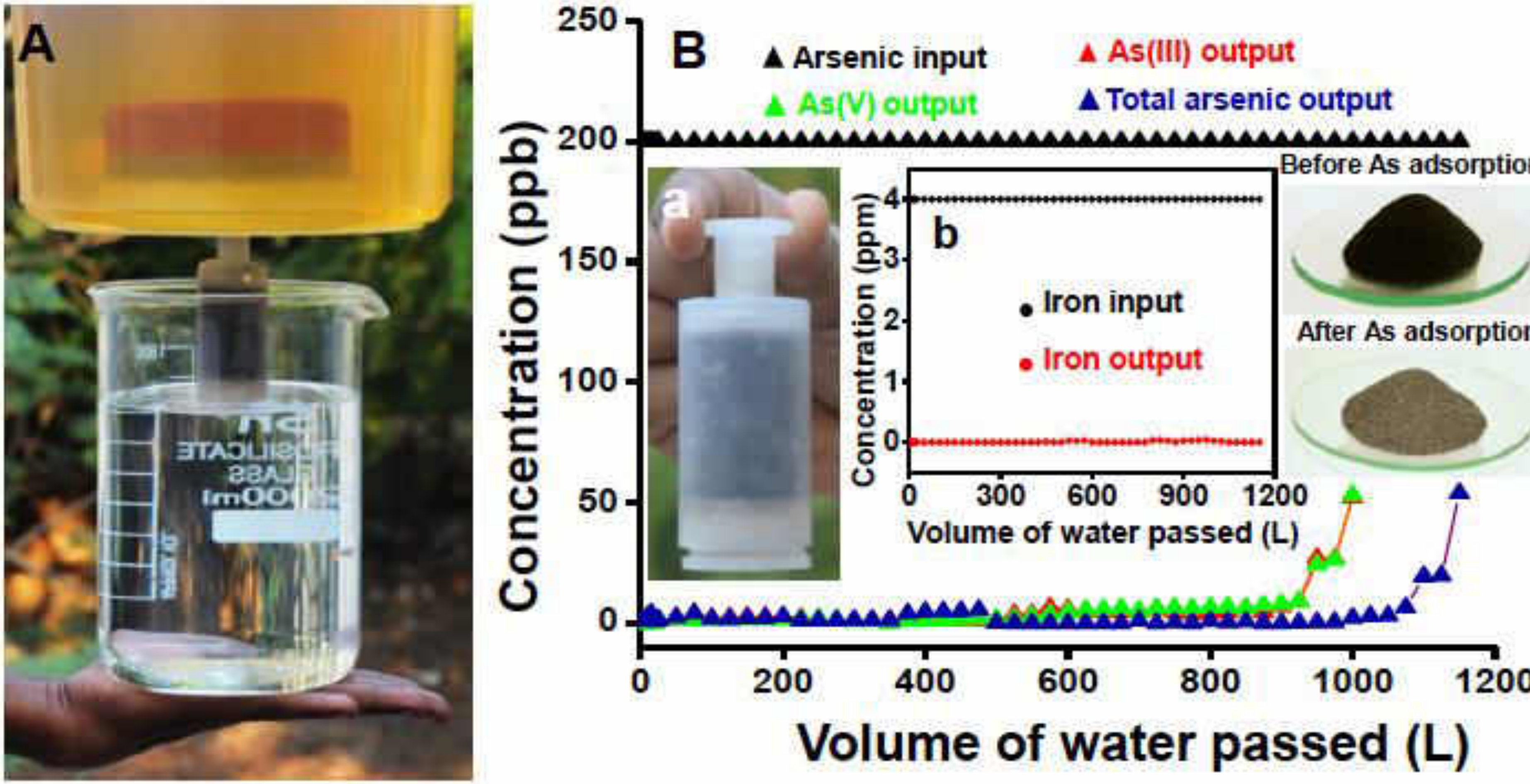
A
Fe2p3/2
711.1
Fe2p1/2
724.6
710.0
723.5
708.9
722.3
c
b
a
Intensity (counts)
B
As3d
As(V)
45.4
44.9
As(III)
44.5
44.3
c
cs
b
bs
a
HO
OH
As
C
c
cl
b
bl
a
A1
B1
E
As(V)aq
As(III)aq
Binding Energy (eV)
Raman Shift (cm-1)

Modeling surfaces



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

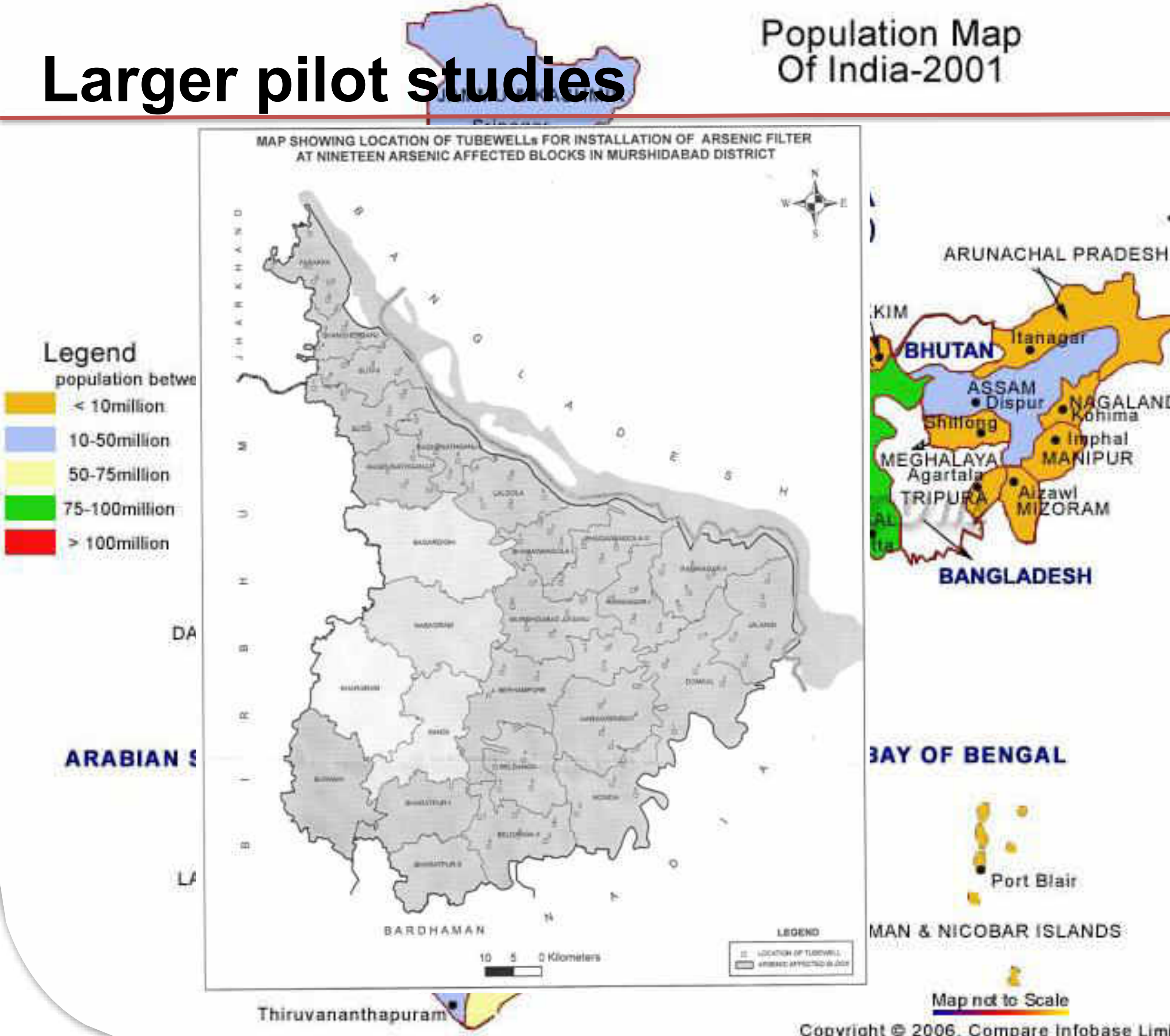
Lab studies



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

Initial pilot studies

Larger pilot studies



Changing the dynamics in the field

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

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

Implementation - From 25 KLD to 1 MLD

Large water supply schemes

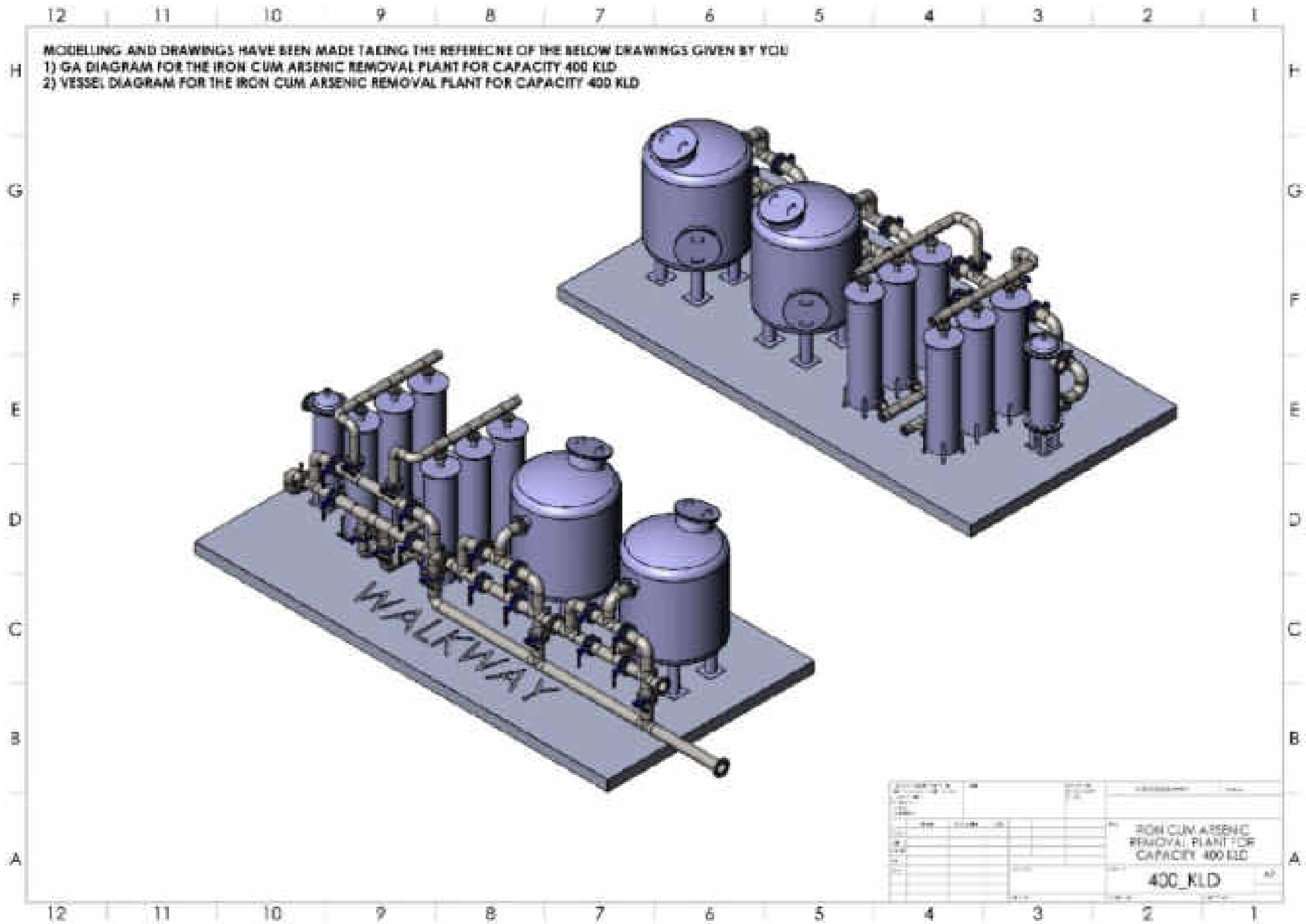
Capacity: above 1 MLD

5 schemes in use across India

Retrofitted Water Purification Plant

Capacity: 0.1-1 MLD

Over 180 units in use across India

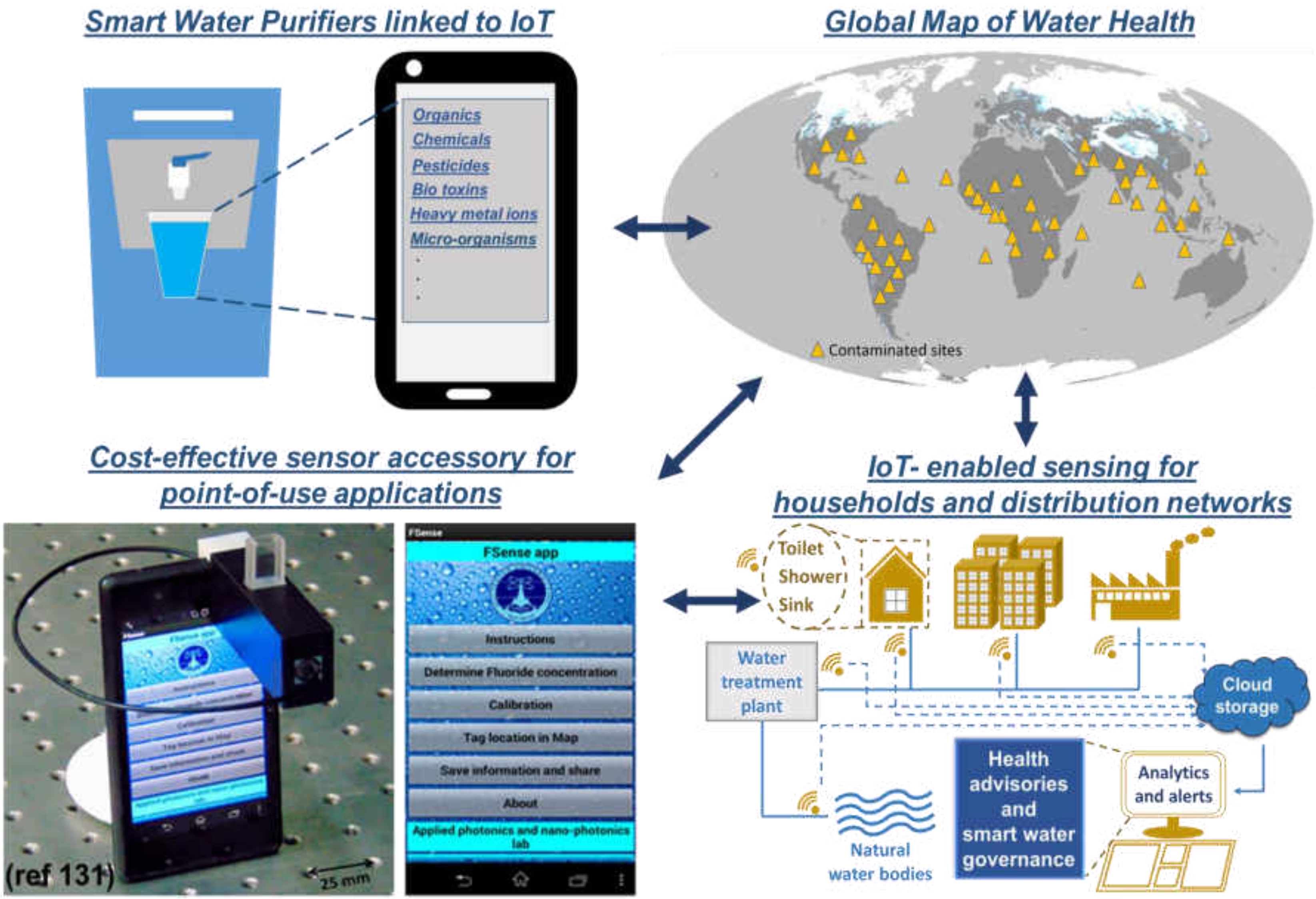

MODELLING AND DRAWINGS HAVE BEEN MADE TAKING THE REFERECNE OF THE BELOW DRAWINGS GIVEN BY YOU
1) GA DIAGRAM FOR THE IRON CUM ARSENIC REMOVAL PLANT FOR CAPACITY 400 KLD
2) VESSEL DIAGRAM FOR THE IRON CUM ARSENIC REMOVAL PLANT FOR CAPACITY 400 KLD
WALKWAY
IRON CUM ARSENIC REMOVAL PLANT FOR CAPACITY 400 KLD
400_KLD

Cleanwater at 2.1 paise per litre!

Calculation for the Tariff to be collected for treated water (Revision if Required)

Sr.No.	Item/Description	Cost / Quantity	Remarks
	Design population	1,071	Plant capacity/70 LPCD
1	Cost of Replacement of Iron removal media	56400	After minimum two years if Iron concentration is more than 5 ppm. But iron concentration is more than 5 ppm at only two to three places. Therefore media may work for 3 years also.
2	Cost of Replacement of Arsenic removal media	978660	After minimum two years if Arsenic concentration is more than 100 ppb. But arsenic concentration is more than 100 ppb at only two to three places. Therefore media may work for 3 years also.
3	Cost of replacement of Activated Carbon	28560	
4	Total cost of Replacement of media	1063620	After minimum two years.
5	Total cost of Replacement of media for one year	531810	
6	Plant capacity	75000	ltr per day
7	Design population	1,071	Plant capacity/70 LPCD
8	Cost per litr of water	2.1 Paise per ltr	0.025 cents
9	Cost of replacement of media	**1.36**	Rs. per head per day =Media replacement cost per year/365/Design population
		40.80	per head per month for 70 LPCD water

Smart water purifiers and big data



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

Waste management

Adsorbents conform to toxicity characteristic leaching procedure

Elemental waste goes back to local environment

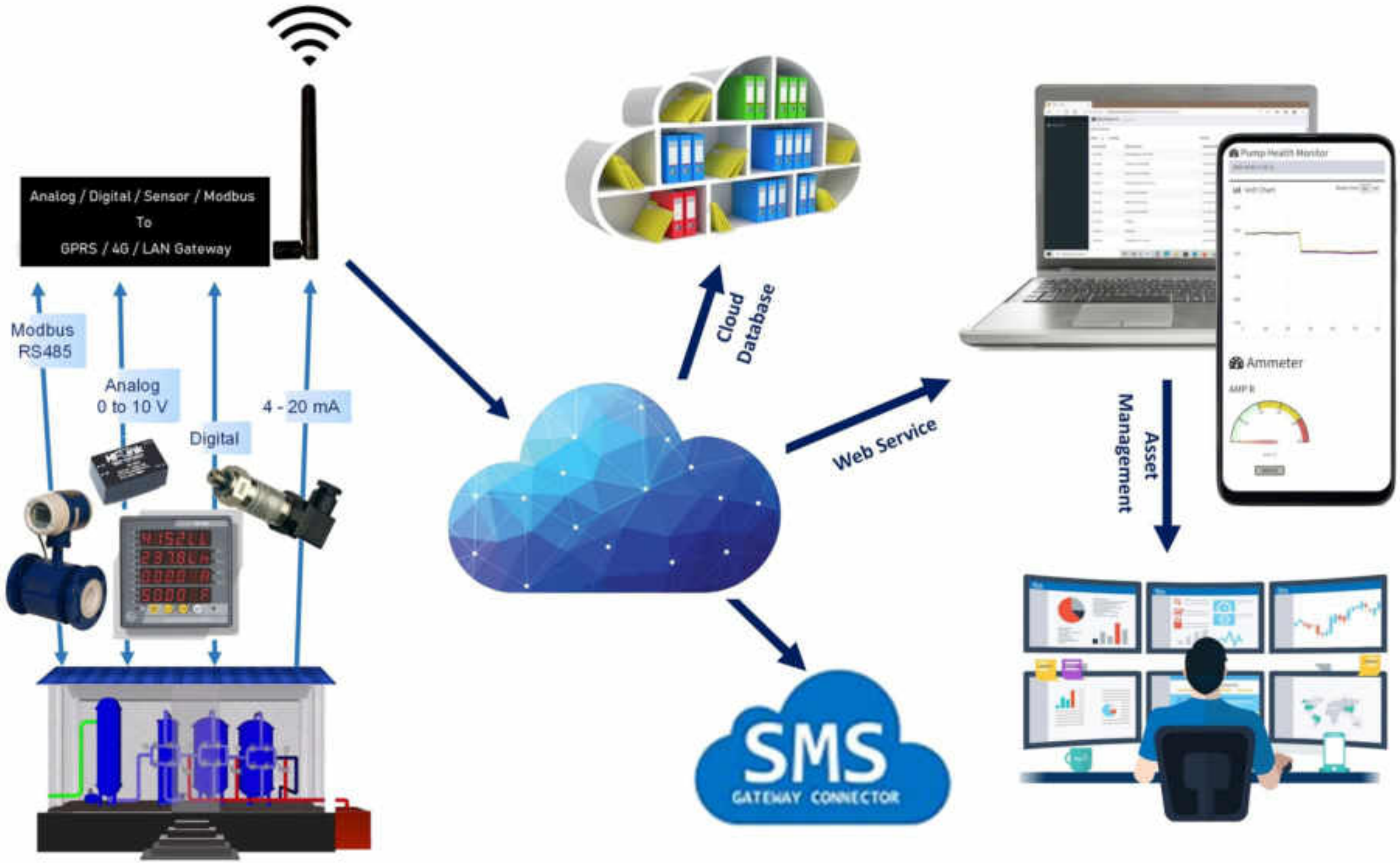
Safe disposal of arsenic (or any other) laden waste

Additional protection could be considered, if necessary

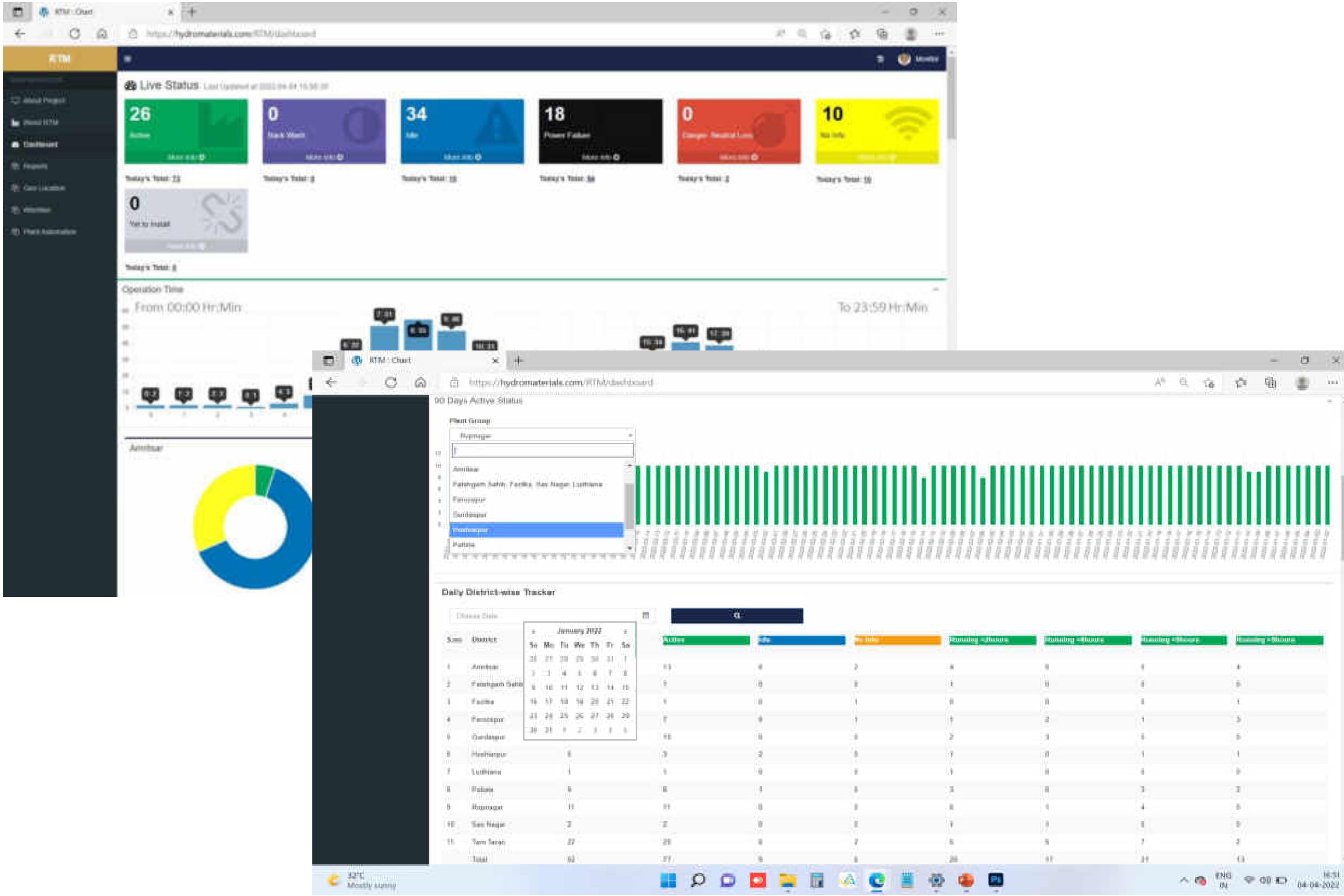
Exploring viable uses

Across the country

Components of IoT architecture implemented by DWSS, GoP

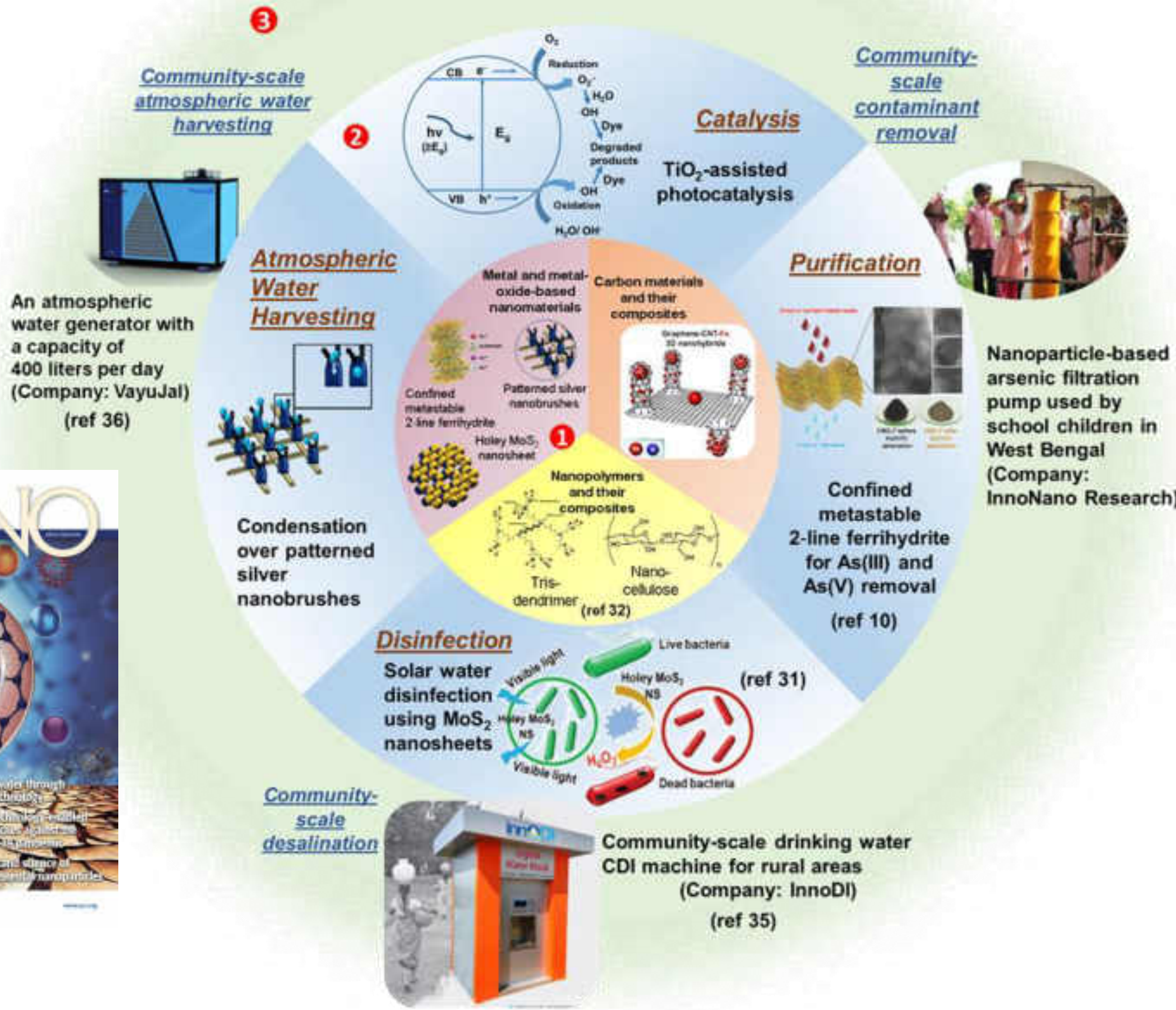


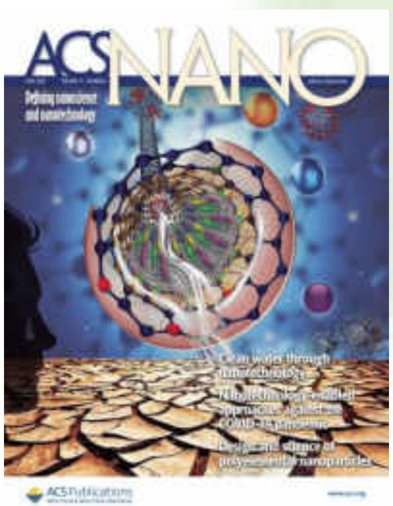
Typical IoT architecture comprises various sensors and meters, communication gateway, Cloud Server, SMS gateway, Webservices and mobile phone application for operator



RTM : Chart
https://hydromaterials.com/RTM/dashboard
RTM
Live Status
26
Active
0
34
Idle
18
Power Failure
0
10
No Info
0
Yet to Install
Operation Time
From 00:00 Hr:Min
To 23:59 Hr:Min
Amritsar
90 Days Active Status
Plant Group
Amritsar
Ferozepur
Gurdaspur
Hoshiarpur
Patiala
Daily District-wise Tracker
January 2022
S.no
District
Active
Idle
No Info
Amritsar
Fazilka
Ferozepur
Gurdaspur
Hoshiarpur
Ludhiana
Patiala
Rupnagar
Tarn Taran
Total

Evolution of materials to products





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

Sensors and new opportunities

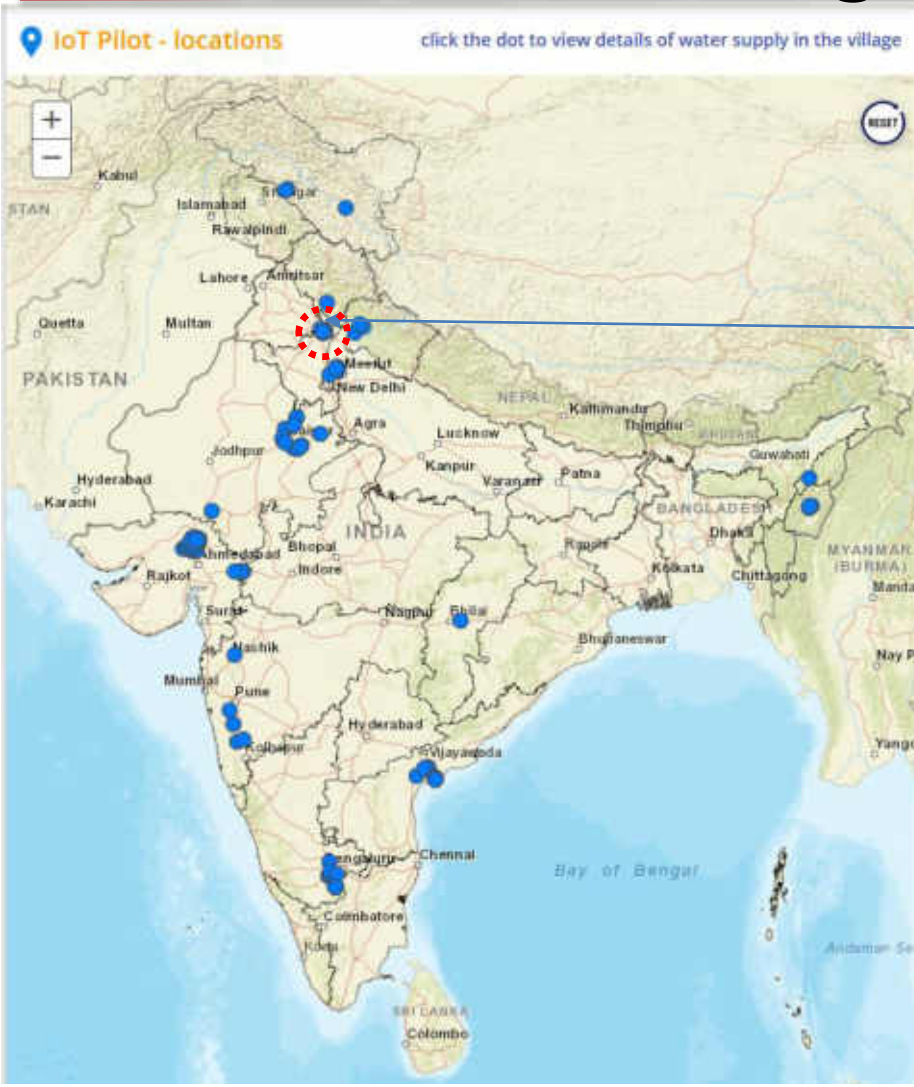
Analog/Grating
Equipment
$ 5~6 Billion (2017)
a few **100k units (2017)**

Ultra compact Low Cost Spectral Sensor Module
~ Billions units (? 2027)

Water quality measurement – In the pipeline

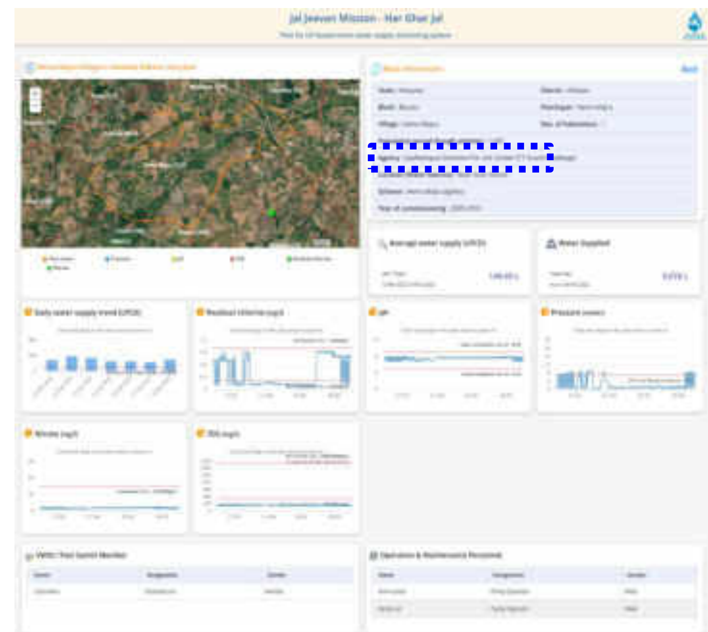
nanoλ

India’s water is being monitored



IITM/IISc

Installations made by four companies

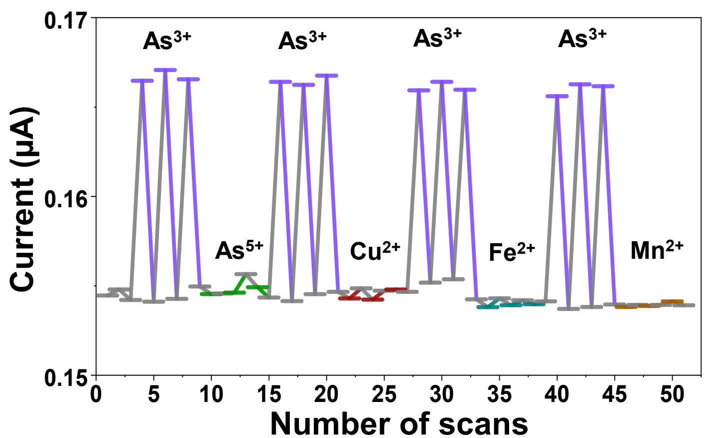


Mobile unit - A reagent free mobile water quality analyser

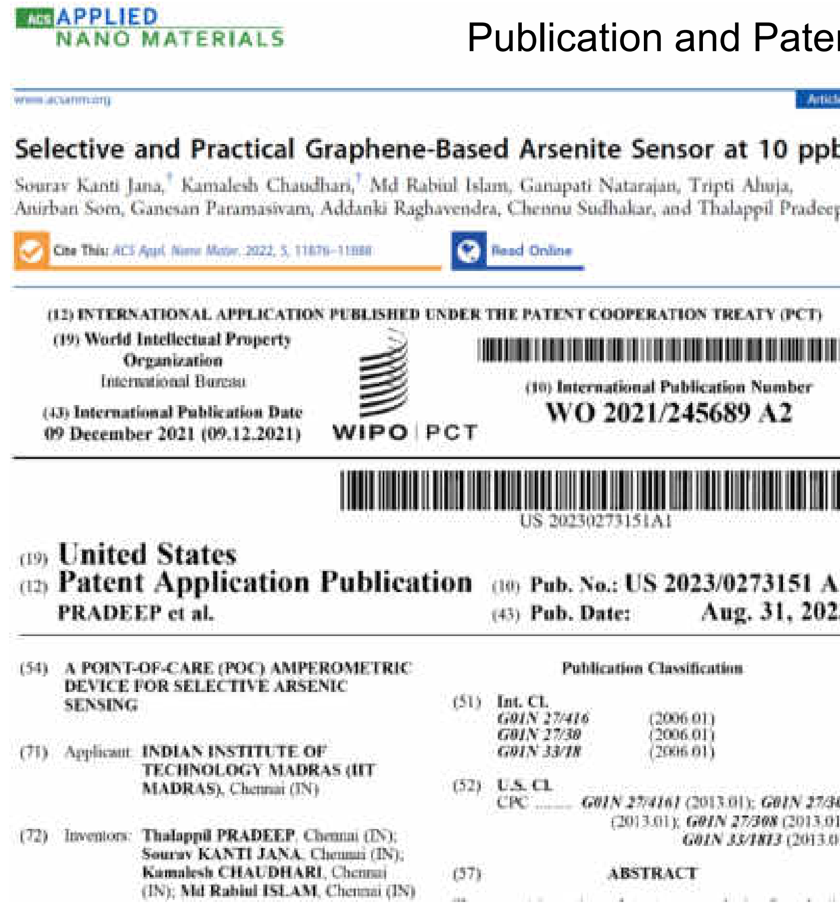
A drop-and-sense reagent free arsenic sensing test strips

IIT Madras patented
Arsenic sensing technology

Reagent free, Reusable test strip with selective arsenic sensing
Drop-and-sense technology with no pretreatment of samples



Publication and Patents


ACS APPLIED NANO MATERIALS

www.acsanm.org Article

Selective and Practical Graphene-Based Arsenite Sensor at 10 ppb

Sourav Kanti Jana,[†] Kamalesh Chaudhari,[†] Md Rabiul Islam, Ganapati Natarajan, Tripti Ahuja, Anirban Som, Ganesan Paramasivam, Addanki Raghavendra, Chennu Sudhakar, and Thalappil Pradeep*

Cite This: ACS Appl. Nano Mater. 2022, 5, 11876−11888 Read Online

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International Bureau

(43) International Publication Date
09 December 2021 (09.12.2021)

WIPO | PCT

(10) International Publication Number
WO 2021/245689 A2

US 20230273151A1

(19) United States
(12) Patent Application Publication
PRADEEP et al.

(10) Pub. No.: US 2023/0273151 A1
(43) Pub. Date: Aug. 31, 2023

(54) A POINT-OF-CARE (POC) AMPEROMETRIC DEVICE FOR SELECTIVE ARSENIC SENSING

(71) Applicant: INDIAN INSTITUTE OF TECHNOLOGY MADRAS (IIT MADRAS), Chennai (IN)

(72) Inventors: Thalappil PRADEEP, Chennai (IN); Sourav KANTI JANA, Chennai (IN); Kamalesh CHAUDHARI, Chennai (IN); Md Rabiul ISLAM, Chennai (IN)

Publication Classification

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G01N 27/30 (2006.01)
G01N 33/18 (2006.01)

(52) U.S. Cl.
CPC G01N 27/4161 (2013.01); G01N 27/307 (2013.01); G01N 27/308 (2013.01); G01N 33/1813 (2013.01)

(57) ABSTRACT


Policy

International Centre for Clean Water

Clathrate hydrates

Ice – why should we care?

Ice is big in scale - 10 percent of the land area on Earth is covered with glacial ice. Glacierized areas cover over 15 million square kilometers.

Ice is there everywhere, including in space - naturally

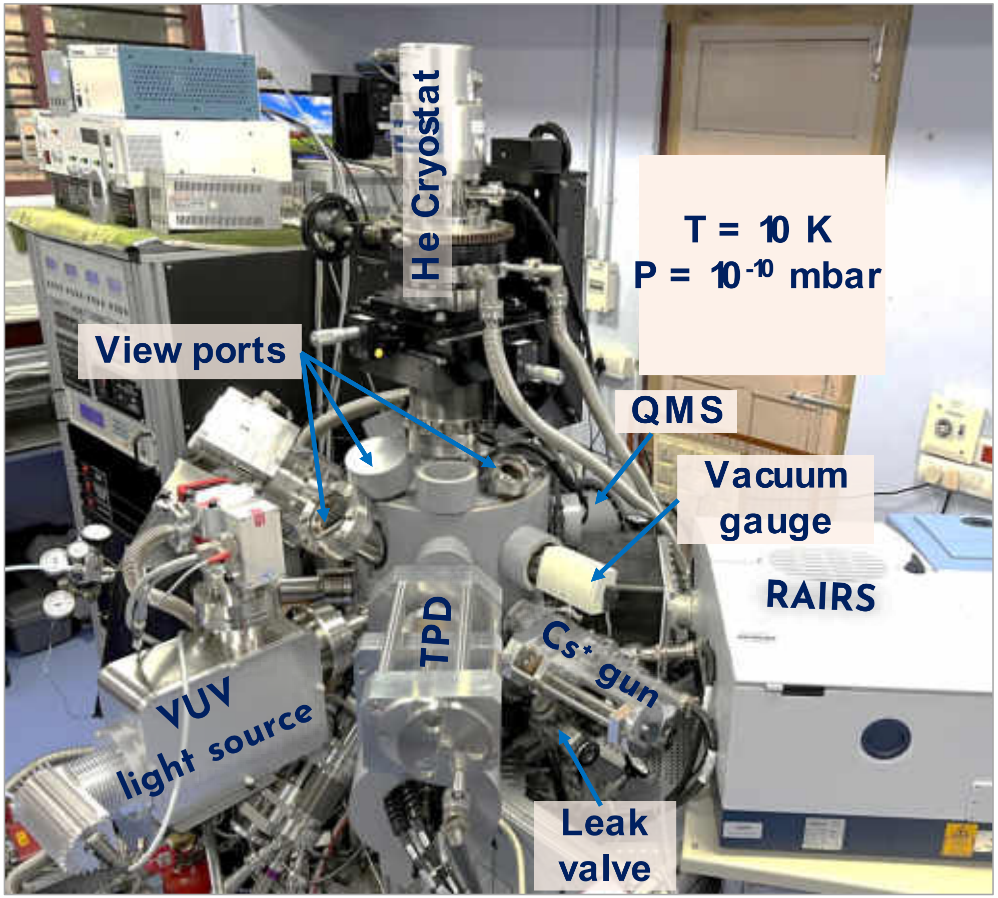
Ice could be a vehicle for life on Earth - astrobiology

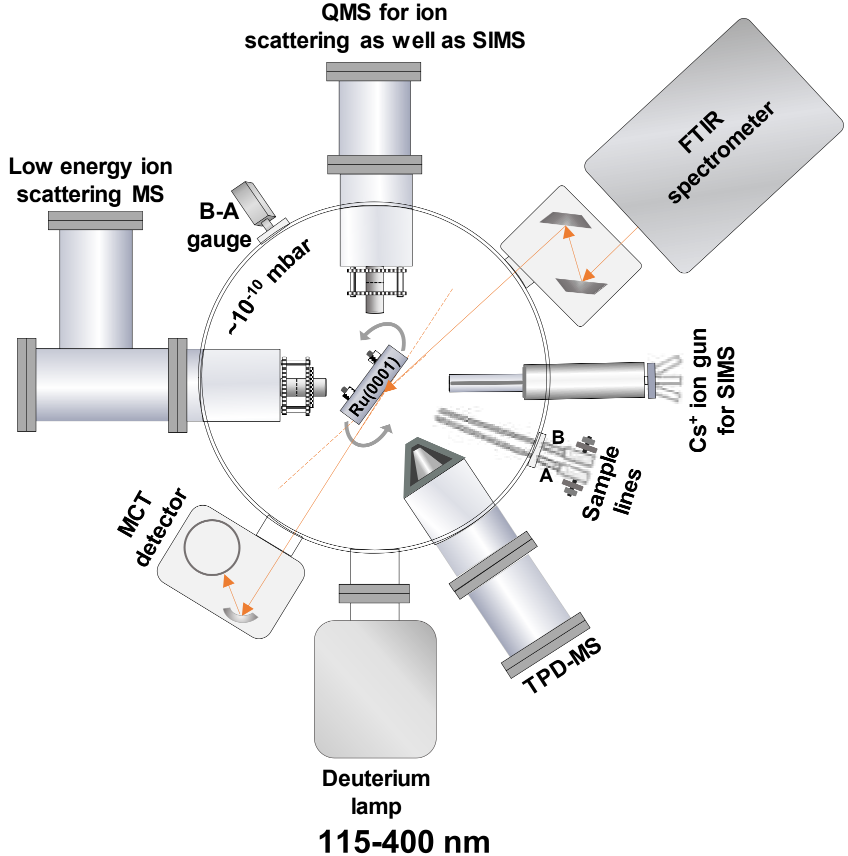
Ice can make clathrates

Water is not understood – especially in its condensed form

Condensed molecular solids are all ices

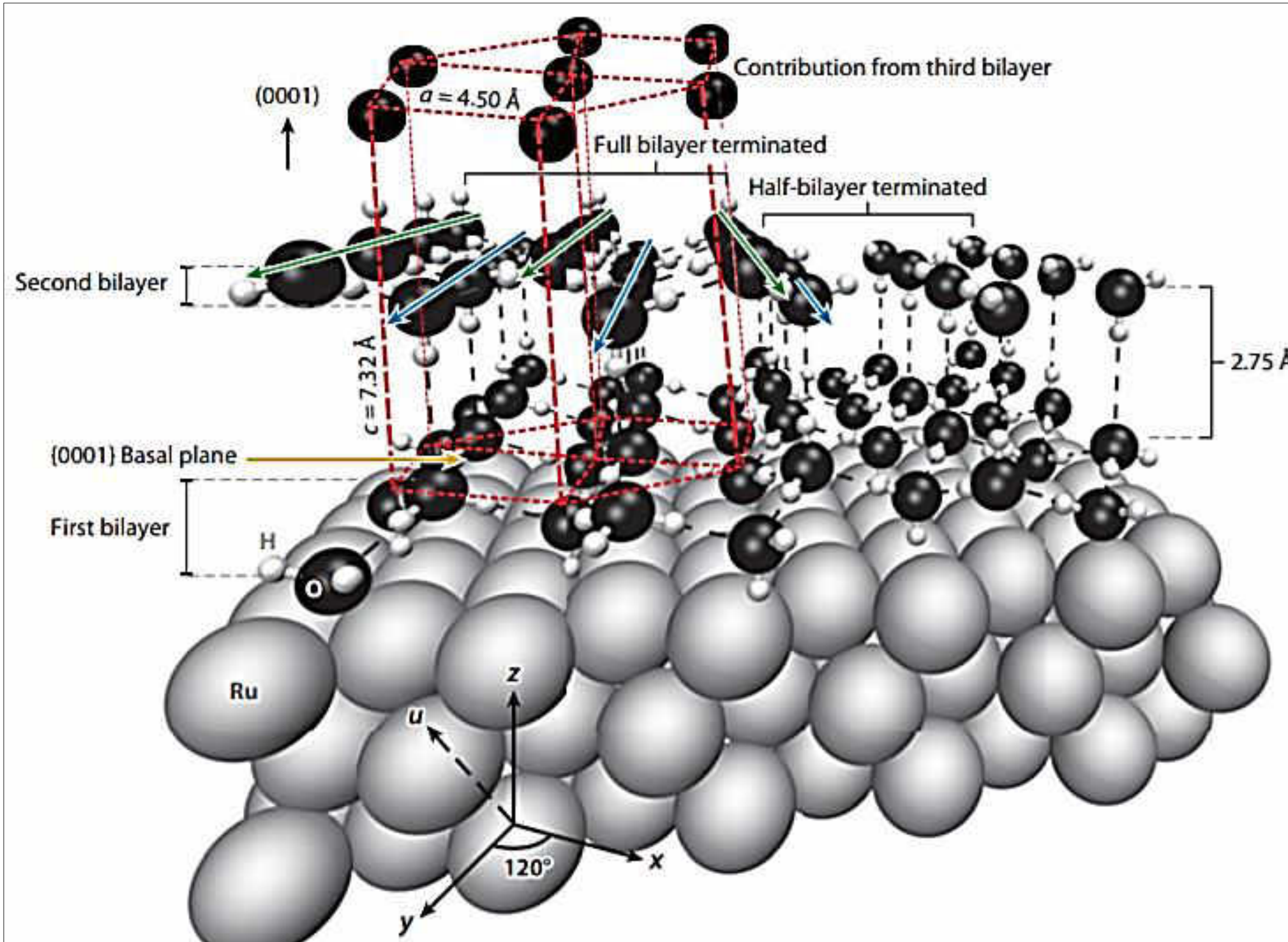
Instrumentation





Bag, S. *et al.*, *Rev. Sci. Instrum.* **2014**, *85*, 014103/1-014103/7

Viswakarma, *G. et al., J. Phys. Chem. Lett.*, **2023**, *14*, 2823–2



Bag, S. *et al.*, *Annu. Rev. Anal. Chem.* **2013**, *6*, 97–118

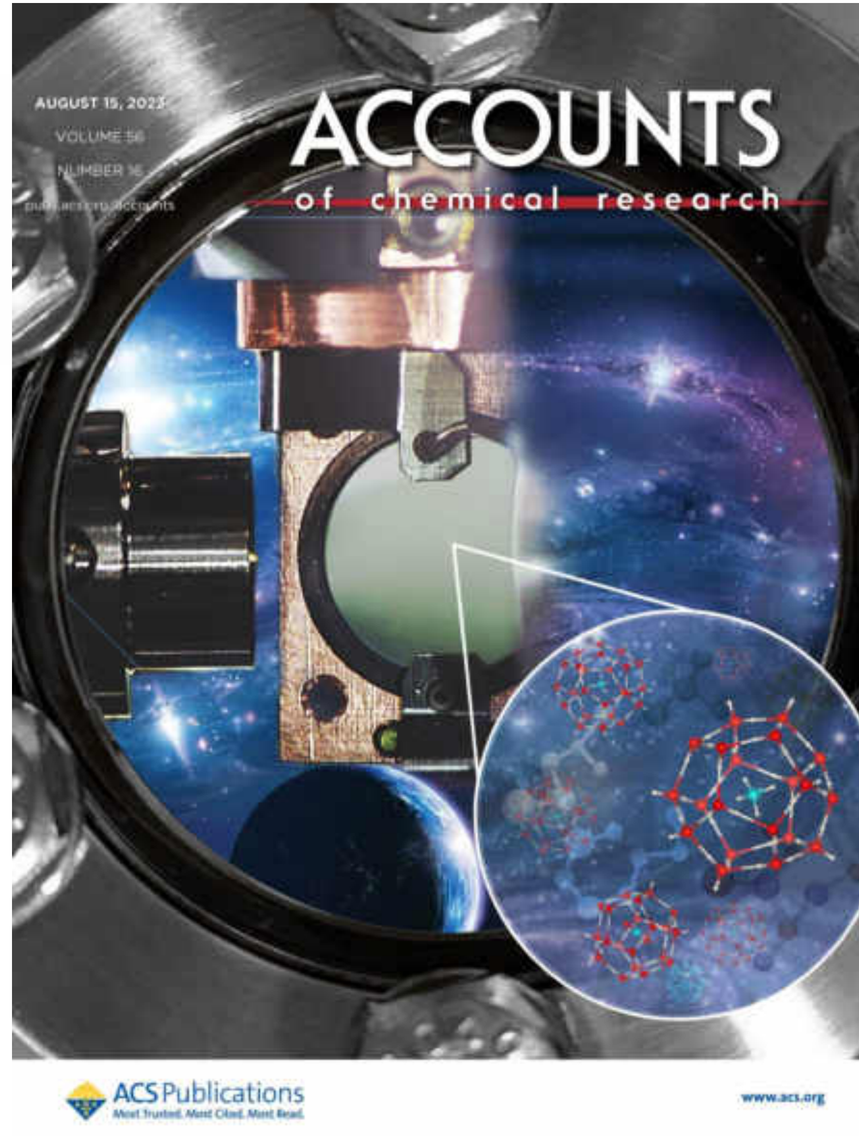
Instrumentation

ACCOUNTS
of chemical research
pubs.acs.org/accounts
Article

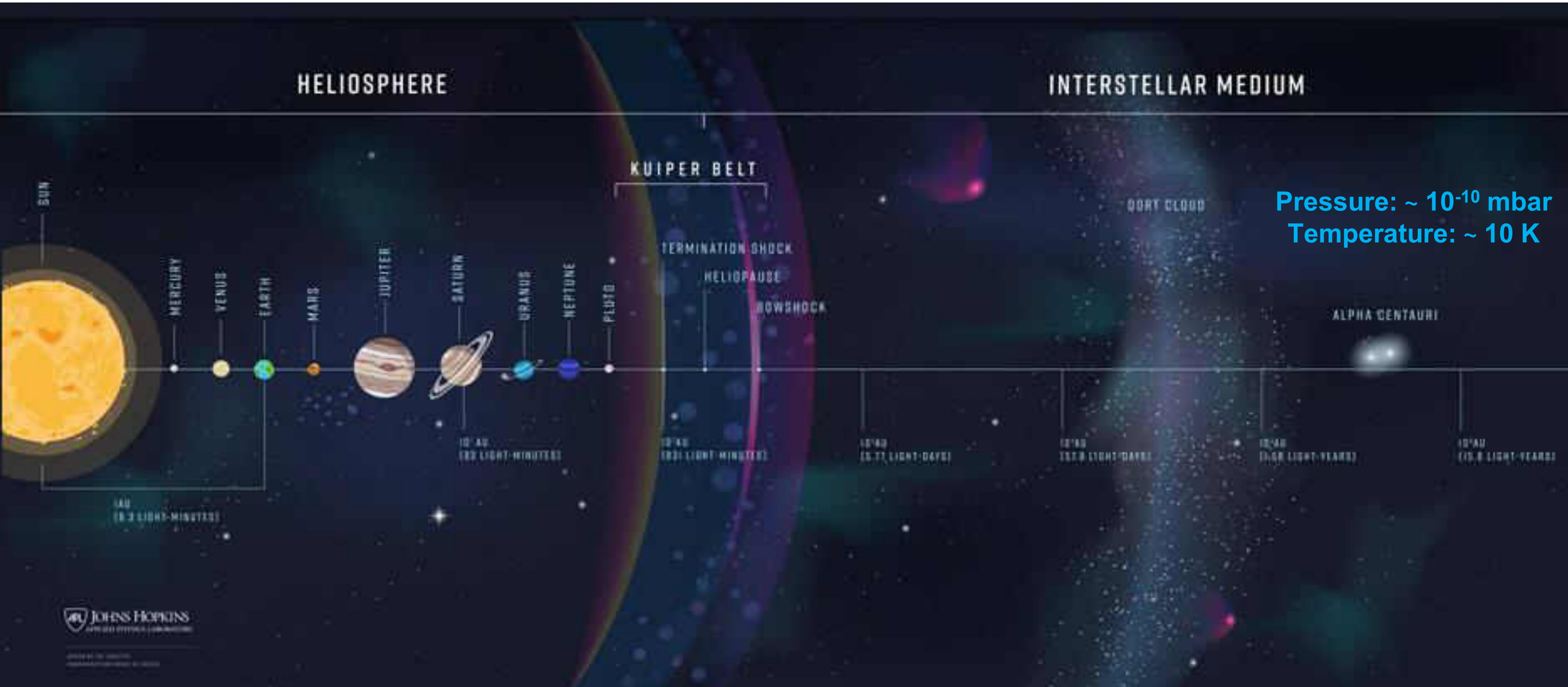
Formation and Transformation of Clathrate Hydrates under Interstellar Conditions

Jyotirmoy Ghosh, Gaurav Vishwakarma, Rajnish Kumar,* and Thalappil Pradeep*

Cite This: https://doi.org/10.1021/acs.accounts.3c00317
Read Online



Interstellar medium

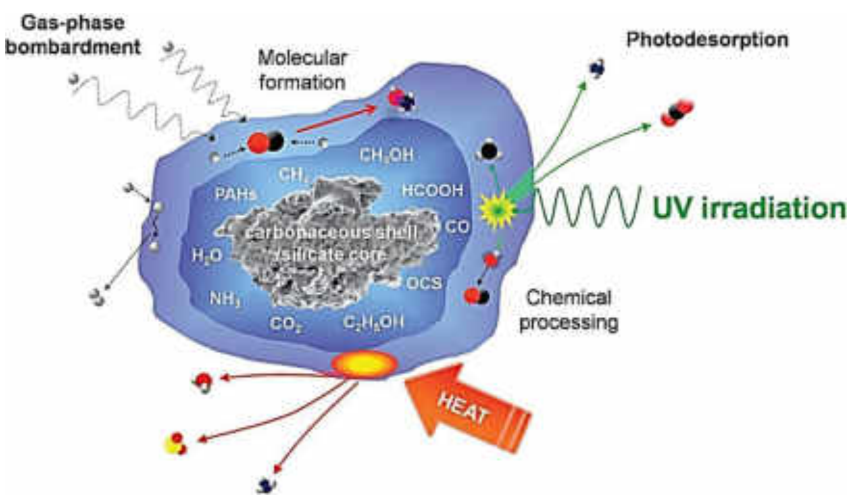


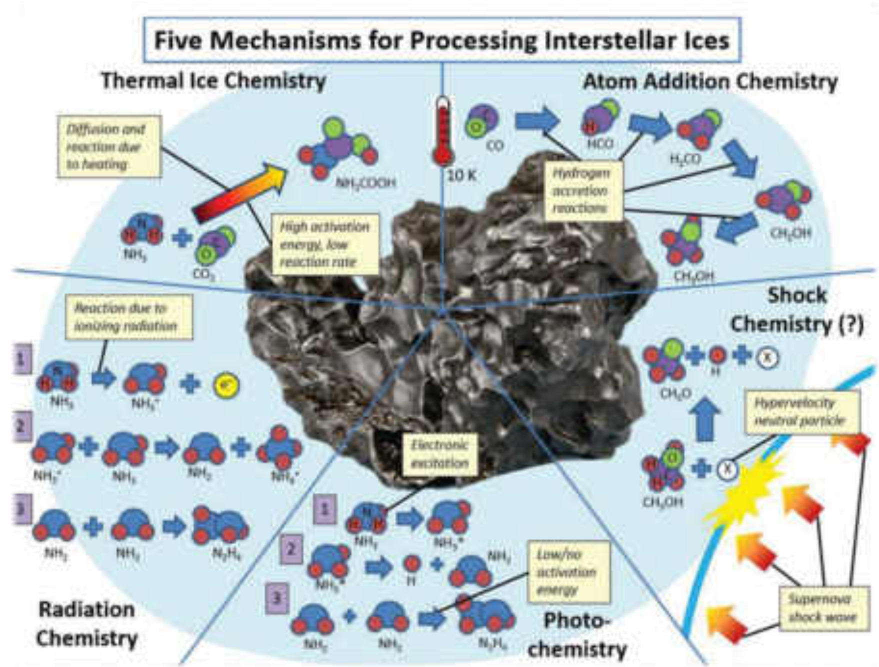
Pressure: ~ 10^{-10} mbar
Temperature: ~ 10 K

Diffuse clouds: T ~ 100 K, n ~ 100 molecules per cm^3
Dense clouds: T ~ 10-100 K, n ~ 10^4-10^8 molecules per cm^3
On Earth sea level: T ~ 300 K, n ~ 3×10^{19} molecules per cm^3

https://spaceref.com/science

Interstellar ices





Silicates and carbonaceous material – 0.01-0.5 µm

Arumainayagam, C. R. *et al., Chem. Soc. Rev.,* **2019**, *48*, 2293–2314

Applications of clathrate hydrates

"Ice on fire" burning of methane hydrate

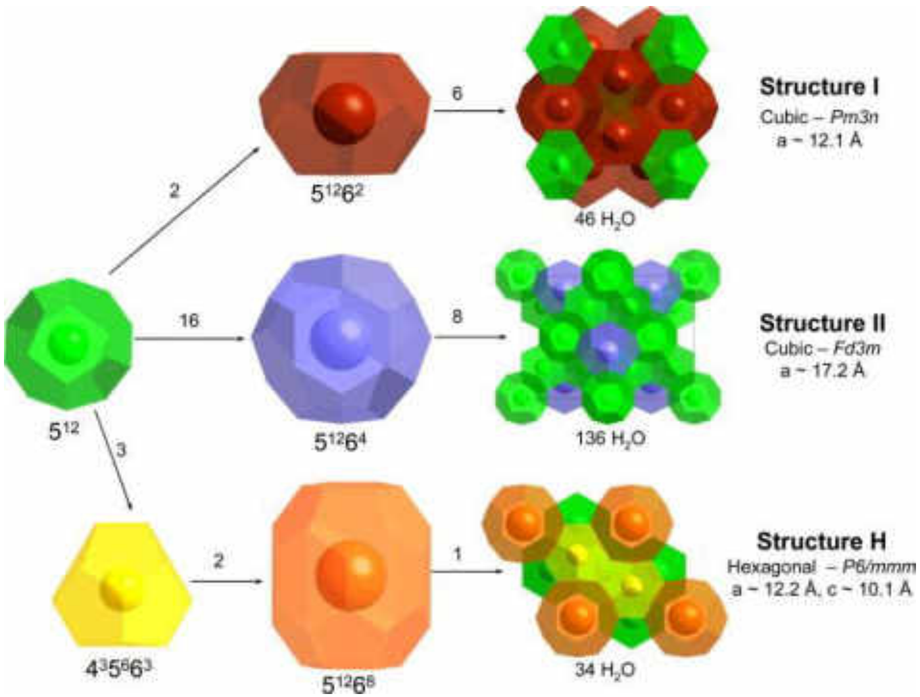
Applications:

- Renewable energy source.
- Storage of natural gases and hydrogen (H_2).
- Separation of flue gases and desalination of seawater.
- Flow assurance in gas pipelines.

Gas hydrate plug recovered from a subsea pipeline

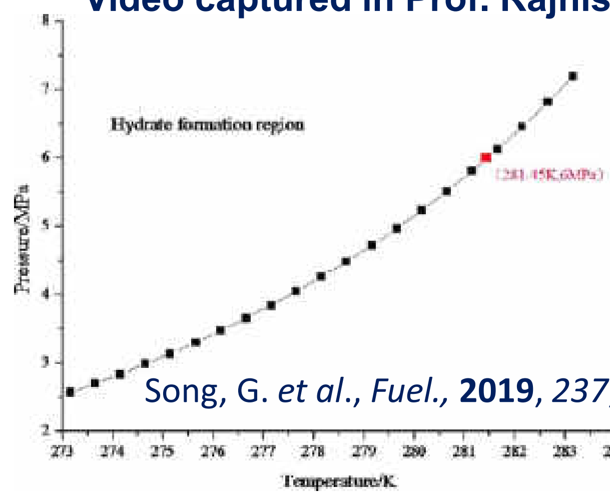
Koh, A.C. *et al., Annu. Rev. Chem. Biomol. Eng.* **2011**, *2*, 237-257

Clathrate hydrates



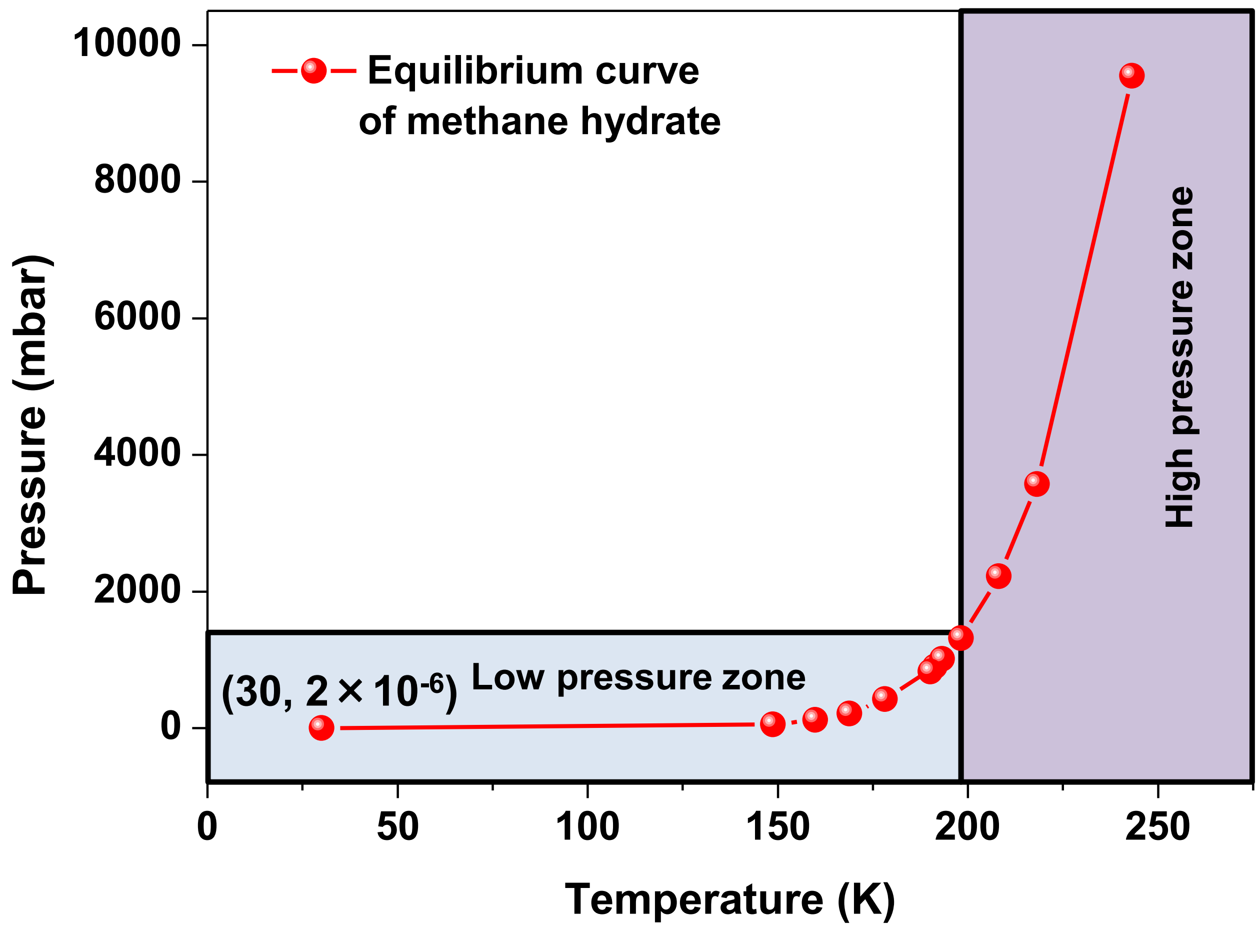
Strobel, T. A. *et al.*, *Chem. Phys. Lett.*, **2009**, *478*, 97–109

Video captured in Prof. Rajnish Kumar's



Song, G. *et al.*, *Fuel.*, **2019**, *237*, 475-485

Clathrate hydrates at extreme low pressure

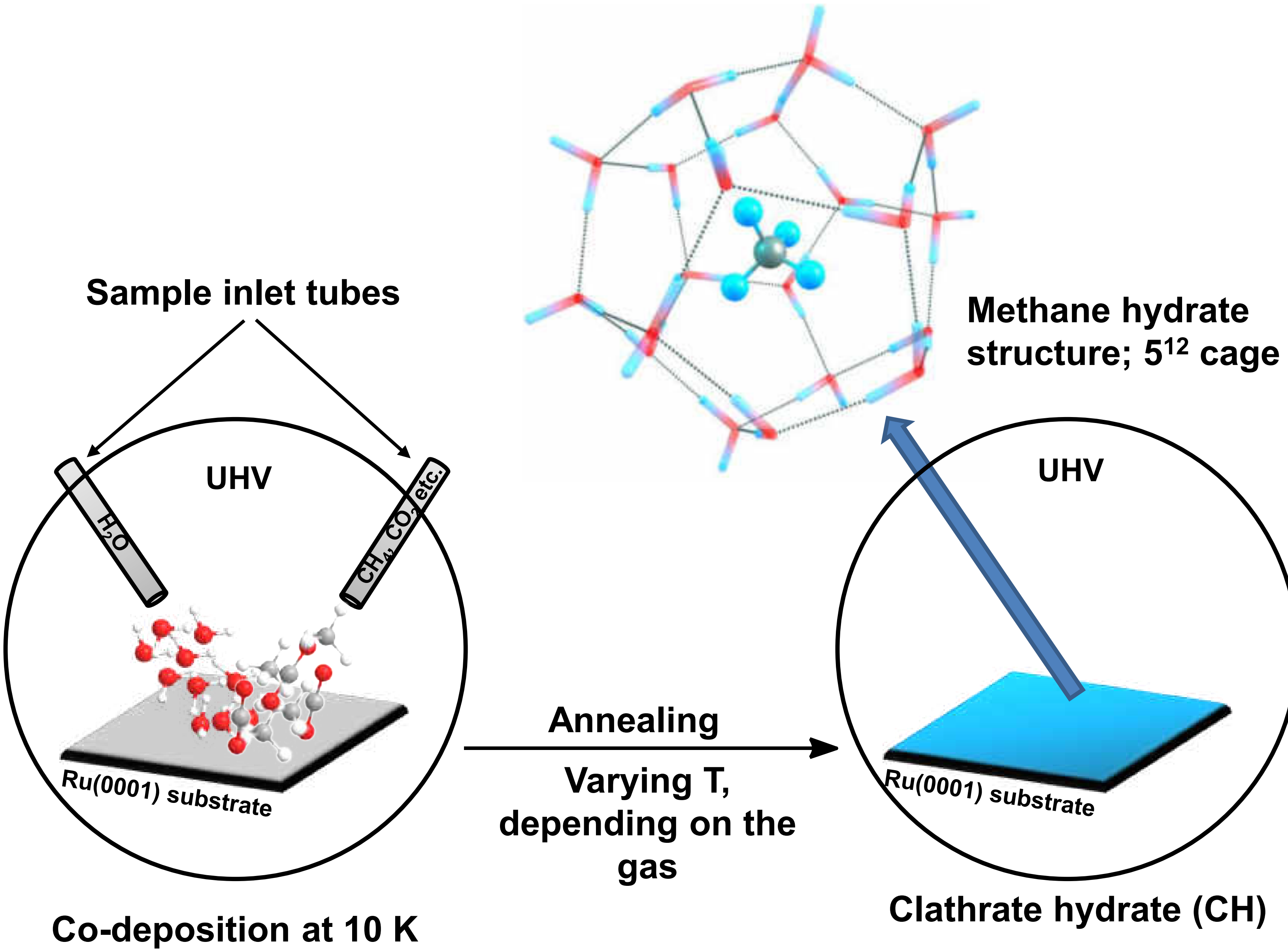


Sloan, E.D.; Koh, C. A., *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press: Boca Raton, FL, 2008

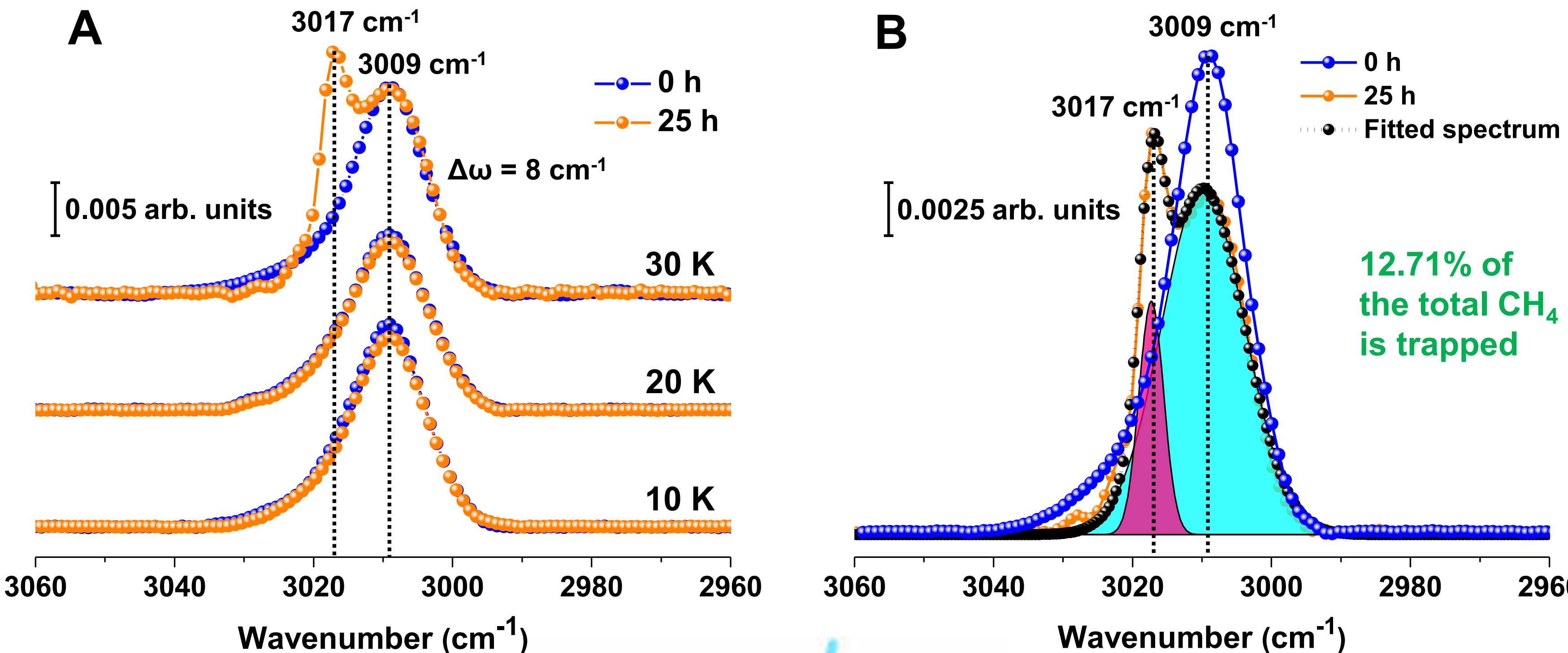
Clathrate hydrates in interstellar environment

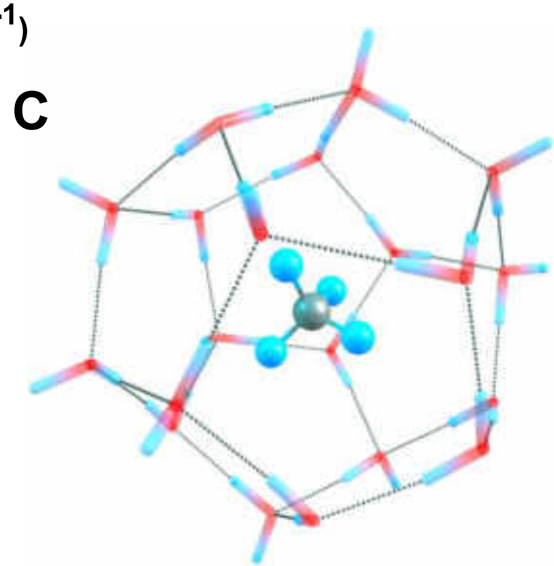
Ghosh, J. *et al., Proc. Natl. Acad. Sci. U.S.A.*, **2019**, *116*, 1526-1531

Experimental method



Clathrate hydrates in interstellar environment



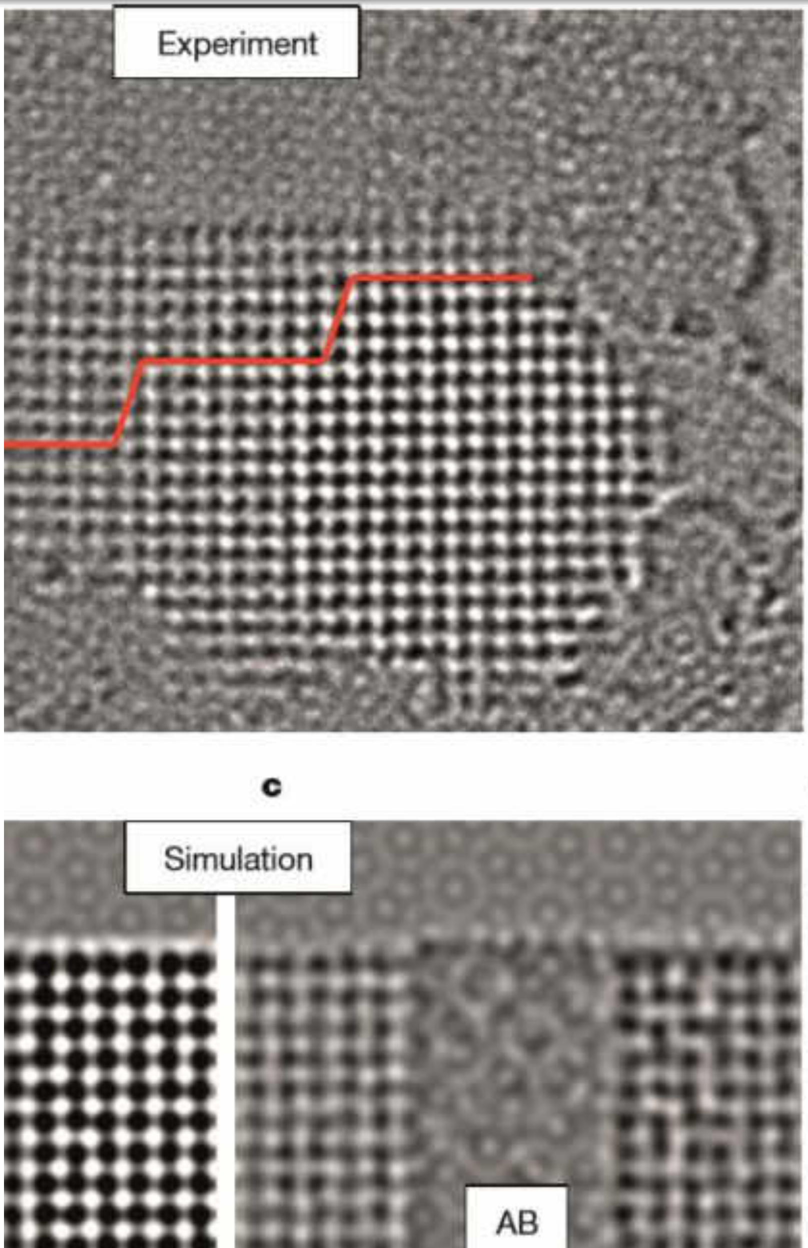


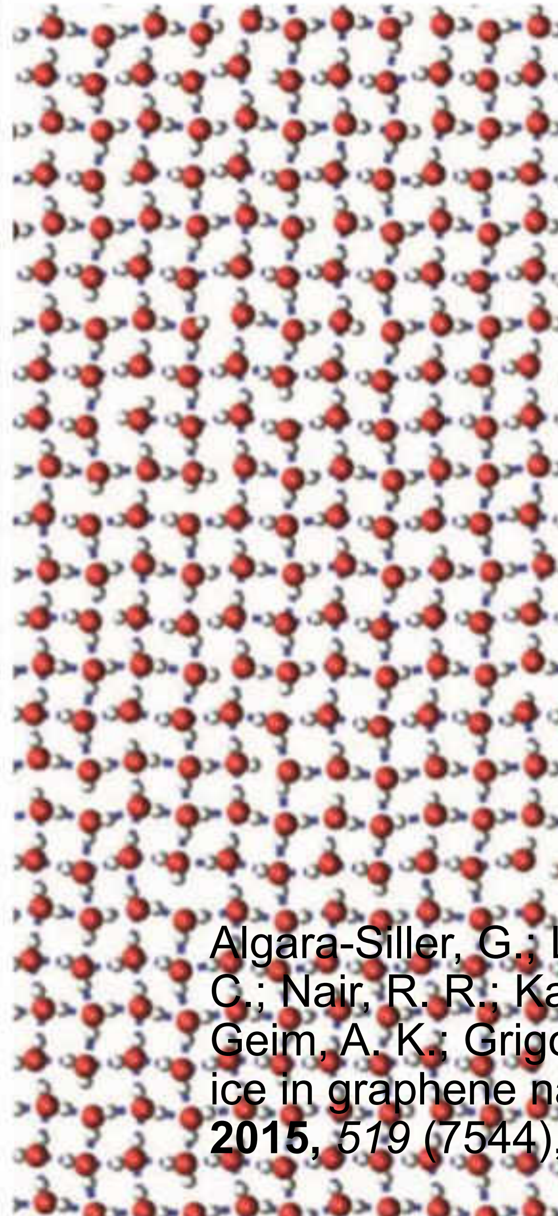
5^{12} cage of CH_4 hydrate

Ghosh, J. *et al., Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116*, 1526-1531

Future

Observing clathrate hydrates?



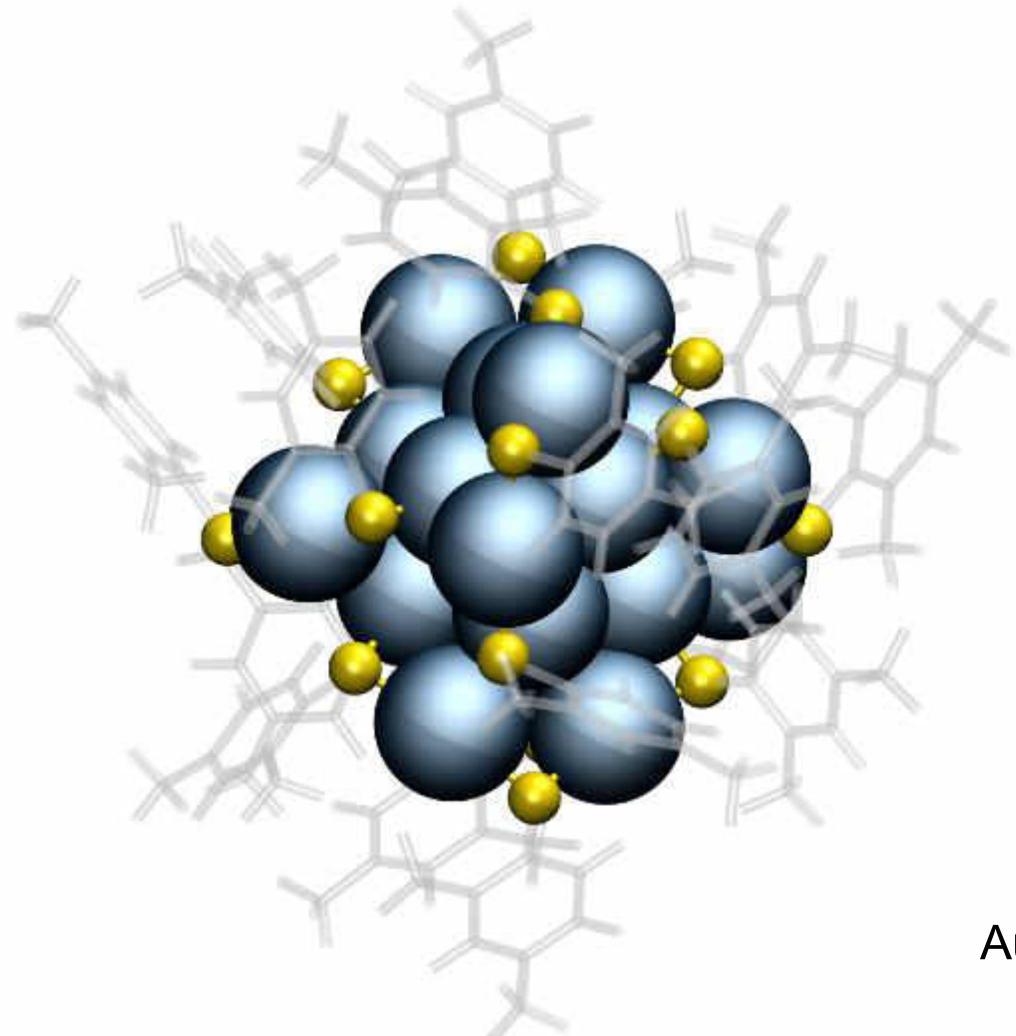


Algara-Siller, G.; Lehtinen, O.; Wang, F. C.; Nair, R. R.; Kaiser, U.; Wu, H. A.; Geim, A. K.; Grigorieva, I. V., Square ice in graphene nanocapillaries. *Nature* **2015**, *519* (7544), 443-445.


M FACILITY

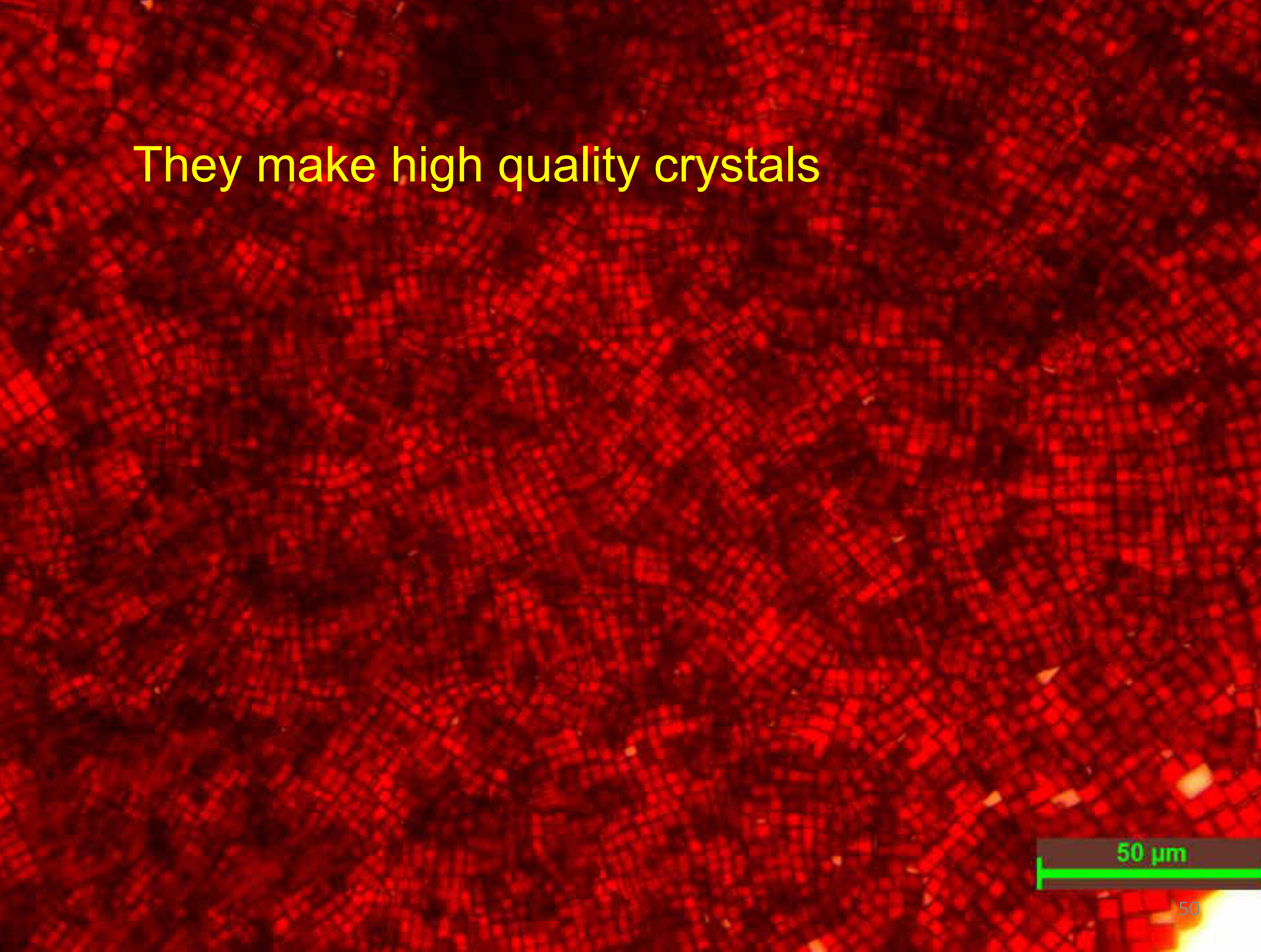
Atomically Precise Clusters

New molecules

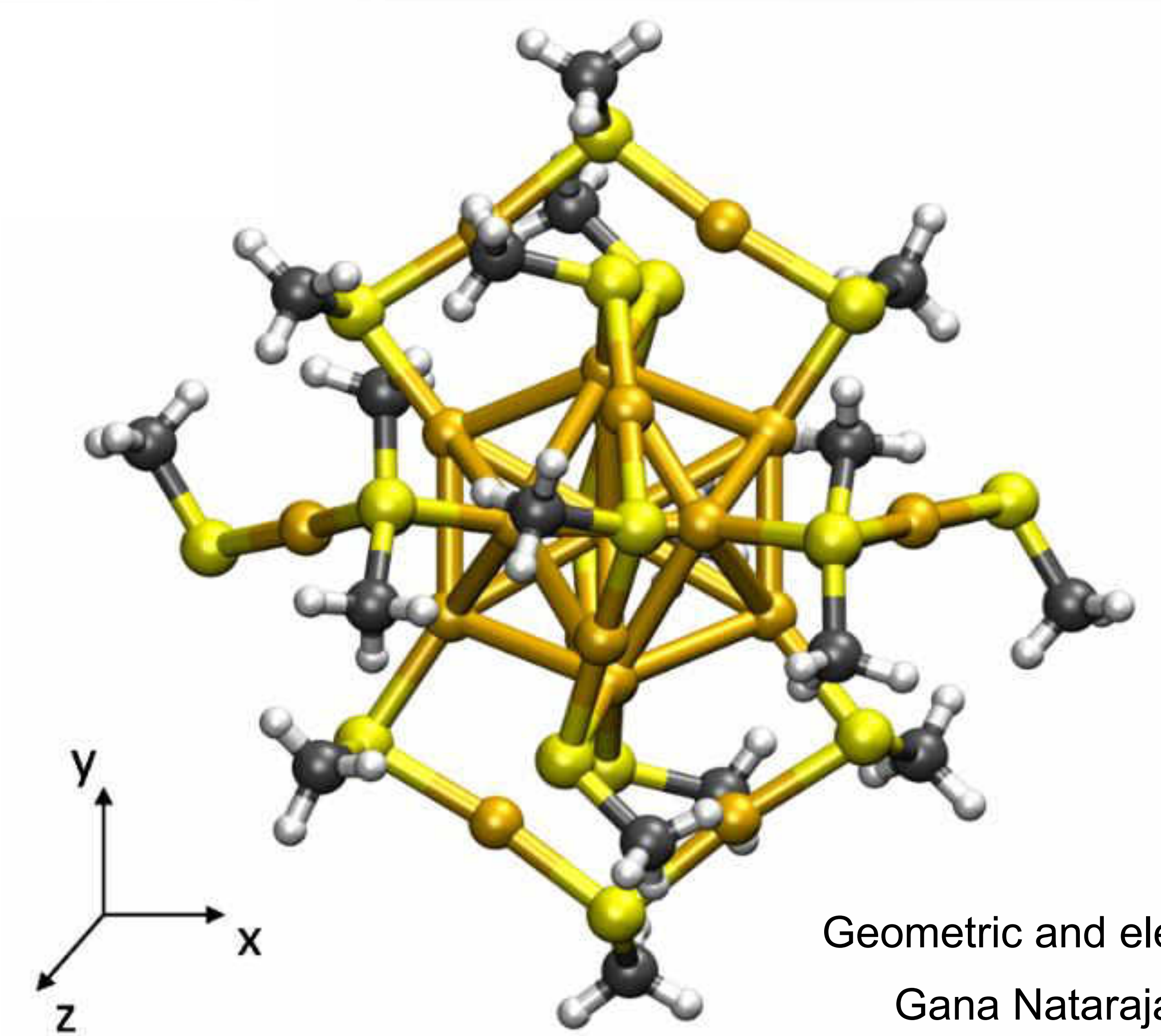


Au_{25}, Ag_{25}, Ag_{29}

They make high quality crystals



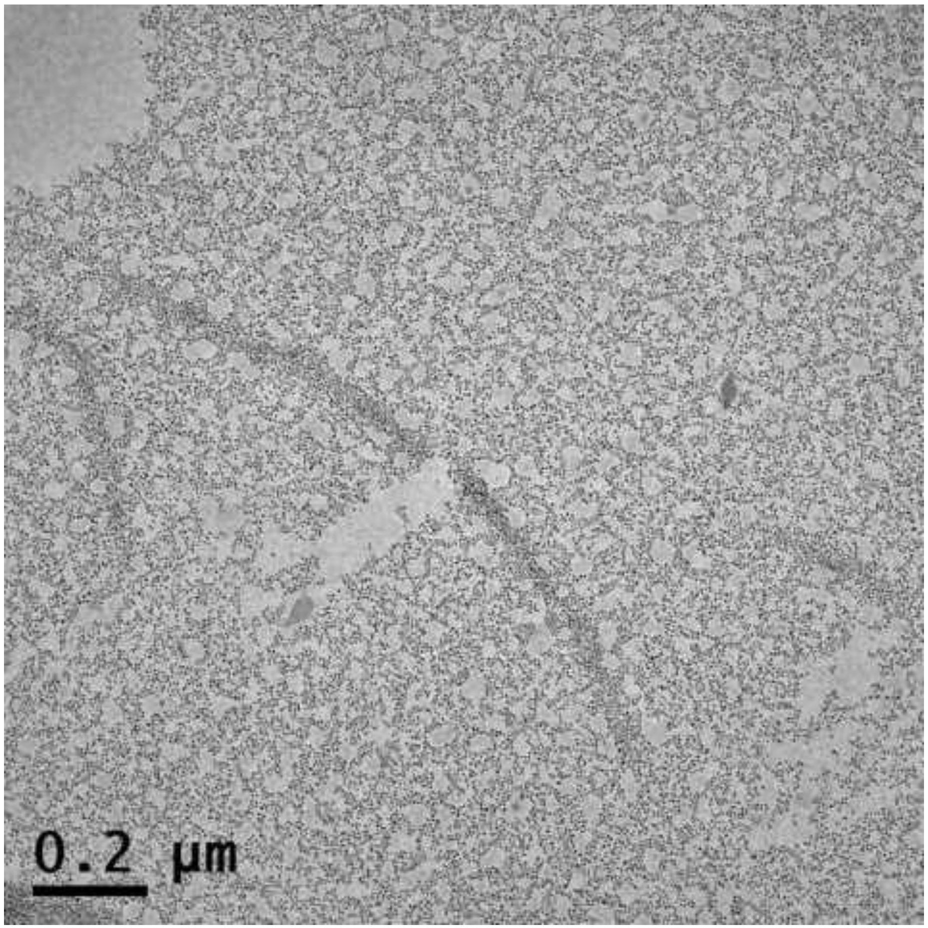
Molecular structure

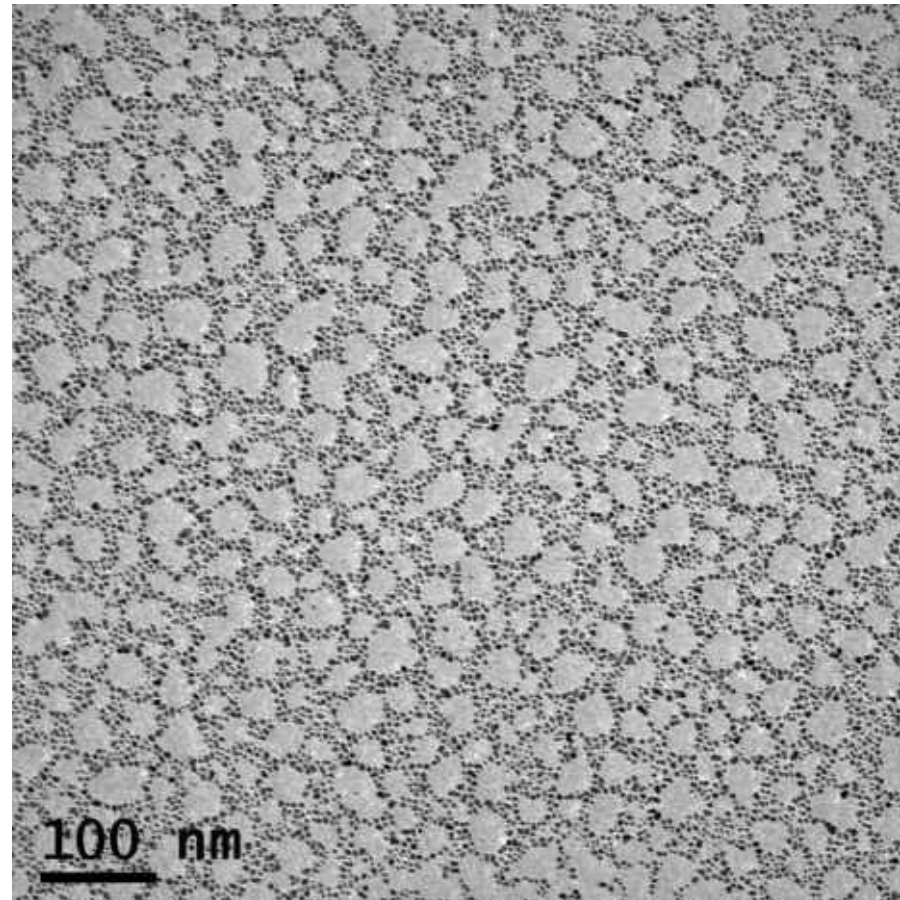


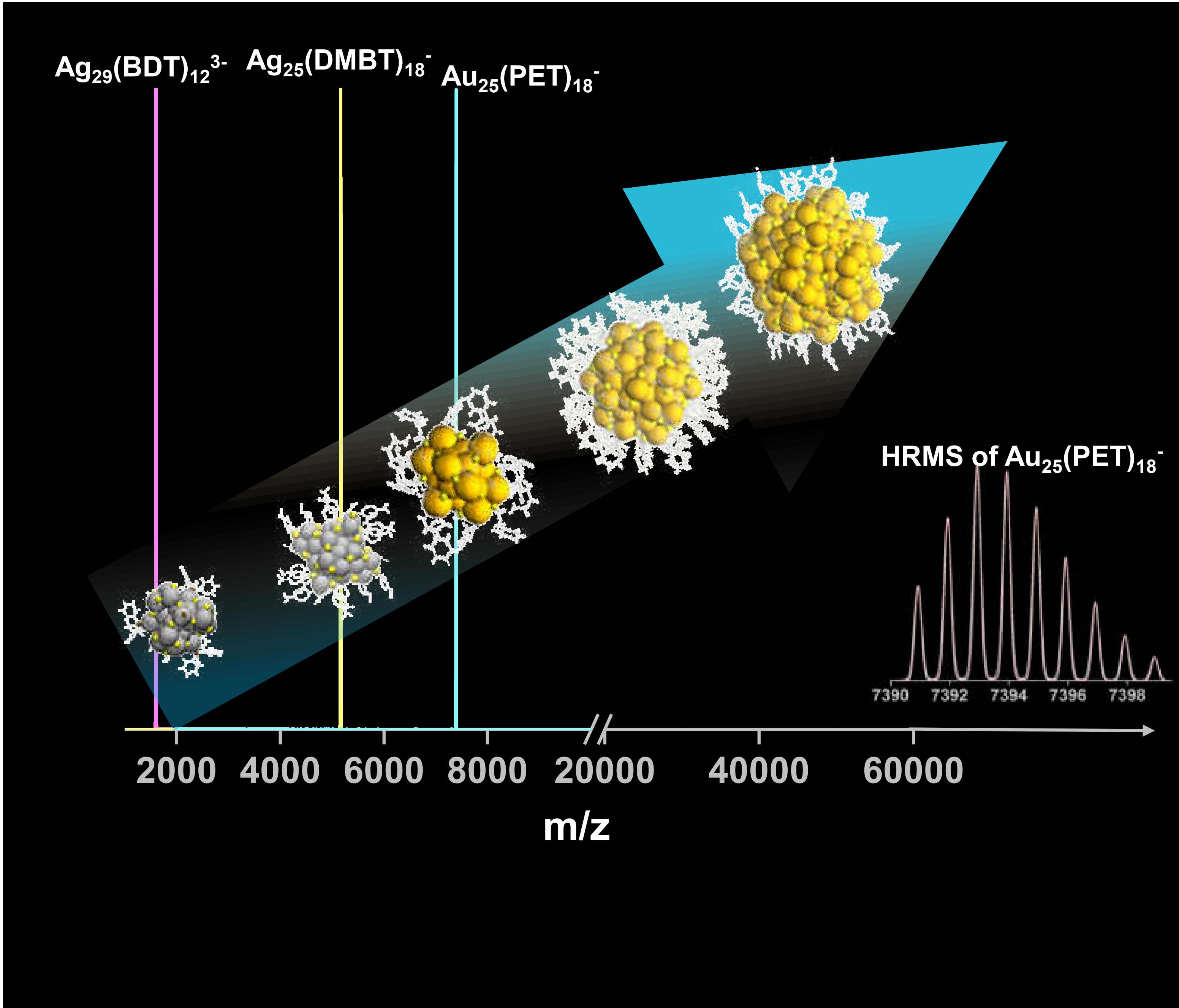
Geometric and electronic shells

Gana Natarajan

TEM images of Au_{25} and Au_{144}

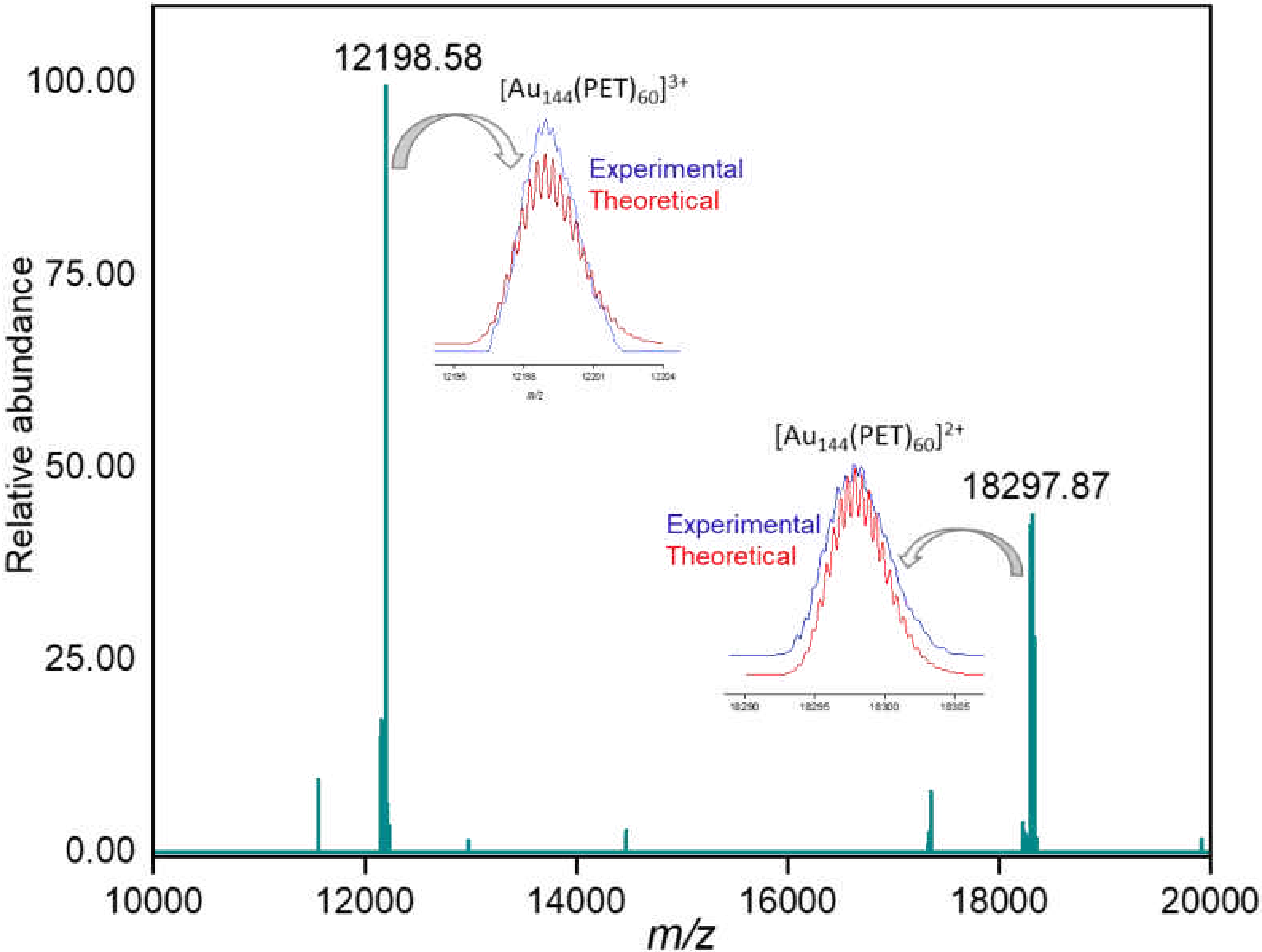




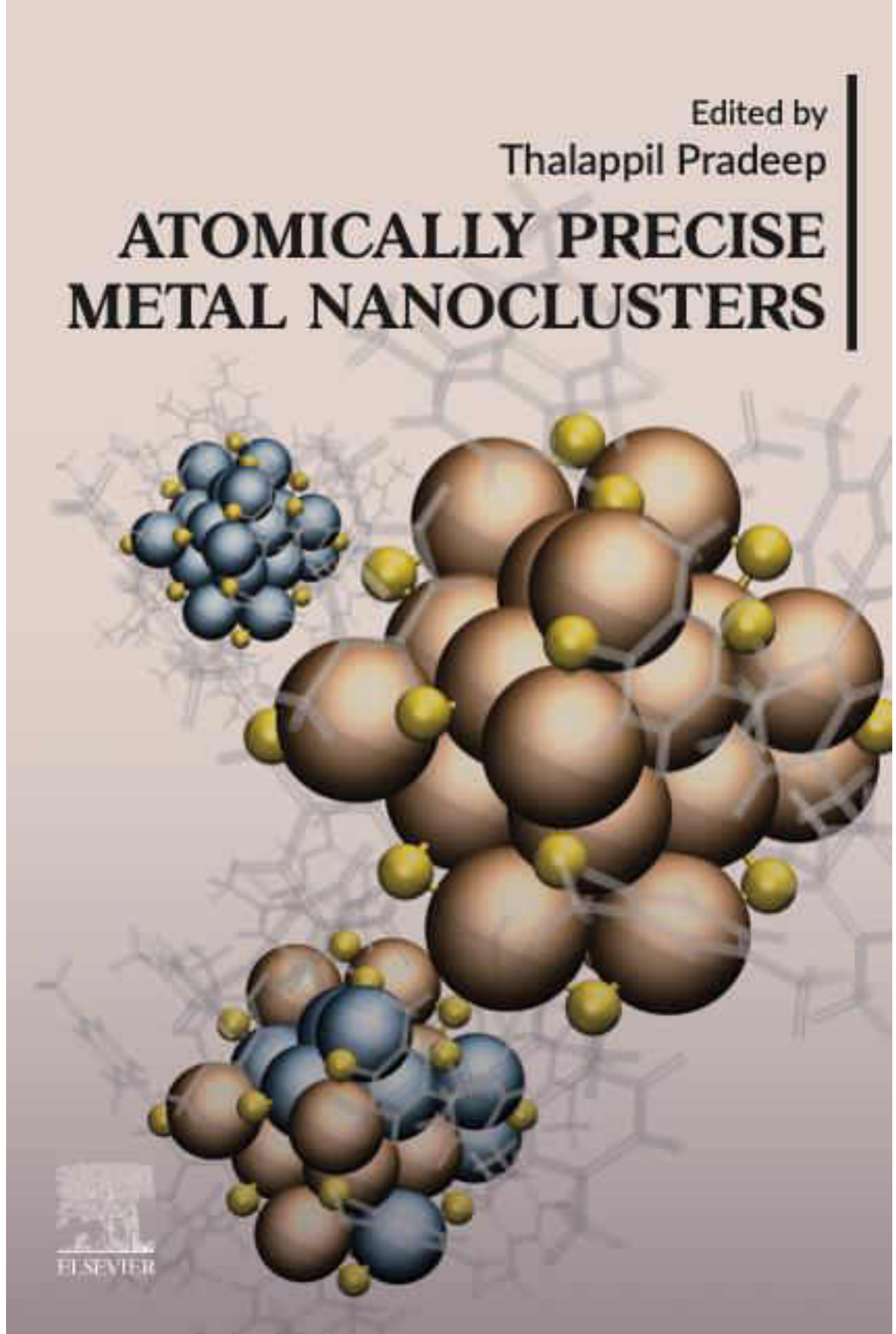


Ag29(BDT)12 3-
Ag25(DMBT)18 -
Au25(PET)18 -
HRMS of Au25(PET)18 -
7390 7392 7394 7396 7398
2000 4000 6000 8000 20000 40000 60000
m/z

$Au_{144}(PET)_{60}$



12198.58
$[Au_{144}(PET)_{60}]^{3+}$
Experimental
Theoretical
$[Au_{144}(PET)_{60}]^{2+}$
18297.87
Experimental
Theoretical
Relative abundance
100.00
75.00
50.00
25.00
0.00
10000
12000
14000
16000
18000
20000
m/z


Edited by
Thalappil Pradeep
ATOMICALLY PRECISE
METAL NANOCLUSTERS
ELSEVIER

Inter-cluster reactions

JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

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Intercluster Reactions between $Au_{25}(SR)_{18}$ and $Ag_{44}(SR)_{30}$

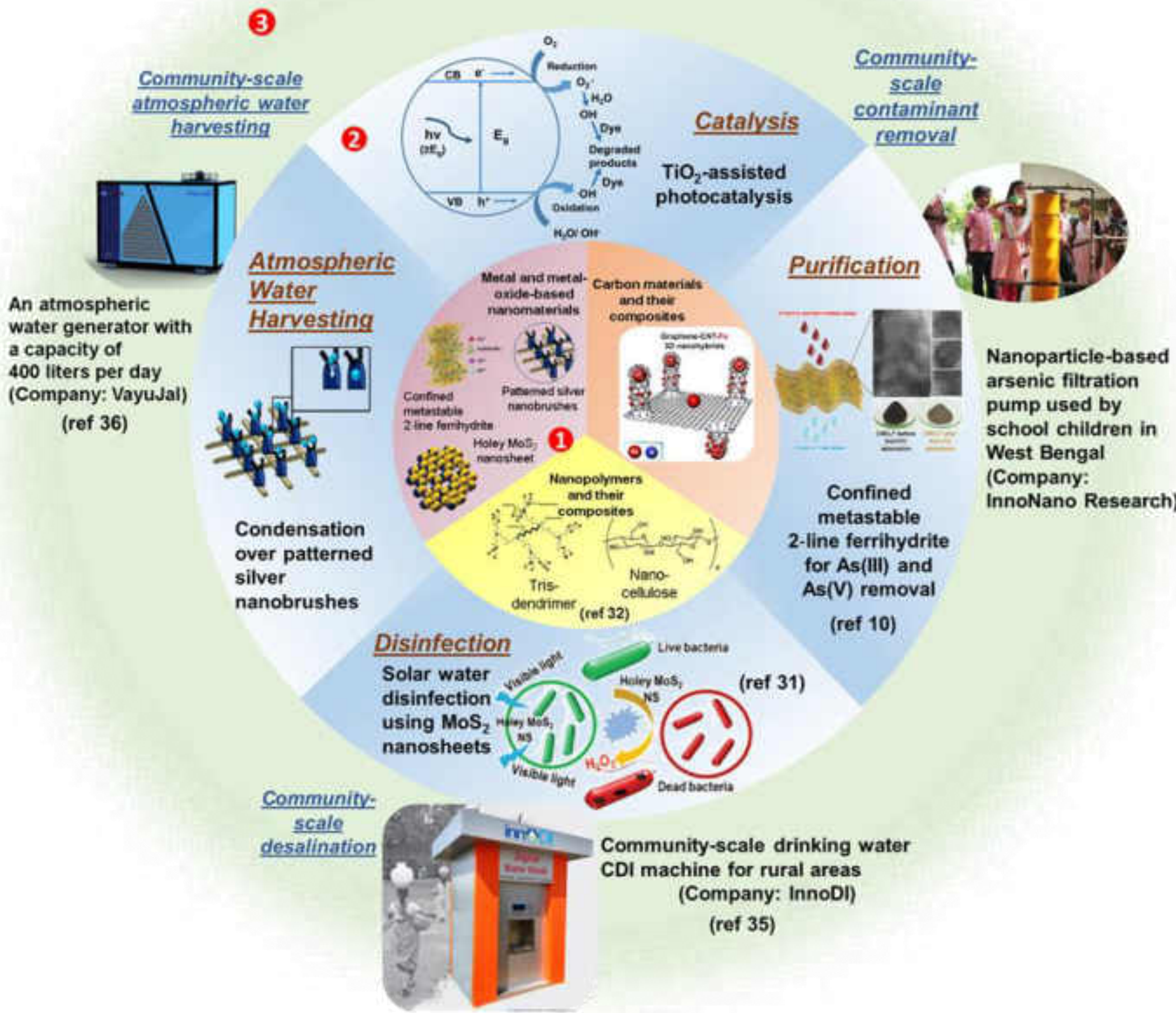
K. R. Krishnadas, Atanu Ghosh, Ananya Baksi, Indranath Chakraborty,[†] Ganapati Natarajan, and Thalappil Pradeep[*]

DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai, 600 036, India

Supporting Information

$$A + B \rightarrow C + D$$

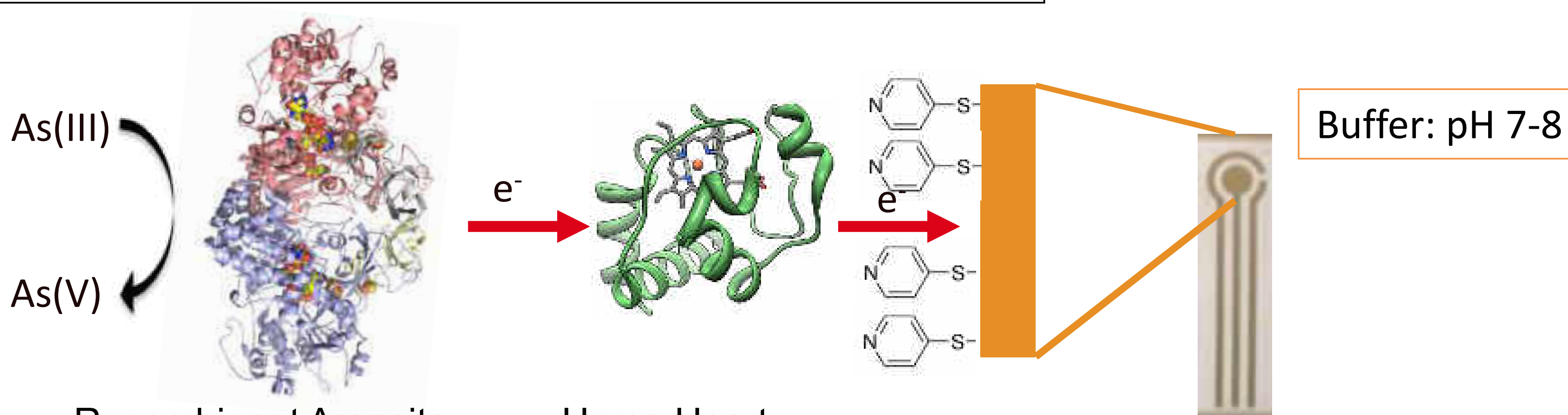
Evolution of materials to products



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

Biosensor Design

1st Generation Design (Mediated Electrochemistry)



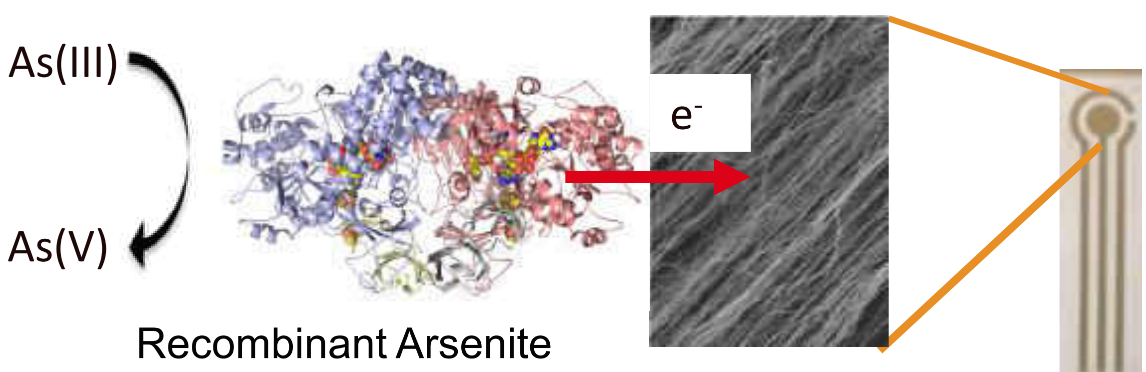
Recombinant Arsenite Oxidase NT-26 Aio

Horse Heart Cytochrome C

Aldrithiol

Low-cost Gold sputtered thin film on PET substrate

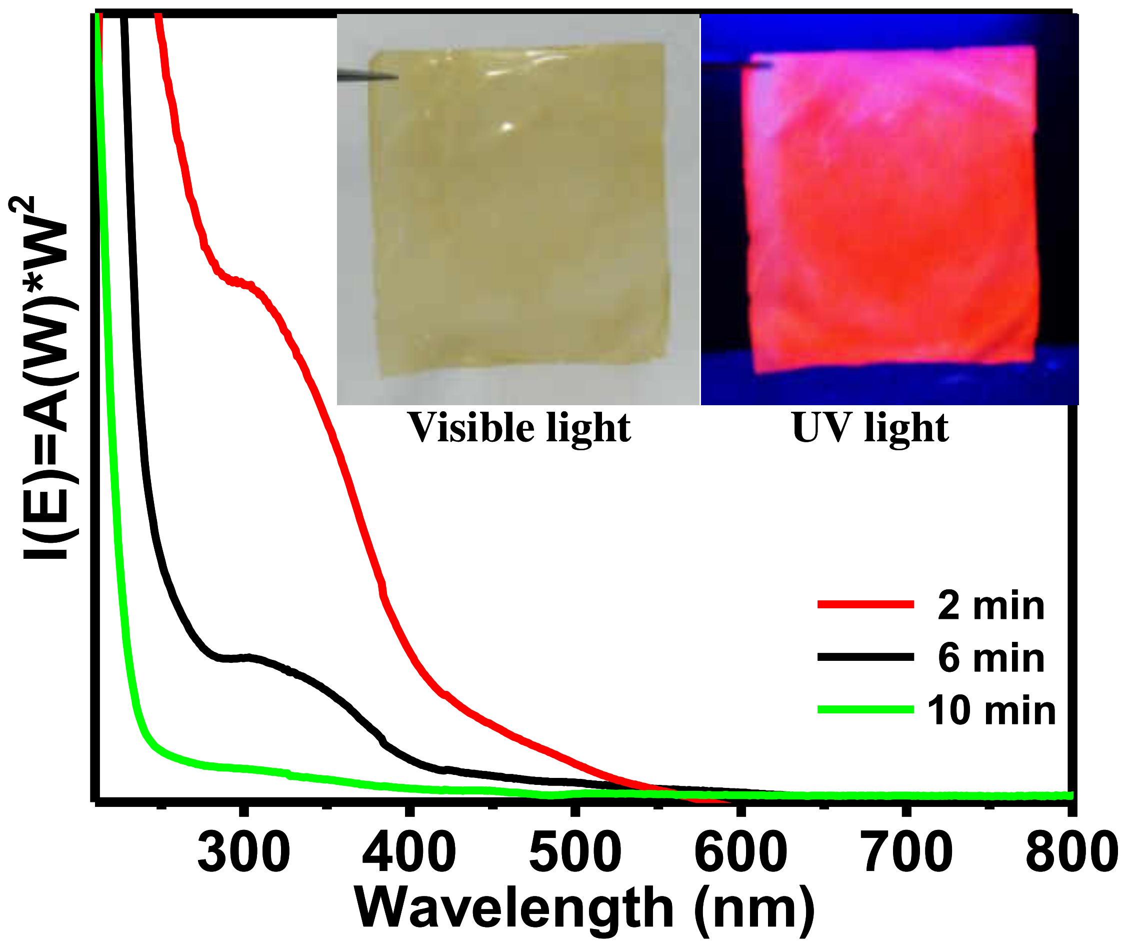
2nd Generation Design (Direct Electron Transfer)



Recombinant Arsenite Oxidase NT-26 Aio

low-cost nanostructured electrodes which interact directly with enzyme (e.g. graphene or CNT).

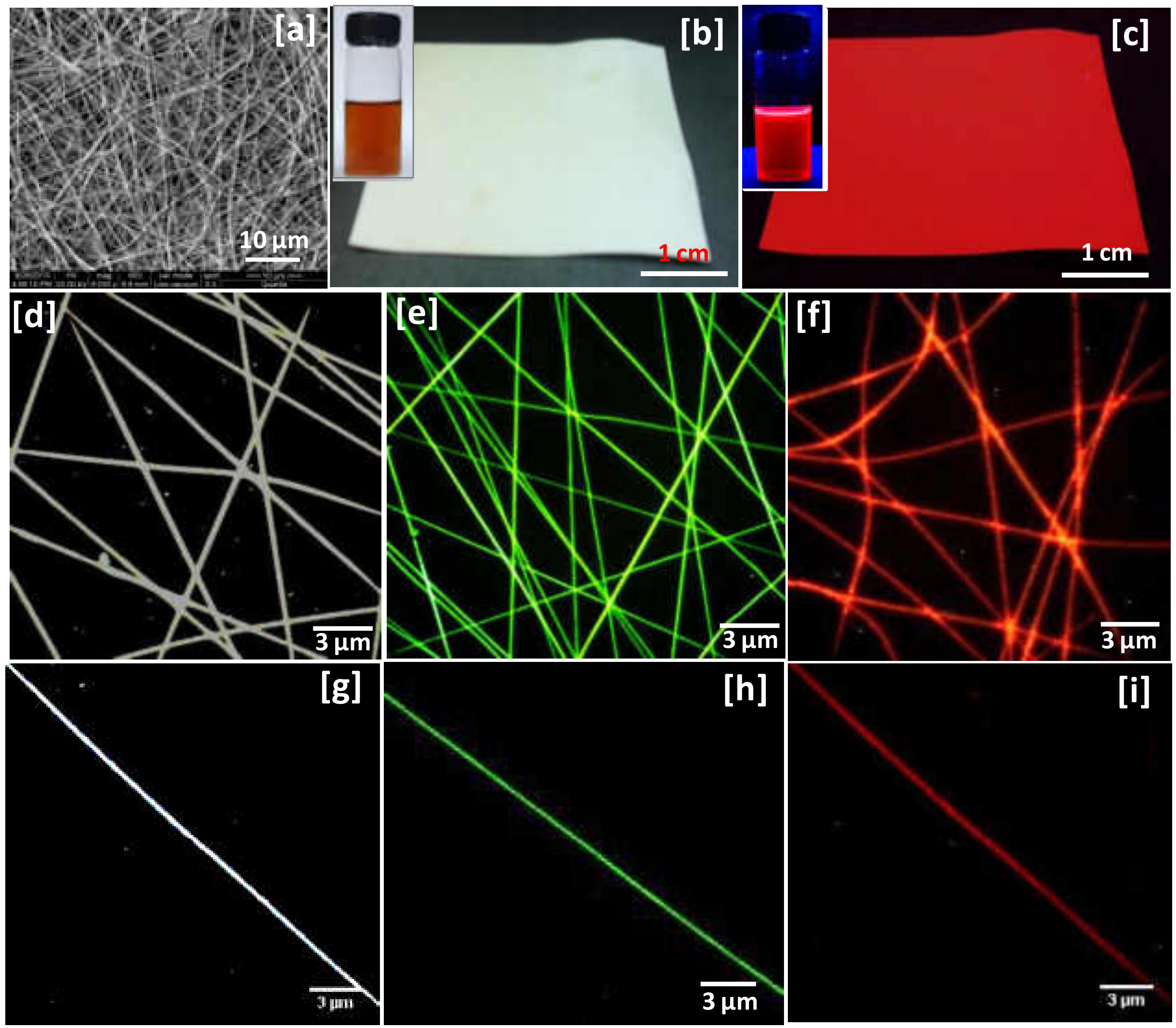
Cluster-based metal ion sensing



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

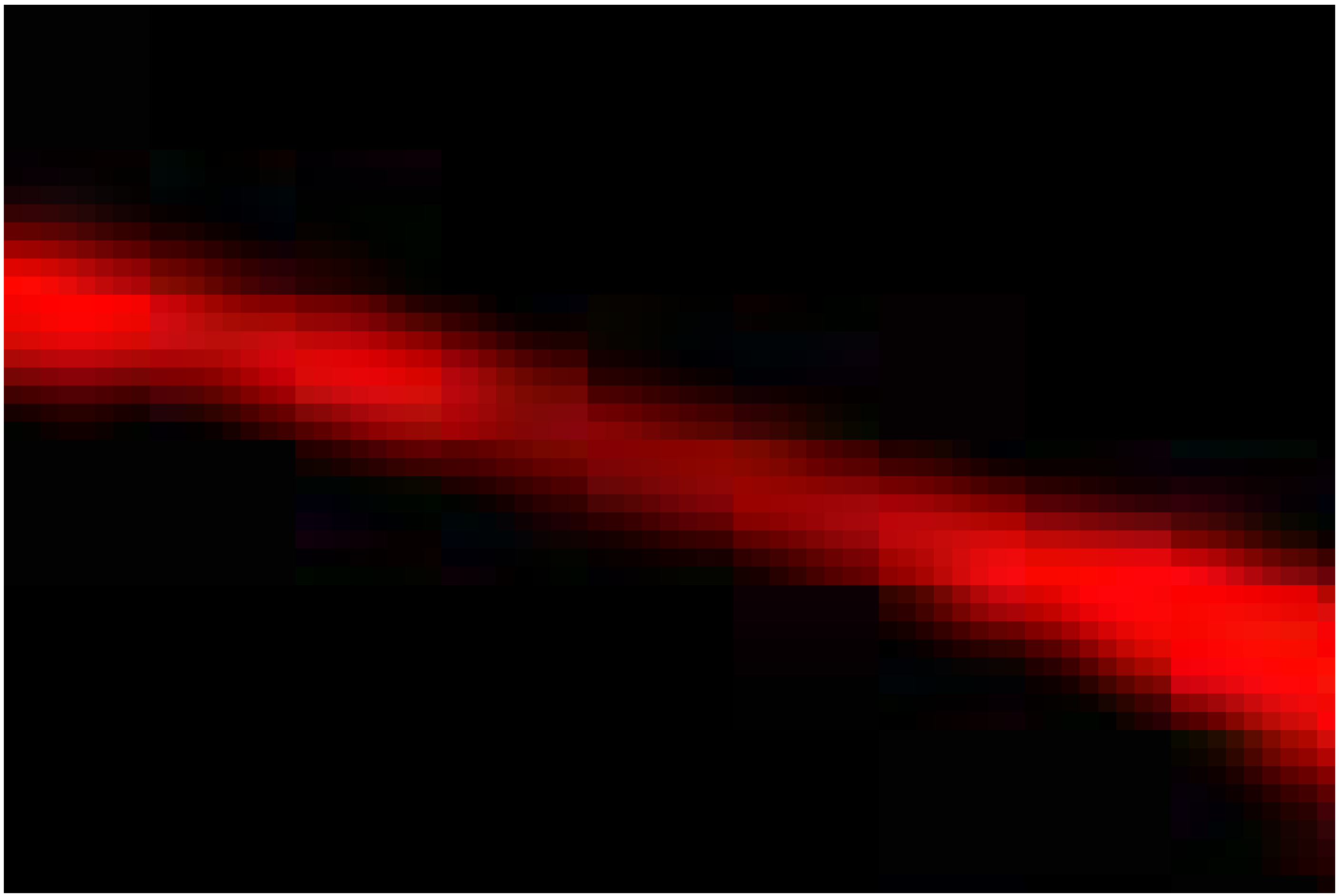
Anu George et al. *ACS Applied Materials & Interfaces*, 2012

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

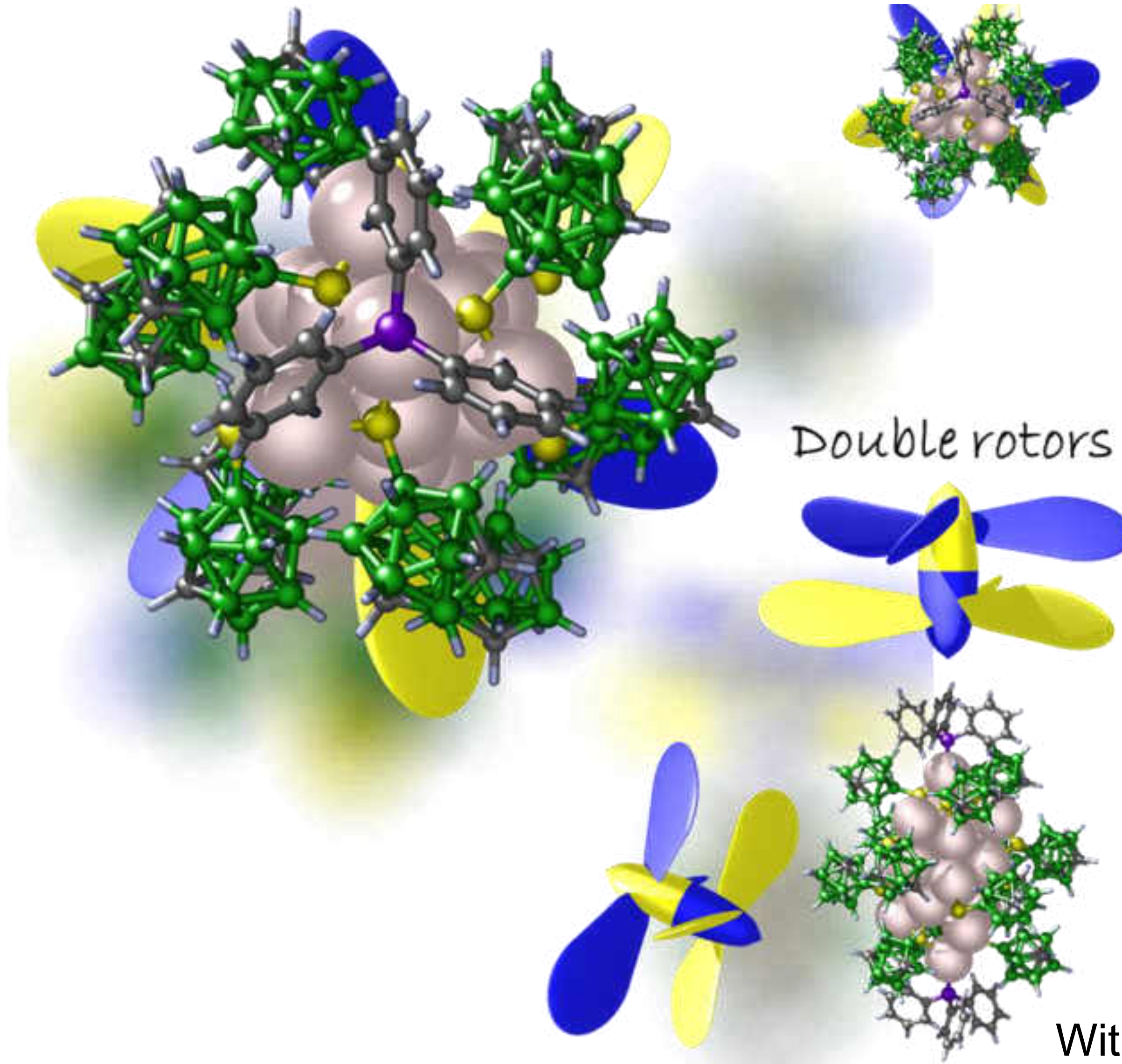


Atanu Ghosh et al. Anal. Chem. 2014.

Mercury quenching experiment using nanofiber

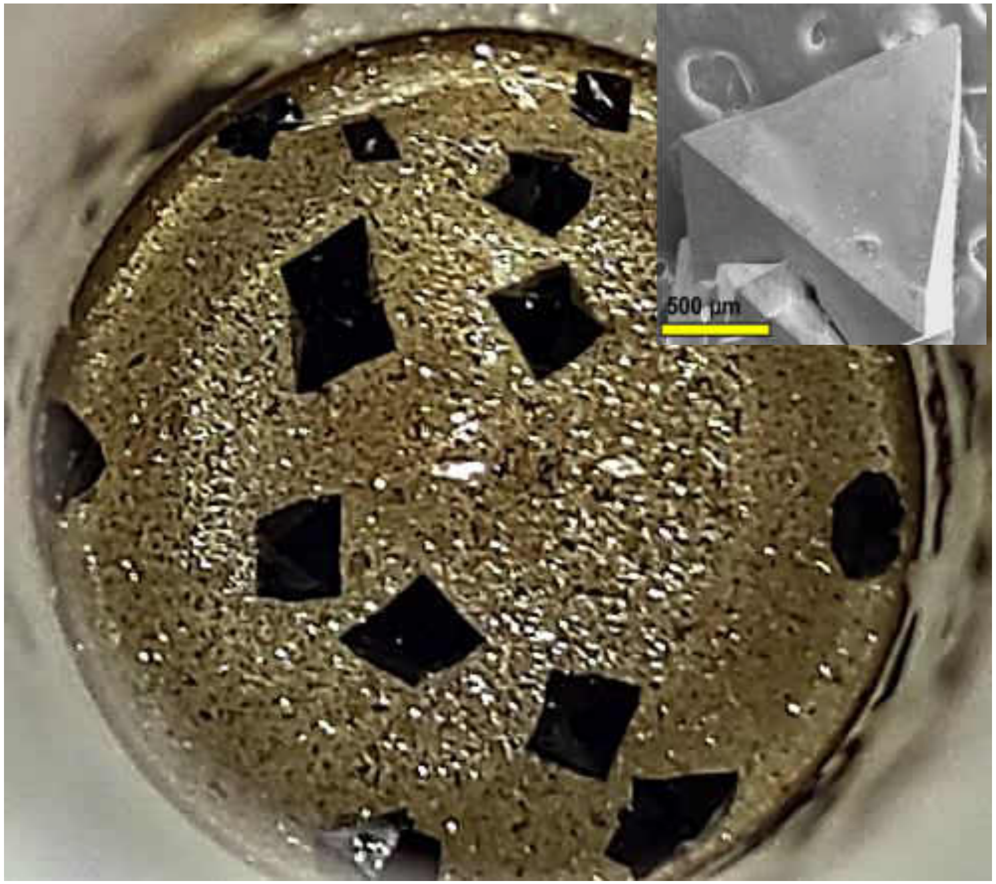
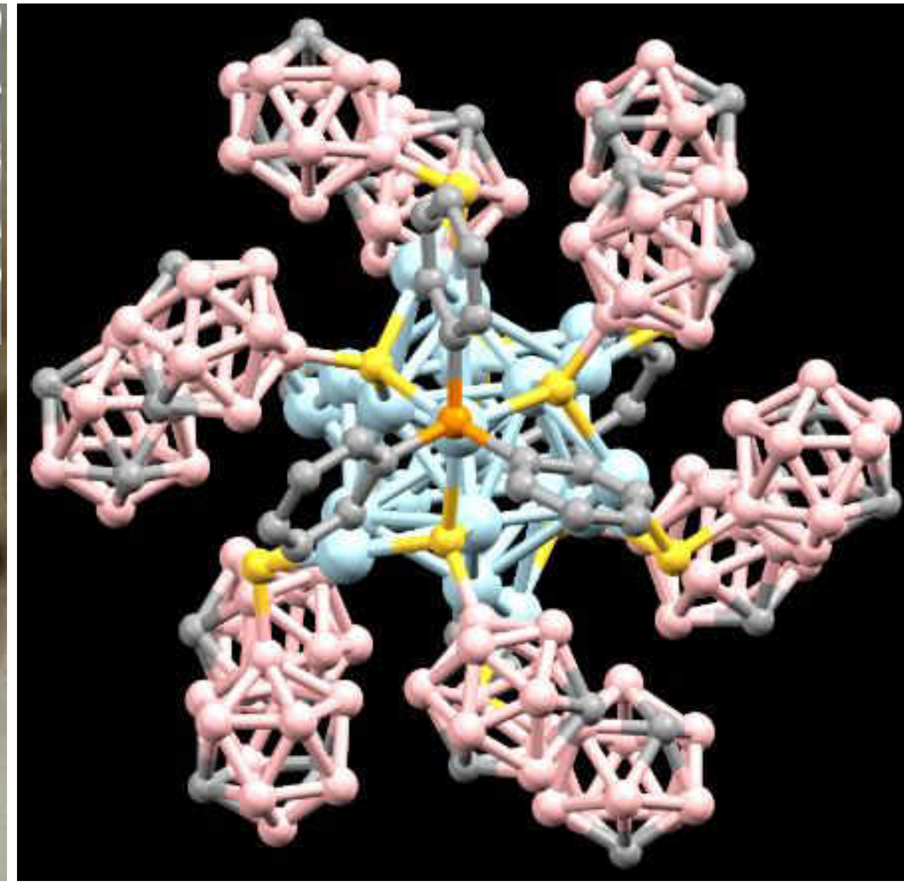


Carborane-thiol protected silver nanomolecule

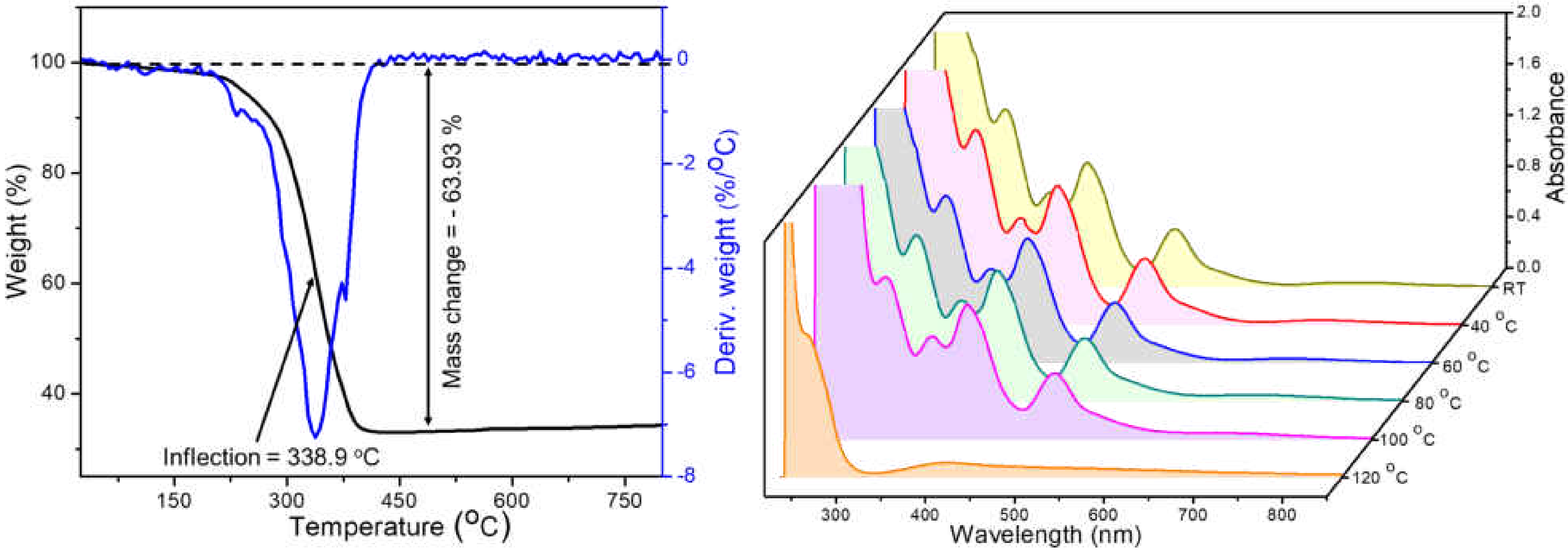


With Tomas Base

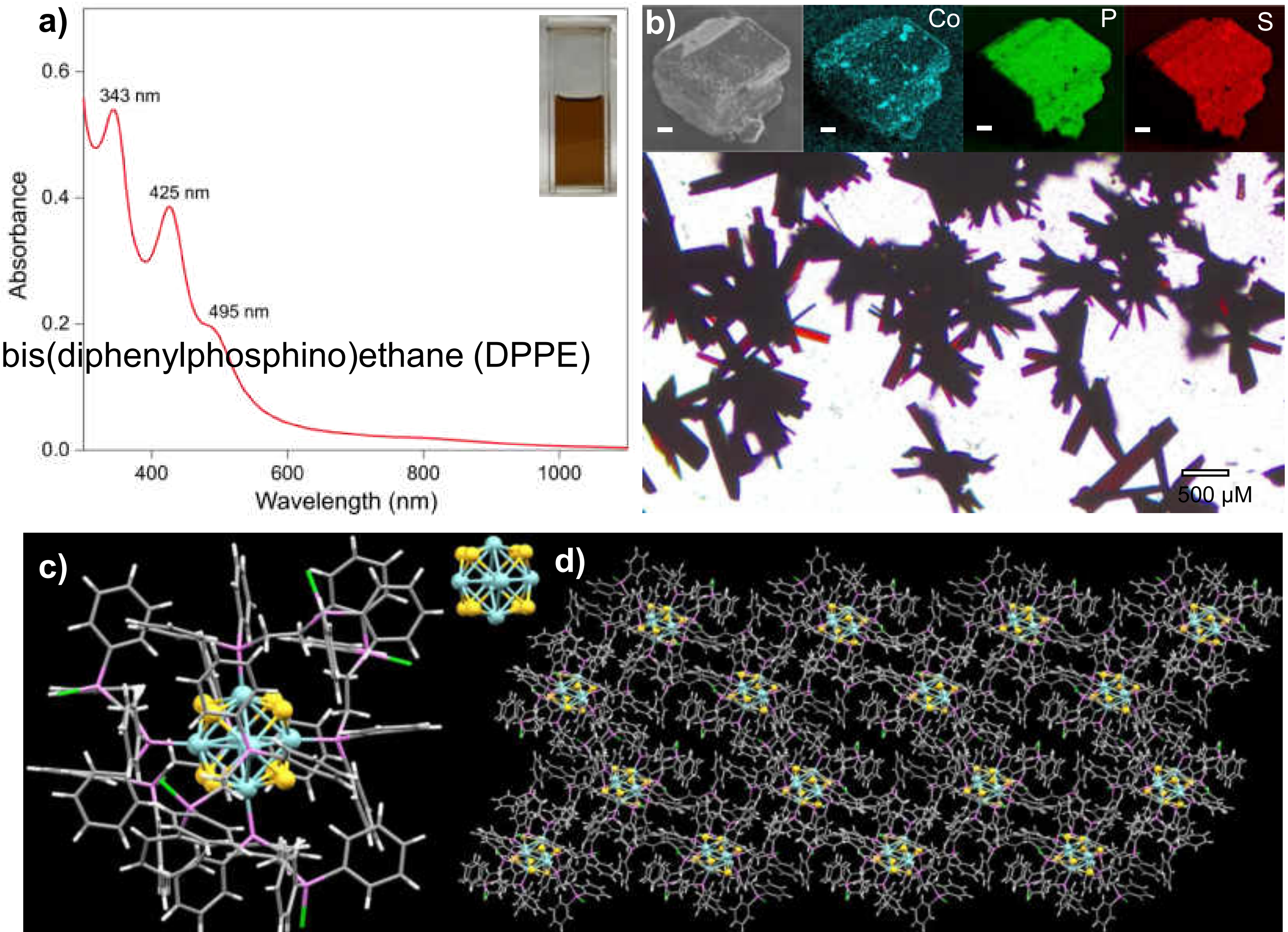
Jana *et*. *al*, Inorganic Chemistry (2022)


500 µm


Thermal stability

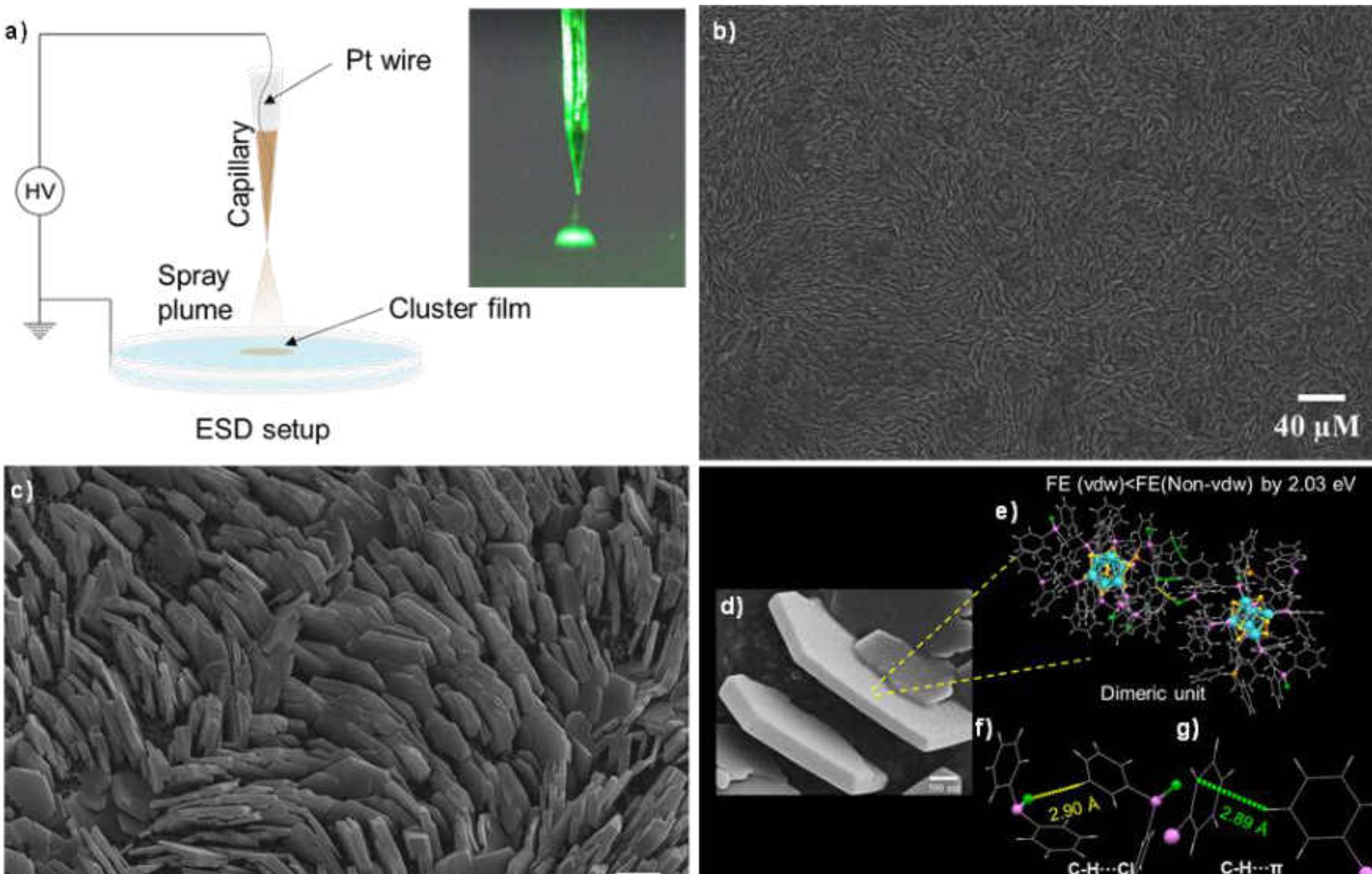


New electrodes - Aligned nanoplates of Co_6S_8



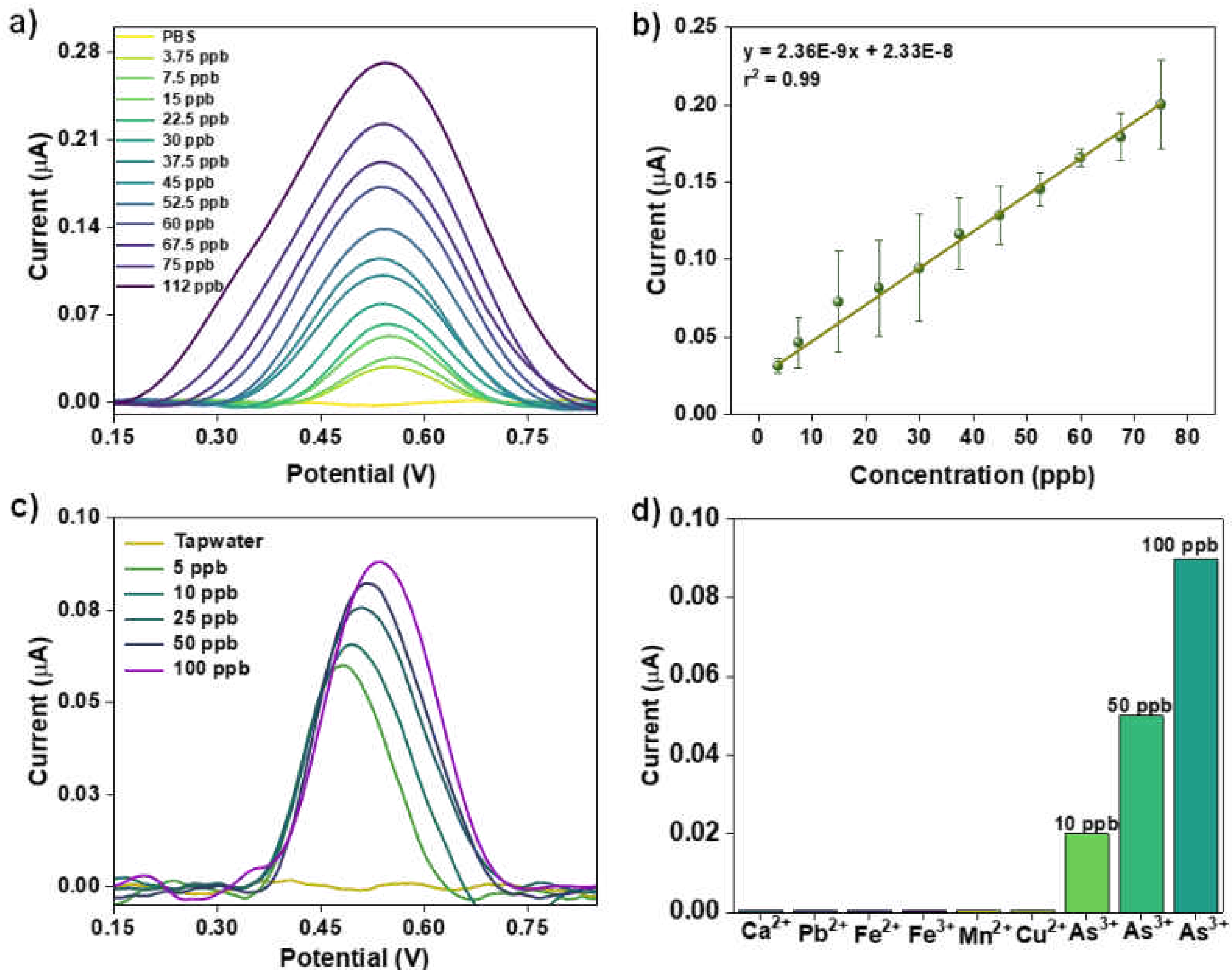
1,2-bis(diphenylphosphino)ethane (DPPE)

Electrospray deposition



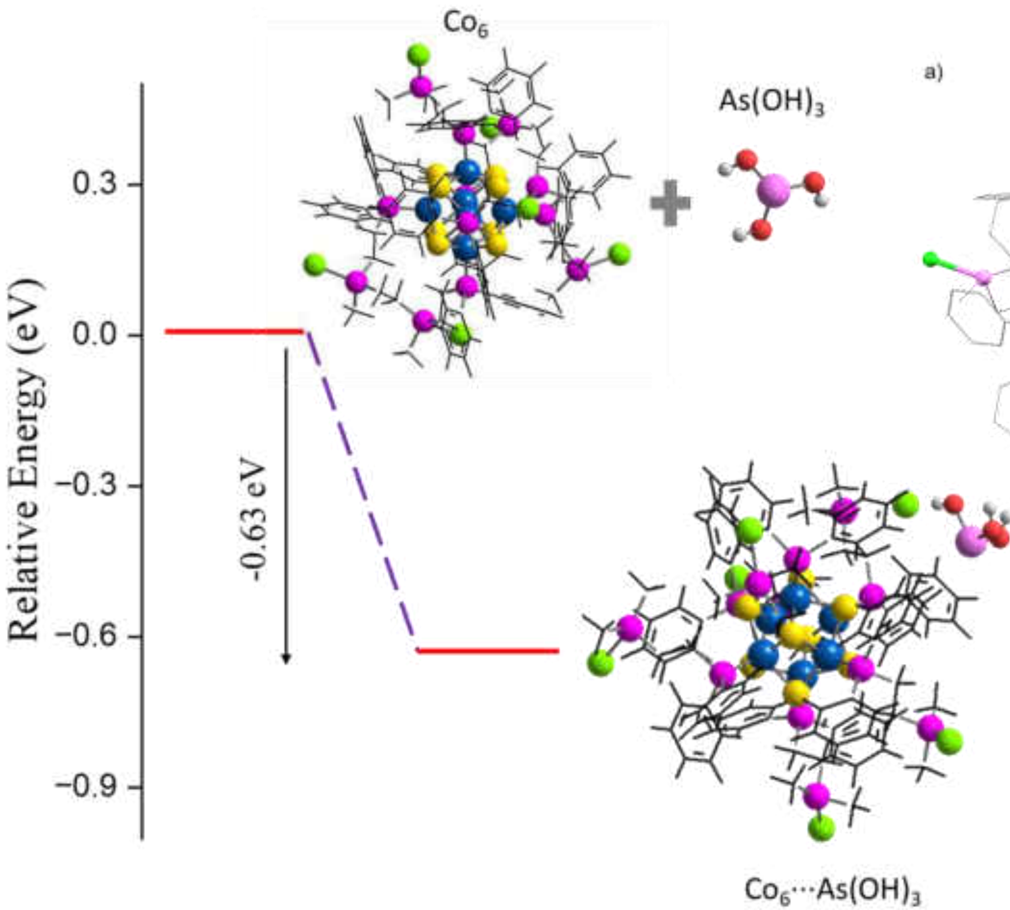
Anagha Jose et. al. ACS Mat. Lett. (2023)

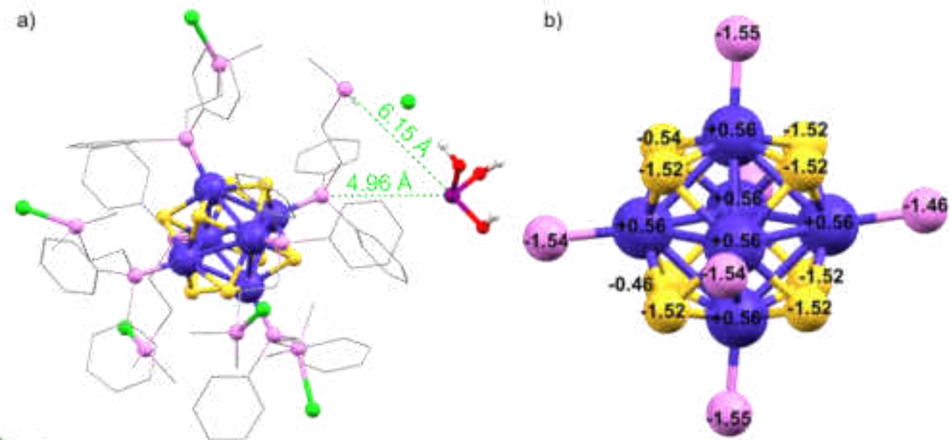
Sensing



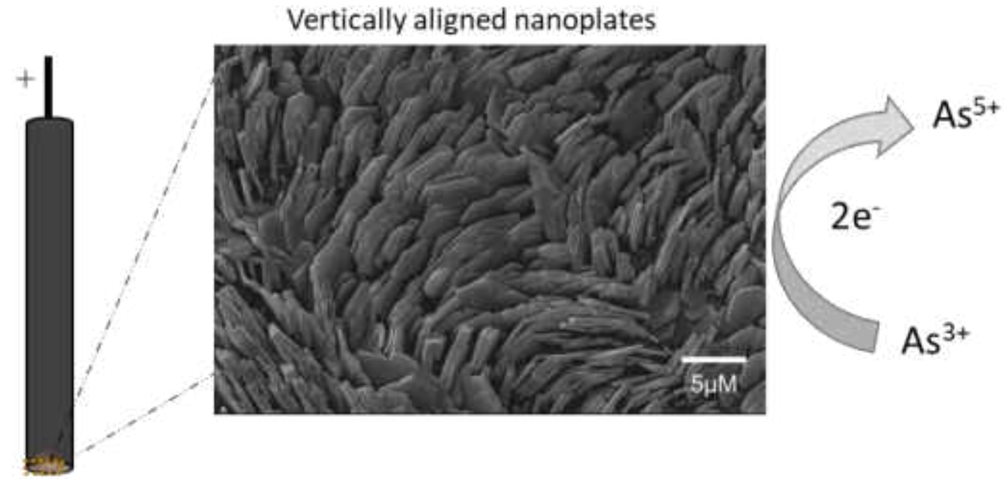
a)
PBS
3.75 ppb
7.5 ppb
15 ppb
22.5 ppb
30 ppb
37.5 ppb
45 ppb
52.5 ppb
60 ppb
67.5 ppb
75 ppb
112 ppb
Current (μA)
Potential (V)
b)
y = 2.36E-9x + 2.33E-8
r² = 0.99
Current (μA)
Concentration (ppb)
c)
Tapwater
5 ppb
10 ppb
25 ppb
50 ppb
100 ppb
Current (μA)
Potential (V)
d)
100 ppb
50 ppb
10 ppb
Current (μA)
Ca2+ Pb2+ Fe2+ Fe3+ Mn2+ Cu2+ As3+ As3+ As3+

Computational insights

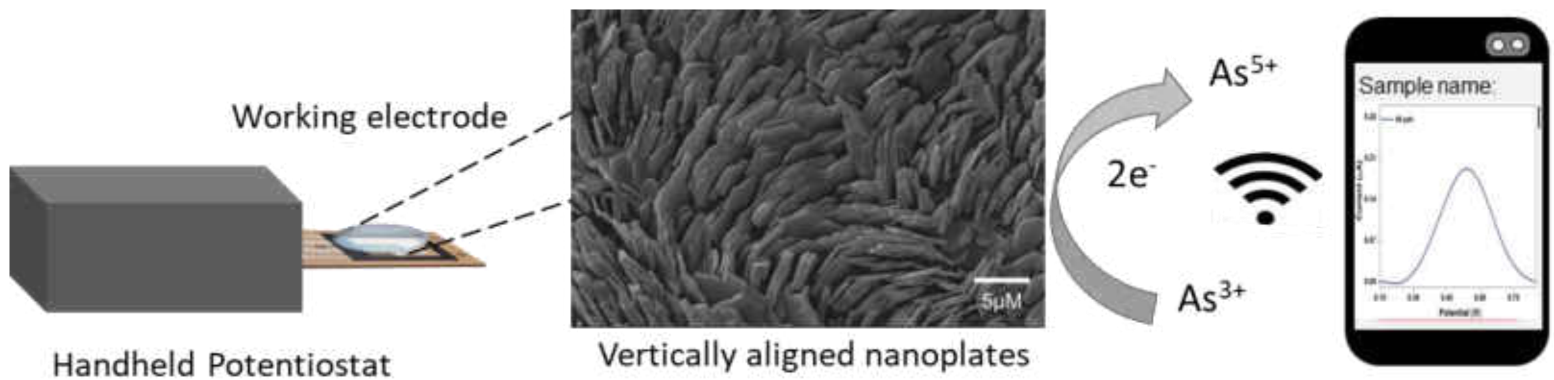




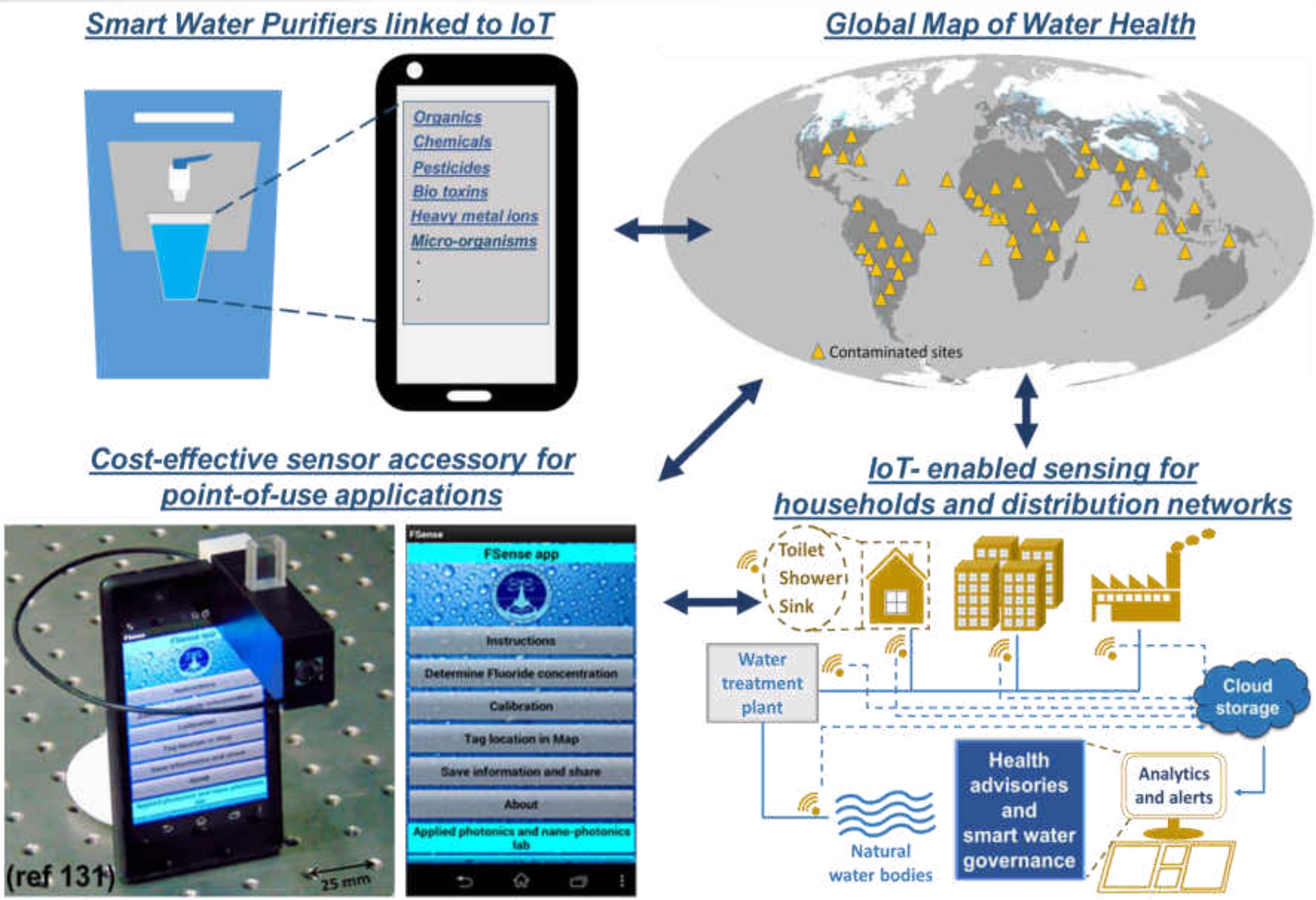
Working electrode



Glassy carbon dropcasted with ESD of Co_6 cluster(WE)

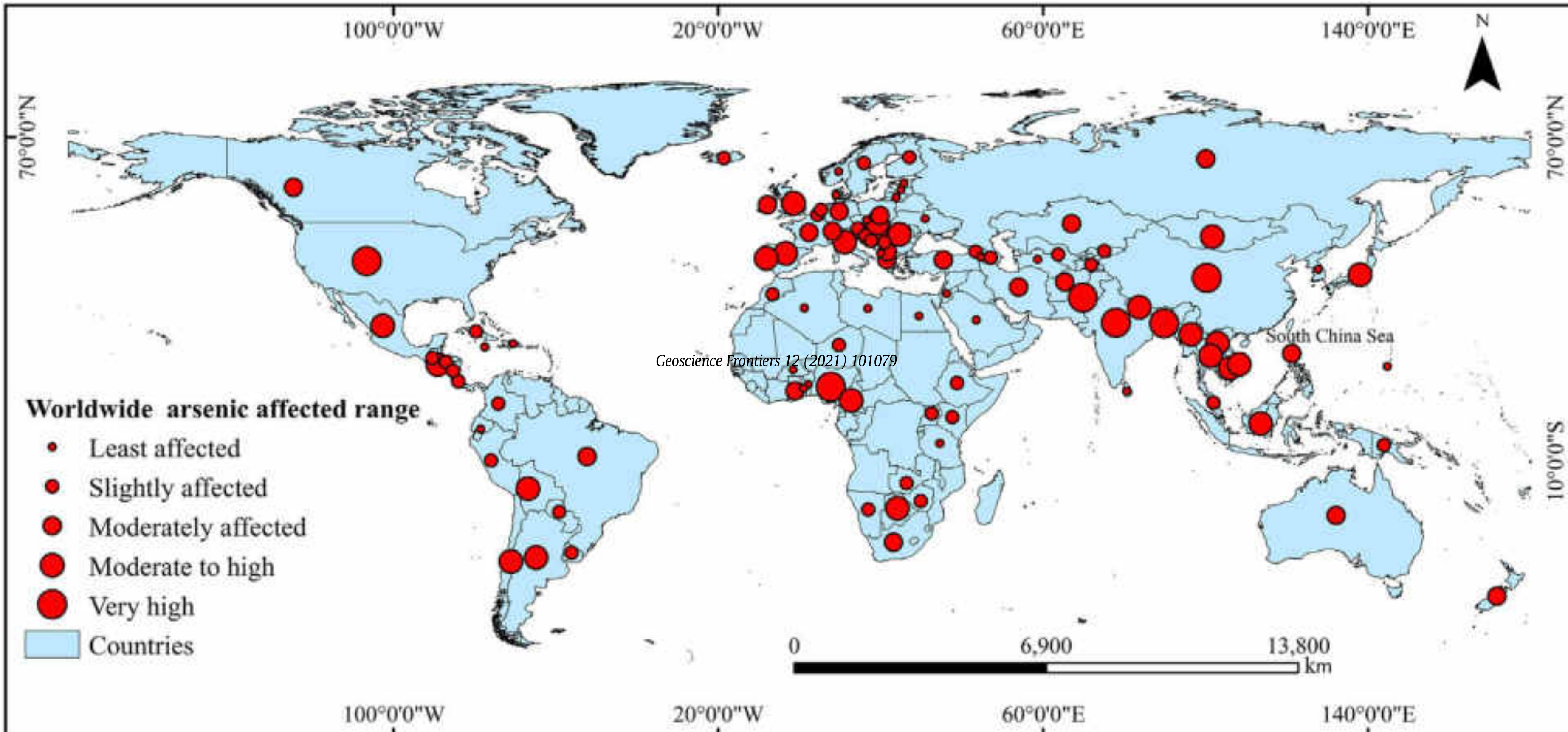


Smart water purifiers and big data



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

Arsenic poisoning across the world



E. Shaji, M. Santosh, K. V. Sarath, Pranav Prakash, V. Deepch and B. V. Divya, Geoscience Frontiers, 12 (2021) 101079.

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Funding: Department of Science and Technology, Government of India

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>25 Post-doctoral fellows, >130 masters students and visitors