Since 1959

Atomically precise clusters for applications

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Co-founder

InnoNano Research Pvt. Ltd.
InnoDI Water Technologies Pvt. Ltd.
VayuJAL Technologies Pvt. Ltd.
Aqueasy Innovations Pvt. Ltd.
Hydromaterials Pvt. Ltd.
EyeNetAqua Pvt. Ltd.
Deepspectrum Analytics Pvt. Ltd.

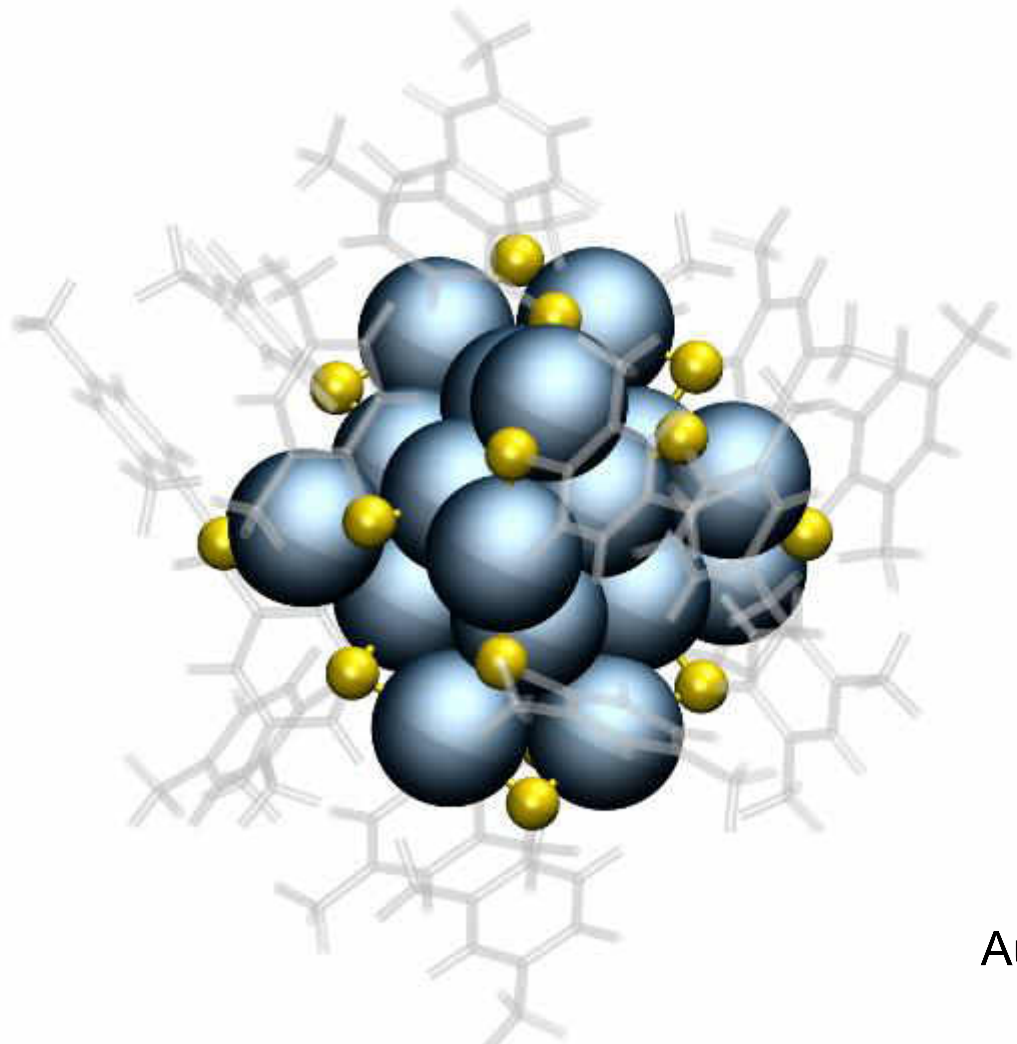
Associate Editor
ACS Sustainable Chemistry & Engineering

Professor-in-charge

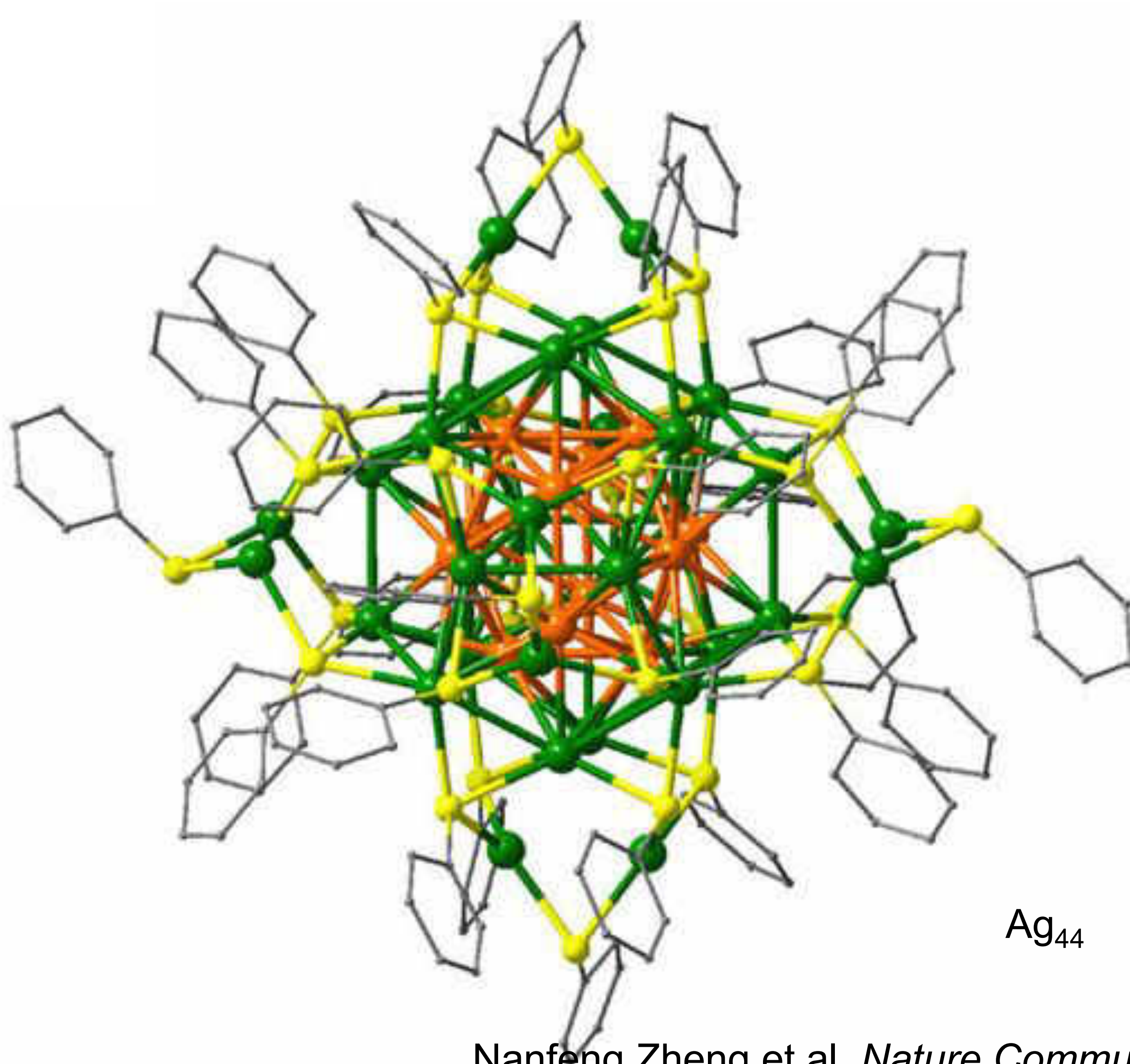
ICCW
International Centre for Clean Water

EFCS 2022, Farook College, January 19-20, 2023

New molecules

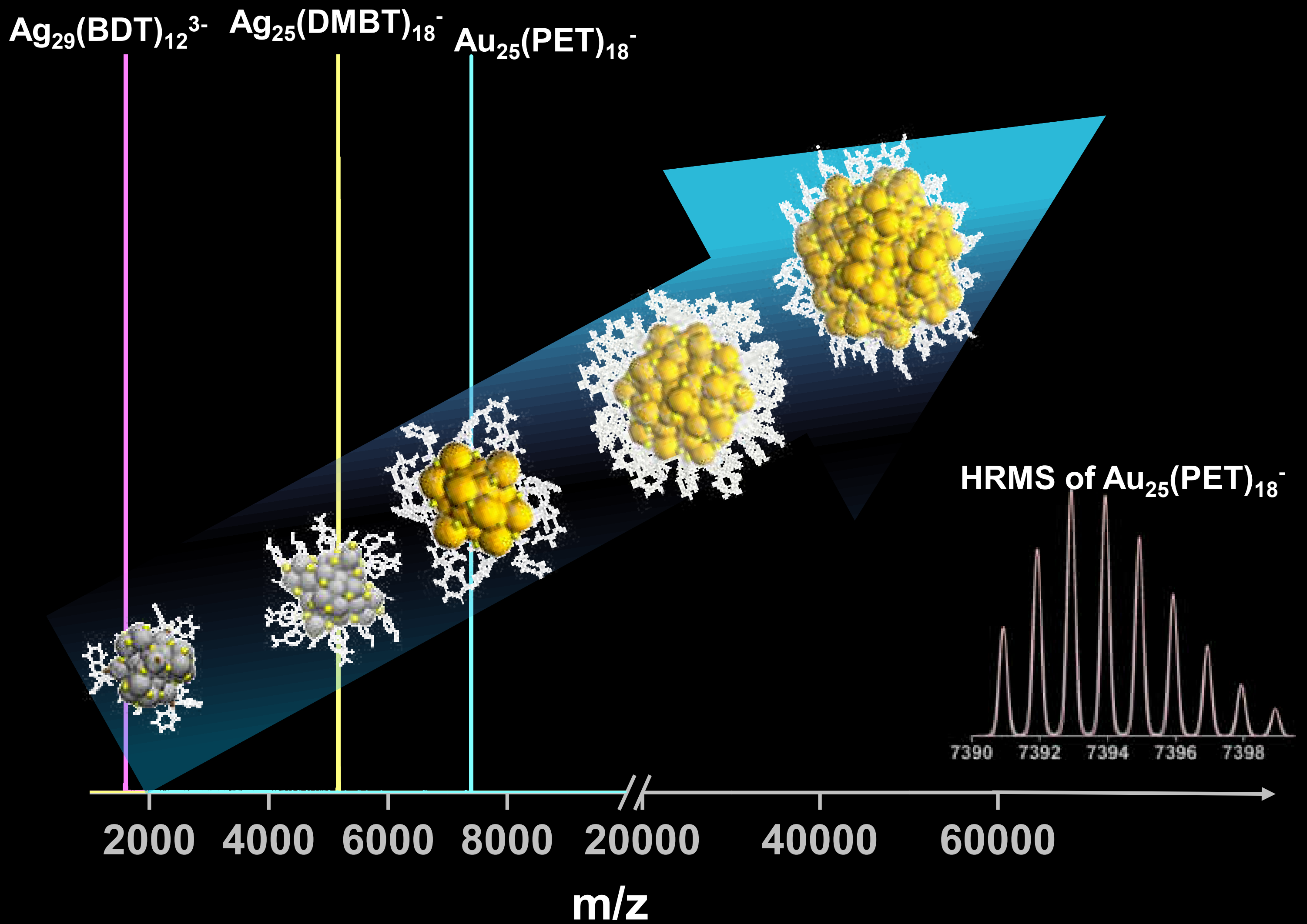


Au_{25}, Ag_{25}, Ag_{29}



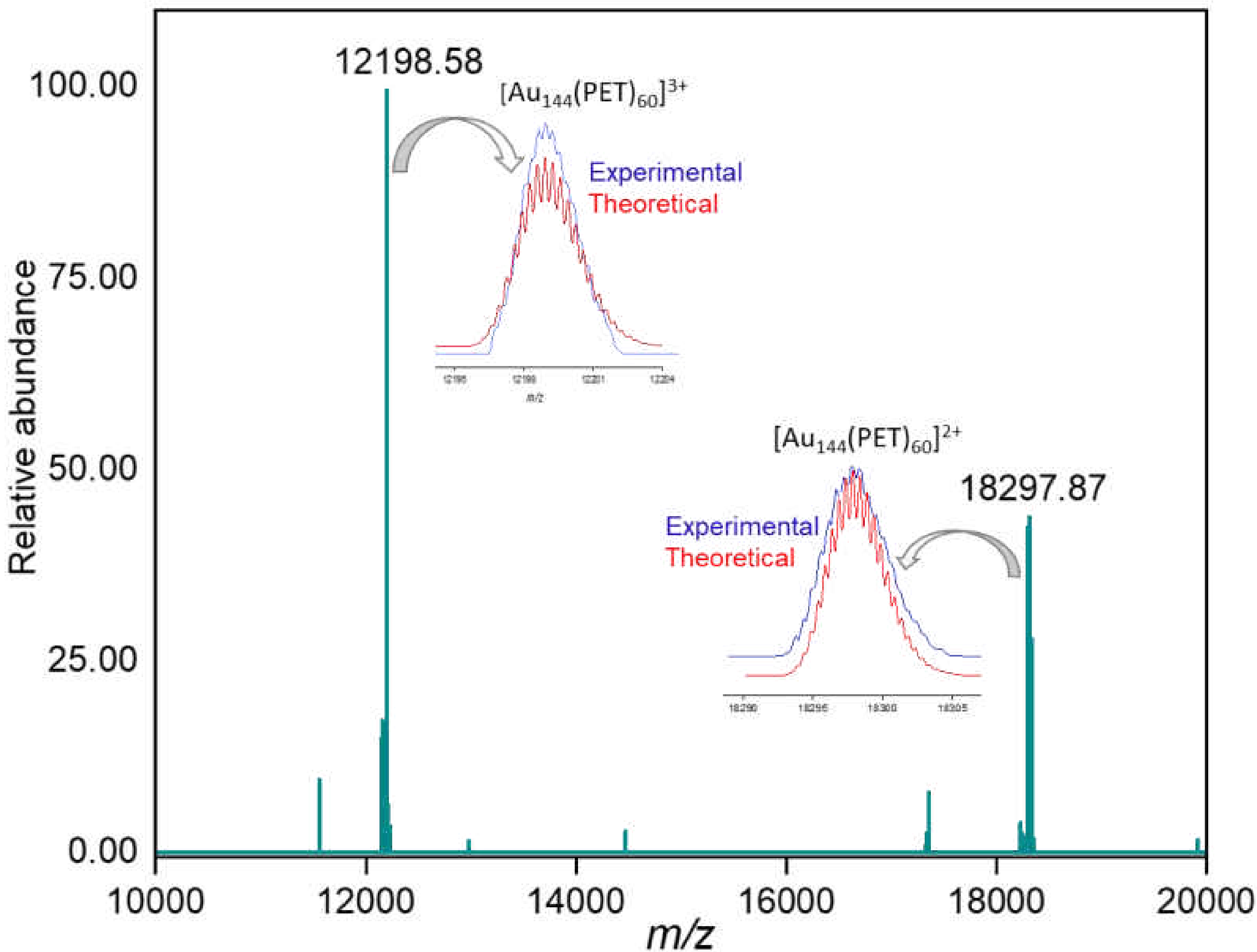
Ag$_{44}$

Nanfeng Zheng et al. *Nature Communications*, 2013
Terry Bigioni et al. *Nature* 2013

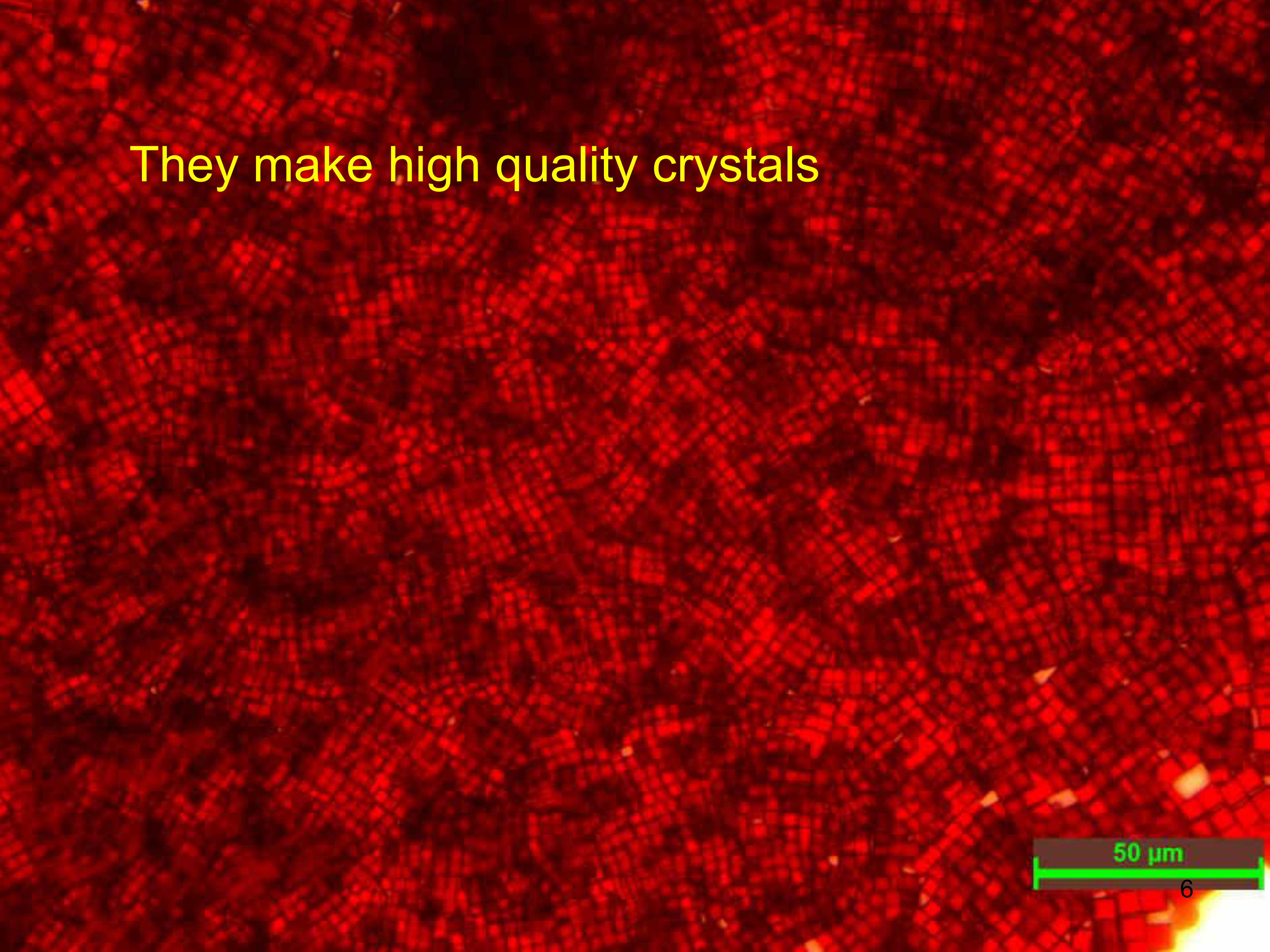


$Ag_{29}(BDT)_{12}^{3-}$
$Ag_{25}(DMBT)_{18}^{-}$
$Au_{25}(PET)_{18}^{-}$
HRMS of $Au_{25}(PET)_{18}^{-}$
7390
7392
7394
7396
7398
2000
4000
6000
8000
20000
40000
60000
m/z

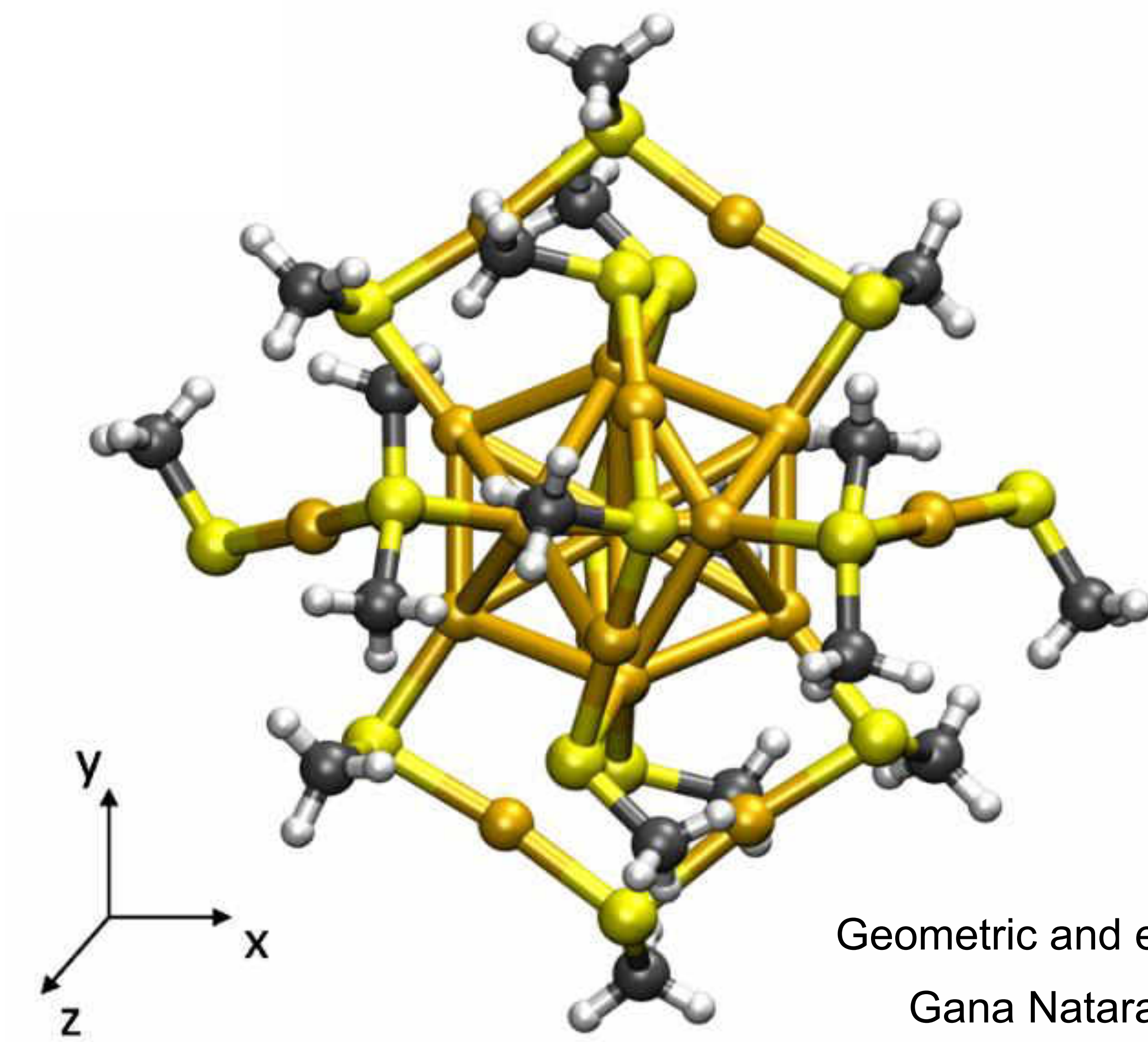
$Au_{144}(PET)_{60}$


12198.58
[Au144(PET)60]3+
Experimental
Theoretical
[Au144(PET)60]2+
18297.87
Experimental
Theoretical
100.00
75.00
50.00
25.00
0.00
Relative abundance
10000
12000
14000
16000
18000
20000
m/z

They make high quality crystals



Molecular structure



Geometric and electronic shells

Gana Natarajan

Molecular materials

ACCOUNTS of chemical research

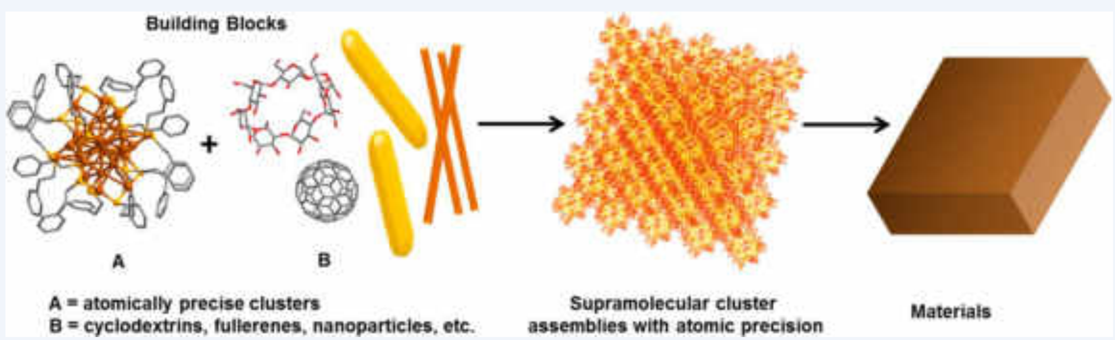
Article

pubs.acs.org/accounts

Approaching Materials with Atomic Precision Using Supramolecular Cluster Assemblies

Papri Chakraborty, Abhijit Nag, Amrita Chakraborty, and Thalappil Pradeep*

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



Molecules and their properties

Chemical formula	H_2O
Molecular weight	18.0148
Critical temperature	373.91°C
Critical pressure	22.05 MPa
Critical density	315.0 kg/m^3
Triple point temperature	0.01°C
Triple point pressure	615.066 Pa
Normal boiling point	100.0°C
Normal freezing point	0.0°C
Density of ice at normal melting point	918.0 kg/m^3
Maximum density, 3.98°C	999.973 kg/m^3
Viscosity, 25°C	0.889 mN s/m^2
Surface tension, 25°C	72 mN/m
Heat Capacity, 25°C	4.1796 kJ/kg.K
Enthalpy of vaporisation, 100°C	2,257.7 kJ/kg
Enthalpy of fusion, 0°C	333.8 kJ/kg
Velocity of sound, 0°C	1.403 km/s
Dielectric constant, 25°C	78.40
Electrical conductivity, 25°C	8 μS/m
Refractive index, 25°C	1.333
Liquid compressibility, 10°C	480. × 10^{-12}m^2/N
Coefficient of thermal expansion, 25°C	256.32 × 10^{-6} K^{-1}
Thermal Conductivity, 25°C	0.608 W/m.K

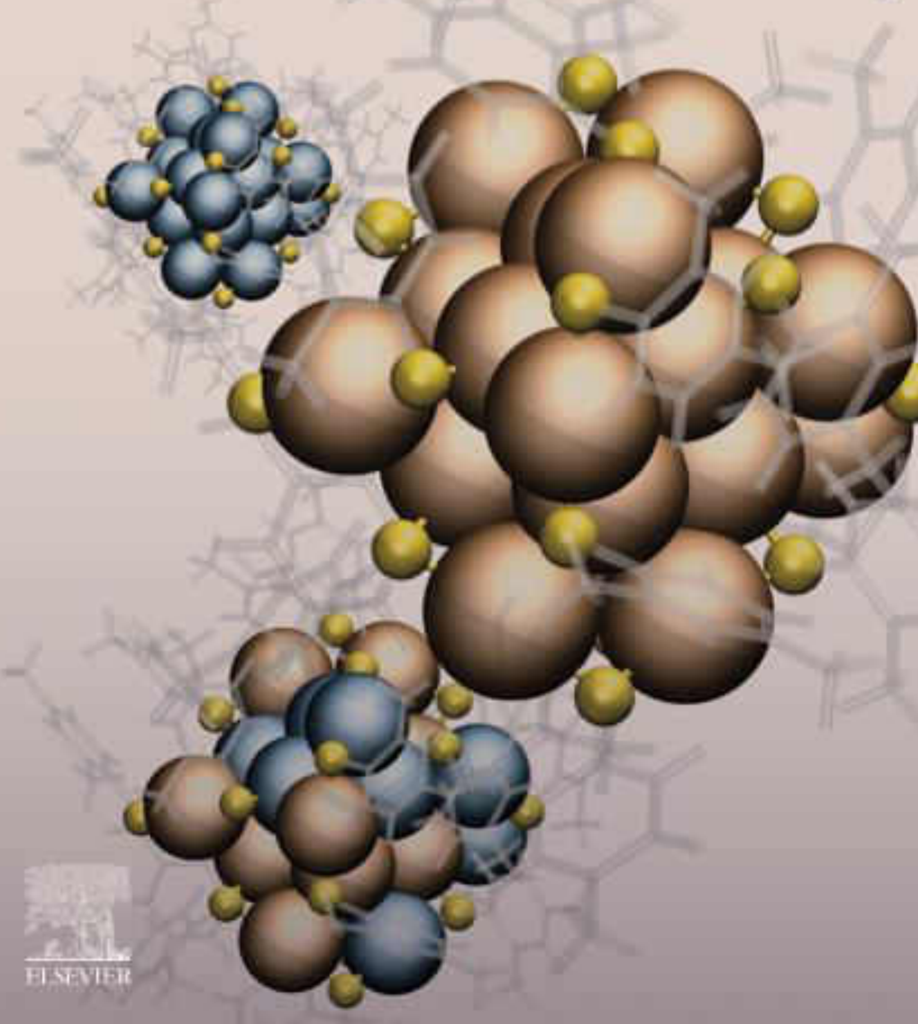
Molecular formula
Molecular weight
Molecular structure
Molecular absorption and emission
Molecular reactions
Molecular assembly
Molecular co-crystals
Ionization potential
Electron affinity

Phases - phase transitions
Physical properties
Electrical, magnetic
Mechanical properties
Electrochemical properties

Future?

Edited by
Thalappil Pradeep

ATOMICALLY PRECISE METAL NANOCLUSTERS



ELSEVIER

Molecular reactions

Reactions on clusters

Reactions <u>between</u> clusters

Inter-cluster reactions

JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

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

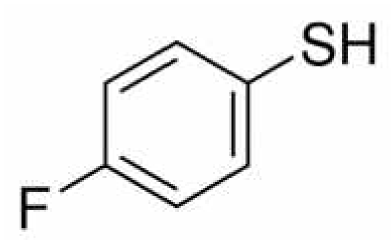
K. R. Krishnadas, Atanu Ghosh, Ananya Baksi, Indranath Chakraborty,[†] Ganapati Natarajan, and Thalappil Pradeep*

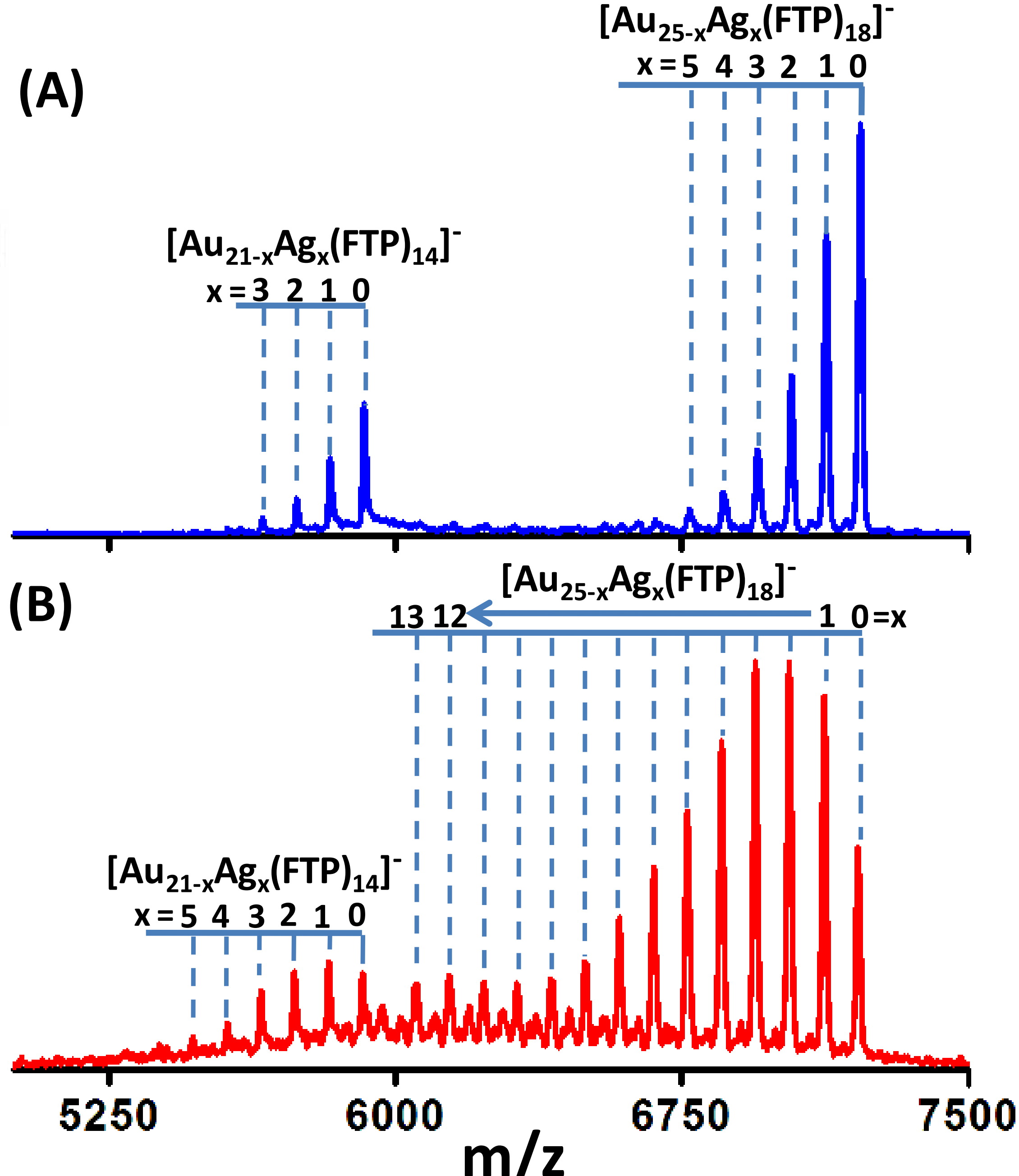
DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai, 600 036, India

Supporting Information

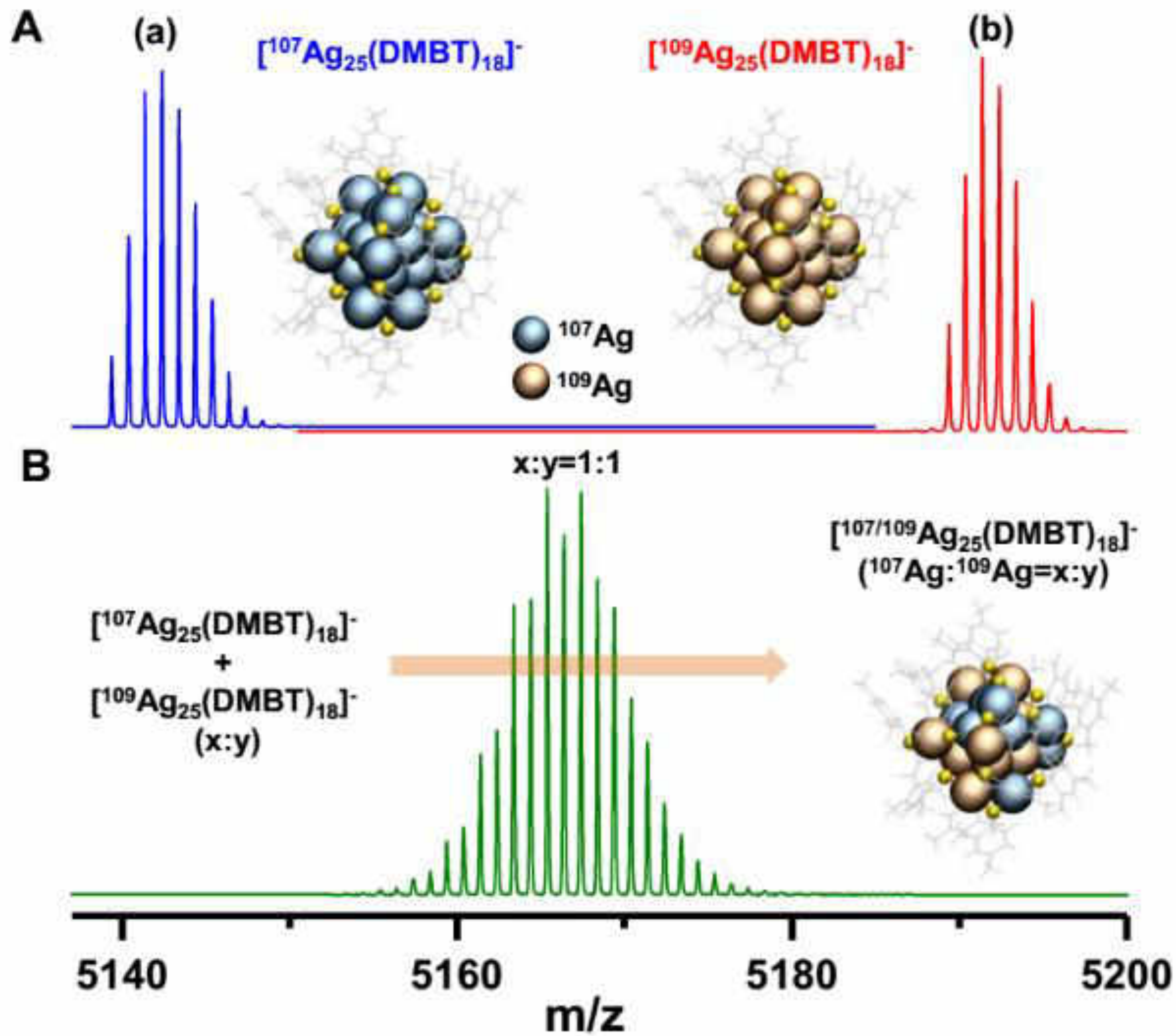
$$A + B \rightarrow C + D$$

$Au_{25}(FTP)_{18} + Ag_{44}(FTP)_{30} \longrightarrow Au_{25-x}Ag_x(FTP)_{18}$



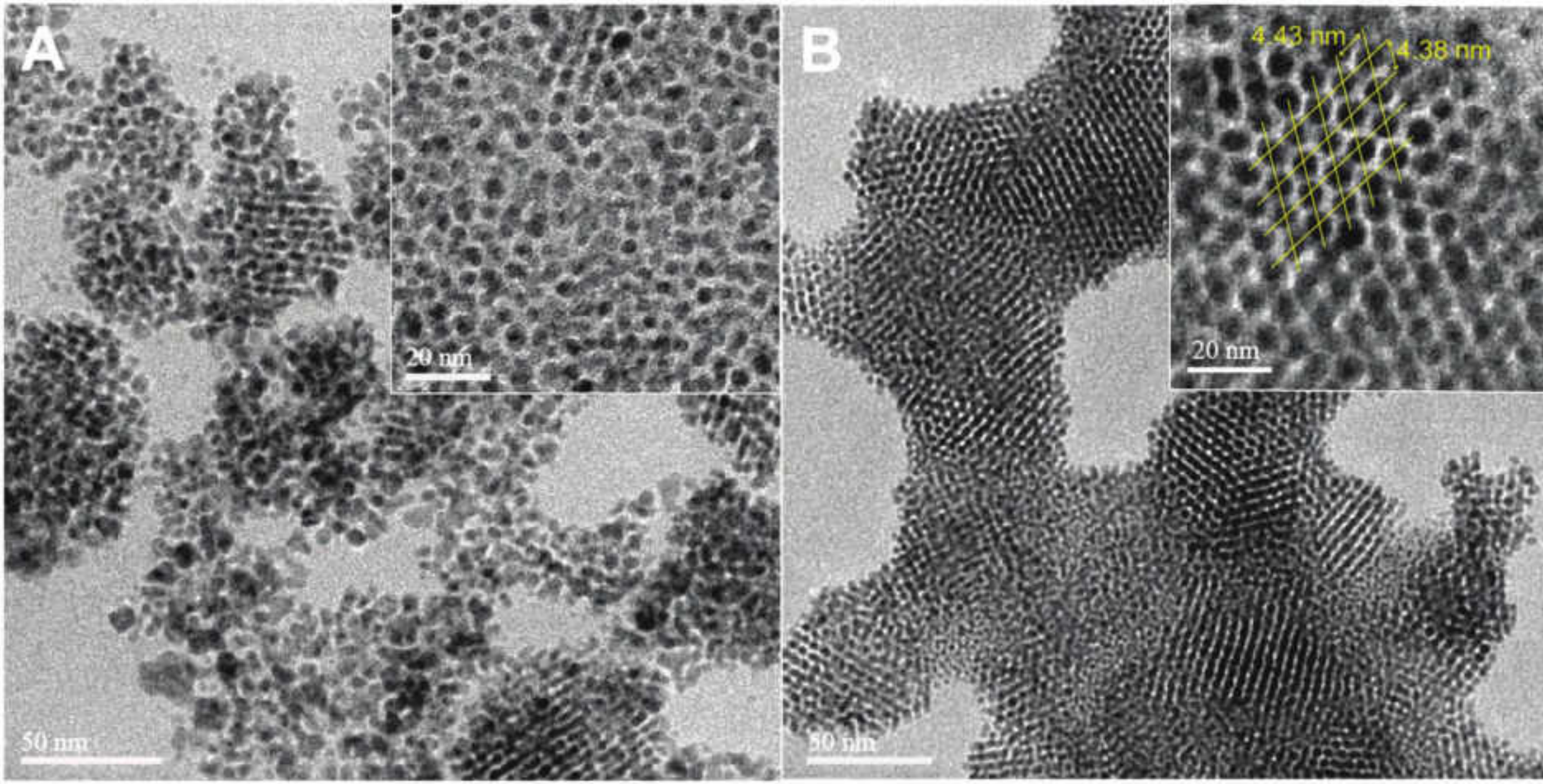


Isotopic exchange



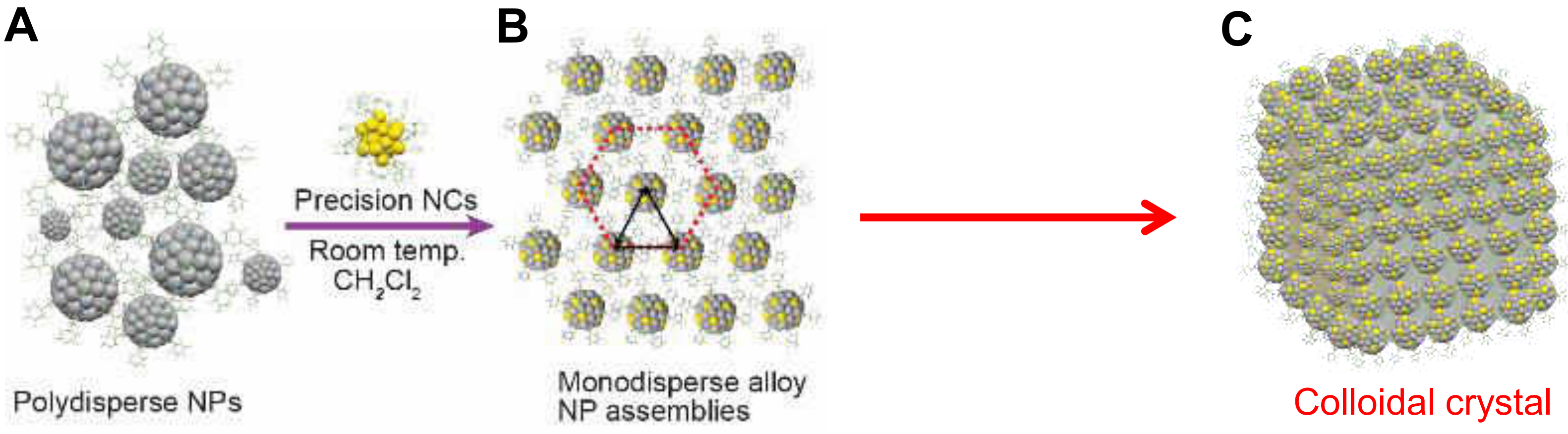
Papri Chakraborti, et. al. Science Advances, 2019.

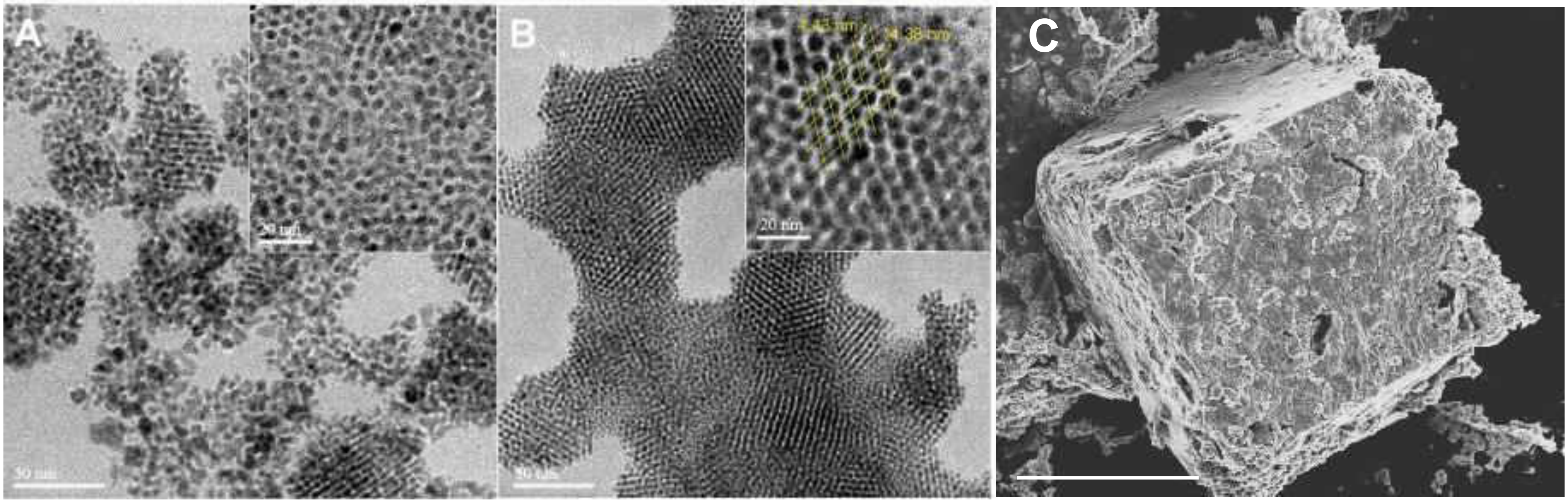
Chemistry in bulk



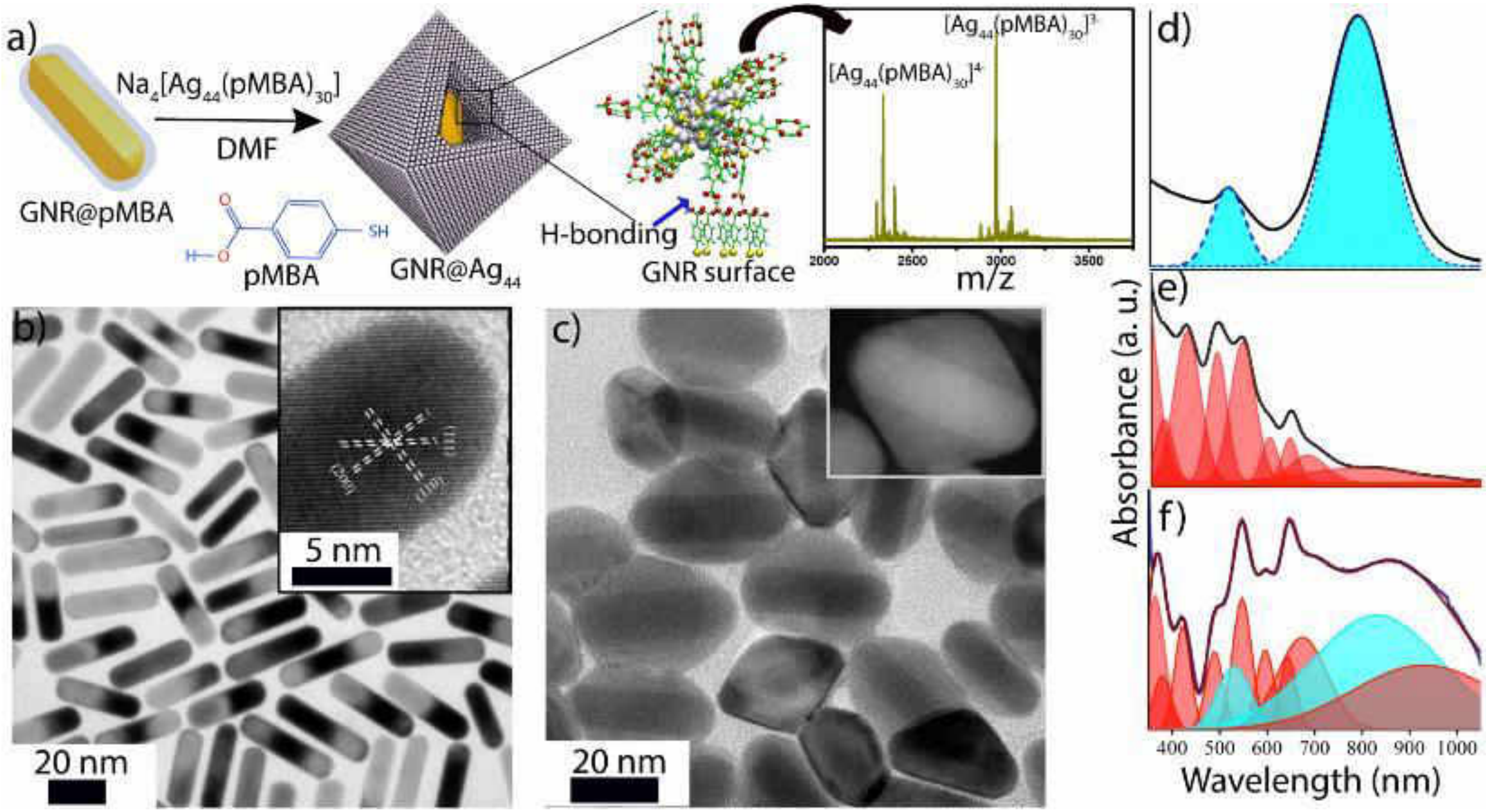
Paulami Bose et al. *Nanoscale* 2020

Crystallization of AgAu NP



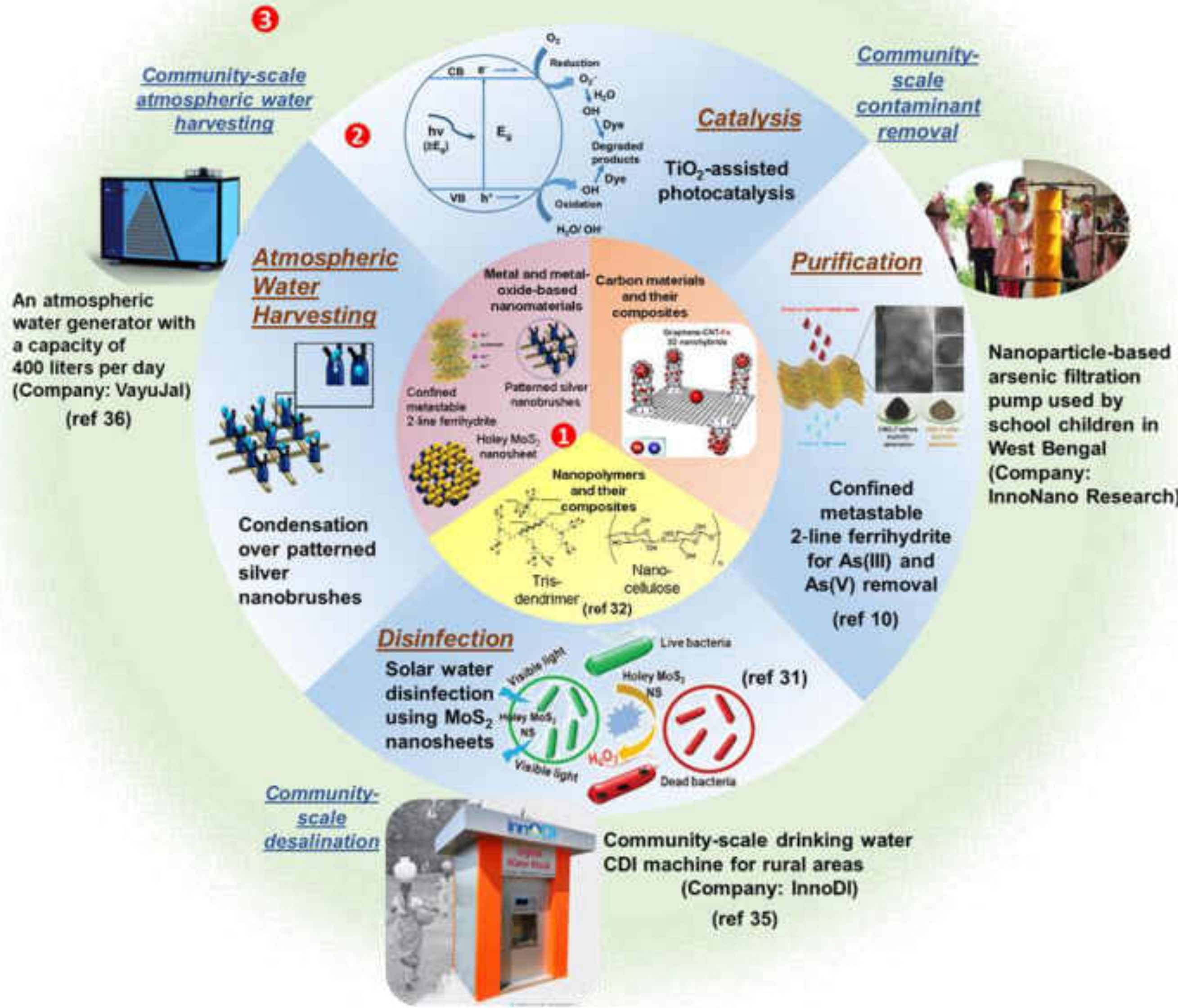


Atomically precise nanocluster assemblies encapsulating plasmonic gold nanorods



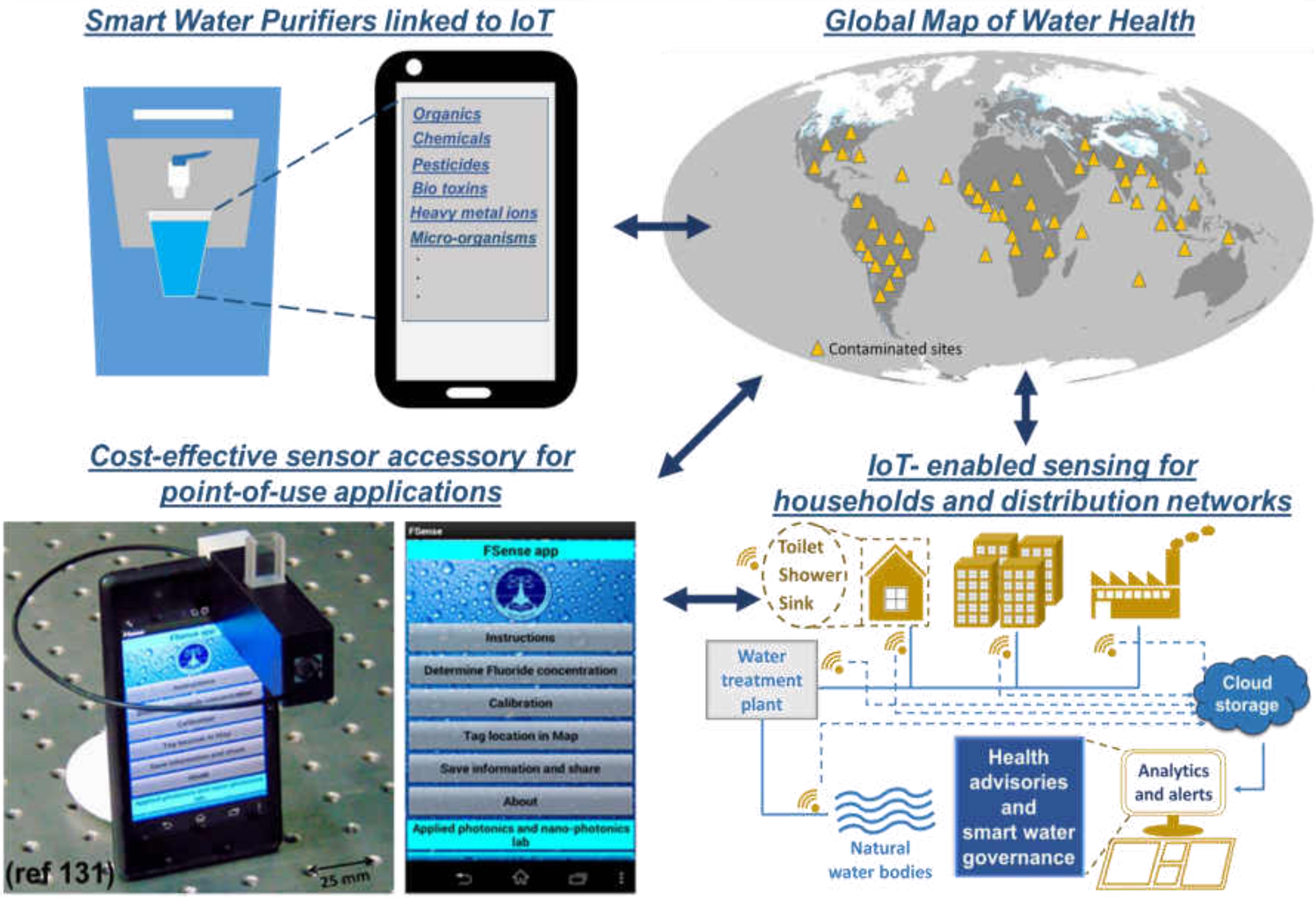
Chakraborty, A. et al., *Angew. Chem. Int. Ed.* **2018,** *57*, 6522–6526.

Evolution of materials to products



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

Smart water purifiers and big data

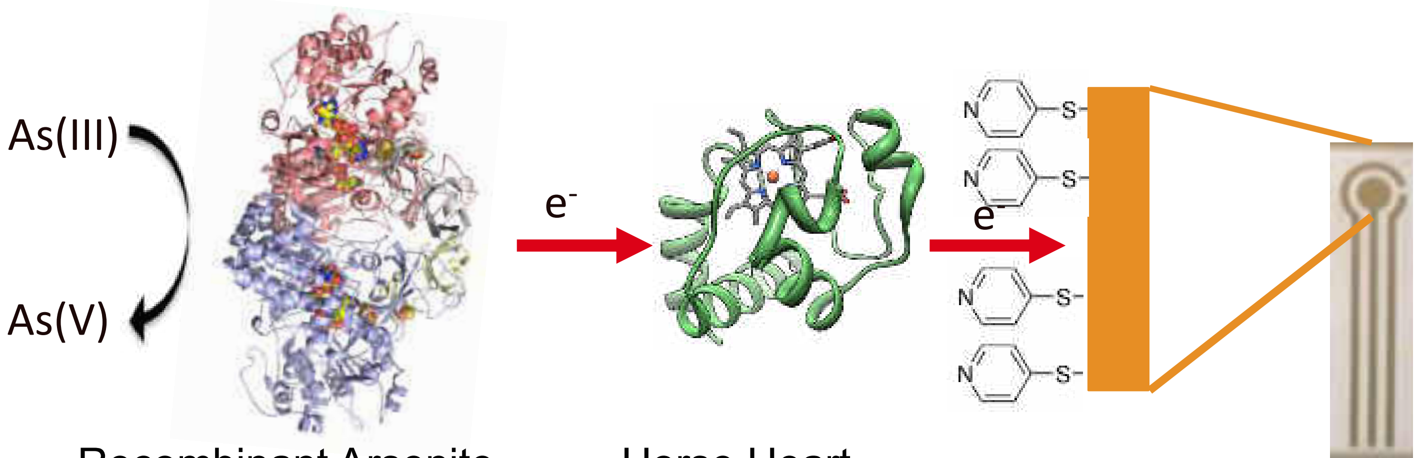


Ankit Nagar and T. Pradeep 14(2020). *ACS Nano*, 6420-6435

Translation to industry

Biosensor Design

1st Generation Design (Mediated Electrochemistry)



Recombinant Arsenite Oxidase NT-26 Aio

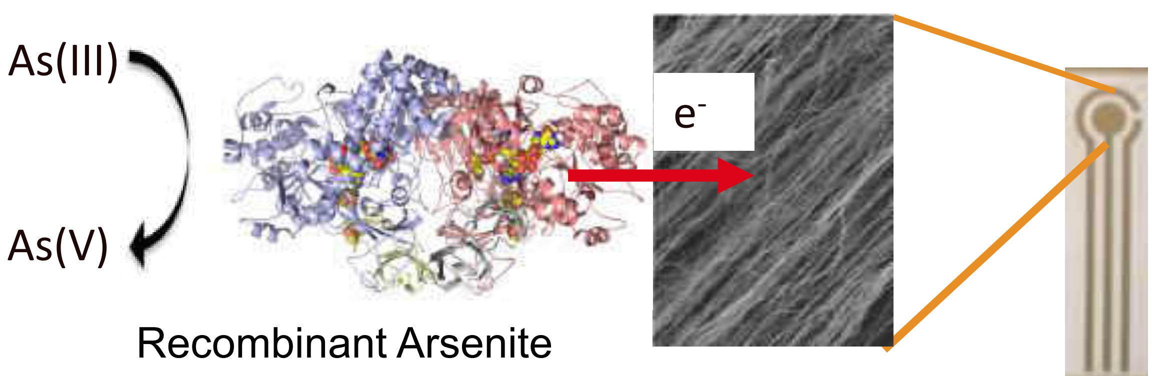
Horse Heart Cytochrome C

Aldrithiol

Low-cost Gold sputtered thin film on PET substrate

Buffer: pH 7-8

2nd Generation Design (Direct Electron Transfer)

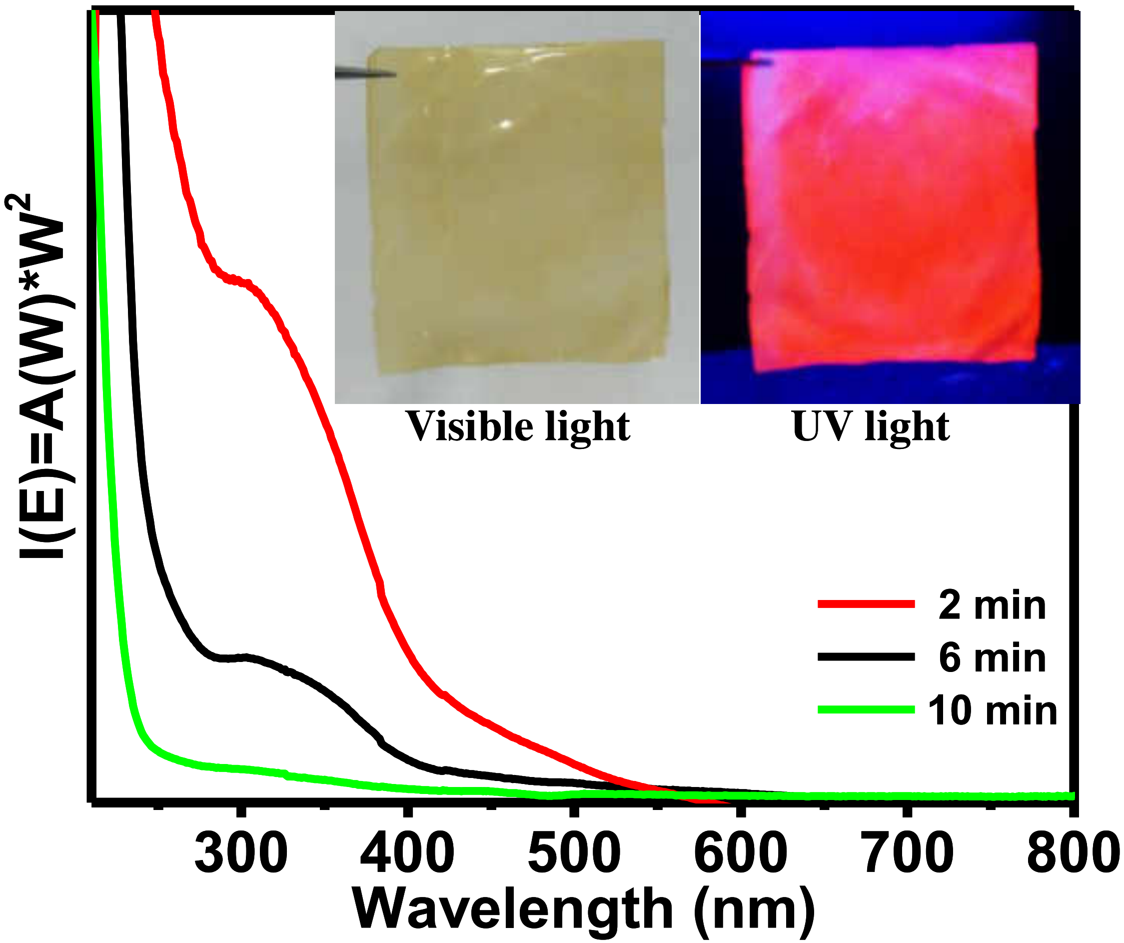


Recombinant Arsenite Oxidase NT-26 Aio

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

Bio-nano Consulting & Imperial College, London

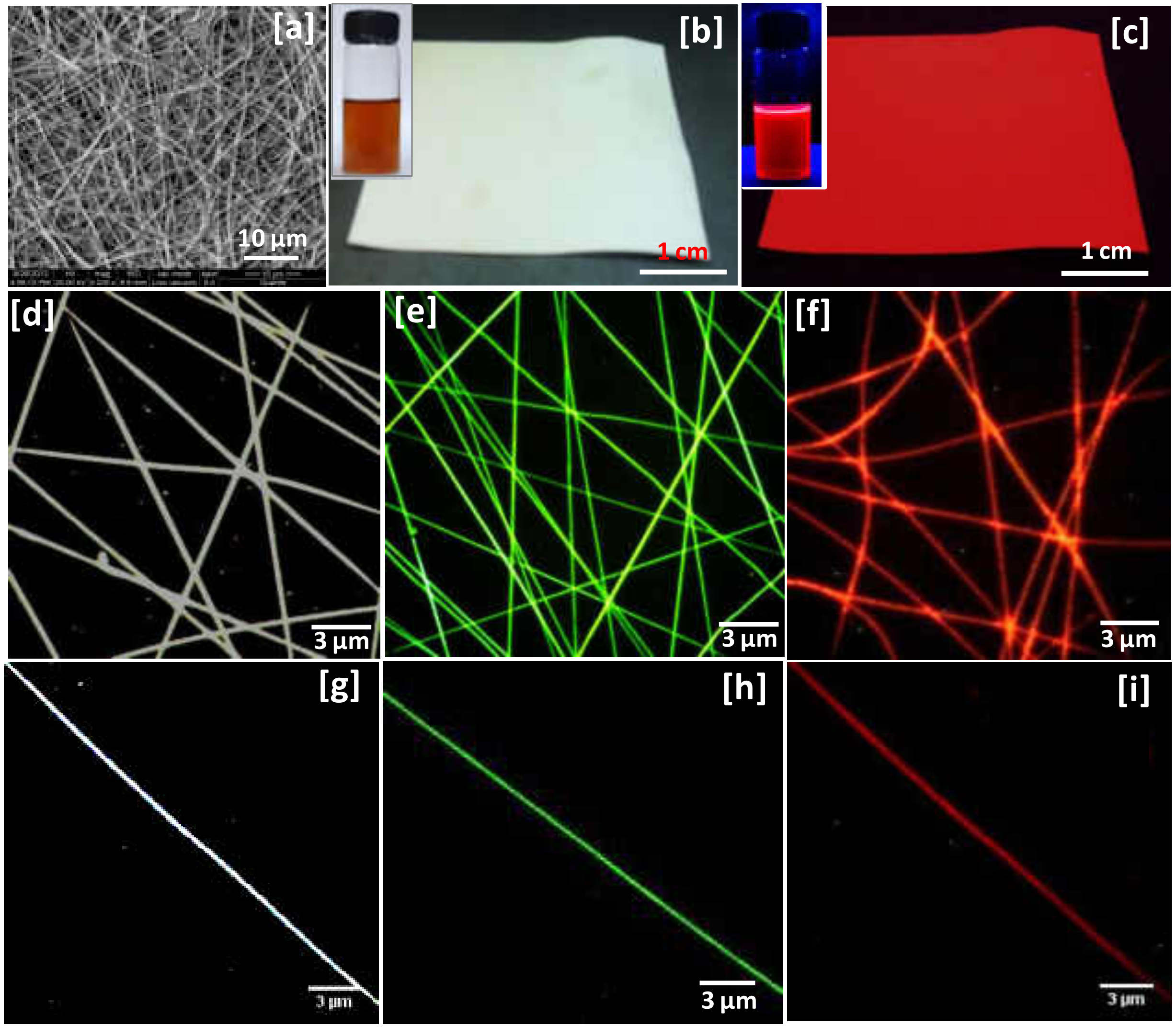
Cluster-based metal ion sensing



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.

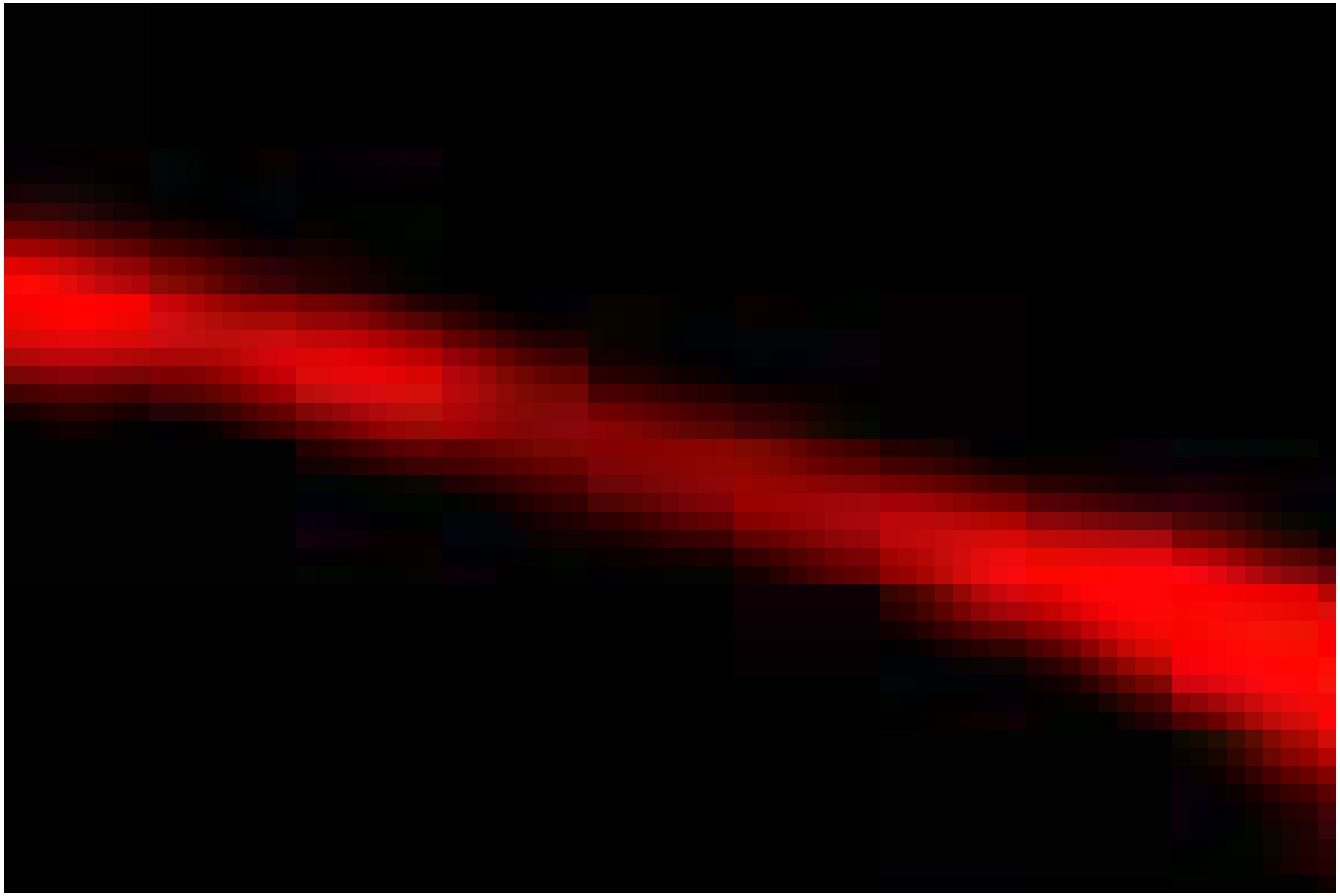
Anu George et al. *ACS Applied Materials & Interfaces*, 2012

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

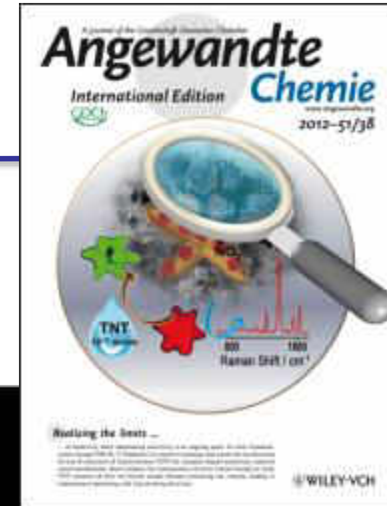


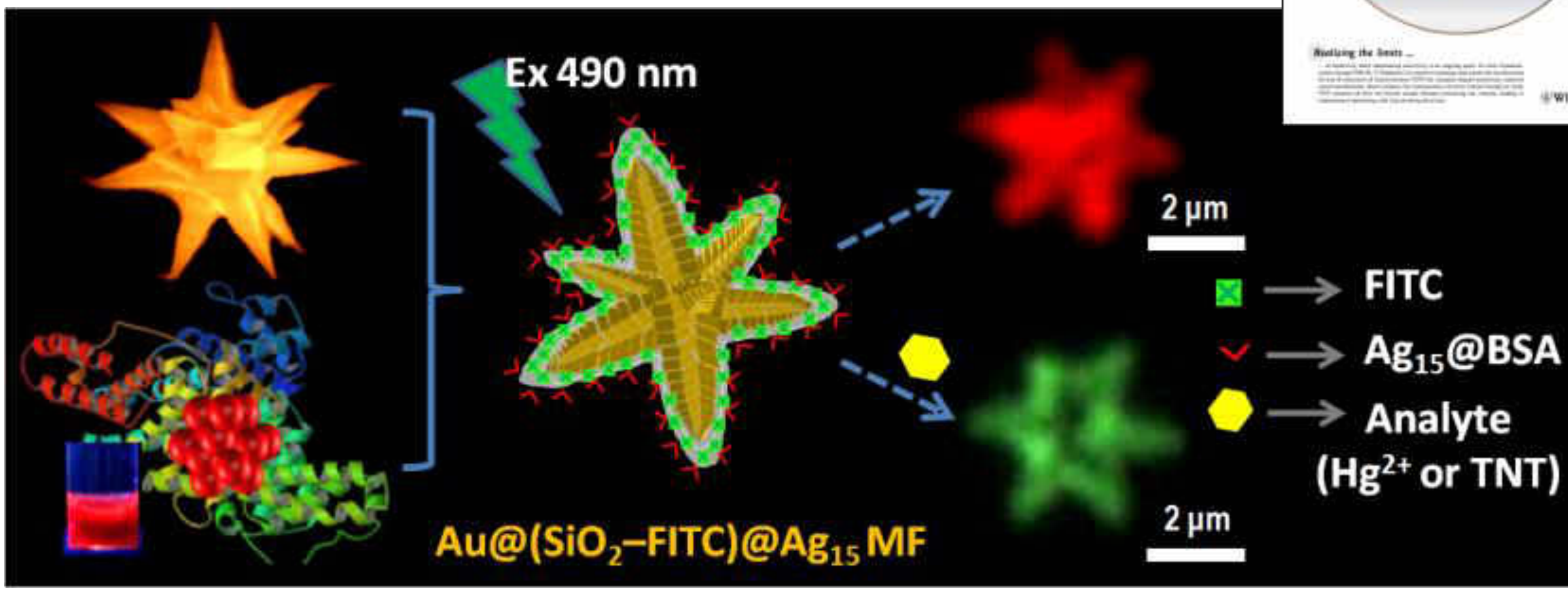
Atanu Ghosh et al. Anal. Chem. 2014.

Mercury quenching experiment using nanofiber



Sub-zeptomolar detection

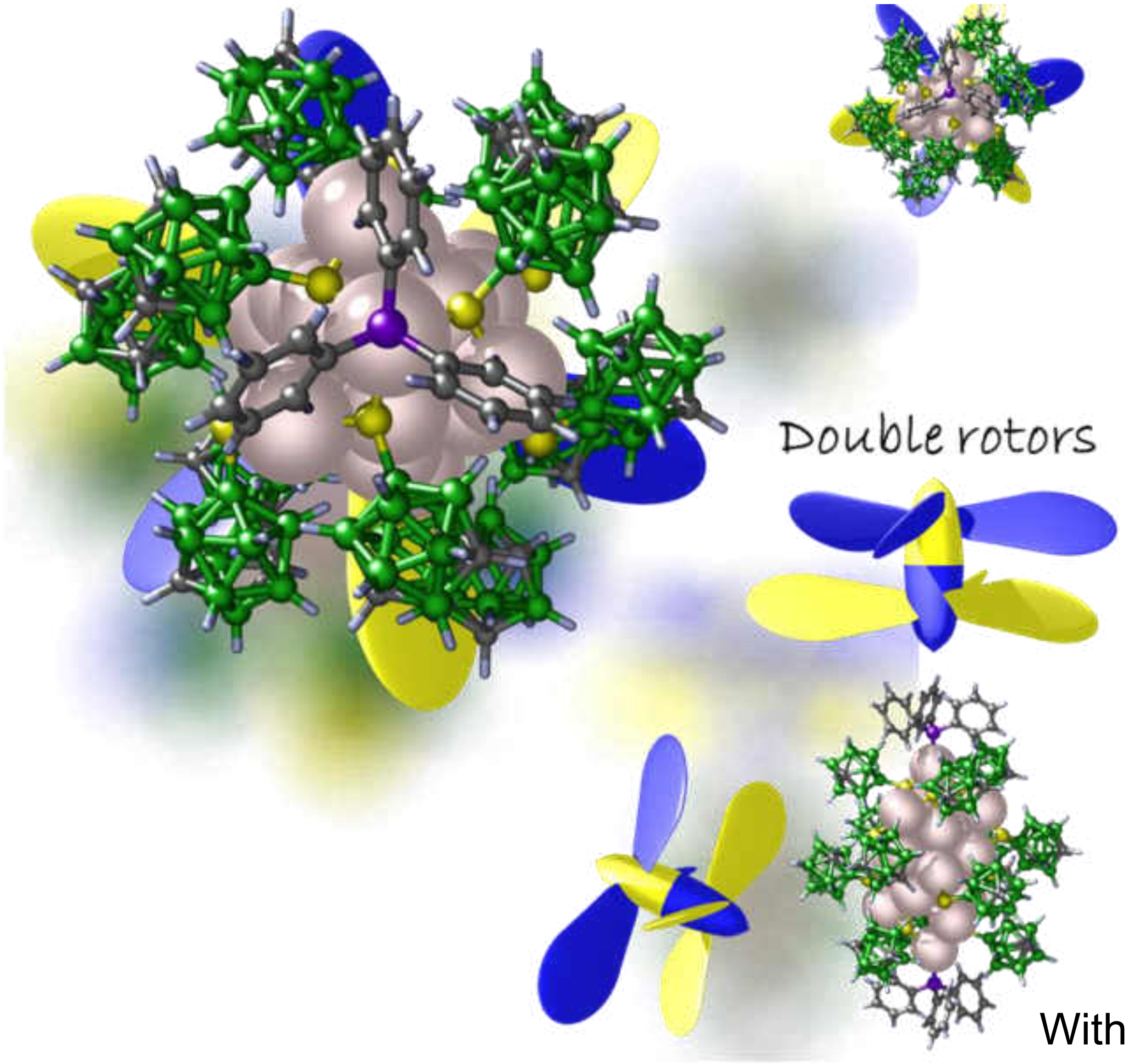




Featured in:
The Hindu, Telegraph, Times of India, etc.
C&E News
and many others

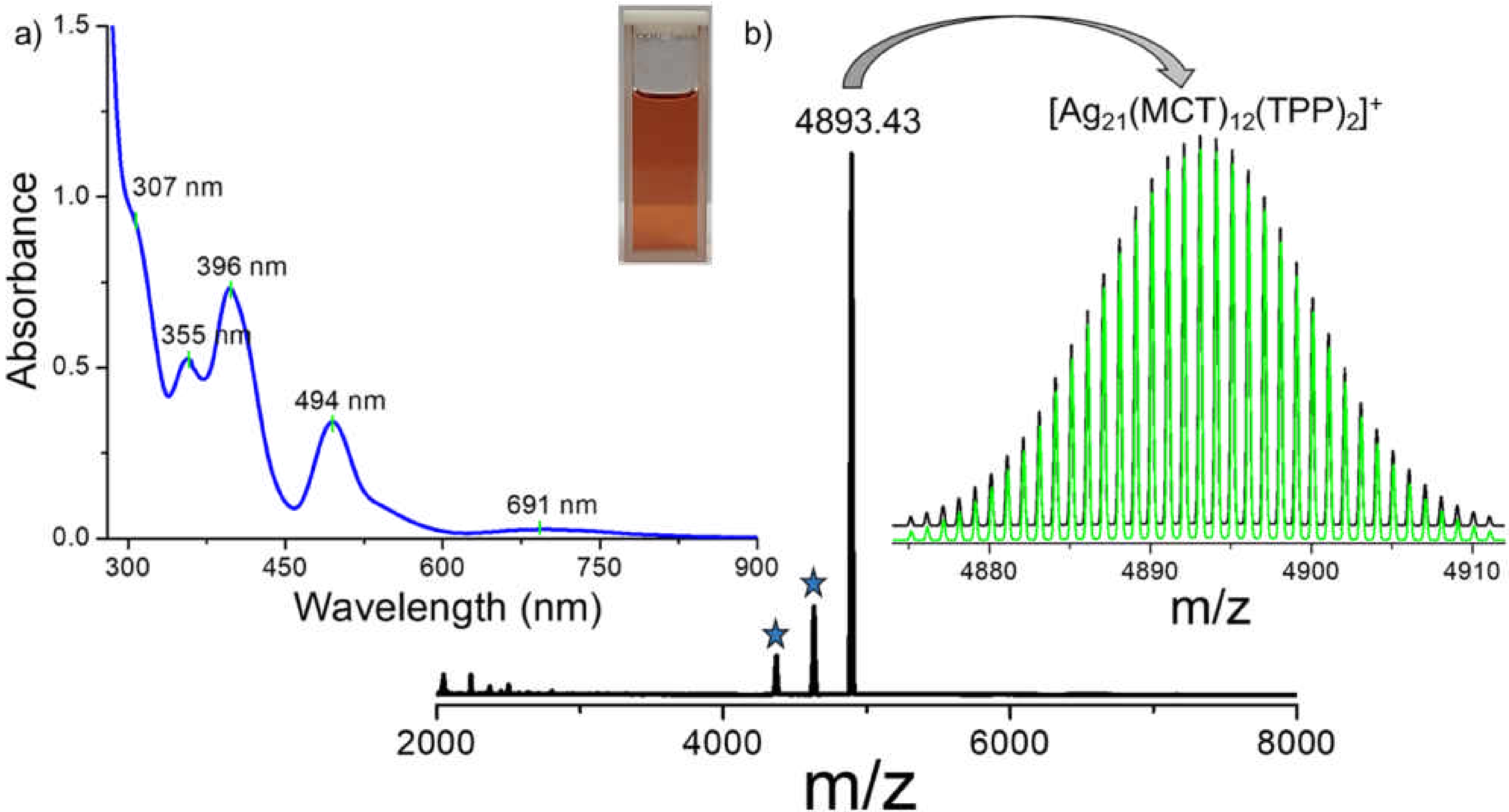
Ammu Mathew, et al. Angew. Chem. Int. Ed. 2012

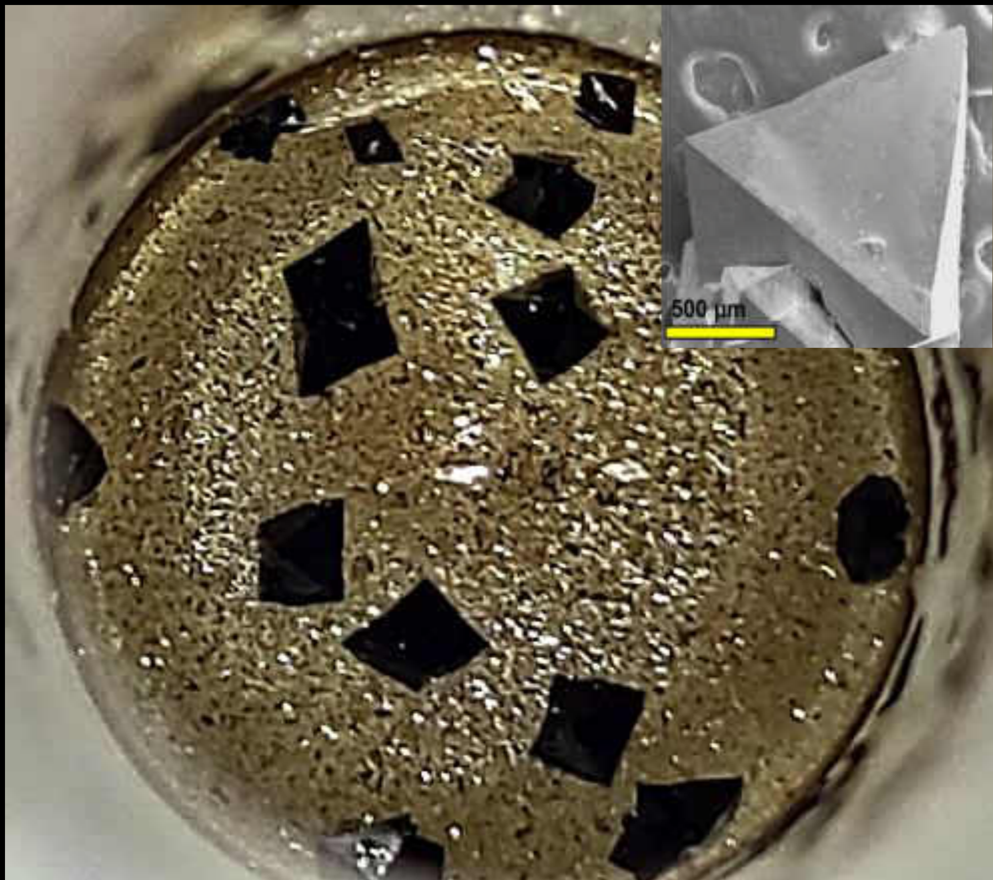
Carborane-thiol protected silver nanomolecule

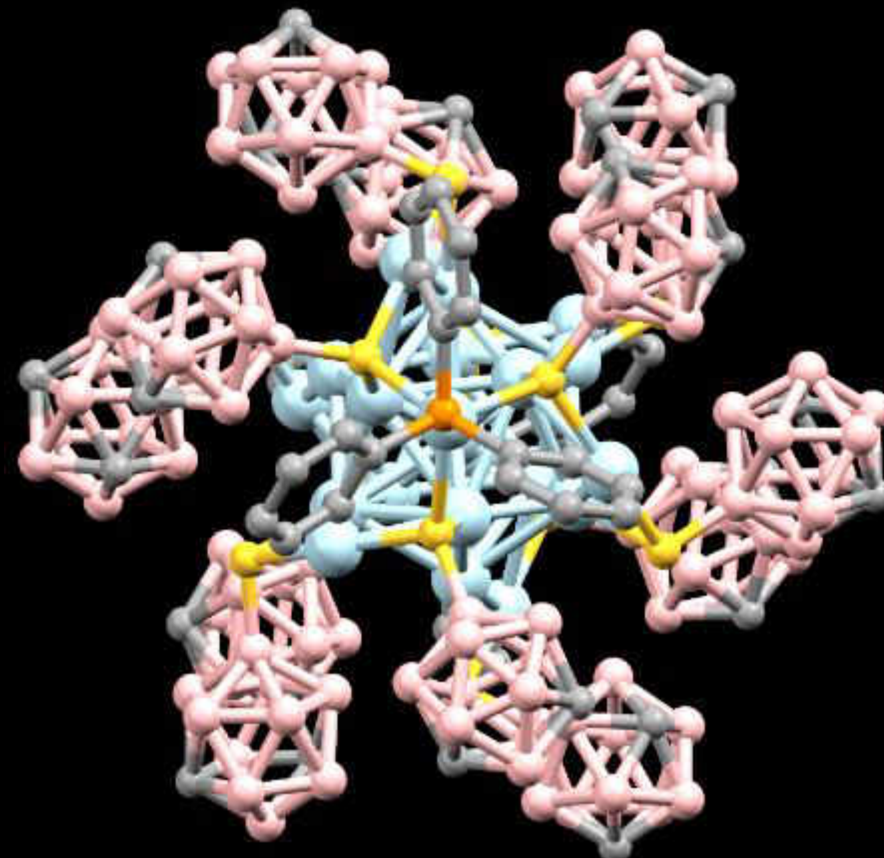


With Tomas Base

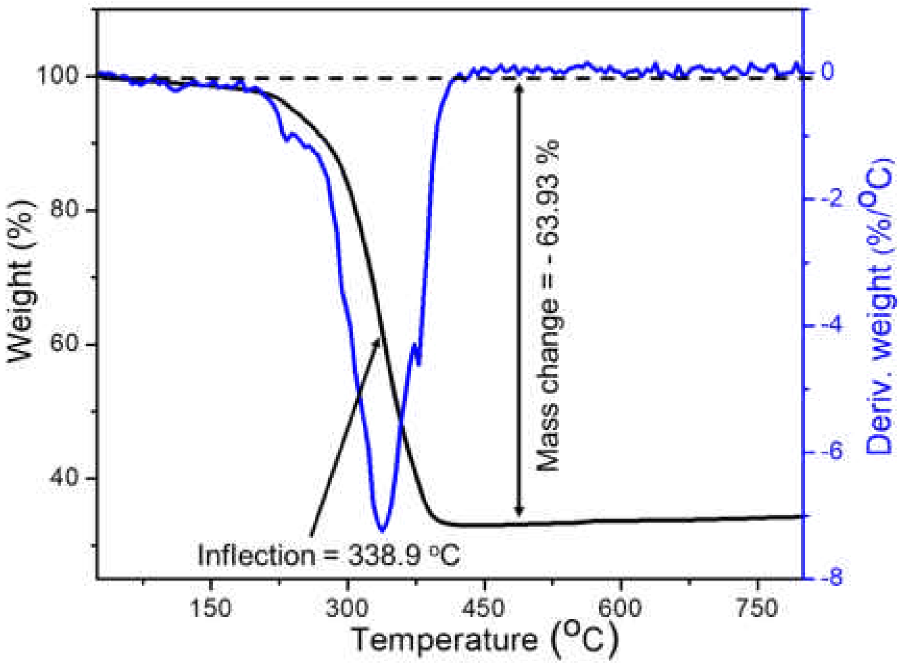
Characterization of Ag_{21}

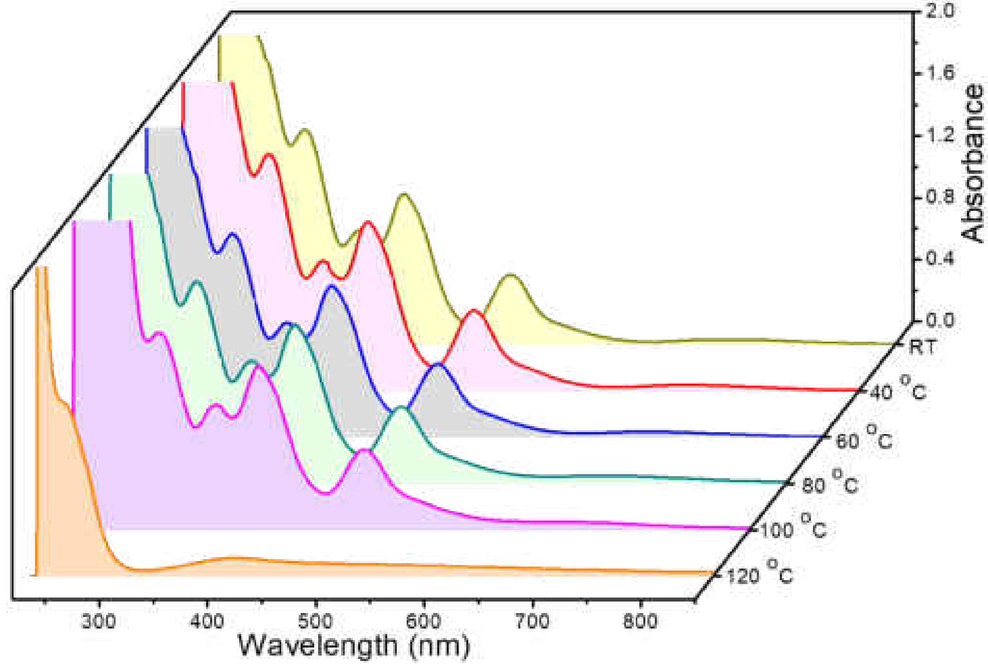



500 μm

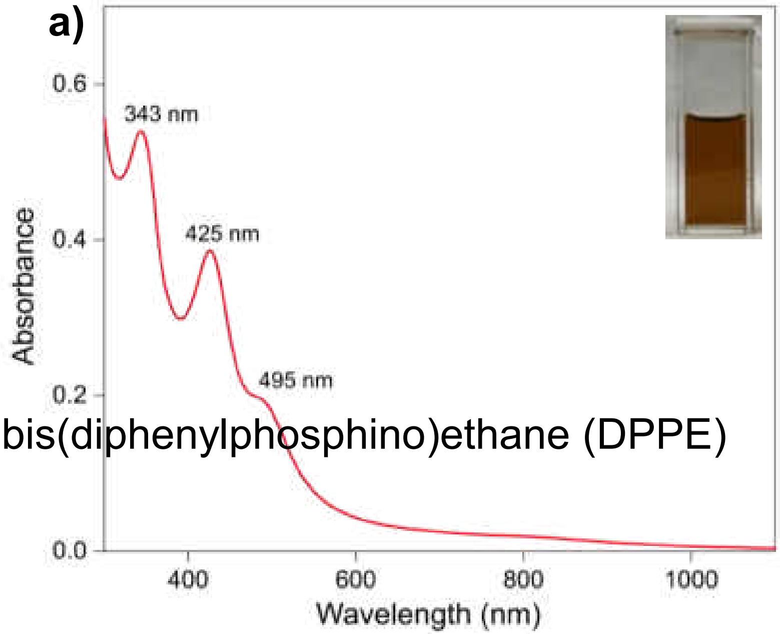


Thermal stability

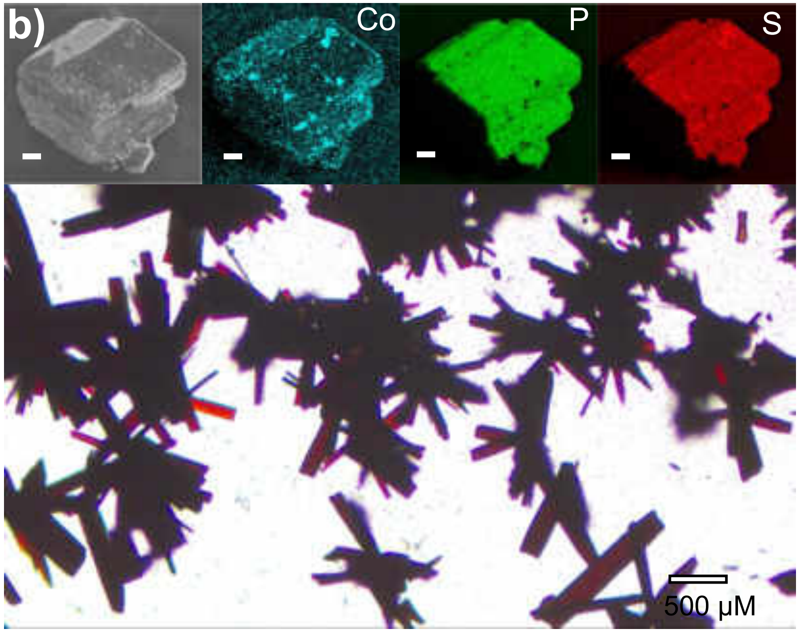


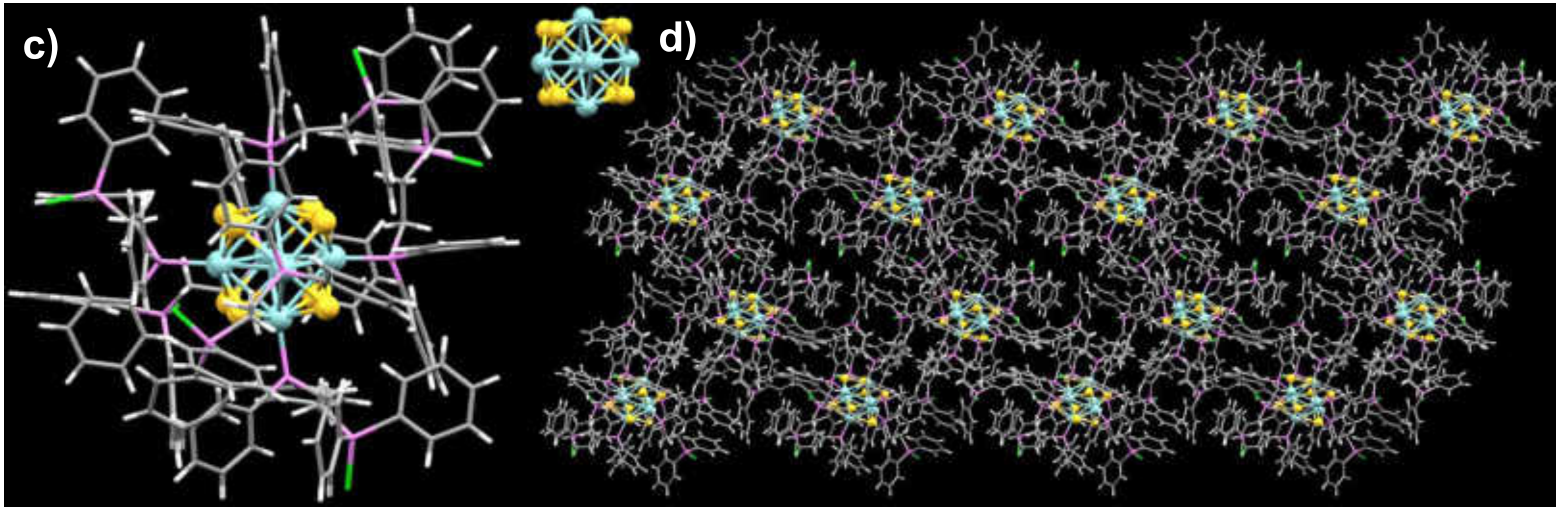


New electrodes - Aligned nanoplates of Co_6S_8

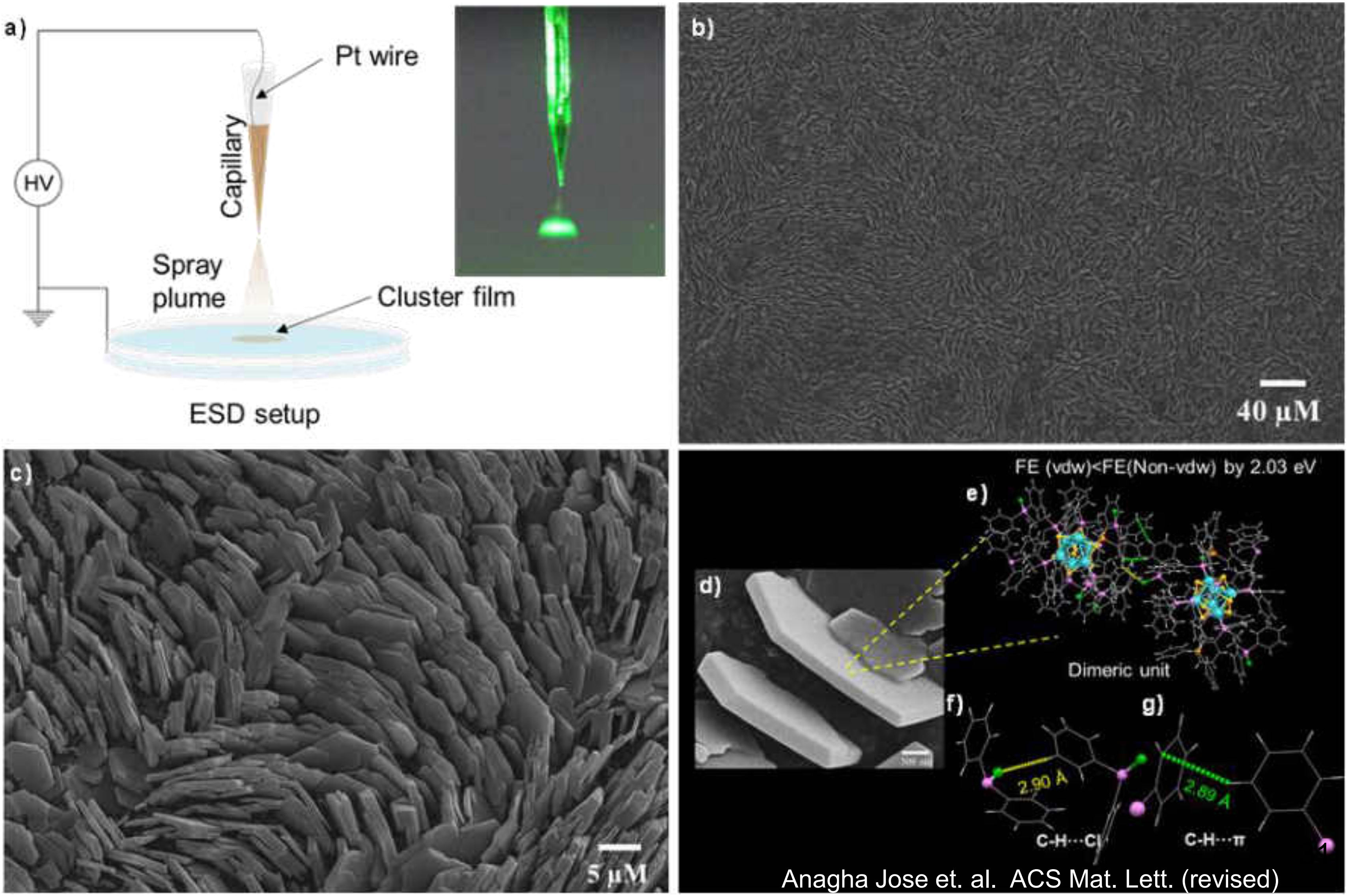


1,2-bis(diphenylphosphino)ethane (DPPE)



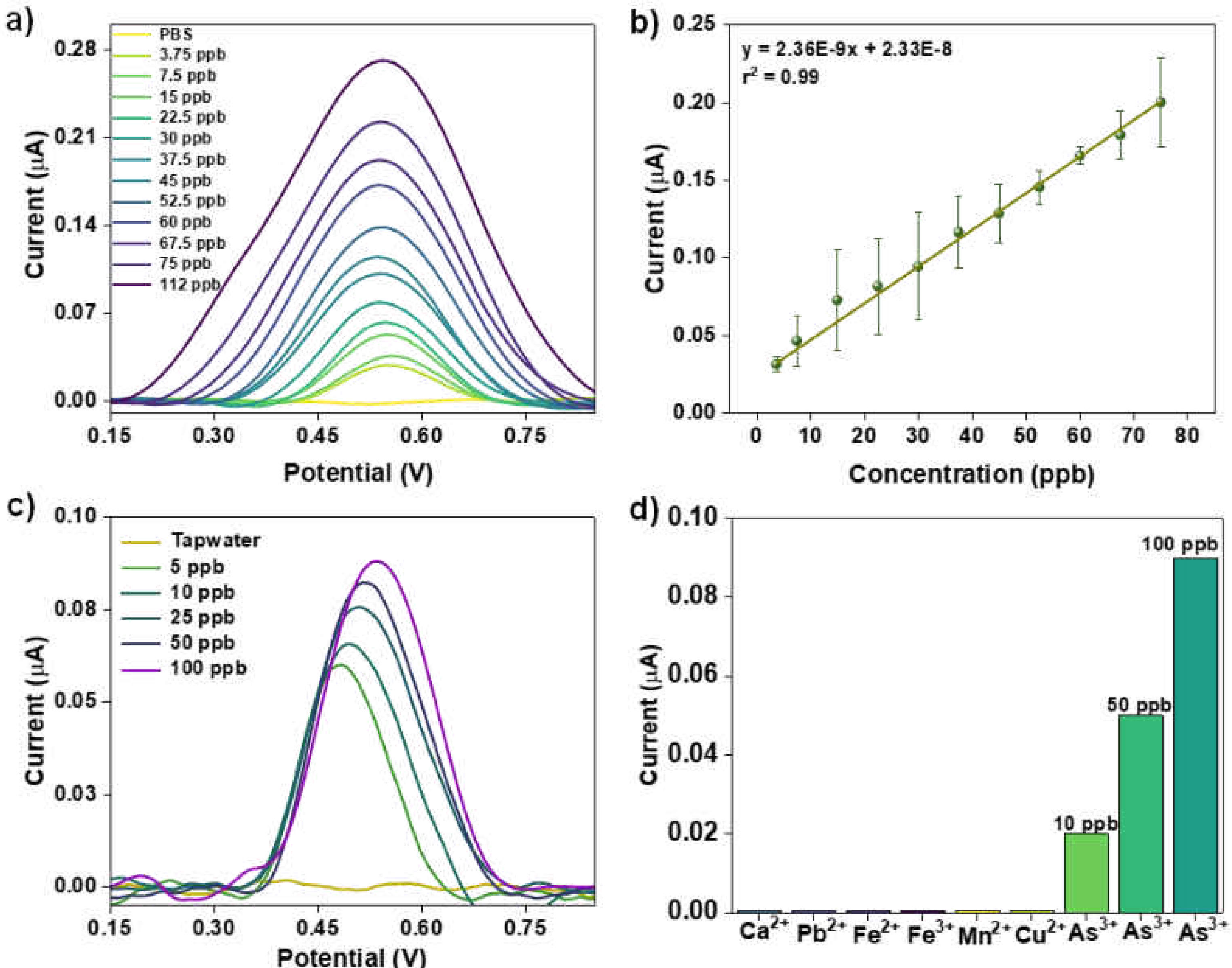


Electrospray deposition

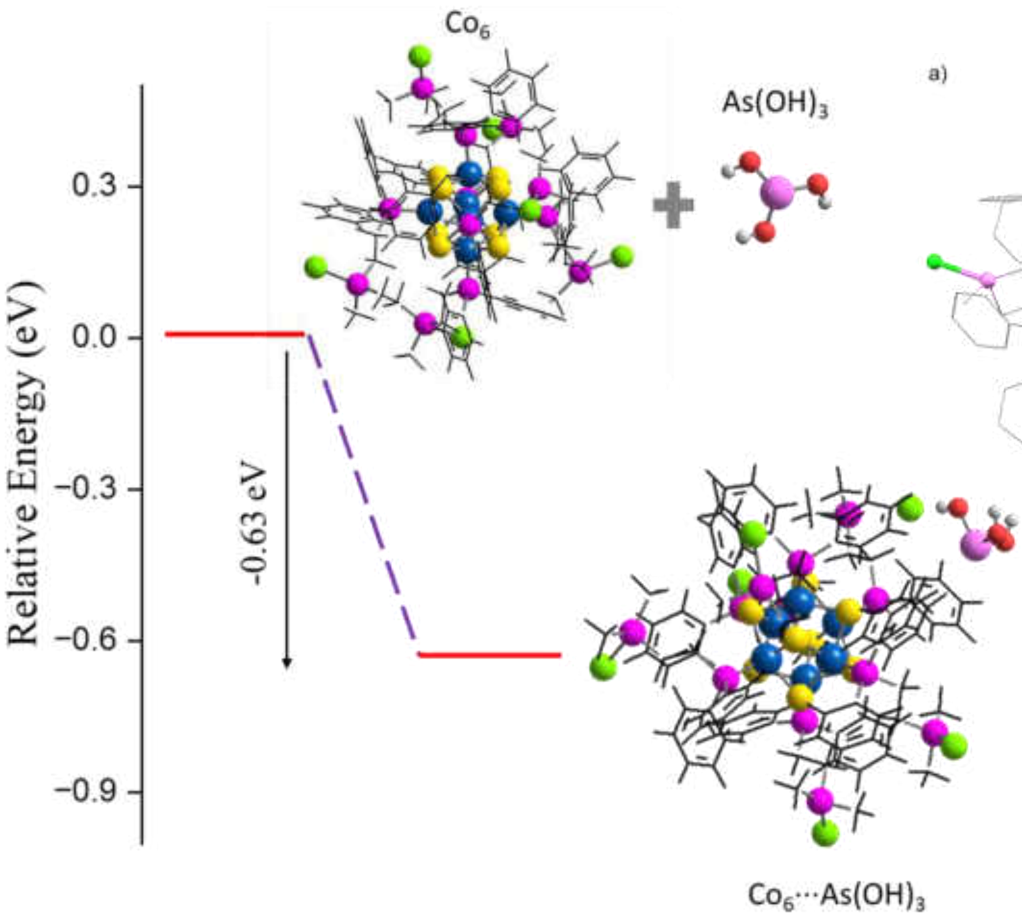


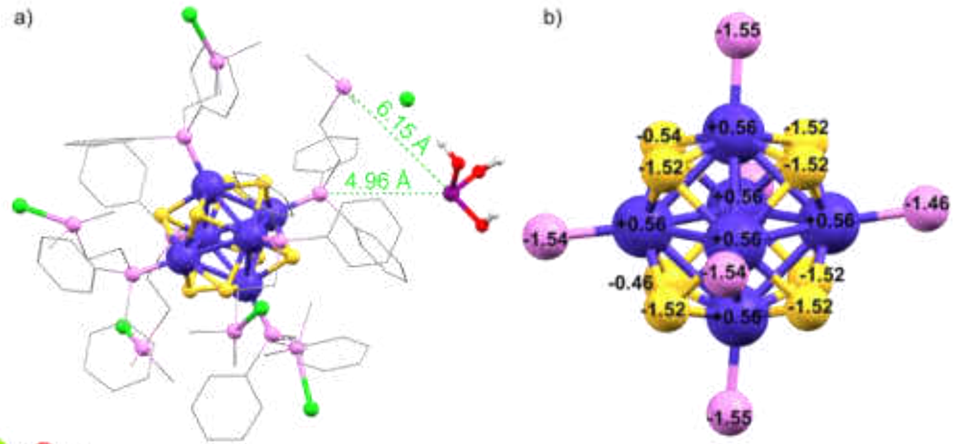
Anagha Jose et. al. ACS Mat. Lett. (revised)

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





Previous As sensor with Co nanoparticles

1 μM= 75 ppb
10 μM= 750 ppb

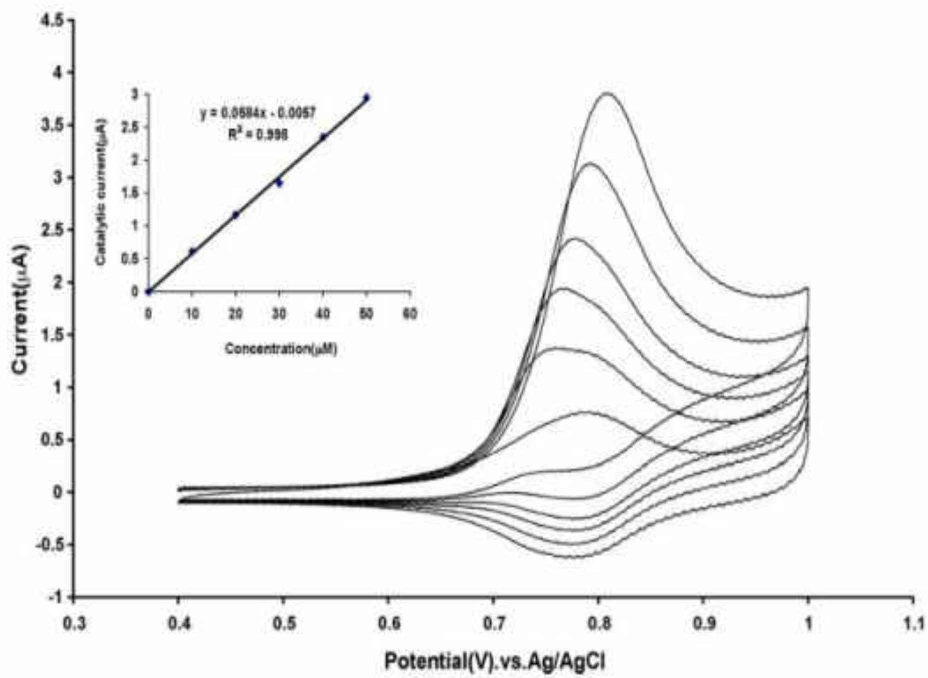


Fig. 4. Cyclic voltammograms of cobalt oxide nanoparticles modified GC electrode in buffer solution pH 7 at scan rate 20 mV s^{-1} with increasing arsenic concentration (from inner to outer) 0.0, 10, 20, 30, 40 and 50 μM. *Inset*: plot of peak current vs. arsenic concentrations.

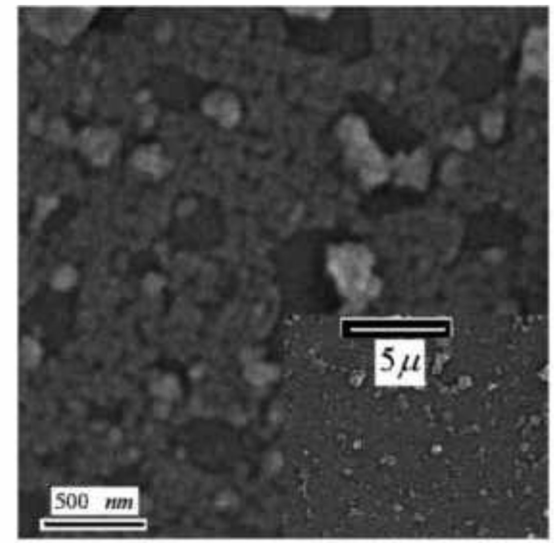
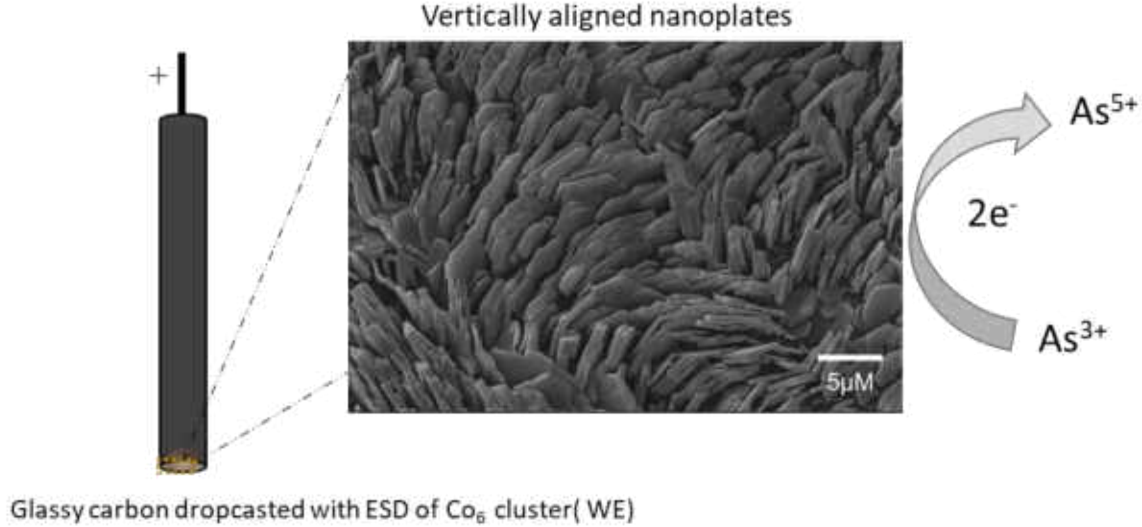


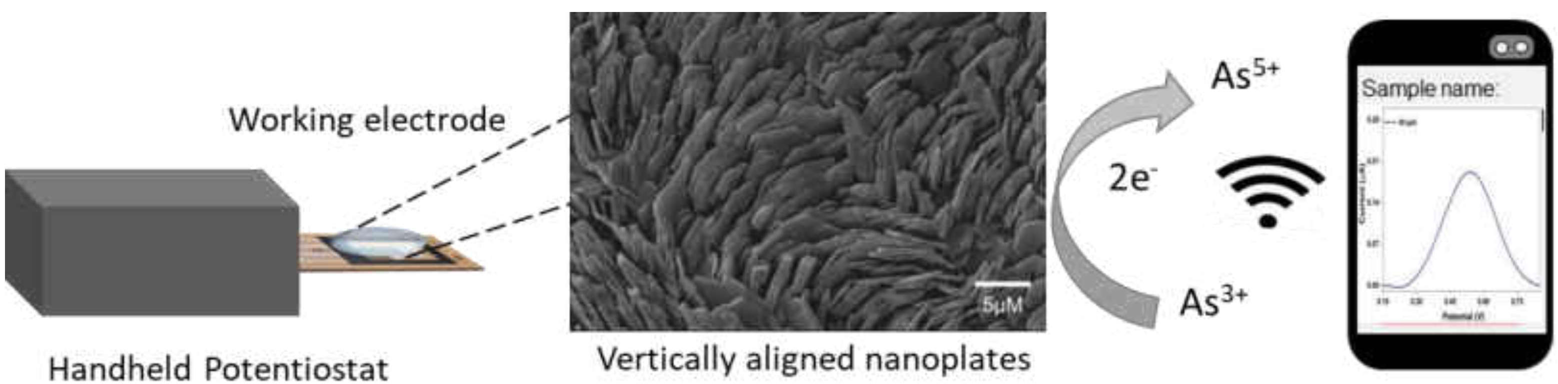
Fig. 1. SEM image of the electrodeposited cobalt oxide on glassy carbon, scale bare 500 nm. *Inset*: The SEM image with lower magnification for the same sample, scale bar is 5.0 μm.

A theoretical LOD of 0.825 ppb using CoOx on a glassy carbon electrode in PBS at pH 7 was reported.

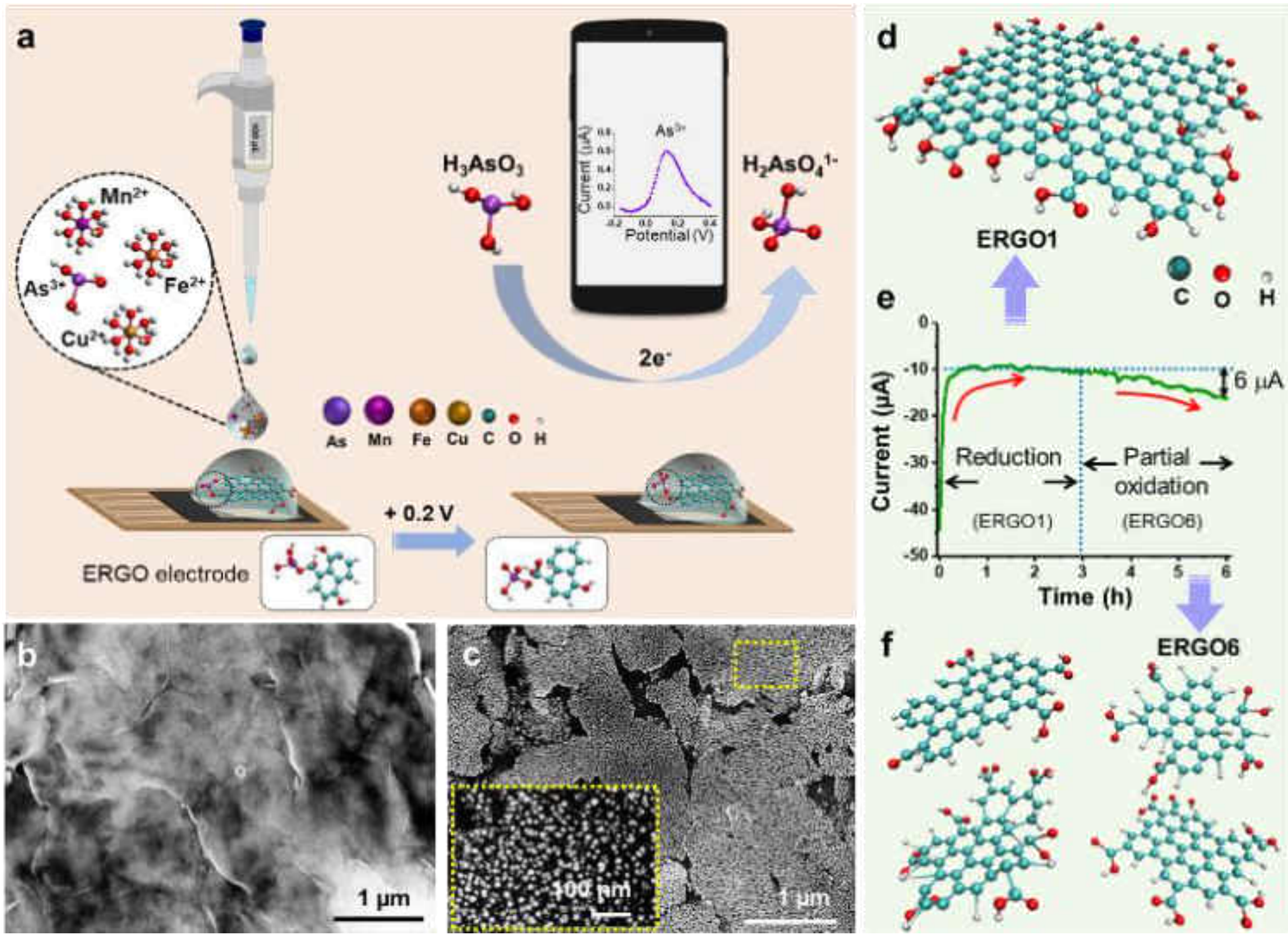
A. Salimi et al. Sensors Actuators, B Chem. 2008, 129 (1), 246–254.

Working electrode

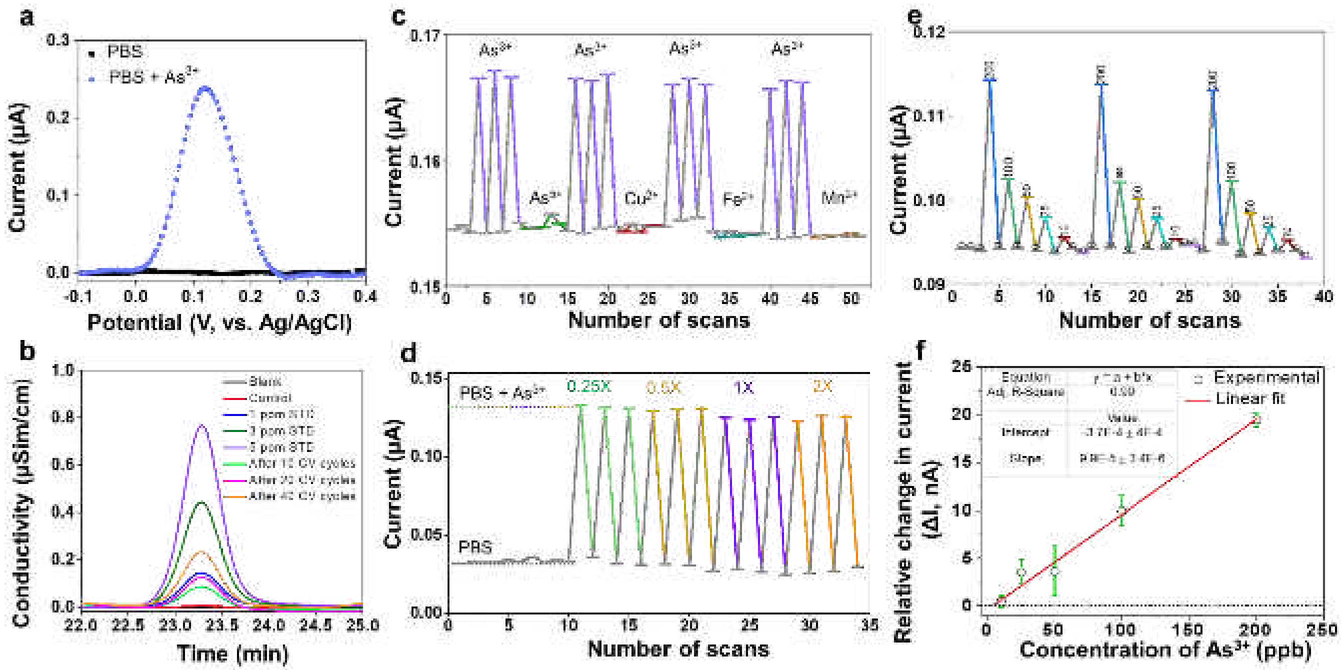




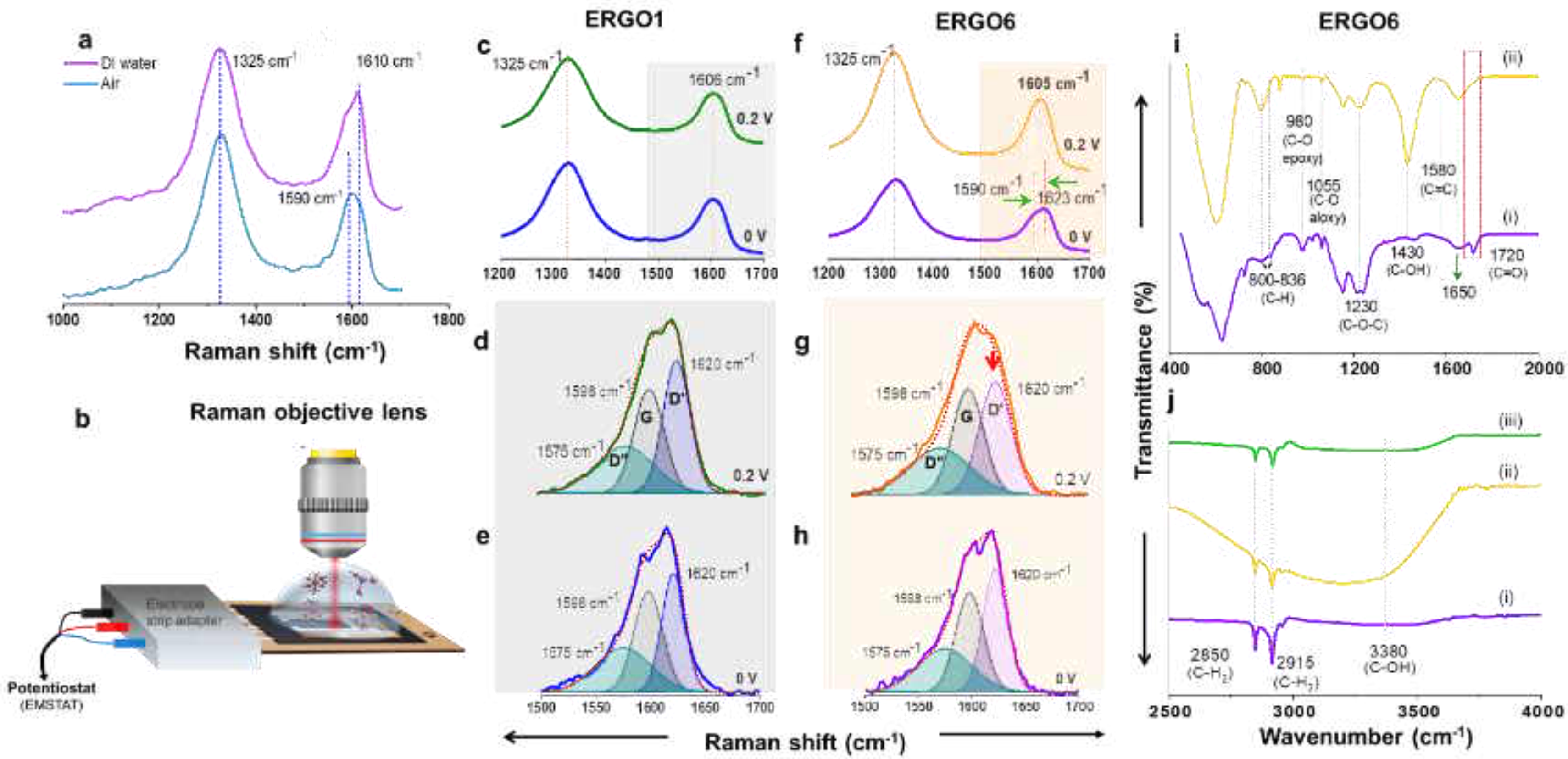
Practical graphene-based arsenite sensor



S. K. Jana et al. ACS Appl. Nano Mater., 5 (2022) 11876−11888.

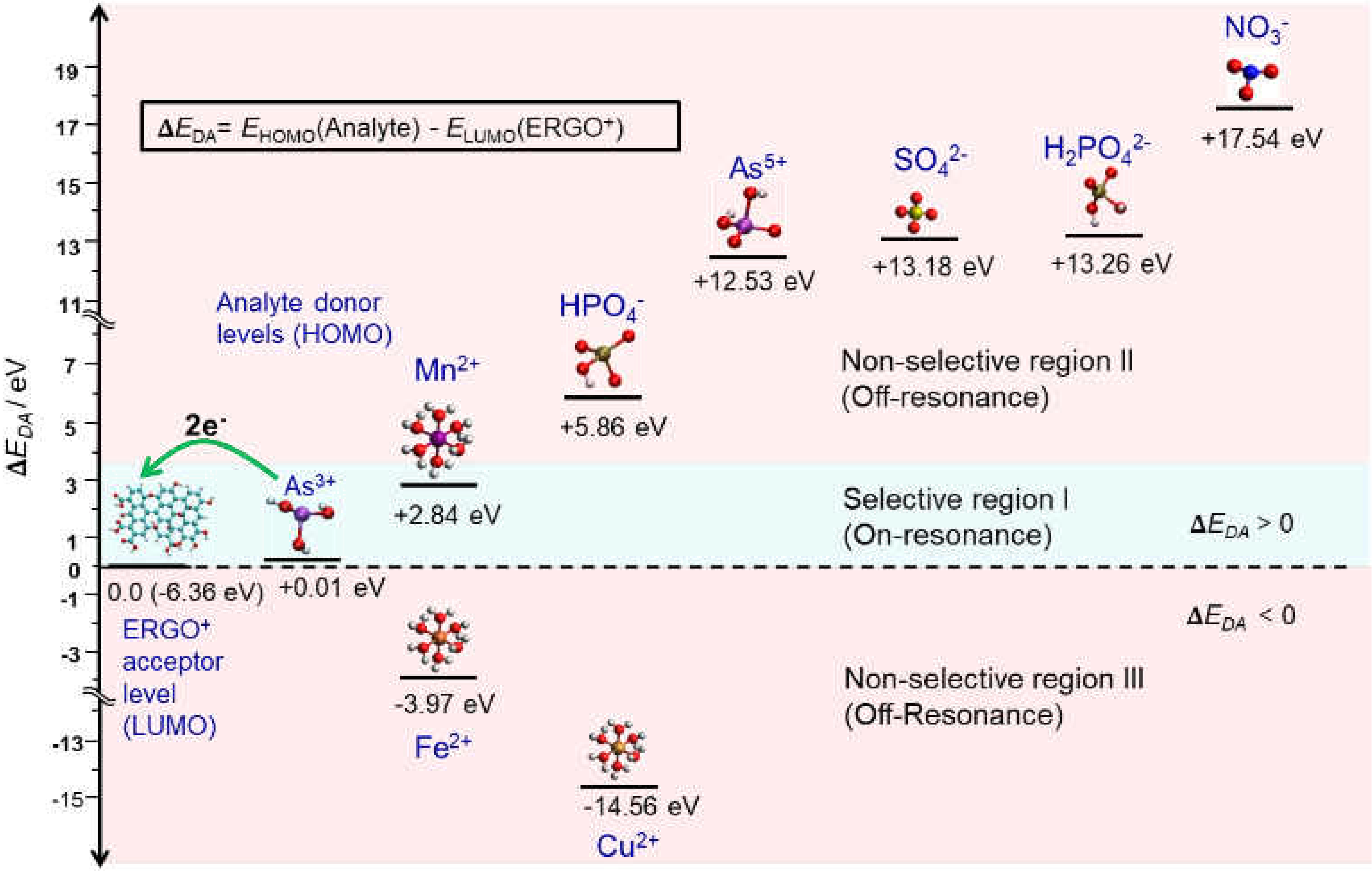


(a) LSV response of ERGO6 without and with 1 ppm As^{3+}, (b) Chronograms obtained from ion chromatography (IC) measurement with the solutions obtained after different number of CV cycles and same measurement with standard (STD) As^{5+} solutions of different concentrations. (c) CA measurement with different concentrations of As^{3+}. (d) Calibration curve showing linearity down to 10 ppb. (e) Interference study performed with several heavy metal ions with ERGO6 electrode. Concentration of As^{3+} was fixed at 200 ppb, while 1 ppm was maintained for interfering ions. (f) Investigation of CA current response of 1 ppm As^{3+} spiked in PBS with different ionic conductivity. We prepared PBS solutions of different conductivity by changing their ionic concentrations and used them further as electrolytes during CA measurements.

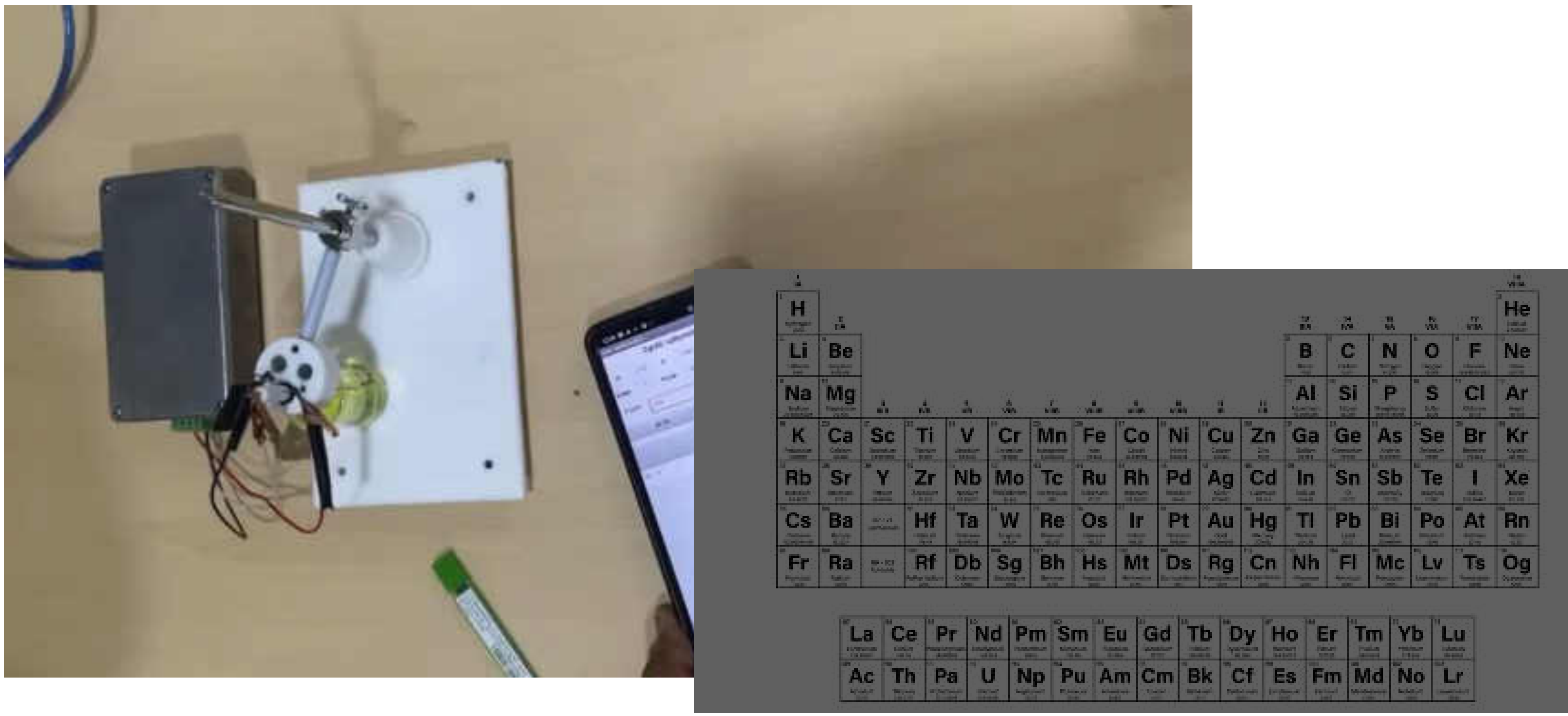


(a) Raman spectra of ERGO6 without (air) and with DI water. (b) Schematic depicts spectro-electrochemical (SPEC) measurement set-up. During SPEC measurements, the Raman objective was focused at the surface of ERGO6 strips with and without As^{3+} containing DI water on it and a DC potential of 0.2 V was applied to the electrode. (c) Raman spectra of ERGO1 in presence of As^{3+} without and with the application of potential (+ 0.2 V). Gaussian peak fitting was performed on the G bands of Raman spectra of ERGO1 (d) with, and (e) without the application of potential. (f) Raman spectra of ERGO6 in presence of As^{3+} without and with application of +0.2 V. Gaussian peak fitting was performed on the G bands of the Raman spectra of ERGO6 (g) with and (h) without the application of potential. Decrease in the intensity of D′ is marked with a downward arrow. FTIR spectra of ERGO6 (i) without (purple trace) and with As^{3+} (yellow trace), (j) FTIR spectra of the same strip without As^{3+} (purple trace), with As^{3+} (yellow trace), and after electrochemical oxidation (green trace) to show the changes in OH deformation peak at higher wavenumber

Origin of selectivity

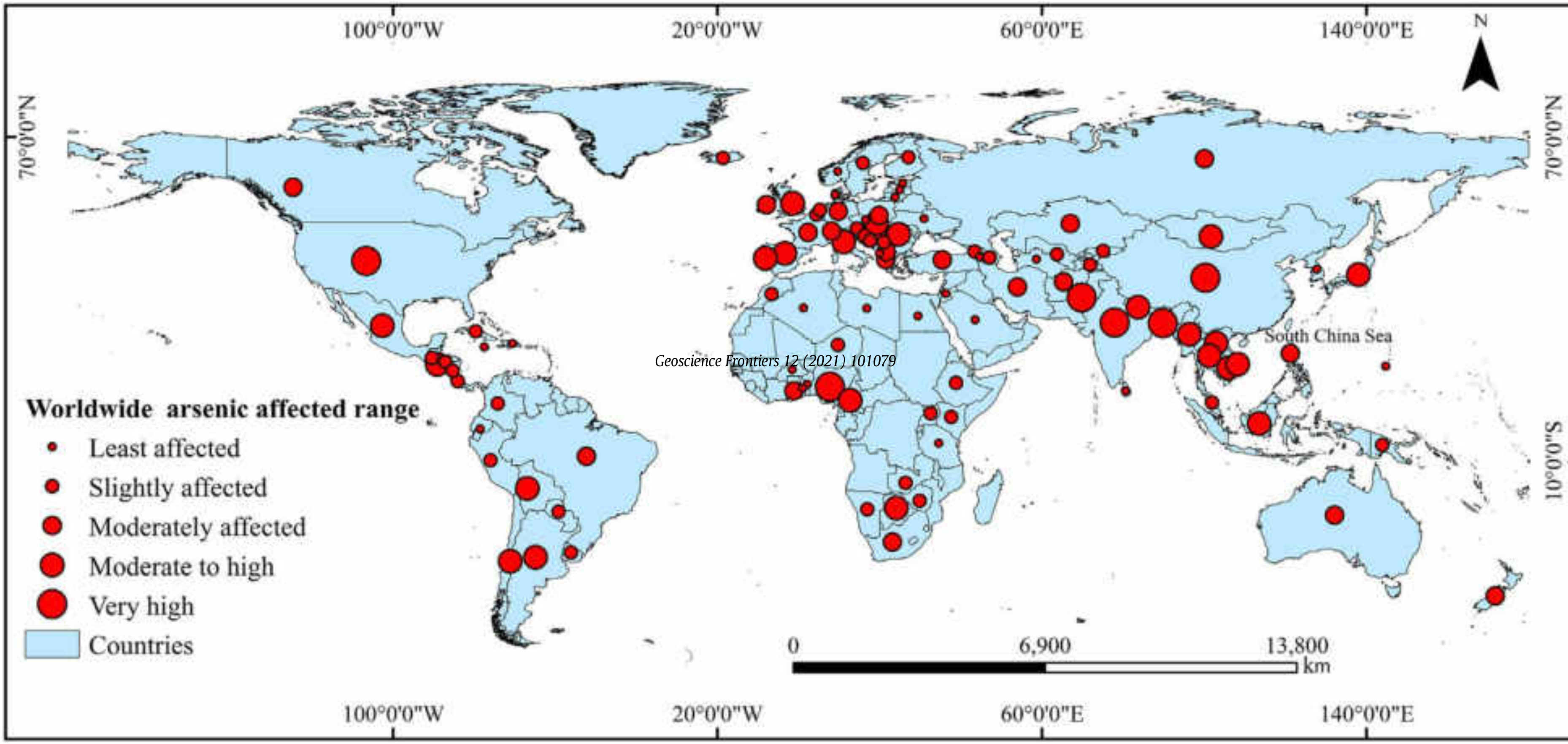


Analytical devices



Sourav Kanti Jana

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.

Collaborators






Tatsuya Tsukuda,
Keisaku Kimura,
Yuichi Negishi,
Uzi Landman,
Hannu Hakkinen,
Rob Whetten

Robin Ras

Nonappa

Tomas Base

Manfred Kappes

Olli Ikkala

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Biswarup Pathak

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G. U. Kulkarni

Vivek Polshettiwar

Shiv Khanna

Department of Science and Technology

Collaborators: Tatsuya Tsukuda, Keisaku Kimura, Yuichi Negishi, Uzi Landman, Rob Whetten, Hannu Hakkinen, Robin Ras, Manfred Kappes, Horst Hahn, Tomas Base, Nonappa, Shiv Khanna, Umesh Waghmare, Chandrabhas Narayana, Giridhar U. Kulkarni, Reji Philip, Vivek Polshettiwar, R. Mukhopadhay, K. V. Adarsh, Biswarup Pathak, Chaitanya Sharma Yamijala

Thank you all