Since 1959

Can Microdroplets Make Soil?

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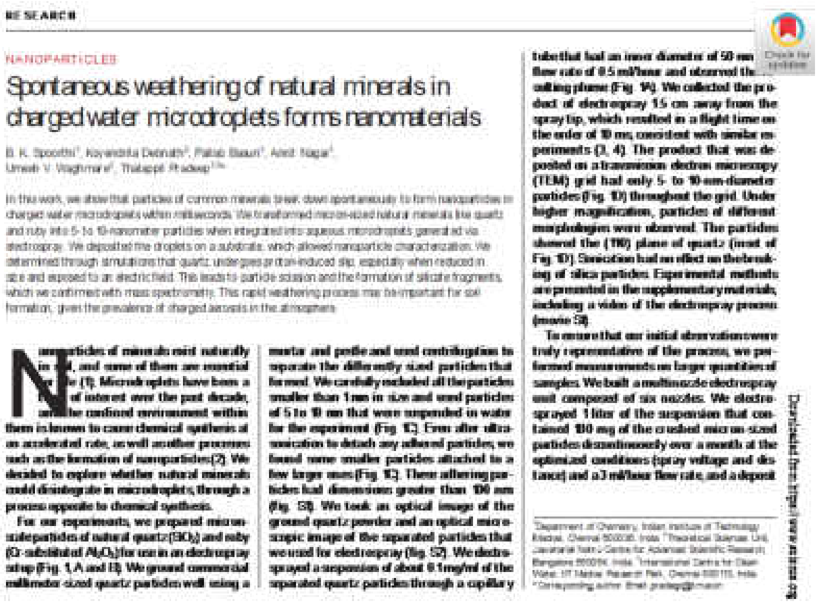
Deepspectrum Analytics Pvt. Ltd.

Professor-in-charge

International Centre for Clean Water

Department of Chemistry, Purdue University, June 17, 2024



RESEARCH

NANOPARTICLES

Spontaneous weathering of natural minerals in charged water microdroplets forms nanomaterials

B. K. Spoorthi[1], Koyendrila Debnath[2], Pallab Basuri[1], Amit Nagar[1], Umesh V. Waghmare[2], Thalappil Pradeep[1,3*]

In this work, we show that particles of common minerals break down spontaneously to form nanoparticles in charged water microdroplets within milliseconds. We transformed micron-sized natural minerals like quartz and ruby into 5- to 10-nanometer particles when integrated into aqueous microdroplets generated via electrospray. We deposited the droplets on a substrate, which allowed nanoparticle characterization. We determined through simulations that quartz undergoes proton-induced slip, especially when reduced in size and exposed to an electric field. This leads to particle scission and the formation of silicate fragments, which we confirmed with mass spectrometry. This rapid weathering process may be important for soil formation, given the prevalence of charged aerosols in the atmosphere.

Nanoparticles of minerals exist naturally in [illegible], and some of them are essential [illegible] (1). Microdroplets have been a [illegible] of interest over the past decade, and the confined environment within them is known to cause chemical synthesis at an accelerated rate, as well as other processes such as the formation of nanoparticles (2). We decided to explore whether natural minerals could disintegrate in microdroplets, through a process opposite to chemical synthesis.

For our experiments, we prepared micron-scale particles of natural quartz (SiO_2) and ruby (Cr-substituted Al_2O_3) for use in an electrospray setup (Fig. 1, A and B). We ground commercial millimeter-sized quartz particles well using a mortar and pestle and used centrifugation to separate the differently sized particles that formed. We carefully excluded all the particles smaller than 1 nm in size and used particles of 5 to 10 nm that were suspended in water for the experiment (Fig. 1C). Even after ultrasonication to detach any adhered particles, we found some smaller particles attached to a few larger ones (Fig. 1C). These adhering particles had dimensions greater than 100 nm (fig. S1). We took an optical image of the ground quartz powder and an optical microscopic image of the separated particles that we used for electrospray (fig. S2). We electrosprayed a suspension of about 0.1 mg/ml of the separated quartz particles through a capillary tube that had an inner diameter of 50 nm [illegible] flow rate of 0.5 ml/hour and observed the [illegible] resulting plume (Fig. 1A). We collected the product of electrospray 1.5 cm away from the spray tip, which resulted in a flight time on the order of 10 ms, consistent with similar experiments (3, 4). The product that was deposited on a transmission electron microscopy (TEM) grid had only 5- to 10-nm-diameter particles (Fig. 1D) throughout the grid. Under higher magnification, particles of different morphologies were observed. The particles showed the (110) plane of quartz (inset of Fig. 1D). Sonication had no effect on the breaking of silica particles. Experimental methods are presented in the supplementary materials, including a video of the electrospray process (movie S1).

To ensure that our initial observations were truly representative of the process, we performed measurements on larger quantities of samples. We built a multinozzle electrospray unit composed of six nozzles. We electrosprayed 1 liter of the suspension that contained 100 mg of the crushed micron-sized particles discontinuously over a month at the optimized conditions (spray voltage and distance) and a 3 ml/hour flow rate, and a deposit

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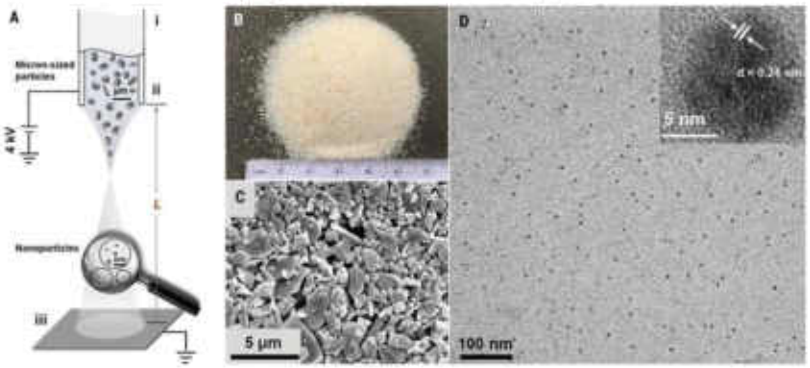


Spoorthi et al., Science 384, 1012–1017 (2024) 31 May 2024

A scale of 1000

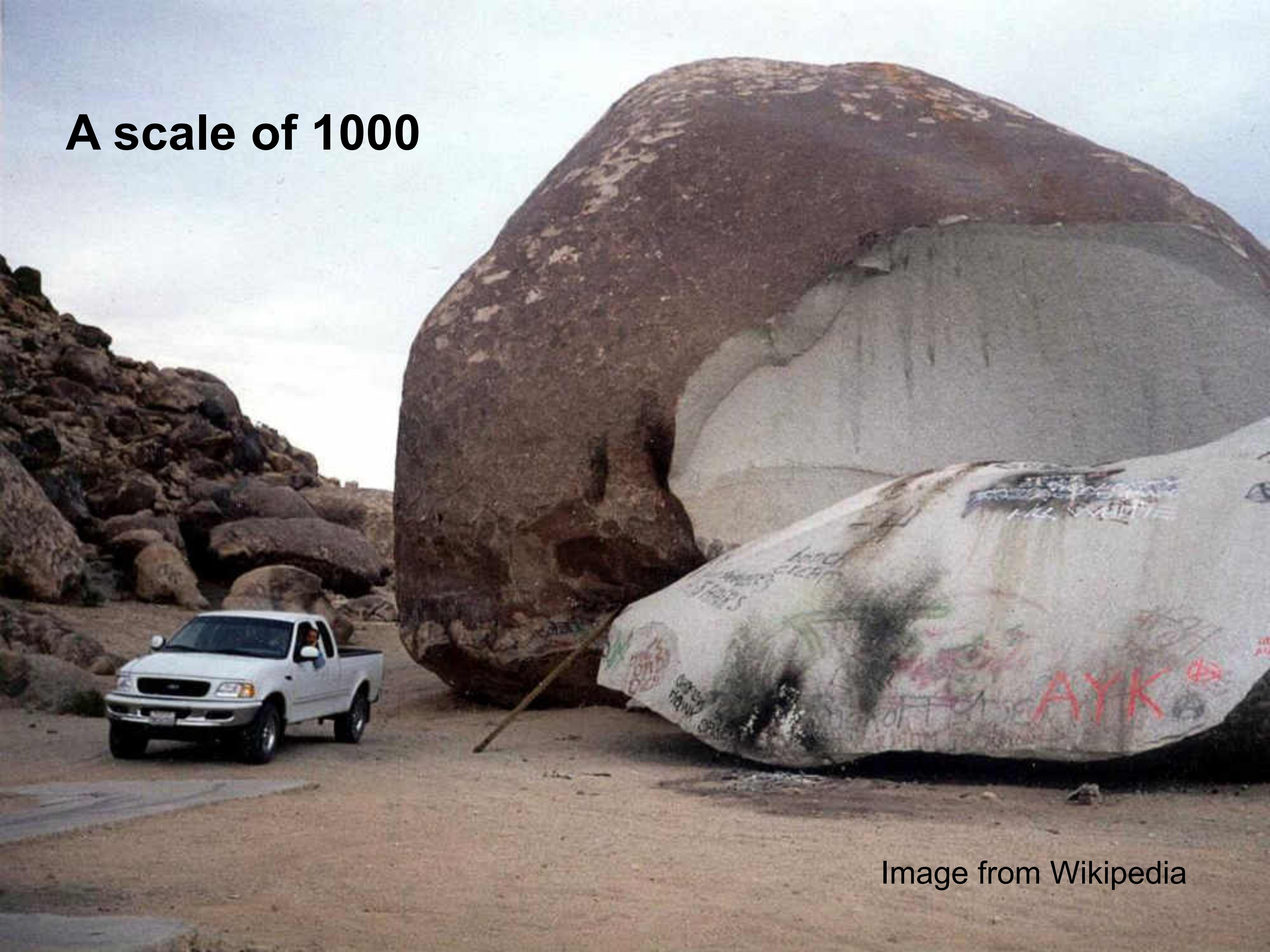
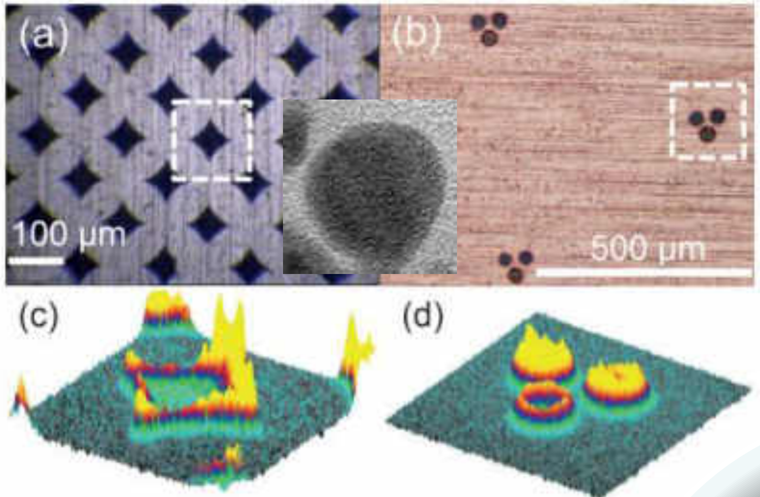


Image from Wikipedia

Functional Nanomaterials



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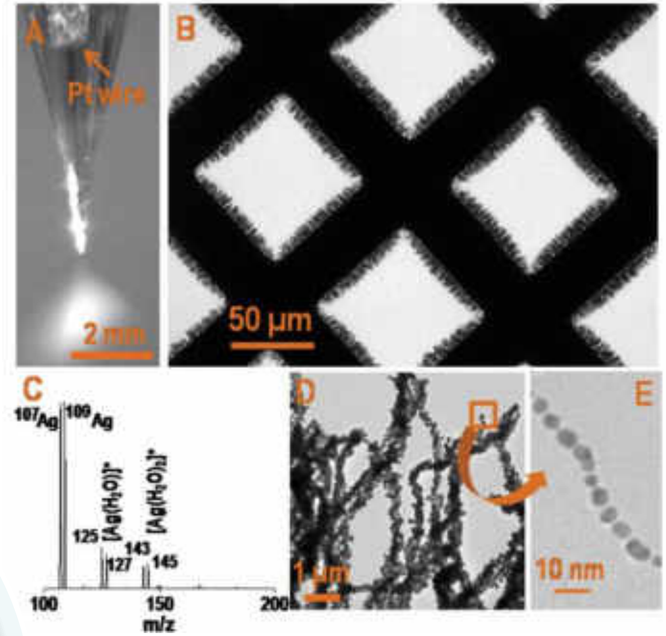

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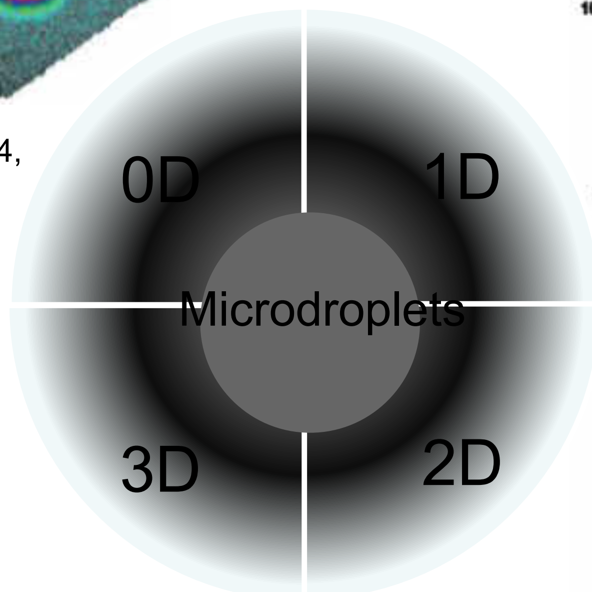
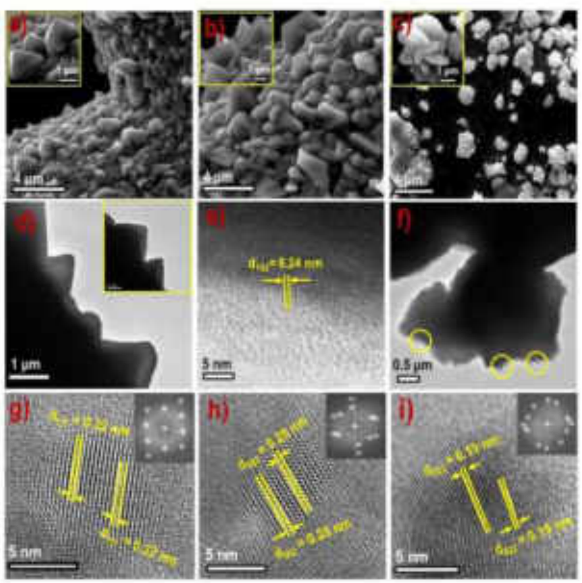
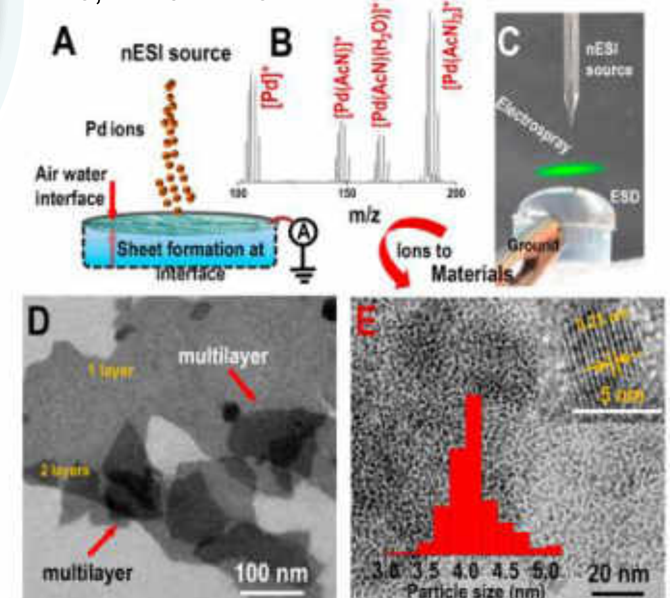




Arijit Jana et. al., *J. Mater. Chem. A,* 2019, 7, 6387–6394.



Depanjan Sarkar, et. al., *J. Phys. Chem. C* 2018, 122, 17777−17783.

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Chemical Science

rsc.li/chemical-science

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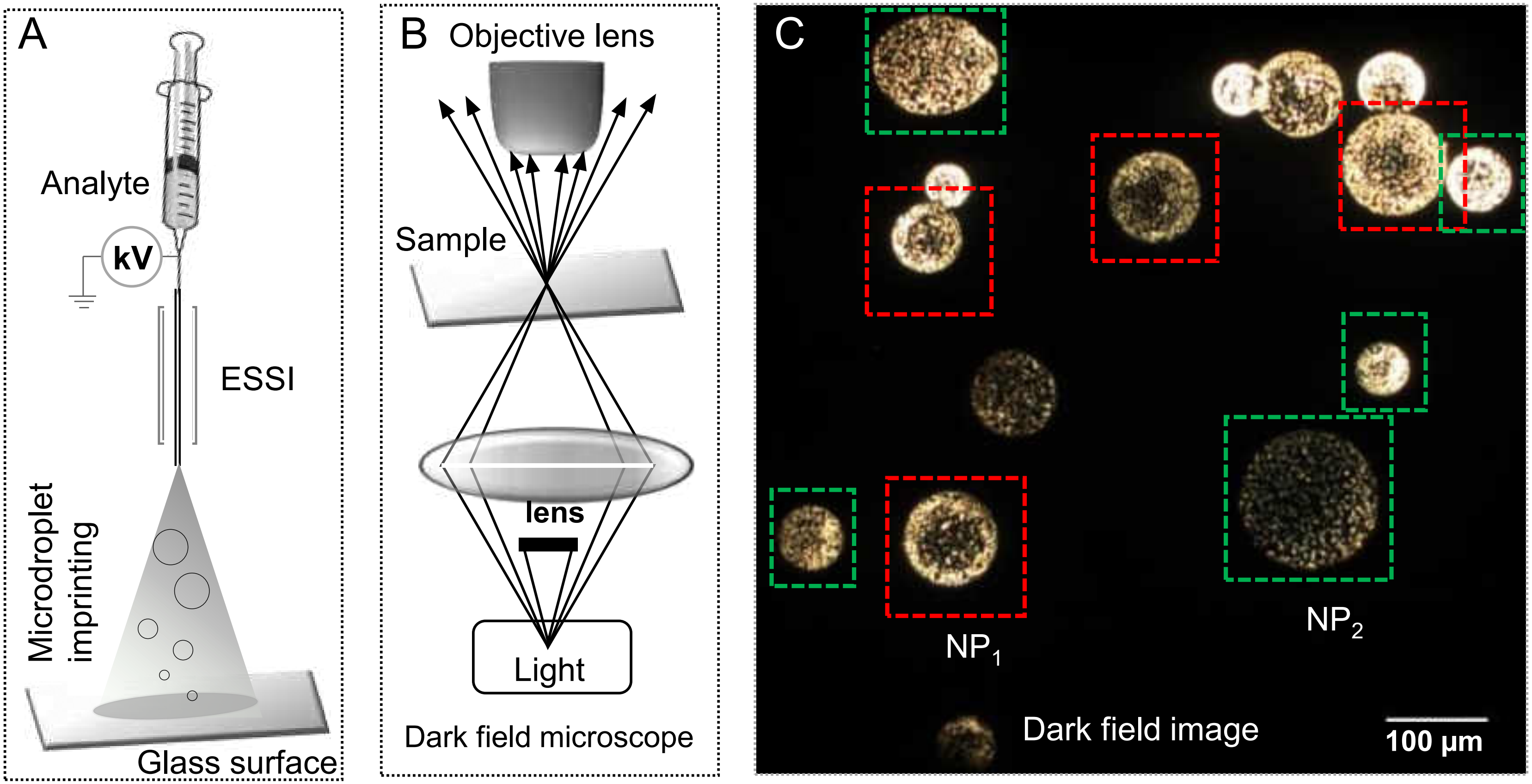
ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE
Thalappil Pradeep *et al.*
Spatial reorganization of analytes in charged aqueous microdroplets

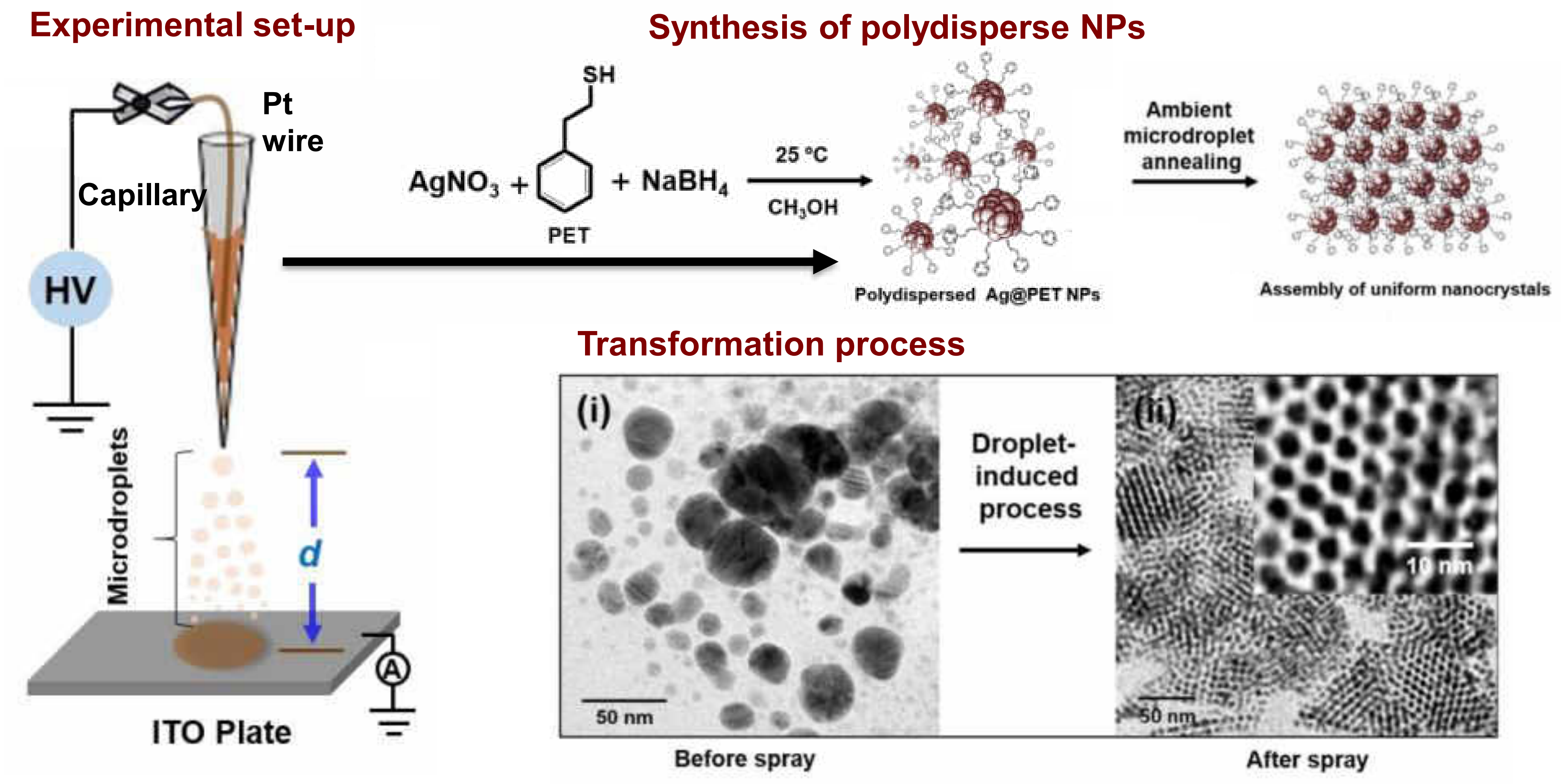
Understanding Microdroplets



Pallab Basuri et. al. *Chem. Sci.,* 2022, 13, 13321–13329.

Transformation of Materials in Microdroplets

Ambient Microdroplet Annealing of Nanoparticles



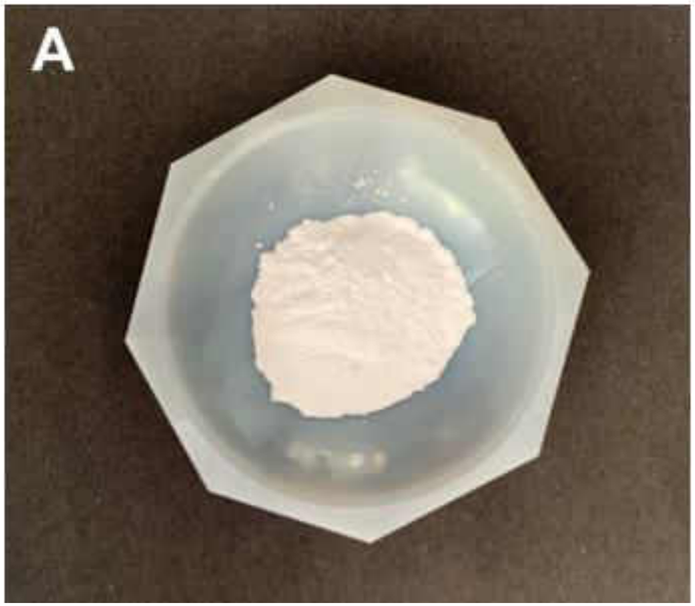
Angshuman Ray Chowdhuri et. al., *Chem. Sci.*, 2021, 12, 6370–6377.


Thanks to ChatGPT

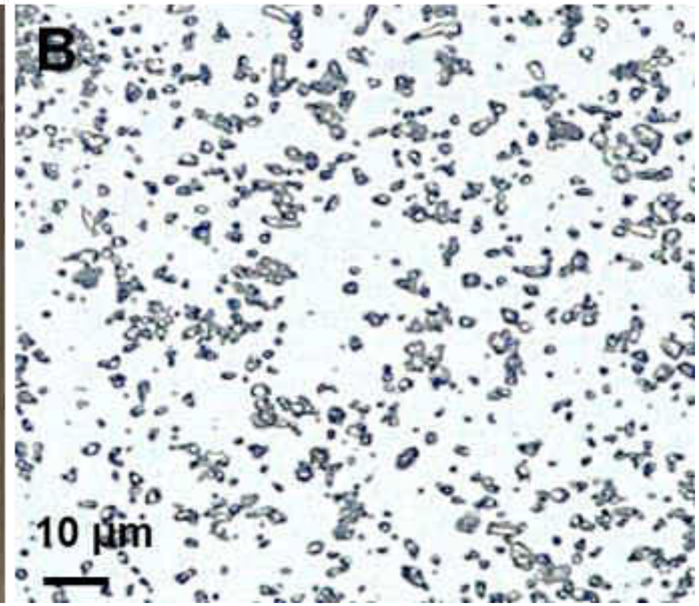
Weathering in Nature

Sand, the Ubiquitous Material

Images from Wikipedia

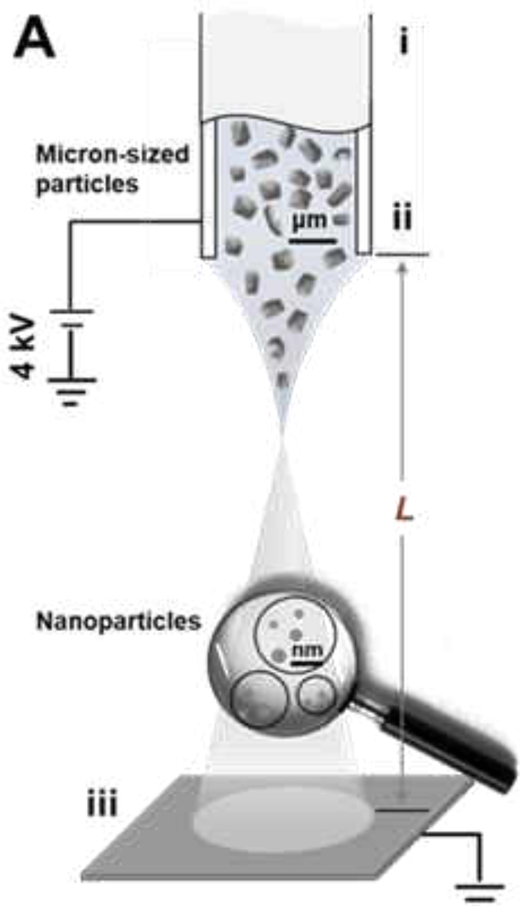


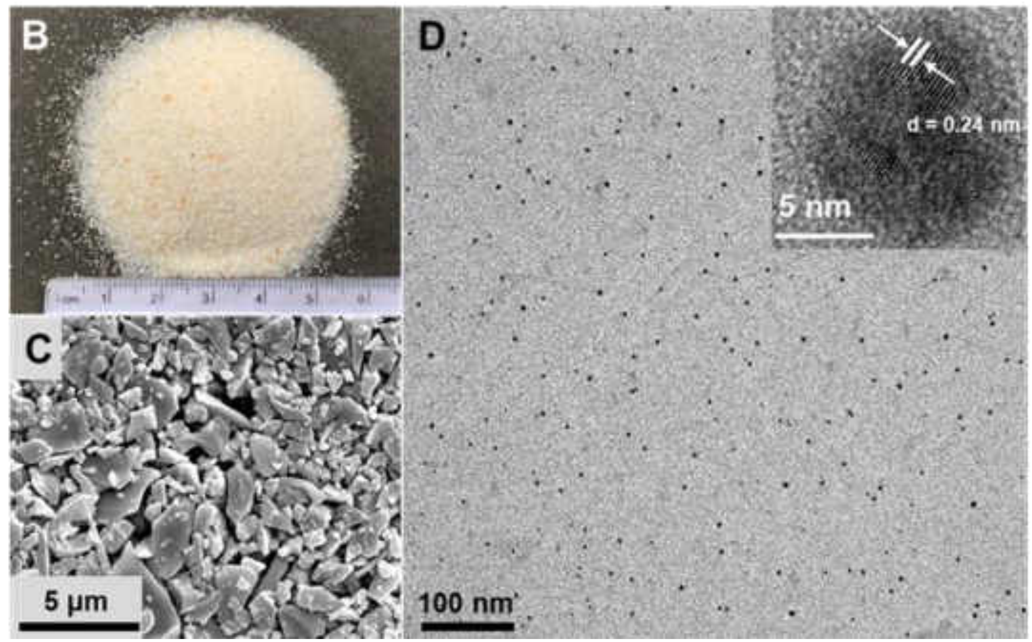
Ground silica



Optical image of silica

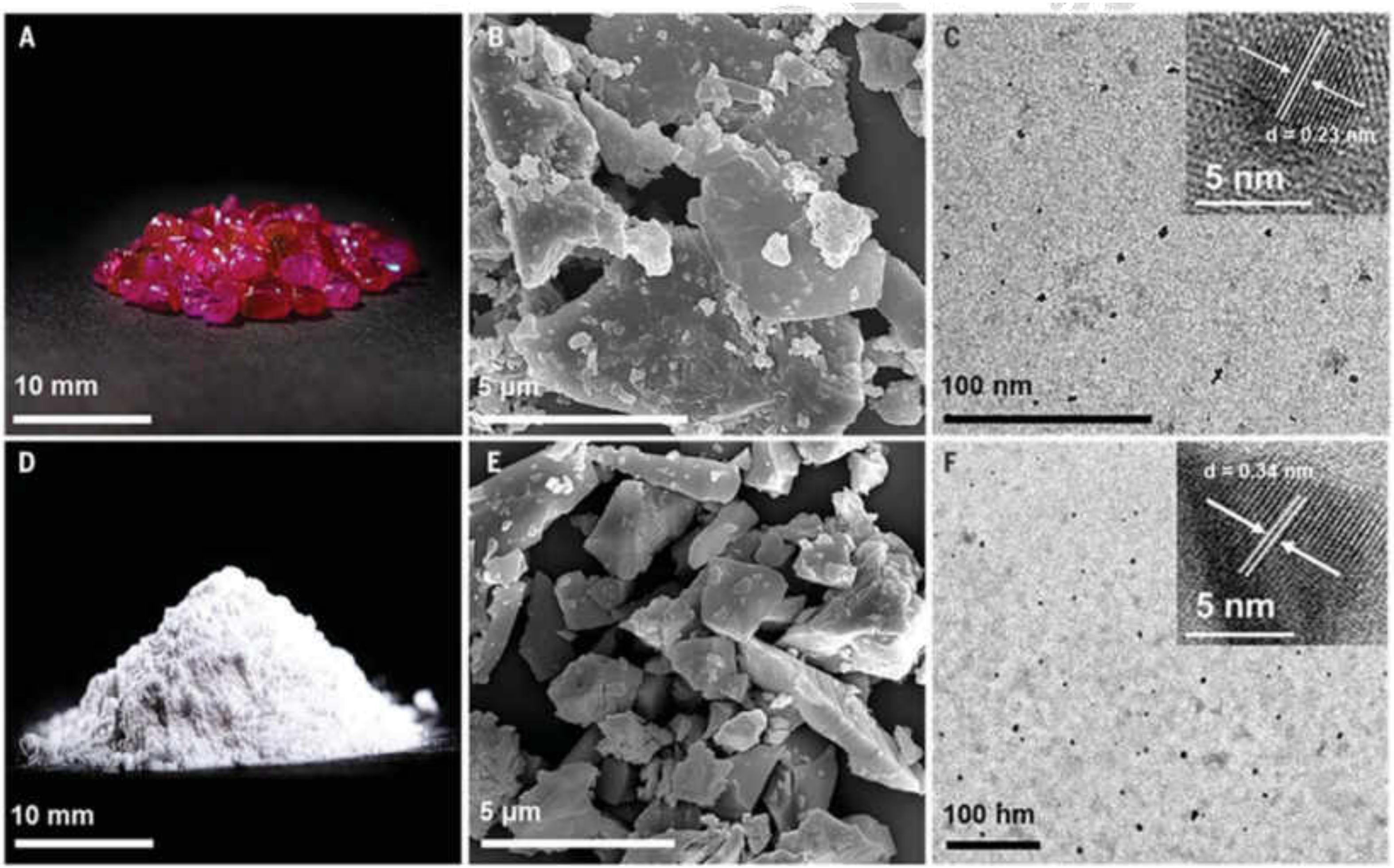
Weathering of Minerals in Microdroplets



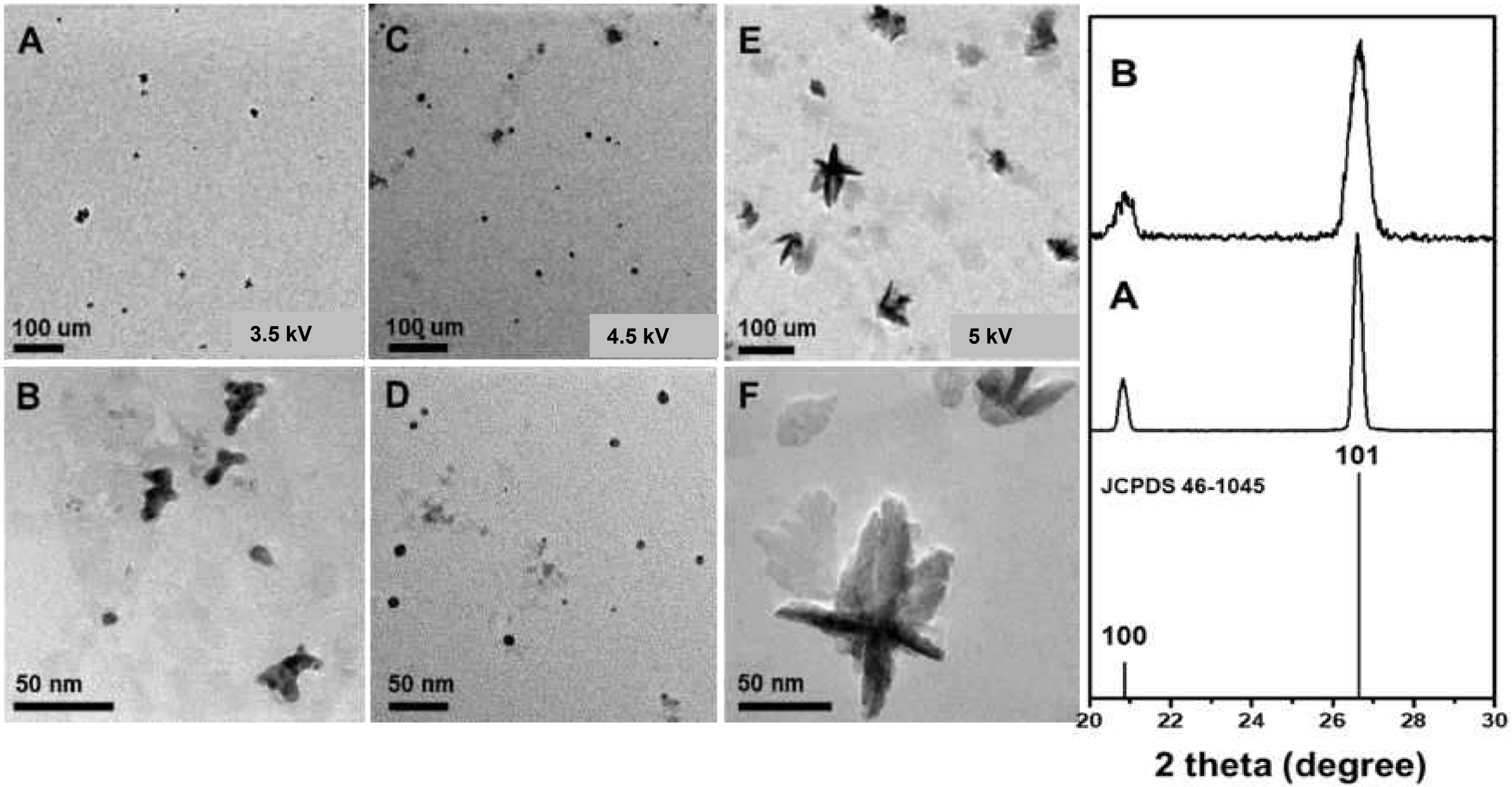


Spoorthi, et. al., *Science*, 2024

Ruby, Fused Alumina



Fragmentation of Silica – Varying Conditions



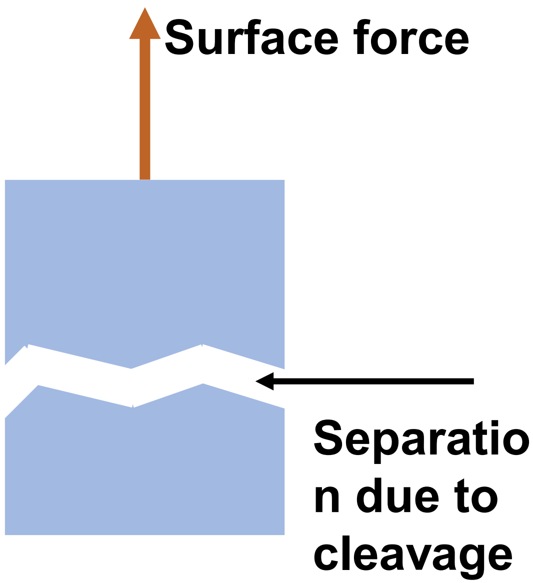
SiO_2 after electrospray

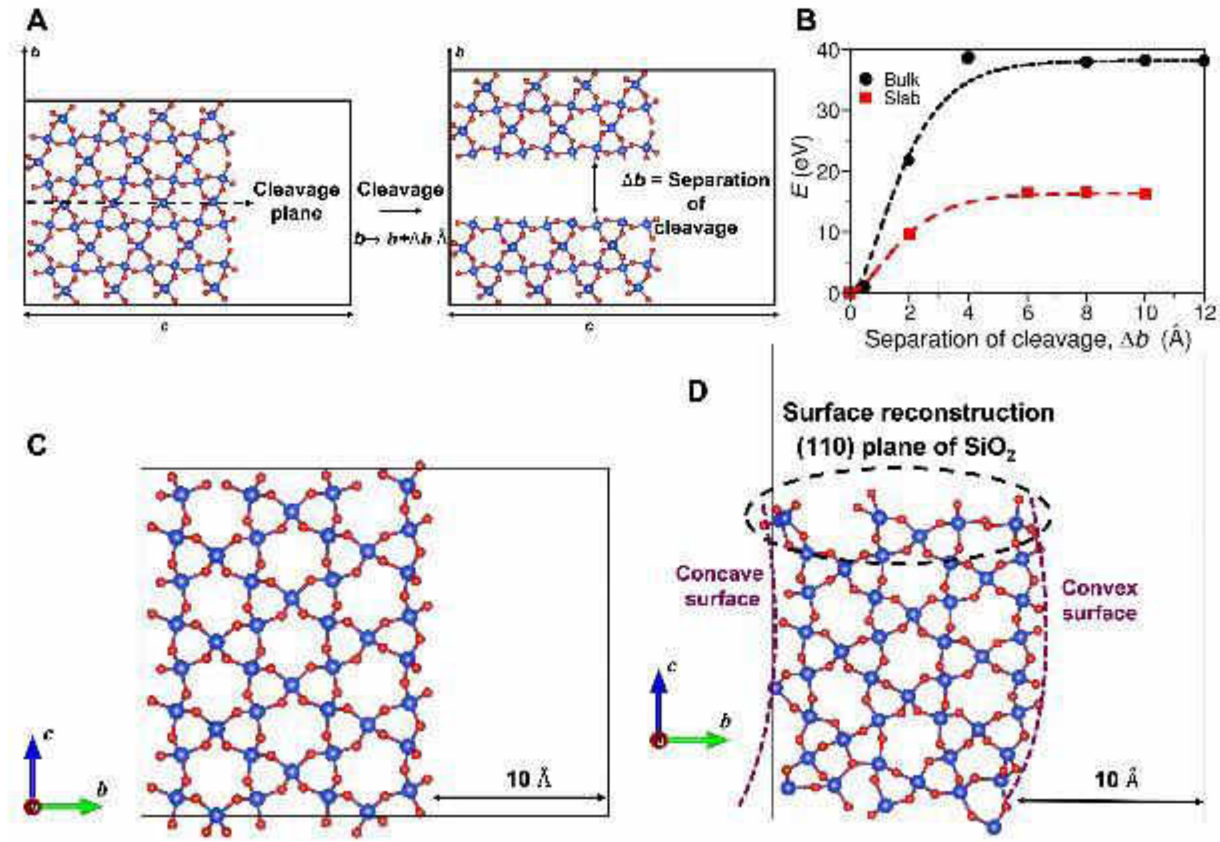
SiO_2 before electrospray

SiO_2 JCPDS data

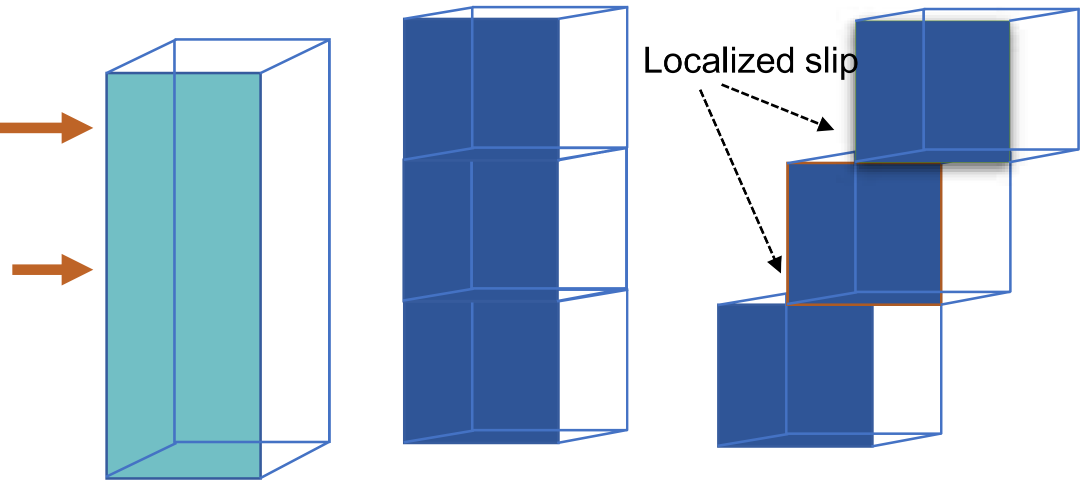
Mechanism: Cleavage

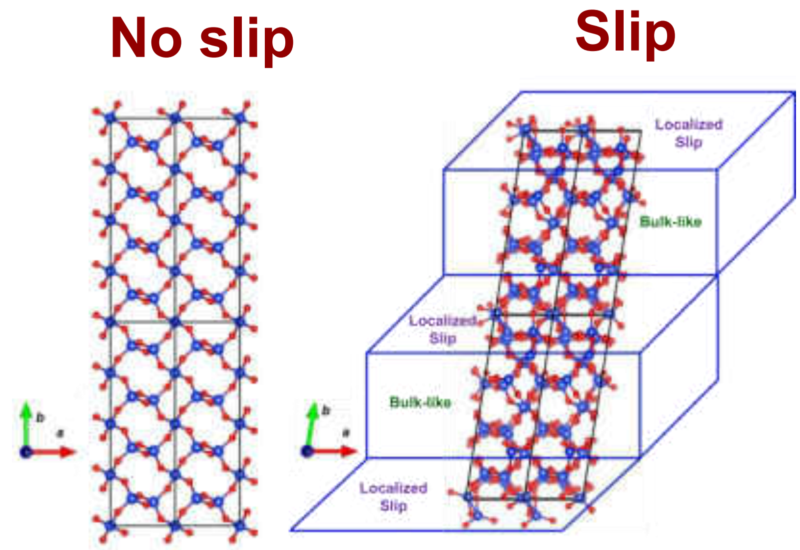
The process of cleavage and surface reconstruction visualized with first-principles simulations





Mechanism: Slip



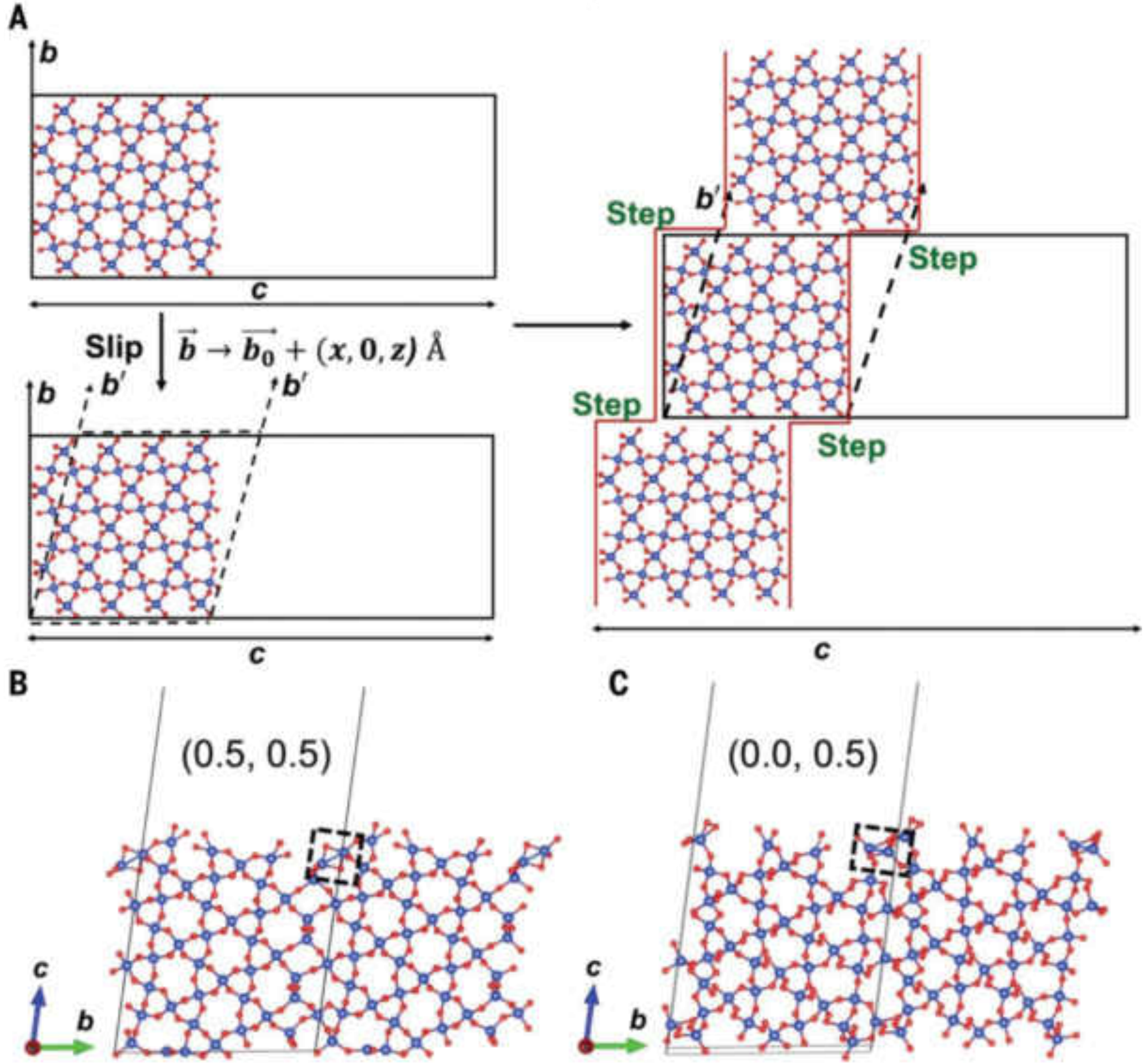


This instability leads to the formation of a stacking fault on the (010) plane, achieved with slip localized at (010) plane

Stacking fault

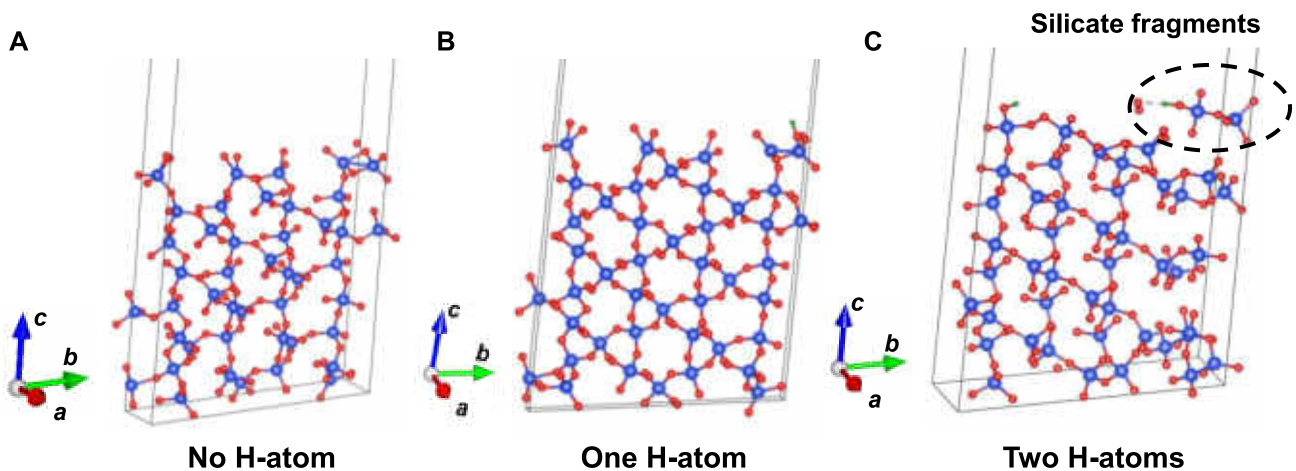
$\vec{b} \rightarrow \overrightarrow{b_0} + (x, 0, z)$.

(x, $z \in [0,1]$) - fractional coordinates

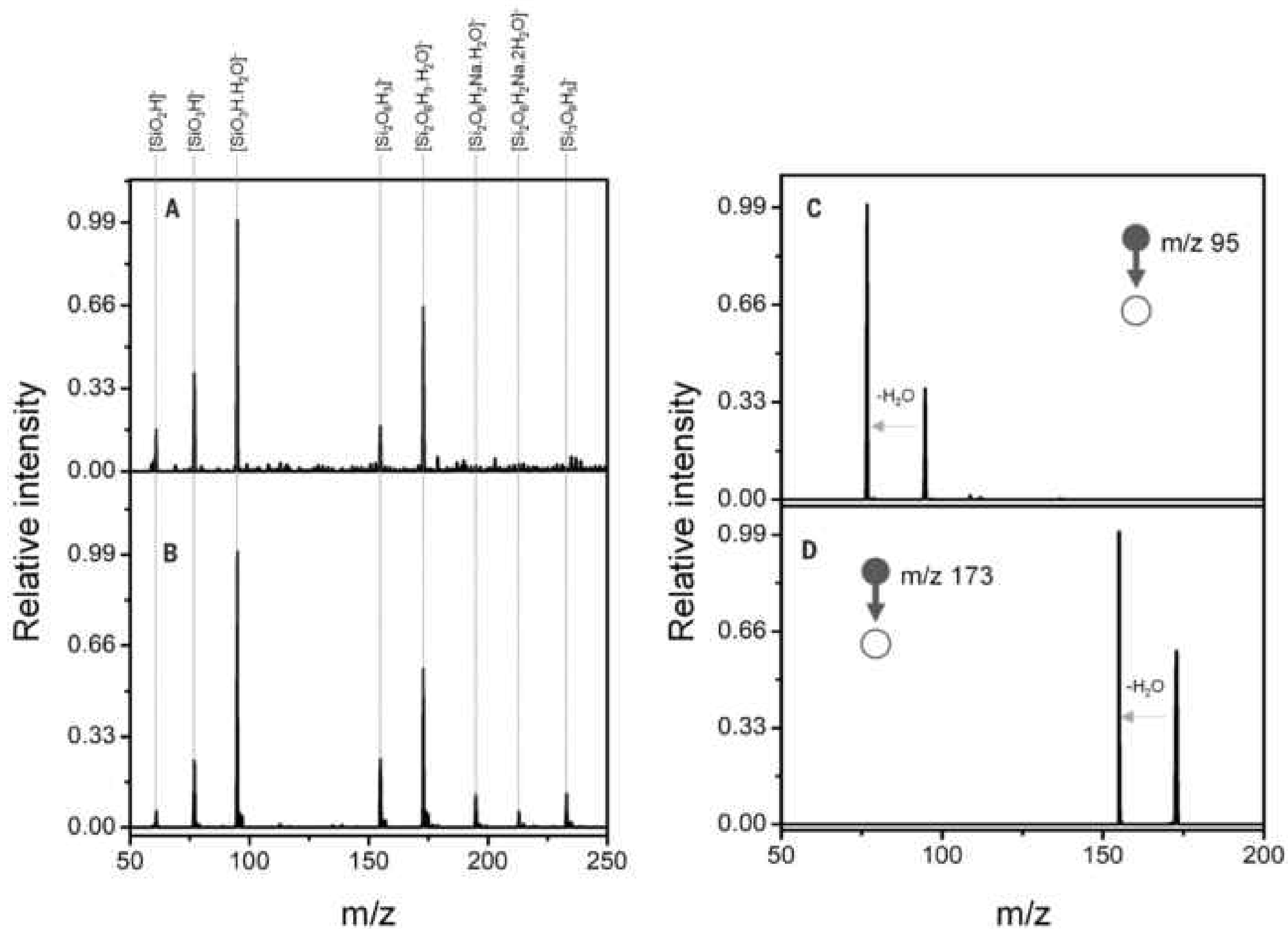

A
b
c
Slip
$\vec{b} \rightarrow \vec{b_0} + (x, 0, z)$ Å
b'
b'
Step
Step
Step
Step
B
(0.5, 0.5)
c
b
C
(0.0, 0.5)
c
b

SFEs of (010) direction with (0, 0), (0, 0.5), (0.5, 0) and (0.5, 0.5) slip configurations on the (110) plane of SiO_2

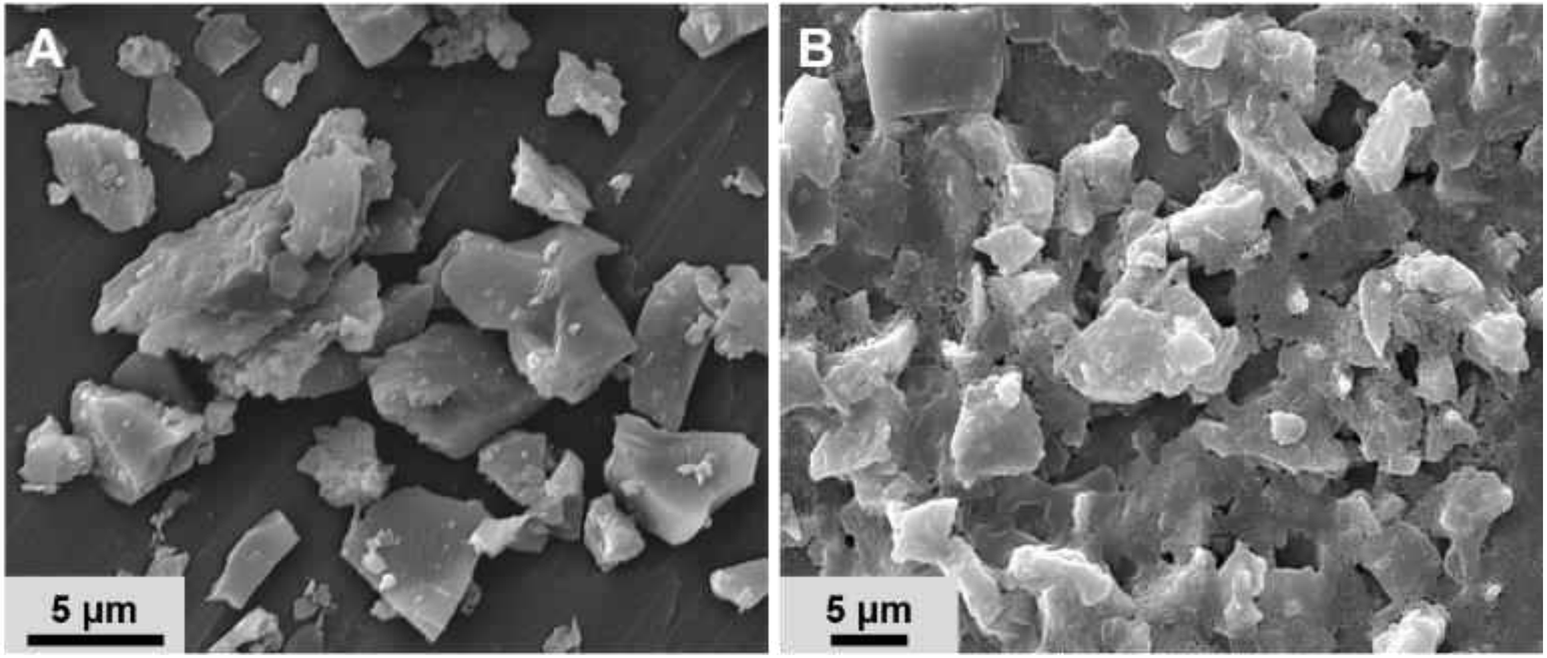
SFE (J/m^2)	Slab					
	x	z	w/o H-atom	1 H-atom	2 H-atoms	E
	0.0	0.0	0	0	0	0
	0.5	**0.5**	**-1.21**	**-0.93**	**-0.88**	**-1.20**
	0.5	0.0	1.20	1.18	0.90	1.12
	0.0	**0.5**	**-0.07**	**0.89**	**-0.83**	**-0.09**



Mass Spectrometry of the Fragments

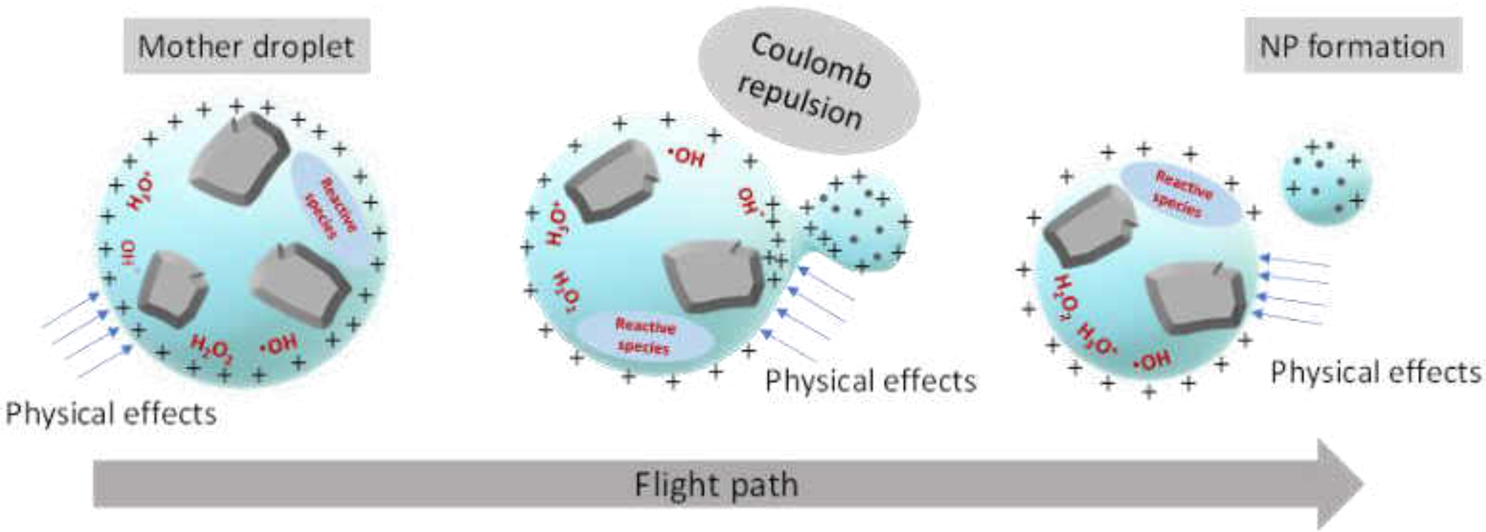


Effect of charged microdroplets on quartz



Increased surface roughness after the spray

Mechanism of nanoparticle formation



Rayleigh, On the equilibrium of liquid conducting masses charged with electricity, Philosophical Magazine, 1882

$Q = 8\pi\, (\epsilon_0\, \gamma R^3)^{1/2}$

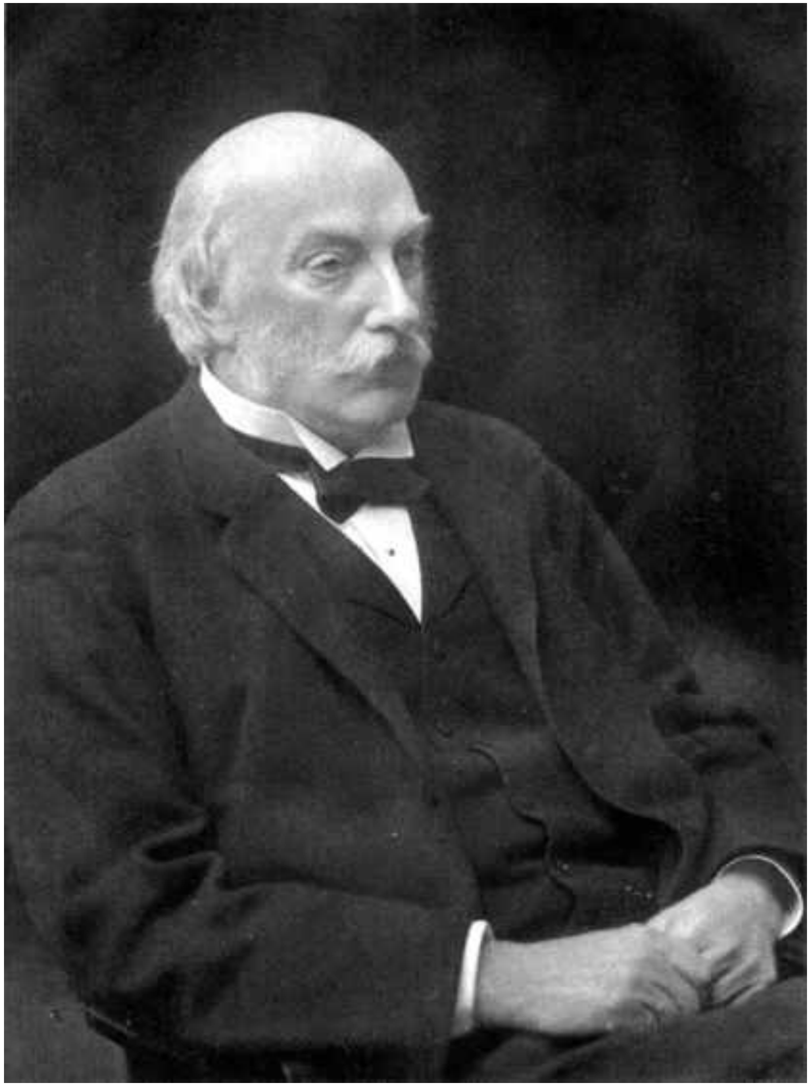
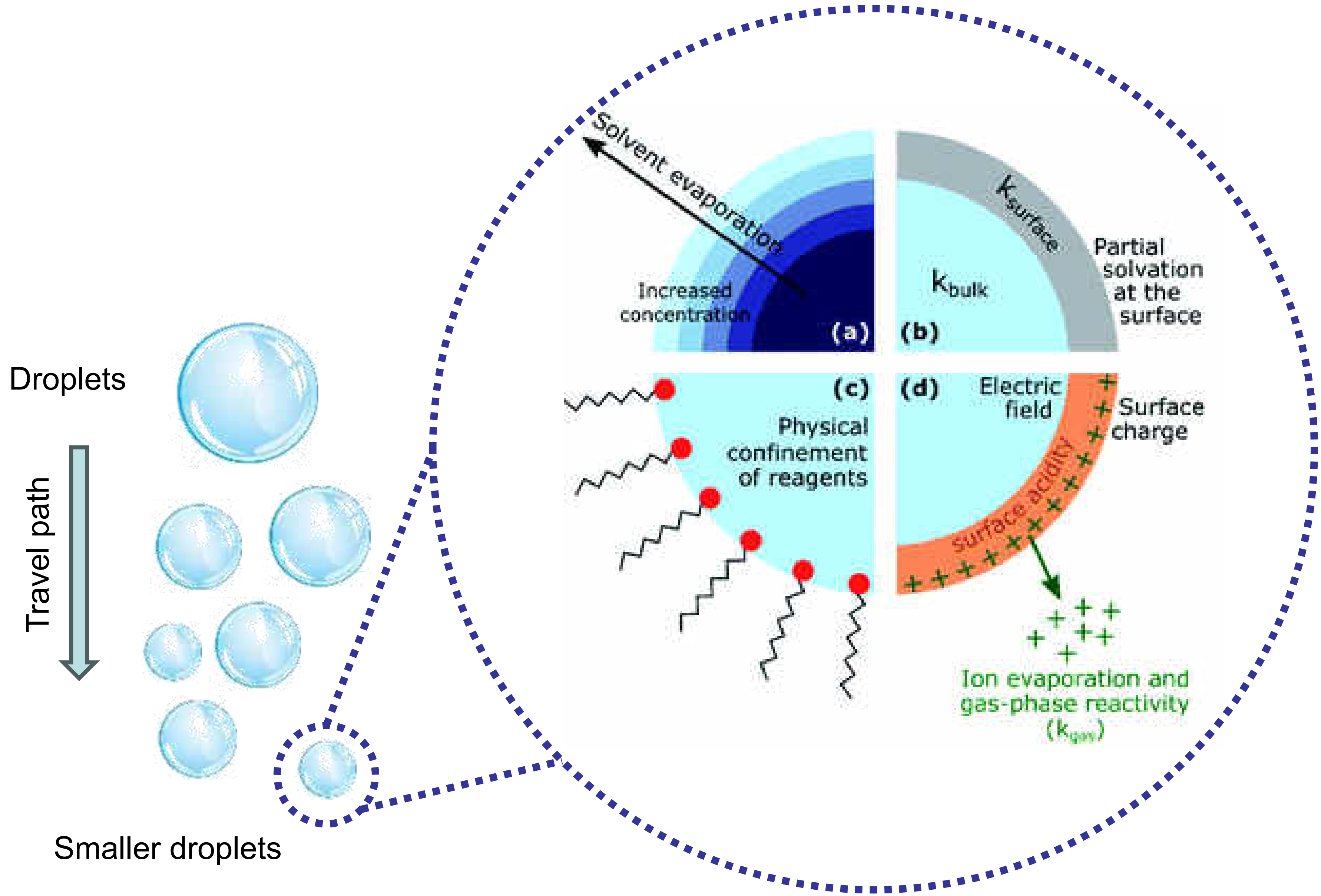


Image from Wikipedia

Understanding Microdroplets



Grazia Rovelli, et. al. *Chem. Sci.*, 2020, 11, 13026–13043.

PERSPECTIVES

CHEMISTRY

Breaking down microdroplet chemistry

Charged microdroplets accelerate mineral disintegration

By **R. Graham Cooks** *and* **Dylan T. Holden**

Charged microdroplets are commonly observed in clouds, sea spray, and other natural aerosols. The chemistry that occurs at the air-water interface of these droplets is often distinct from that observed in bulk solution, which is of considerable interest because chemical reactions can be accelerated at this boundary (*1*, *2*). This may have implications for environmental processes such as the weathering of rocks, which contributes to soil formation. On page 1012 of this issue, Spoorthi *et al*. (*3*) report that micrometer-scale mineral particles can rapidly break down into nanoparticles when in charged aqueous microdroplets (see the figure). This points to a potential role for atmospheric water droplets in the natural disintegration of minerals.

To examine material degradation, Spoorthi *et al*. borrowed methodology used to accelerate bond-forming chemical reactions. By spraying an aqueous suspension of microparticles of natural minerals, the authors produced nanoparticles of minerals in high yield. Specifically, Spoorthi *et al*. used an electrospray device to emit a jet of liquid droplets (by applying high voltage) containing mineral particles of natural quartz, ruby, or synthetic alumina that ranged in size from 1 to 5 μm in diameter. The authors observed the production of nanoparticles that were 5 to 10 nm in diameter. Moreover, the fragmentation occurred in approximately 10 ms.

Such material degradation and chemical synthesis experiments are united by the extremes of chemical reactivity that occur at the air-water interface, where reagents are partially solvated (*4*). Whether formed through nebulization, splashing from a surface, or other means, microdroplet populations will include droplets with nonzero net charges. The small radius of curvature in a microdroplet produces a very strong electric field (*5*) that can support a double layer of electric charge at the air-water interface. The change in geometry (radius of curvature) converts a two-dimensional air-water interface with limited electric field into a sphere with an electric field of a strength approaching the order of chemical bond energies (3 to 4.5 eV/Å). Coulombic fission (the splitting of charged microdroplets due to excess charge overcoming the surface tension) and evaporative processes further increase the surface area, reduce the radius of curvature, and augment the surface electric field of the droplet.

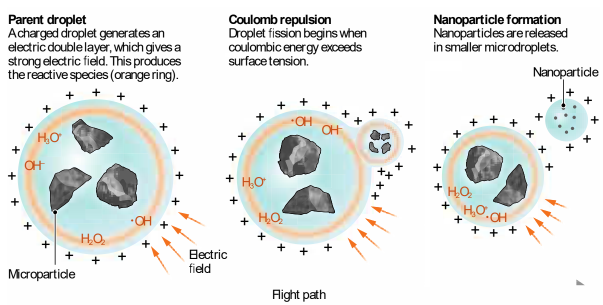
The unusual chemical nature of the air-water interface results in much remarkable chemistry. For example, amino acids in water undergo dehydration to form peptides in this environment (*6*), whereas bulk water simply solvates amino acids. The superacidic interface activates amino acids and removes water to yield peptides. In addition to such acid-base reactions, redox chemistry results from the formation of strong oxidants and reductants from water at the interface. For example, a high hydronium ion (H_3O^+) concentration at the interface derived from fleetingly charged surface water molecules ($H_2O^{\bullet+}/H_2O^{\bullet-}$) coexists with oxidative species such as hydrogen peroxide (H_2O_2) and OH•. These redox species enable a variety of spontaneous chemical transformations, including carbon-oxygen O) bond cleavage in phosphonates, which yields the corresponding phosphonic acid (*7*), and in the Baeyer-Villiger oxidation of aryl ketones to give esters (*8*). These considerations thereby enable simultaneous acid-base and oxidation-reduction chemistry in a single population of droplets (*7*).

Through their study, Spoorthi *et al*. have added natural weathering to a list of processes in which accelerated interfacial microdroplet reactions play an important role. Other processes include those in the atmosphere, both natural and anthropogenic, the latter typified by pollution that involves nitrate photochemistry (*9*). A substantial number of accelerated catalyst-free microdroplet reactions form the basis for chemical syntheses that generate a variety of small molecules (*10*), including the facile and high-throughput functionalization of drugs. This latter approach can be scaled up so that microdroplet reactions produce substantial small-molecule products. Prebiotic chemistry, including peptide and nucleotide formation, is another process that is accelerated at the microdroplet air-water interface (*11*).

The millisecond timescale of quartz degradation reported by Spoorthi *et al*. matches the known microsecond-to-millisecond timescale for accelerated bond-formation and bond-cleavage chemical reactions in microdroplets (*1*). This reinforces the conclusion that the chemical basis for accelerated weathering lies in the powerful acidic and hydrolytic nature of the air-water interface. The authors further suggest a role for the superacid interface in inducing slippage at crystal plane boundaries in quartz and ruby fragmentation. Their simulations show that individual protons inserted into the slip configuration mineral

Micro-to-nano transitions in minerals at the air-water interface

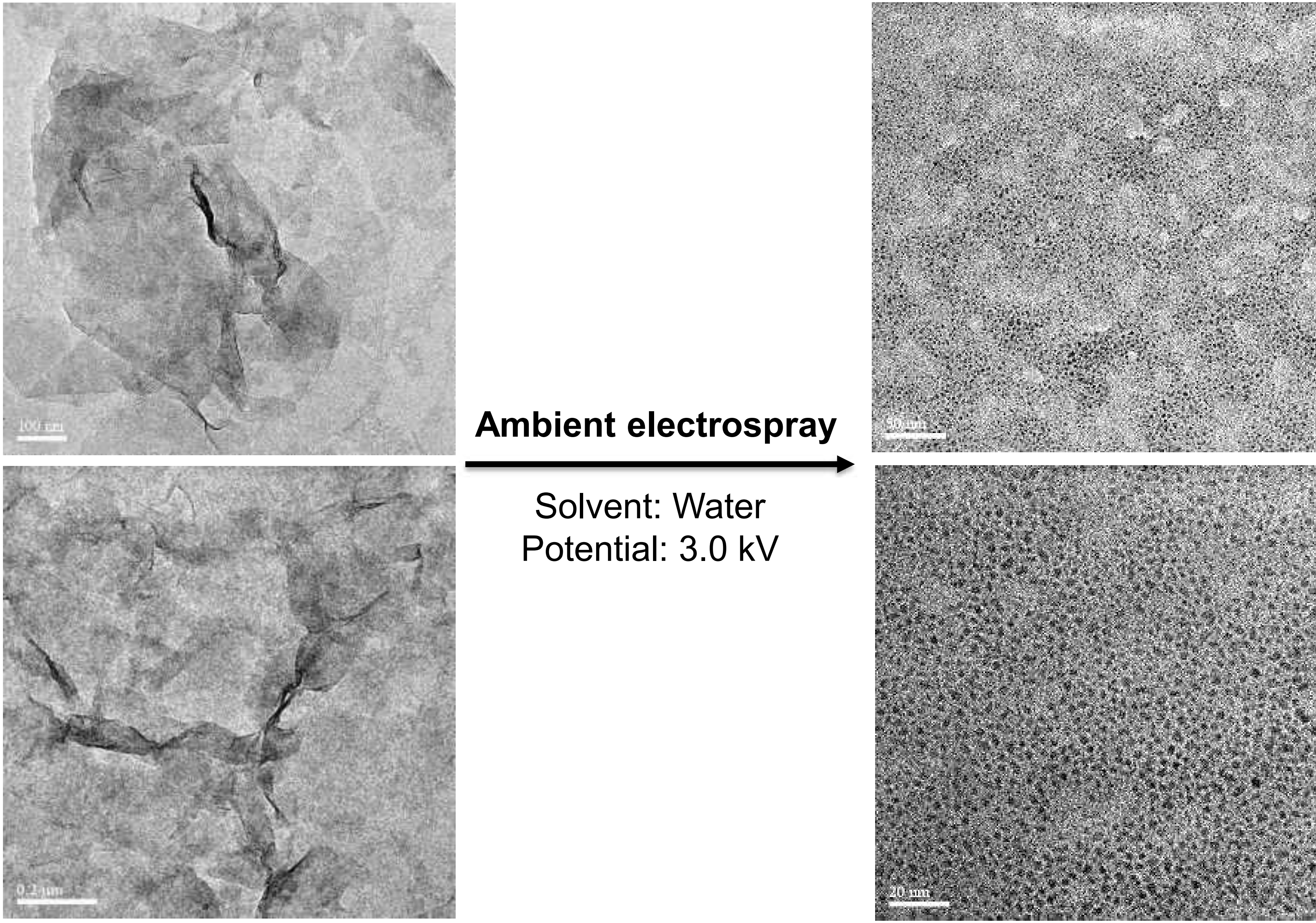
Reactions that promote mineral disintegration are accelerated at the air-water interface of microdoplets. Key reactive species are the result of the effects of a high electric field at the surface of the water droplets.



GRAPHIC: K. HOLOSKI/ *SCIENCE*

Department of Chemistry, Purdue University, West Lafayette, IN, USA. Email: cooks@purdue.edu

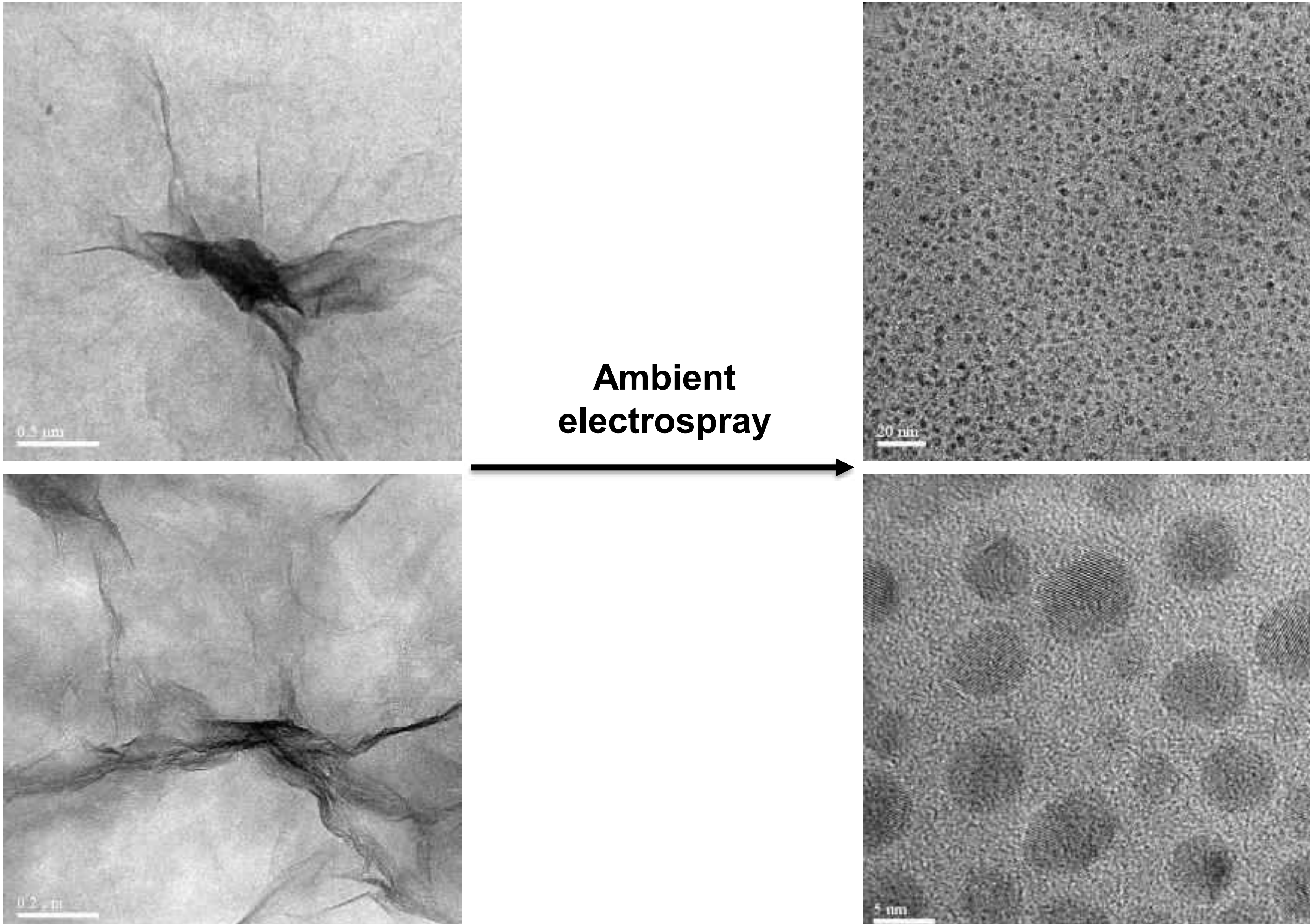
MoS_2 Nanosheets



MoS_2 Nanosheet

MoS_2 Nanoparticles

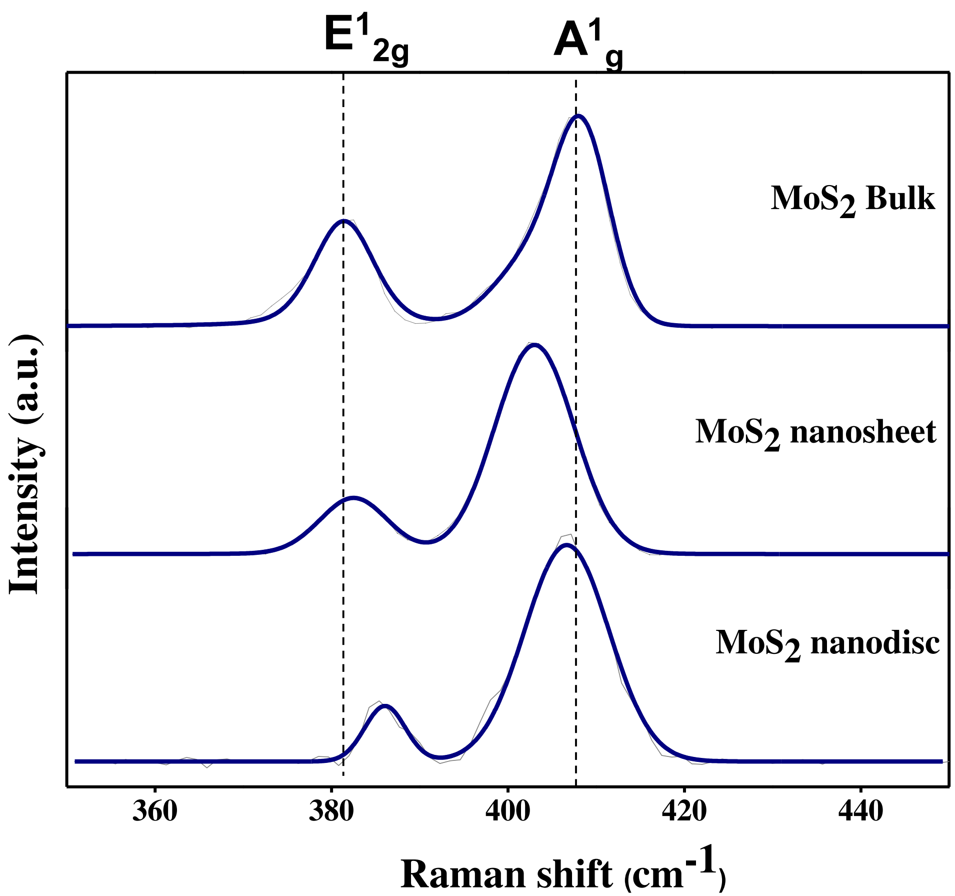
Graphene Oxide

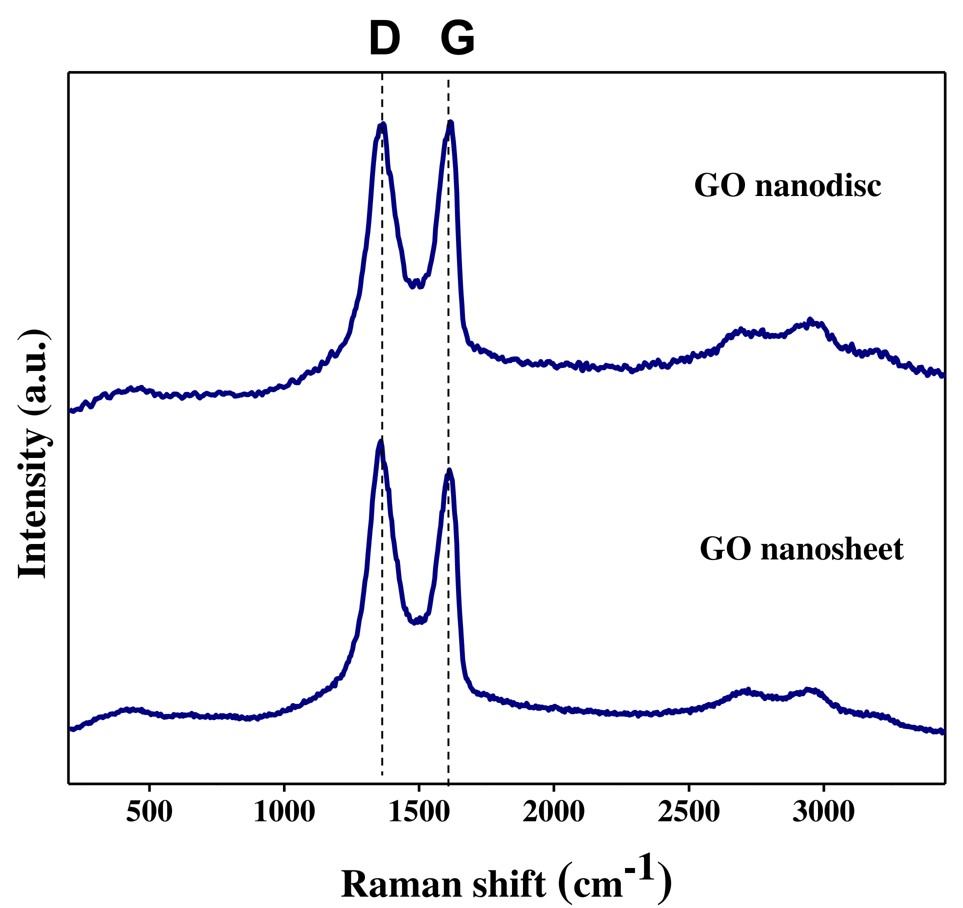


Graphene oxide nanosheet

Graphene oxide nanodiscs

Raman Spectra of MoS_2 and Graphene Oxide Nanosheets



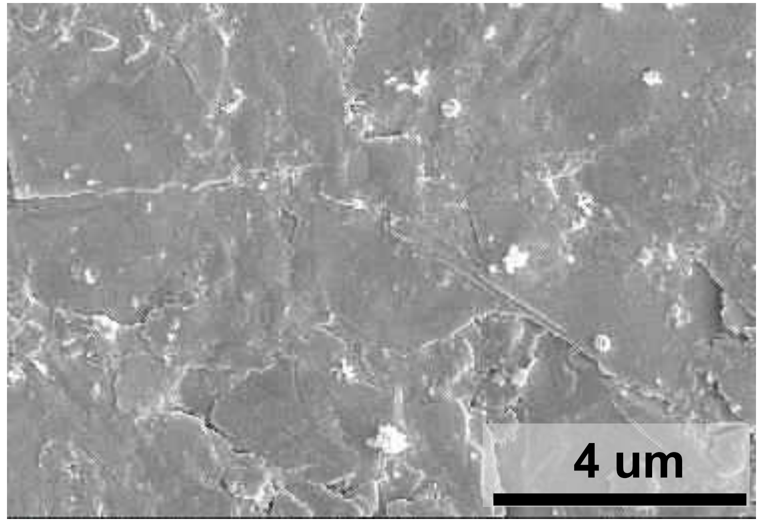


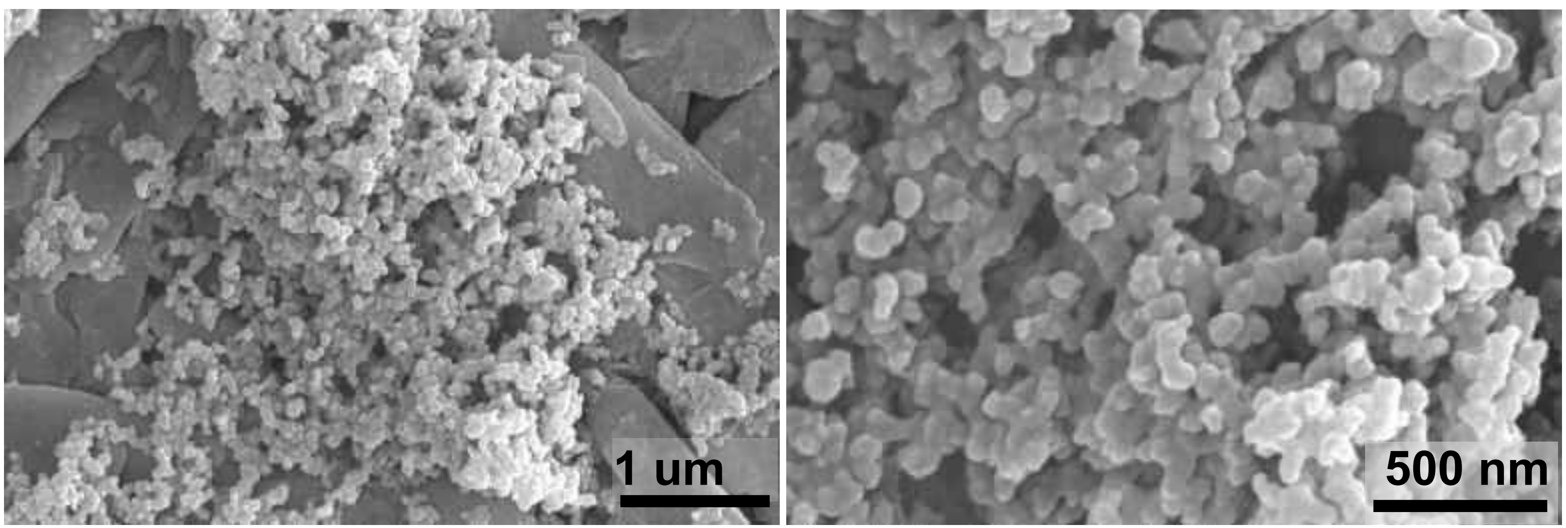
	E^1_{2g} (cm^{-1})	A^1_g (cm^{-1})
Bulk	381.34	407.67
NS	382.88	402.95
ND	386.01	406.67

Relative peak intensity

Charged Droplets on MoS_2 Bulk

Bulk MoS_2 surface before the spray



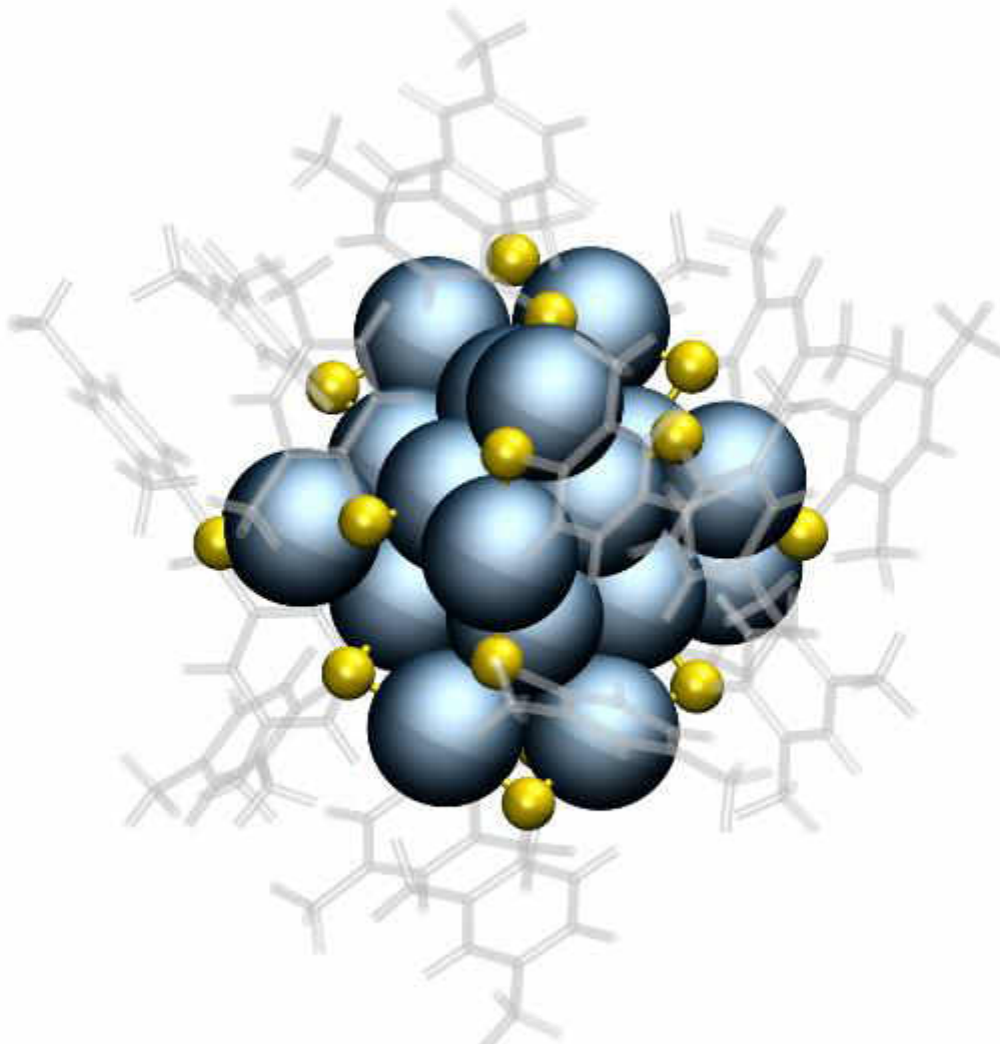


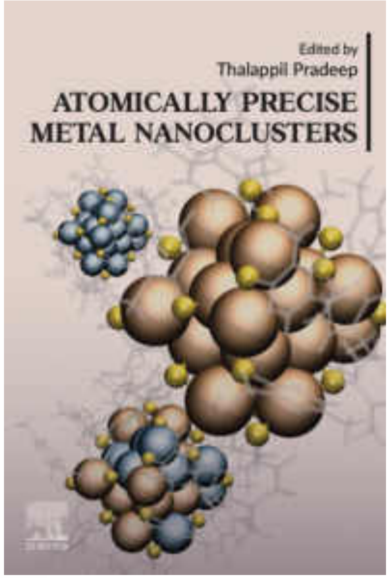
Appearance of microspheres after the water spray on MoS_2

Marcasite, FeS_2

Image from Wikipedia

New molecules





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

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

PNAS

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

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Madras, Chennai 600 036, India

Edited by Eric Hoek, University of California,

(received for review November 21, 2012)

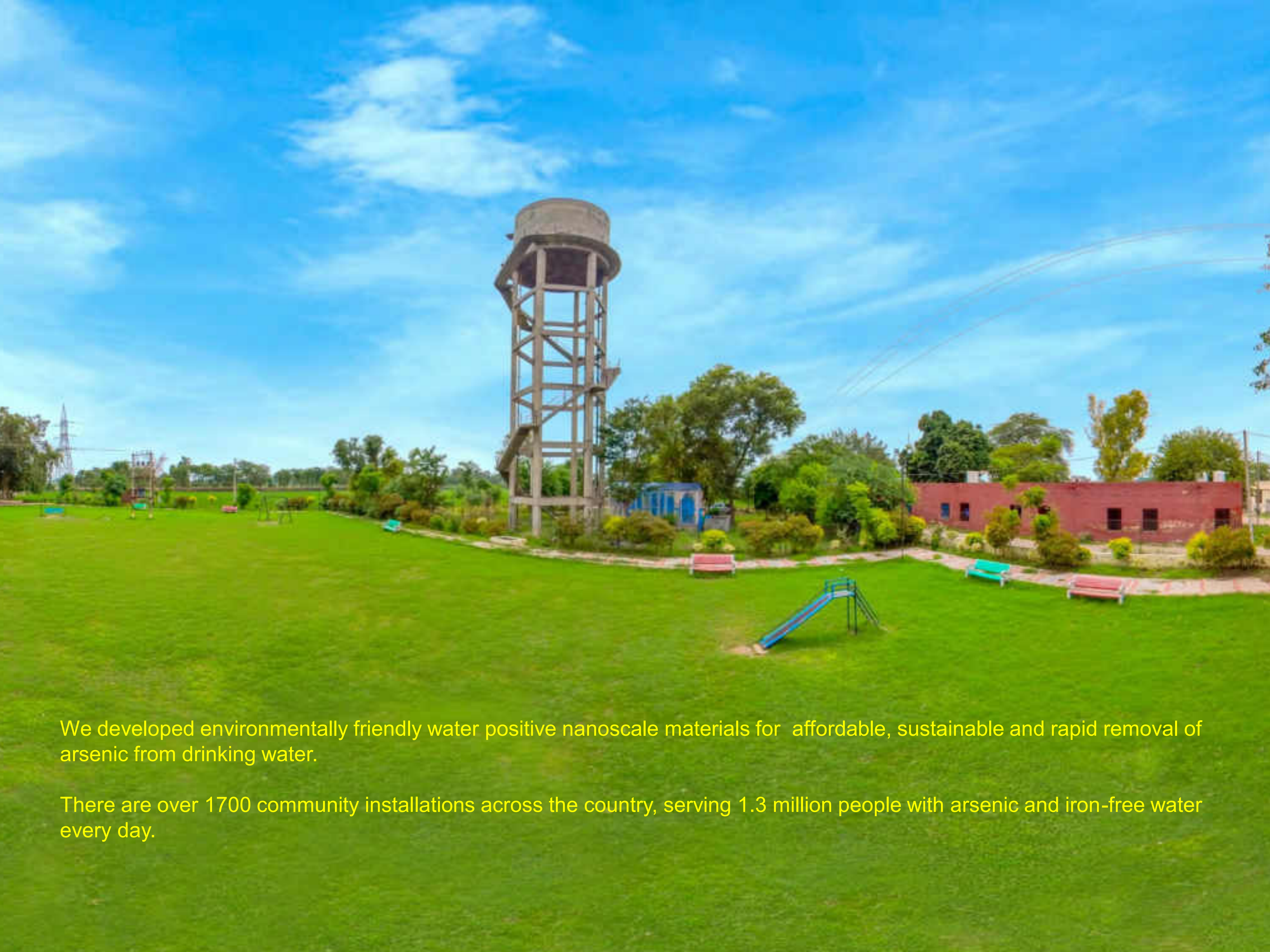
Creation of affordable materials for cons
water is one of the most promising ways
drinking water for all. Combining the
composites to scavenge toxic species
other contaminants along with the ab
affordable, all-inclusive drinking water
without electricity. The critical proble
synthesis of stable materials that can
uously in the presence of complex s
drinking water that deposit and caus
surfaces. Here we show that such con
be synthesized in a simple and effective
out the use of electrical power. The na
sand-like properties, such as higher shea
forms. These materials have been used
water purifier to deliver clean drinking
ily. The ability to prepare nanostructu
ambient temperature has wide releva
water purification.

vailable; and (*c*) continued retention
matrix is difficult.
ate a unique family of nanocrystalline
n granular composite materials pre-
ature through an aqueous route. The
mposition is attributed to abundant -O-
on chitosan, which help in the crys-
oxide and also ensure strong covalent
surface to the matrix. X-ray photo-
) confirms that the composition is rich
ps. Using hyperspectral imaging, the
aching in the water was confirmed.
to reactivate the silver nanoparticle
al antimicrobial activity in drinking
osites have been developed that can
ts in water. We demonstrate an af-
device based on such composites de-
nd undergoing field trials in India, as
spread eradication of the waterborne

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

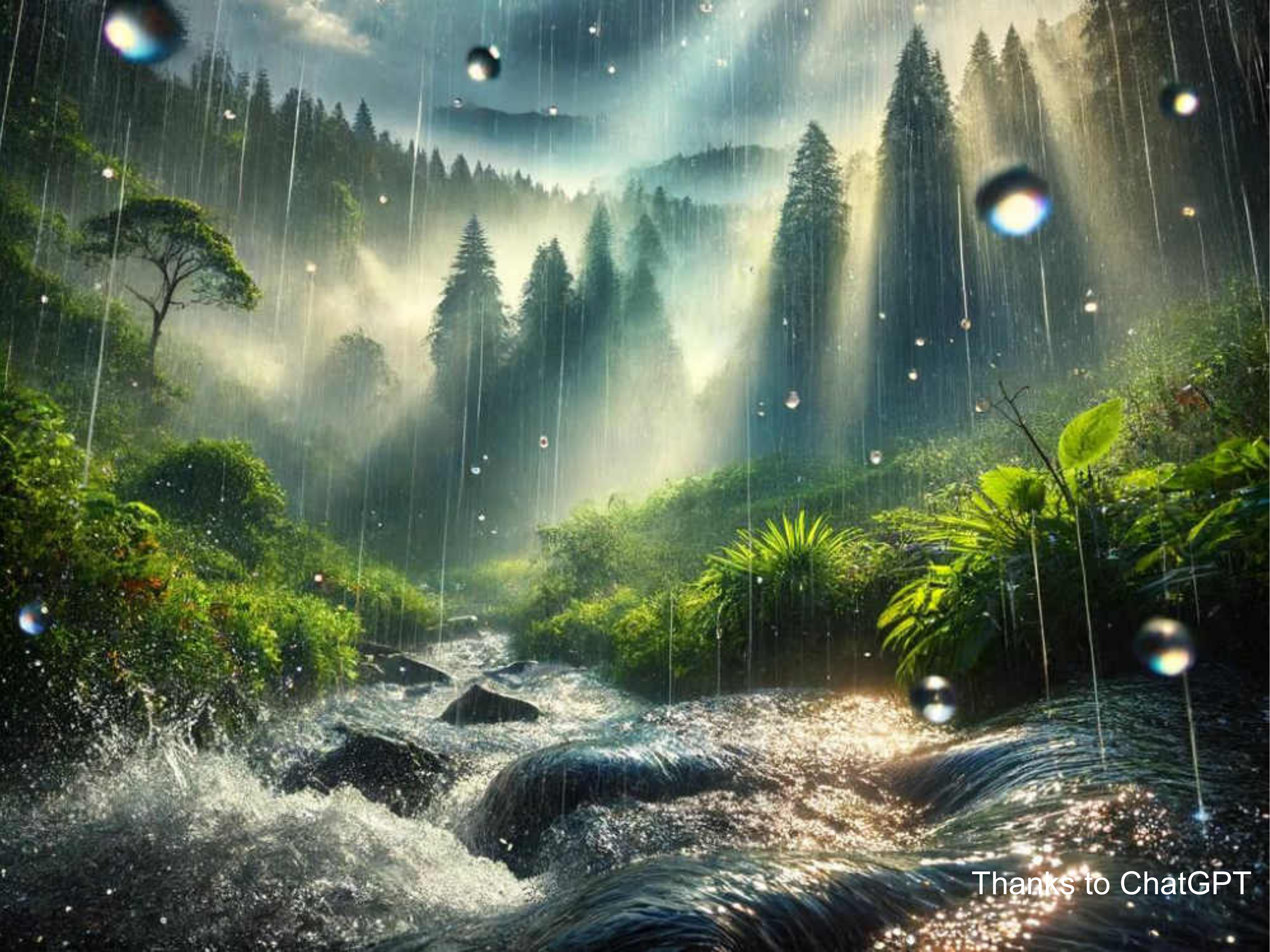
Results and Discussion

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



We developed environmentally friendly water positive nanoscale materials for affordable, sustainable and rapid removal of arsenic from drinking water.

There are over 1700 community installations across the country, serving 1.3 million people with arsenic and iron-free water every day.


Thanks to ChatGPT

Vision

Make soil using processed wastewater and make deserts bloom.

Thanks to ChatGPT

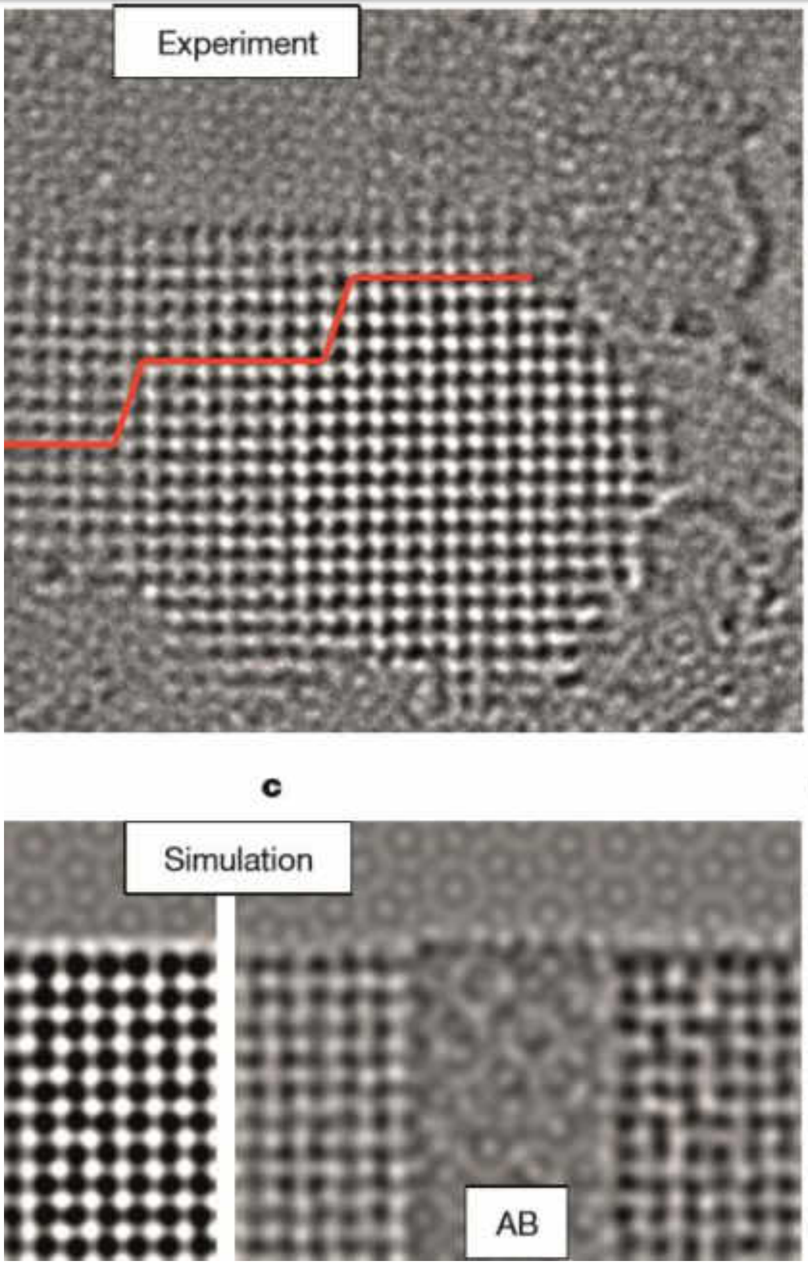
Conclusions

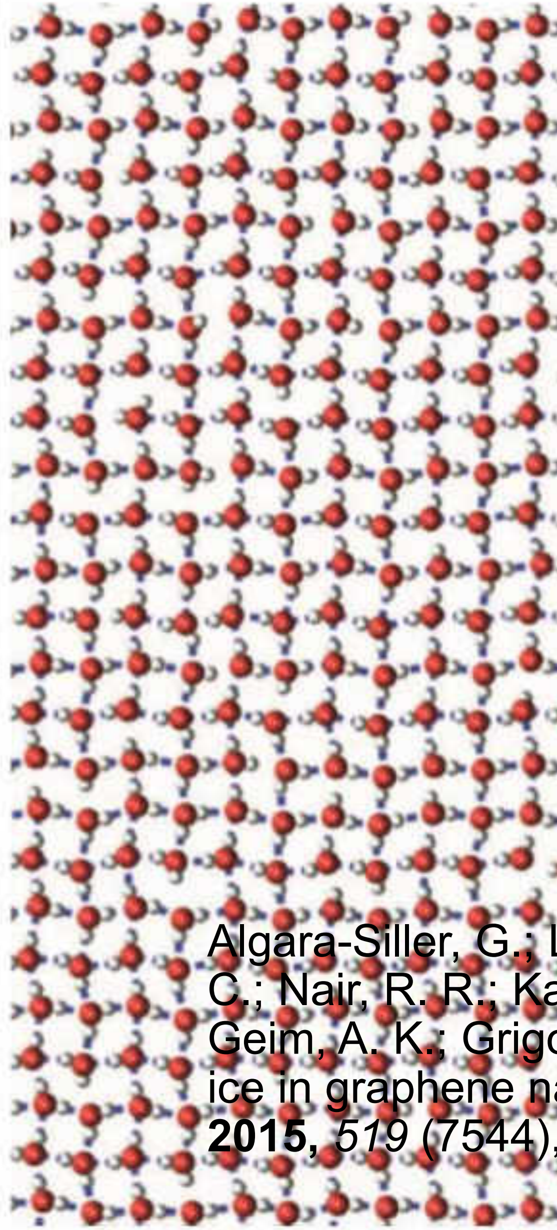
Natural minerals break spontaneously in charges water microdroplets
It occurs only in water… so far
Studies on a variety of materials
Facile due to proton-induced slip
Detailed investigations are essential to know more
Implications to the production of specific nanomaterials and soil in general

International Centre for Clean Water


IIT Madras Research Park

Observing water





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.


Department of Science and Technology

Thank you all

Microdroplets are Everywhere

COVID-19

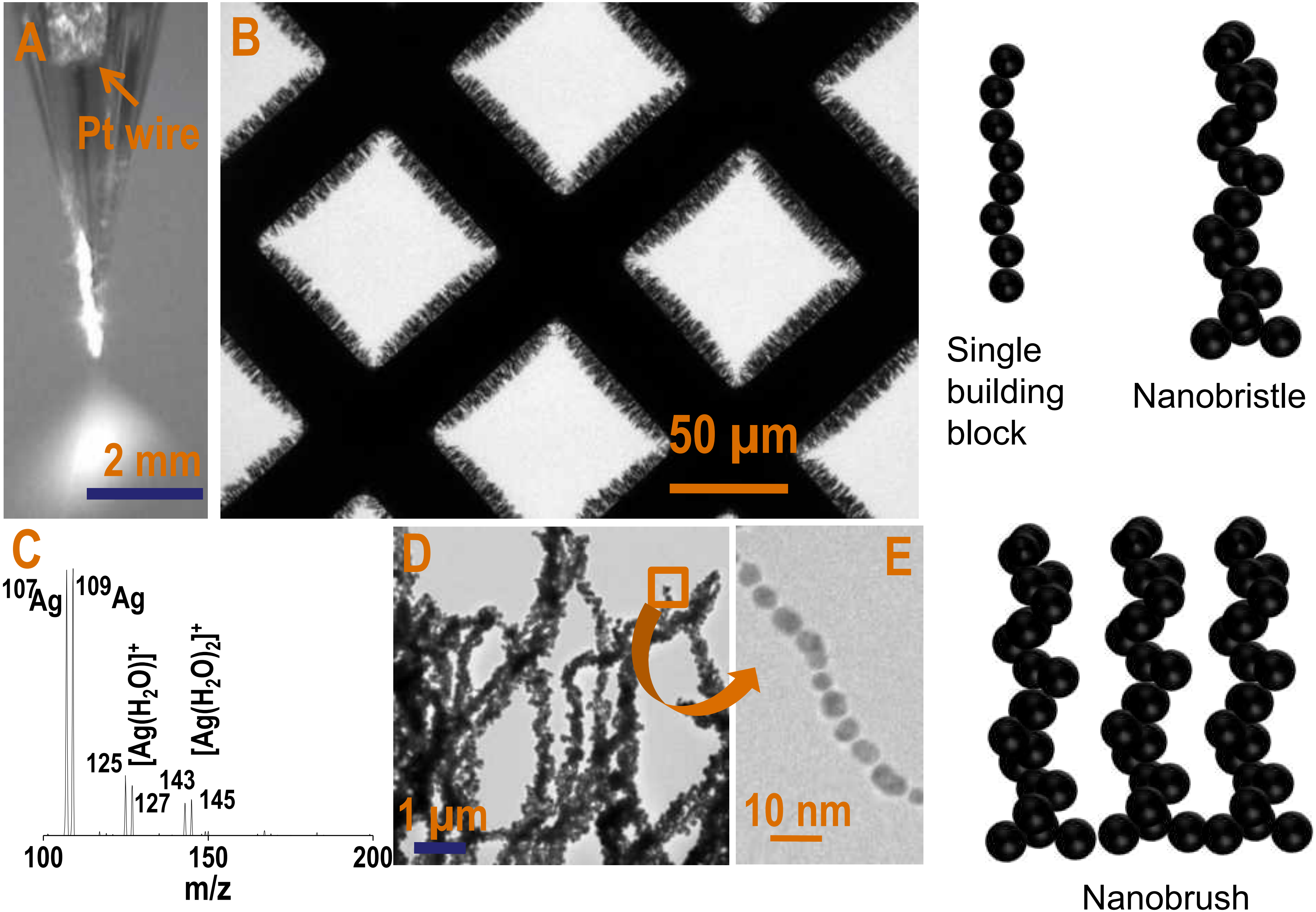
Painting

Hair sprays

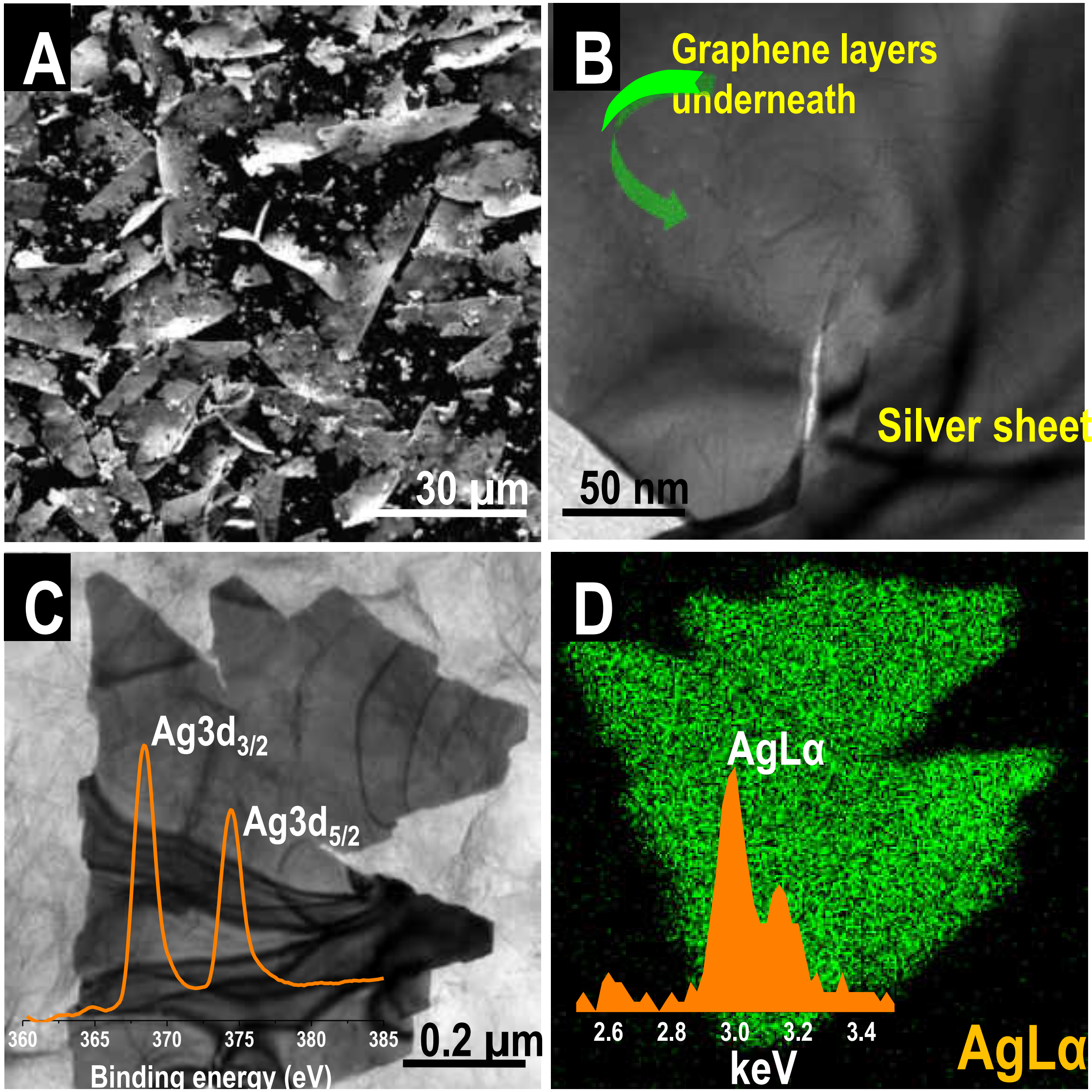
Perfumes

Agriculture

1D Nanomaterials



2D Nanomaterials



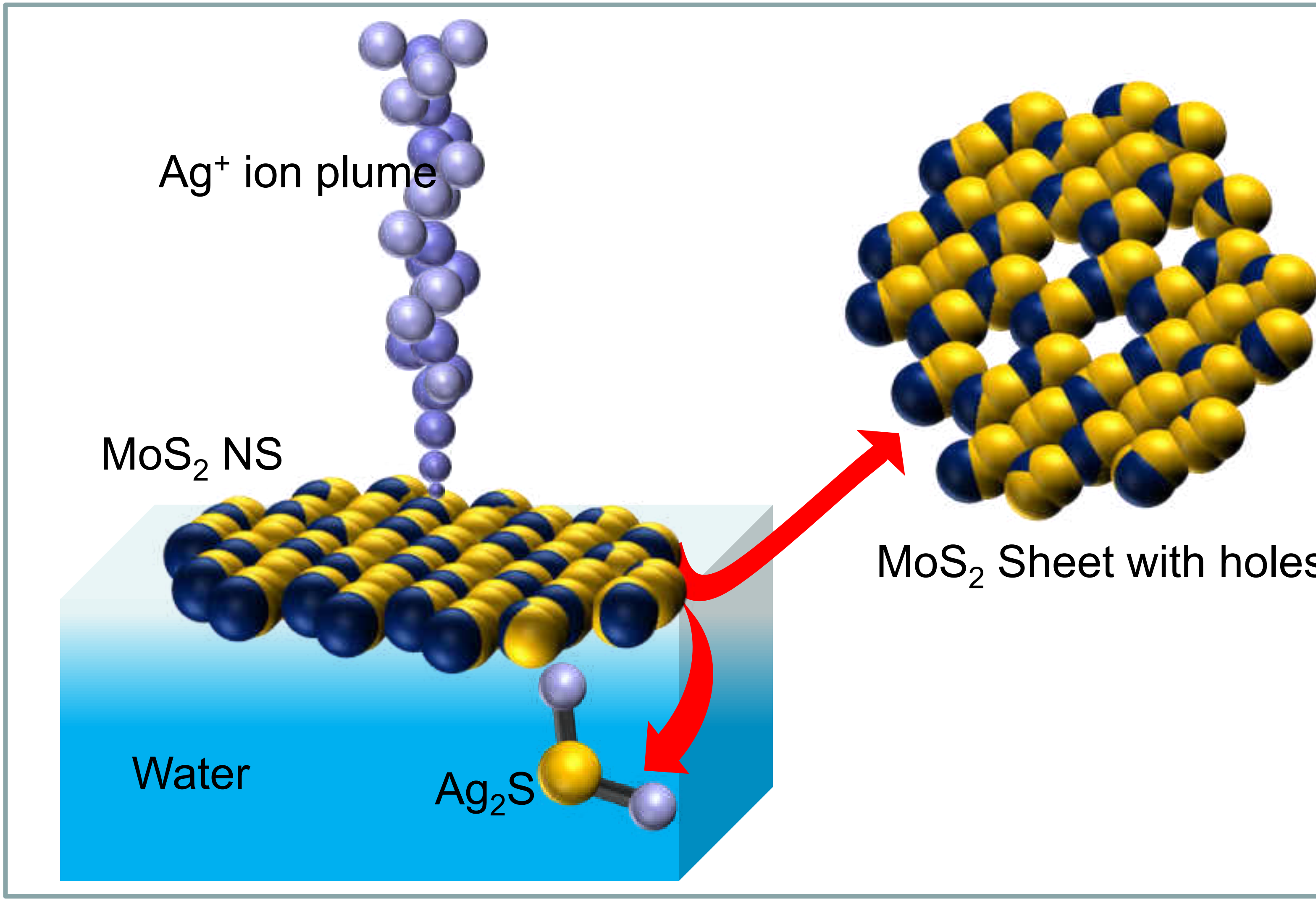
Ag^{+} ions

Room temperature

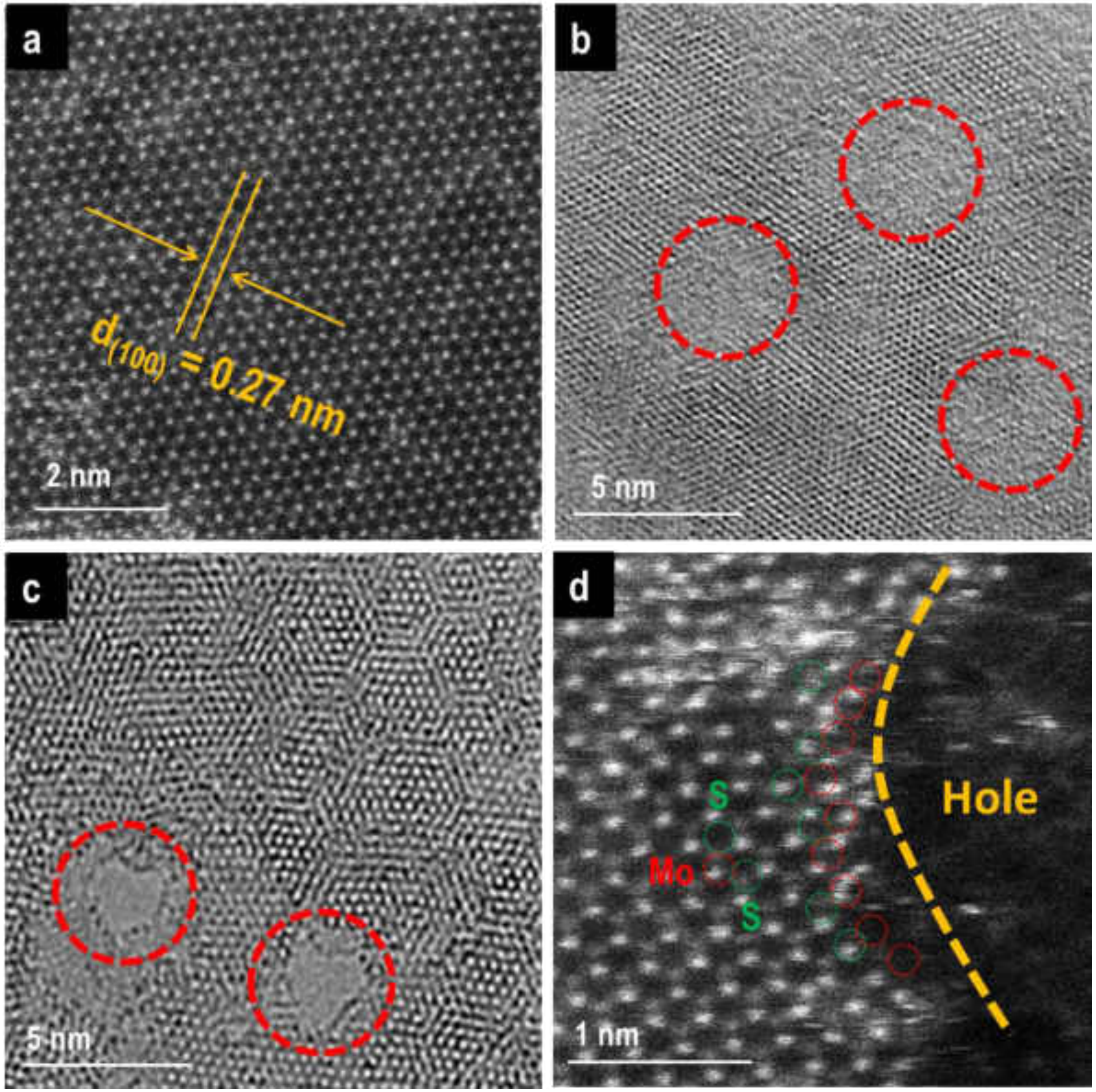
Single crystalline Ag metallic sheet

Depanjan Sarkar et. al., *Small,* 2024, Article ASAP.

Surface Modification Using Charged Microdroplets

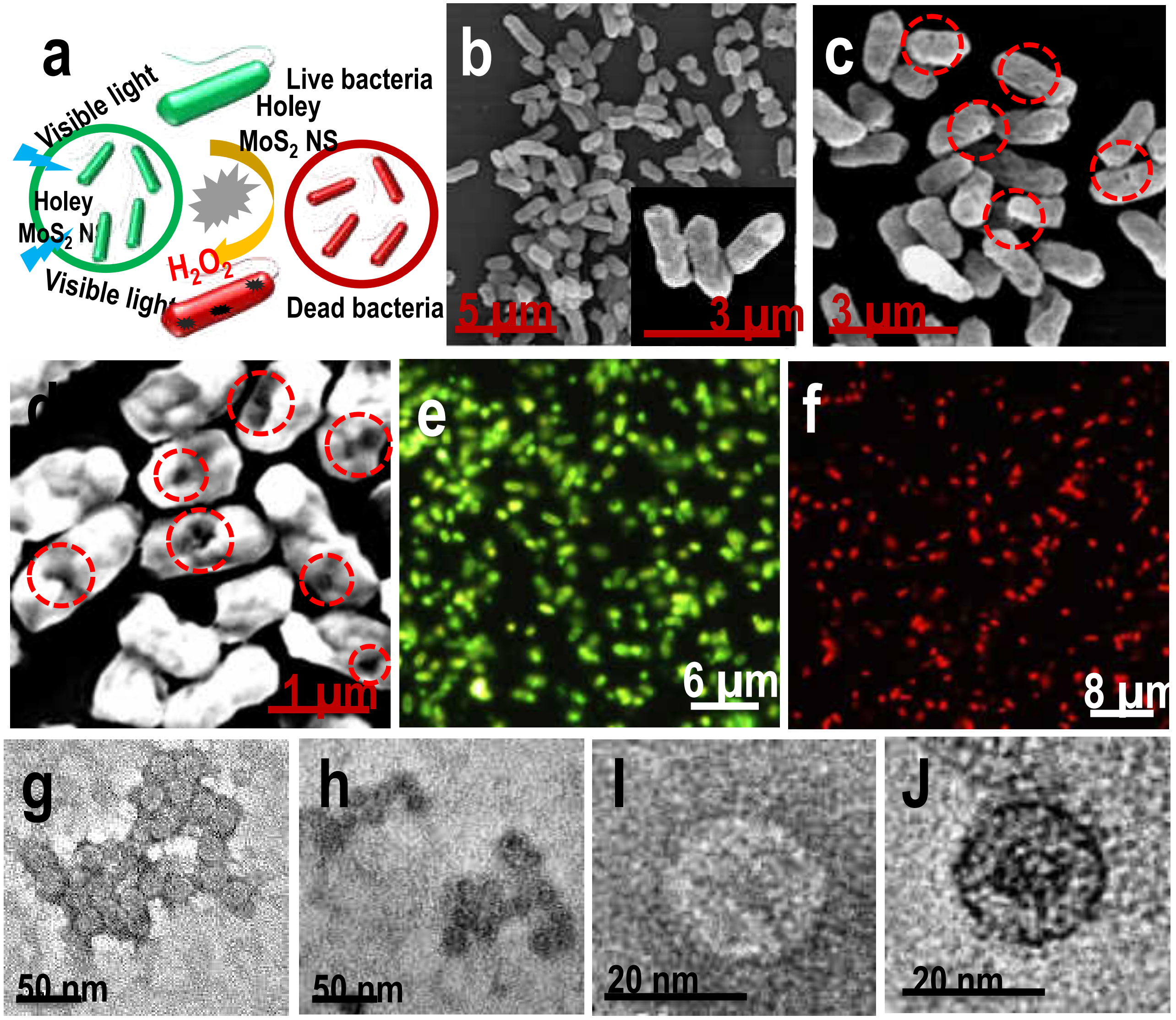


Fabrication of Holey MoS_2 NSs



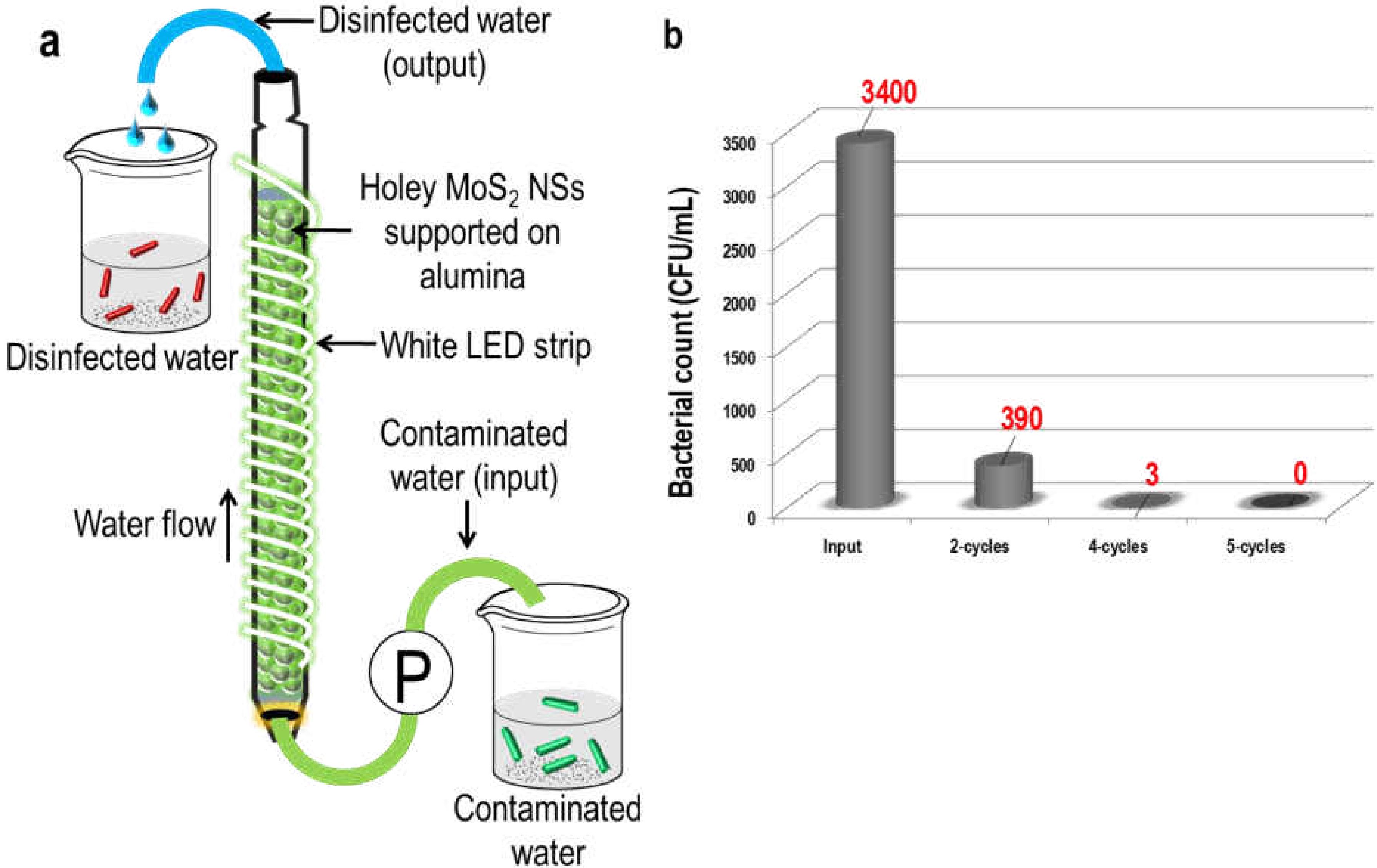
Depanjan Sarkar et. al., *Global Challenges,* 2018, 2, 1800052.

Application: Water Disinfection

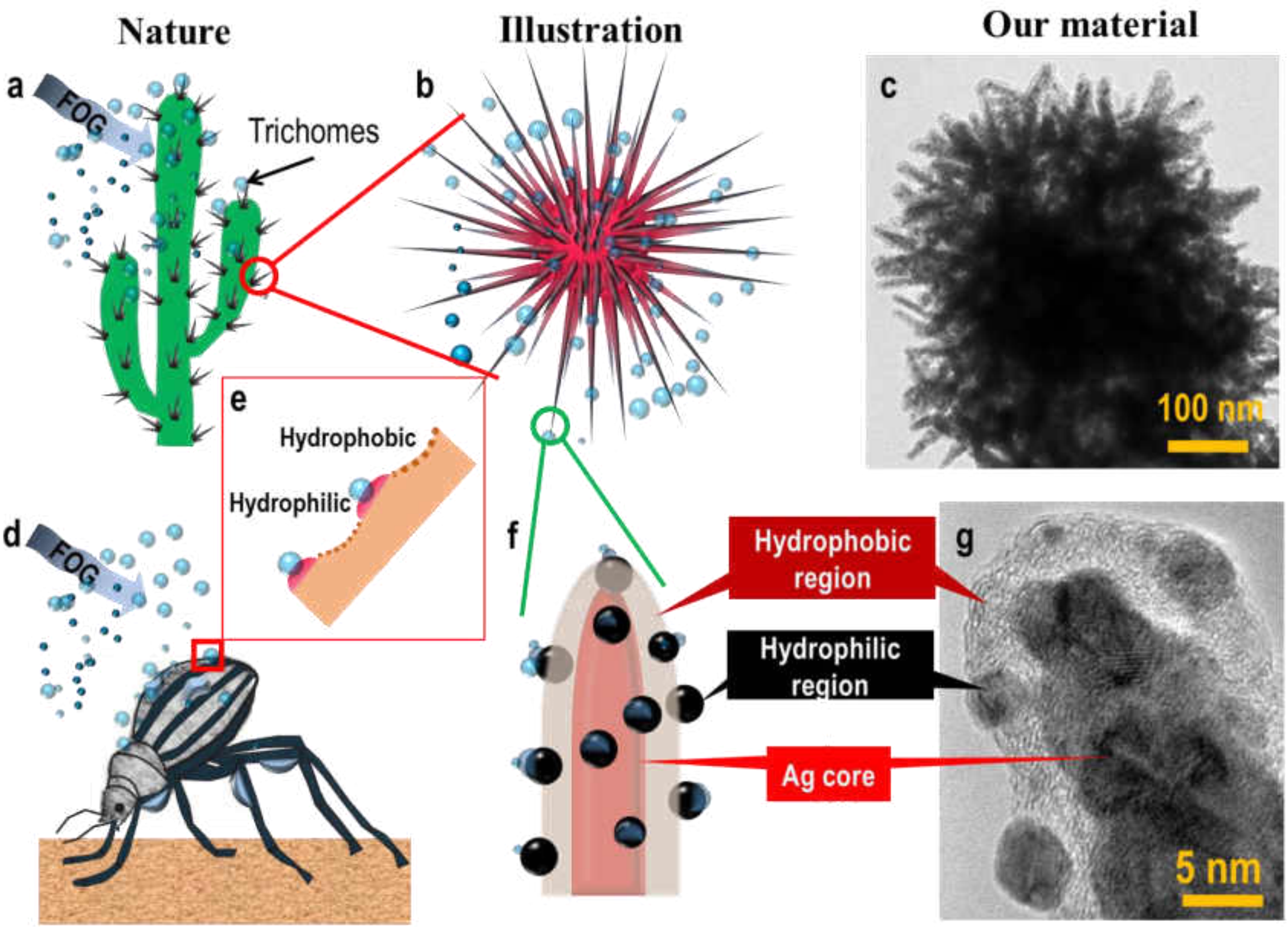


Depanjan Sarkar et. al., *Global Challenges,* 2018, 2, 1800052.

Application: Water Disinfection

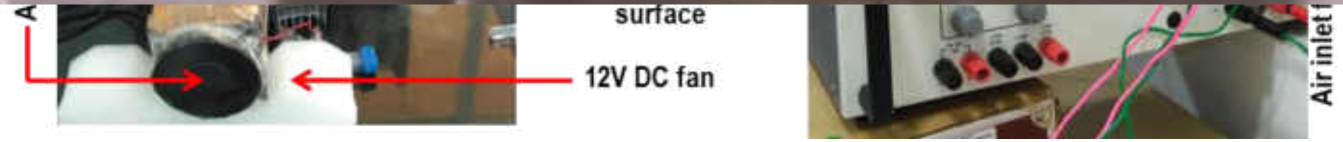


Patterned Surfaces Using Microdroplets



Depanjan Sarkar et. al., *Adv. Mater. Interfaces*, 2018, 1800667.

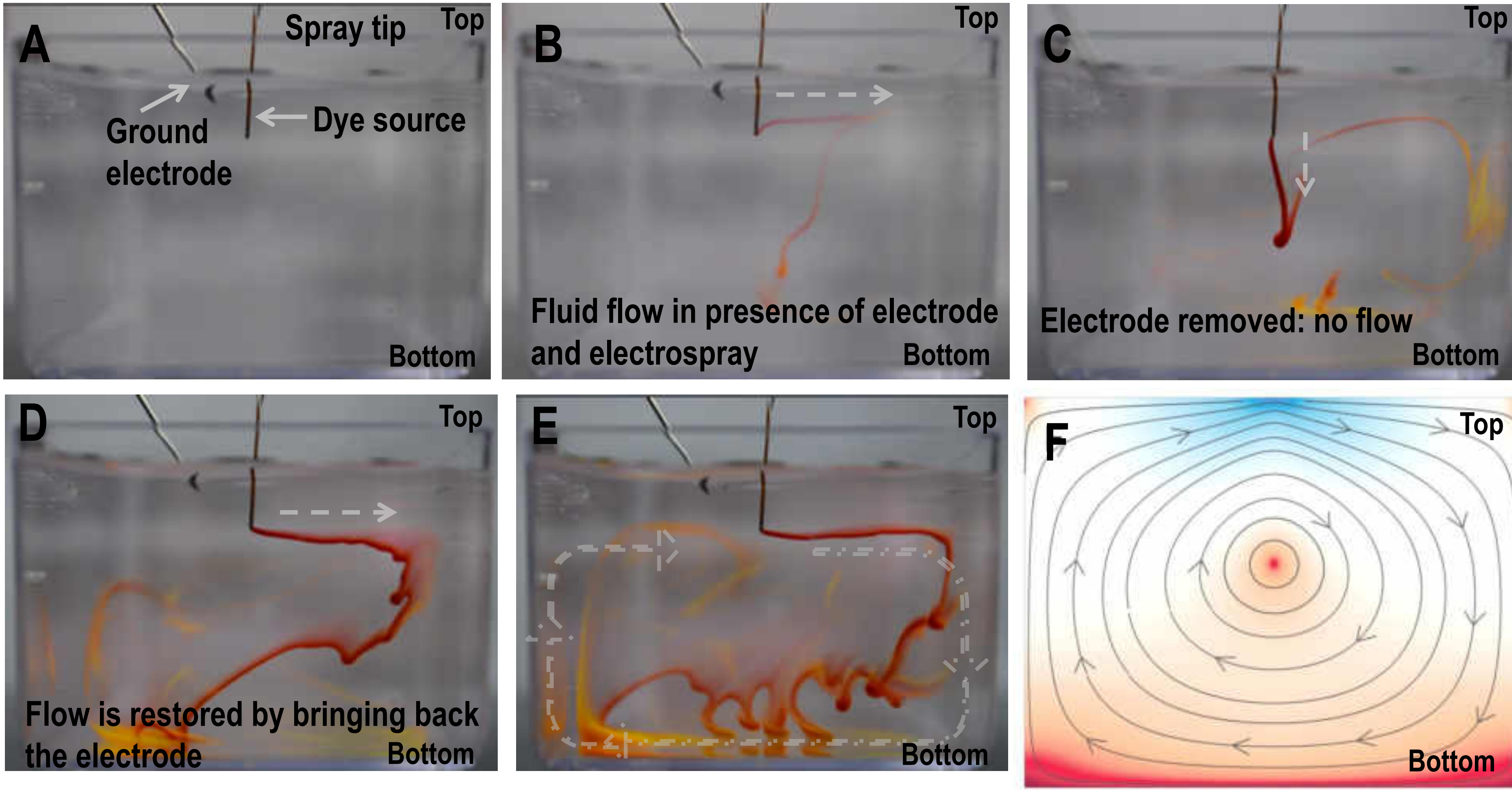
Atmospheric Water Capture



Efficiency of 56.6 L m^{-2} d^{-1}

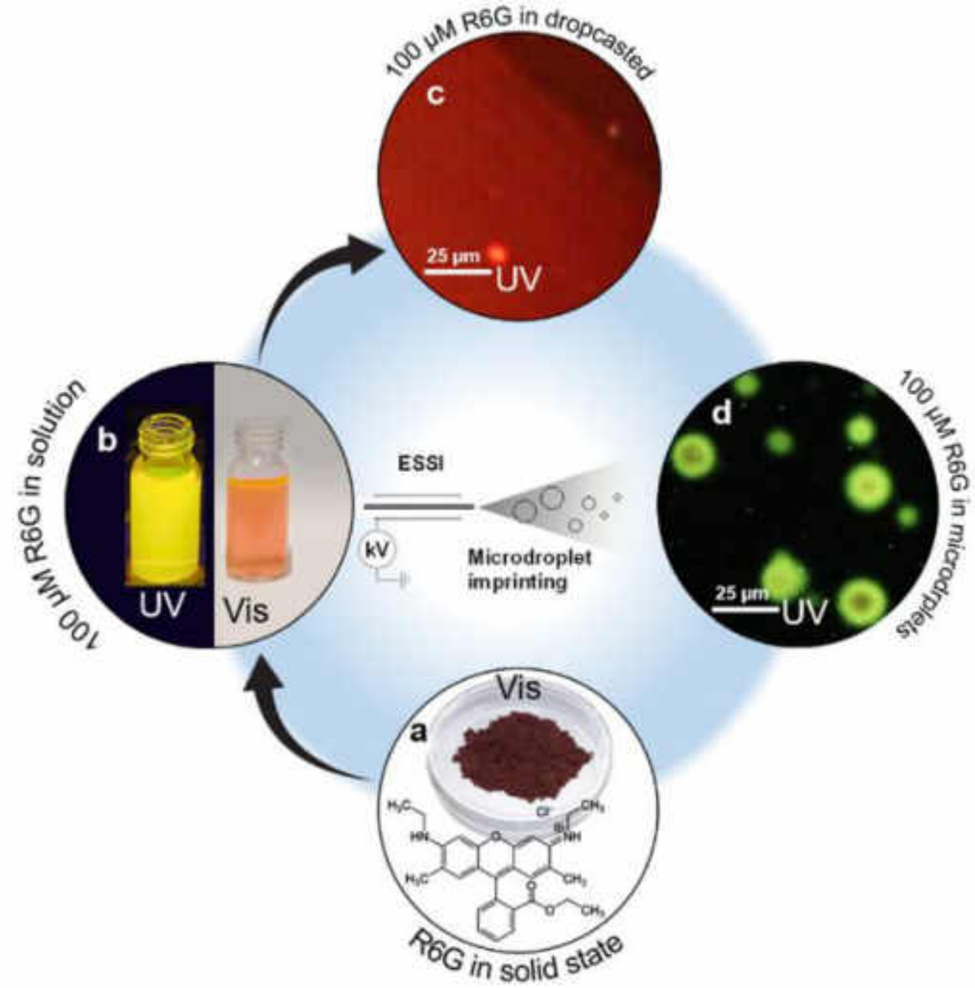
Understanding Microdroplets

Electrohydrodynamic flow in the liquid surface induced by microdroplet deposition



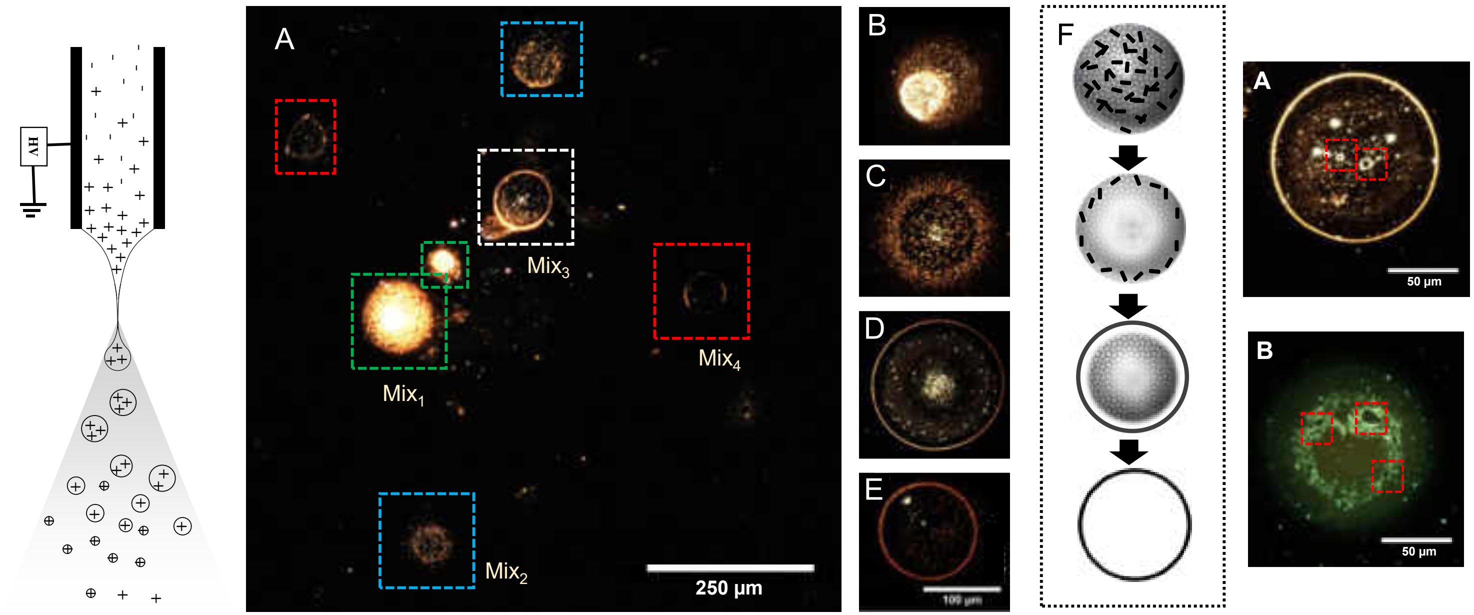
Depanjan Sarkar et.al., *J. Phys. Chem. C,* 2018, 122, 17777−17783.

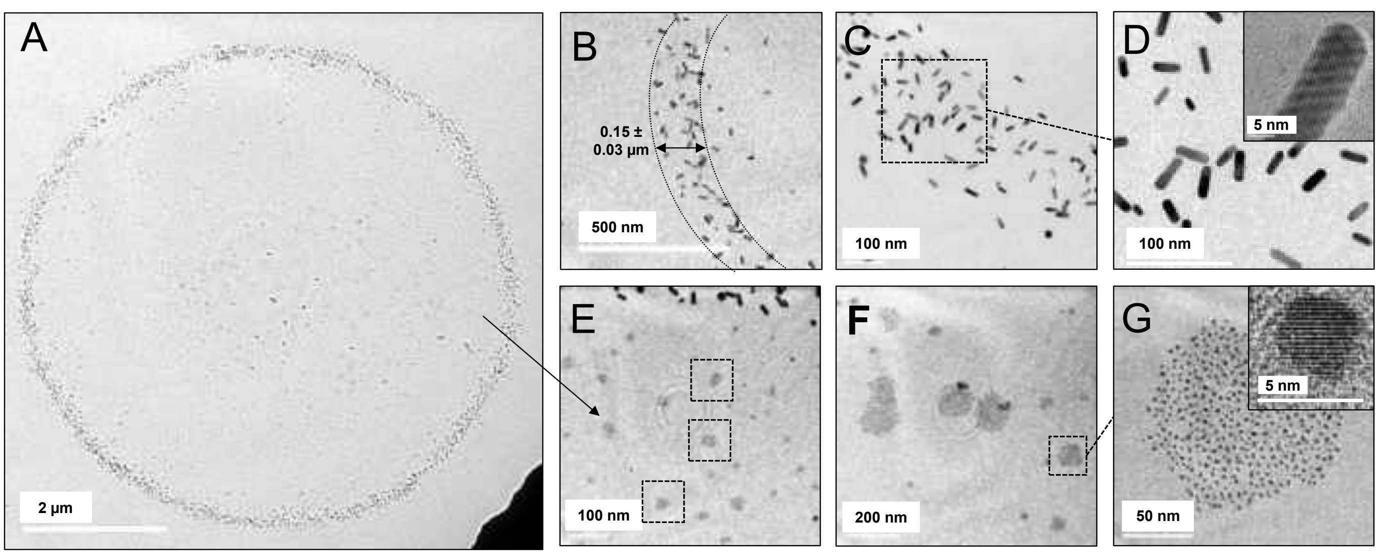
Understanding Microdroplets



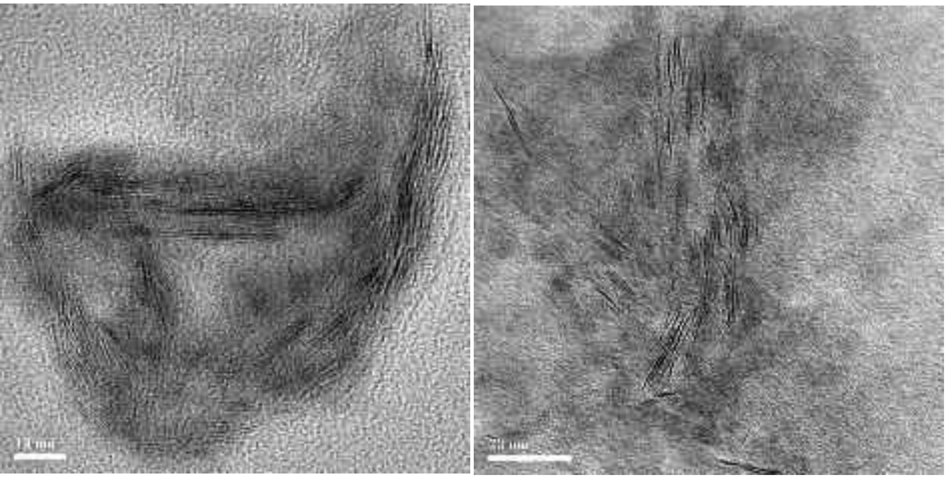
Pallab Basuri et. al., *Chem. Commun.*, 2022, 58, 12657–12660

Understanding Microdroplets

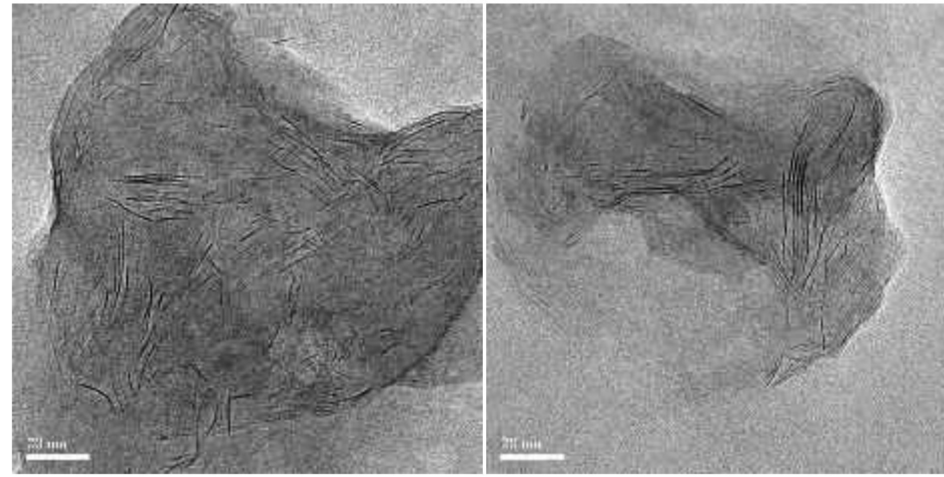




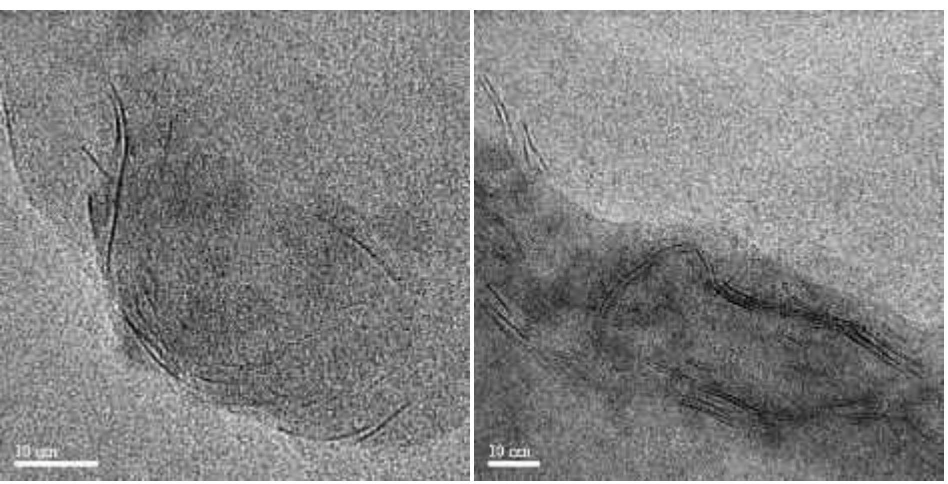
100% Methanol



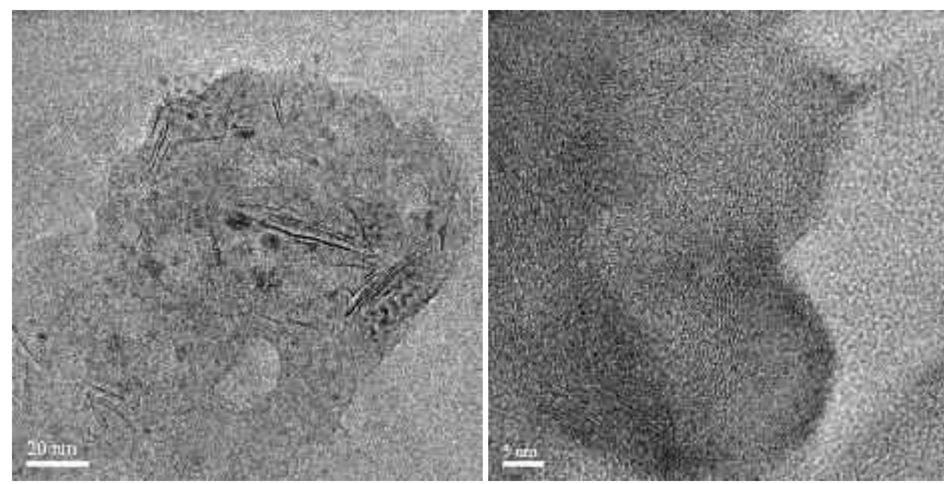
75:25 Methanol: Water

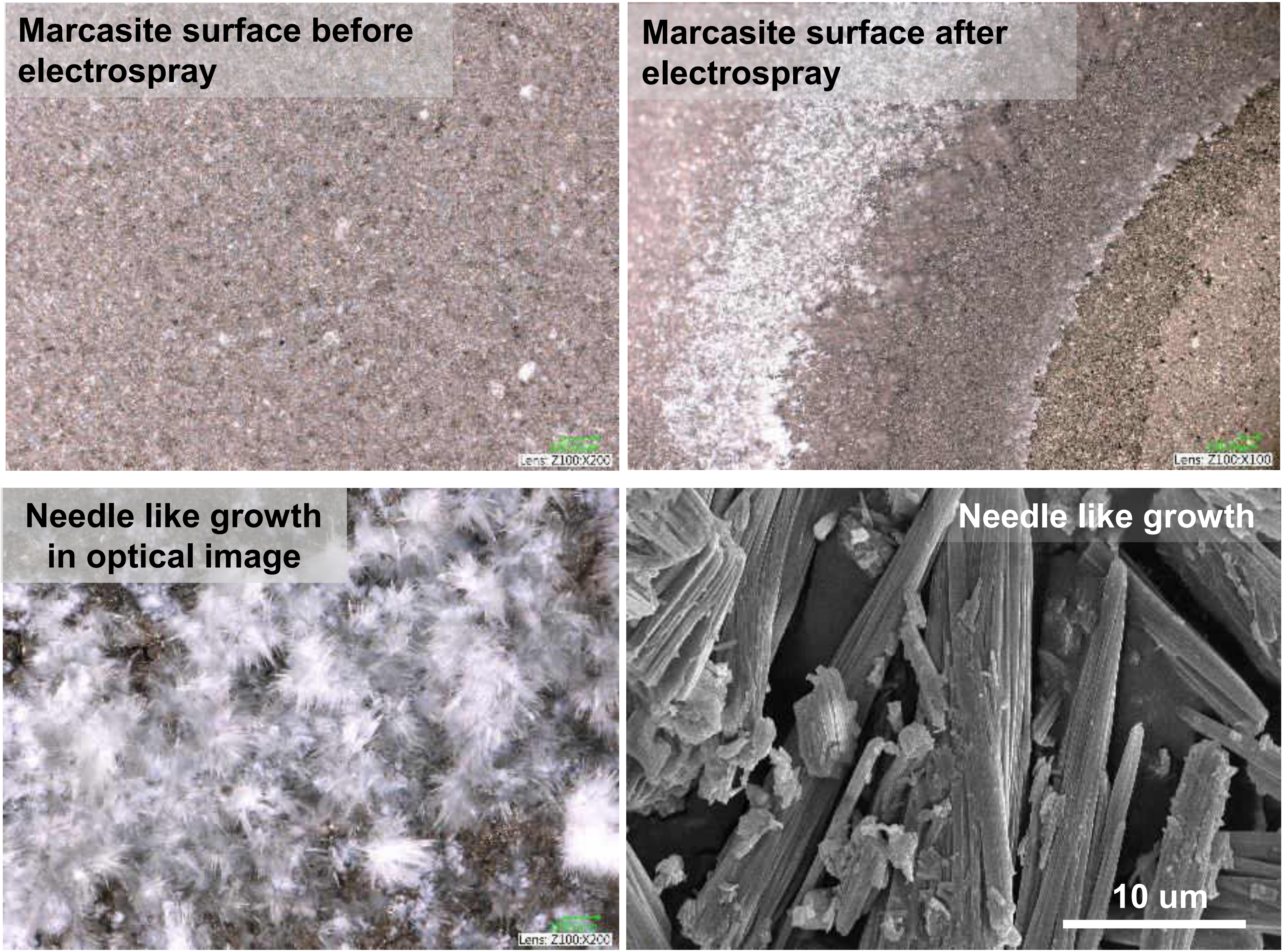


50:50 Methanol: Water



25:75 Methanol: Water




Marcasite surface before electrospray
Lens: Z100:X200
Marcasite surface after electrospray
Lens: Z100:X100
Needle like growth in optical image
Lens: Z100:X200
Needle like growth
10 um

Collaborators






Robin Ras

Nonappa

Tomas Base

Manfred Kappes

Olli Ikkala

Horst Hahn

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

Biswarup Pathak

K. V. Adarsh

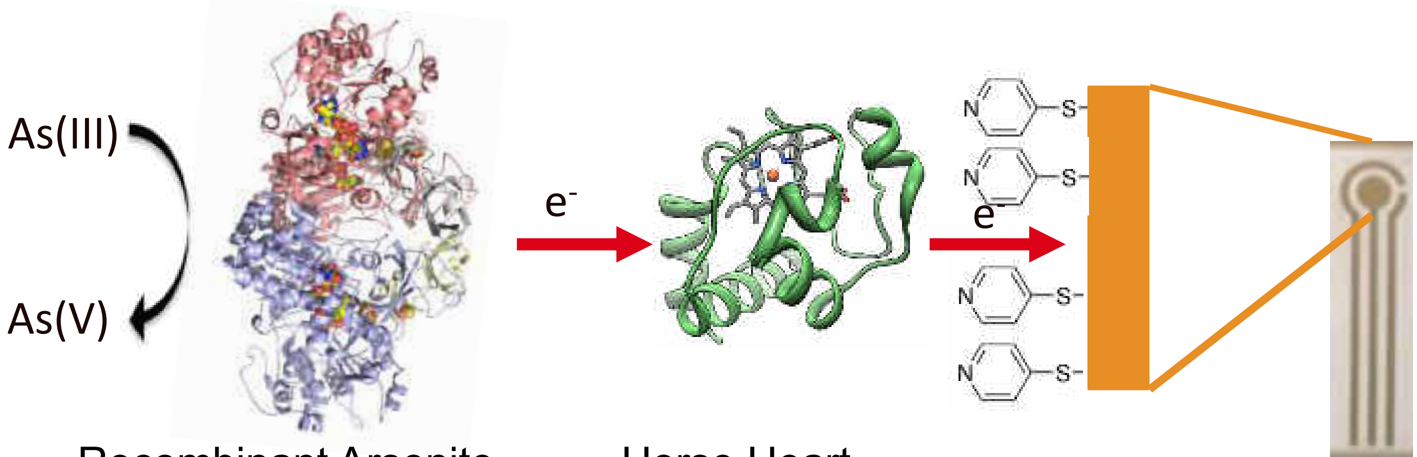
G. U. Kulkarni

Vivek Polshettiwar

Shiv Khanna

Biosensor Design

1st Generation Design (Mediated Electrochemistry)



Buffer: pH 7-8

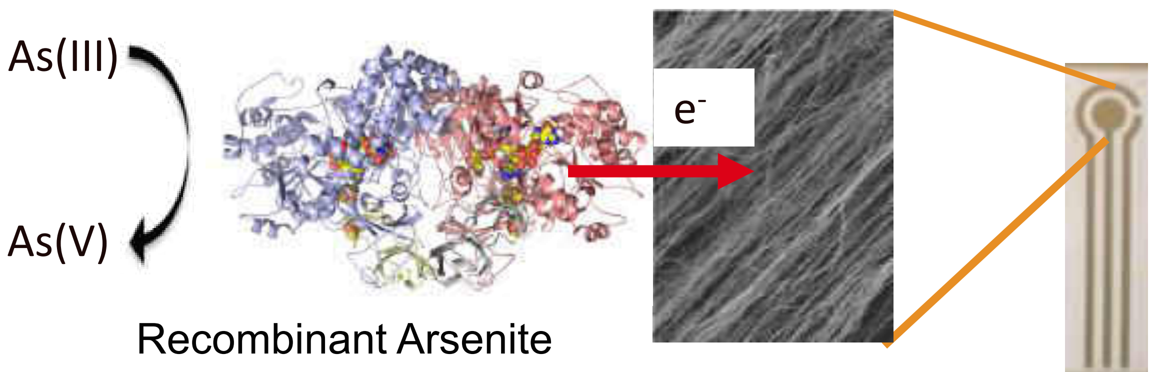
Recombinant Arsenite Oxidase NT-26 Aio

Horse Heart Cytochrome C

Aldrithiol

Low-cost Gold sputtered thin film on PET substrate

2nd Generation Design (Direct Electron Transfer)

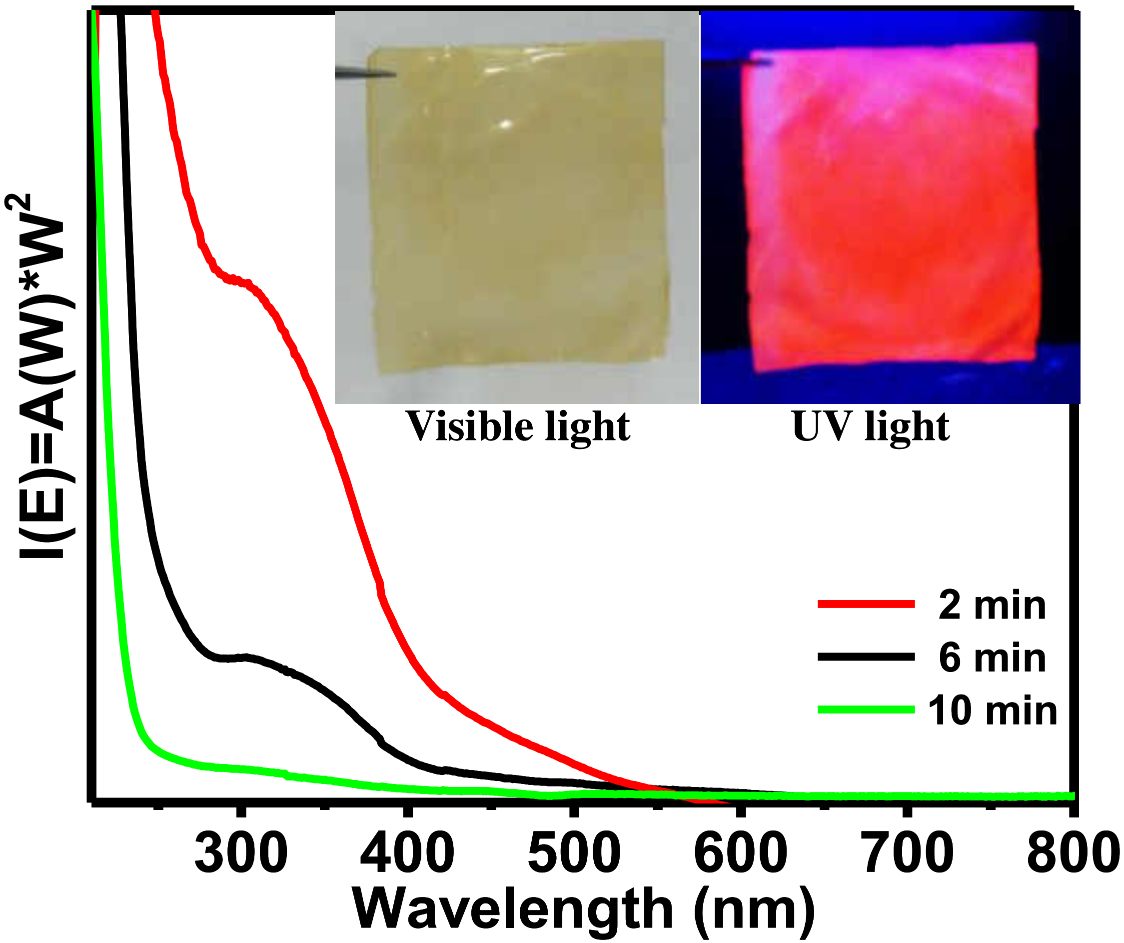


low-cost nanostructured electrodes which interact directly with enzyme (e.g. graphene or CNT).

Recombinant Arsenite Oxidase NT-26 Aio

Bio-nano Consulting & Imperial College, London

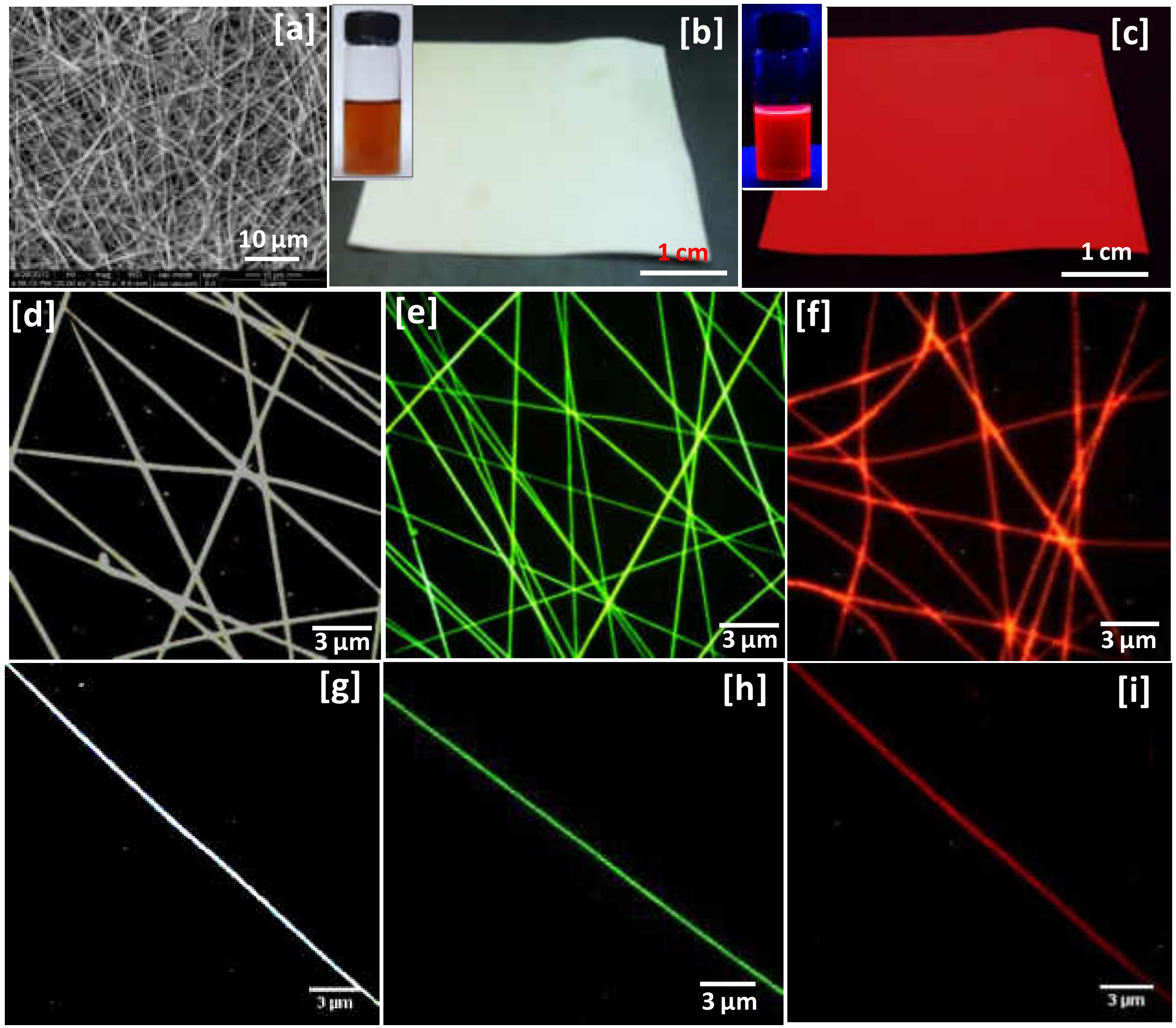
Cluster-based metal ion sensing



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.

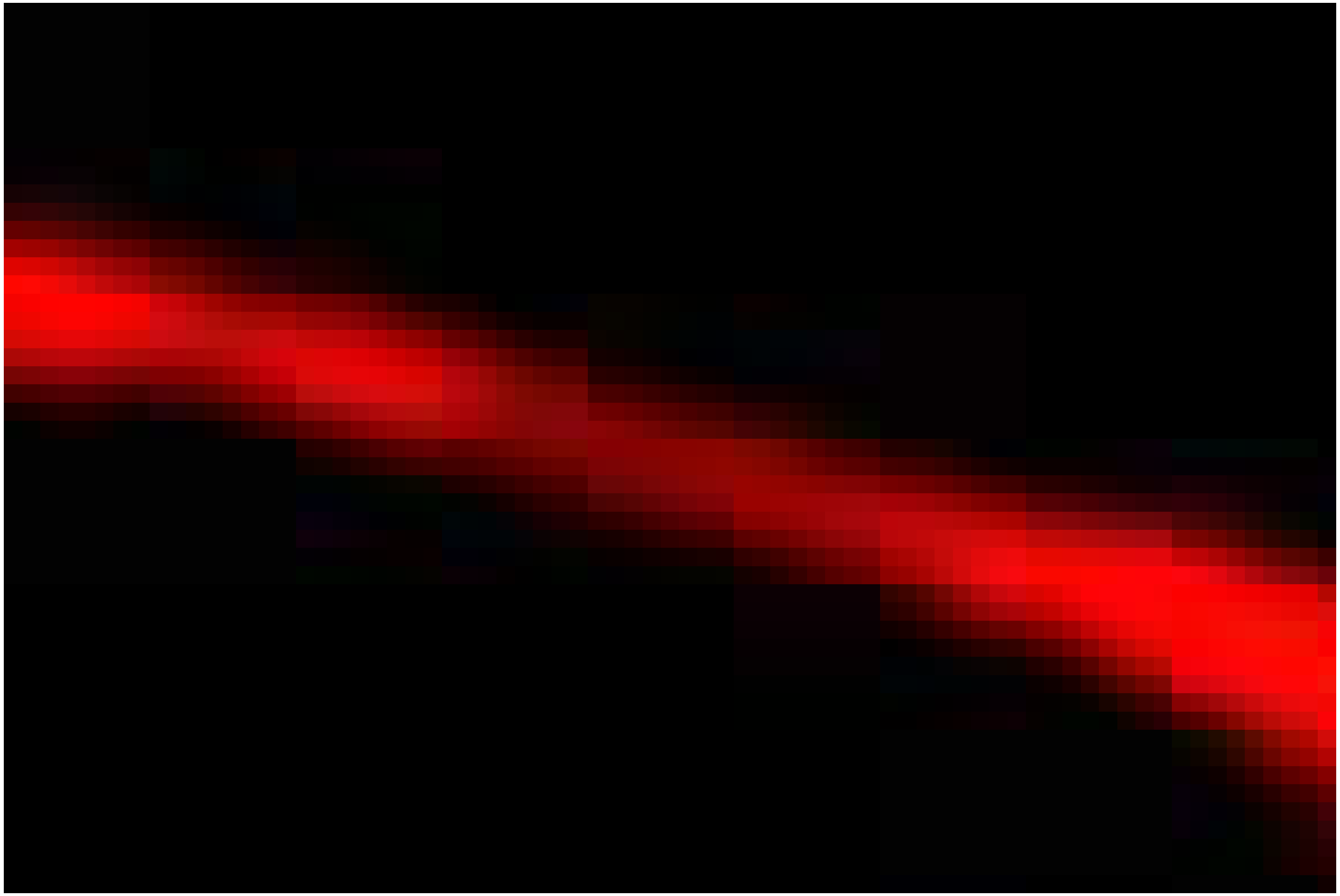
Anu George et al. *ACS Applied Materials & Interfaces*, 2012

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

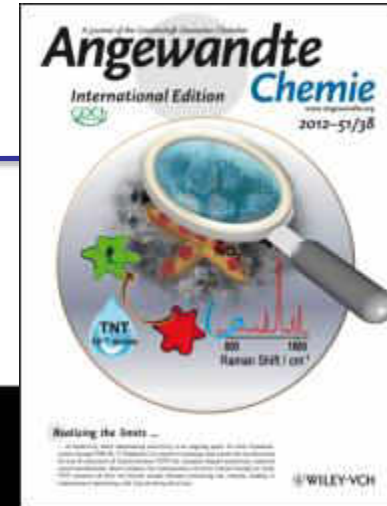


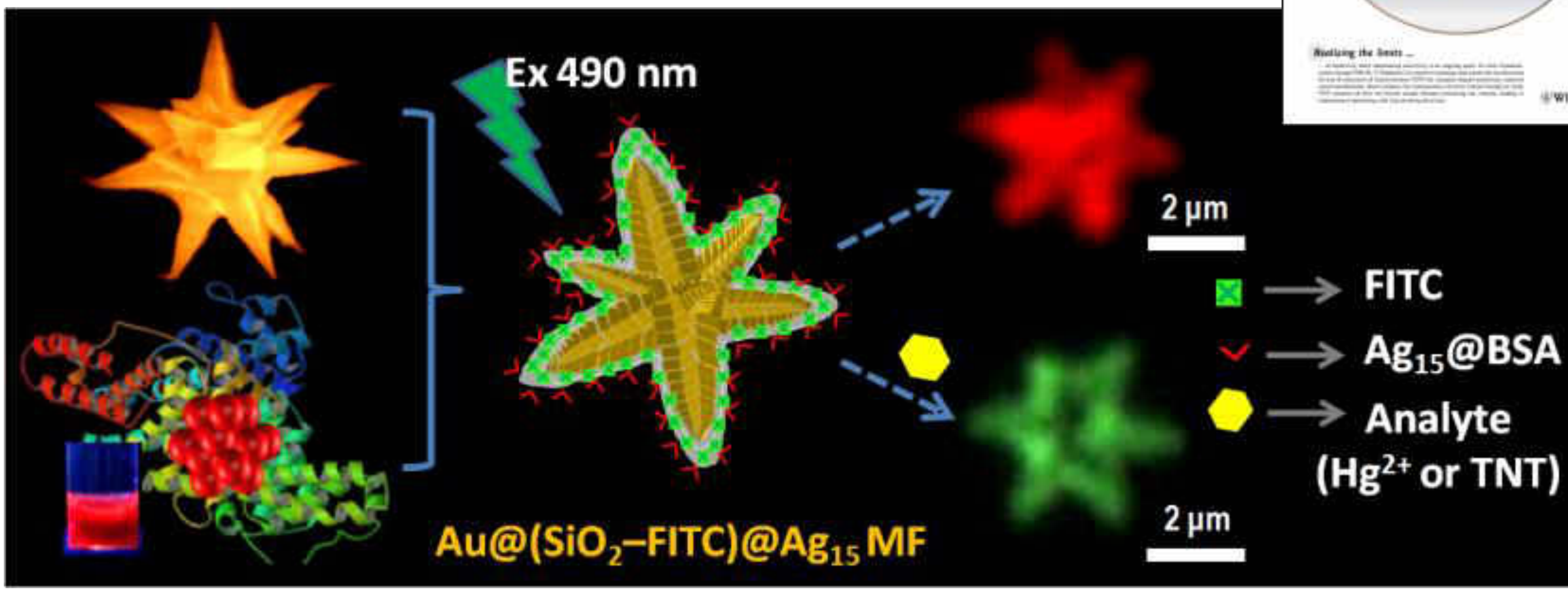
Atanu Ghosh et al. Anal. Chem. 2014.

Mercury quenching experiment using nanofiber



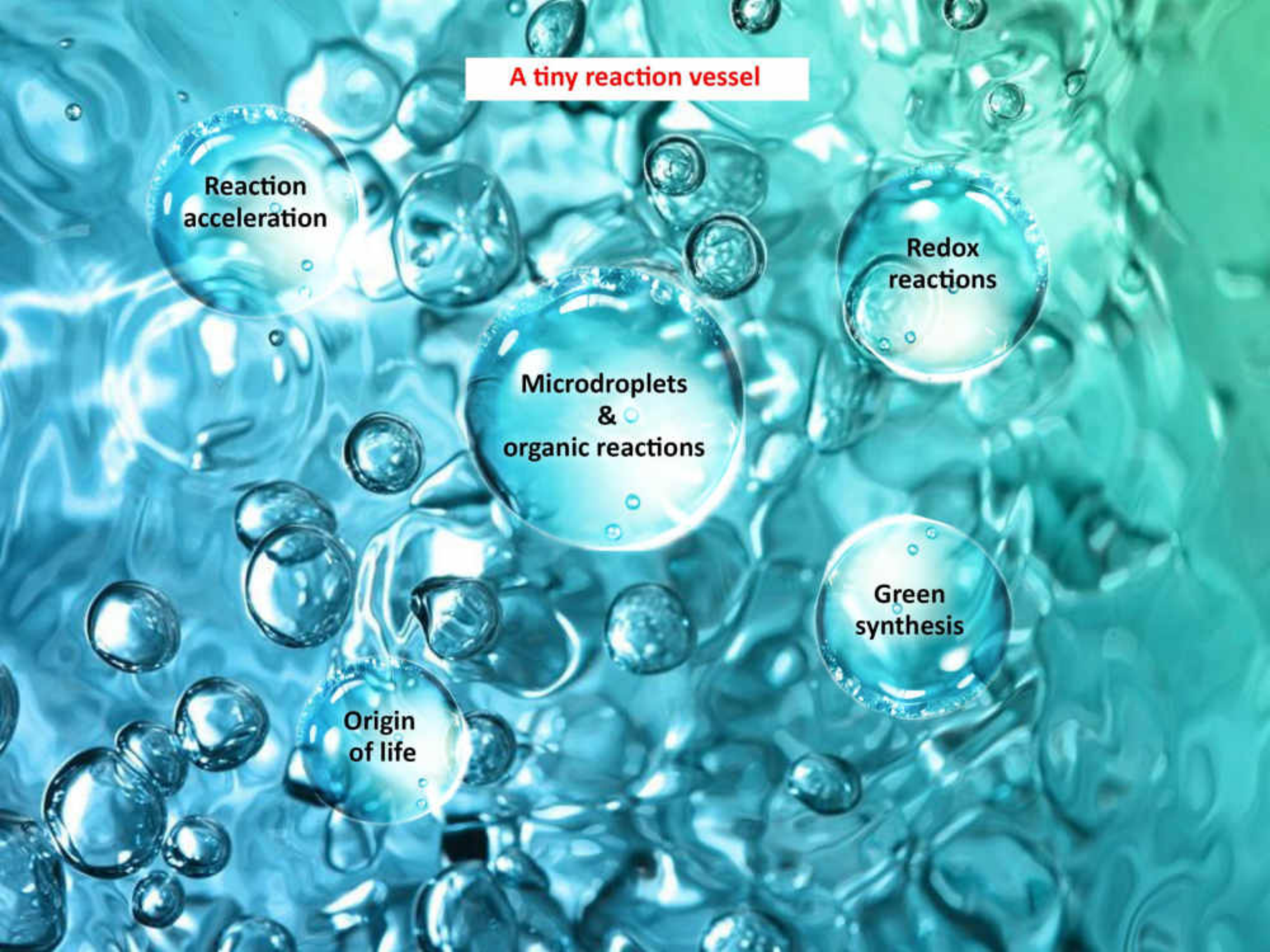
Sub-zeptomolar detection



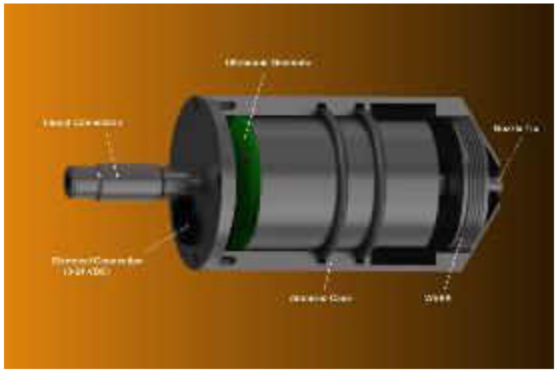


Featured in:
The Hindu, Telegraph, Times of India, etc.
C&E News
and many others

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

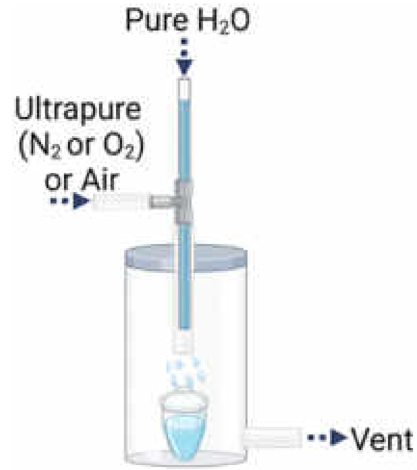

A tiny reaction vessel
Reaction acceleration
Redox reactions
Microdroplets & organic reactions
Green synthesis
Origin of life

Ways of Production of Microdroplets

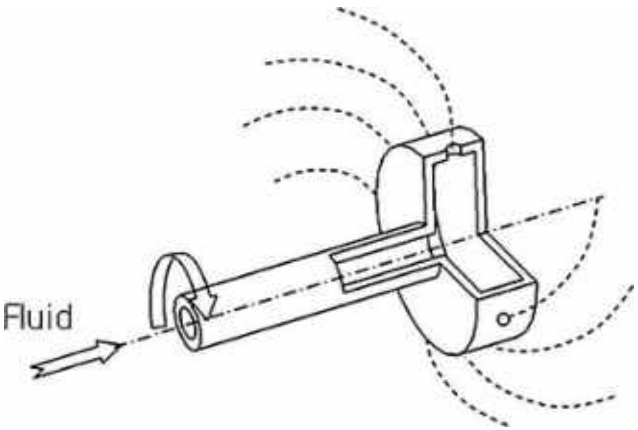


Ultrasonic

Production of fine droplets by high-frequency sound waves

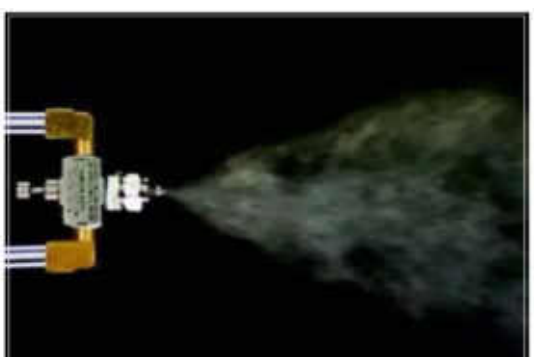


Nebulization



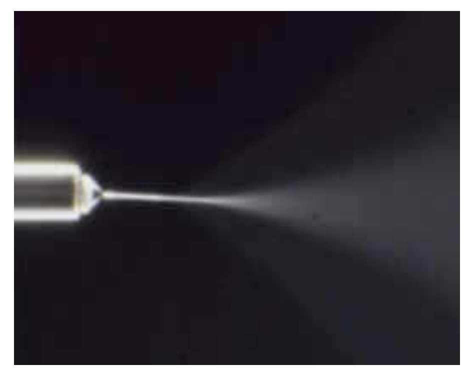
Rotary atomizers

Production of fine droplets by high speed rotation



Hydraulic

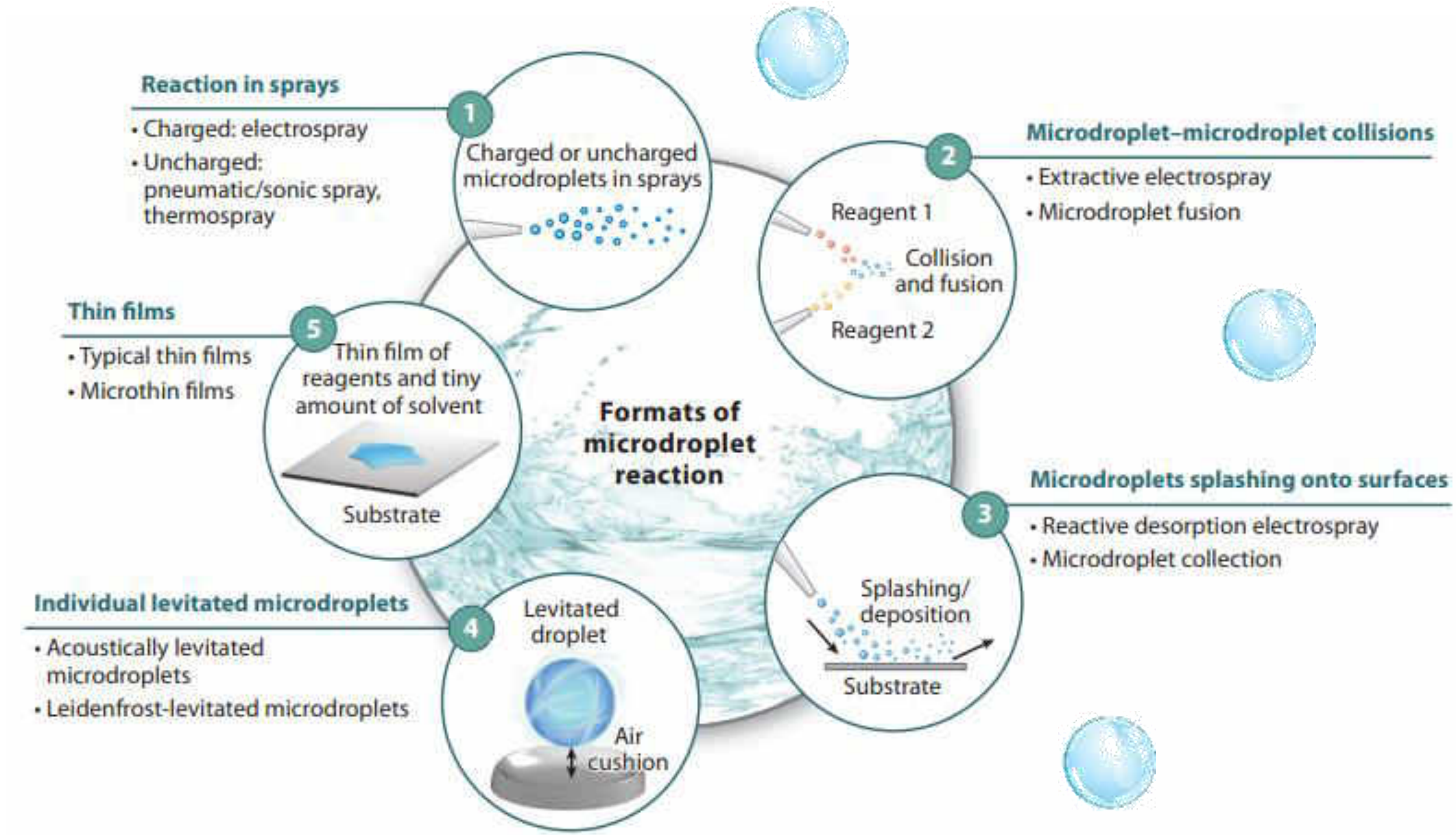
Production of fine droplets by applying hydraulic pressure



Electrospray

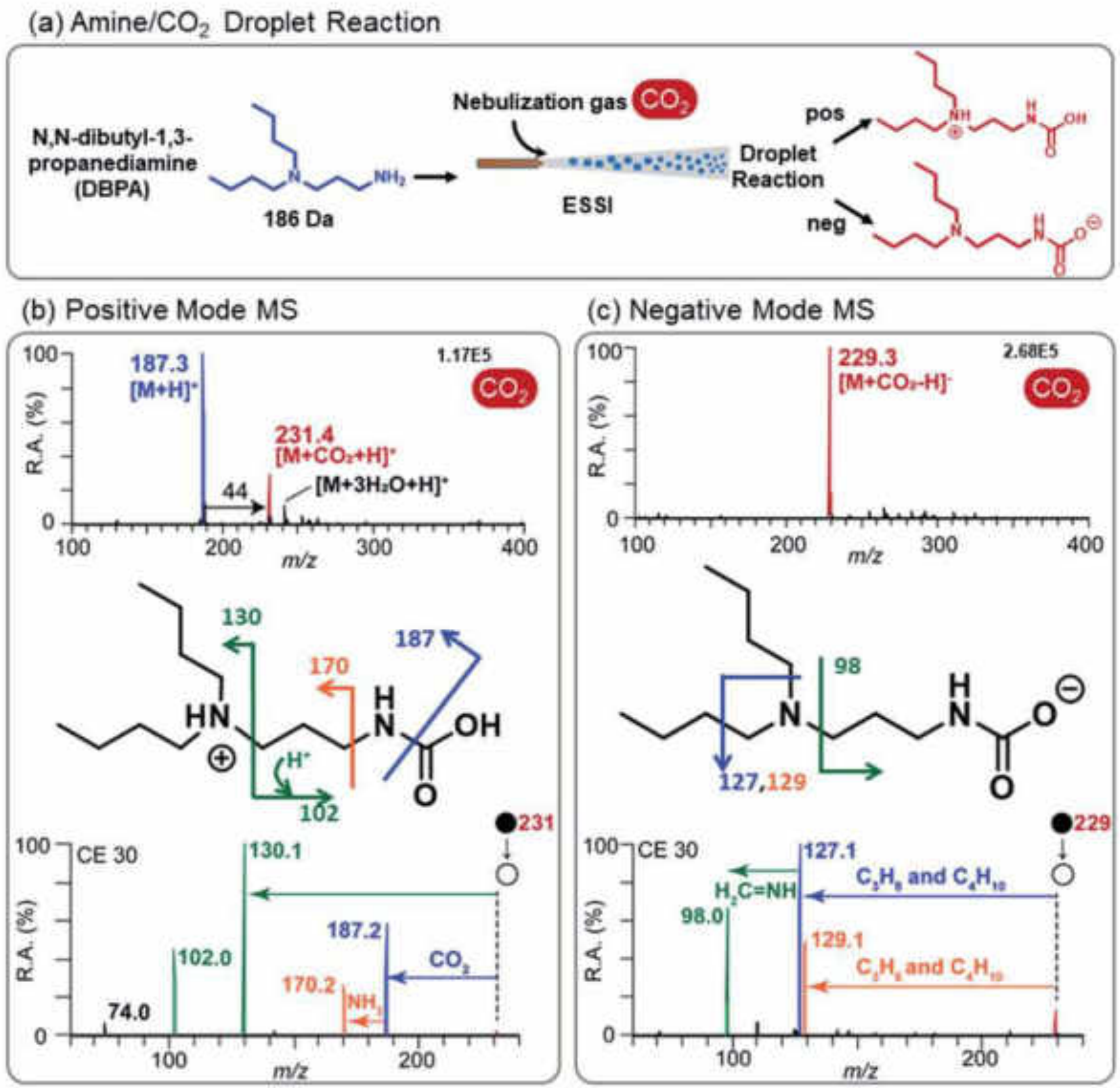
Images from the Internet

Reaction Acceleration in Microdroplets



Z. Wei, et al., Annu. Rev. Phys. Chem., 2020, 71, 31–51.

Reaction Acceleration in Microdroplets

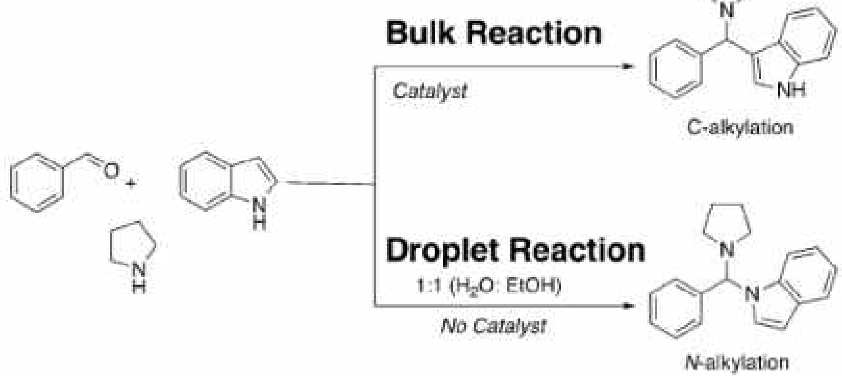


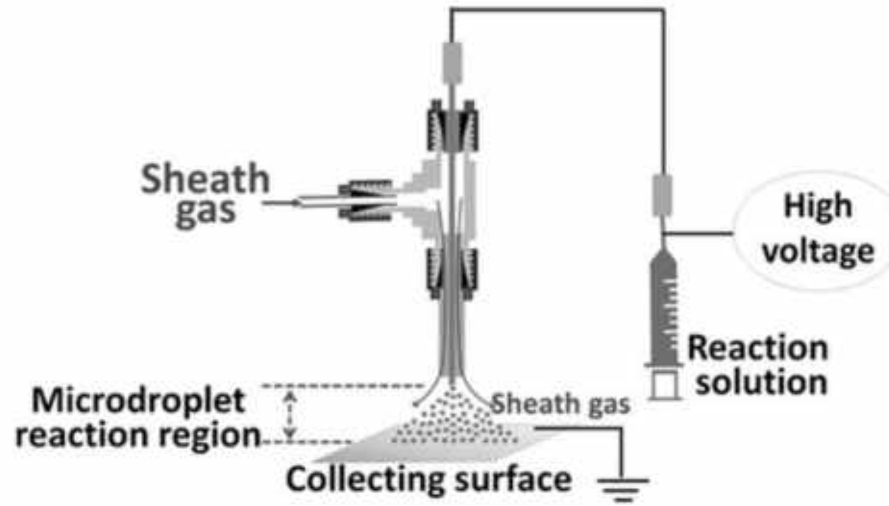
- Carbon dioxide undergoes C–N bond formation reactions with amines at the interface of droplets to form carbamic acids
- ESI – MS displays the reaction products in the form of the protonated and deprotonated carbamic acid

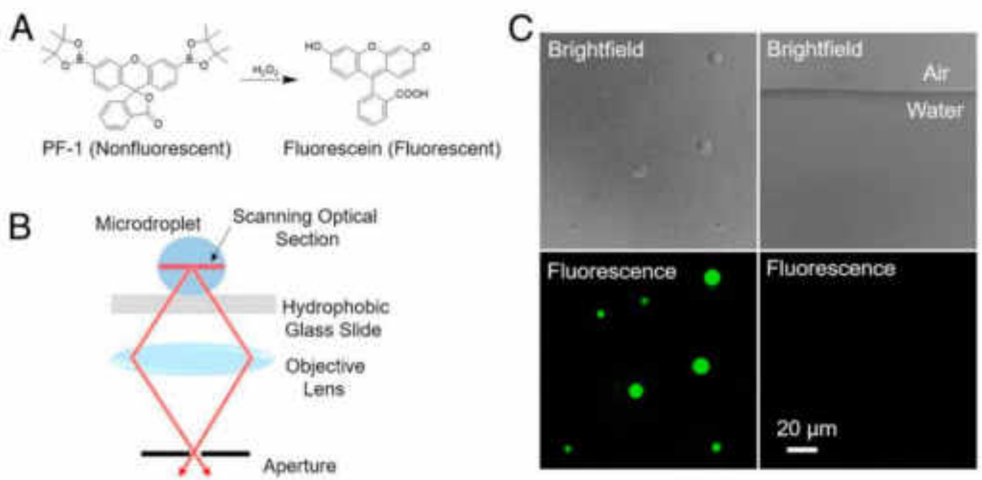
K. H. Huang, et al., Chem. Sci., 2021, 12, 2242-2250

Reactions Different from Bulk

First chemoselective N-alkylation of Indole in aqueous microdroplets







At air-water interface

$$H_2O \longrightarrow H^+ + OH^-$$

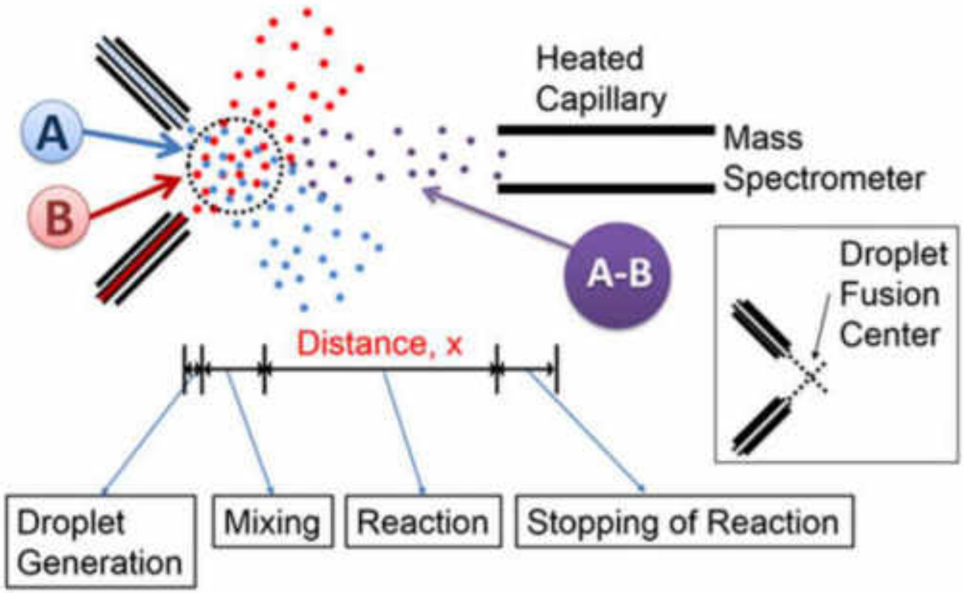
$$OH^- \xrightarrow{\vec{E},\ \Delta pH} OH^{\bullet} + e^- (solv)$$

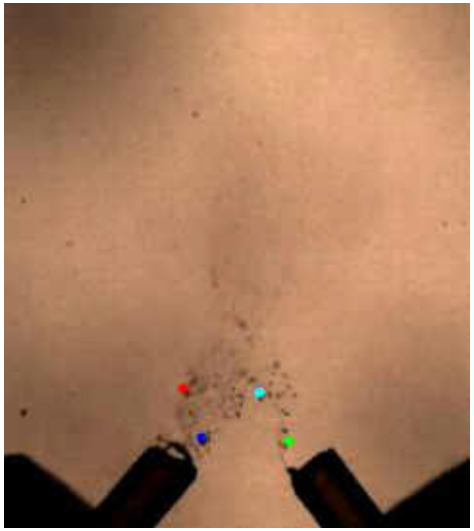
$$OH^{\bullet} + OH^{\bullet} \longrightarrow H_2O_2$$

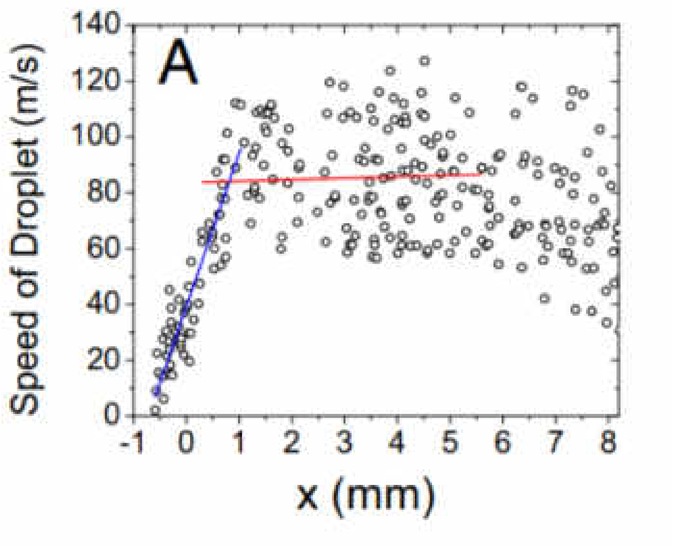
E. Gnanamani, et al., Angew. Chem. Int. Ed., 2020, *59*, 3069-3072.

J. K. Lee, et al., Proc. Natl. Acad. Sci. *U.S.A.*, 2019, 116, 19294-19298.

Reaction Kinetics Studies in Microdroplets

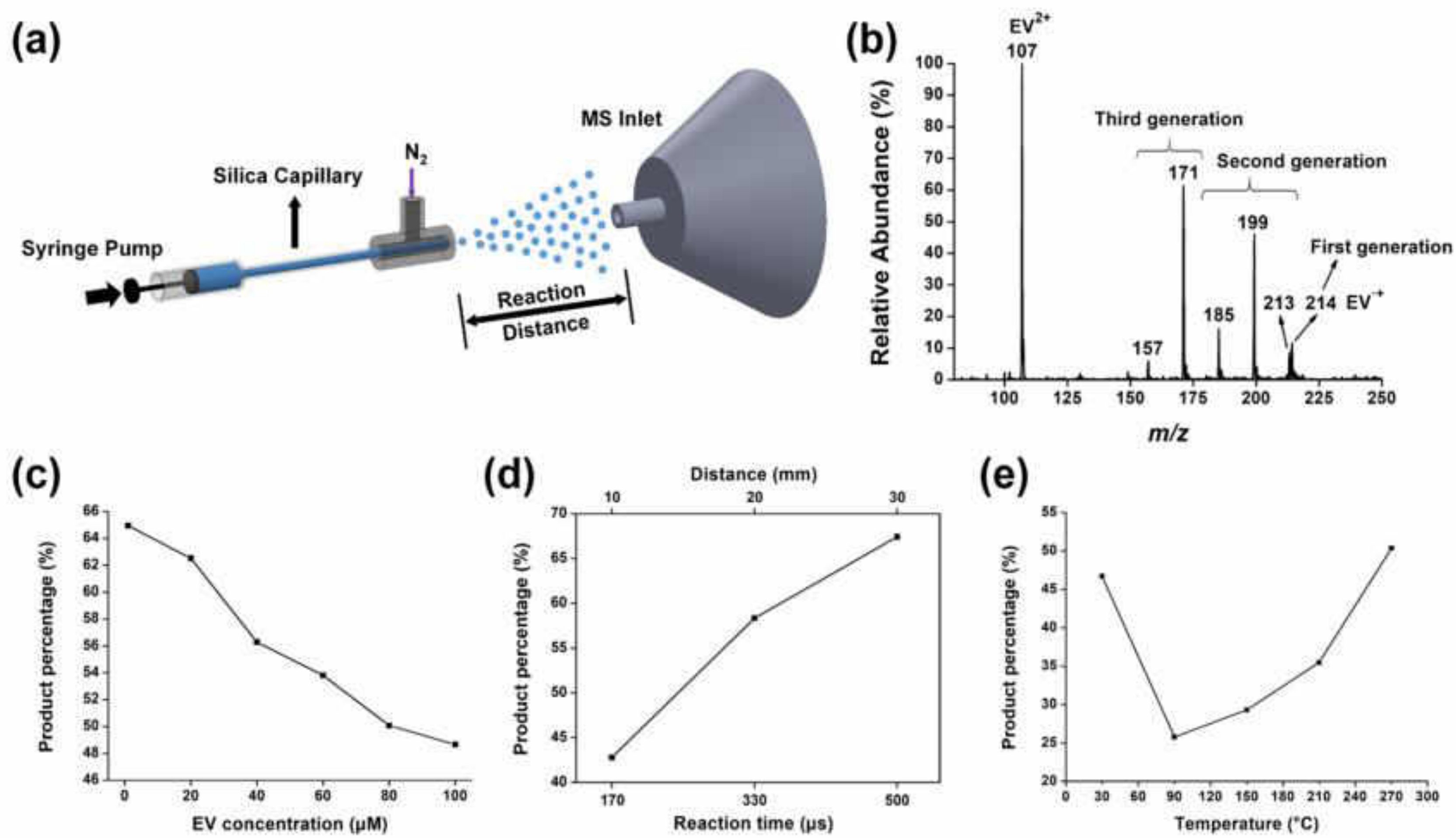






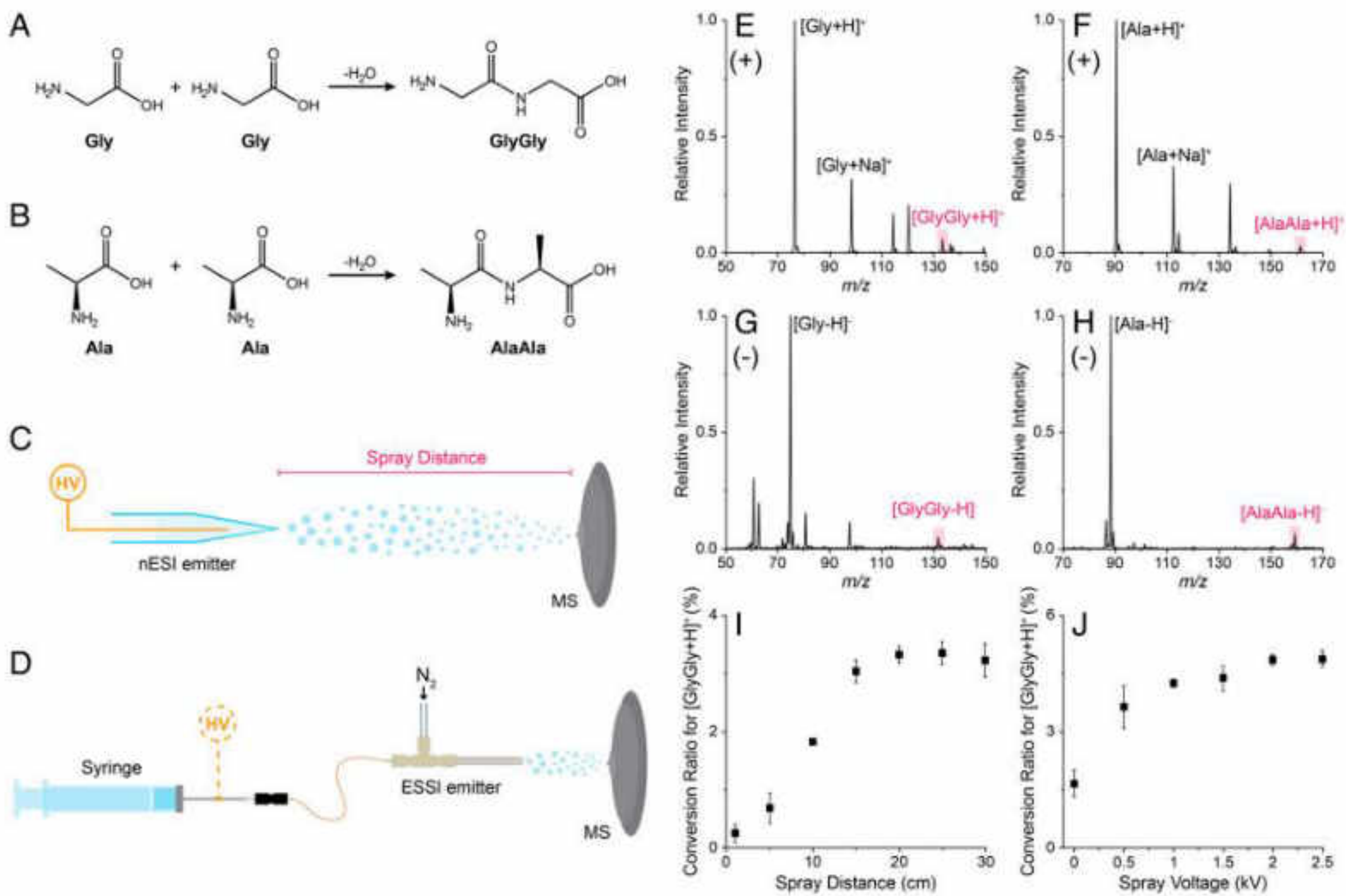
J. K. Lee, et al., Proc. Natl. Acad. Sci. U. S. A., 2015, **112**, 3898–3903.

Degradation of Reluctant Molecules



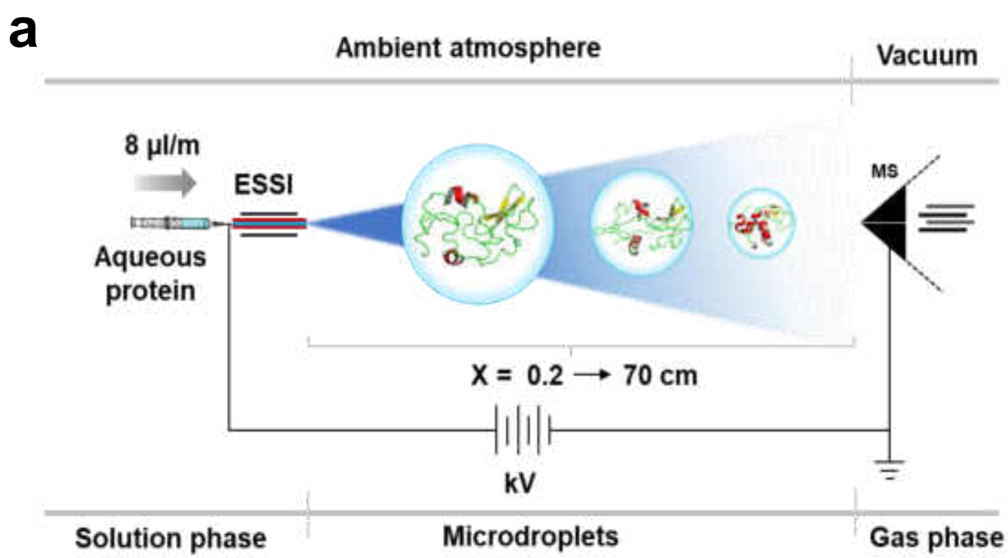
C. Gong, et al., J. Am. Chem. Soc., 2022, 144, 8, 3510–3516.

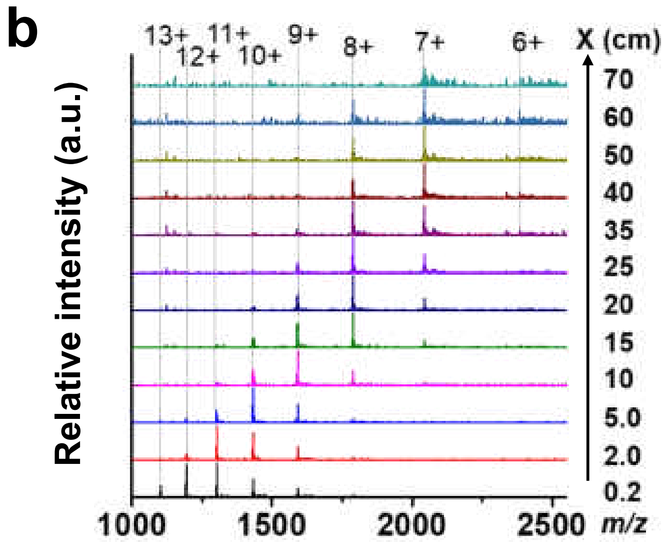
Peptide Bond Formation



D. T. Holden, et al., Proc. Natl. Acad. Sci. U.S.A., 2022, 119, e2212642119.

Proteins in Microdroplets

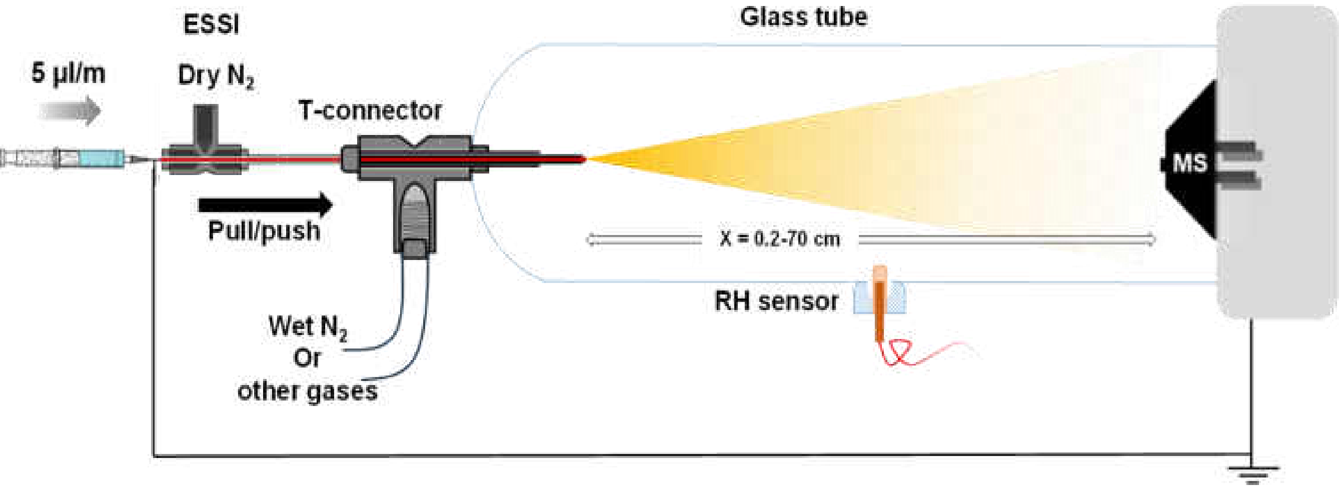


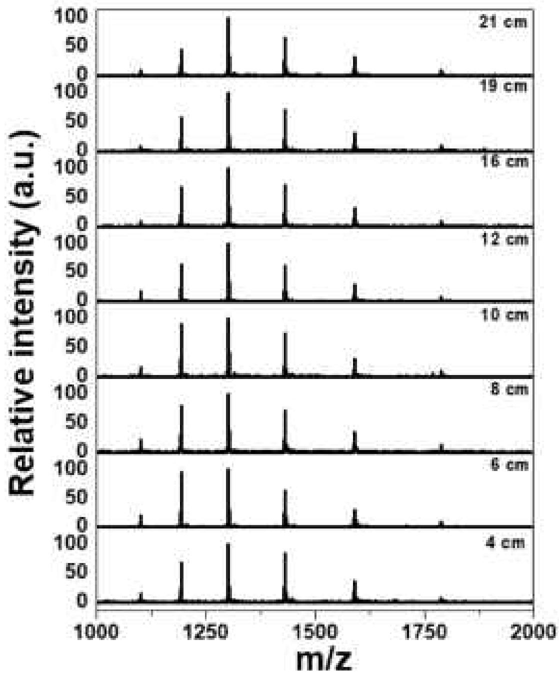


Schematic of the experimental set-up

Stacked mass spectra of lysozyme at different distance

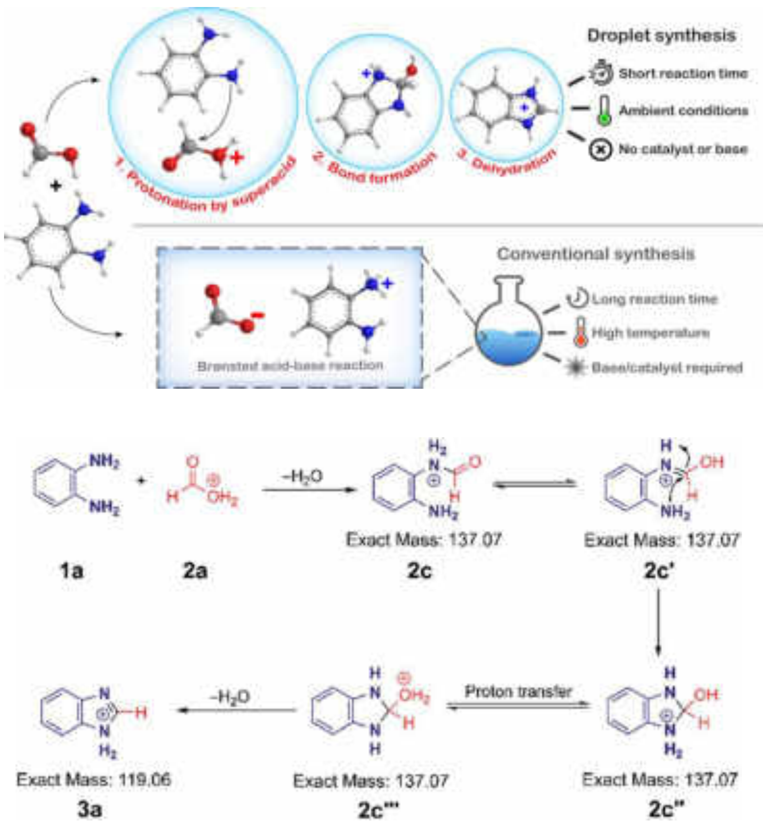
Proteins in Microdroplets



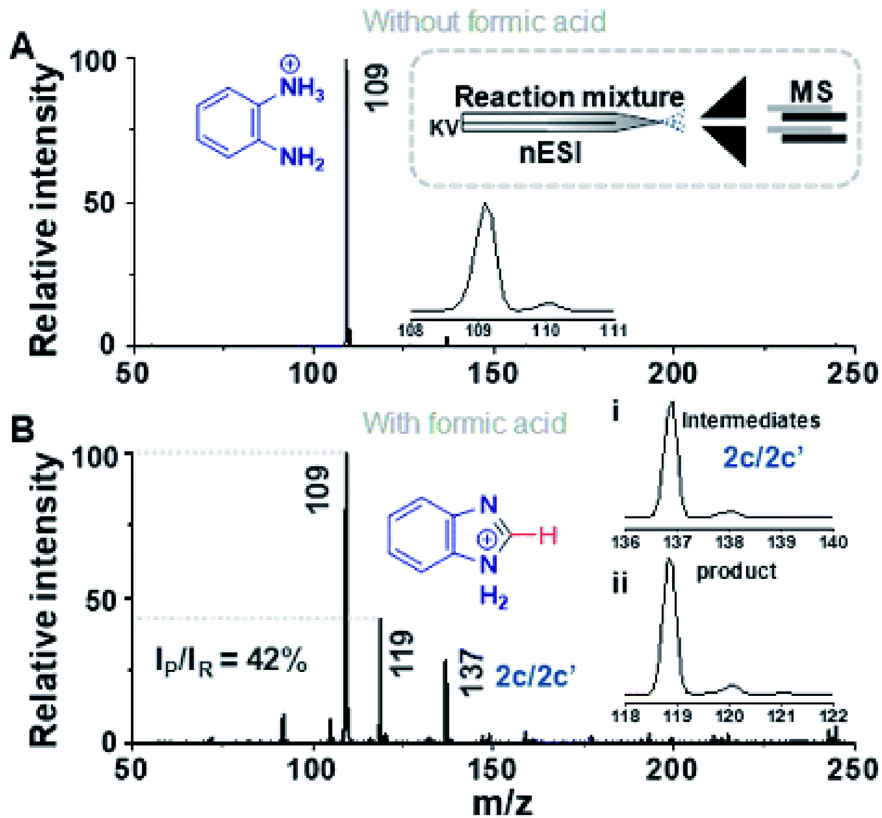


Chemistry in Microdroplets

Accelerated Microdroplet Synthesis of Benzimidazoles by Nucleophilic Addition to Protonated Carboxylic Acids



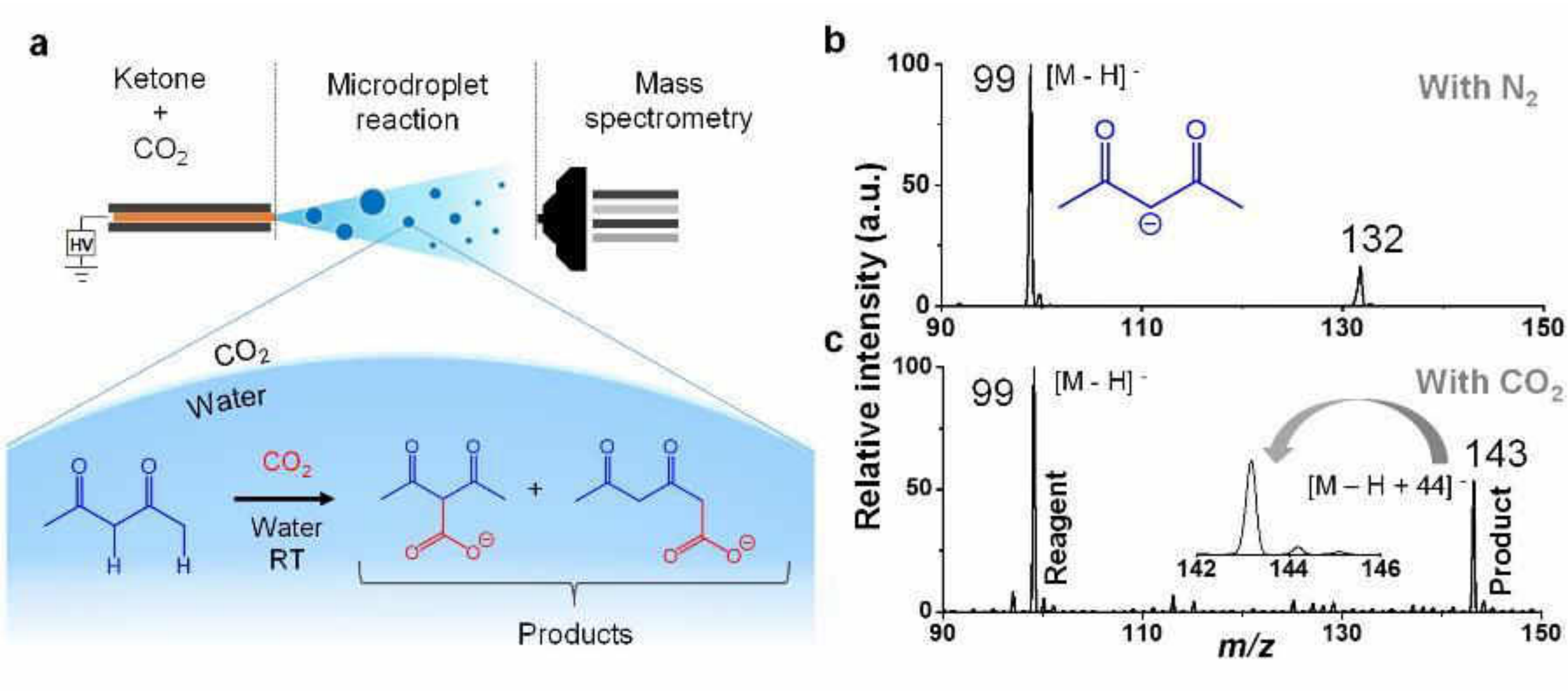
Proposed mechanism



Mass spectra of the reaction mixture

Pallab Basuri et.al., Chem. Sci. 2020, 11 (47), 12686-12694.

Spontaneous α-C-H carboxylation of ketones by gaseous CO_2 at the air-water interface of aqueous microdroplets

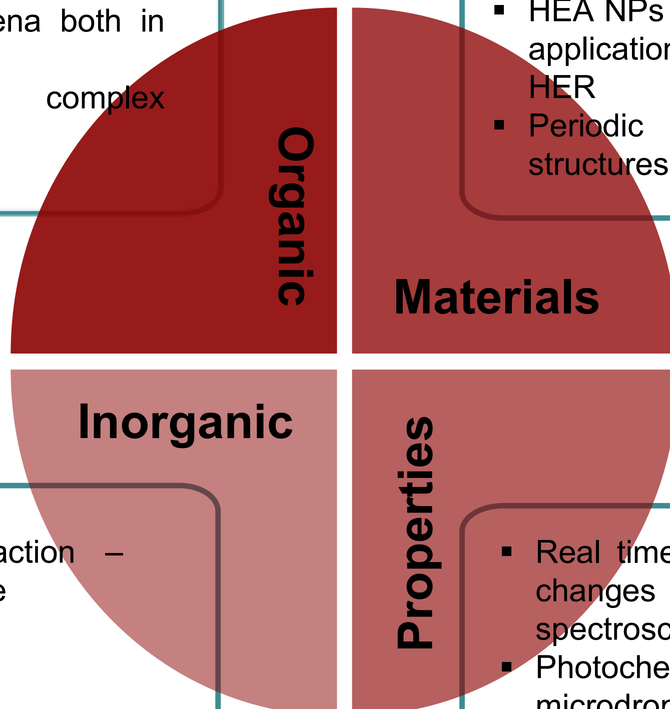


Pallab Basuri et. al., Angew. Chem. Int. Ed. 2024, Article ASAP.

What's Next

- Degradation phenomena both in VOC and PFAs
- Fragmentation of complex biomolecules

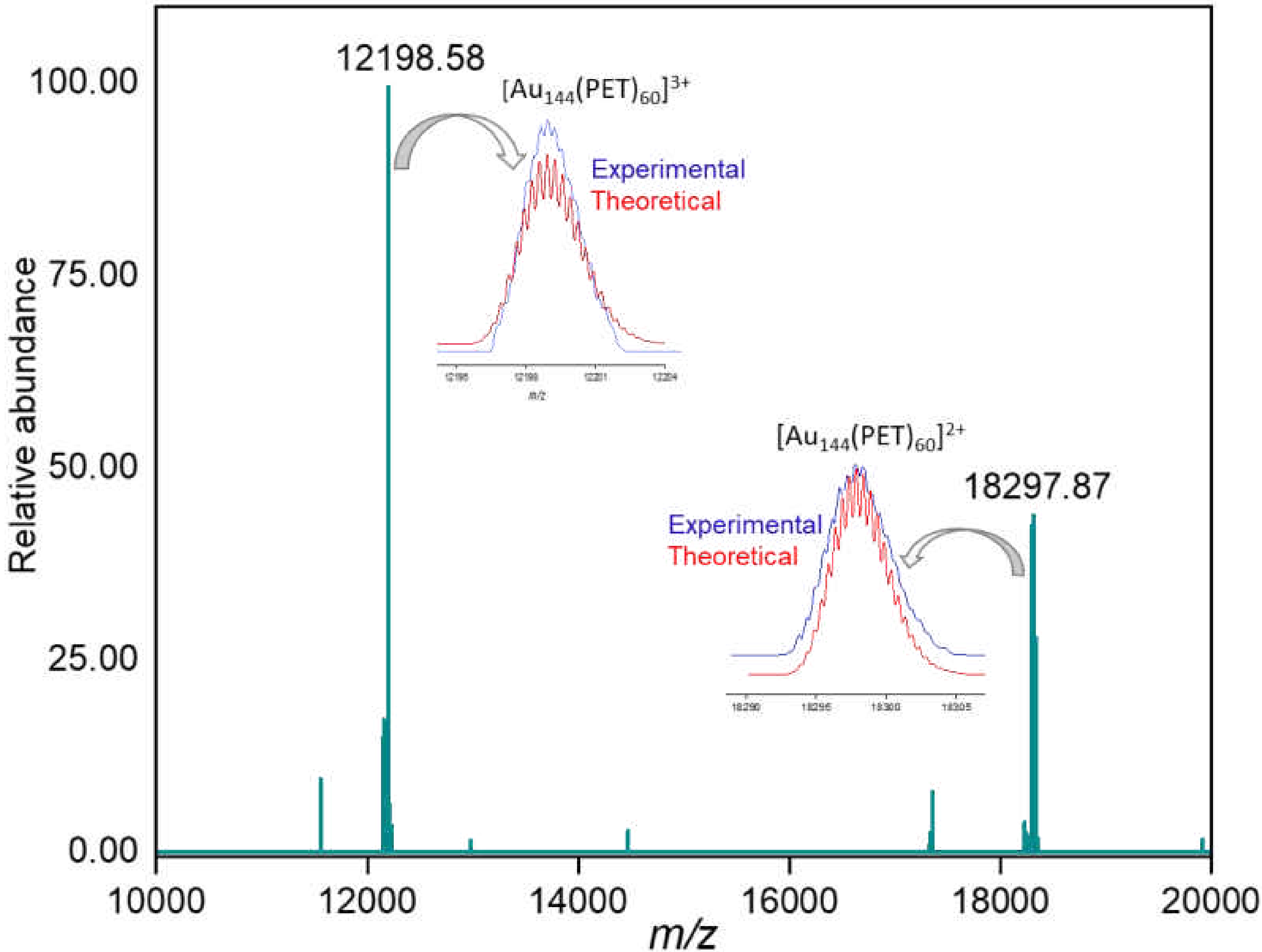
- HEA NPs for potential electrochemical applications, like CO_2 reduction and HER
- Periodic table – Different metal structures



- Iron (II) related reaction – Atmospheric relevance
- Phase transformation
- Minerals

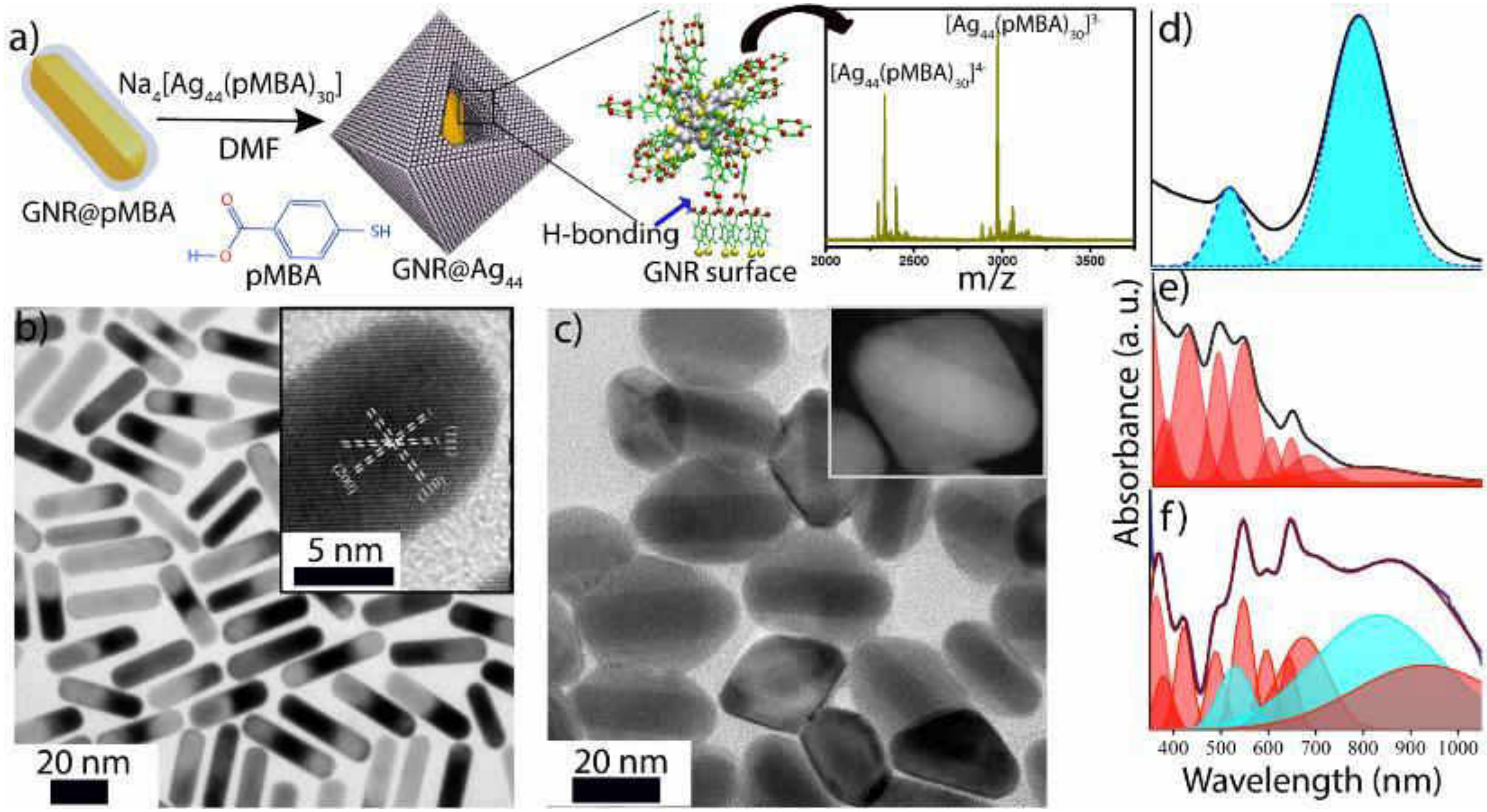
- Real time measurement of structural changes in microdroplet using in-situ spectroscopy
- Photochemical reactions in microdroplets

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



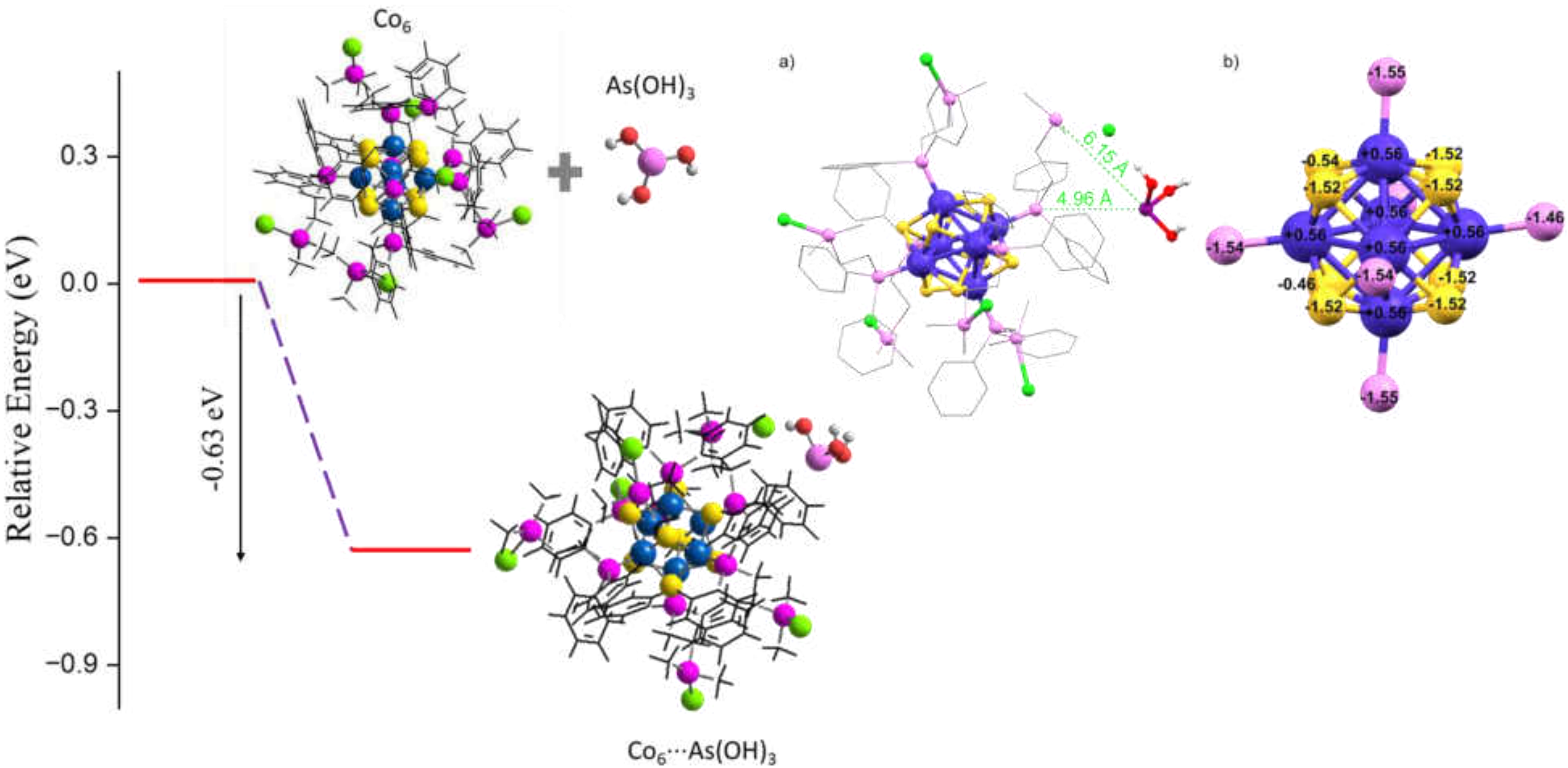
12198.58
$[Au_{144}(PET)_{60}]^{3+}$
Experimental
Theoretical
$[Au_{144}(PET)_{60}]^{2+}$
18297.87
Experimental
Theoretical
Relative abundance
100.00
75.00
50.00
25.00
0.00
10000
12000
14000
16000
18000
20000
m/z

Atomically precise nanocluster assemblies encapsulating plasmonic gold nanorods

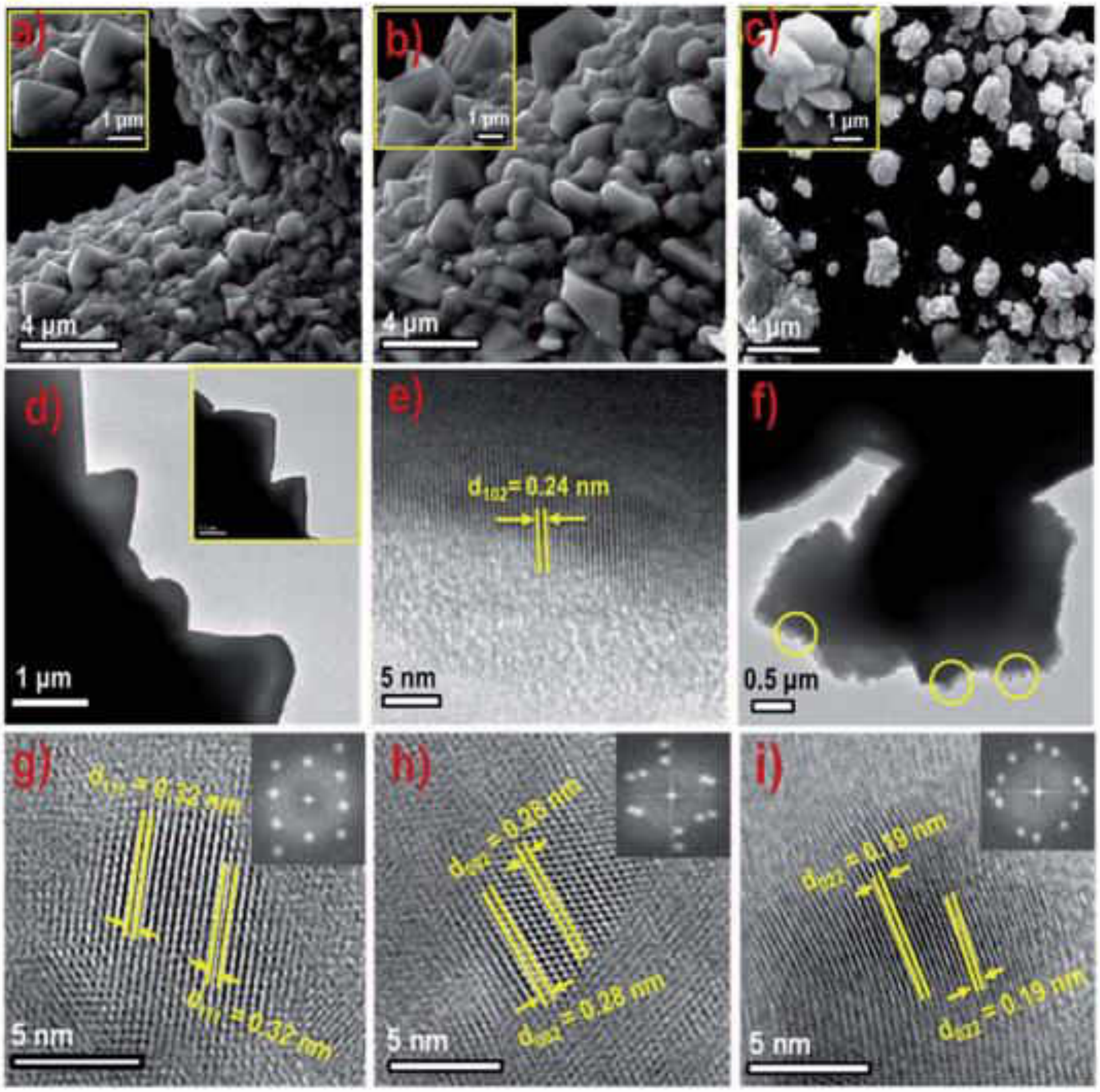


Chakraborty, A. et al., Angew. Chem. Int. Ed. **2018,** 57, 6522–6526.

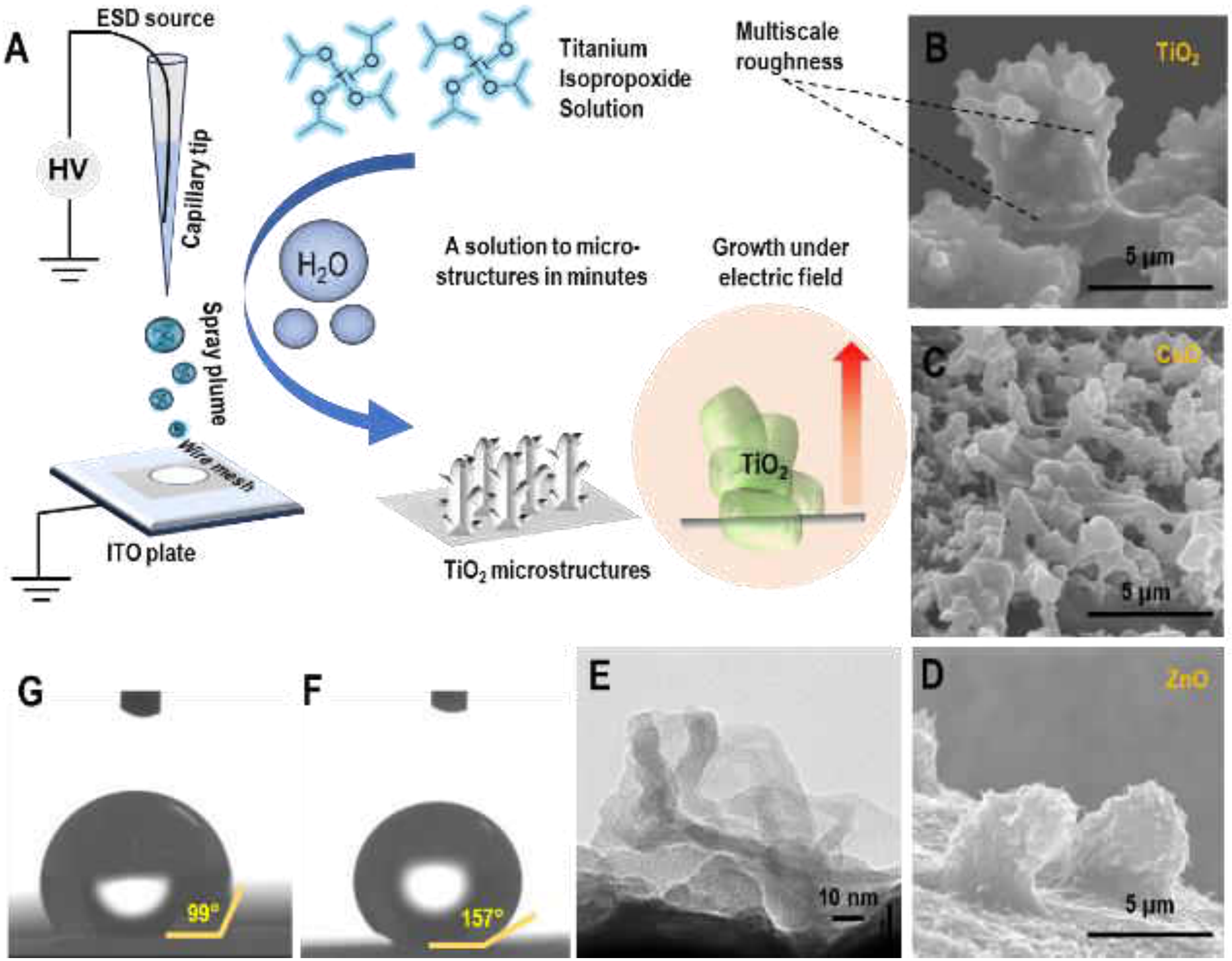
Computational insights



Surface Modification using Charged Microdroplets

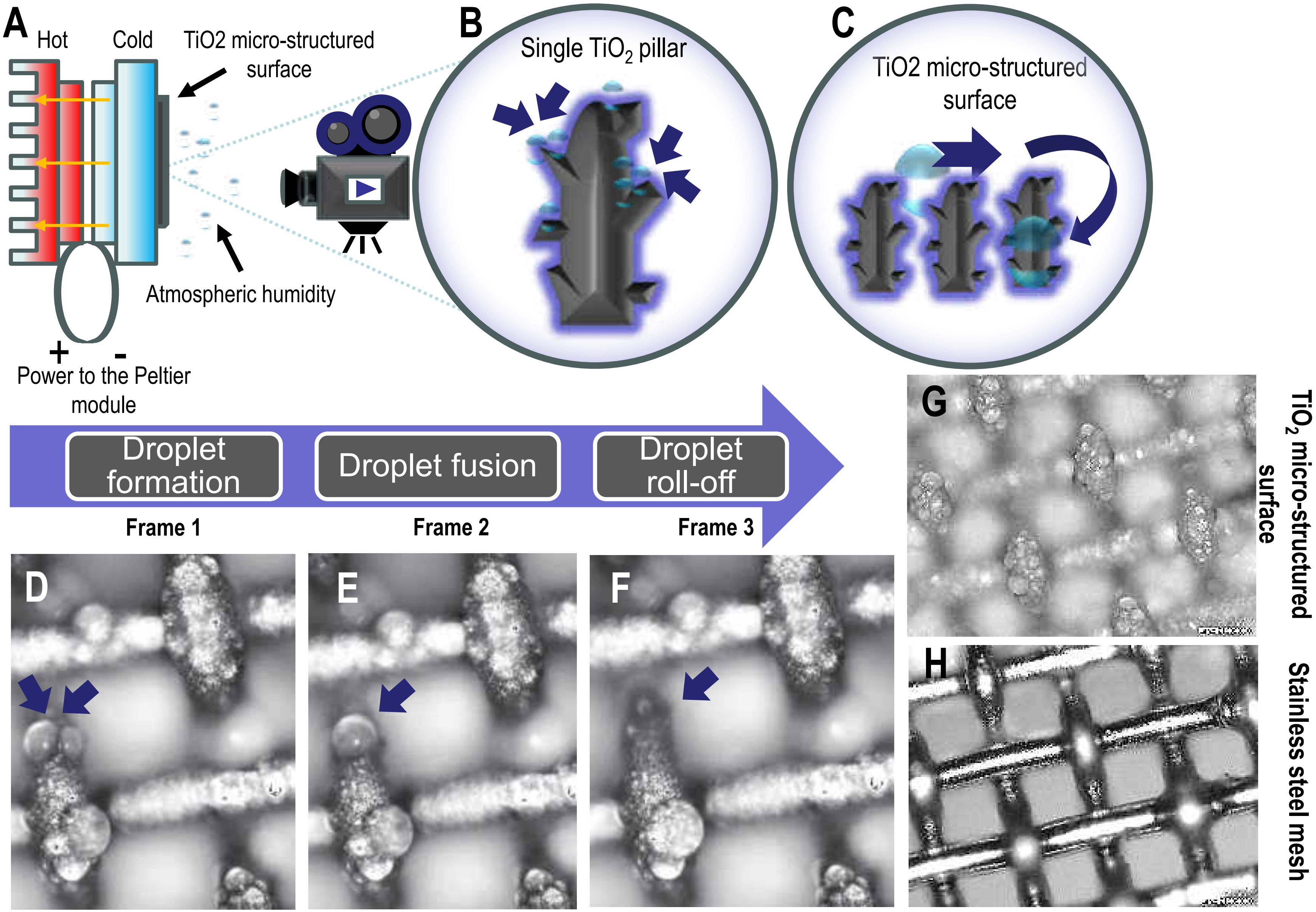


Standalone Surface for Simultaneous Water Harvesting and Treatment



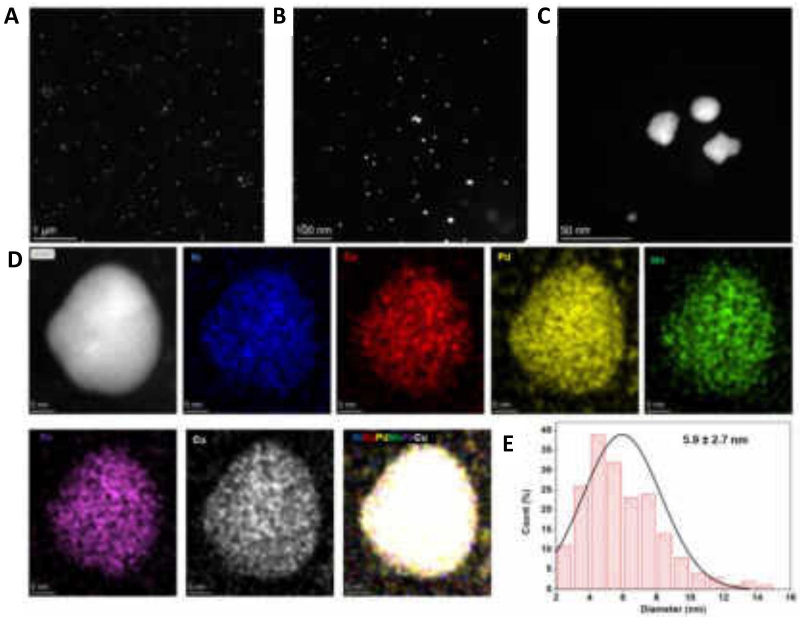
Keerthana Unni et. al., *ACS Sustainable Chemistry and Engineering*, (Under Review).

Atmospheric Water Capture

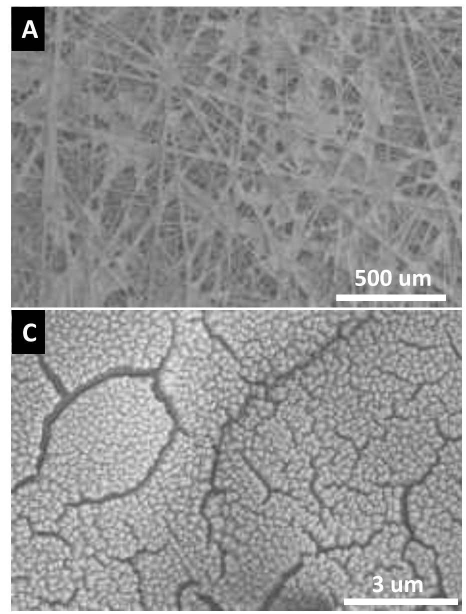


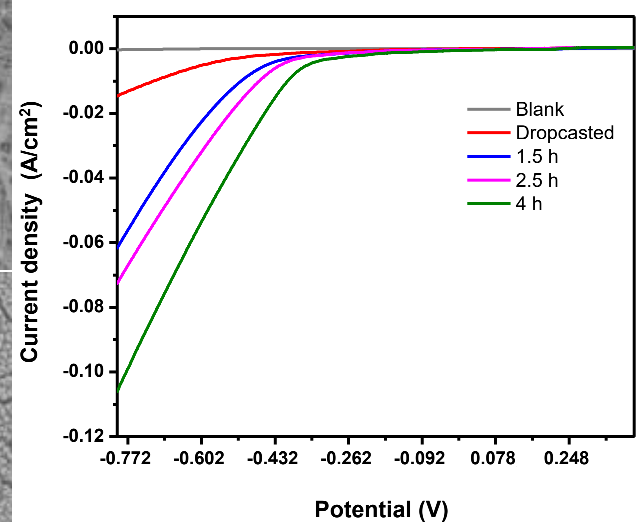
High Entropy Alloy in Charged Microdroplets

Ni, Co, Pd, Mn, Fe, Cu



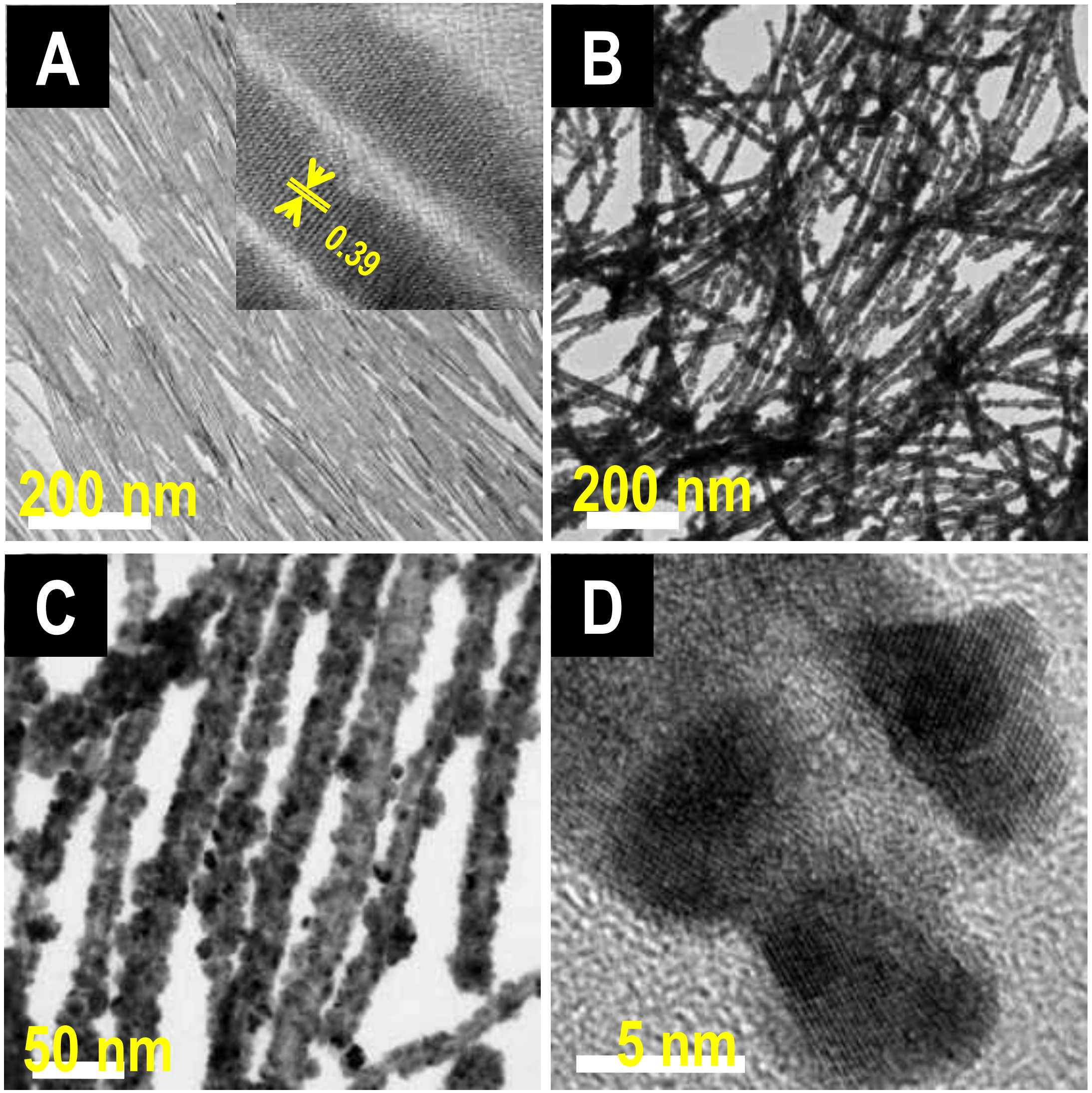
Ni, Co, Pd, Mn, Fe, Cu

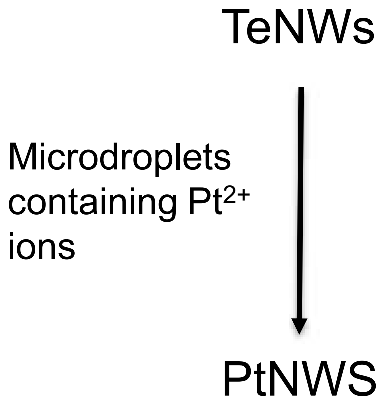




Spoorthi et. al. Unpublished.

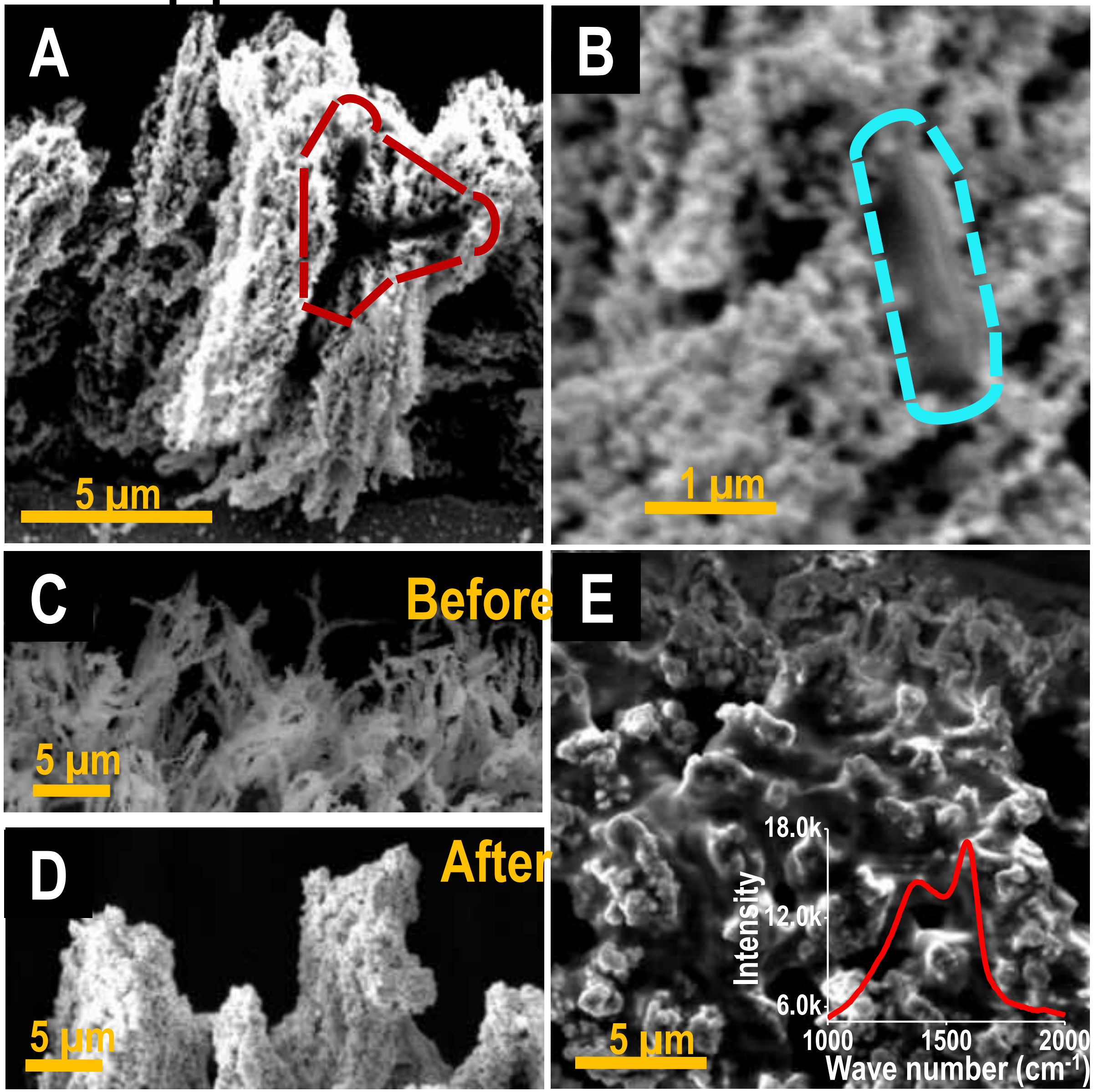
Surface Modification using Charged Microdroplets





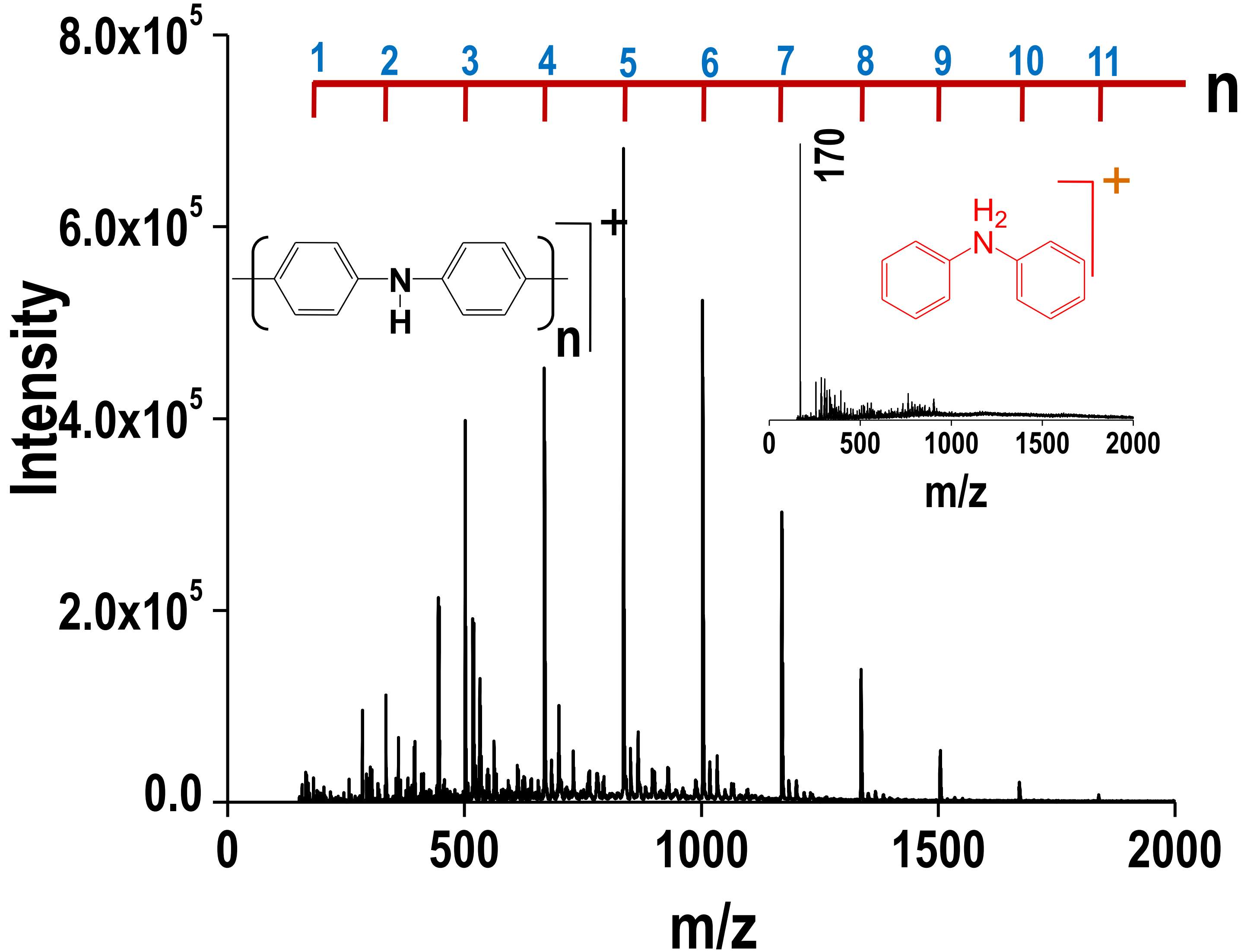
Depanjan Sarkar et. al., Anal.Chem. 2017, 89, 11378−11382.

Applications: Air Filtration



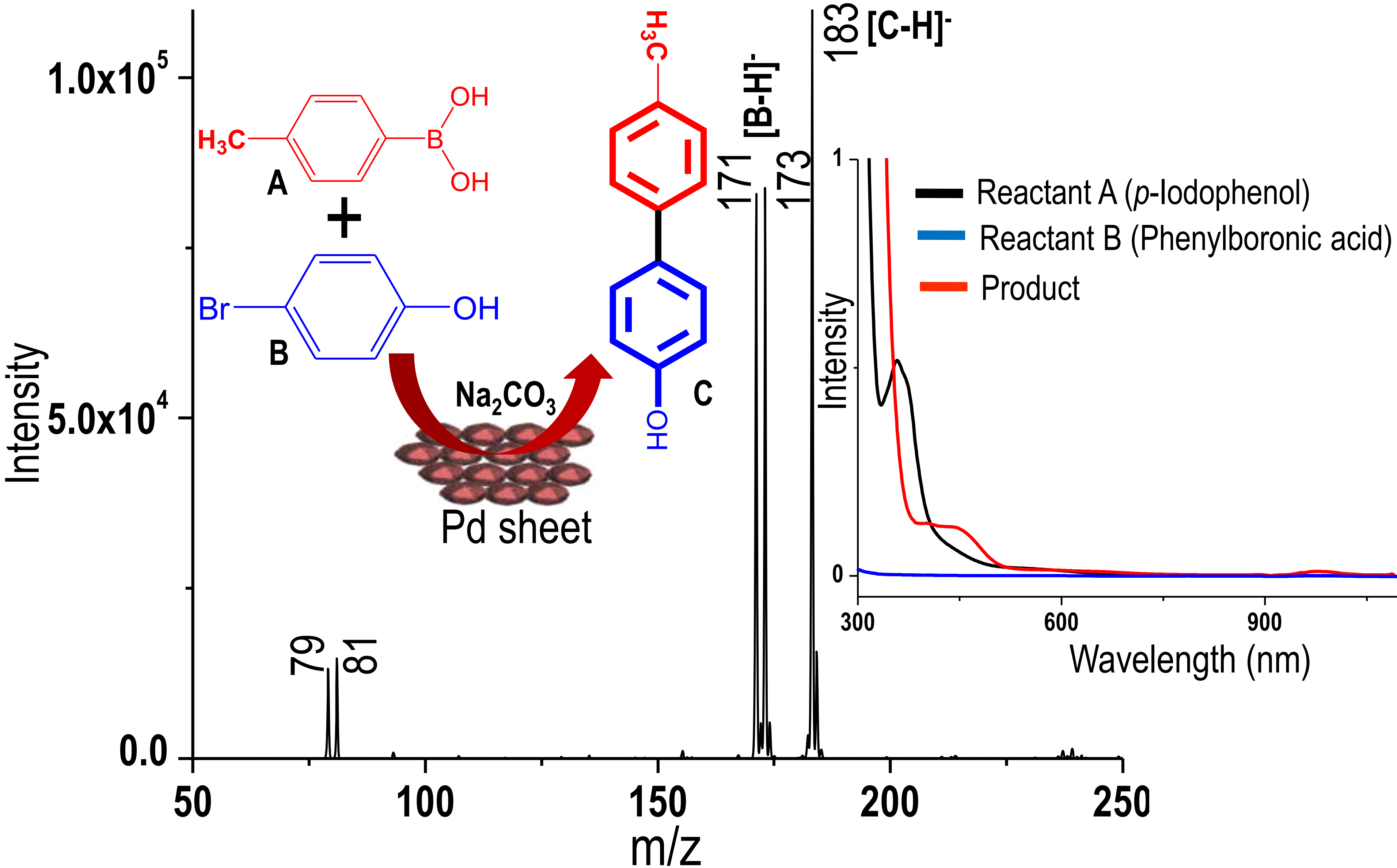
Depanjan Sarkar et. al., *Adv. Mater.* 2016, 28, 2223–2228.

Applications: Catalysis



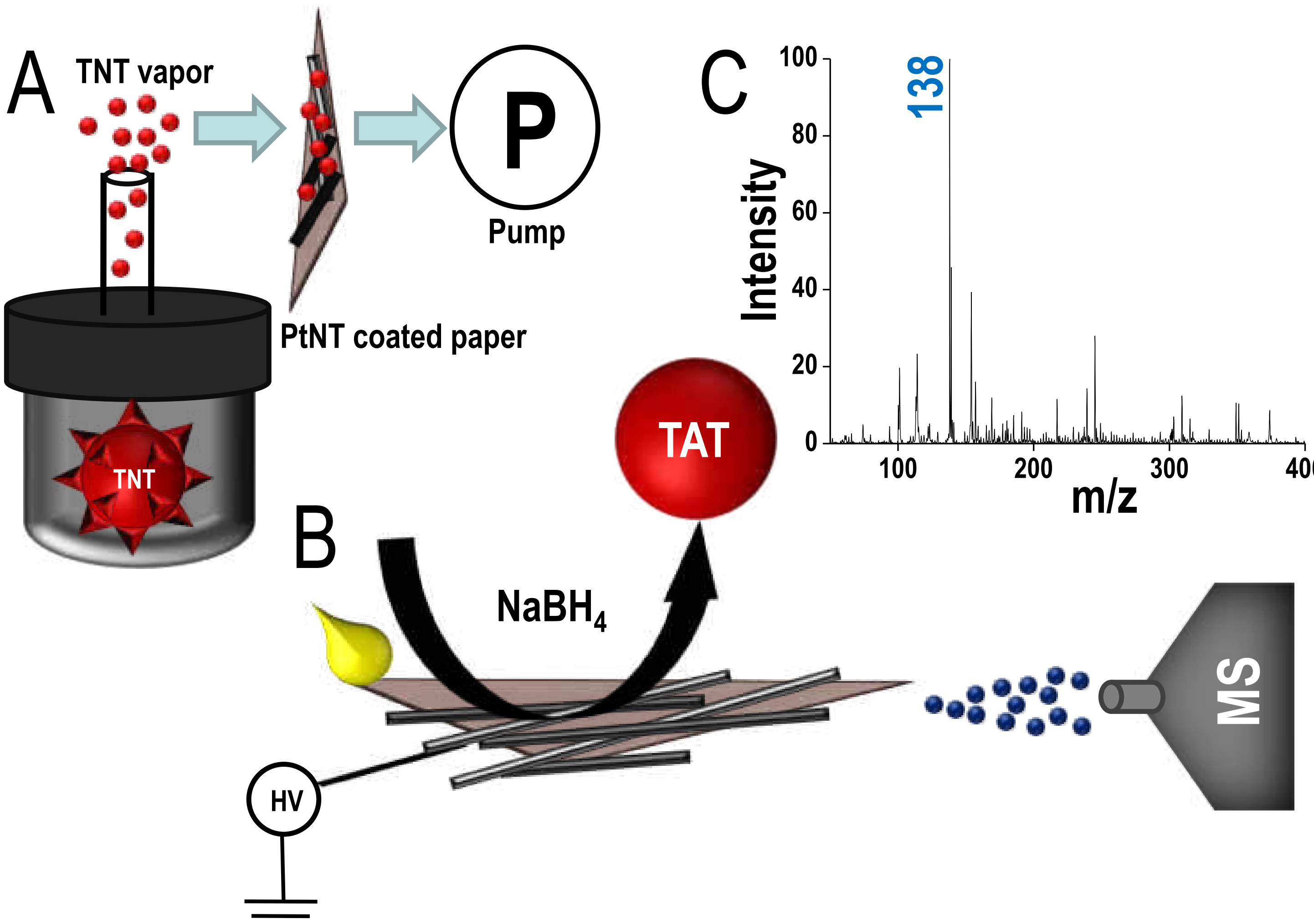
Depanjan Sarkar, et. al., *J. Phys. Chem. C* 2018, 122, 17777−17783.

Applications: Catalysis



Coupling reaction using Pd NPNS as catalyst

Applications: Vapor Detection



Vapor phase detection of 2,4,6-trinitrotoluene

Matter in Confinement: Atomically Precise Clusters and Microdroplets

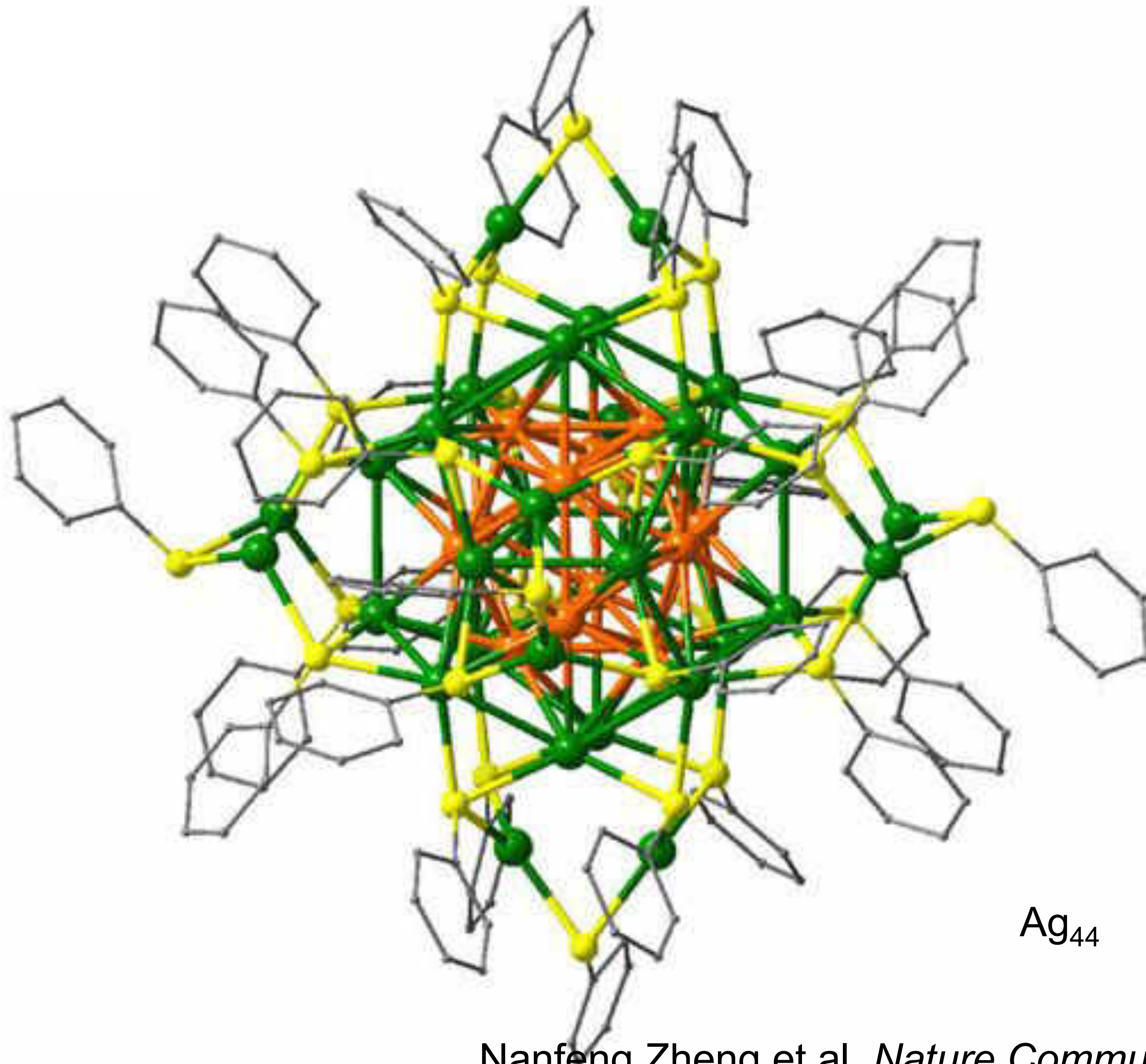
Introduction to our work

Atomically precise clusters

Clean water using advanced materials

Ice chemistry

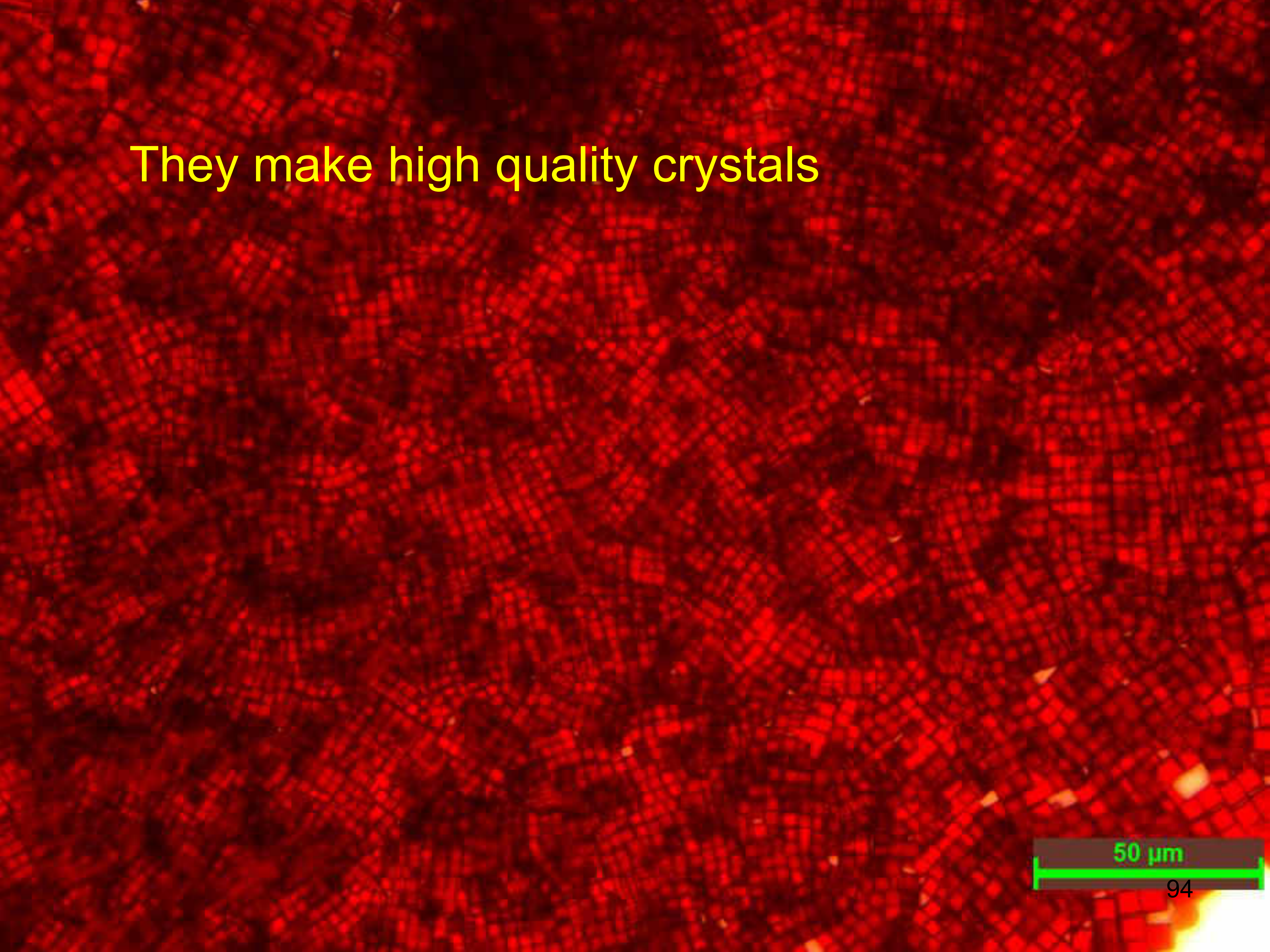
Microdroplets



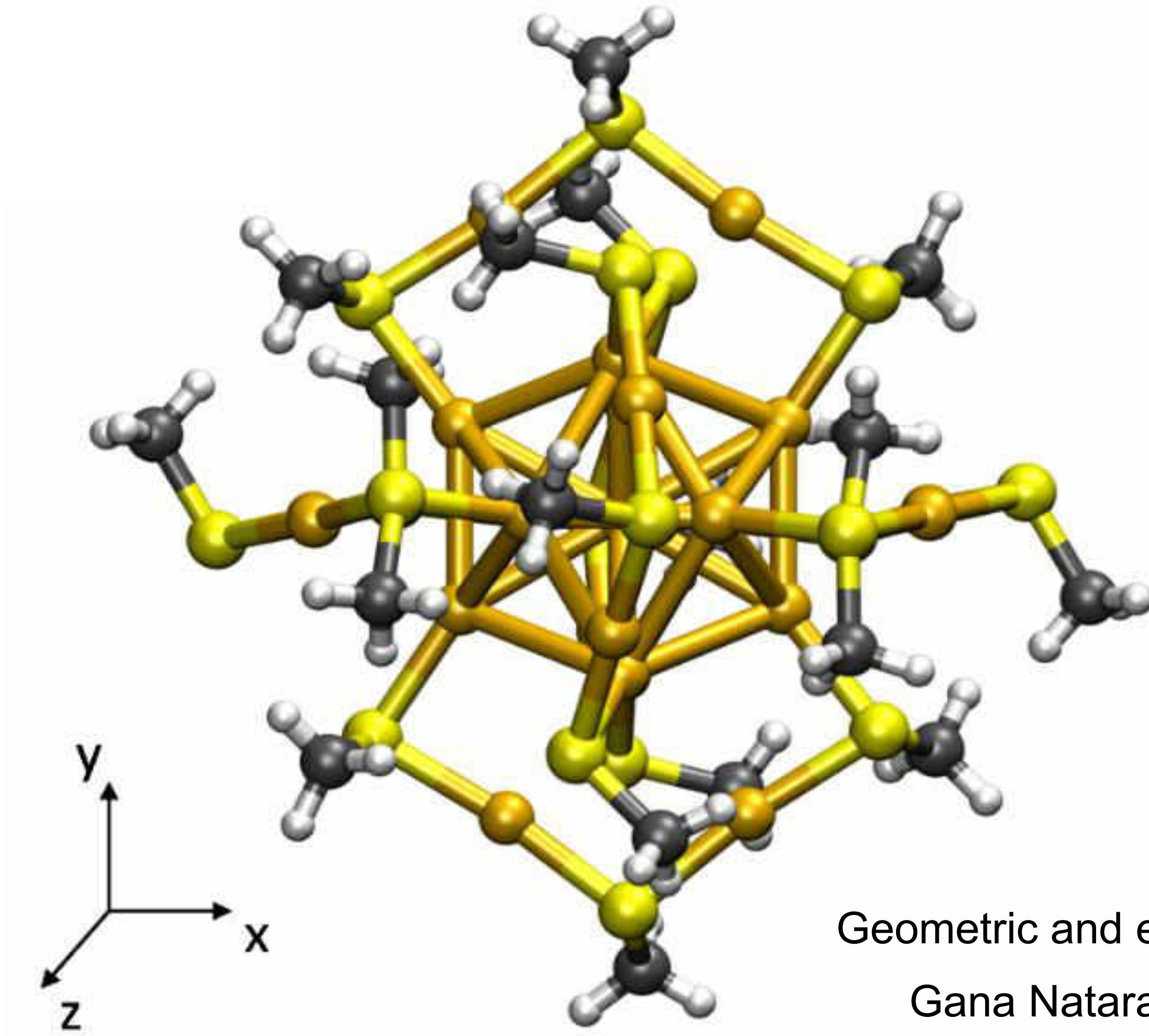
Ag_{44}

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

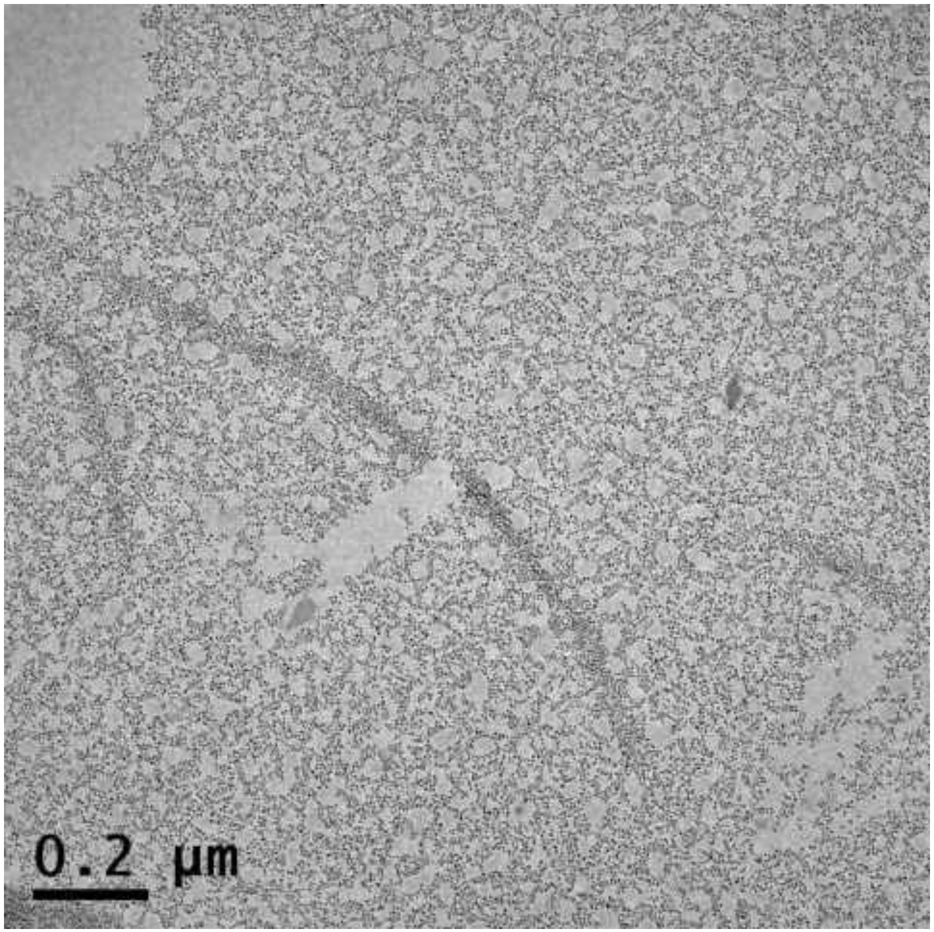
They make high quality crystals

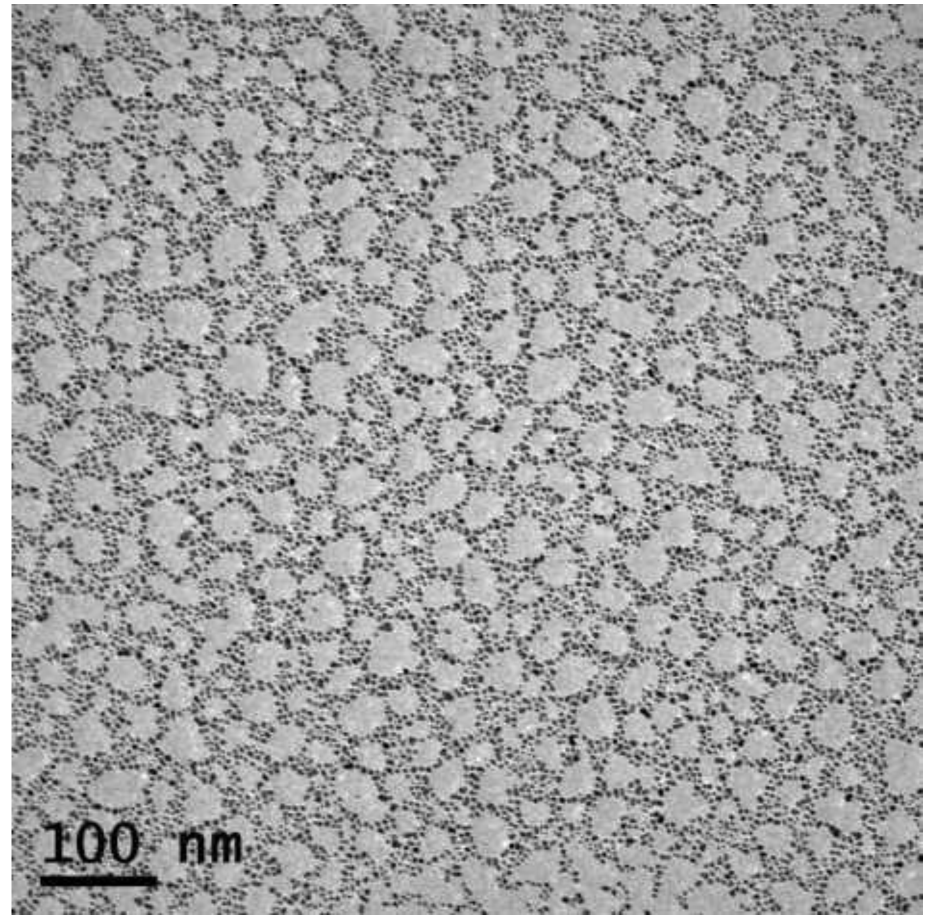


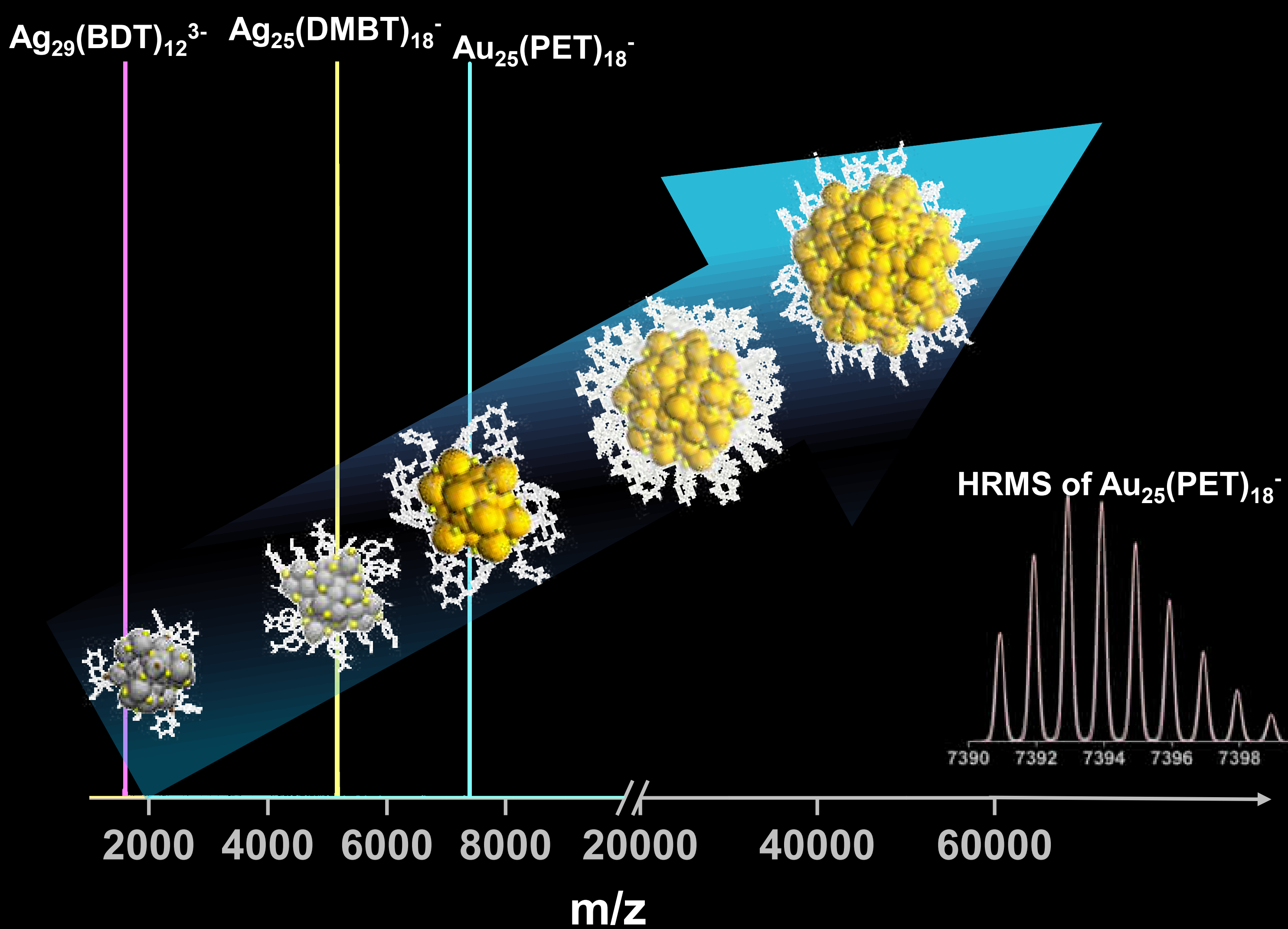
Molecular structure



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







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

Molecular materials

ACCOUNTS of chemical research

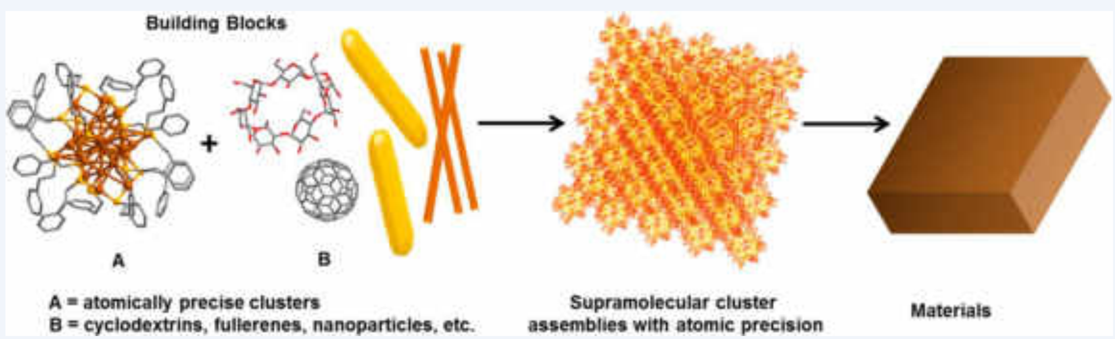
Article

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. $\times$ 10^{-12}m^2/N
Coefficient of thermal expansion, 25°C	256.32 $\times$ 10^{-6} K^{-1}
Thermal Conductivity, 25°C	0.608 W/m.K

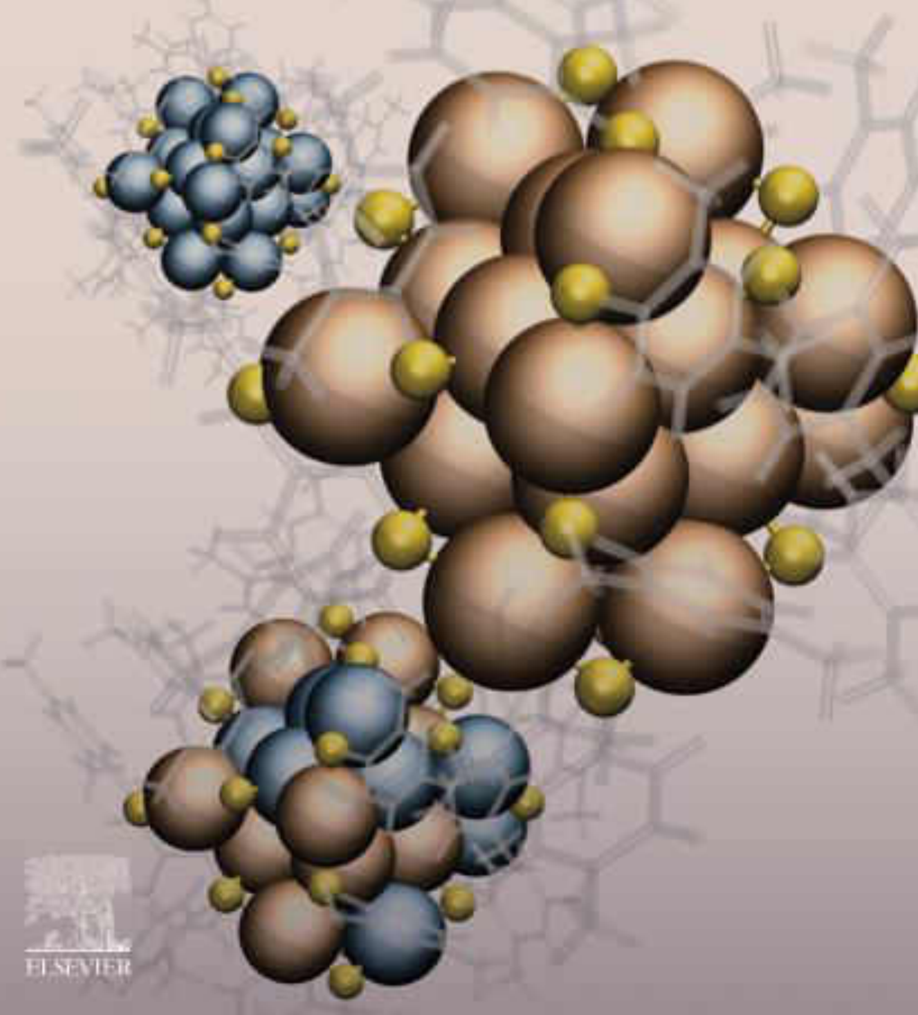
Molecular formula
Molecular weight
Molecular structure
Molecular absorption and emission
Molecular reactions
Molecular assembly
Molecular co-crystals
Ionization potential
Electron affinity

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 $Ag_{44}(SR)_{30}$

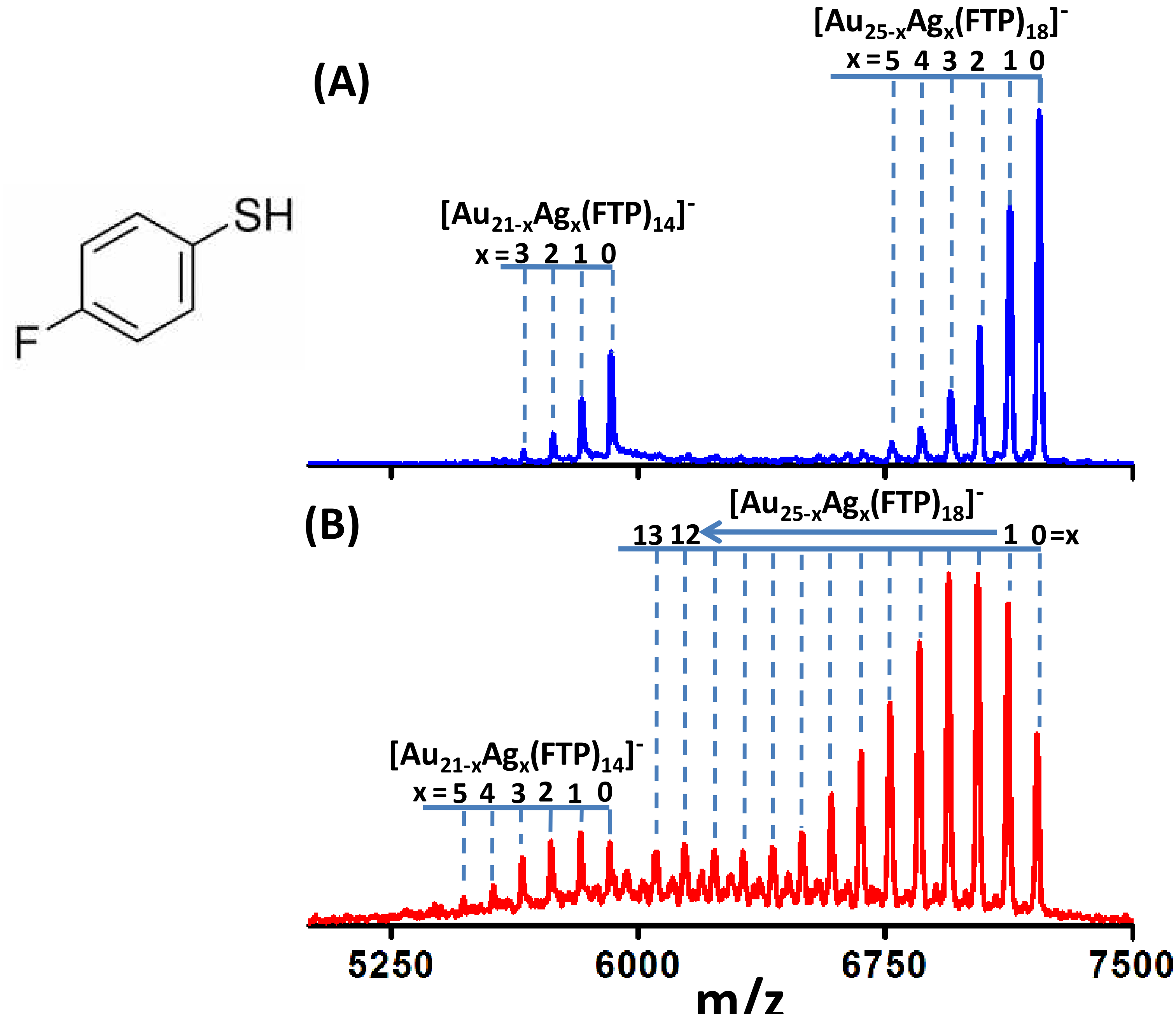
K. R. Krishnadas, Atanu Ghosh, Ananya Baksi, Indranath Chakraborty,[†] Ganapati Natarajan, and Thalappil Pradeep*

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

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

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

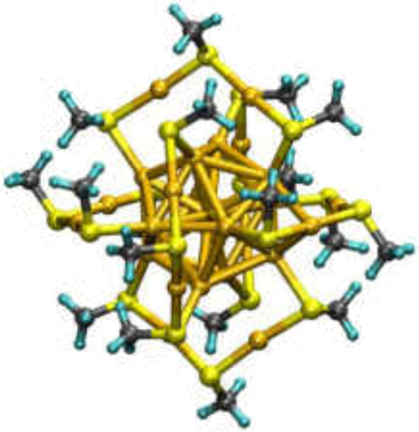


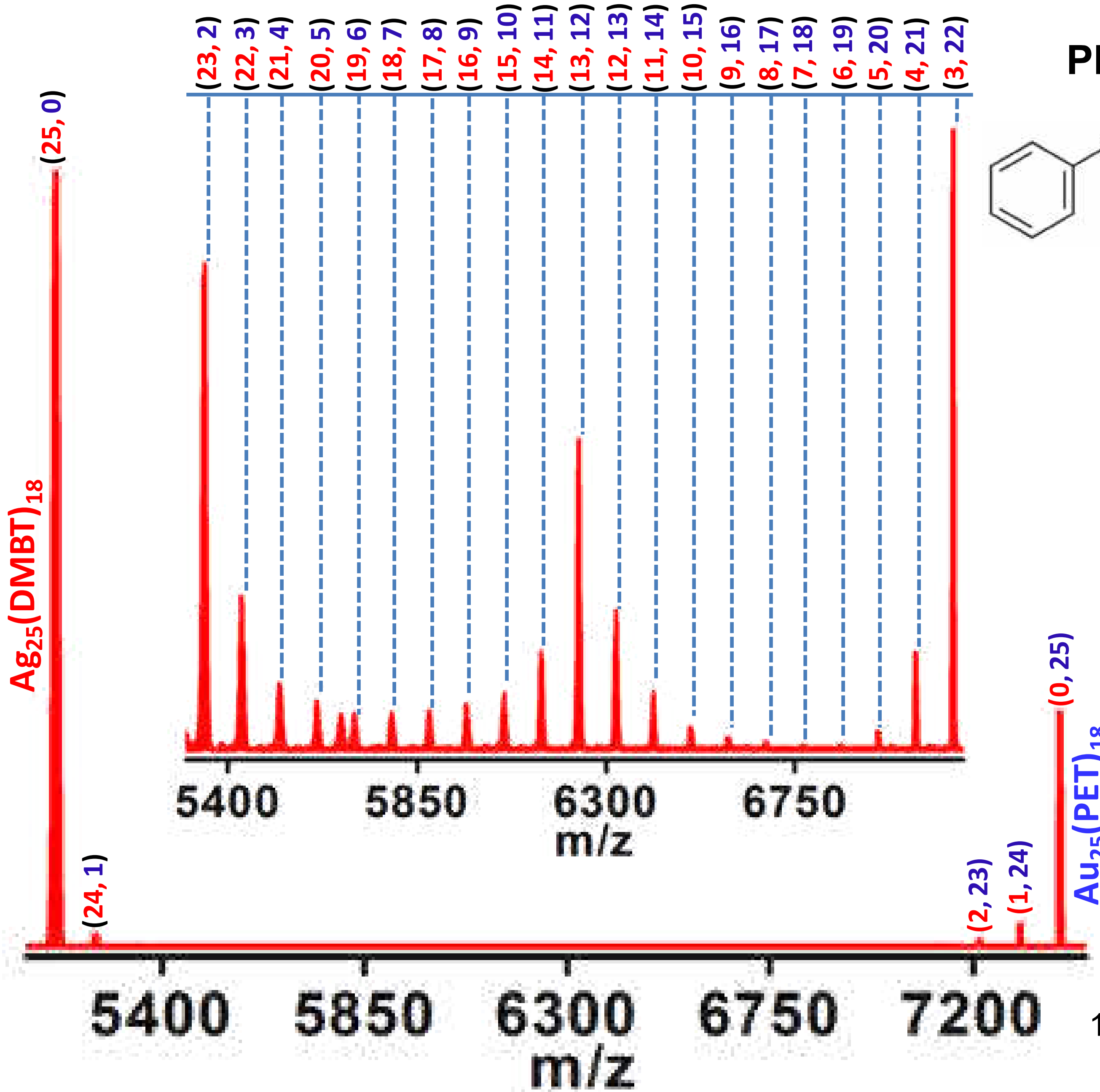
Ag_{25}-Au_{25} experiments

K. R. Krishnadas et al. *Nature Commun.* 2016

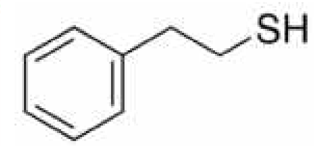
Reaction between $Au_{25}(PET)_{18}$ and $Ag_{25}(DMBT)_{18}$

DMBT

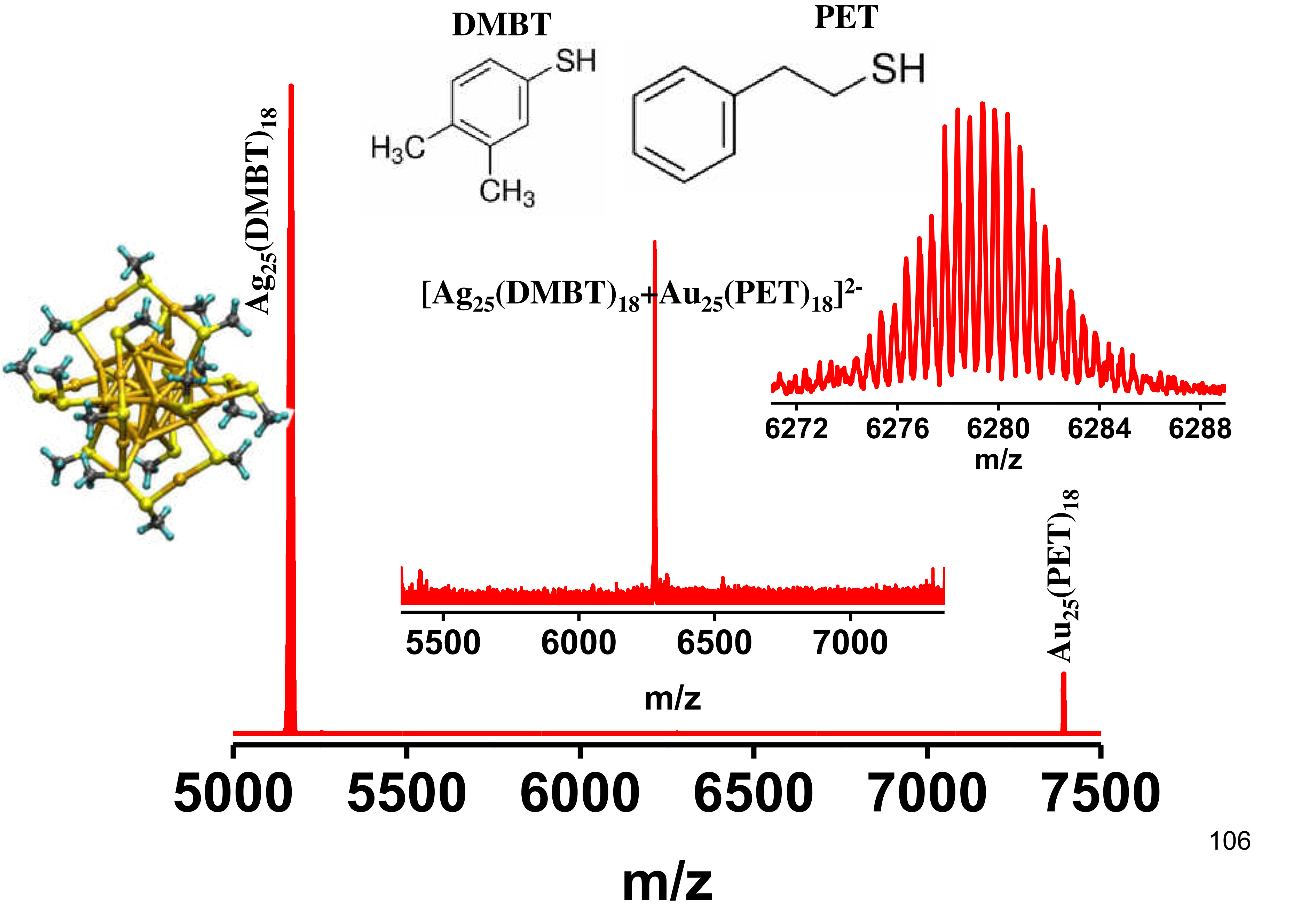




PET

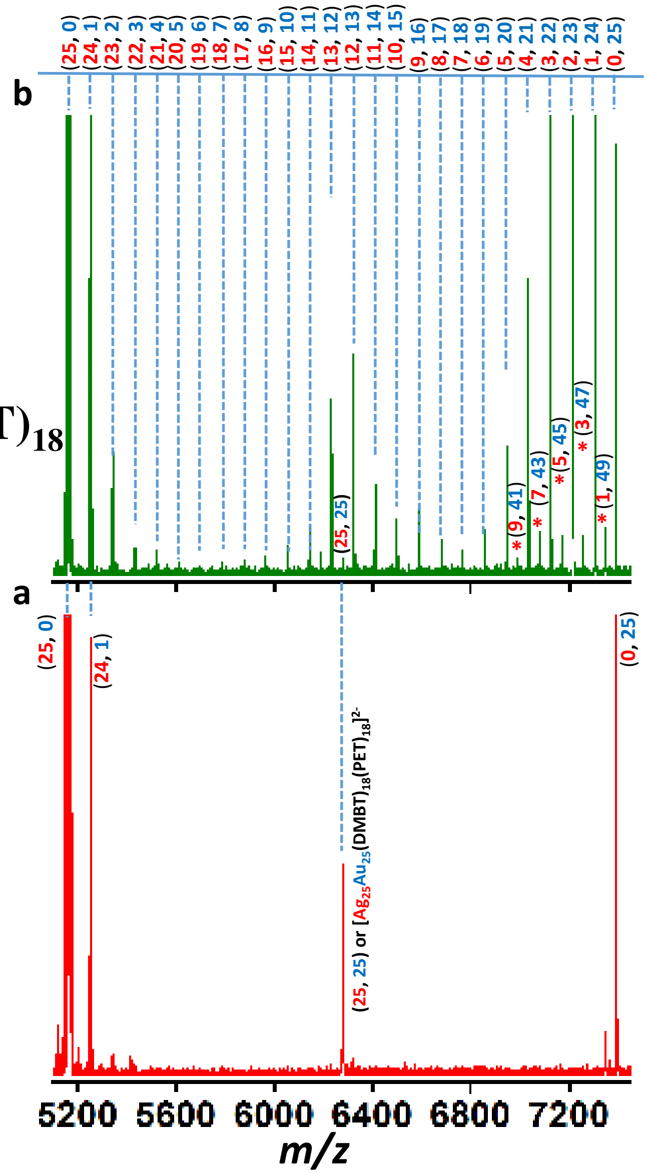


$[Ag_{25}(DMBT)_{18}+Au_{25}(PET)_{18}]^{2-}$



Evolution of alloy clusters from the dianionic adduct, $[Ag_{25}Au_{25}(DMBT)_{18}(PET)_{18}]^{2-}$

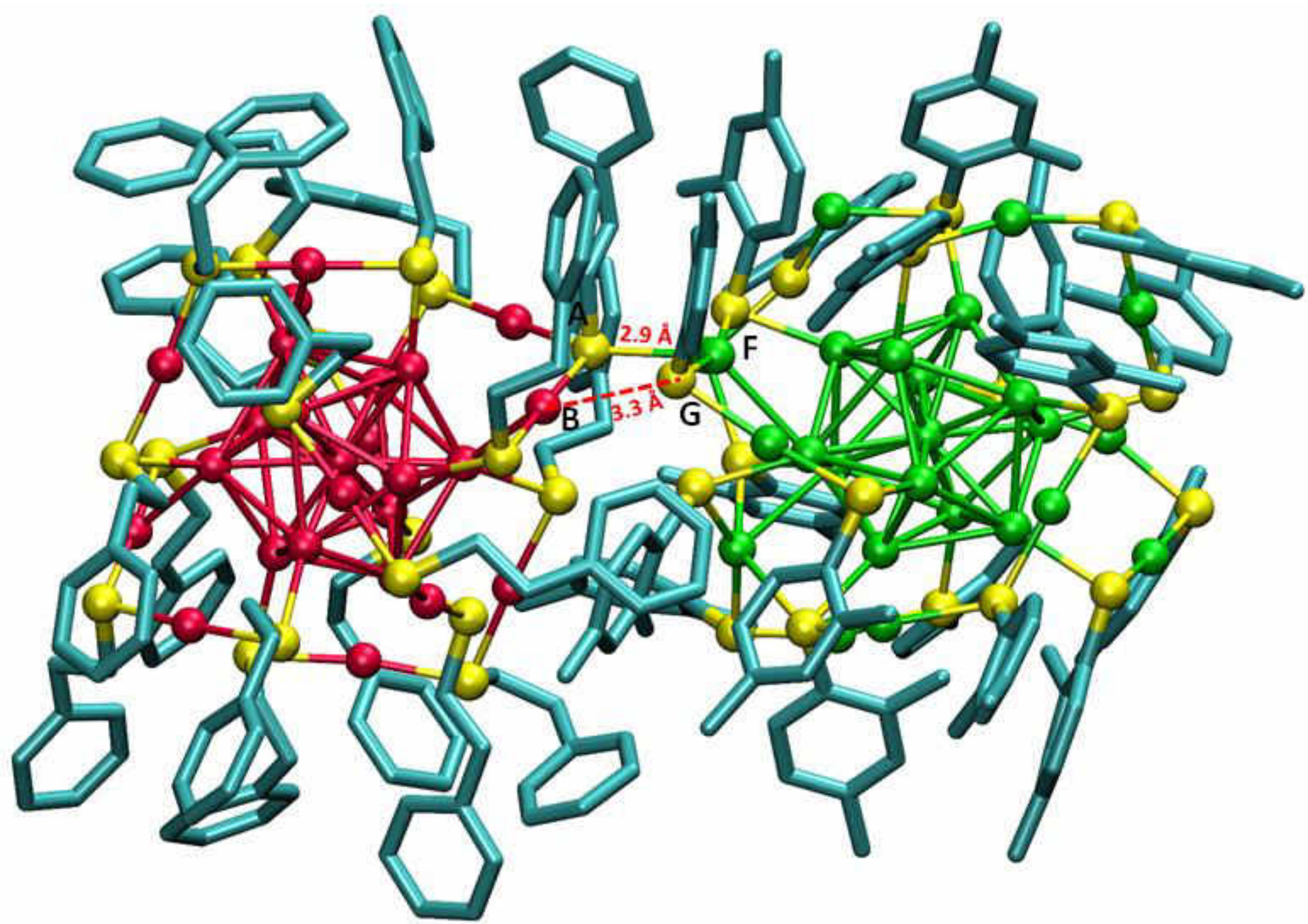
$Ag_{25}(DMBT)_{18}:Au_{25}(PET)_{18}$
0.3:1.0

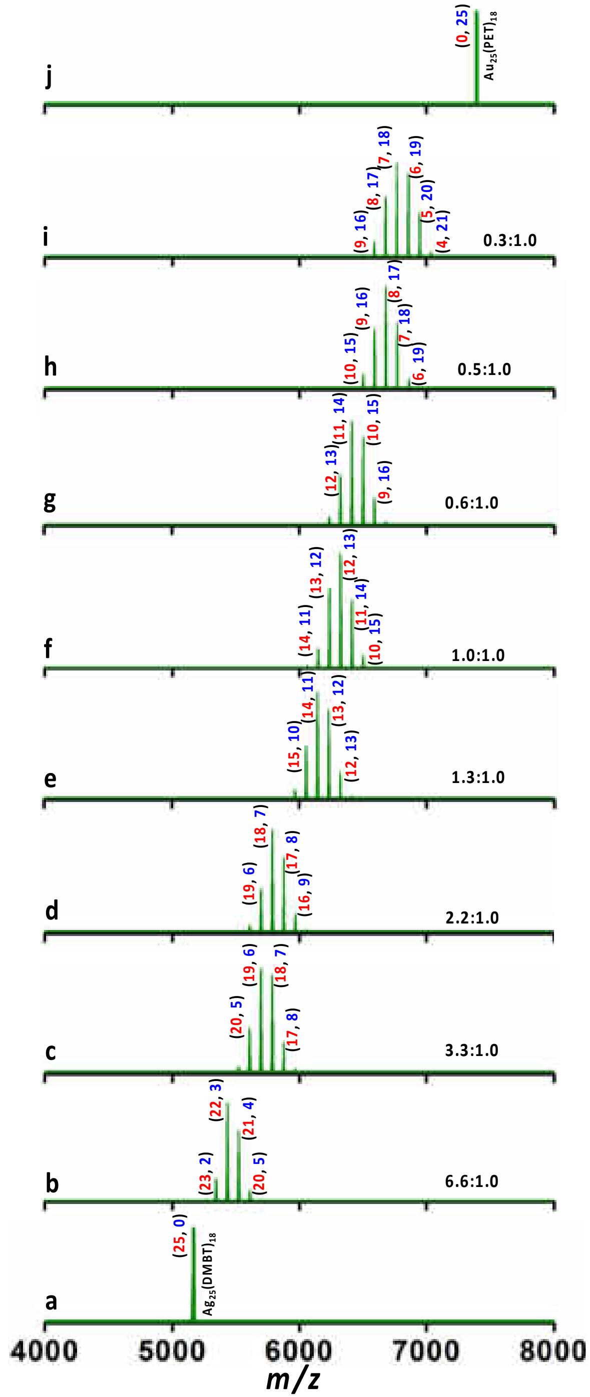


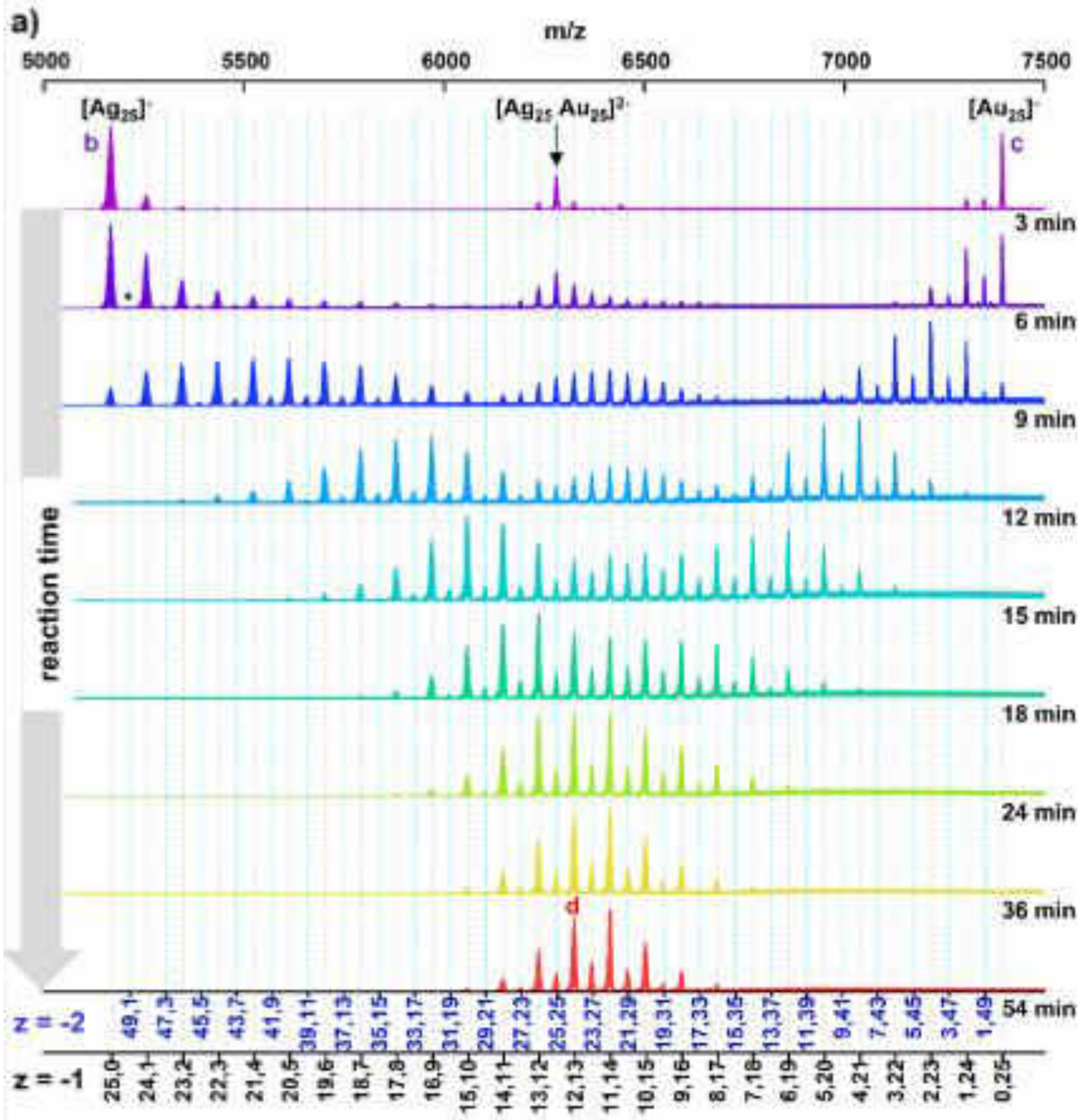
within 5 min

within 2 min

Optimized structure of $[Ag_{25}Au_{25}(DMBT)_{18}(PET)_{18}]^{2-}$



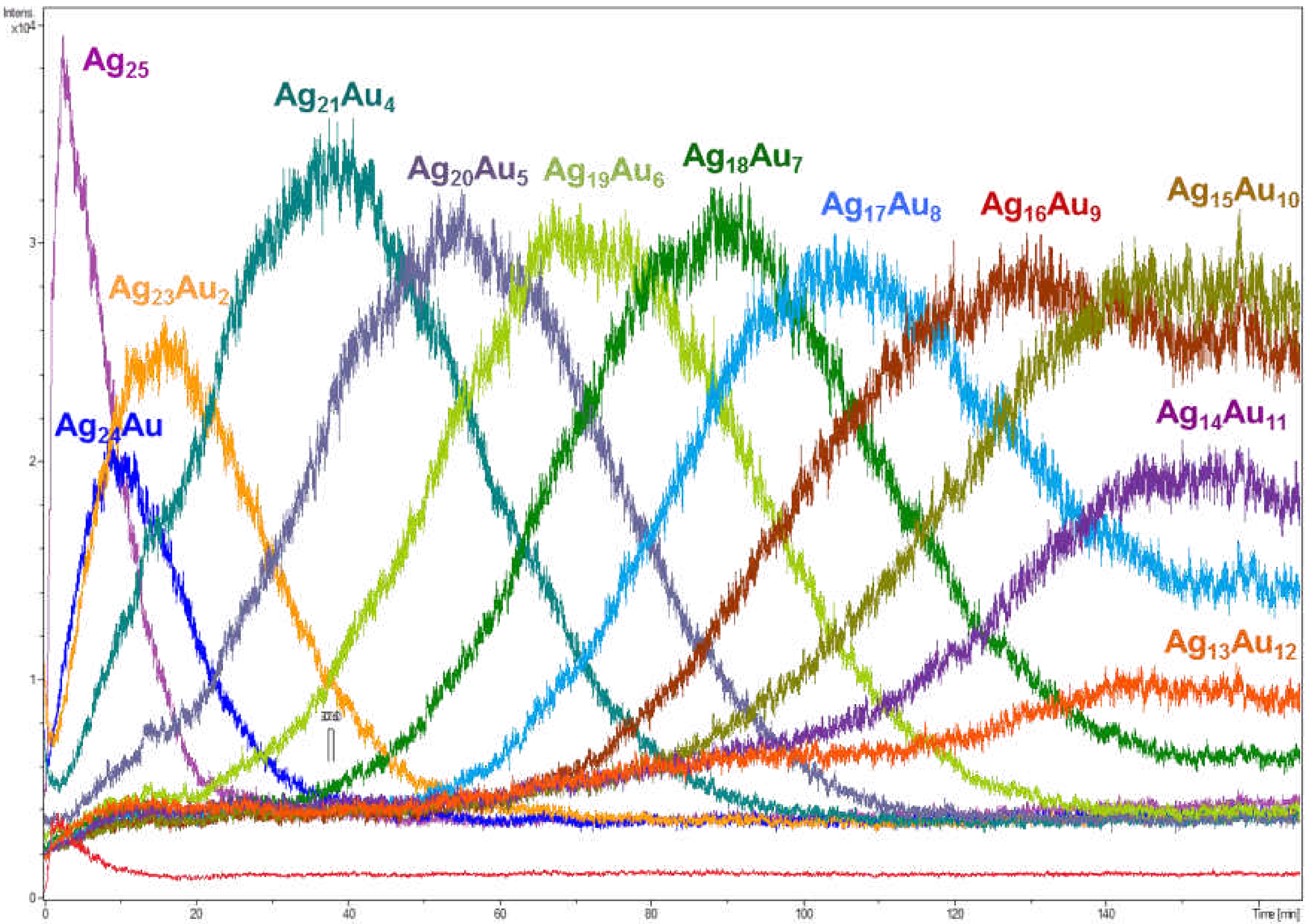

j
(0, 25)
Au25(PET)18
i
0.3:1.0
(9, 16)
(8, 17)
(7, 18)
(6, 19)
(5, 20)
(4, 21)
h
0.5:1.0
(10, 15)
(9, 16)
(8, 17)
(7, 18)
(6, 19)
g
0.6:1.0
(12, 13)
(11, 14)
(10, 15)
(9, 16)
f
1.0:1.0
(14, 11)
(13, 12)
(12, 13)
(11, 14)
(10, 15)
e
1.3:1.0
(15, 10)
(14, 11)
(13, 12)
(12, 13)
d
2.2:1.0
(19, 6)
(18, 7)
(17, 8)
(16, 9)
c
3.3:1.0
(20, 5)
(19, 6)
(18, 7)
(17, 8)
b
6.6:1.0
(23, 2)
(22, 3)
(21, 4)
(20, 5)
a
(25, 0)
Ag25(DMBT)18
4000
5000
6000
7000
8000
m/z



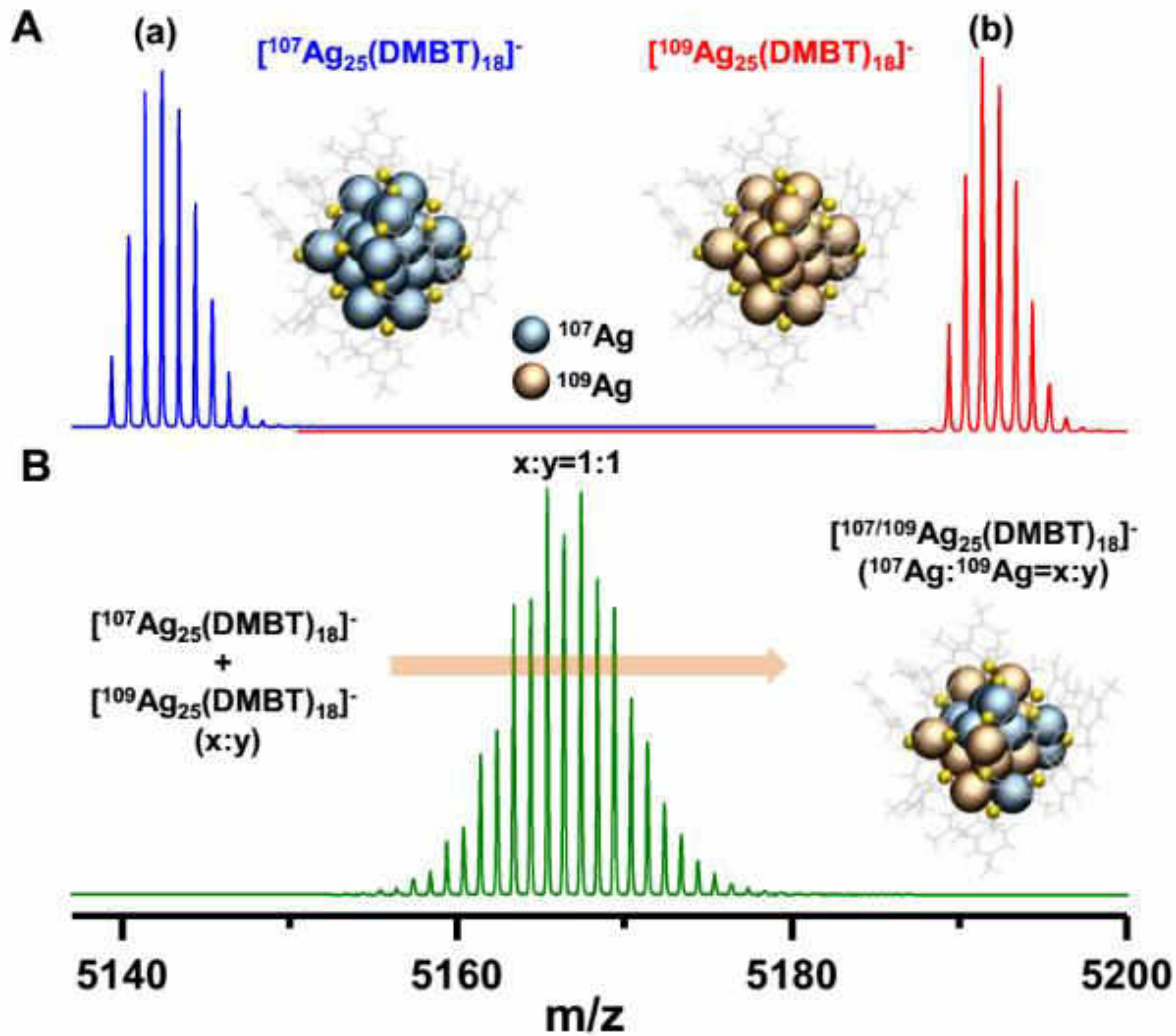
Manfred Kappes, KIT

M. Neumaier, A. Baksi, et. al., *JACS* 2021

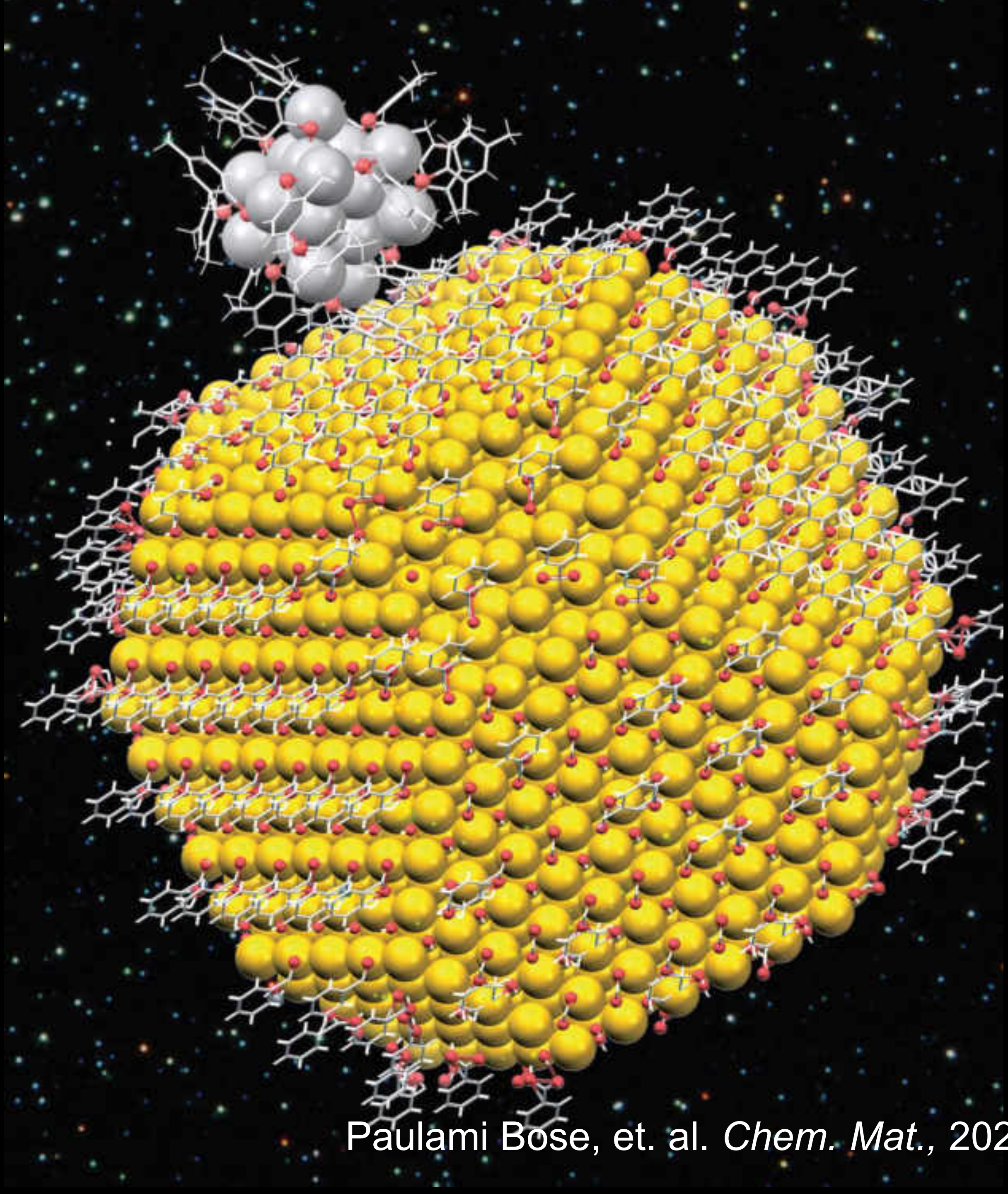
Kinetics of the exchange (monitored on the Ag_{25} side)



Isotopic exchange

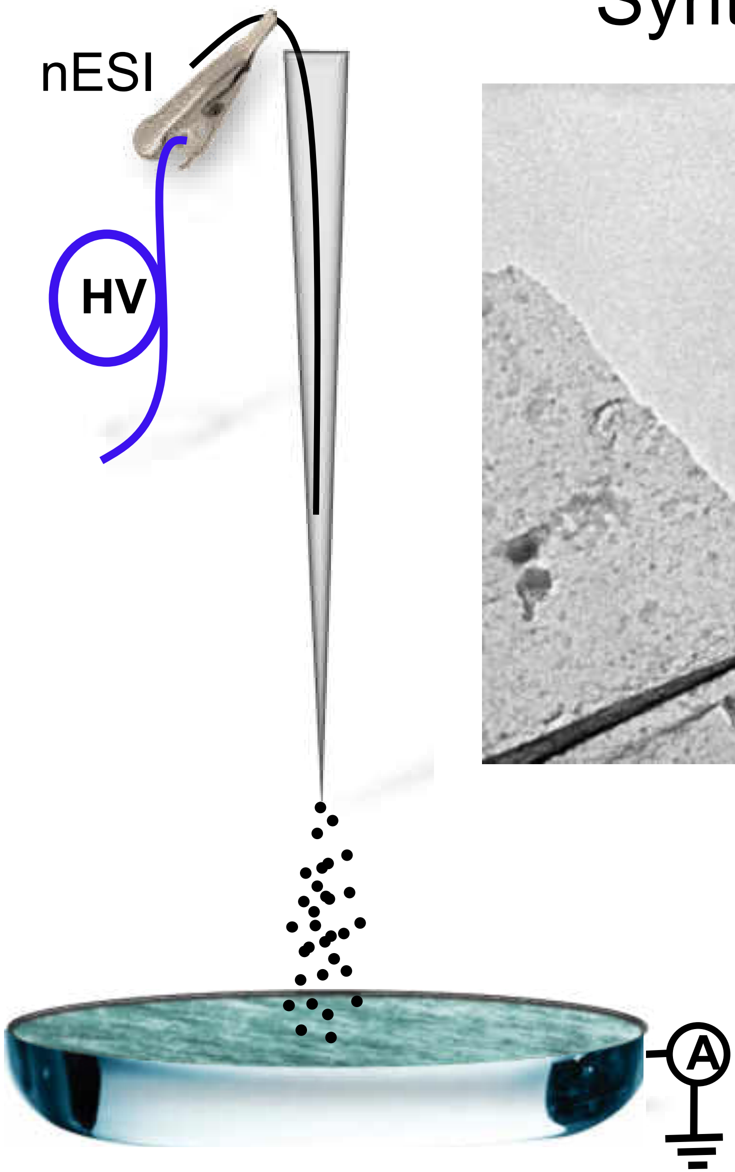


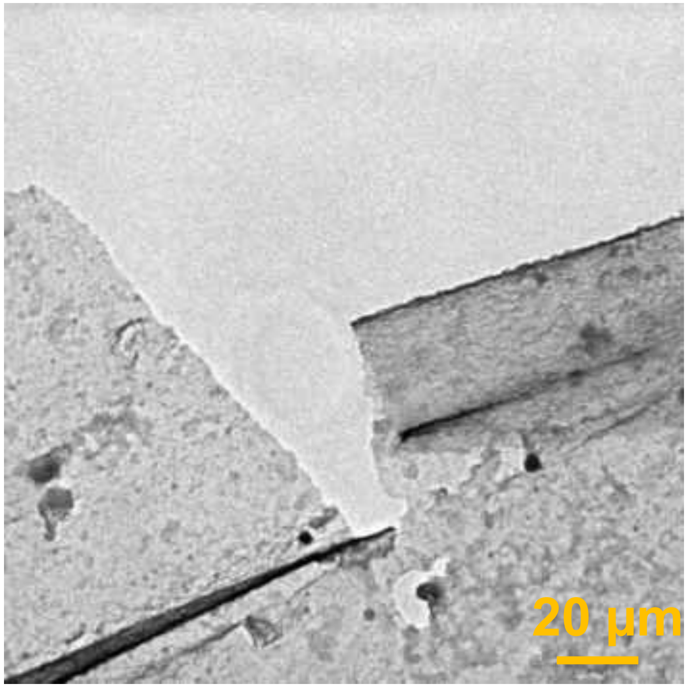
Papri Chakraborti, et. al. *Science Advances*, 2019.

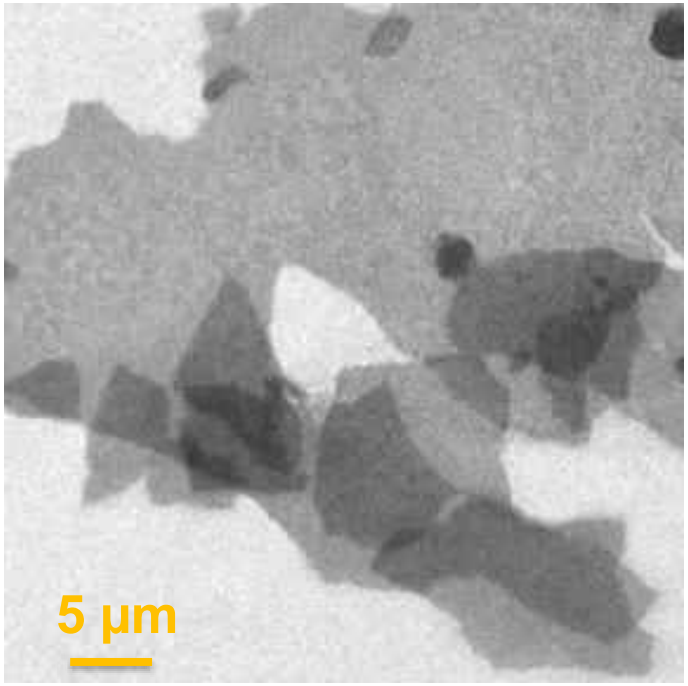


Paulami Bose, et. al. *Chem. Mat.,* 2024 (in Press).

Synthesis Strategies



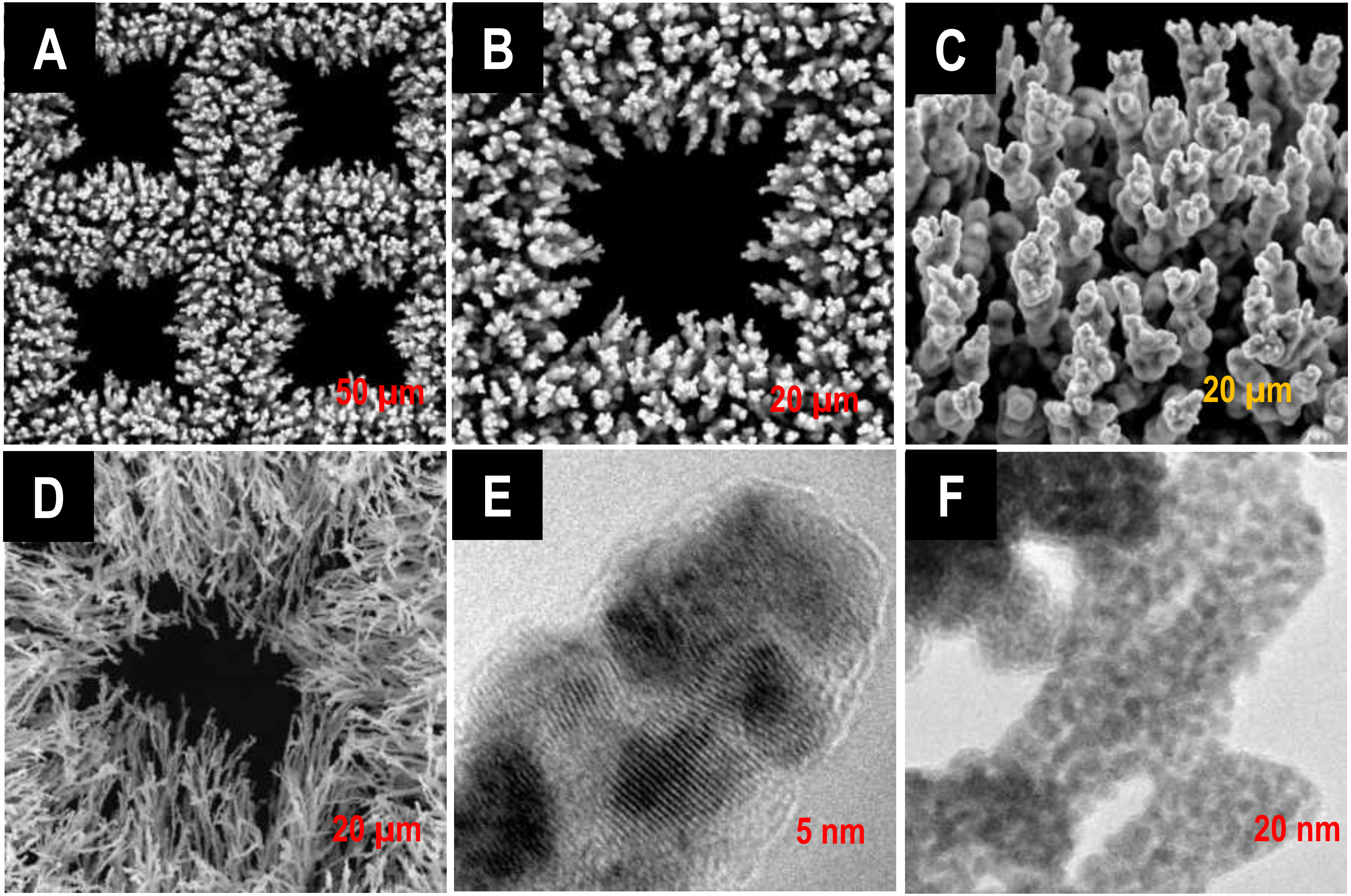




All these are possible because it is an ambient process!

Sustainable process with a minimal carbon footprint.

Bimetallic Nanobrushes

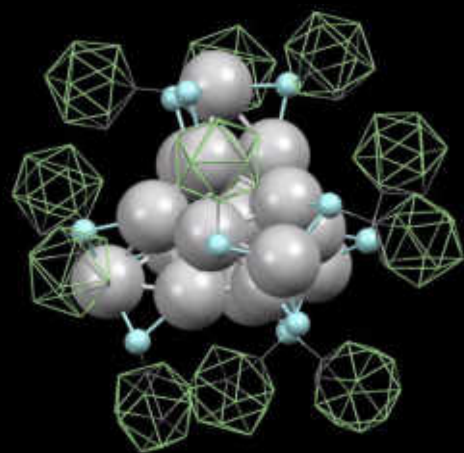


Formation of Ag-Pd bimetallic brushes

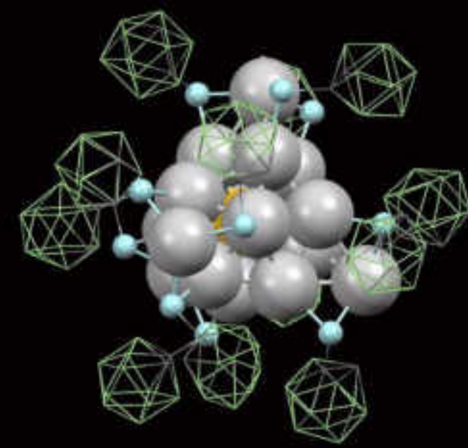
Fabrication of Micro-Nano Structures Using Microdroplets for Atmospheric Water Capture


Nature is a best teacher, a great source of wisdom

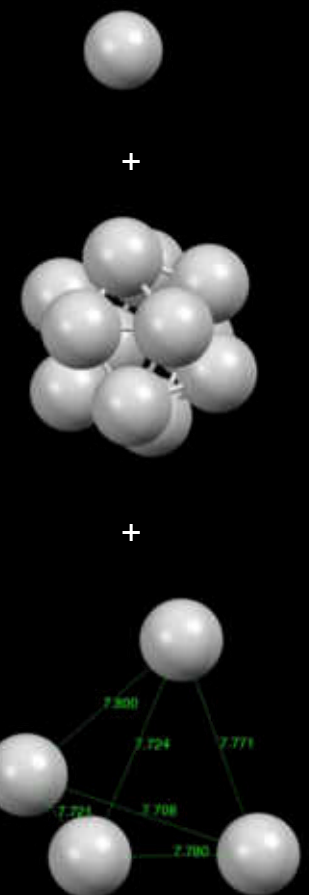
Carboranethiol protected clusters

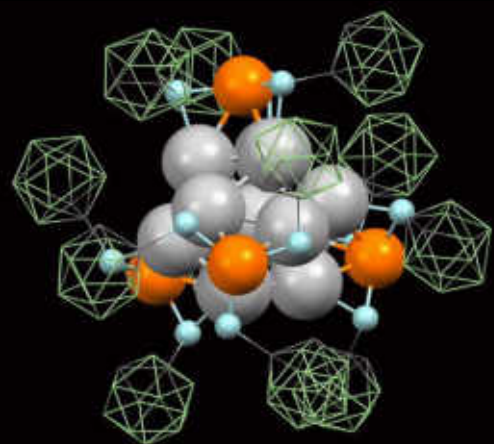


Ag_{17}

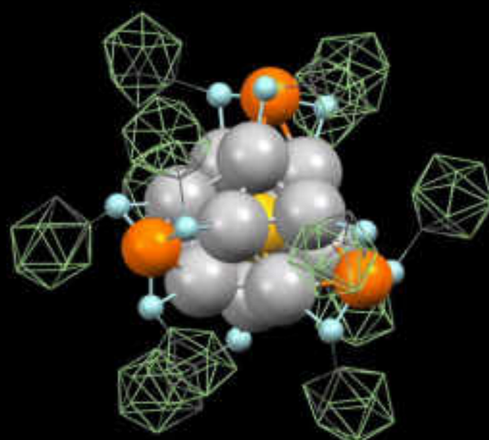


$Au@Ag_{16}$





$Ag_{13}@Cu_4$

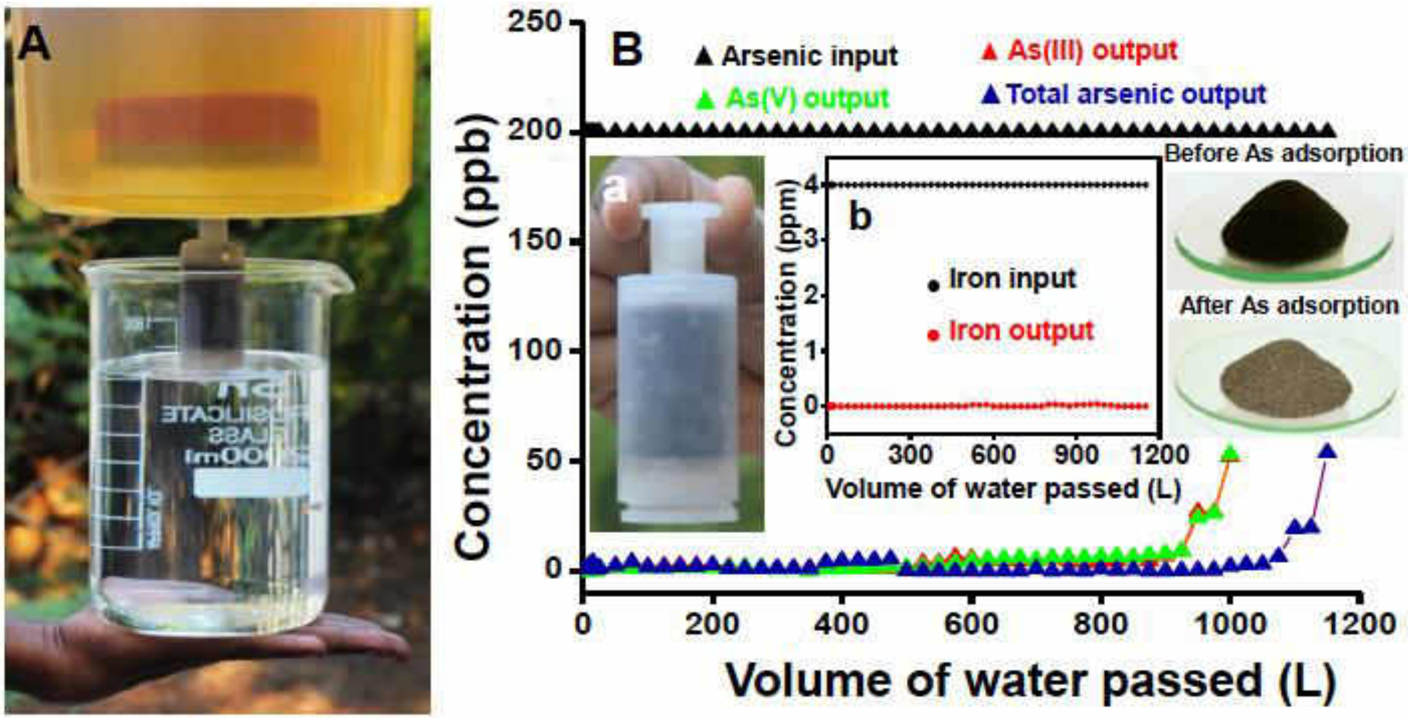


$Au@Ag_{12}@Cu_4$

Vivek Yadav, et. al. Unpublished

Clean water using advanced materials

Range of materials, their affordability and safety



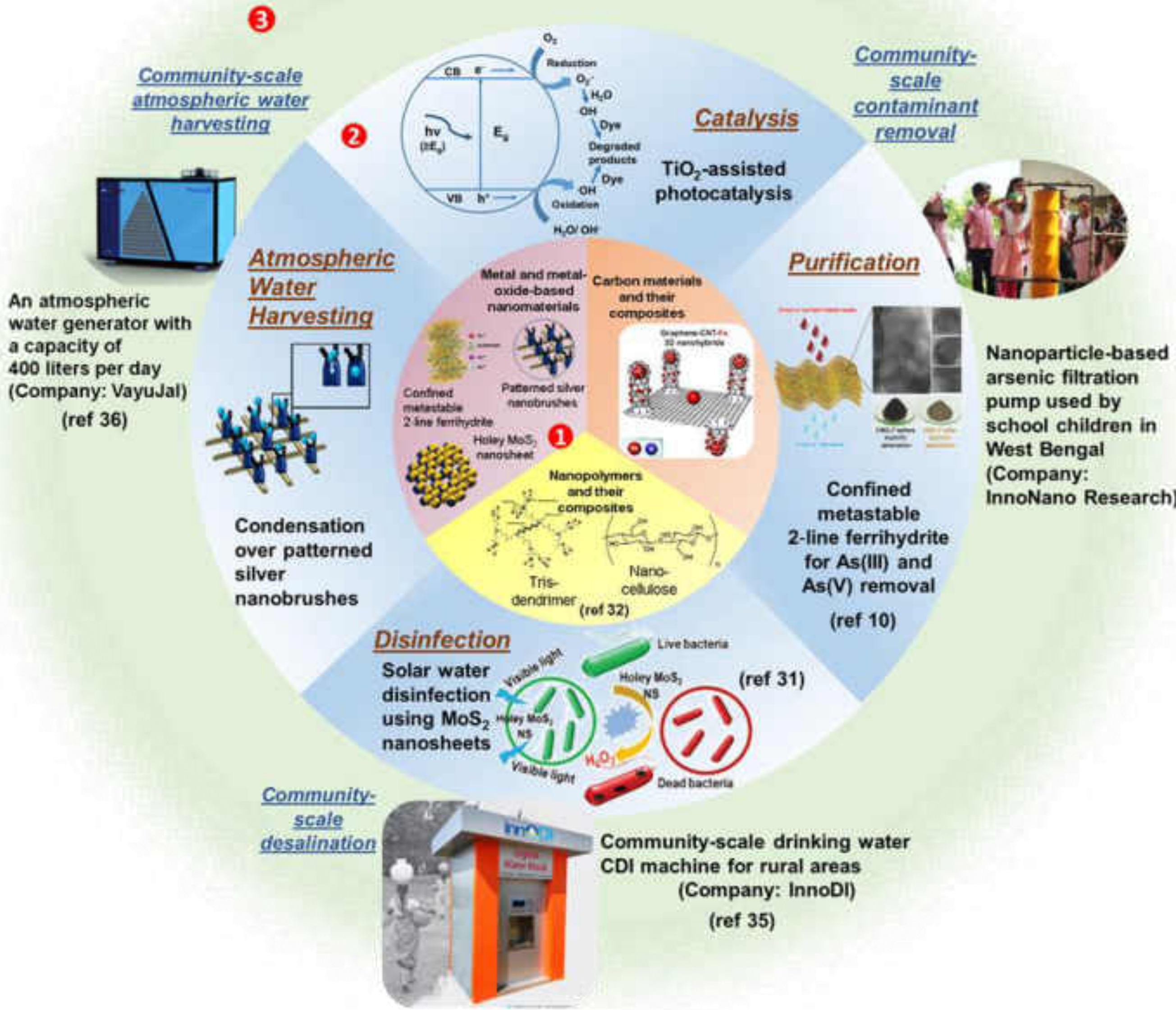
Safety of spent media, TCLP

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

Clean water for everyone

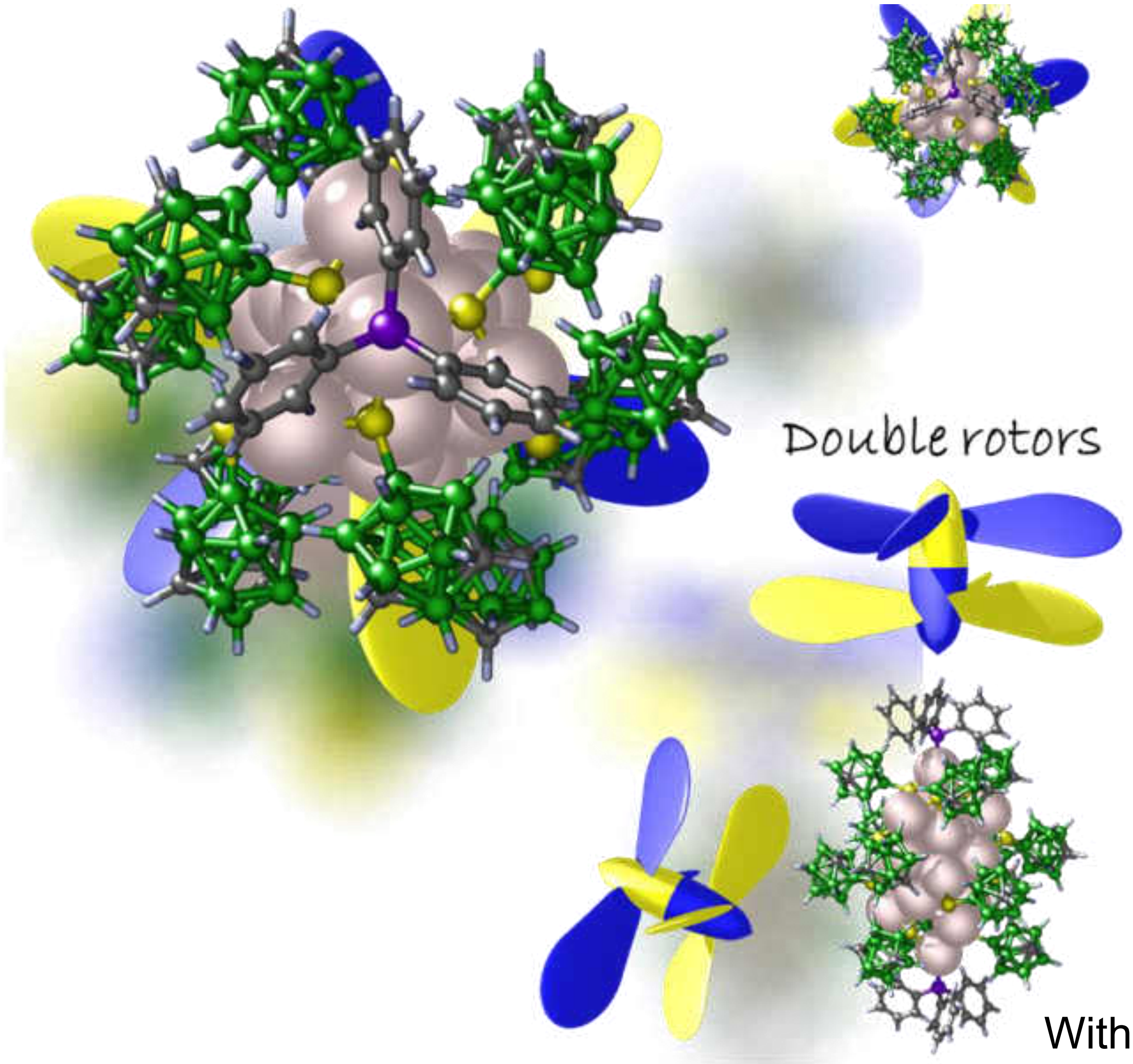
ACS Sustainable Chemistry & Engineering Editorial,
December 2016

Evolution of materials to products

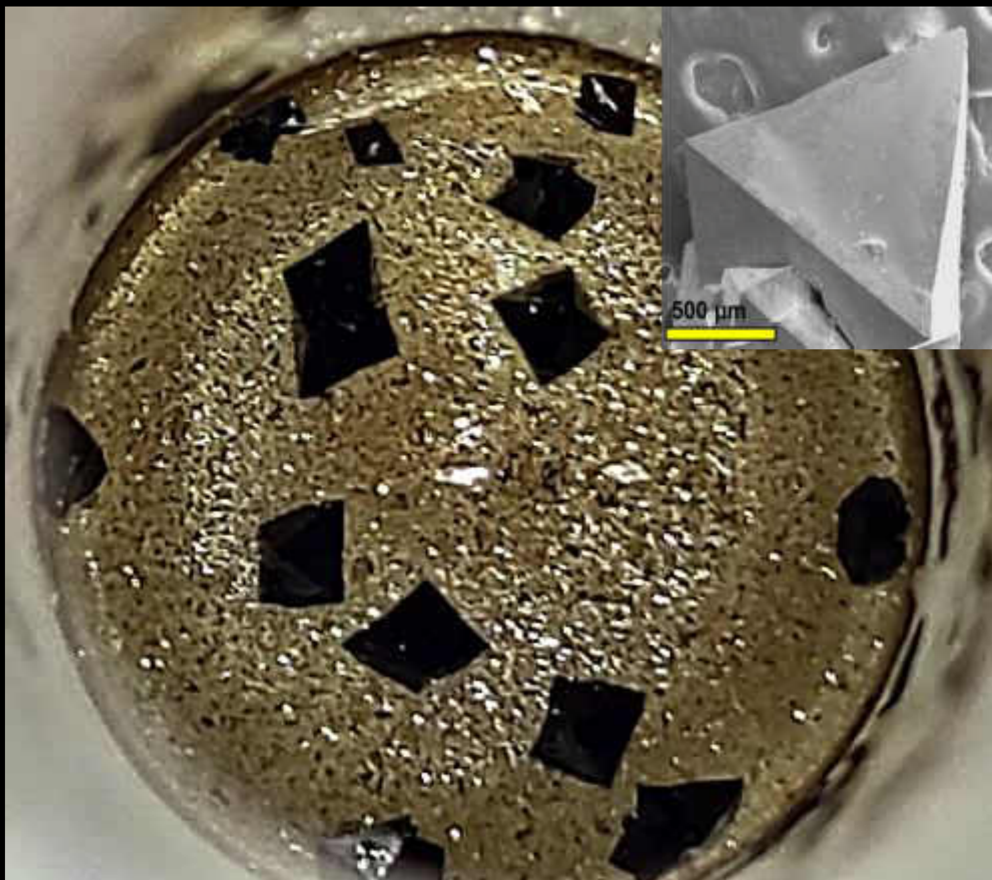


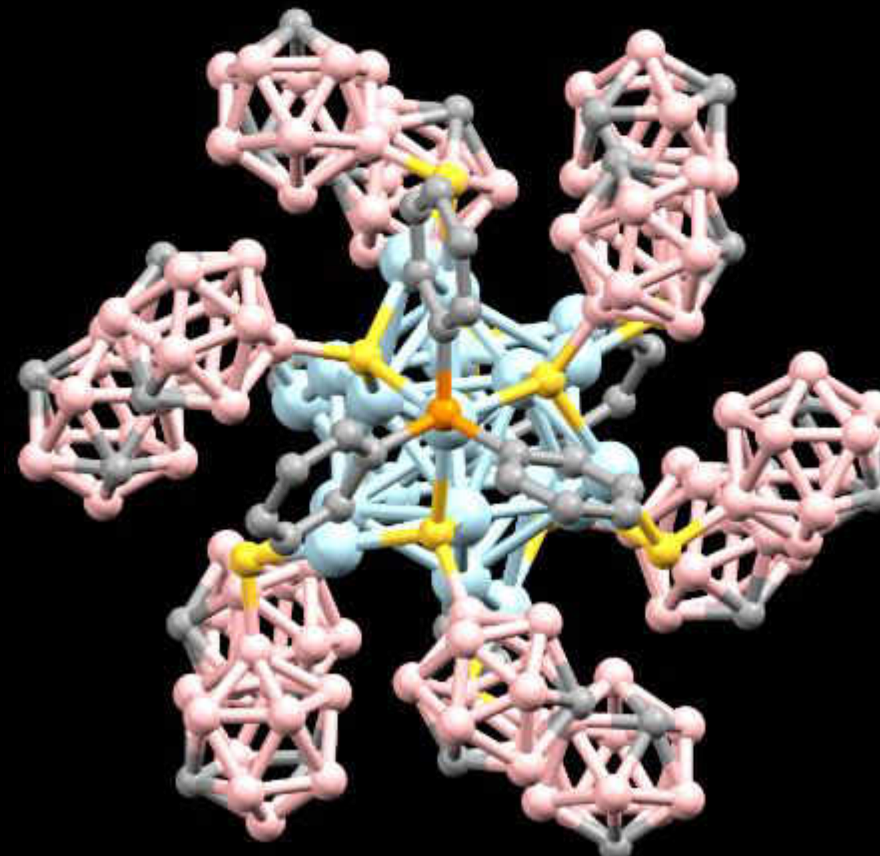
Ankit Nagar and T. Pradeep 14(2020). *ACS Nano*, 6420-6435

Carborane-thiol protected silver nanomolecule

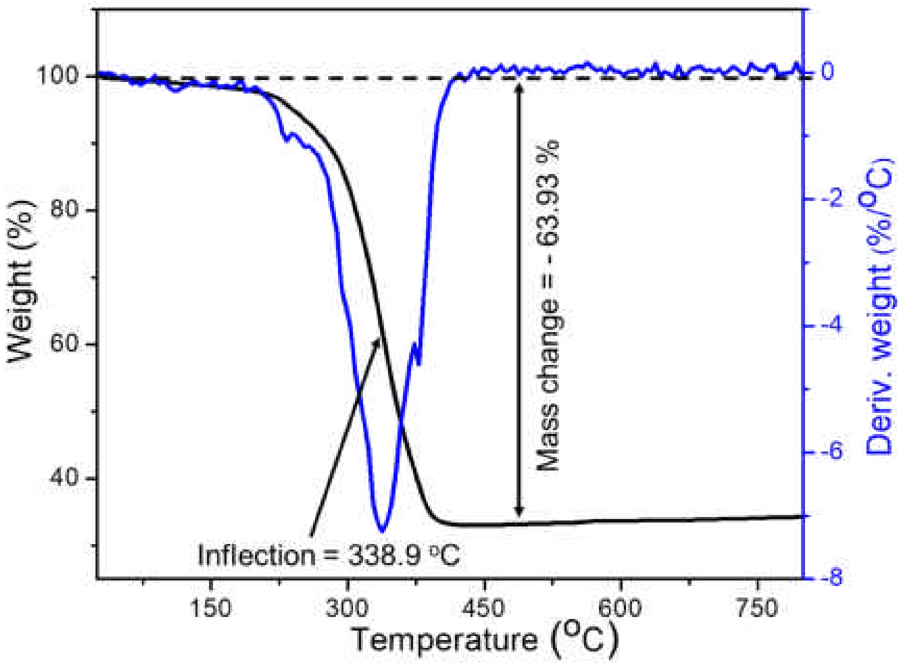


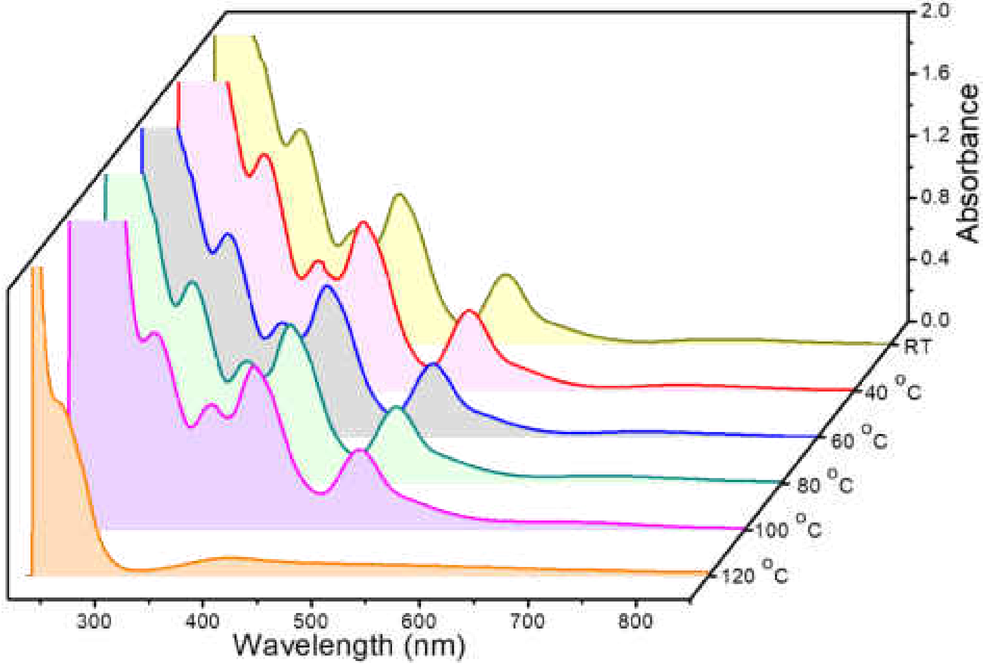
With Tomas Base


500 µm

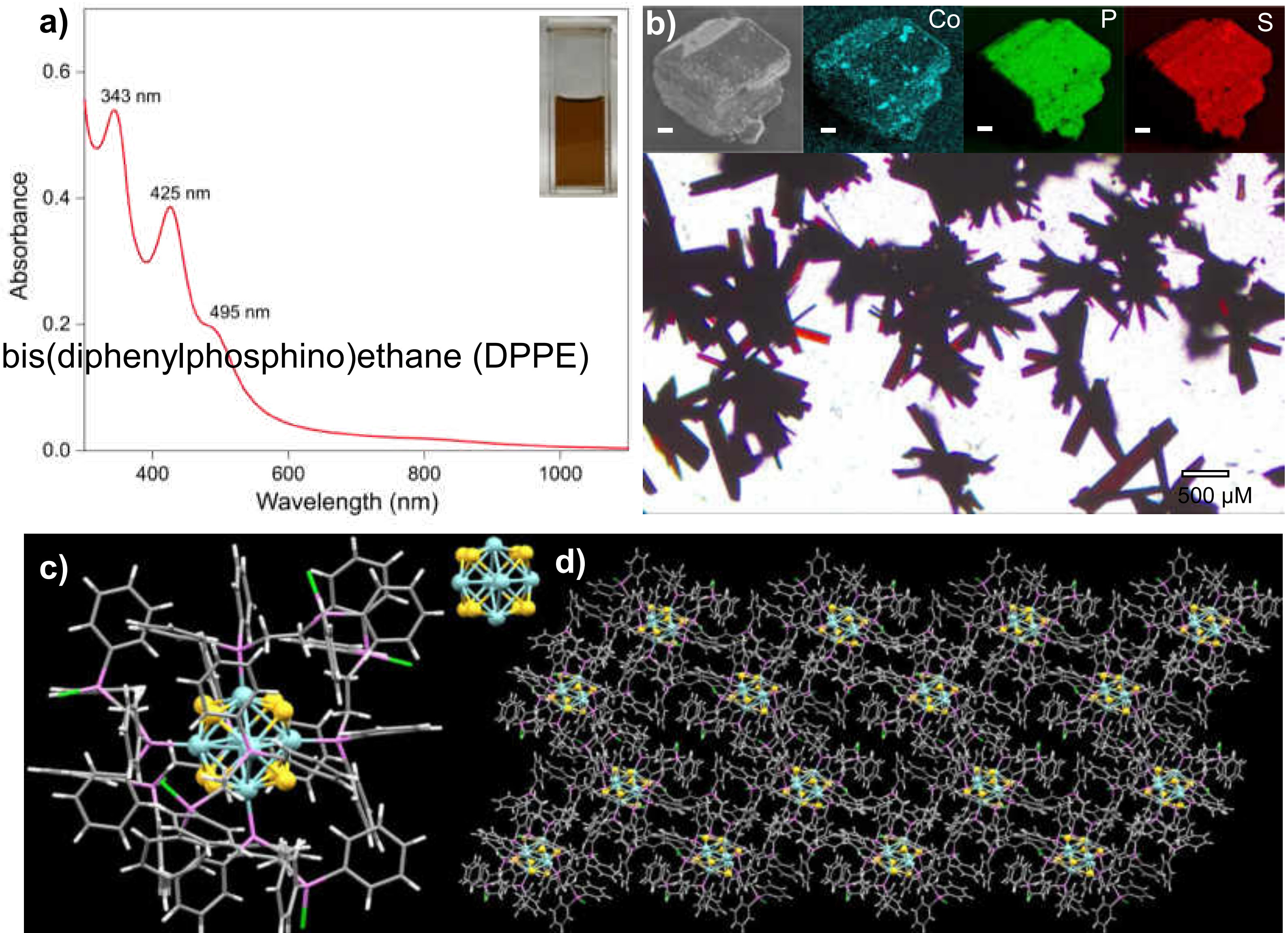


Thermal stability



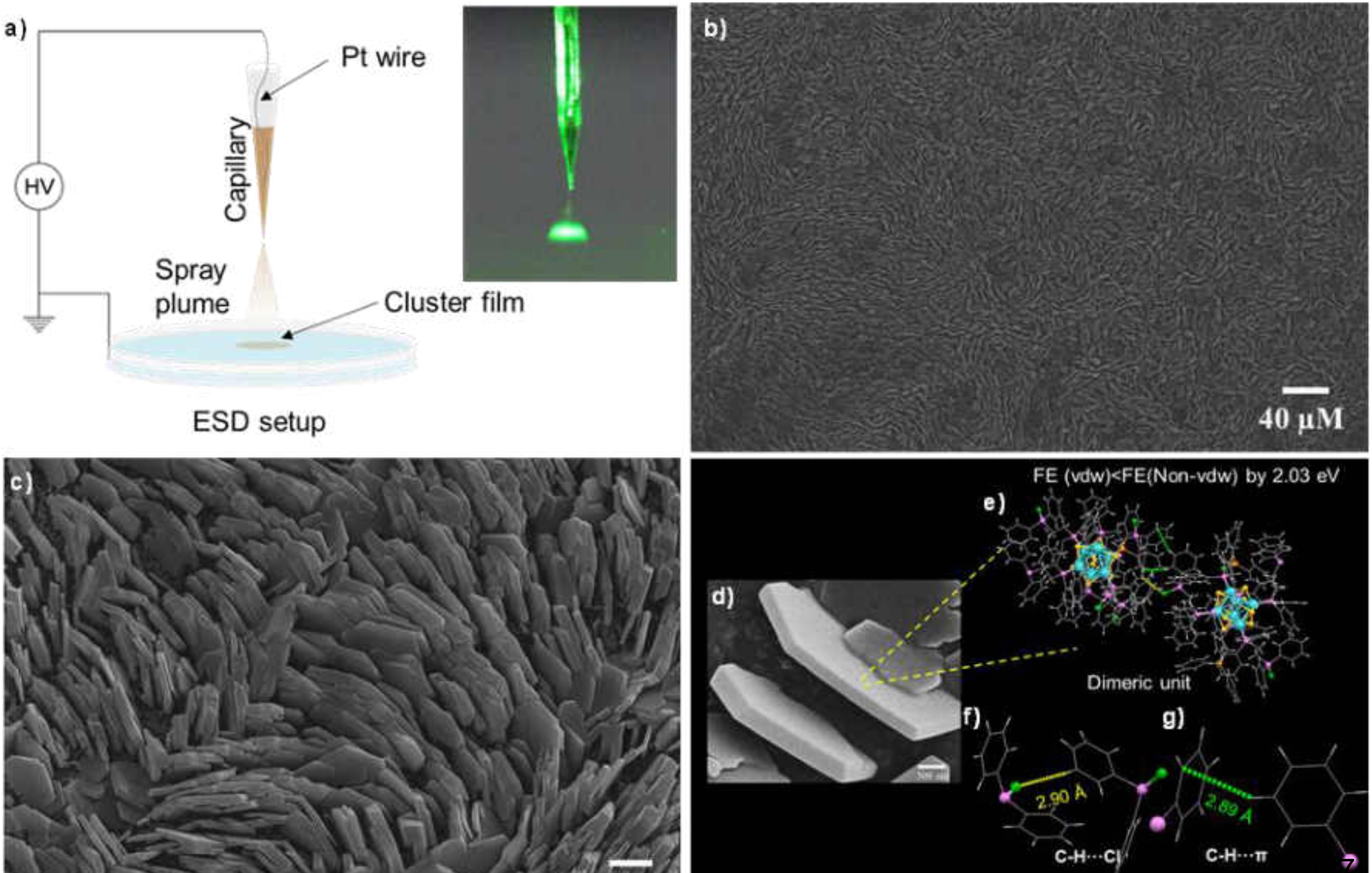


New electrodes - Aligned nanoplates of Co_6S_8



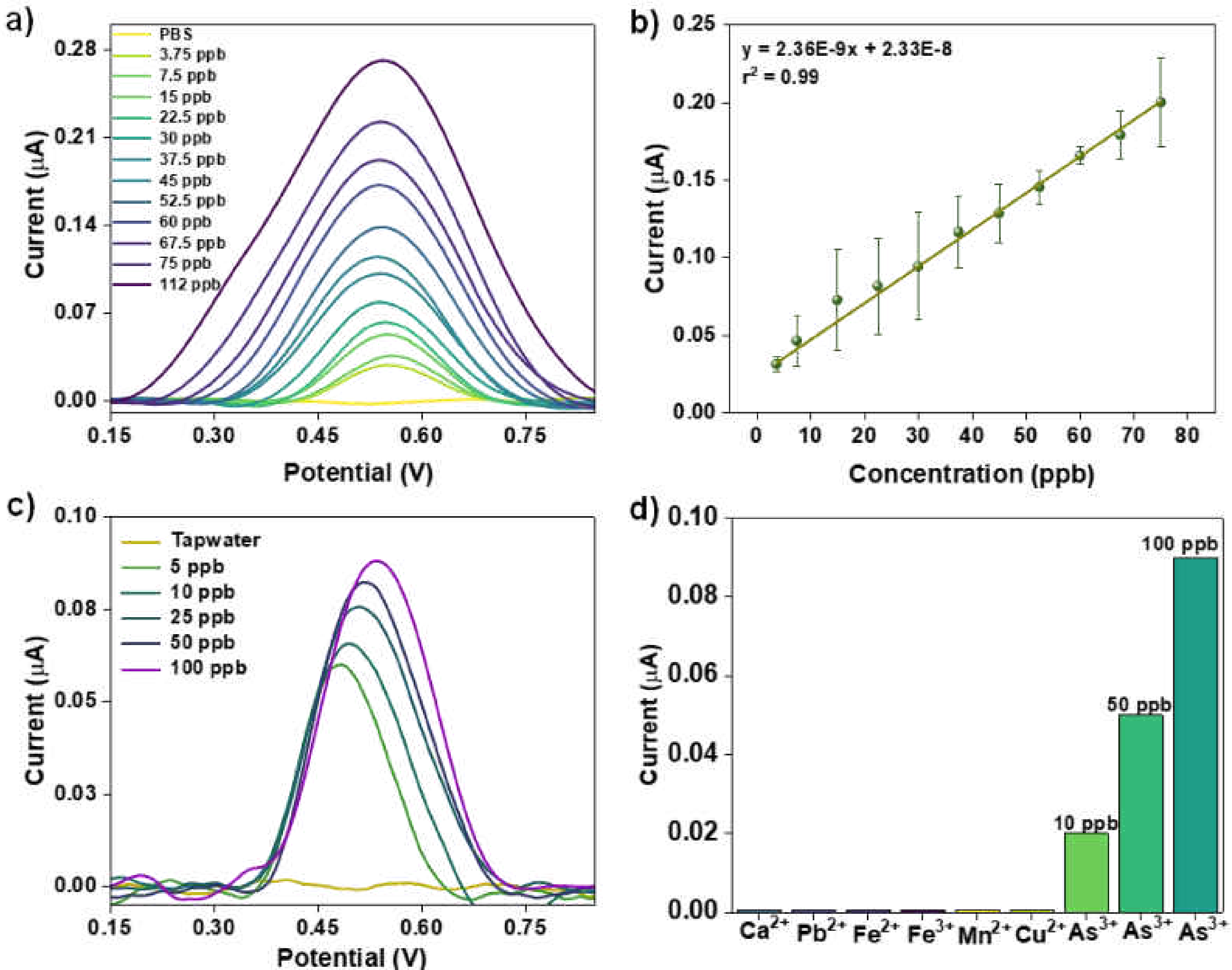
1,2-bis(diphenylphosphino)ethane (DPPE)

Electrospray deposition



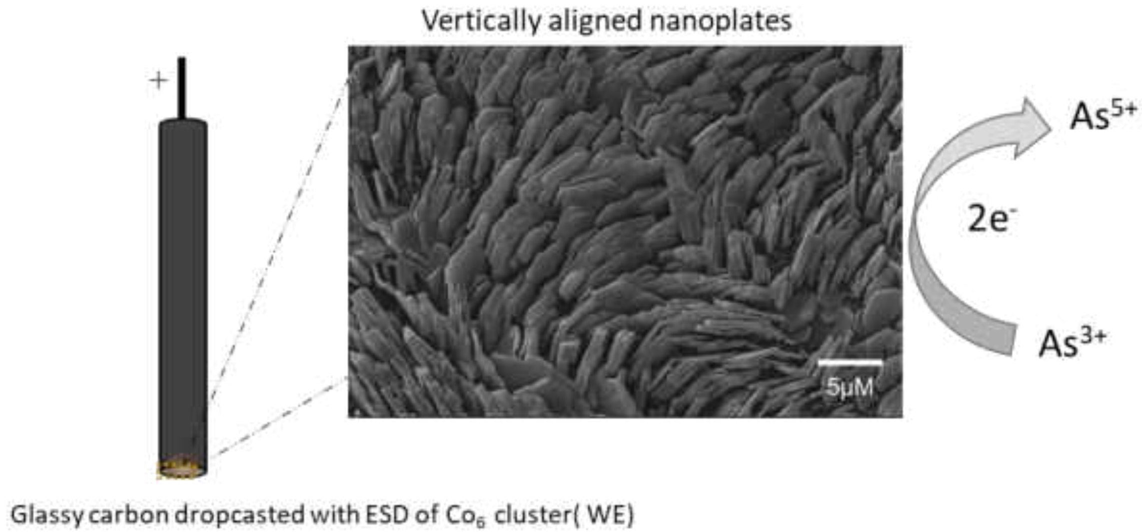
Anagha Jose et. al. *ACS Mat. Lett.* (2023)

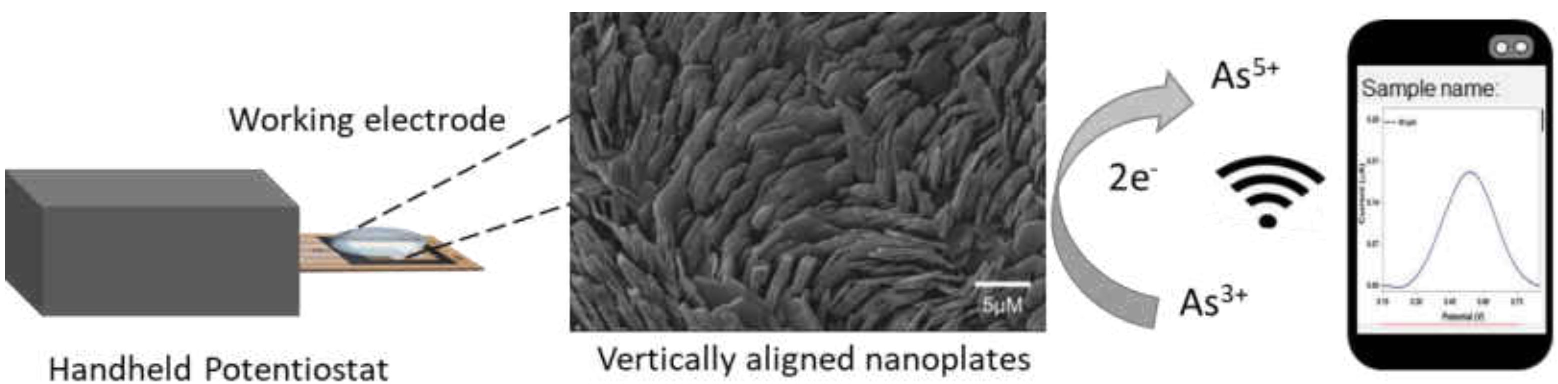
Sensing



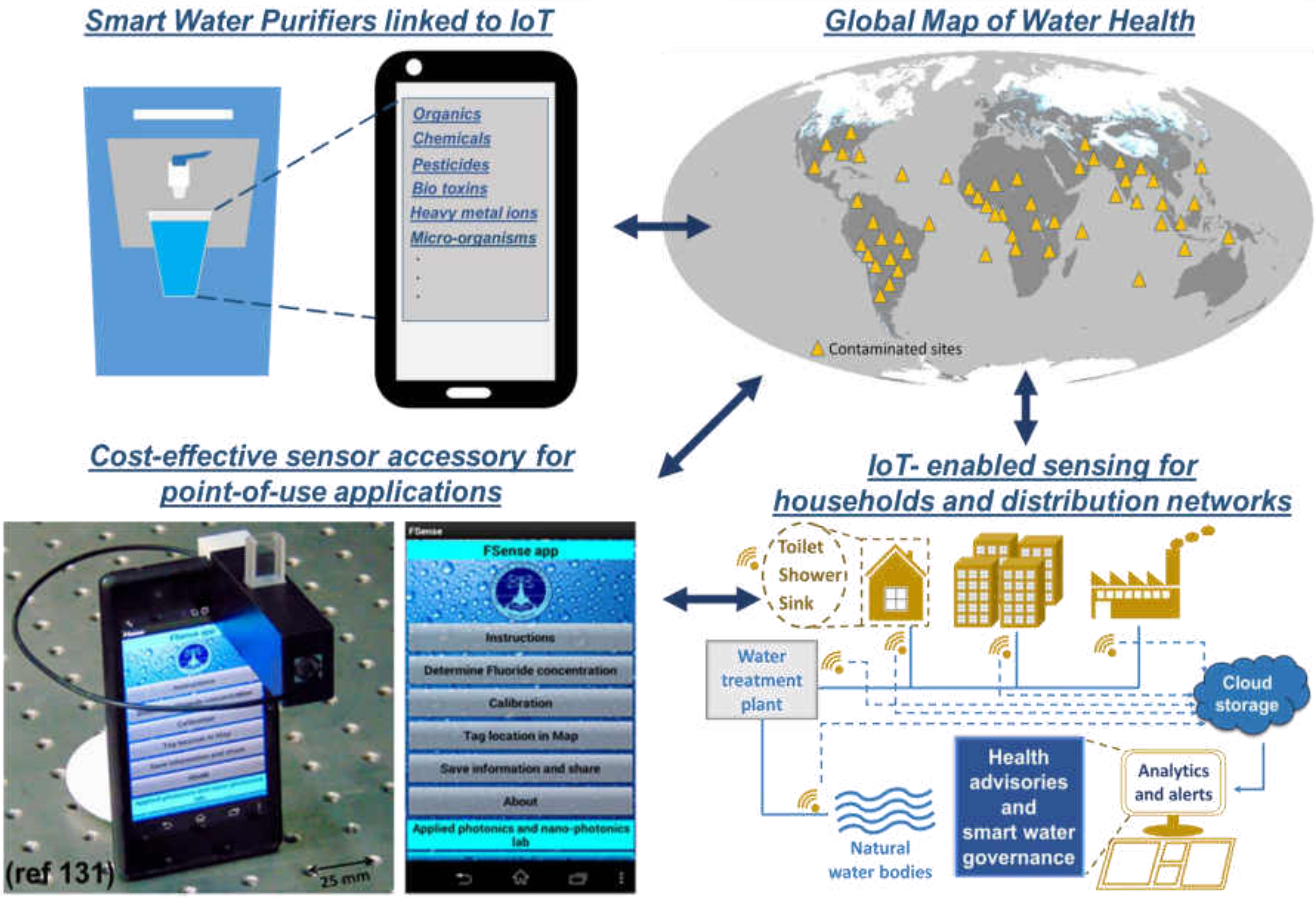
a)
PBS
3.75 ppb
7.5 ppb
15 ppb
22.5 ppb
30 ppb
37.5 ppb
45 ppb
52.5 ppb
60 ppb
67.5 ppb
75 ppb
112 ppb
0.28
0.21
0.14
0.07
0.00
Current (μA)
0.15
0.30
0.45
0.60
0.75
Potential (V)
b)
y = 2.36E-9x + 2.33E-8
r² = 0.99
0.25
0.20
0.15
0.10
0.05
0.00
Current (μA)
0
10
20
30
40
50
60
70
80
Concentration (ppb)
c)
Tapwater
5 ppb
10 ppb
25 ppb
50 ppb
100 ppb
0.10
0.08
0.05
0.03
0.00
Current (μA)
0.15
0.30
0.45
0.60
0.75
Potential (V)
d)
100 ppb
50 ppb
10 ppb
0.10
0.08
0.06
0.04
0.02
0.00
Current (μA)
Ca2+
Pb2+
Fe2+
Fe3+
Mn2+
Cu2+
As3+
As3+
As3+

Working electrode



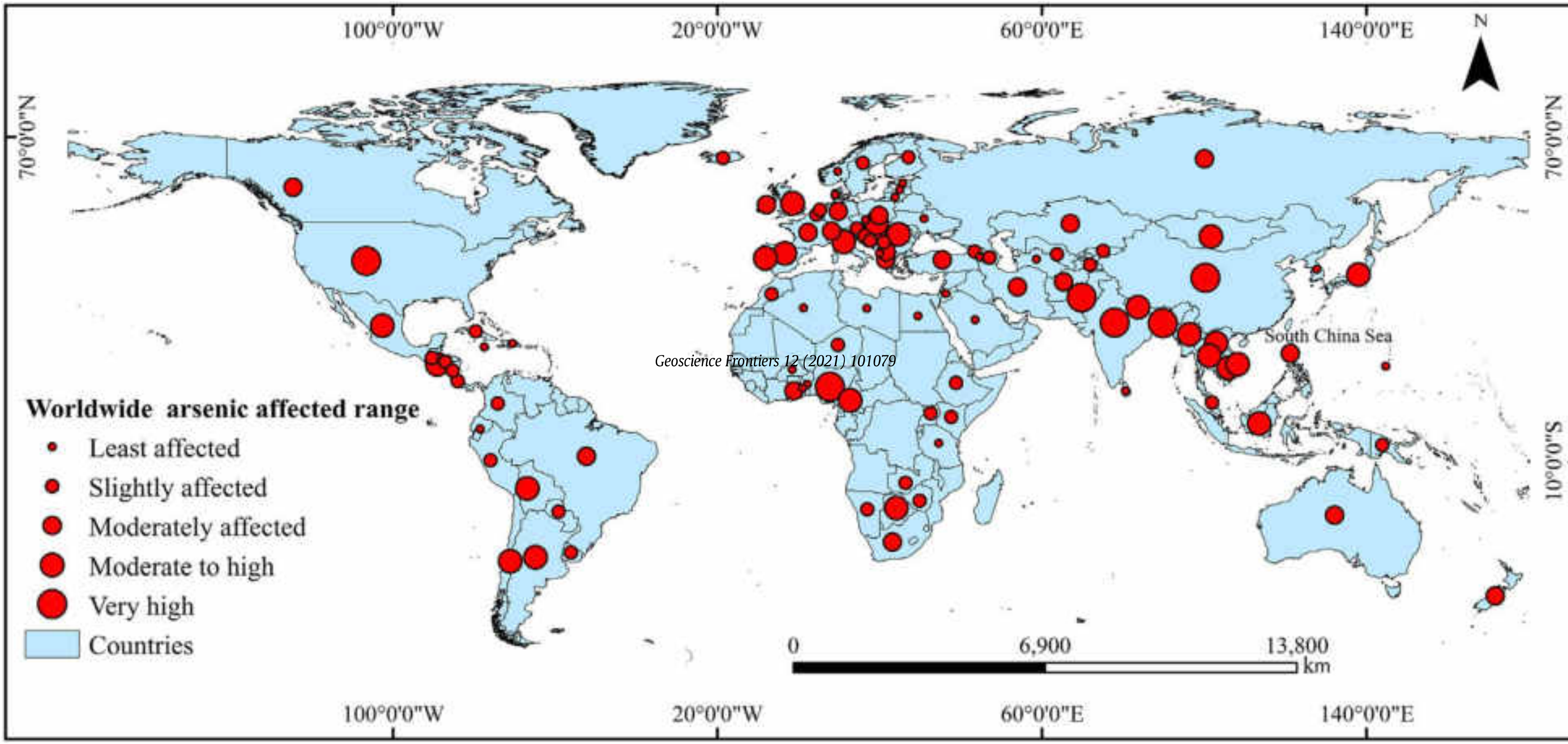


Smart water purifiers and big data



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

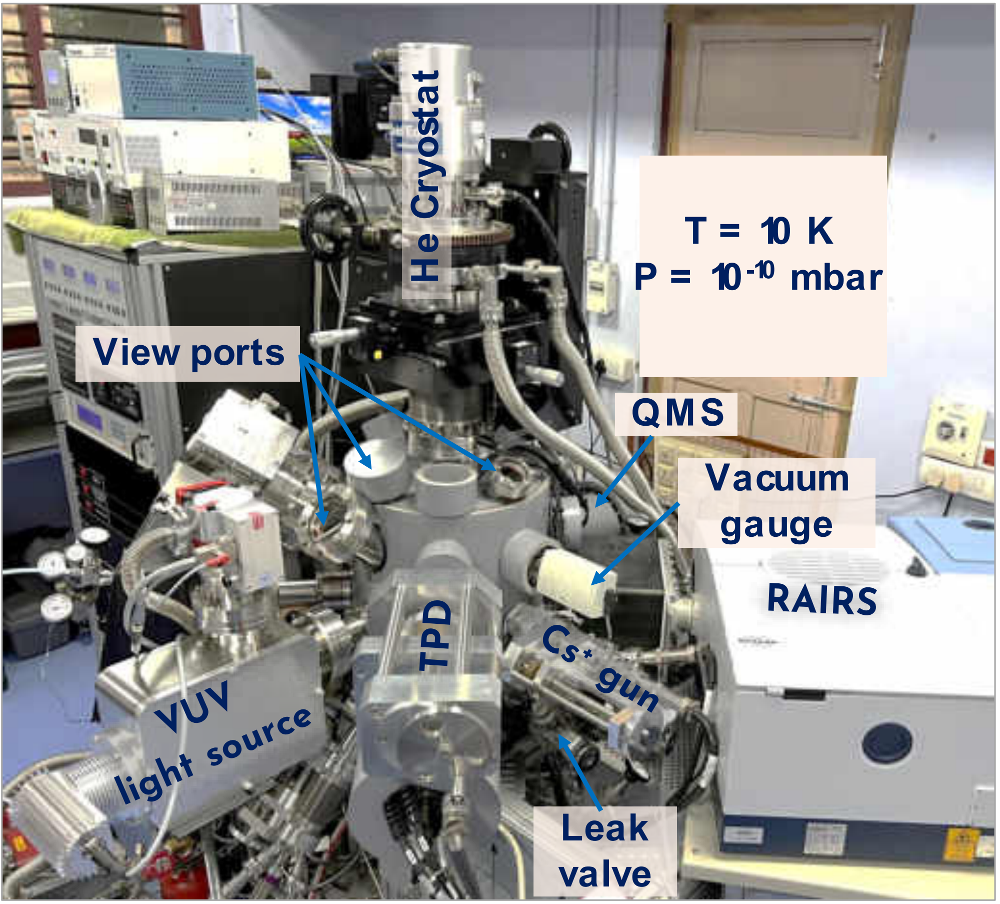
Arsenic poisoning across the world

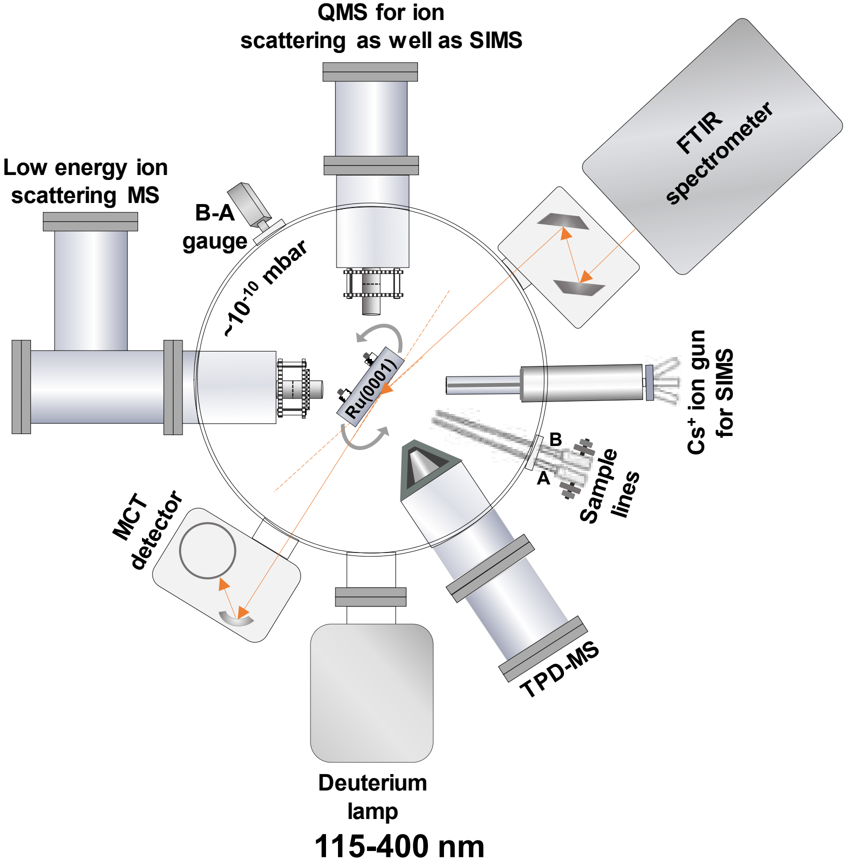


E. Shaji, M. Santosh, K. V. Sarath, Pranav Prakash, V. Deepch and B. V. Divya, *Geoscience Frontiers*, 12 (2021) 101079.

Ice chemistry

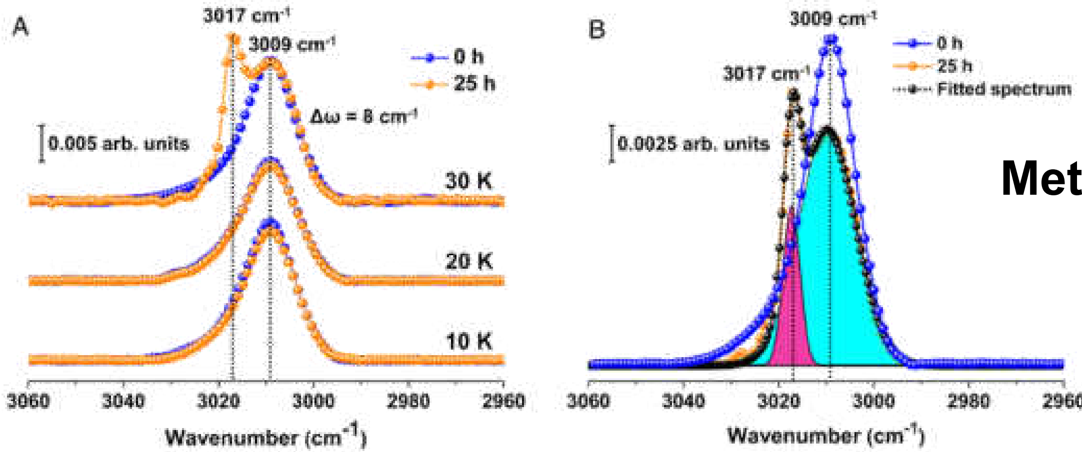
Instrumentation



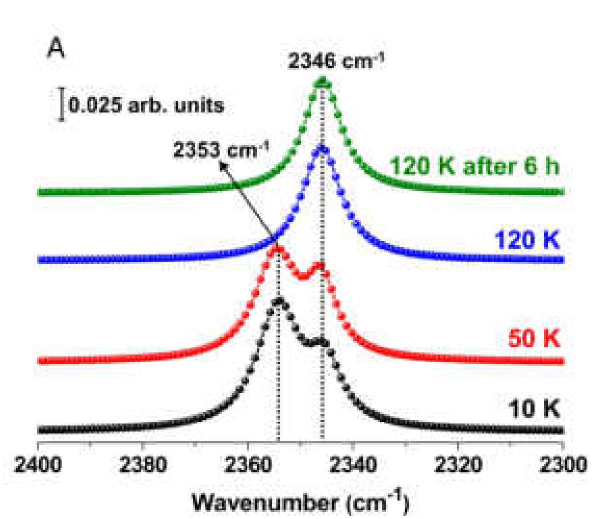


Ice instrument located in HSB-148, IIT Madras Viswakarma, *G. et al., J. Phys. Chem. Lett.*, **2023**, *14*, 2823–2

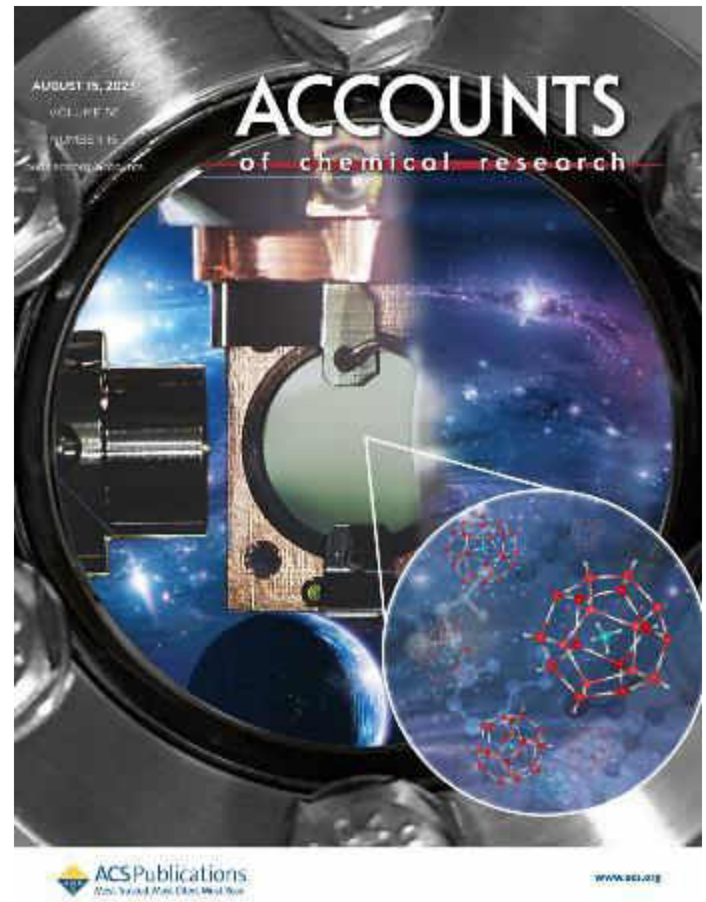
CH in ultrahigh vacuum



Methane CH



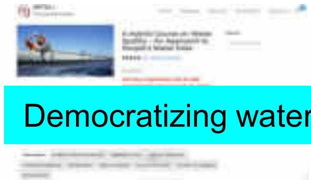
Carbon dioxide CH



Ghosh, J. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.*, **2018,** *116*, 1526-1531

Microdroplets

Activities for the next ten years



Democratizing water

People’s water data
Innovation for all

Innovation course

Teaching

Clean water for all
International centre for clean water

Innovation

Partnerships

Joint courses
Virtual labs
Indian campuses

Droplet weathering

Research

Droplets
Clean water

AMRIT Technology,
Reached millions

Outreach

Media
Global visibility
Academies

Tiny Reaction Vessels