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# Can MicroDroplets Make Soil?

A path to sustainable nanotechnology



Matter in confinement for sustainability

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International Centre for Clean Water



# Science

## RESEARCH

### NANOPARTICLES

## Spontaneous weathering of natural minerals in charged water microdroplets forms nanomaterials

B. K. Spoorthi<sup>1</sup>, Kavyashila Debnath<sup>2</sup>, Palash Basu<sup>1</sup>, Anil Nagai<sup>1</sup>, Umesh V. Vaghmare<sup>1</sup>, Thalapatt P. Radhak<sup>1,3</sup>

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 rutile) 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 etch, especially when reduced in size and exposed to an electric field. This leads to particle etching 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.

**N**anoparticles of minerals exist naturally in soil, and some of them are essential for life (1). Microscale studies have been a of interest over the past decade, because the confined environment within them is known to cover 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 microscale particles of natural quartz ( $\text{SiO}_2$ ) and rutile ( $\text{TiO}_2$ -substituted  $\text{Al}_2\text{O}_3$ ) for use in an electrospray setup (Fig. 1, A and B). We ground commercial millimeter-sized quartz particles well using a

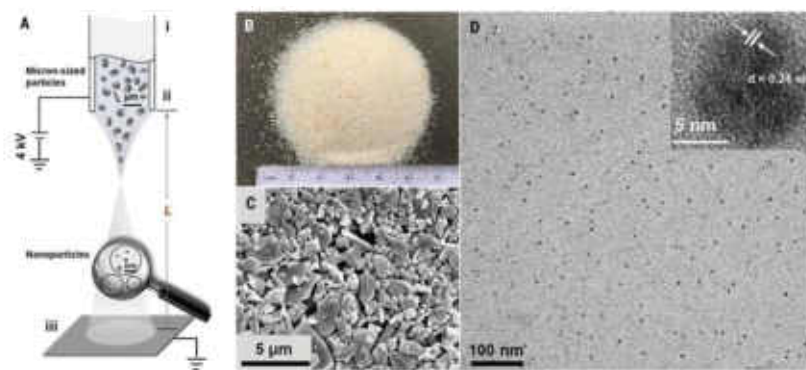
mortar and pestle and used centrifugation to separate the differently sized particles that formed. We carefully excluded all the particles smaller than 1  $\mu\text{m}$  in size and used particles of 5 to 10  $\mu\text{m}$  that were suspended in water for the experiment (Fig. 1C). Even after ultra-sonication to detach any adhered particles, we found some smaller particles attached to a few large ones (Fig. 1C). These adhering particles had dimensions greater than 100 nm (Fig. 1D). 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. 1E). We electrosprayed a suspension of about 6 mg/ml of the separated quartz particles through a capillary

tube that had an inner diameter of 50  $\mu\text{m}$ , flow rate of 0.5 ml/hour and observed the exiting plume (Fig. 1F). We collected the product of electrospray 15 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. 1G) throughout the grid. Under higher magnification, particles of different morphologies were observed. The particles showed the (110) plane of quartz (inset of Fig. 1G). 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 0.5 ml/hour flow rate, and a deposit

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**A scale of 1000**

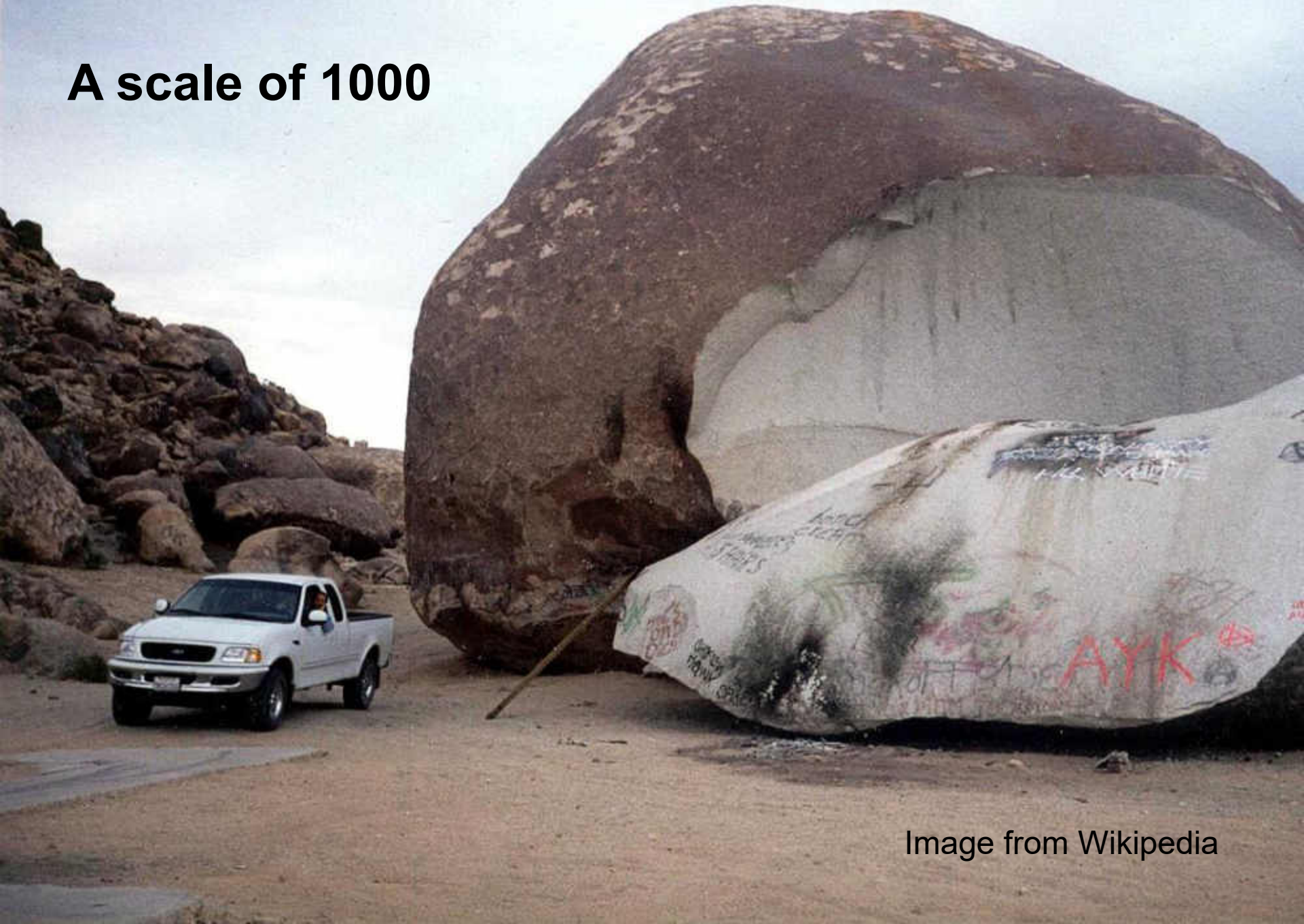
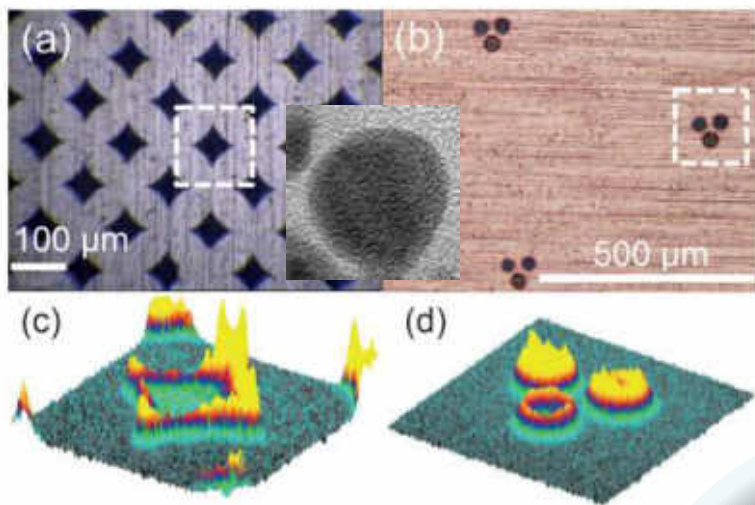


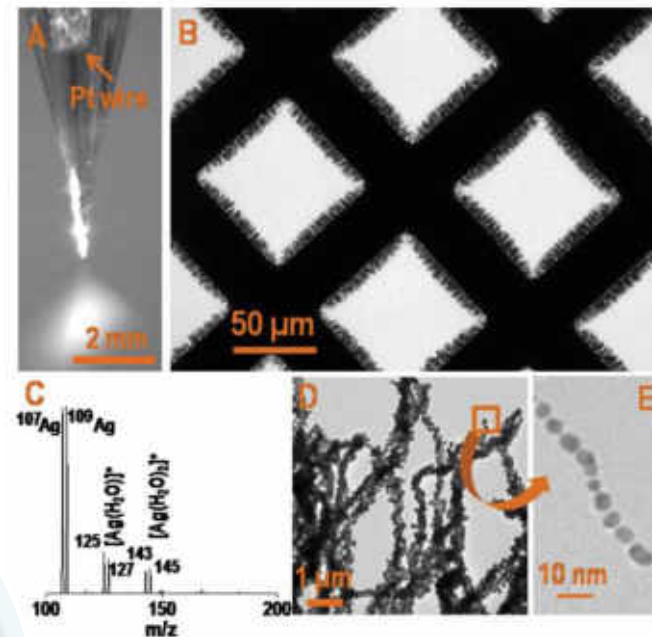
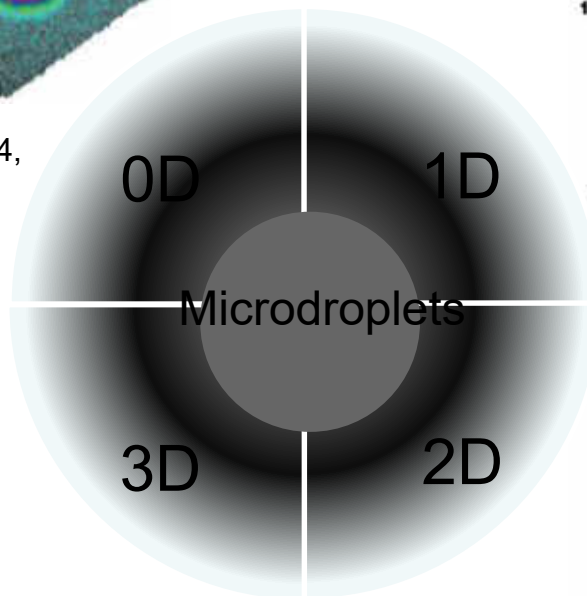
Image from Wikipedia

# **Functional Nanomaterials**

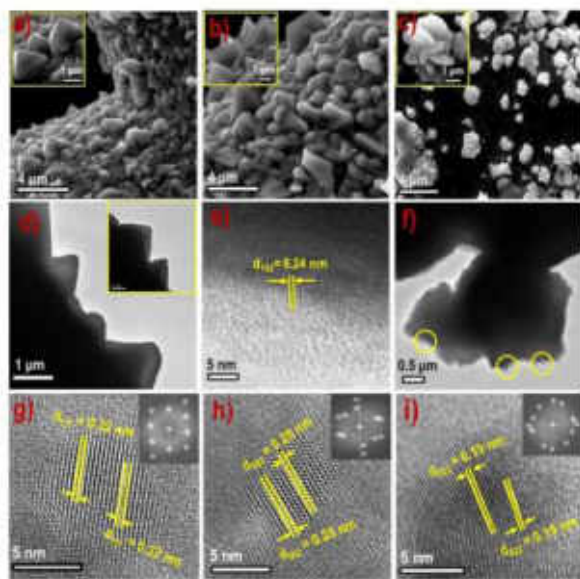




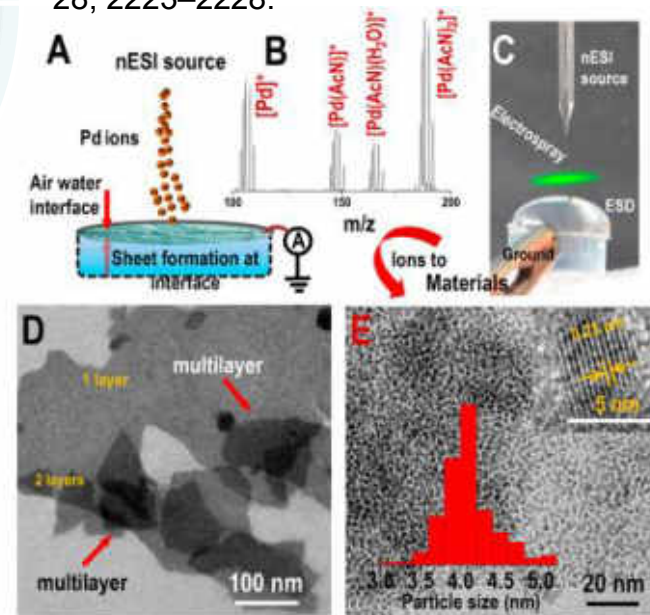
Anyin Li, et. al., *Angew. Chem. Int. Ed.* 2014, 53, 12528–12531.



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



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



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

# Chemical Science

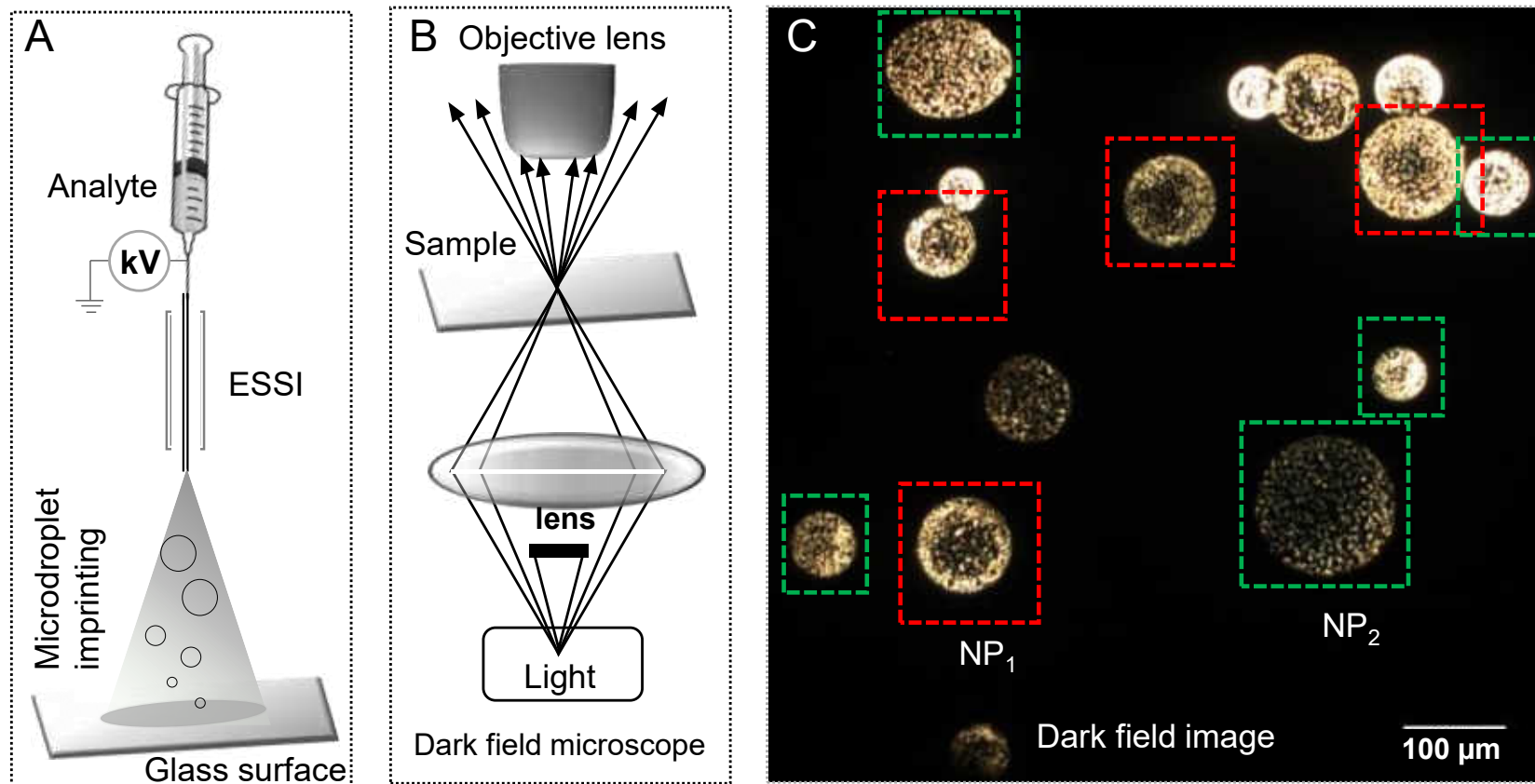
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Pages 13251–13634

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# Understanding Microdroplets

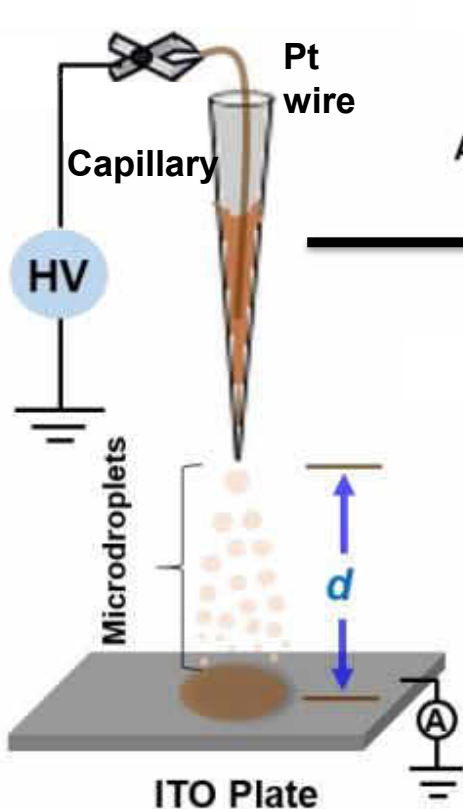


# **Transformation of Materials in Microdroplets**

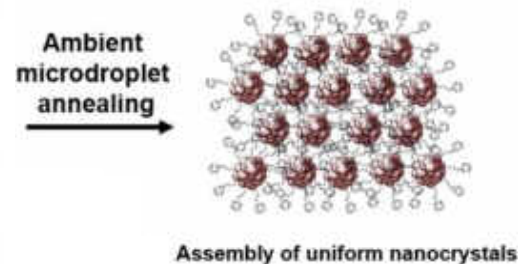
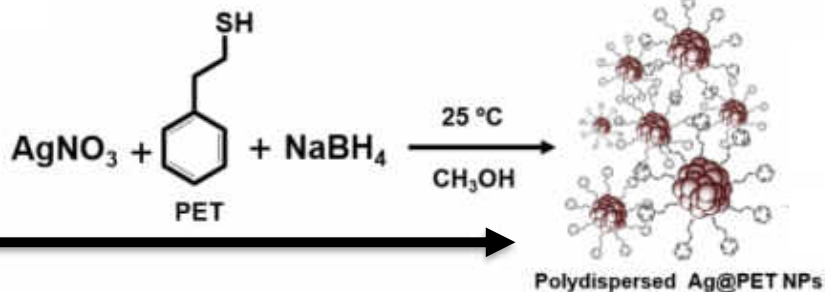


# Ambient Microdroplet Annealing of Nanoparticles

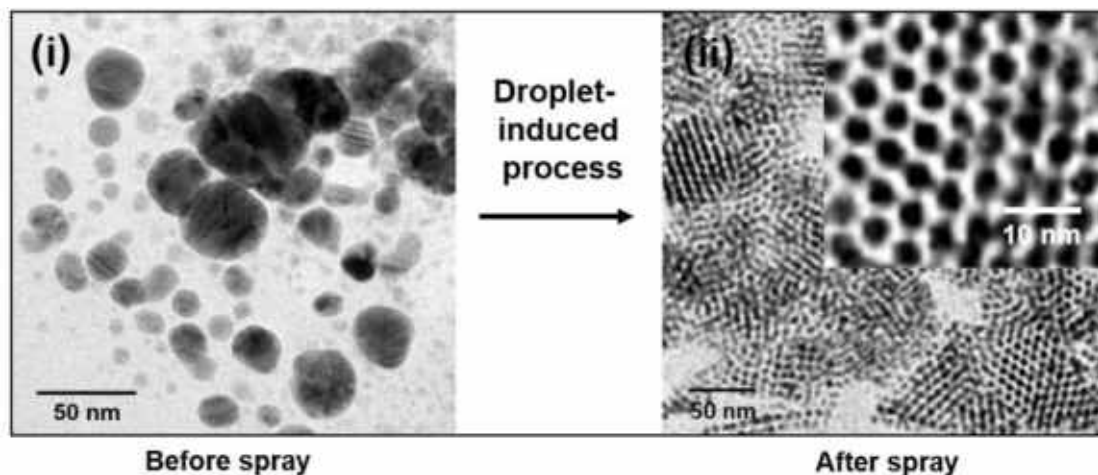
## Experimental set-up



## Synthesis of polydisperse NPs



## Transformation process





Thanks to ChatGPT

# Weathering in Nature





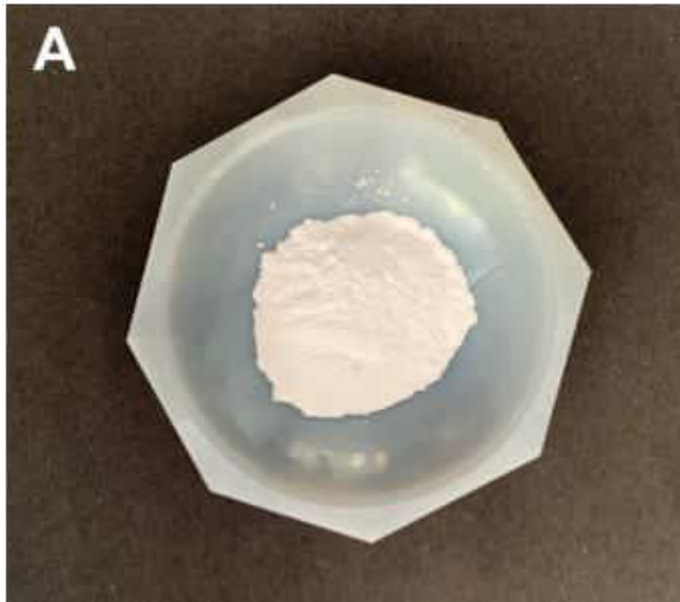
# Sand, the Ubiquitous Material



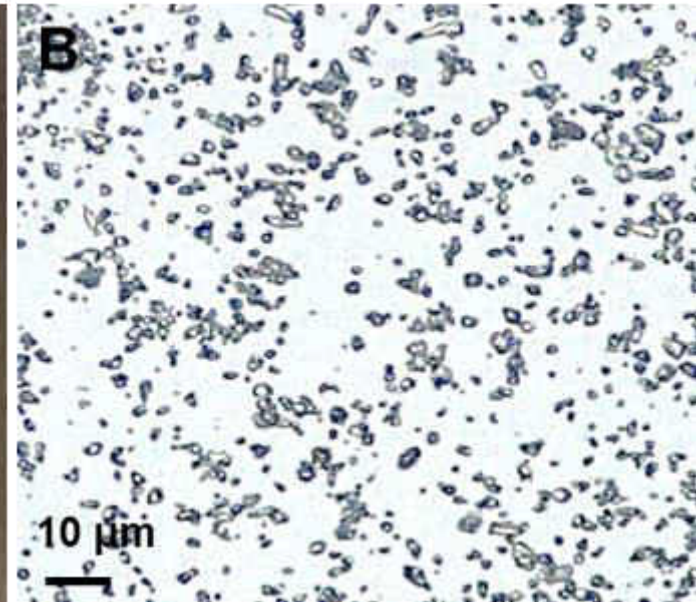
Images from Wikipedia





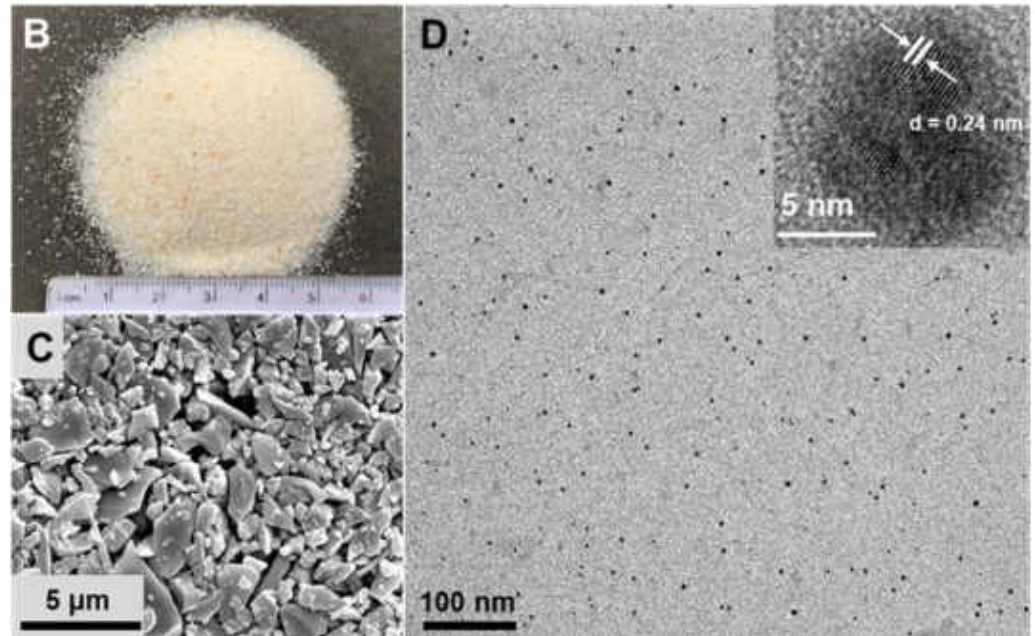
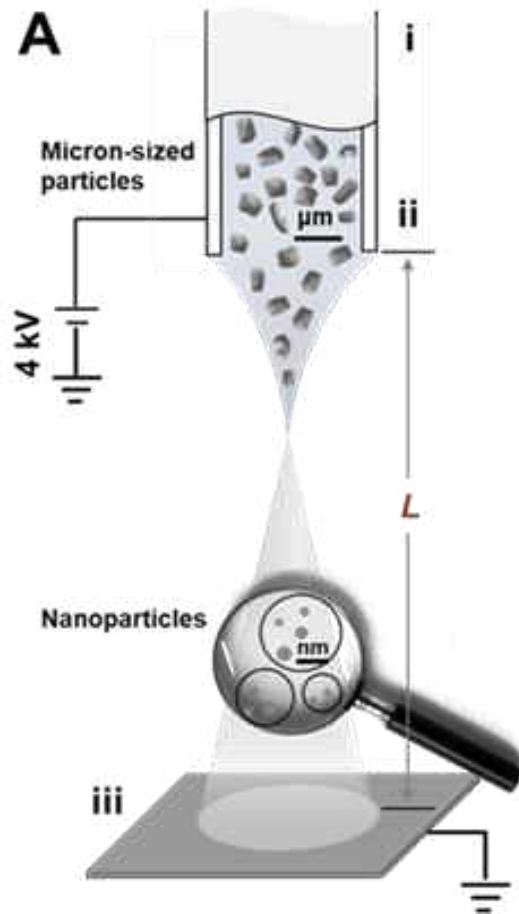


**Ground silica**

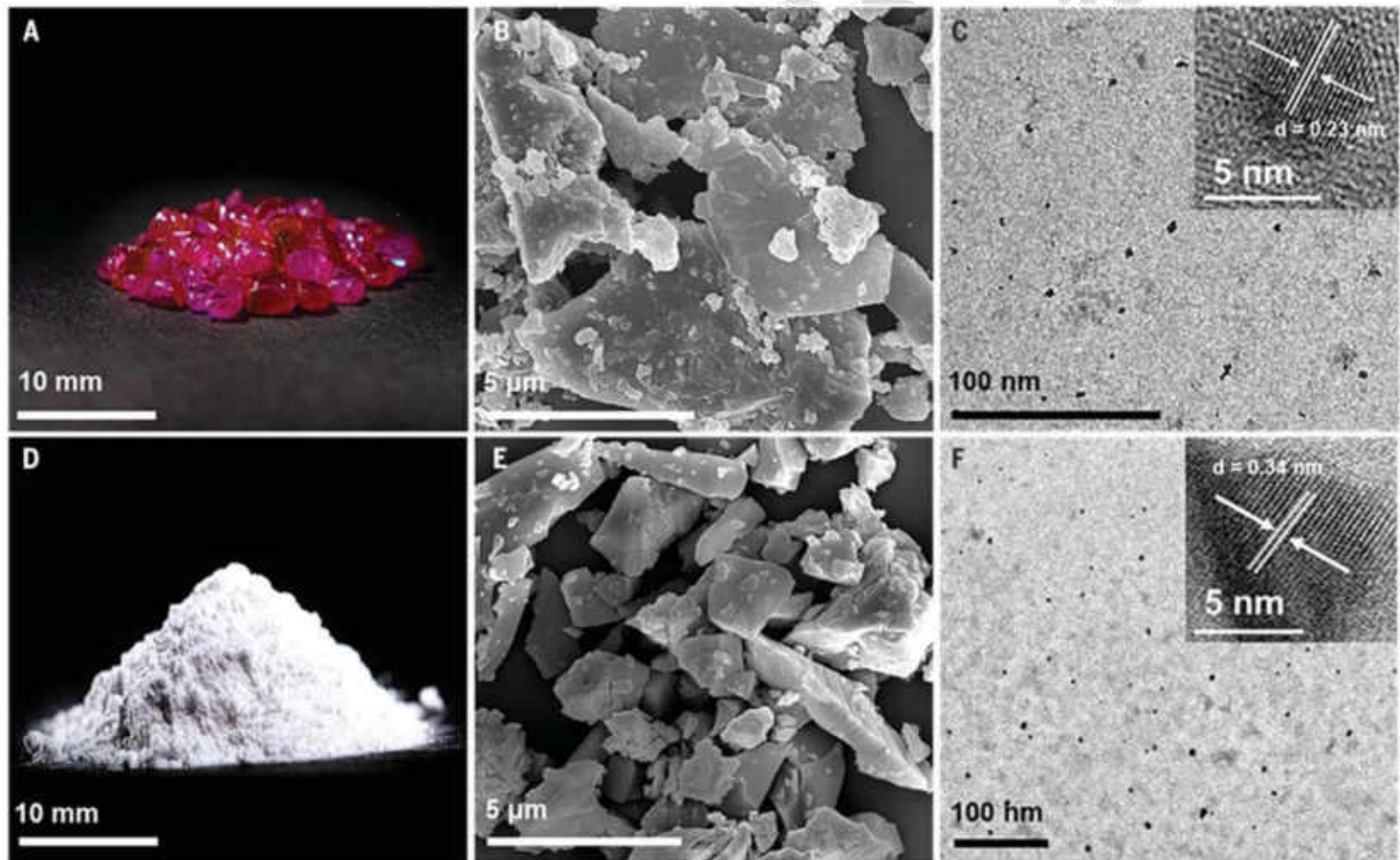


**Optical image of silica**

# Weathering of Minerals in Microdroplets

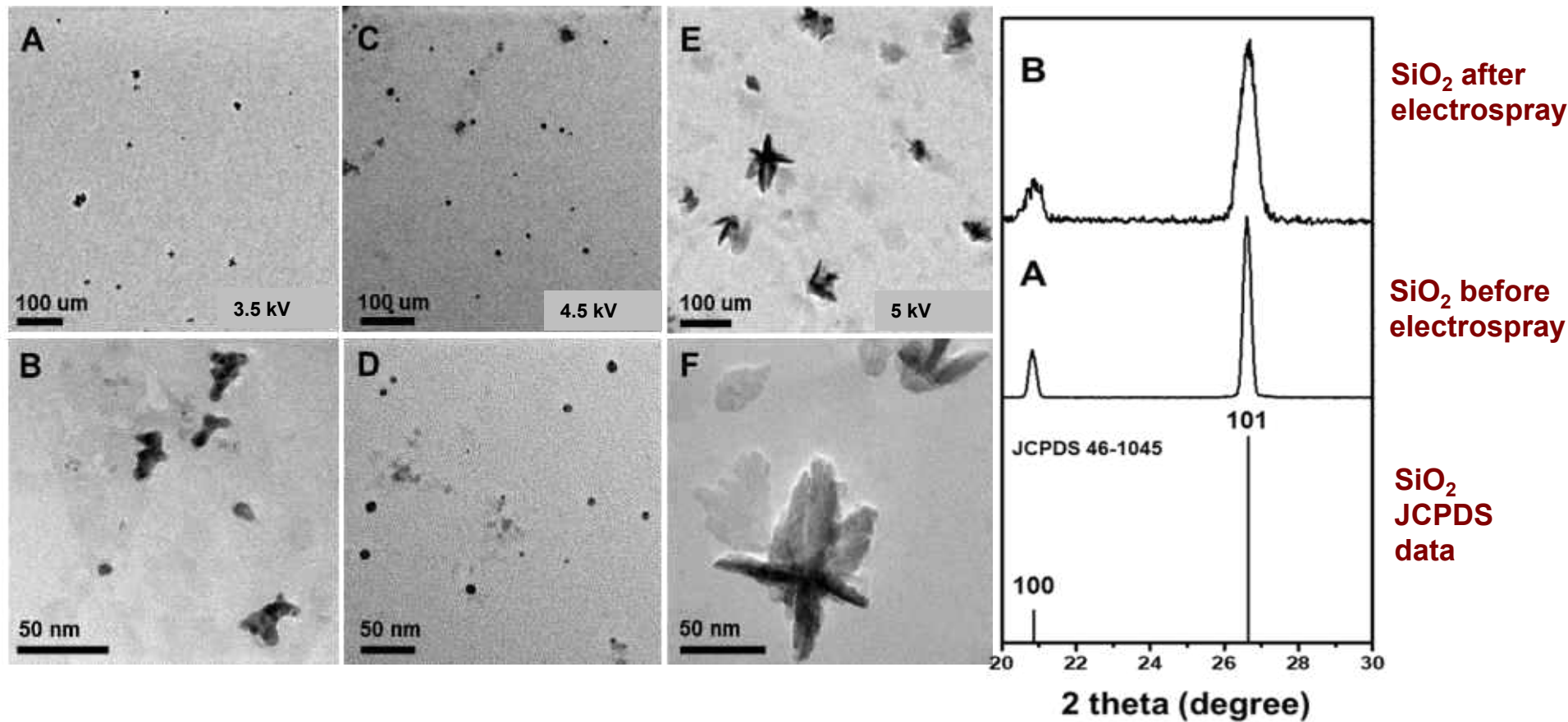


# Ruby, Fused Alumina



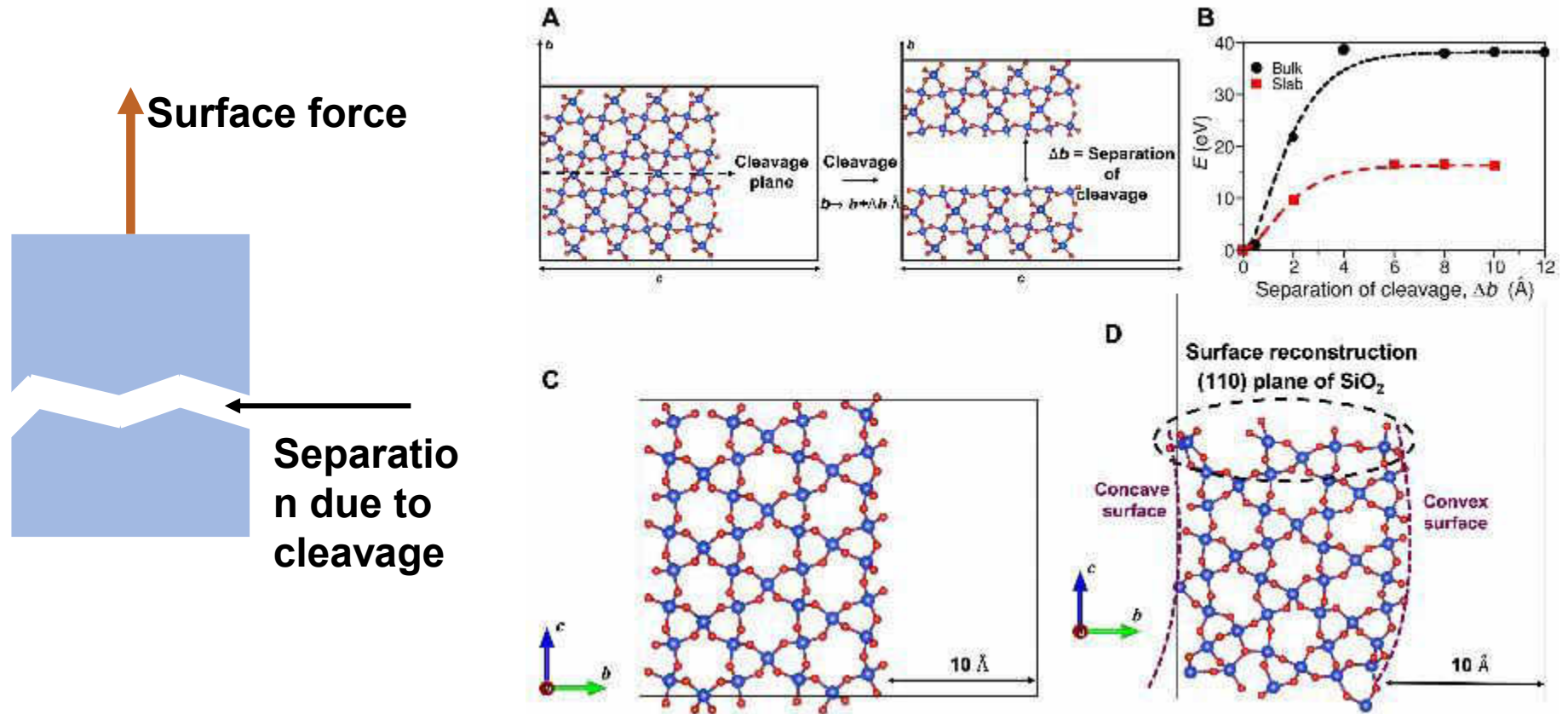


# Fragmentation of Silica – Varying Conditions

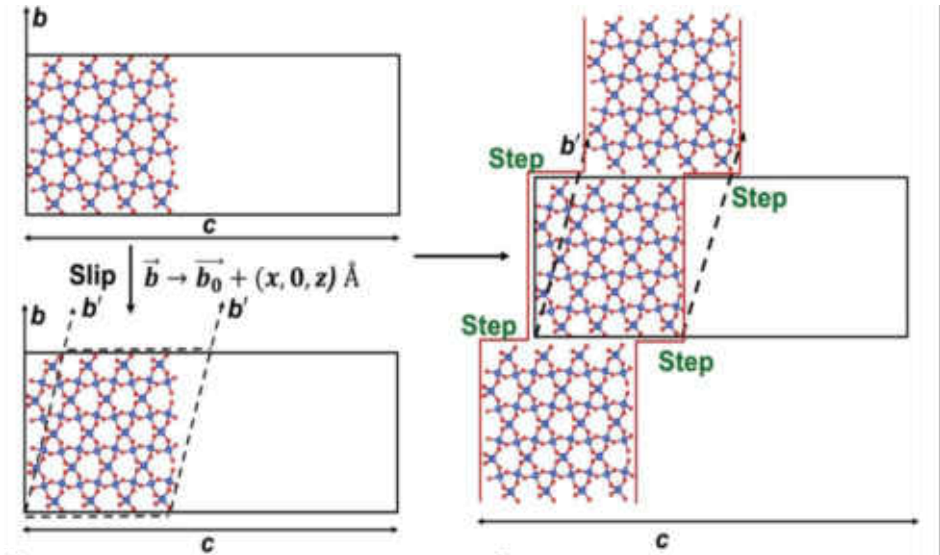
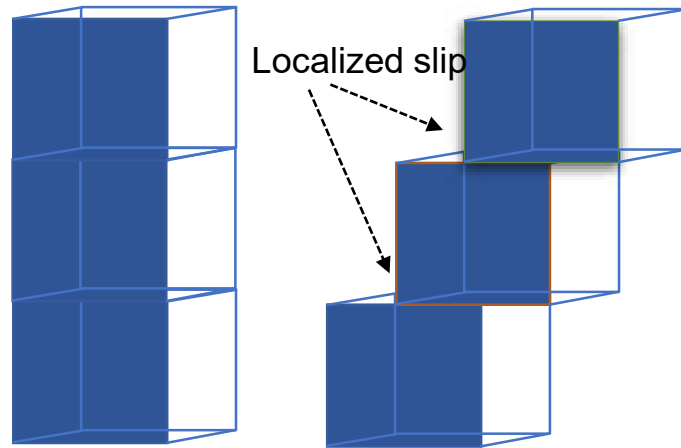


# Mechanism: Cleavage

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

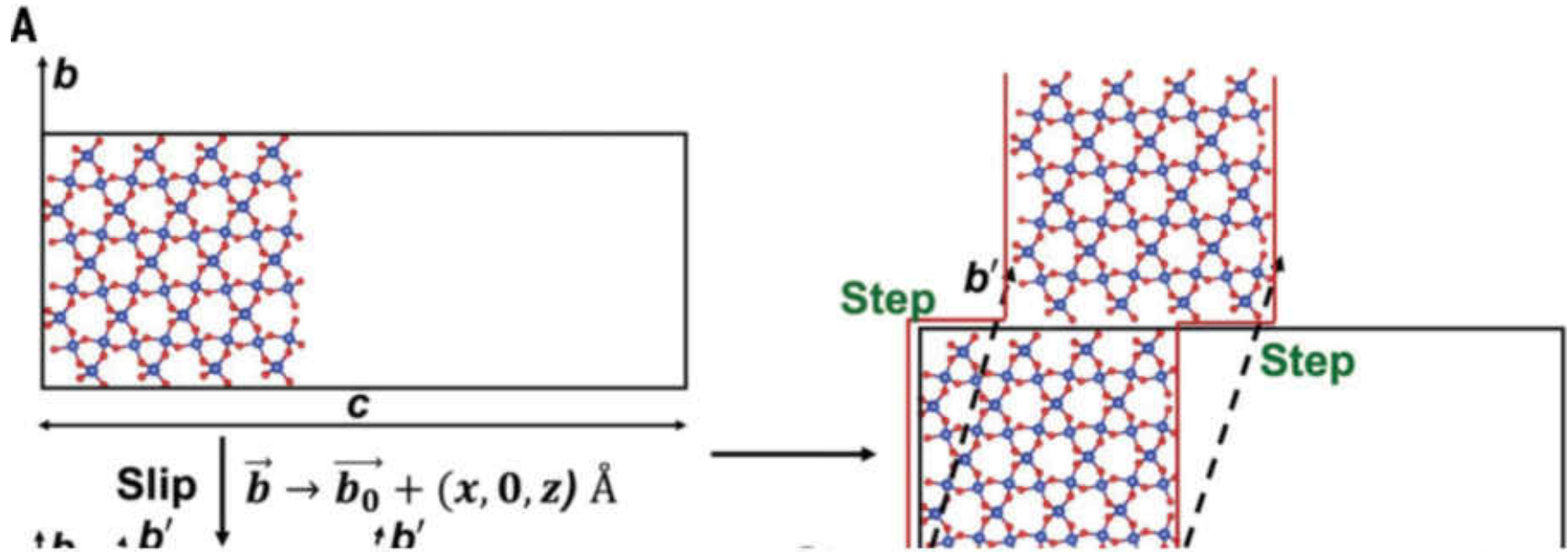
Stacking fault

$$\vec{b} \rightarrow \vec{b}_0 + (x, 0, z).$$

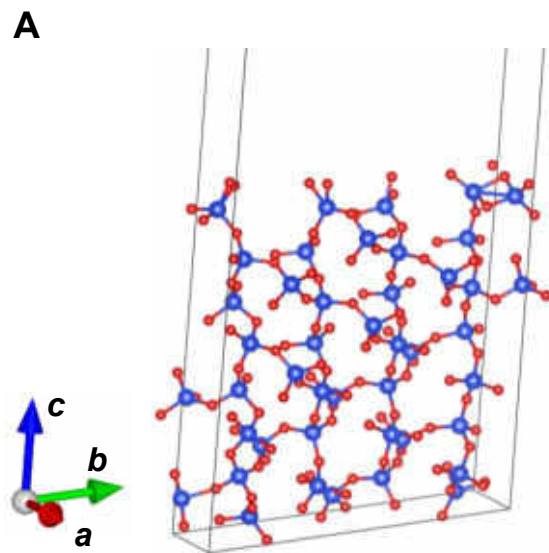
$(x, z \in [0, 1])$  - fractional coordinates

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<sub>2</sub>

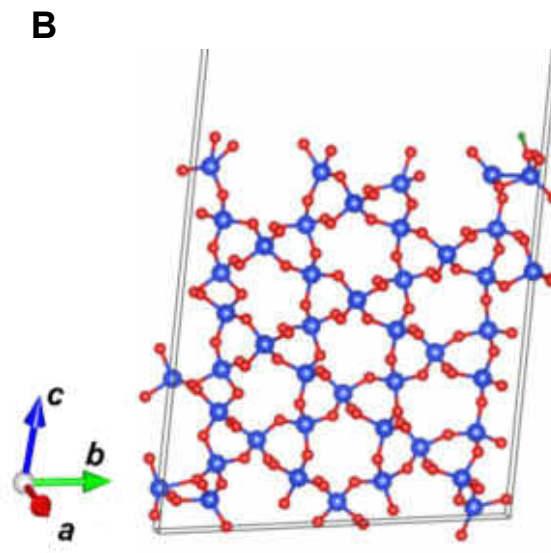
SFE ( $J/m^2$ )	Slab					
	$x$	$z$	w/o H-atom	1 H-atom	2 H-atoms	$E$
	0.0	0.0	0	0	0	0
	<b>0.5</b>	<b>0.5</b>	<b>-1.21</b>	<b>-0.93</b>	<b>-0.88</b>	<b>-1.20</b>
	0.5	0.0	1.20	1.18	0.90	1.12
	<b>0.0</b>	<b>0.5</b>	<b>-0.07</b>	<b>0.89</b>	<b>-0.83</b>	<b>-0.09</b>



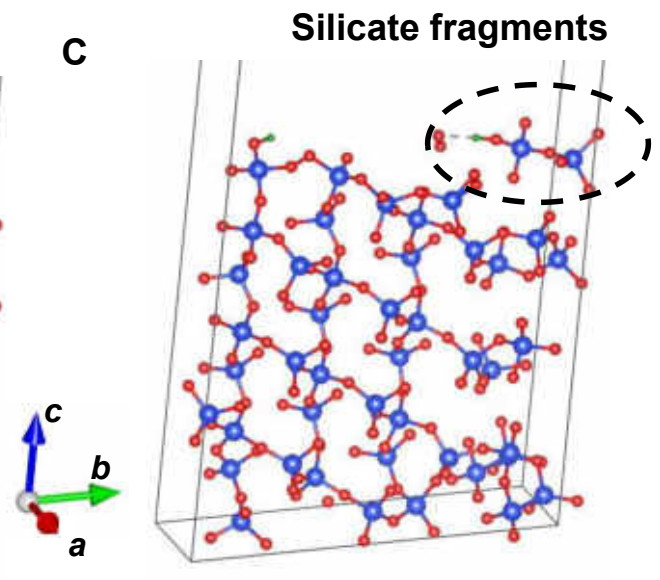




**No H-atom**

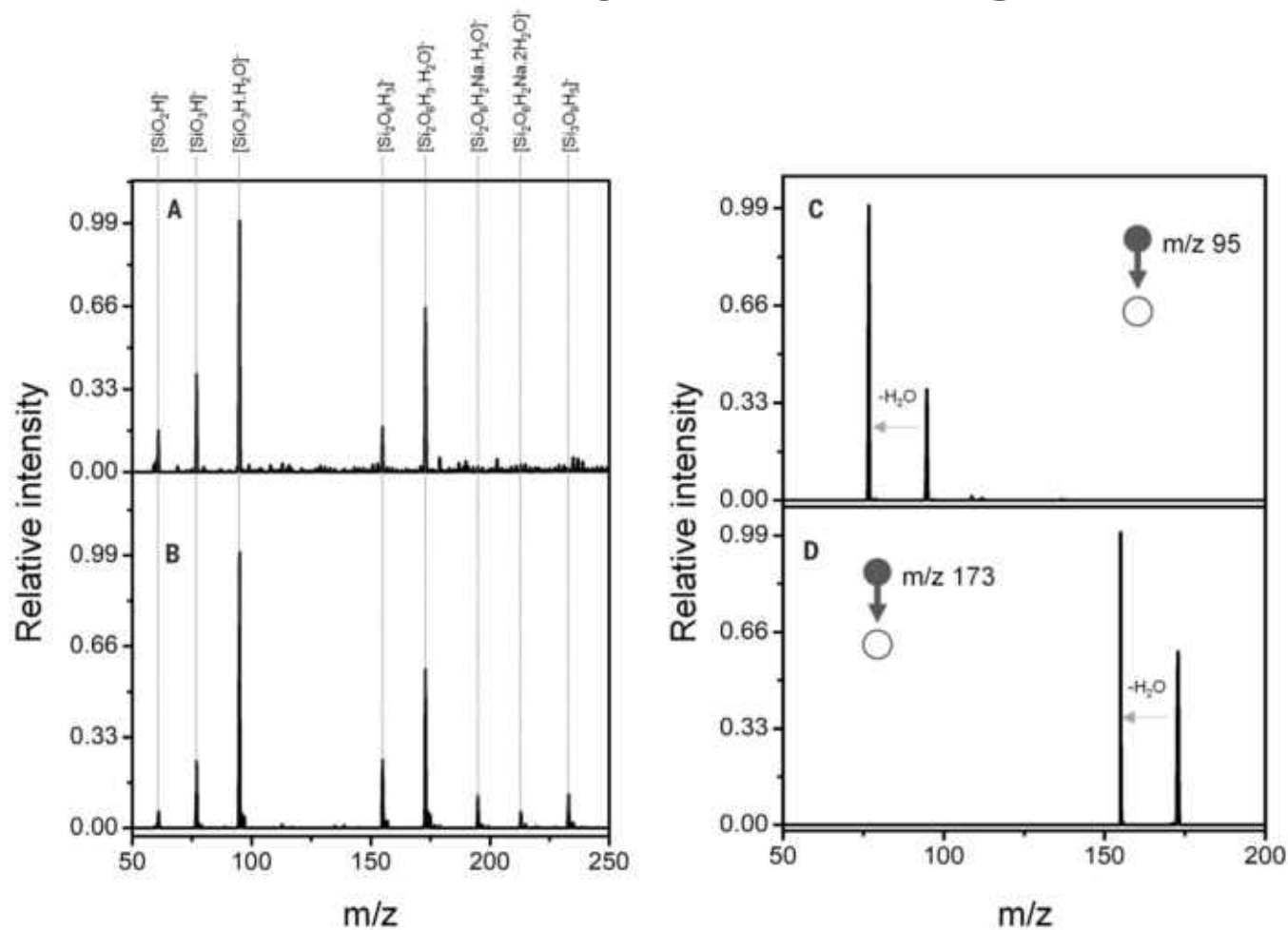


**One H-atom**

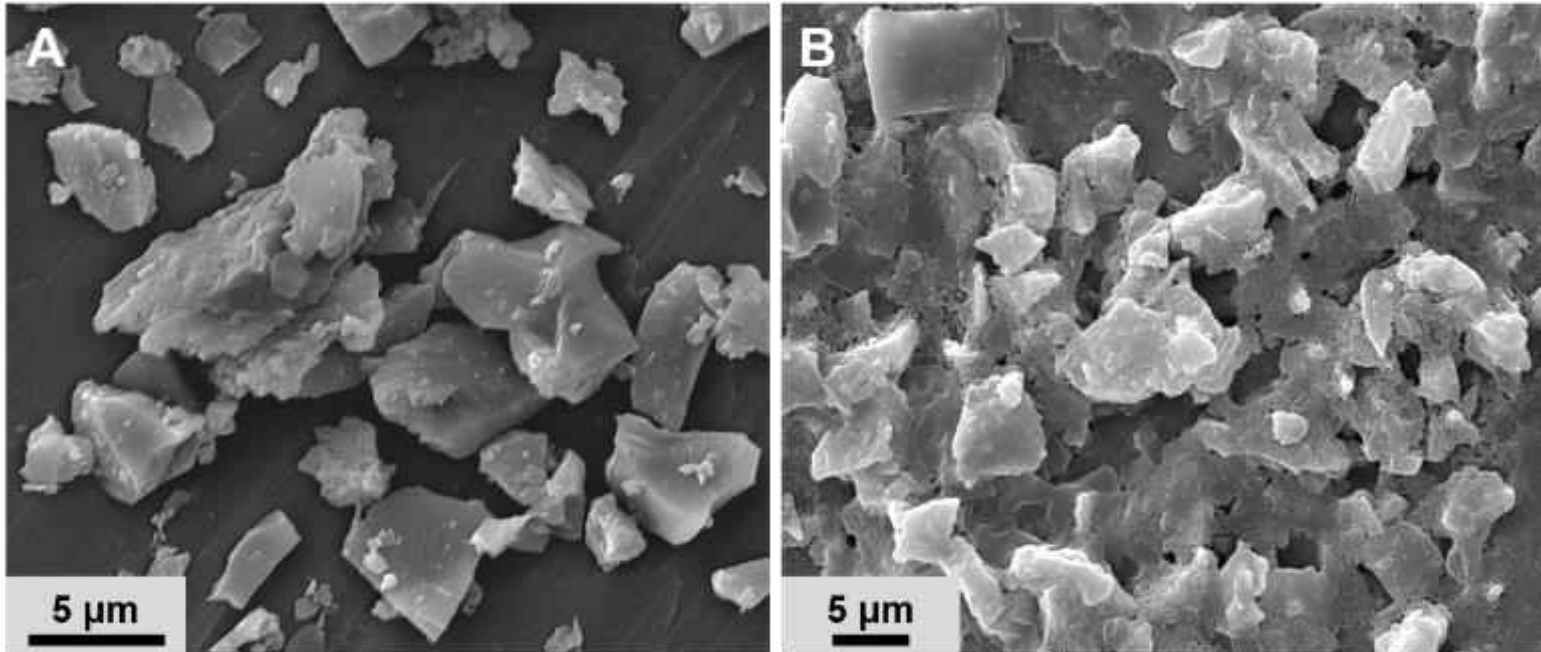


**Two H-atoms**

# Mass Spectrometry of the Fragments

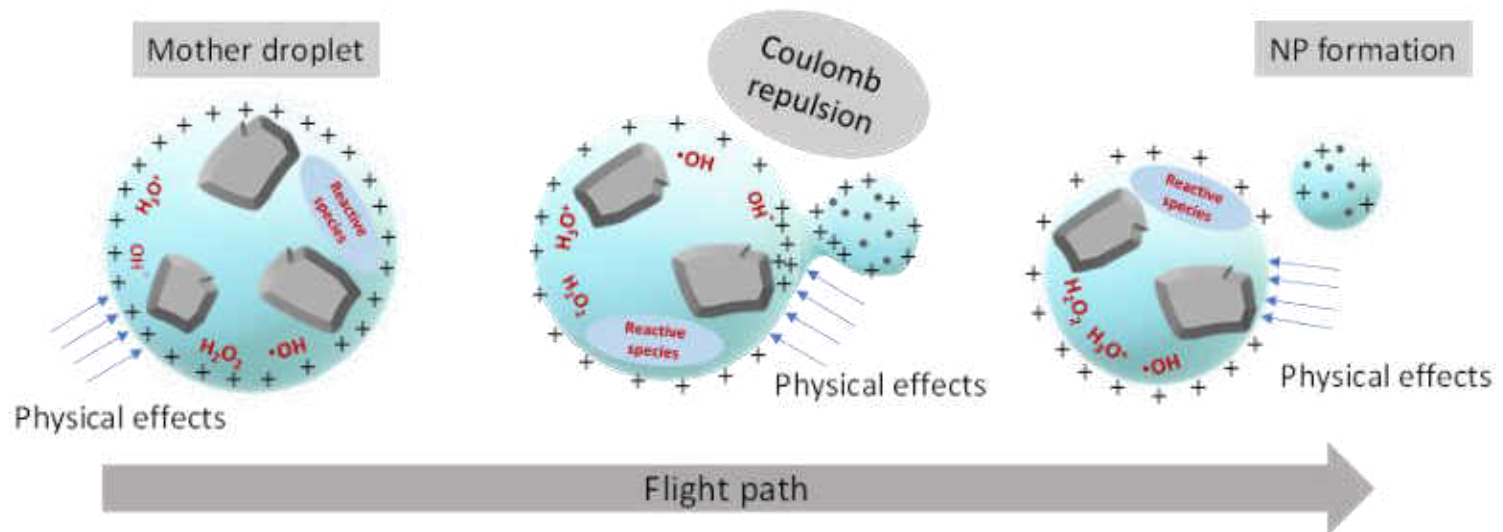


# Effect of charged microdroplets on quartz



Increased surface roughness after the spray

# Mechanism of nanoparticle formation





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

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

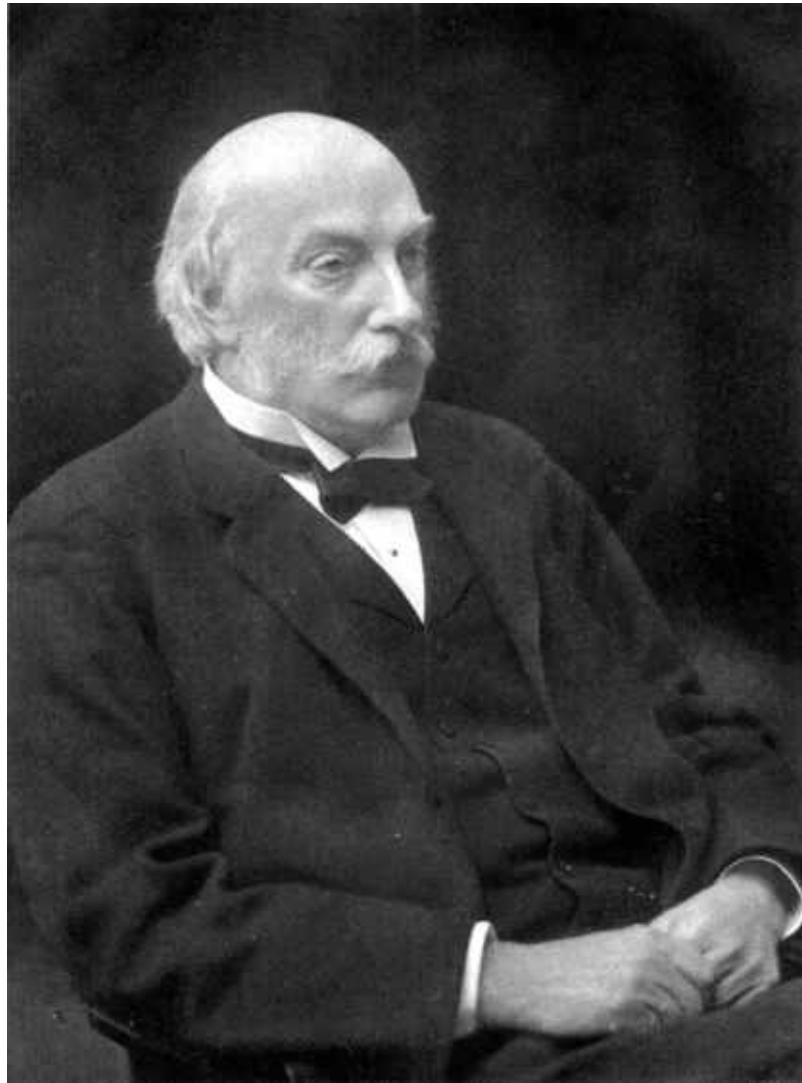
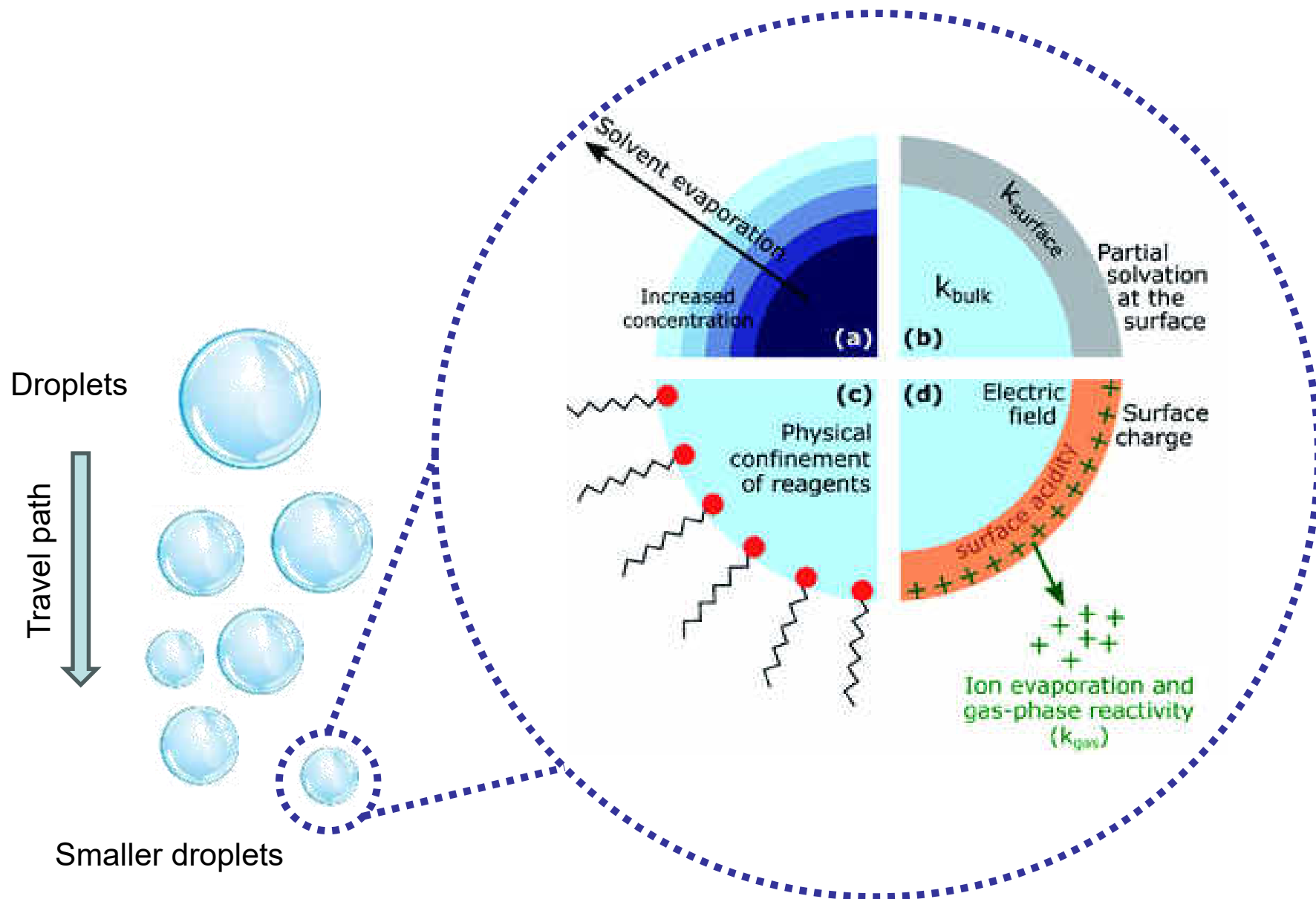


Image from Wikipedia

# Understanding Microdroplets



## 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 what is 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 102 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  $\mu\text{m}$  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 ( $\text{H}_3\text{O}^+$ ) concentration at the interface derived from fleetingly charged surface water molecules ( $\text{H}_2\text{O}^+/\text{H}_2\text{O}^-$ ) coexists with oxidative species such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and  $\text{OH}^\bullet$ . These redox species enable a variety of spontaneous chemical trans-

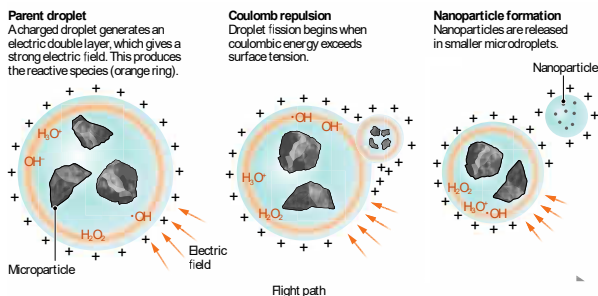
formations, including carbon-oxygen (O) bond cleavage in phosphonates, which yields the corresponding phosphonic acid (7), and in the Baeyer-Villiger oxidation of aryl ketones to give esters (8). These considerations thereby enable simultaneous acid-base and oxidation-reduction chemistry in a single 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 (7). 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

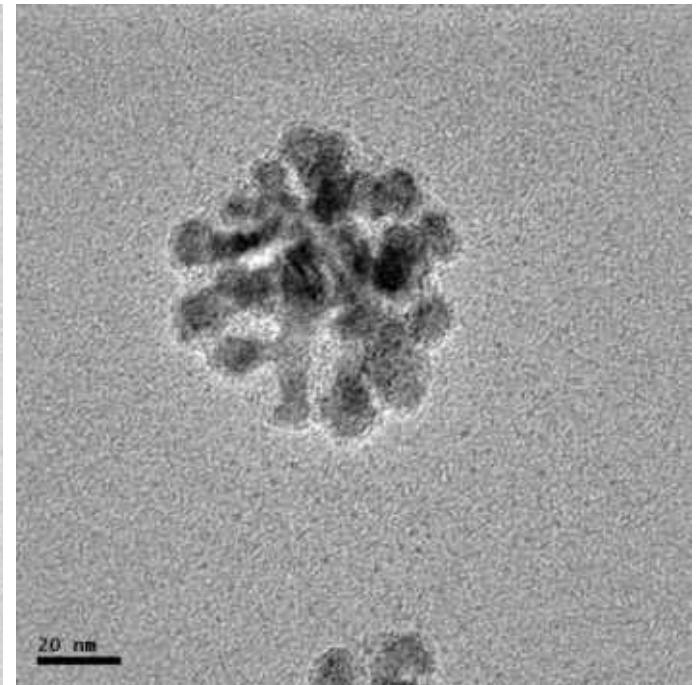
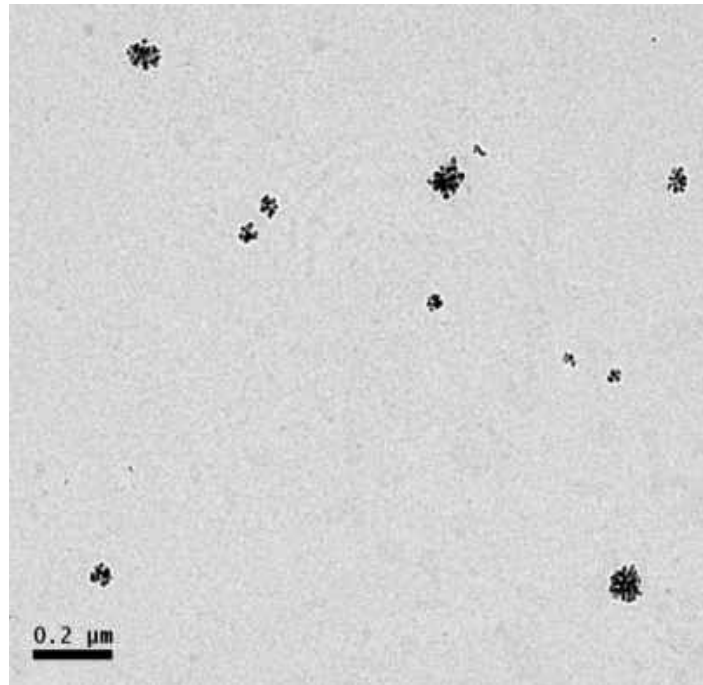
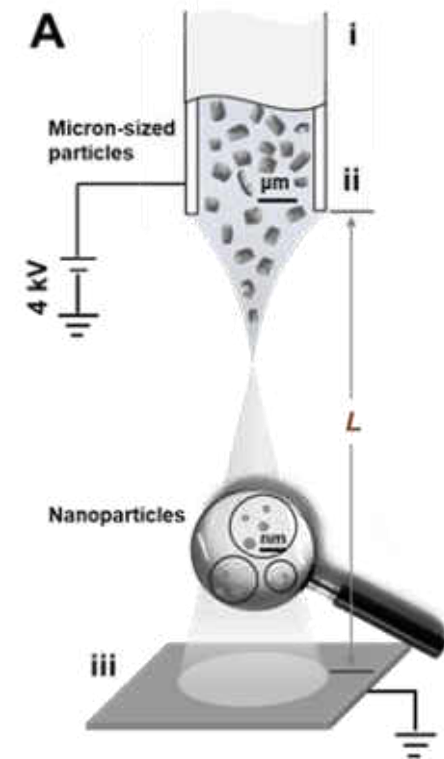
Reactions that promote mineral disintegration are accelerated at the air-water interface of microdroplets. Key reactive species are the result of the effects of a high electric field at the surface of the water droplets.



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

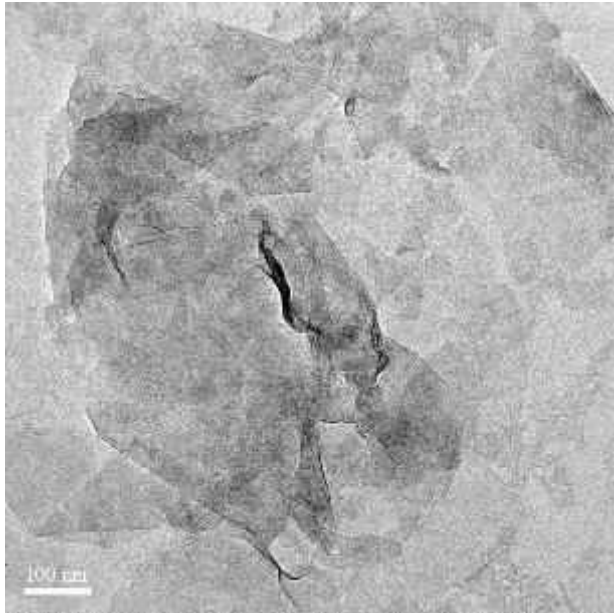


# How do they form?



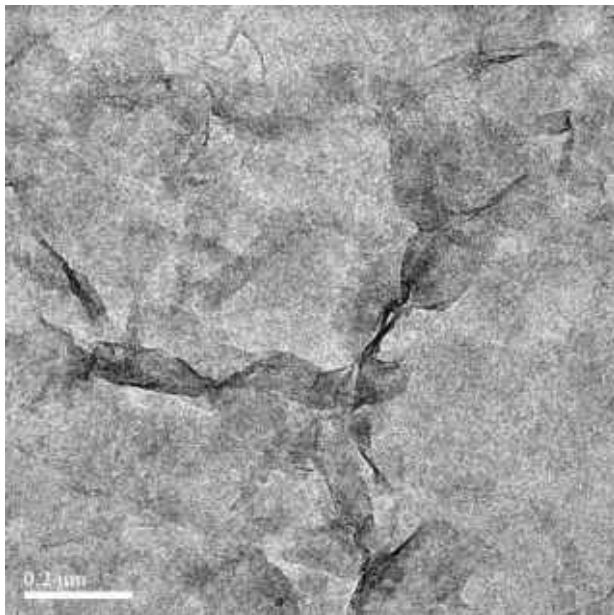


# MoS<sub>2</sub> Nanosheets

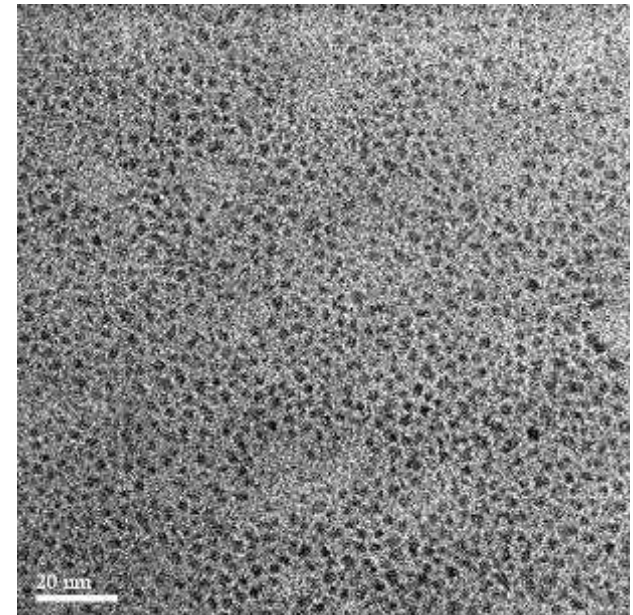
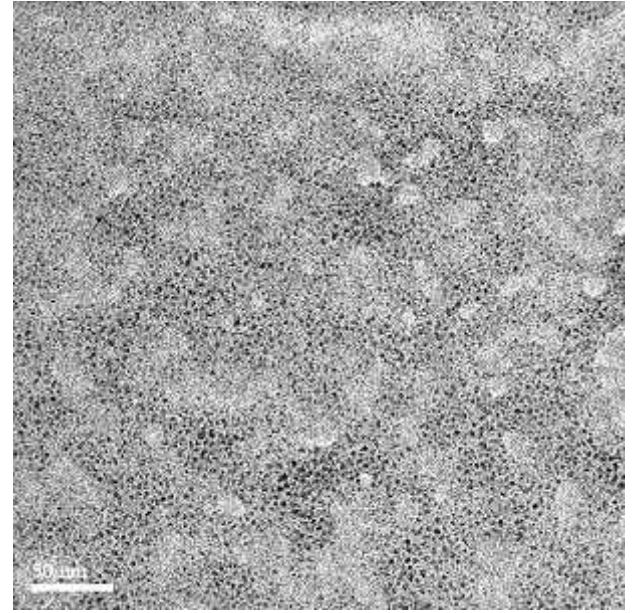


**Ambient electrospray**

Solvent: Water  
Potential: 3.0 kV

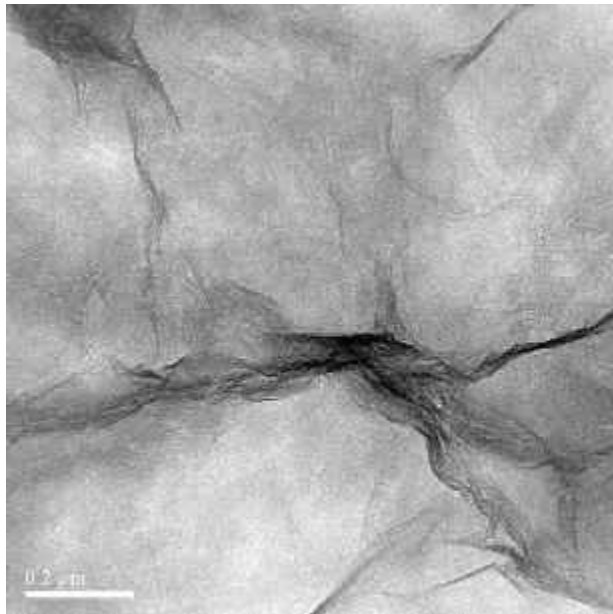
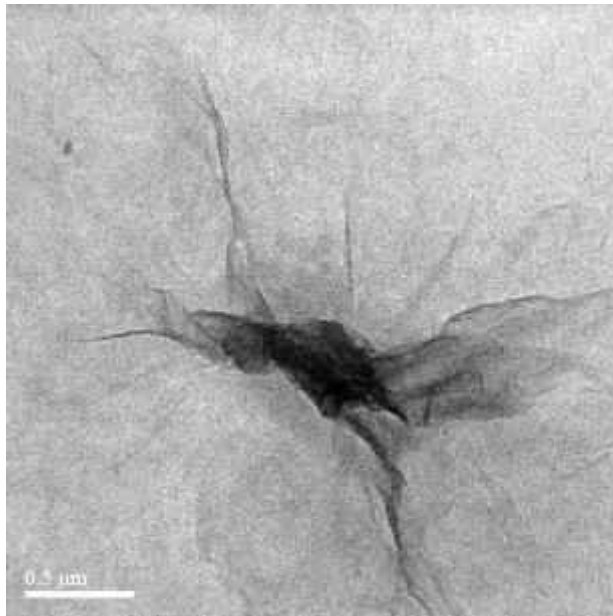


MoS<sub>2</sub> Nanosheet



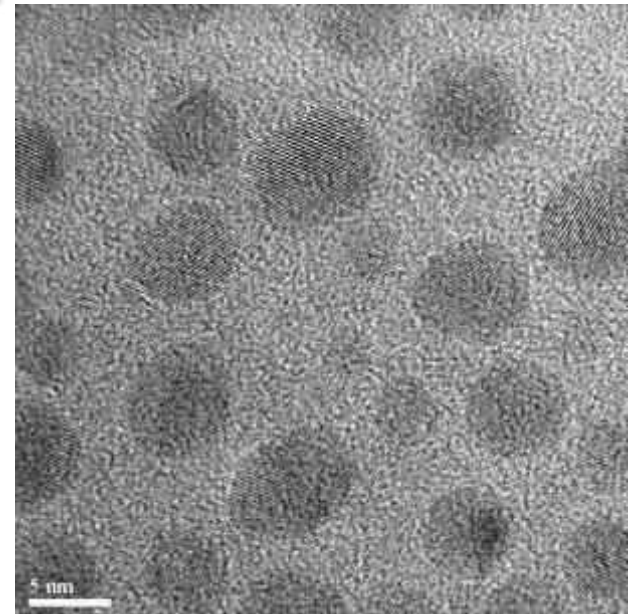
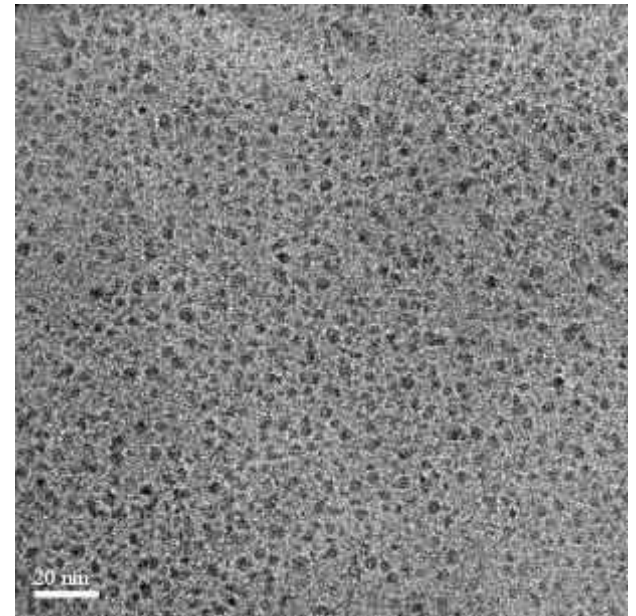
MoS<sub>2</sub> Nanoparticles

# Graphene Oxide



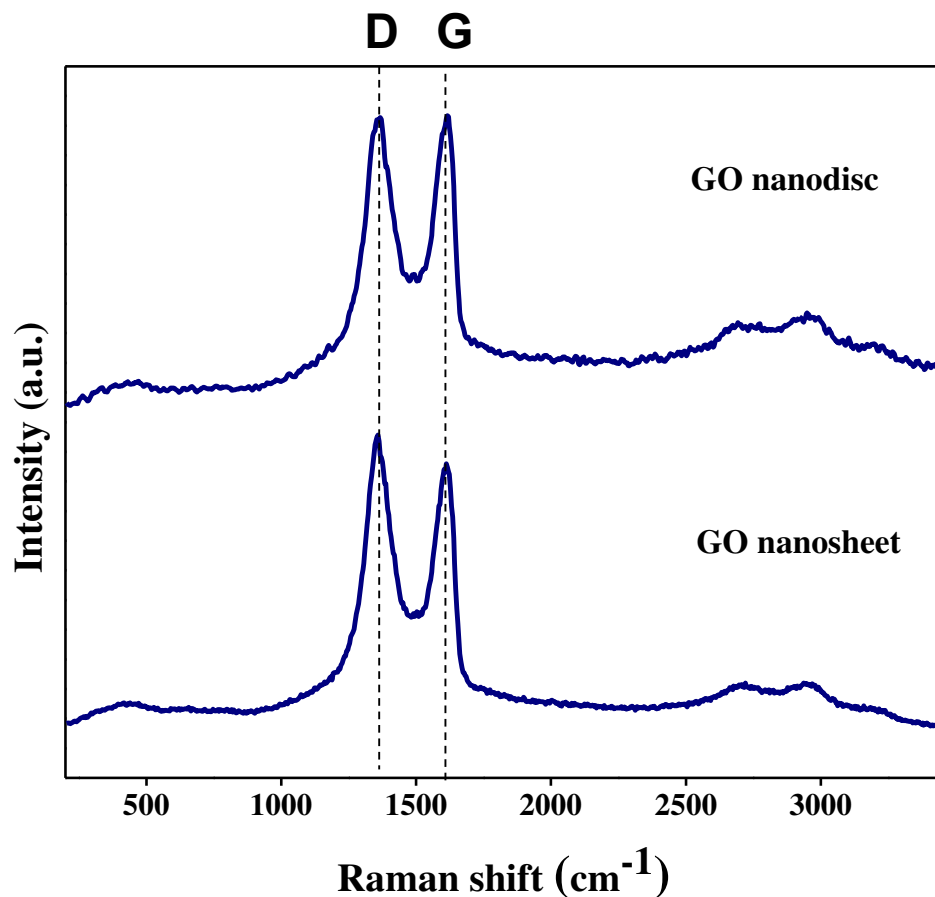
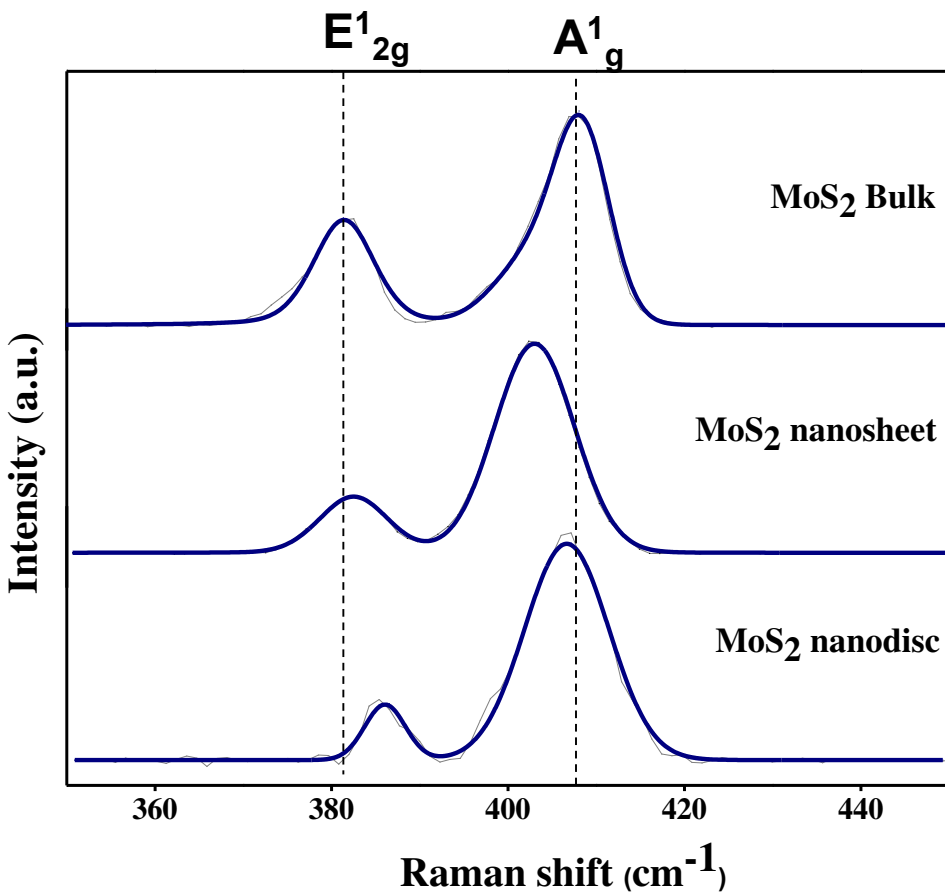
Graphene oxide nanosheet

Ambient  
electrospray



Graphene oxide nanodiscs

# Raman Spectra of MoS<sub>2</sub> and Graphene Oxide Nanosheets

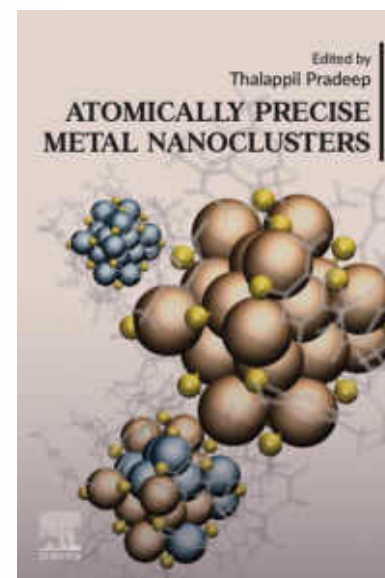
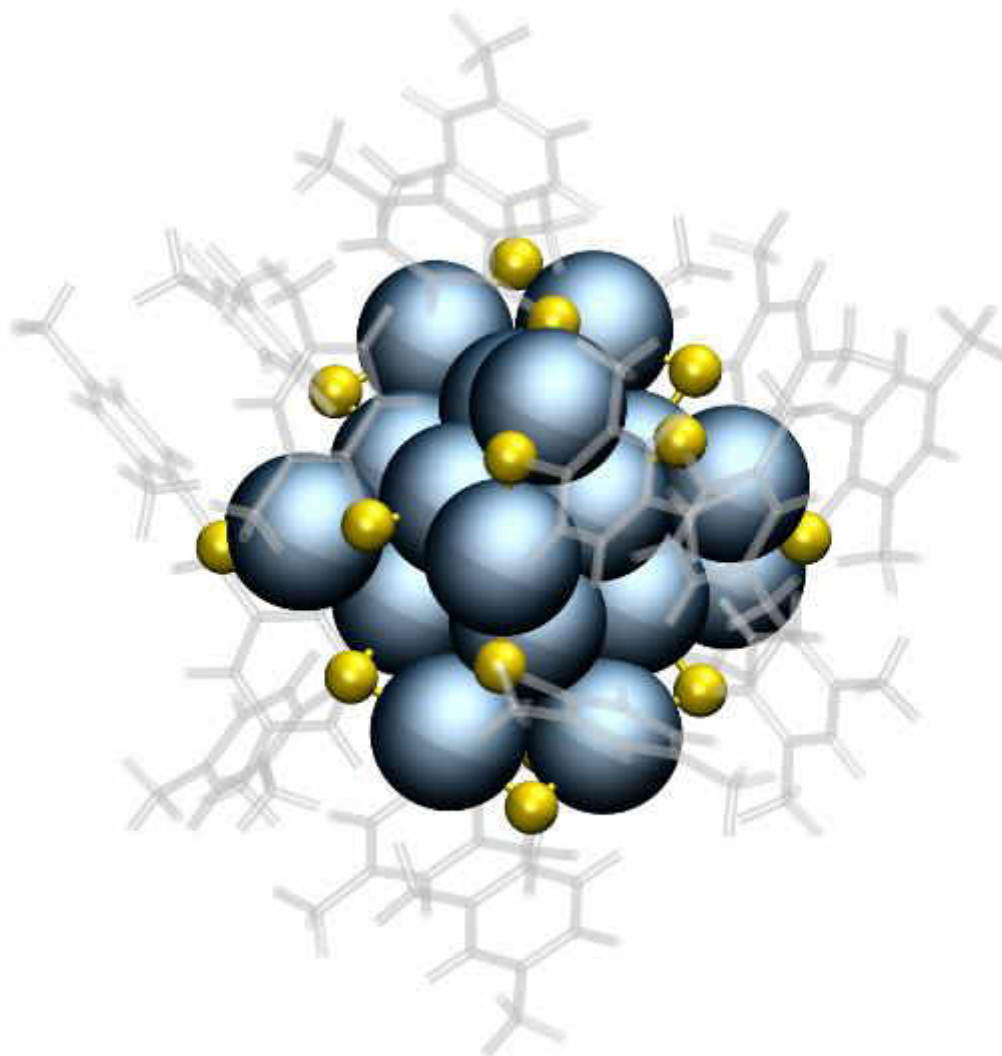


Relative peak intensity

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

# New molecules

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$\text{Au}_{25}$ ,  $\text{Ag}_{25}$ ,  $\text{Ag}_{29}$

# Carboranethiol-protected $\text{Ag}_{17}$ , $\text{AuAg}_{16}$ , $\text{Ag}_{13}\text{Cu}_4$ and $\text{AuAg}_{12}\text{Cu}_4$ Nanoclusters

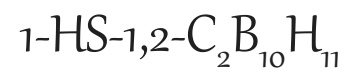
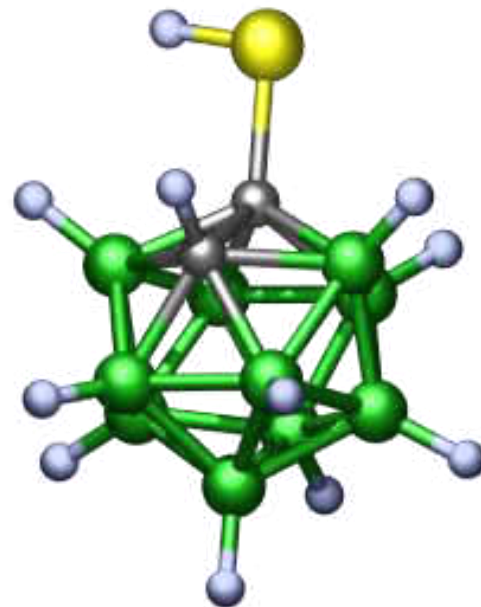
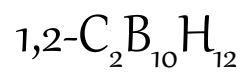
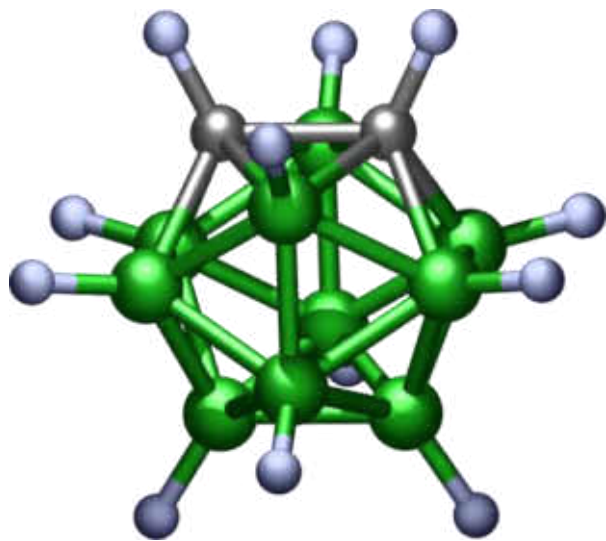
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Vivek Yadav  
Prime Minister's Research Fellow  
c/o Prof. T. Pradeep  
Department of Chemistry  
Indian Institute of Technology Madras  
India

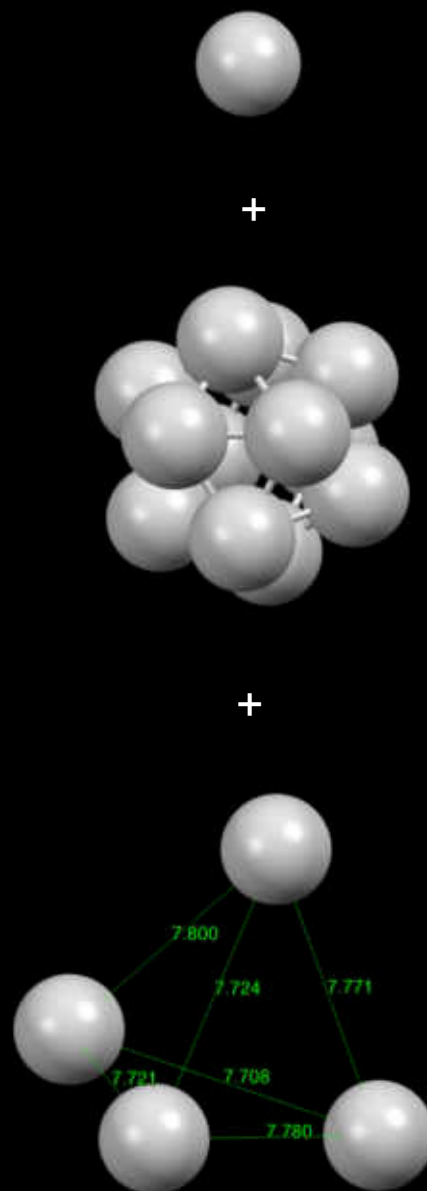
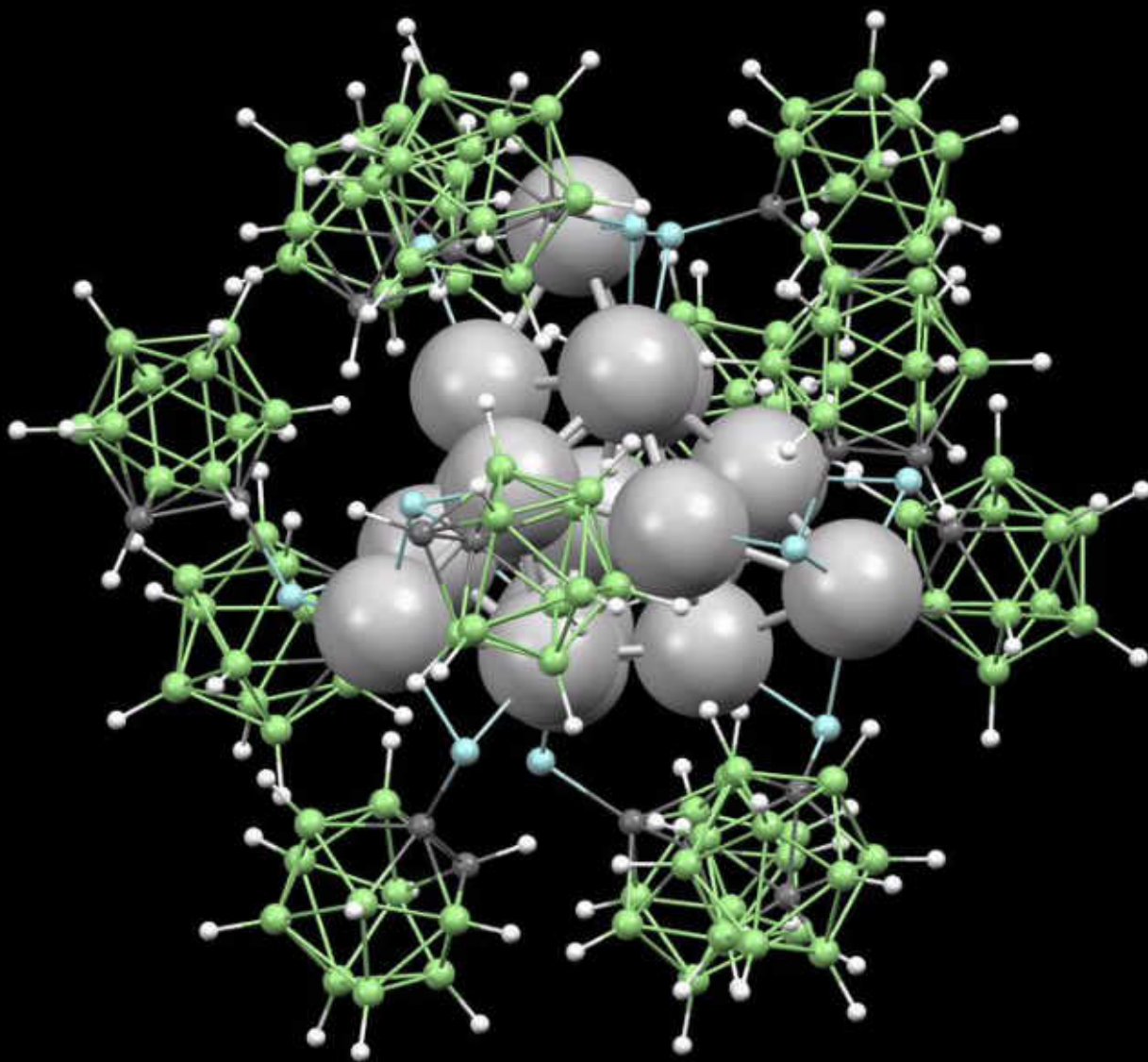
Vivek Yadav et al., *Nature Communications*, Revised and submitted.



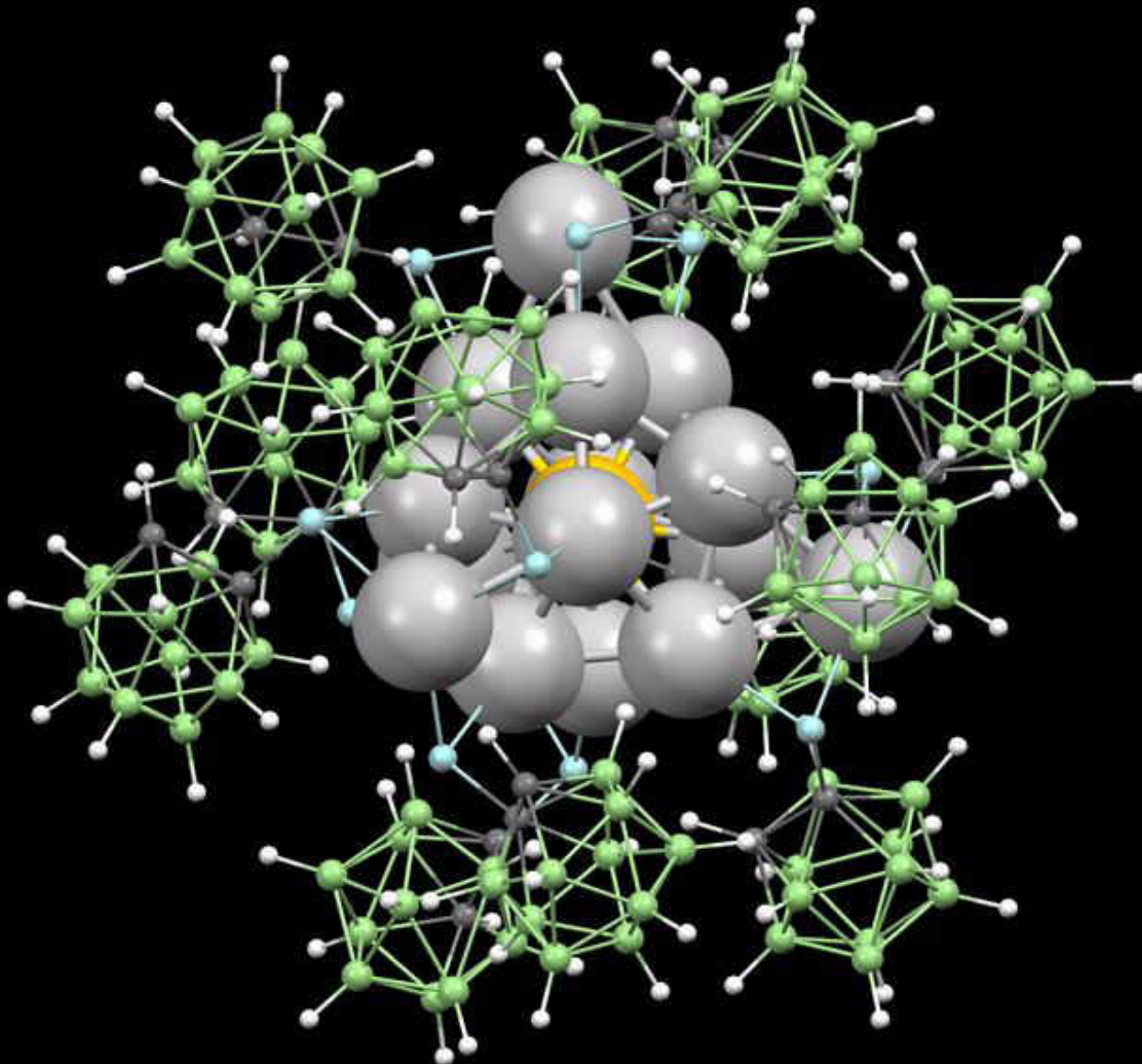
## About the Ligand



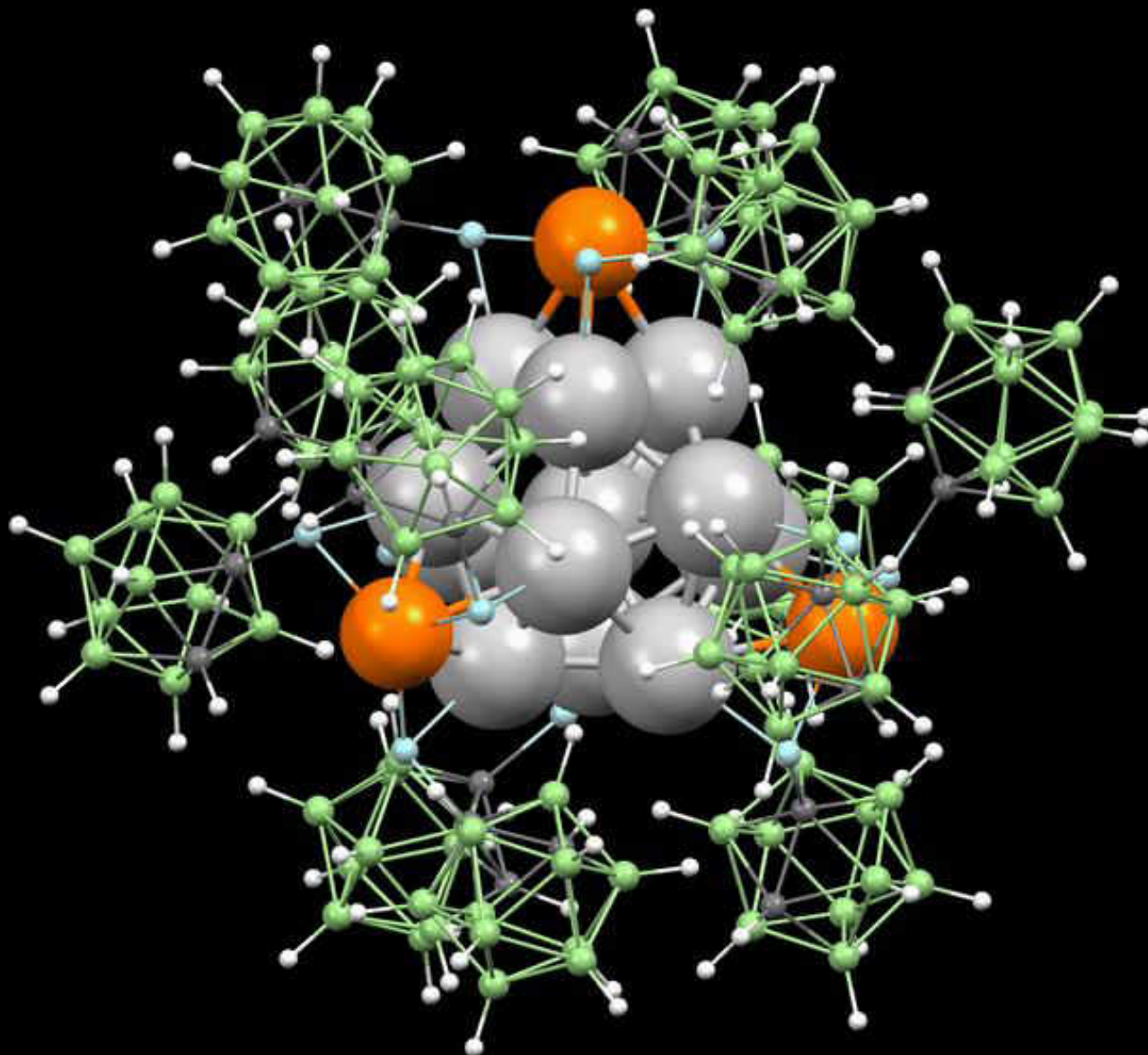
# Structure of $[\text{Ag}_{17}(\text{o}_1\text{-CBT})_{12}]^{3-}$ Nanocluster



# Structure of AuAg<sub>16</sub> Nanocluster

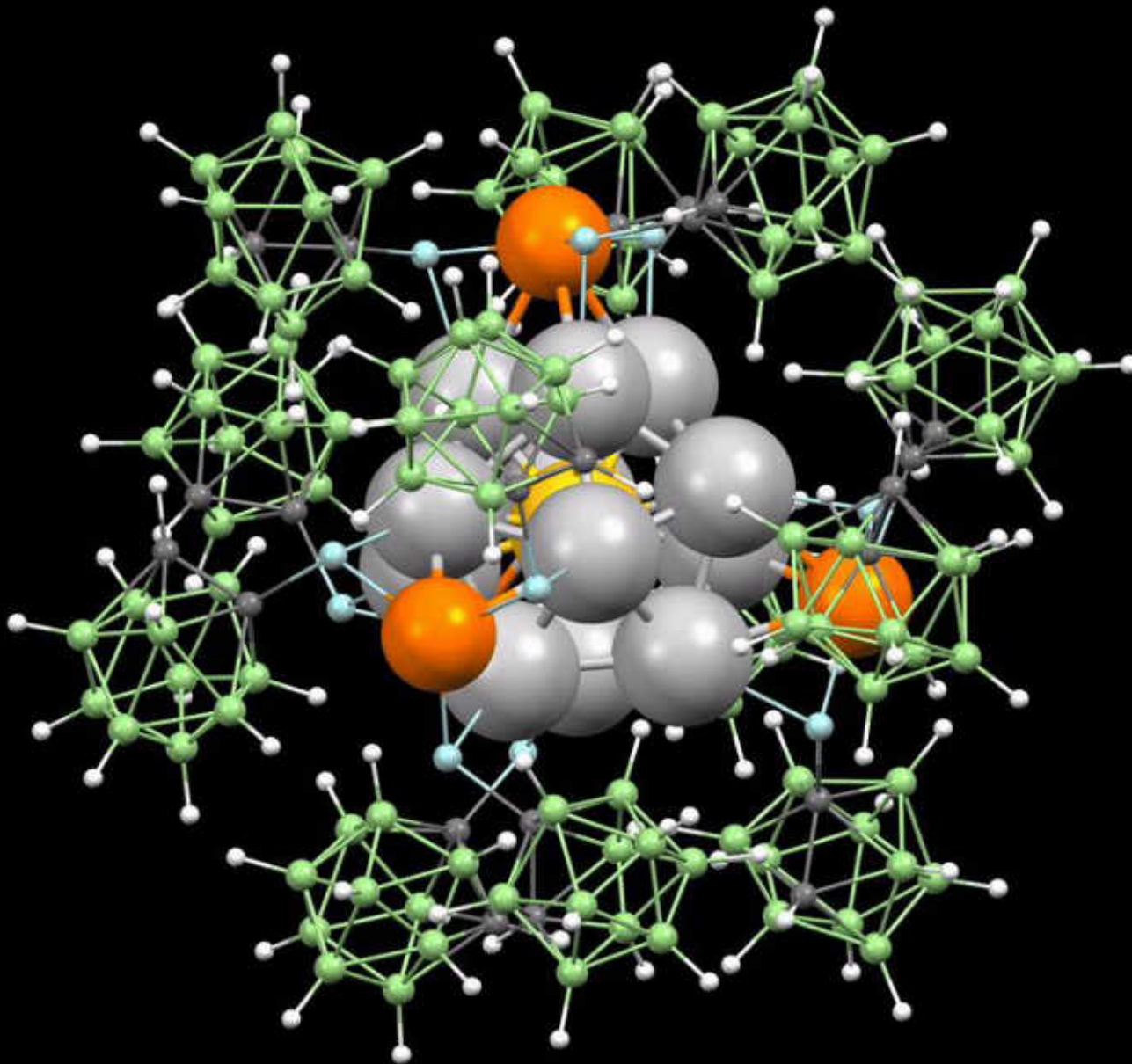


# Structure of $\text{Ag}_{13}\text{Cu}_4$ Nanocluster



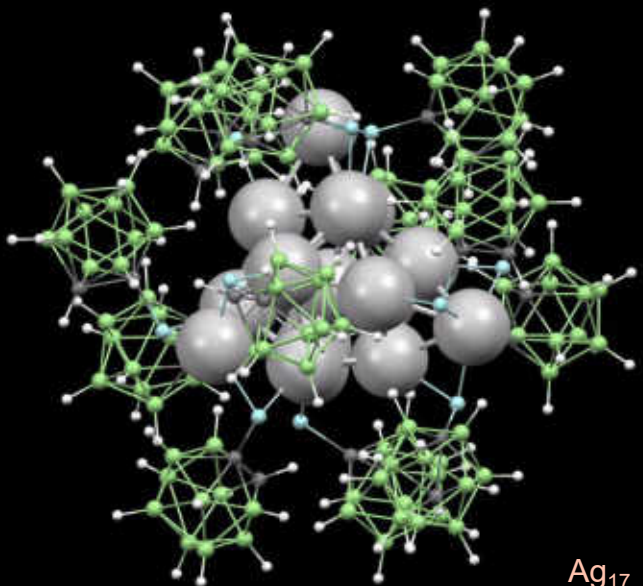


# Structure of AuAg<sub>12</sub>Cu<sub>4</sub> Nanocluster

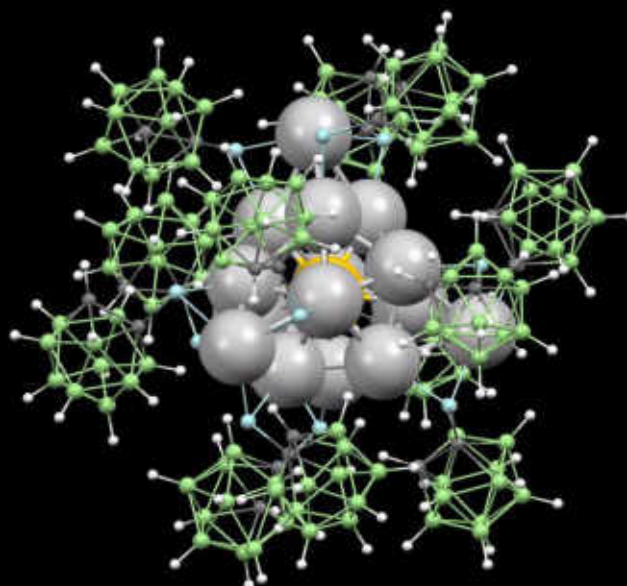




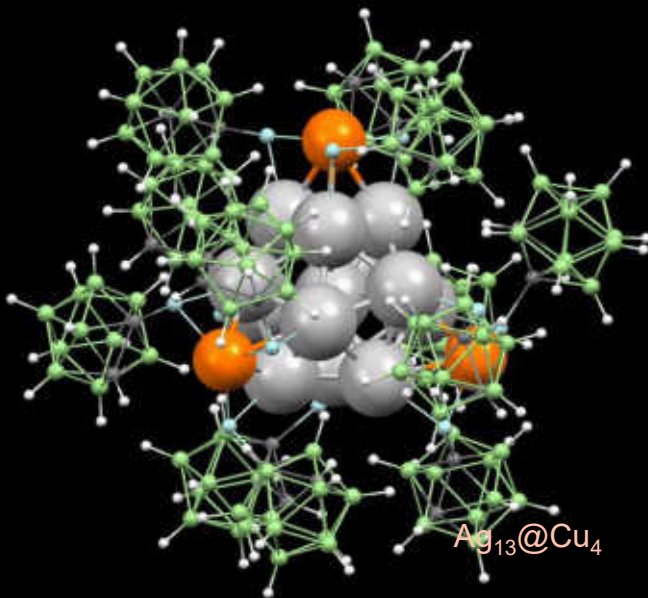
# Structure of $M_{17}$ Nanoclusters



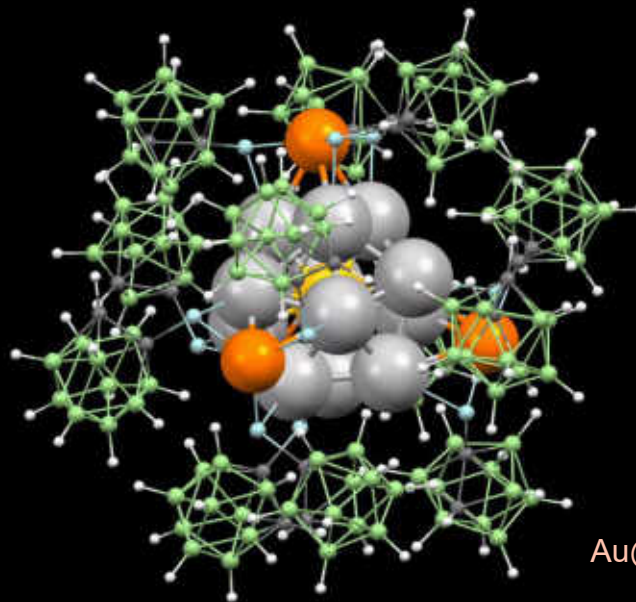
$Ag_{17}$



$Au@Ag_{16}$

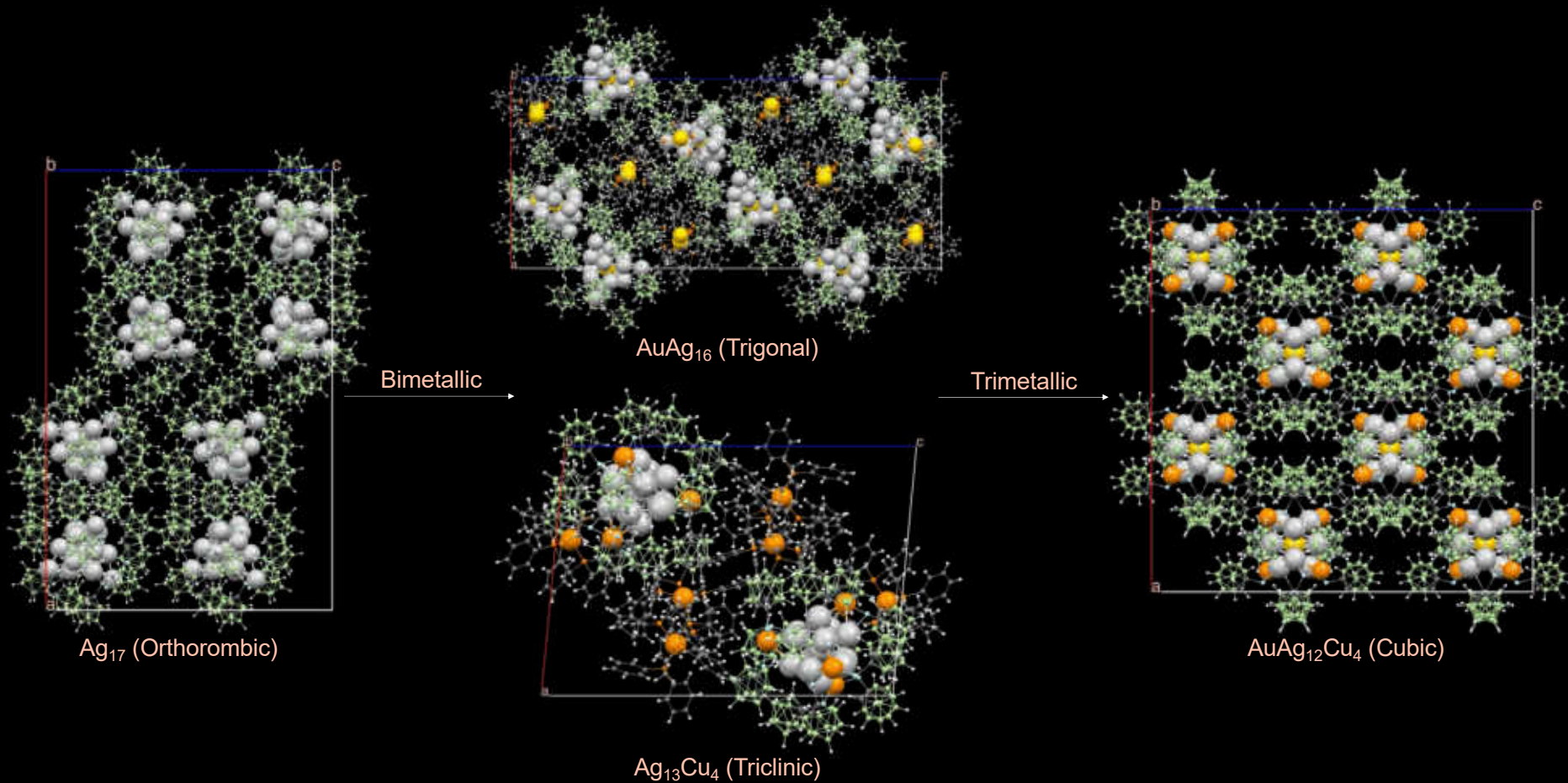


$Ag_{13}@Cu_4$



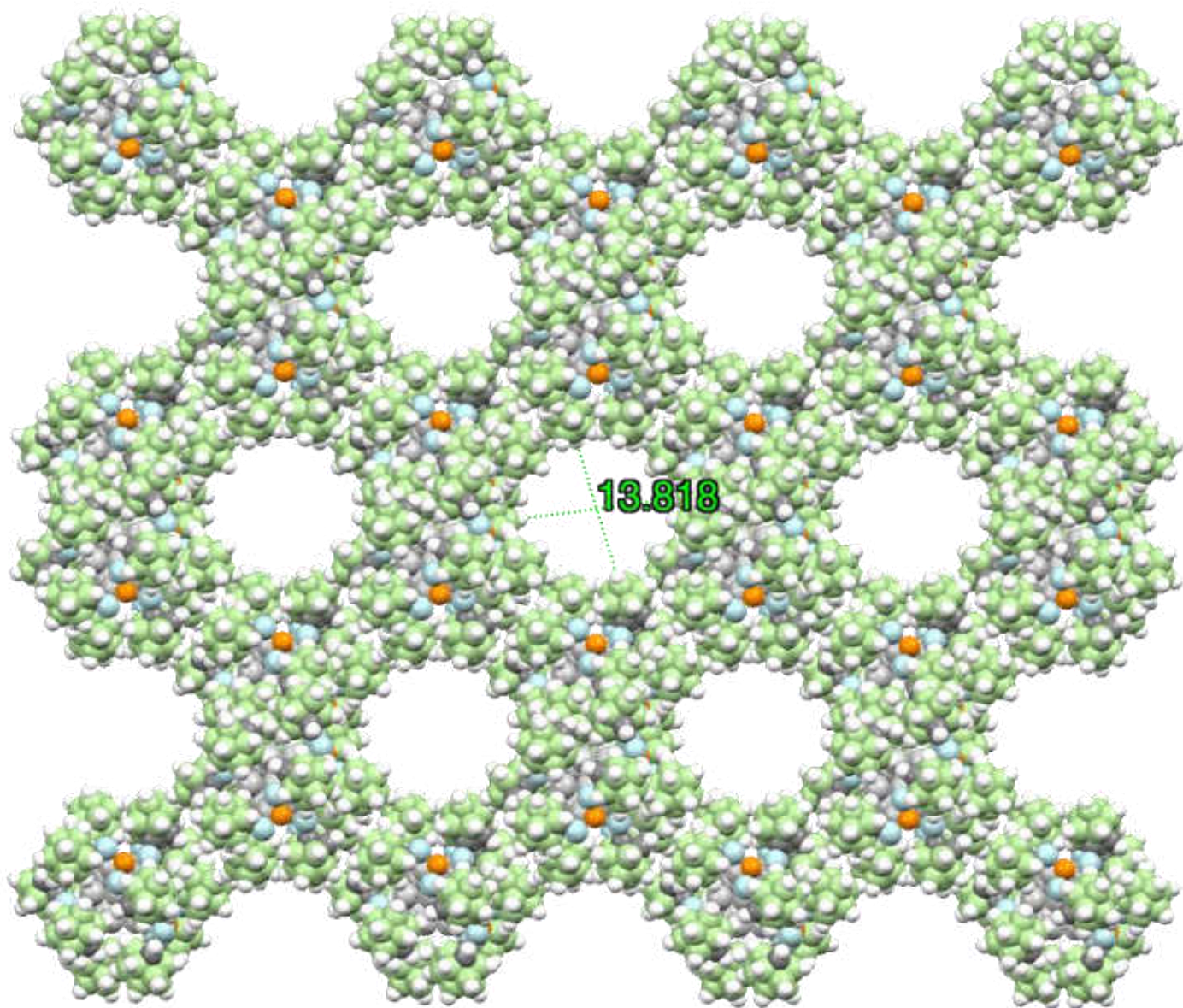
$Au@Ag_{12}@Cu_4$

# Packing of $M_{17}$ Nanoclusters





# Structural Pores of AuAg<sub>12</sub>Cu<sub>4</sub> Nanoclusters





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

Mohan Udhaya Sankar<sup>1</sup>, Sahaja Aigal<sup>1</sup>, Shihabudheen M. Maliyekkal<sup>1</sup>, Amrita Chaudhary, Anshup, Avula Anil Kumar, Kamalesh Chaudhari, and Thalappil Pradeep<sup>2</sup>

<sup>1</sup>Unit of Nanoscience and Thematic Unit of Ex

Edited by Eric Hoek, University of California,

Creation of affordable materials for cons water is one of the most promising way 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 can 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 ility. The ability to prepare nanostructu ambient temperature has wide releva water purification.

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



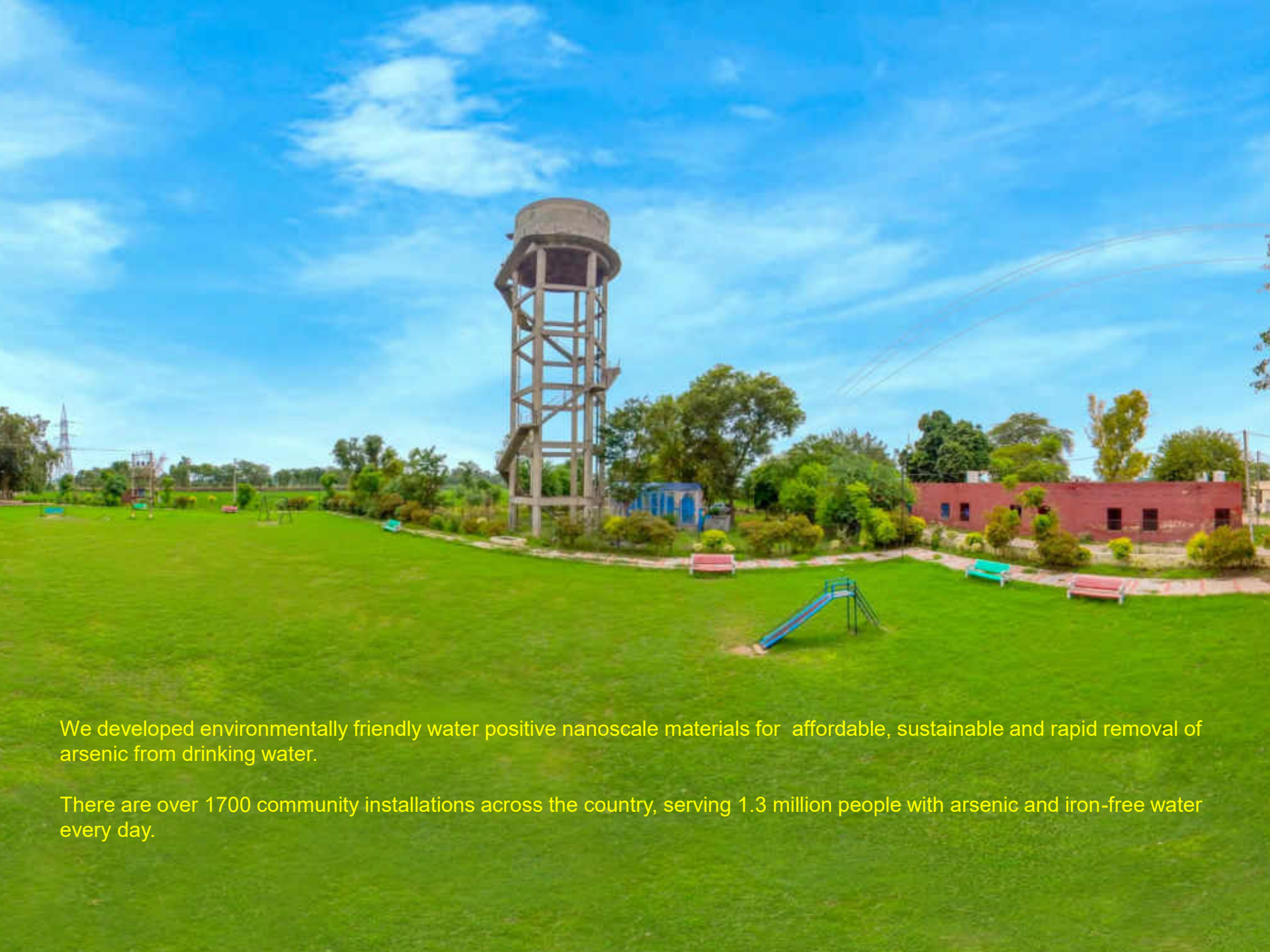
Madras, Chennai 600 036, India

(received for review November 21, 2012)

available; 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 ial antimicrobial activity in drinking osites have been developed that can its in water. We demonstrate an af- device based on such composites de- und undergoing field trials in India, as :spread eradication of the waterborne

RESULTS AND DISCUSSION

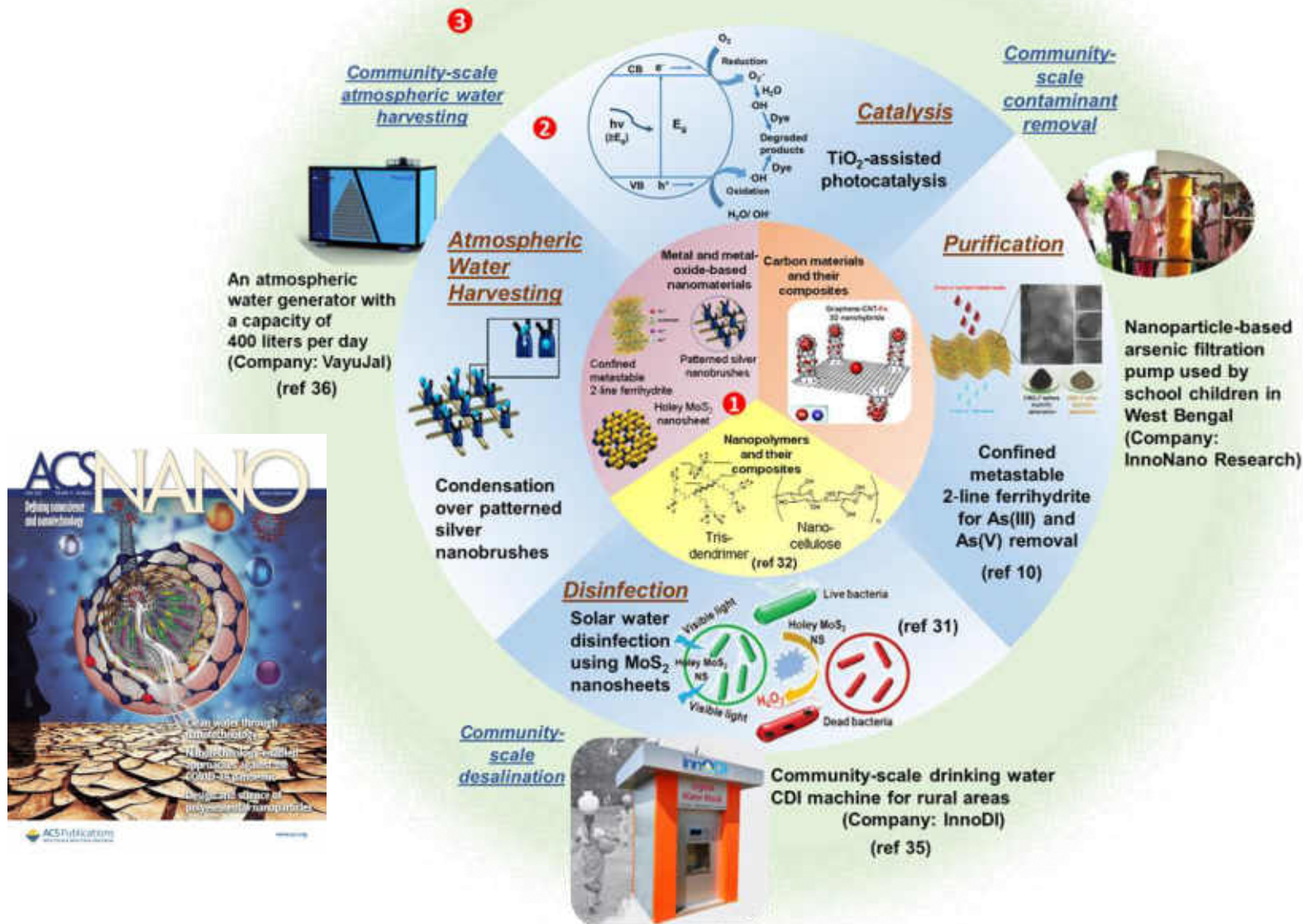




We developed environmentally friendly water positive nanoscale materials for affordable, sustainable and rapid removal of arsenic from drinking water.

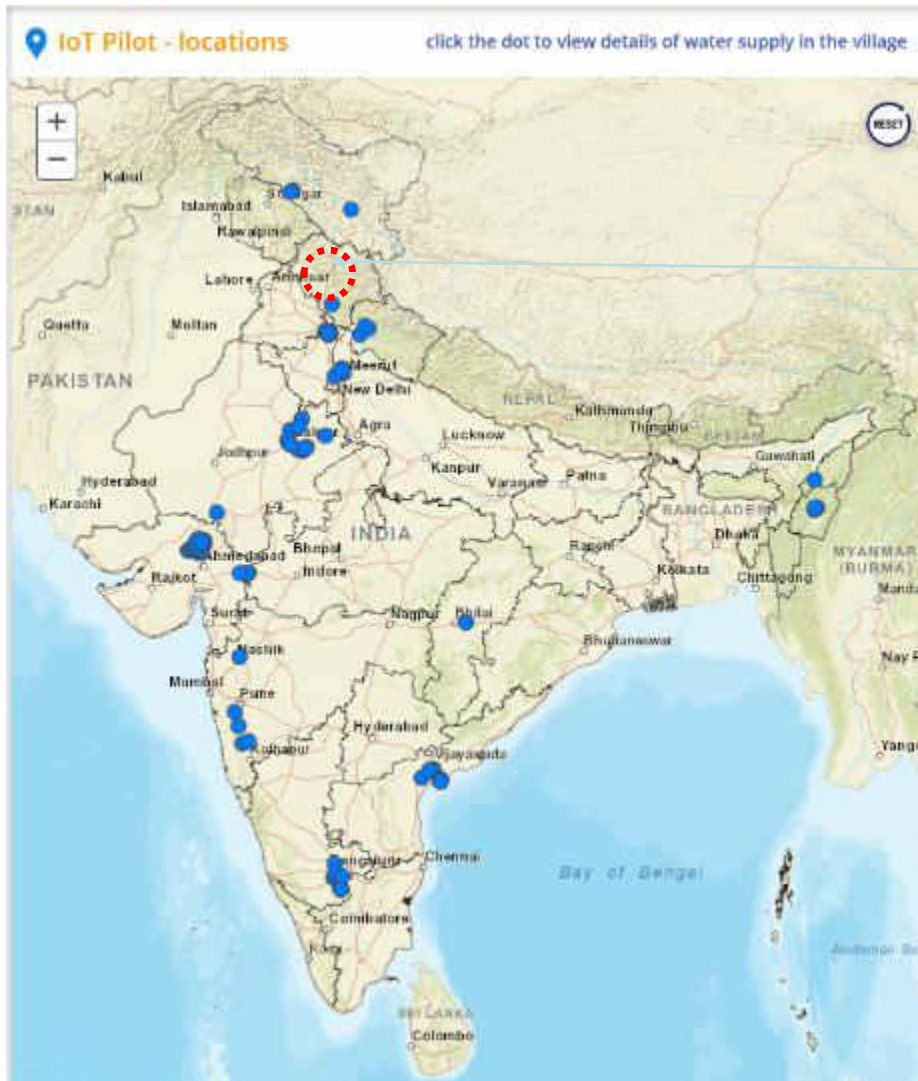
There are over 1700 community installations across the country, serving 1.3 million people with arsenic and iron-free water every day.

# Evolution of materials to products



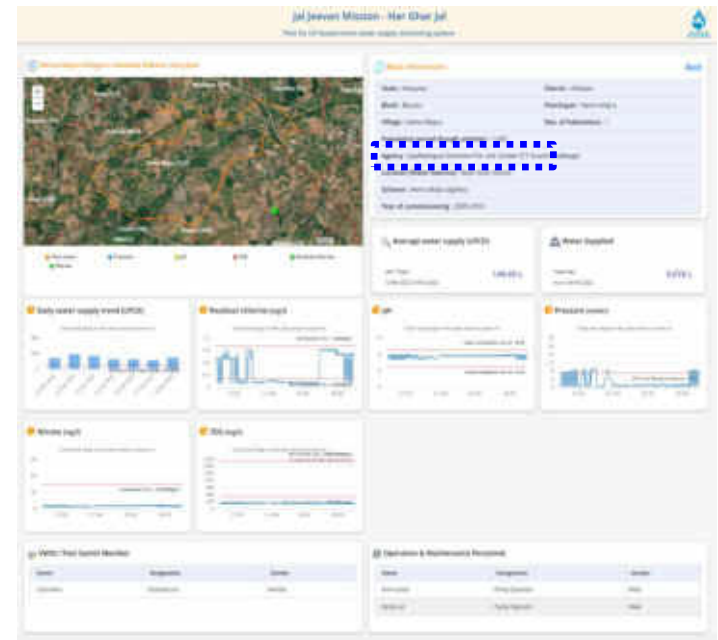


# India's water is being monitored



IITM/IISc

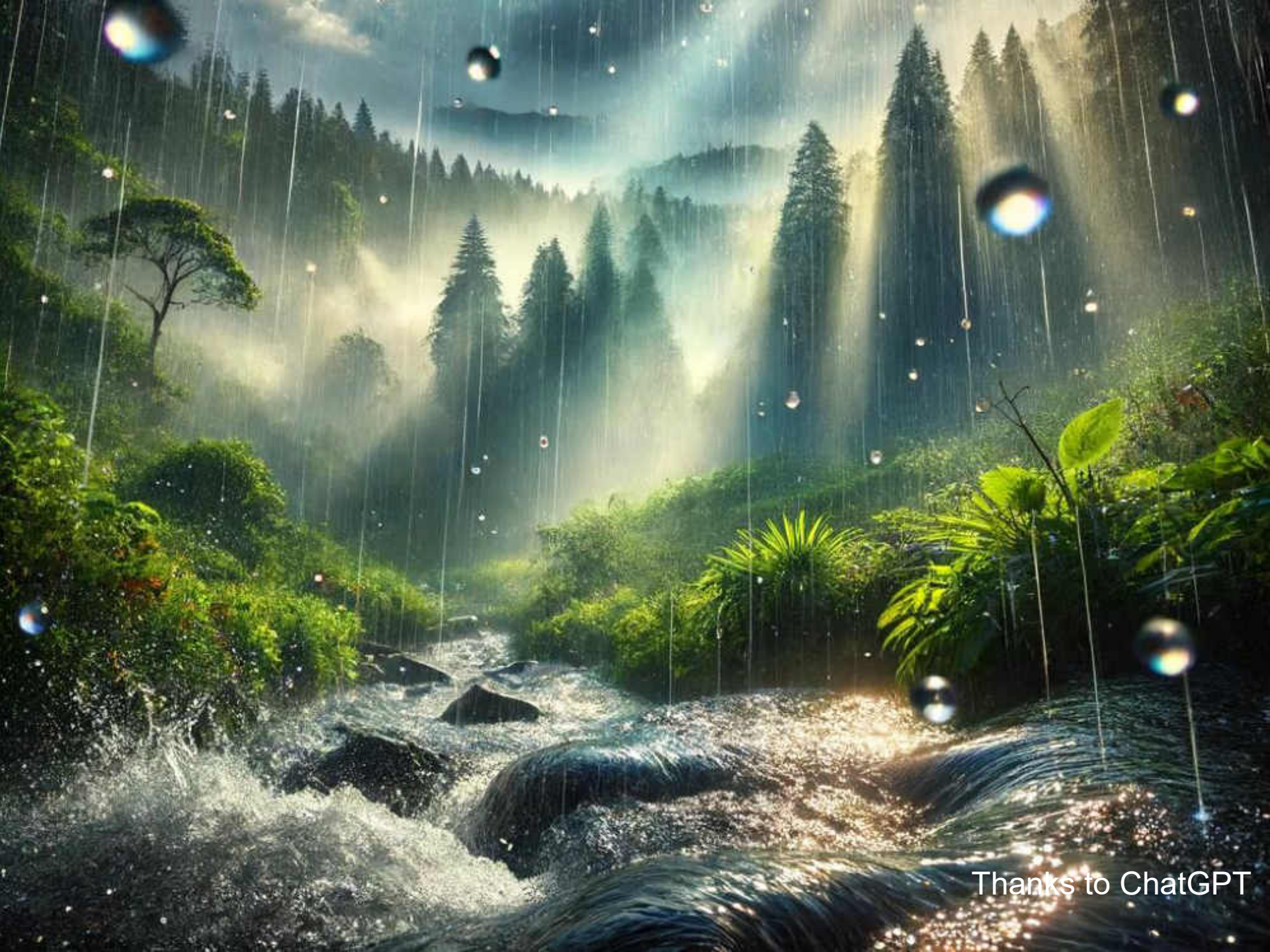
Installations made by four companies



# People's Water Data

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Thanks to ChatGPT



# Vision

Make soil using  
processed wastewater  
and make deserts  
bloom.



Thanks to ChatGPT

# Conclusions

Natural minerals break spontaneously in charged 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

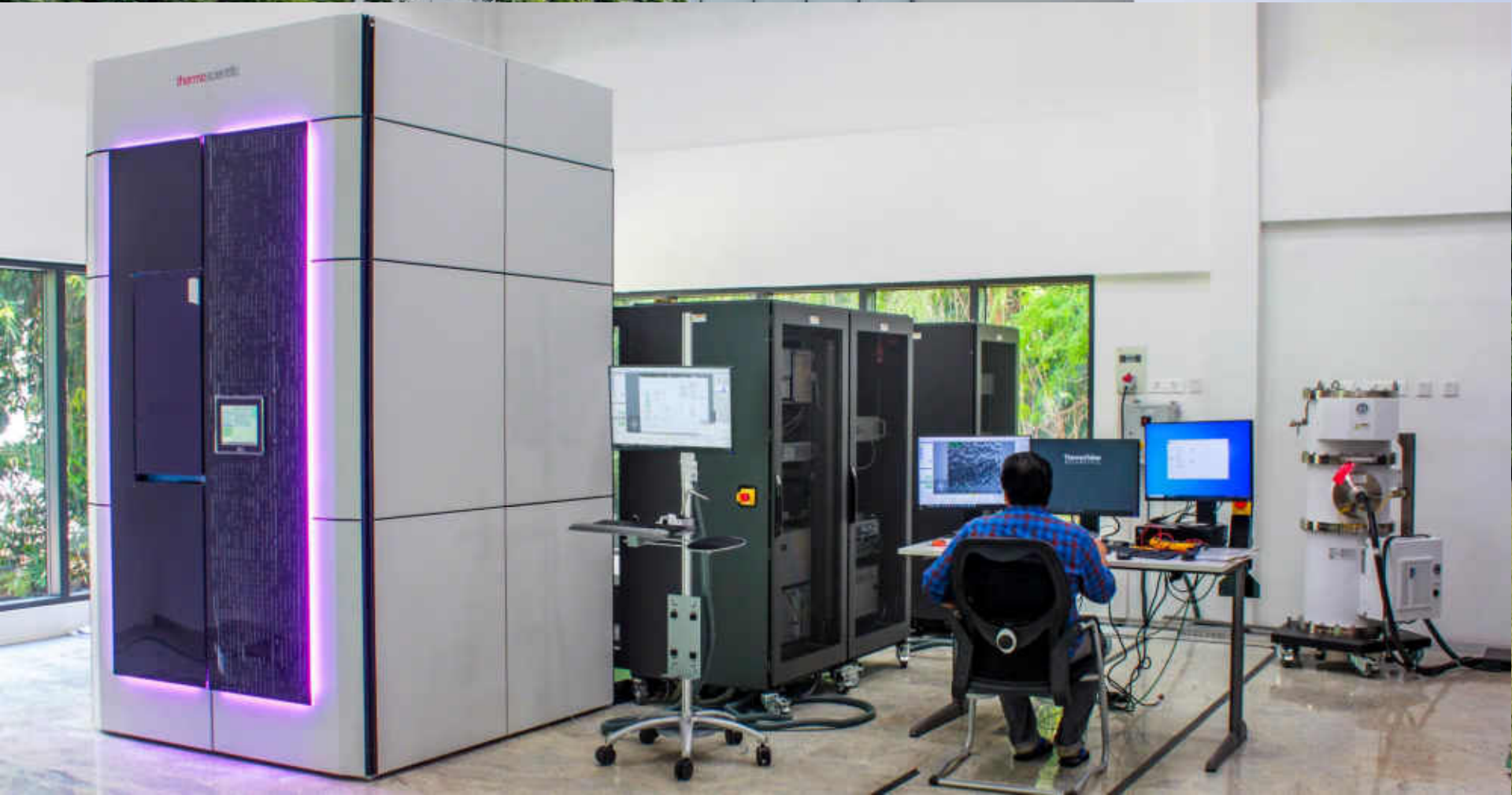
Implications to the production of specific nanomaterials and soil in general

There is a new category of materials called atomically precise clusters, which are fascinating.

Carborane thiol protected new clusters are new additions to this family

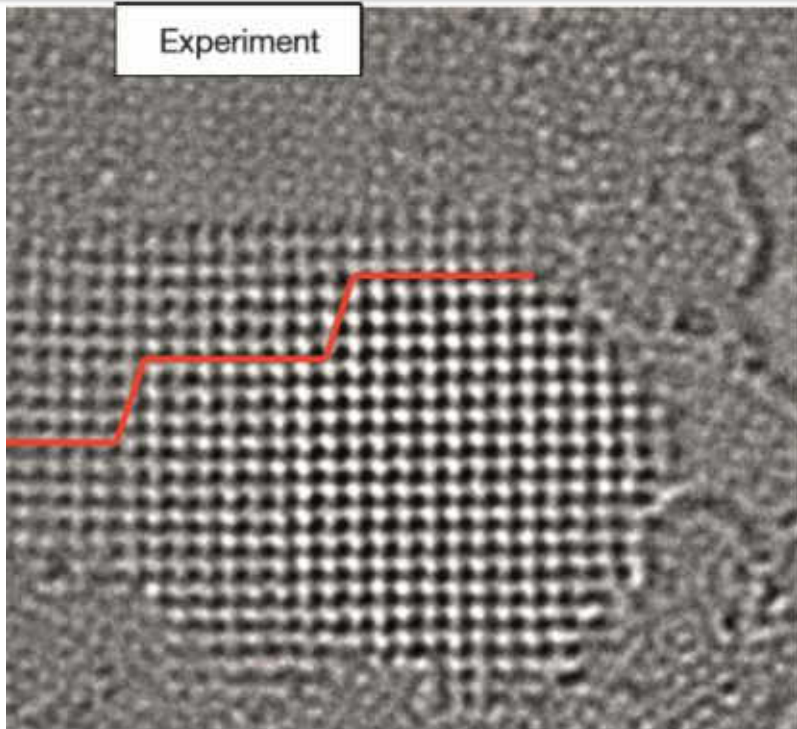
Clean water can be provided with advanced materials

Technologies based on them are being used across the country

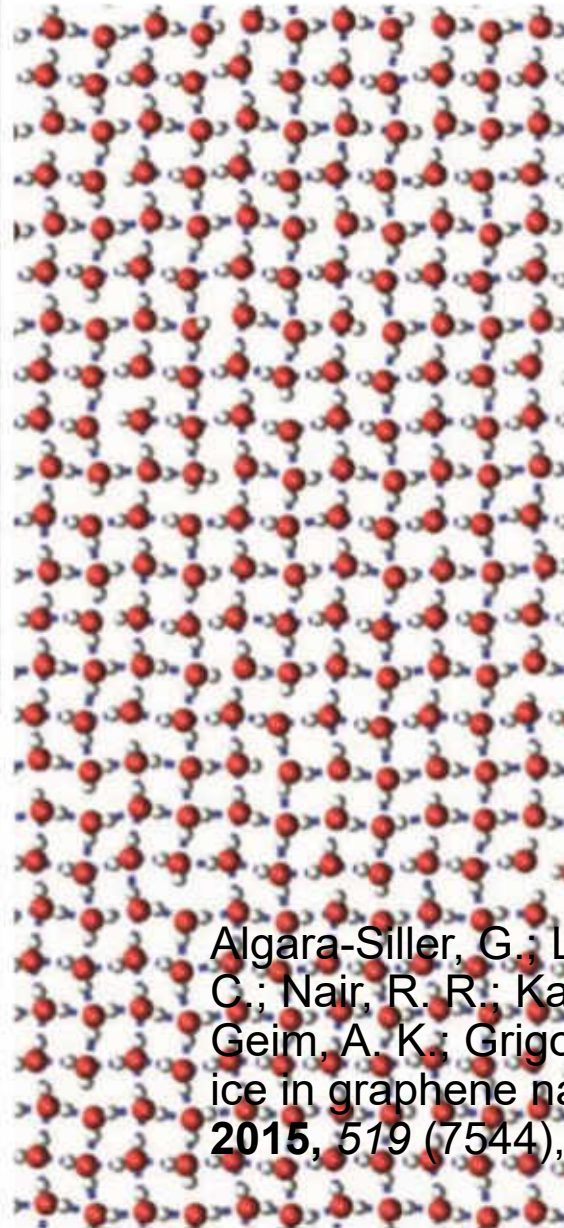
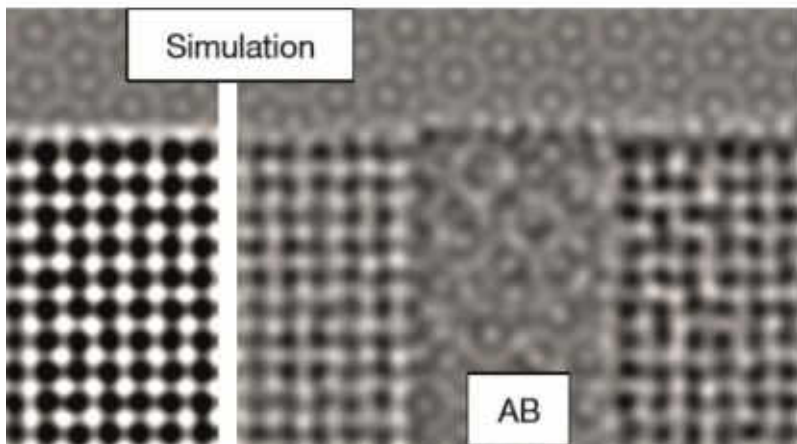




# Observing water



c



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.





International Centre for Clean Water





## Other collaborators



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Tomas Base



Horst Hahn



Biswarup Pathak



K. V. Adarsh

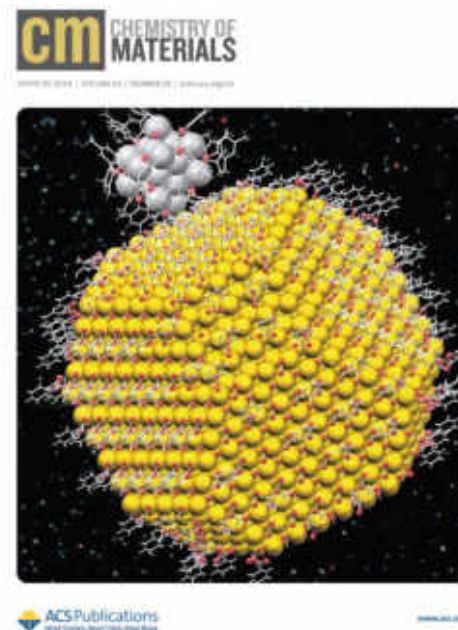


G. U. Kulkarni



Vivek Polshettiwar

Department of Science and Technology  
Institute of Eminence  
Many Outstanding Individuals







# Indian Institute of Technology Madras



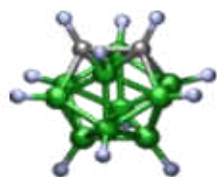
Bhaskar Ramamurthi/V. Kamakoti

## Thank you all

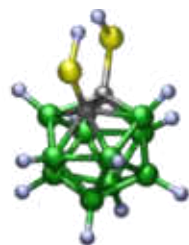




# Building Blocks: Carborane Thiols



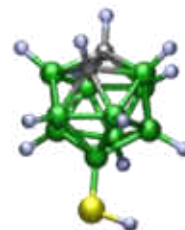
1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>



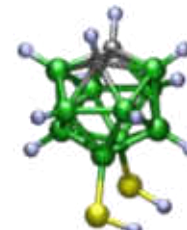
1,2-(HS)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>



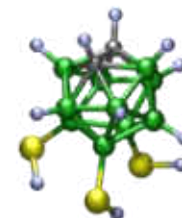
1-HS-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>



9-HS-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>



9,12-(HS)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>



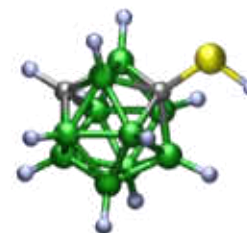
8,9,12-(HS)<sub>3</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>9</sub>



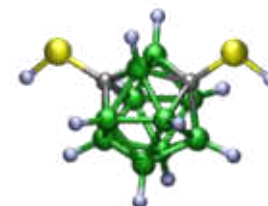
1,7-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>



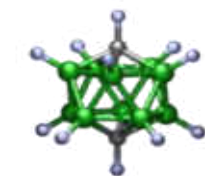
9-HS-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>



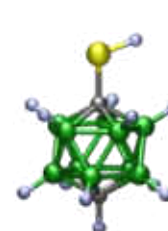
1-HS-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>



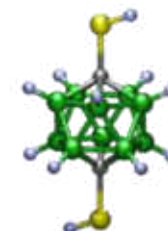
1,7-(HS)<sub>2</sub>-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>



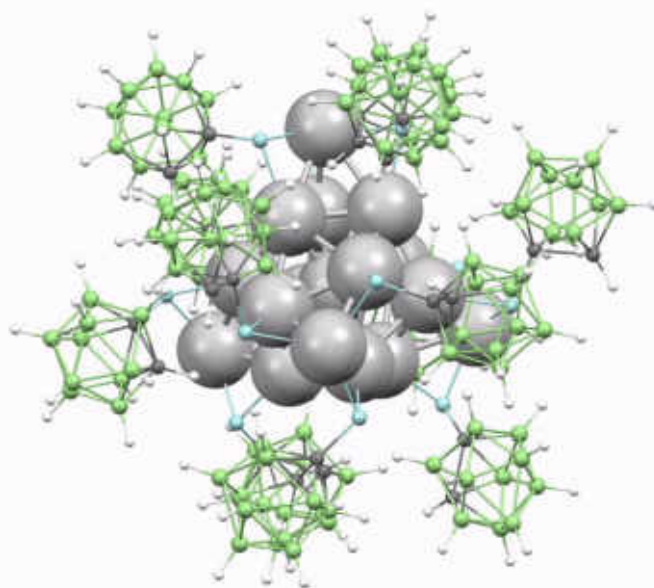
1,12-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>



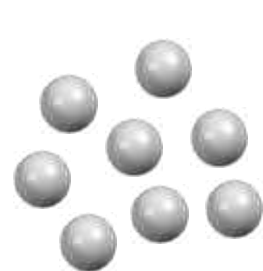
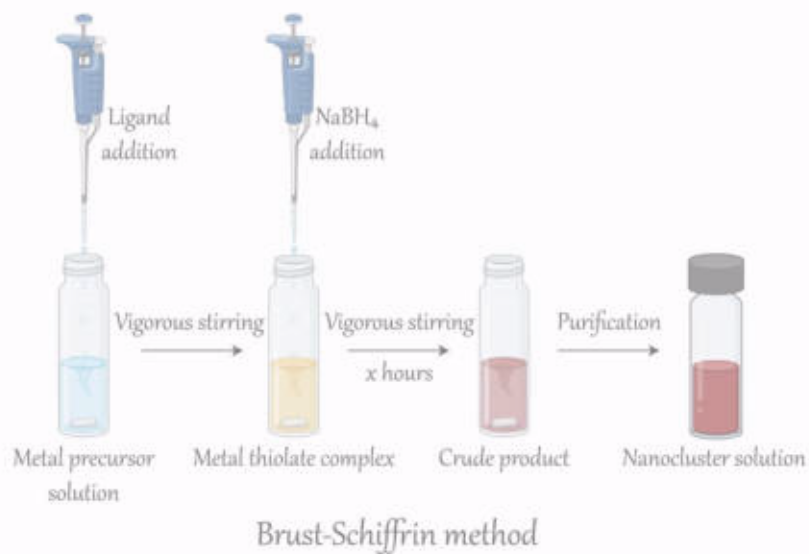
1-HS-1,12-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>



1,12-(HS)<sub>2</sub>-1,12-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>



# Synthesis Schematic of $[\text{Ag}_{17}(\text{o}_1\text{-CBT})_{12}]^{3-}$ Nanocluster

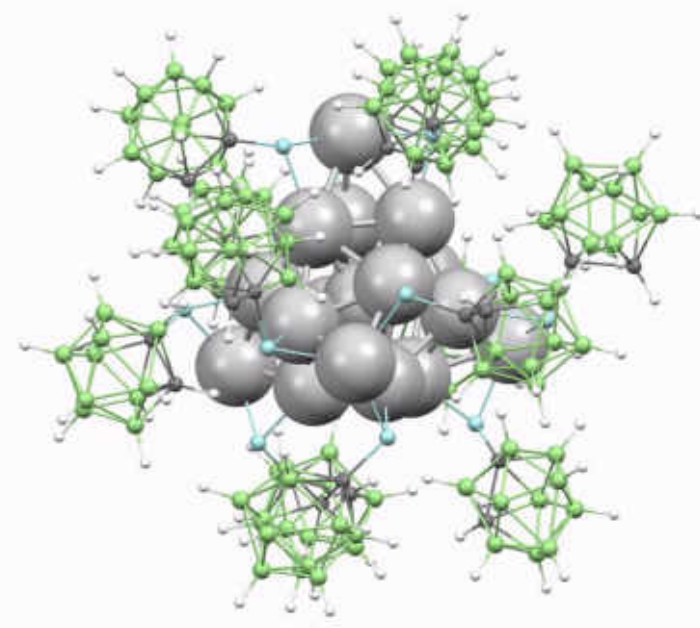


Ag Solution

+

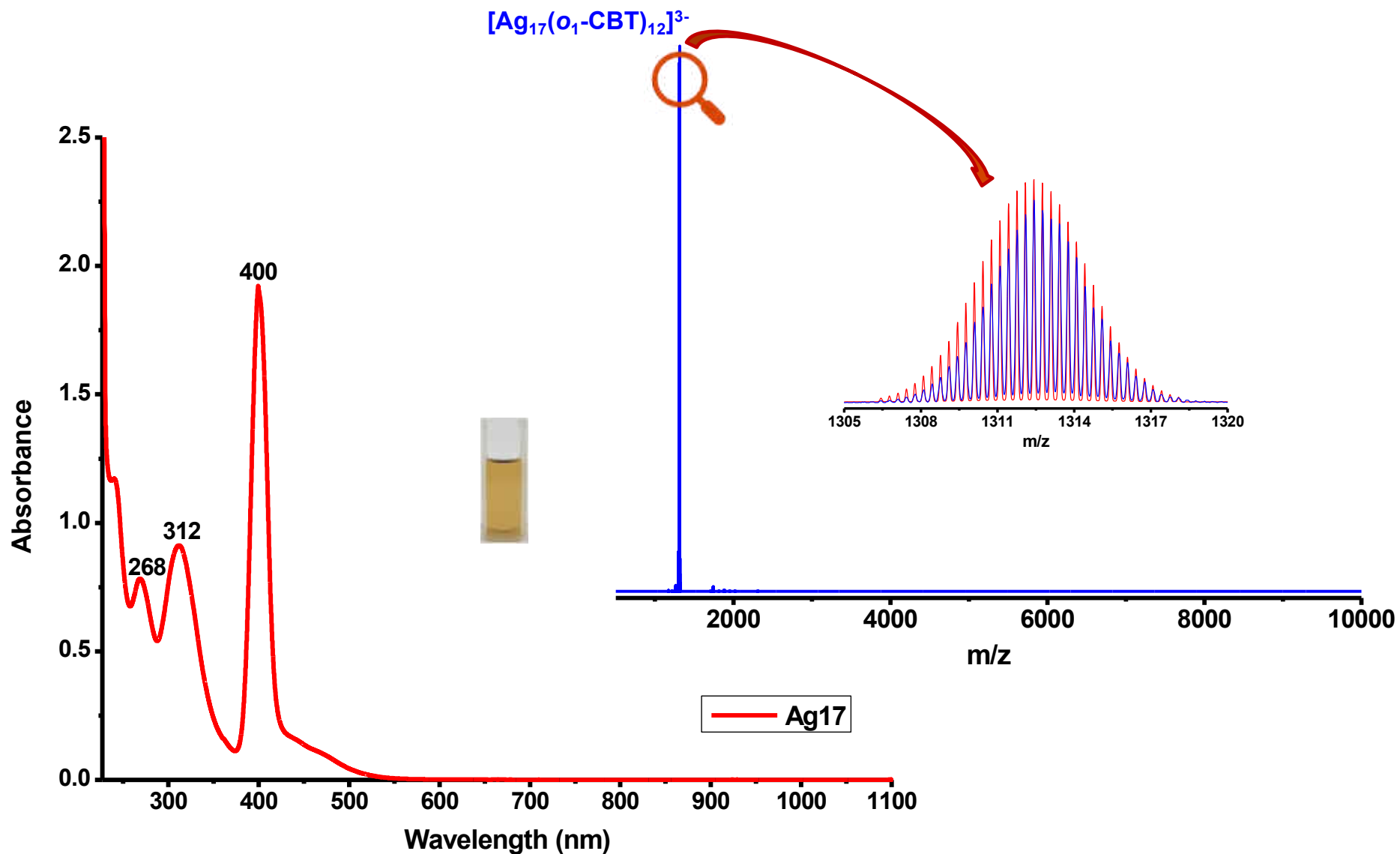


$\text{o}_1$ -Carborane  
Thiol

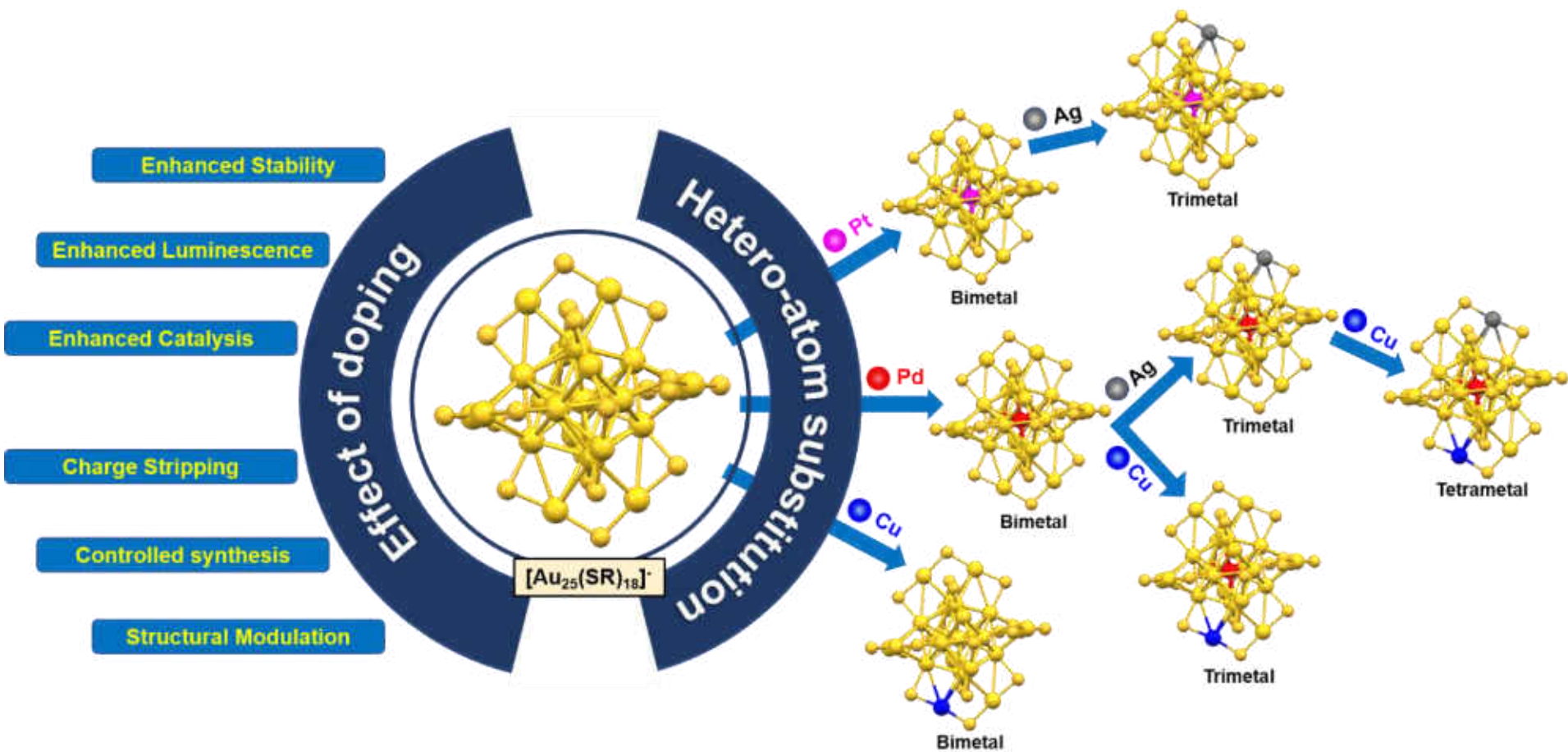


$[\text{Ag}_{17}(\text{o}_1\text{-CBT})_{12}]^{3-}$

# Characterisation of $[\text{Ag}_{17}(\text{o}_1\text{-CBT})_{12}]^{3-}$ Nanocluster

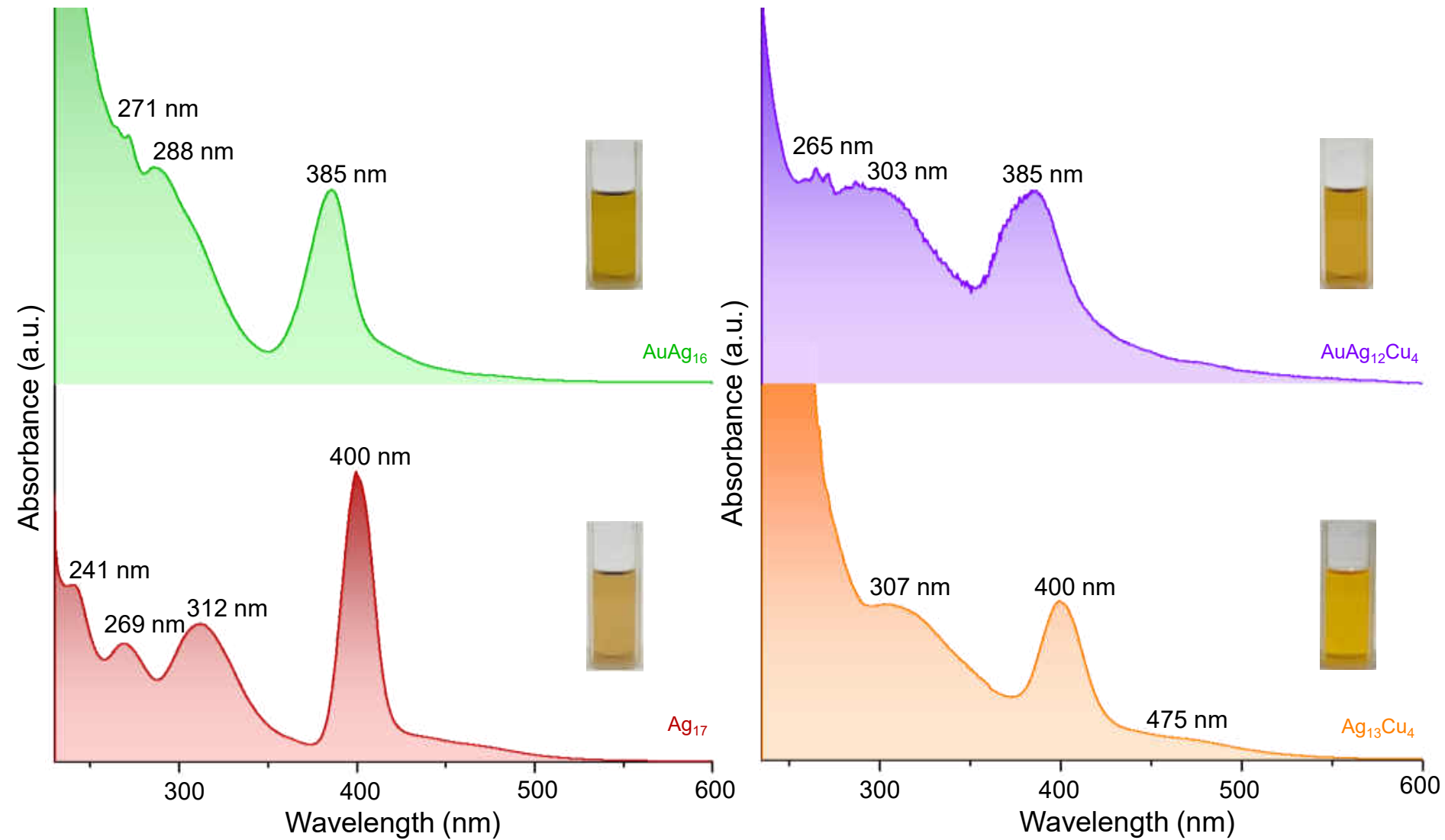


# Alloying of Nanoclusters: The Work Plan

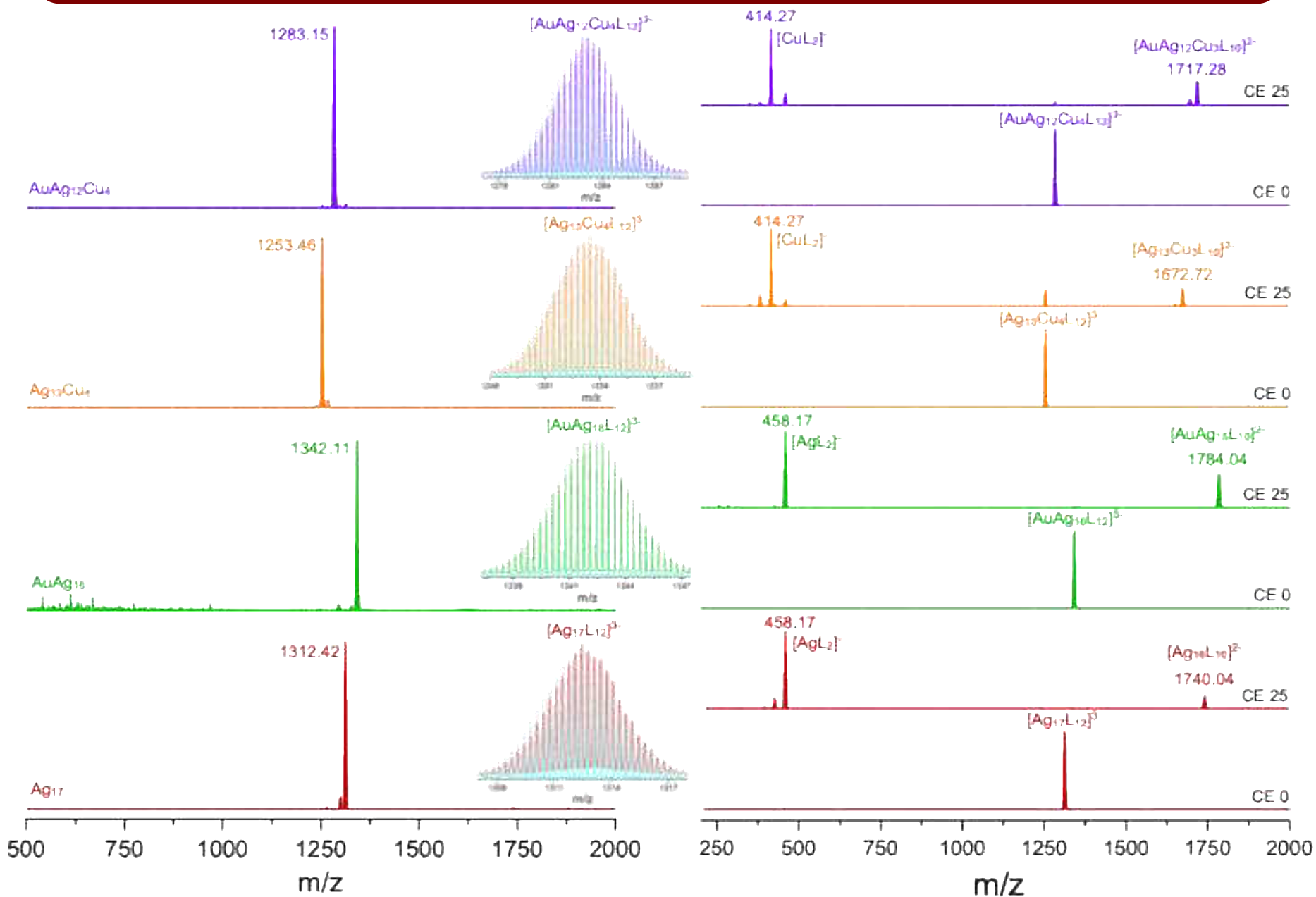




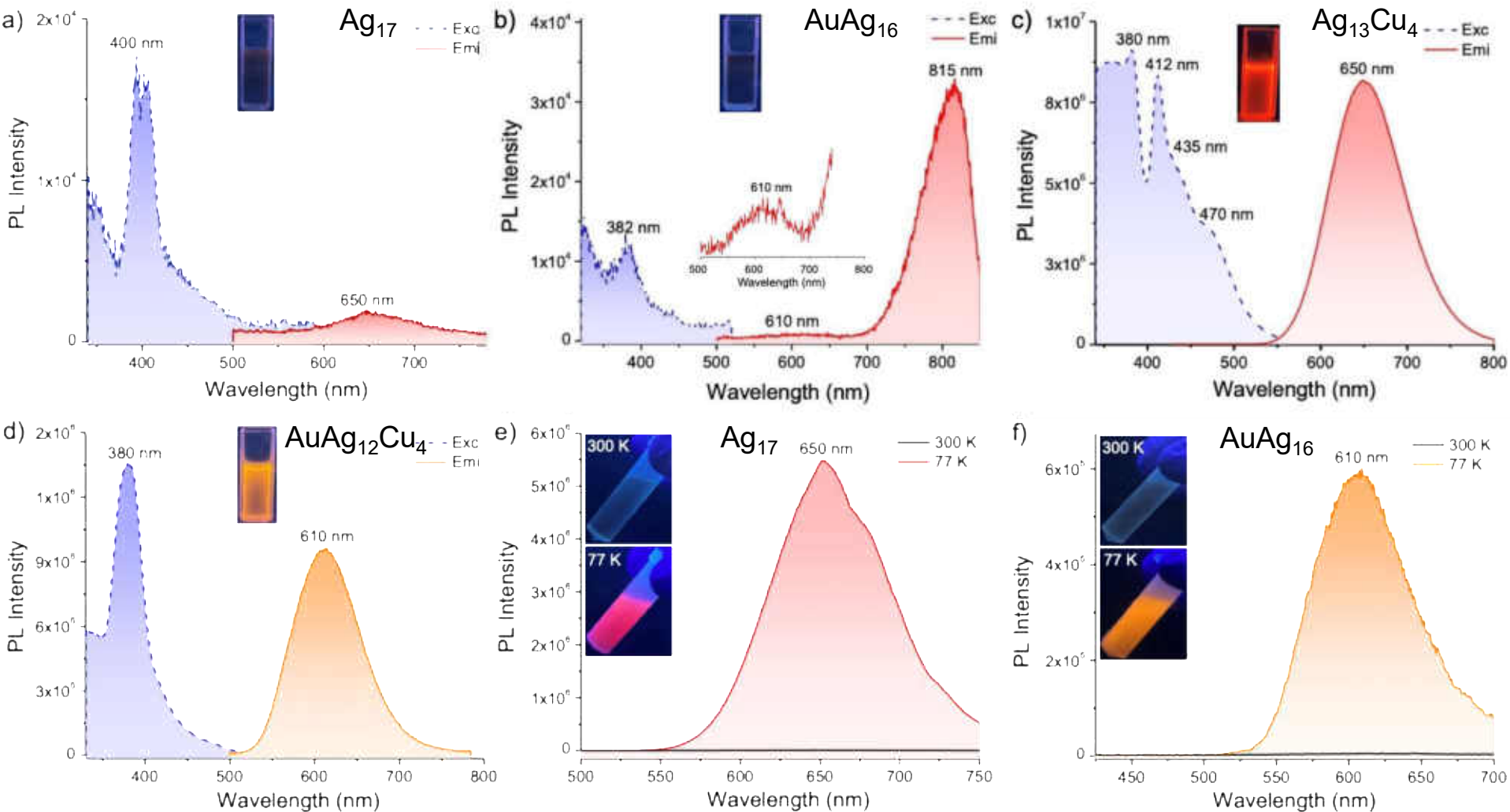
# UV-Vis of M<sub>17</sub> Nanoclusters



# Mass Spec of M<sub>17</sub> Nanoclusters

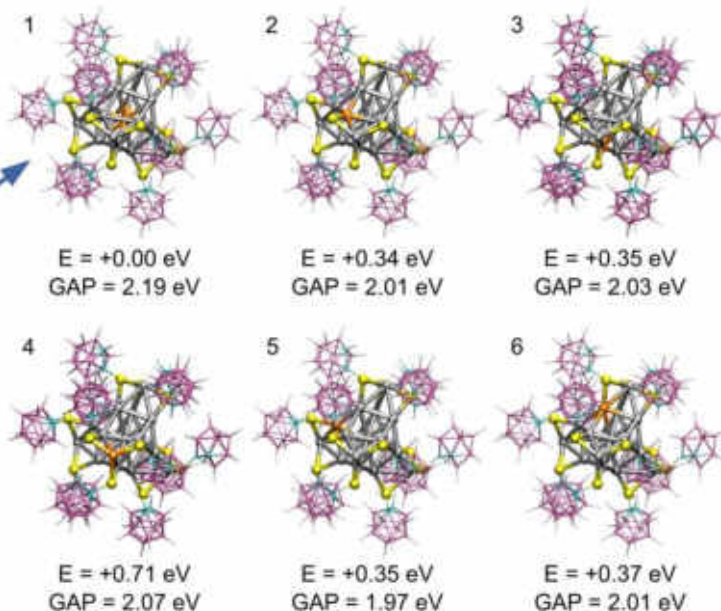


# Photoluminescence of $M_{17}$ Nanoclusters

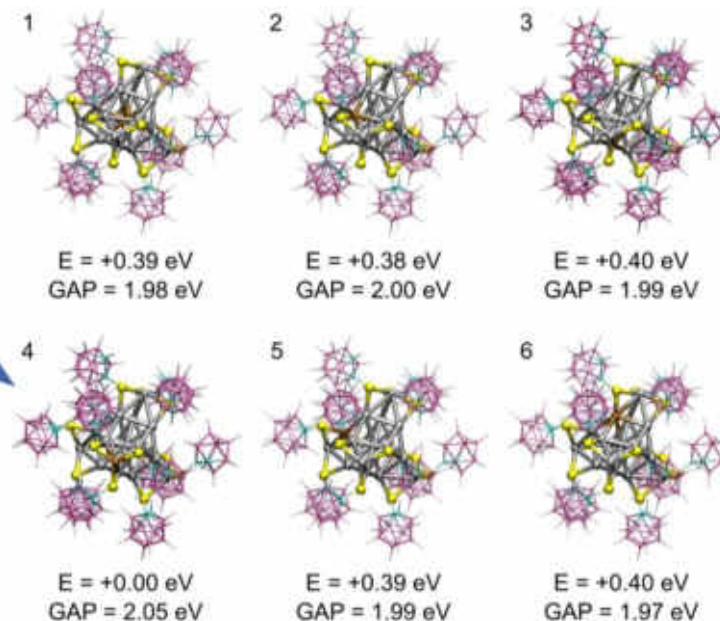


# Theoretical Understanding

Energetically best doping position for Au is in the center of the metal core.



Energetically best doping position for Cu is at the metal-ligand interface, in the  $\text{Cu}(\text{SR})_3$  units.





# Theoretical Understanding

