



Since 1959

Can Water Microdroplets Make Soil?

A path to sustainable nanotechnology



Matter in confinement for sustainability

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International Centre for Clean Water



Science



RENAULT

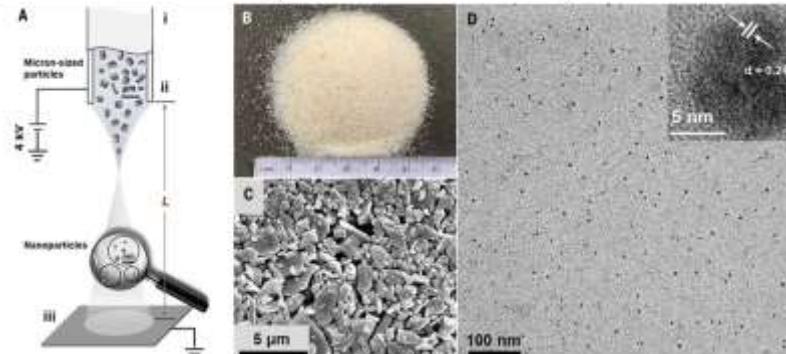
NANOPARTICLES

Spontaneous weathering of natural minerals in charged water microdroplets forms nanomaterials

E. K. Sponzaia¹, Ruyendrik Debruyne², Phébén Bouari¹, André Nepp¹,
Léonard M. Mertens², Philippe Chabot^{1,2*}

In this work, we studied particle of common minerals breakdown spontaneously to form nanoparticulate-shaped surface nanostructures without any外加 factors. We found mineral-sized natural mineral fibers can spontaneously break into 5-10 nm size particles when integrated into aqueous microdroplets generated via electrospray. We hypothesized the dissolution is substrate, which has nanoparticle characteristics. We determined through simulation that quartz undergoes preferential dissolution upon when subjected to an electric field. This leads to particle dissolution and the formation of silica fragments, which are stabilized with surface charges. This physical breaking process may be important for all minerals, due to the presence of charged areas on the surfaces.

For our experiments, we prepared microdisks with SiO_2 -Si dioxide-siloxane (Si) (SiO₂) containing 10% amorphous SiO_2 (Si). Porous microdisks containing 10% amorphous SiO_2 (Si) (Fig. 1, SiO_2 -Si dioxide-siloxane (Si) (SiO₂)) were obtained by dissolving SiO_2 in CH_2Cl_2 -CH₃COCH₃-CH₃COCH₃ (1:1:1) and adding SiO_2 to the solution.



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

A scale of 1000

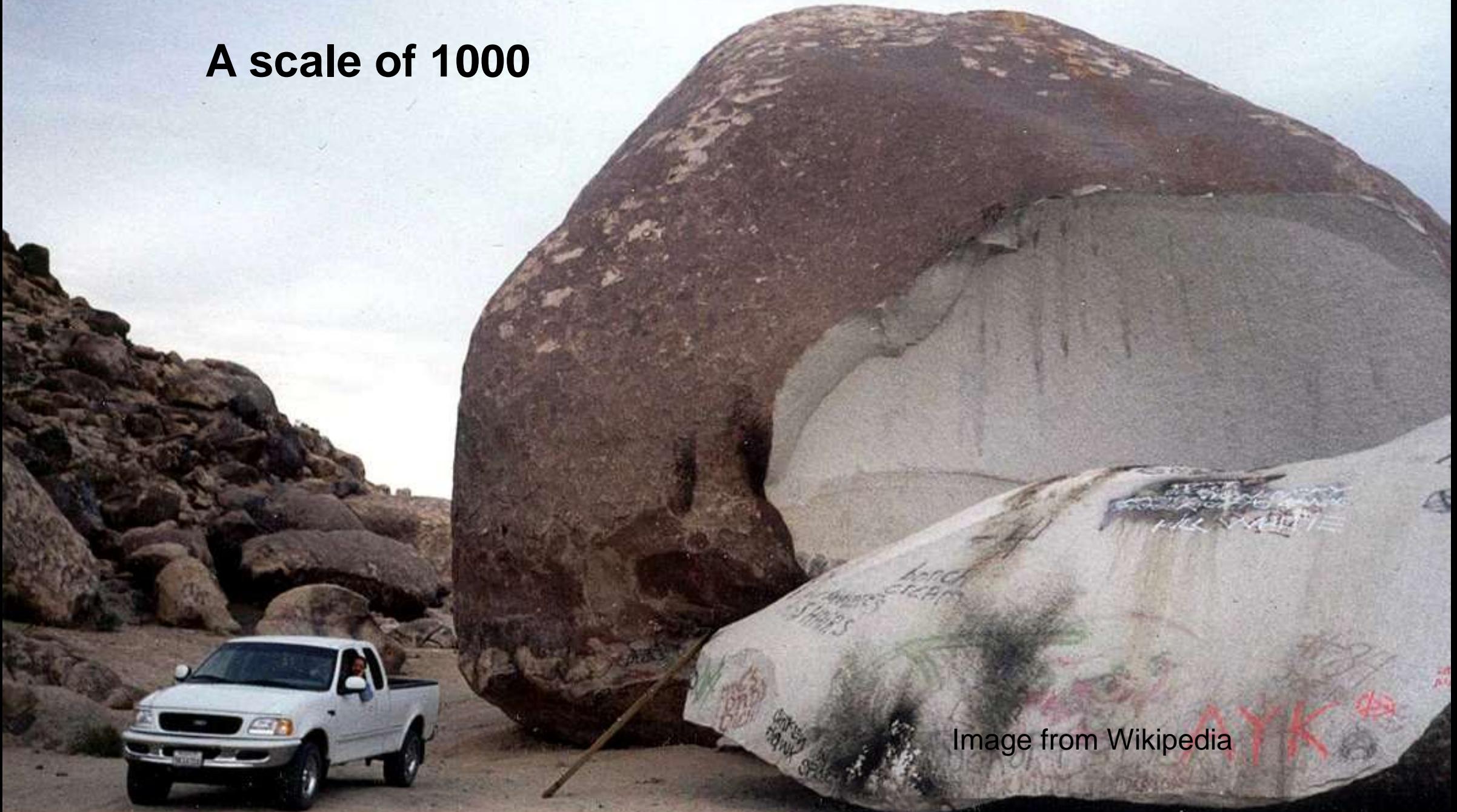
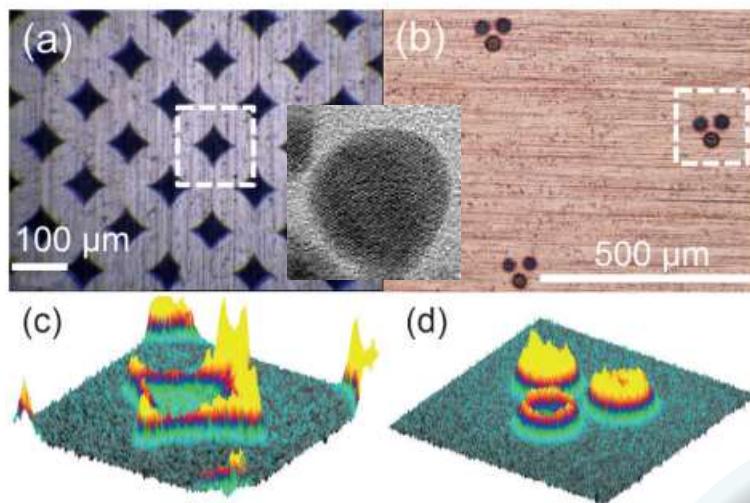
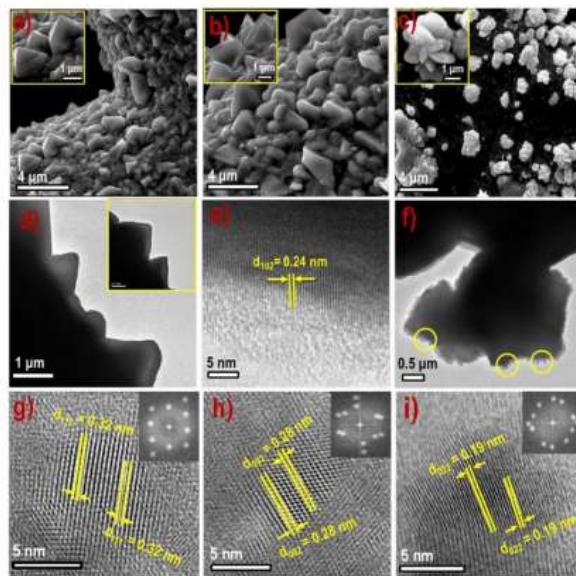


Image from Wikipedia

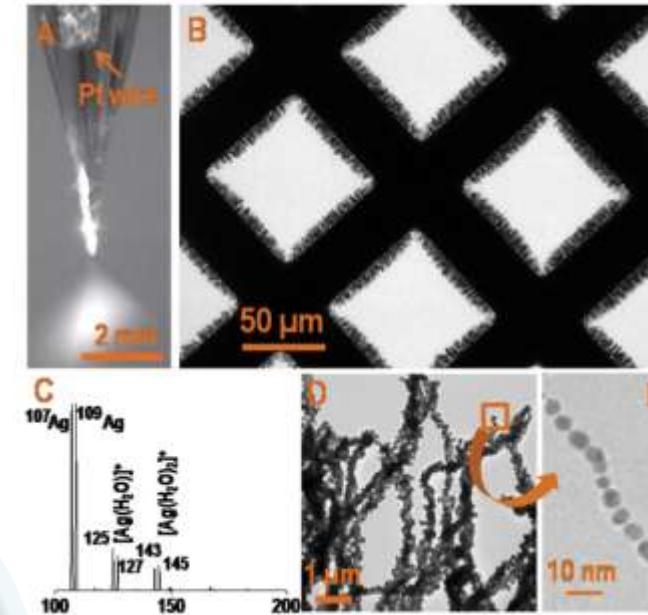
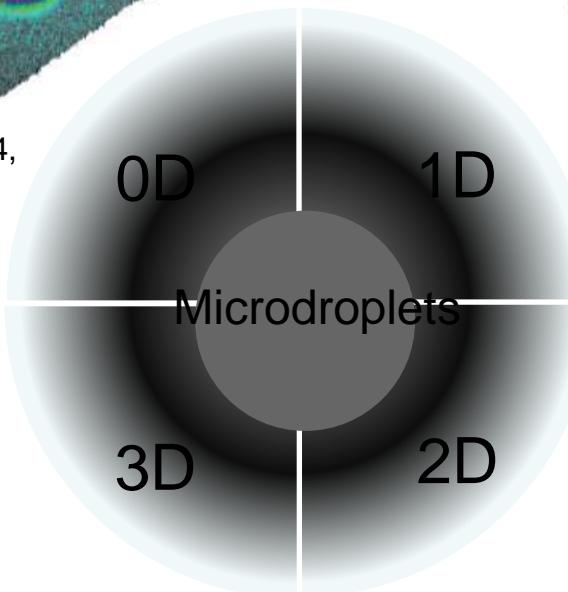
Functional Nanomaterials



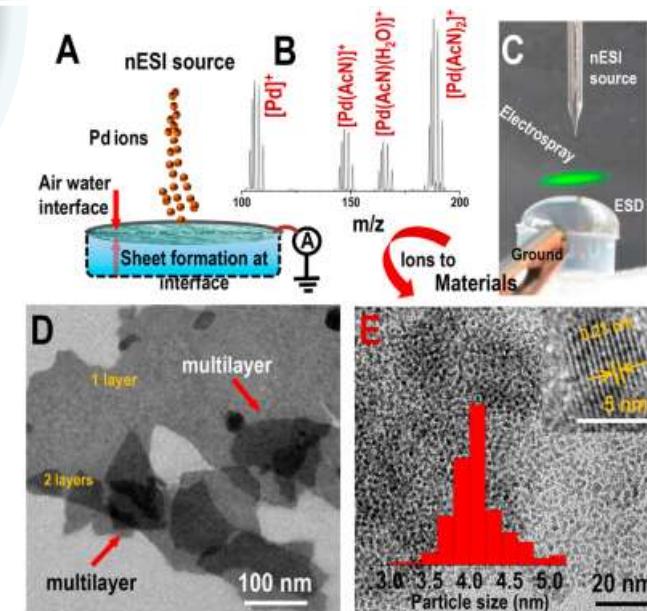
Anyin Li, et. al., *Angew. Chem. Int. Ed.* 2014, 53, 12528 –12531.



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



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



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



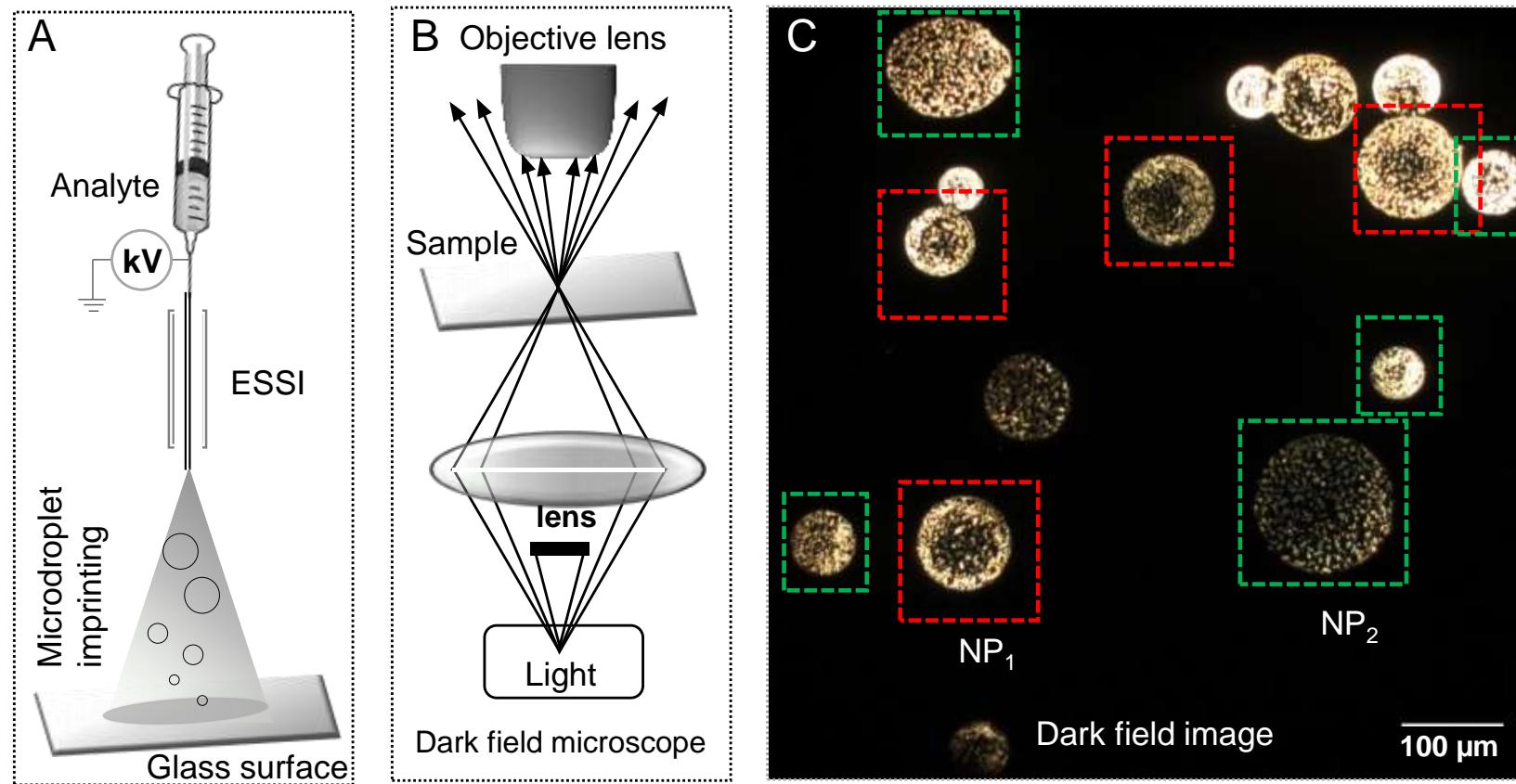
Chemical Science

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ISSN 2041-6539

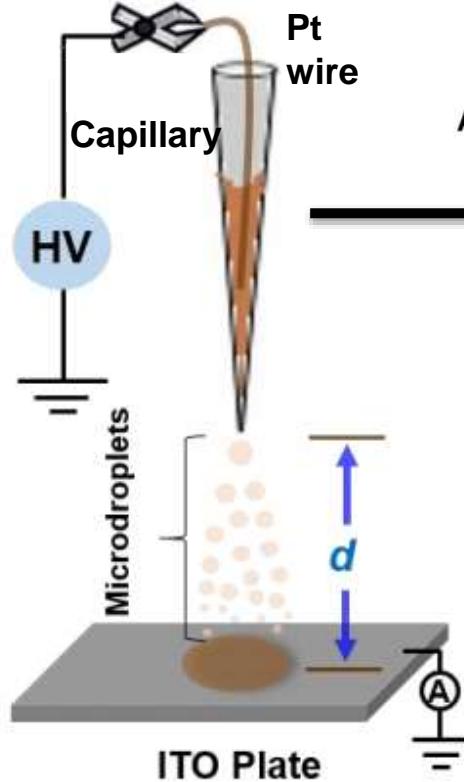
Understanding Microdroplets



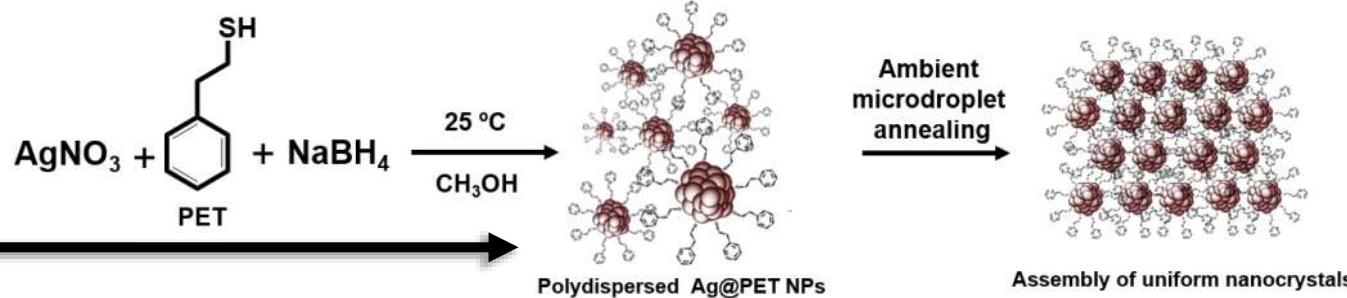
Transformation of Materials in Microdroplets

Ambient Microdroplet Annealing of Nanoparticles

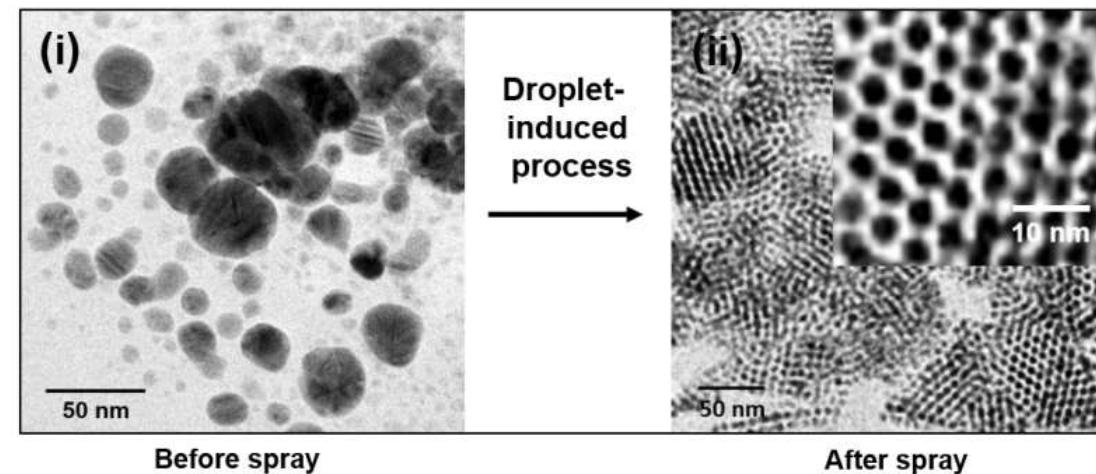
Experimental set-up



Synthesis of polydisperse NPs



Transformation process





Thanks to ChatGPT

Weathering in Nature

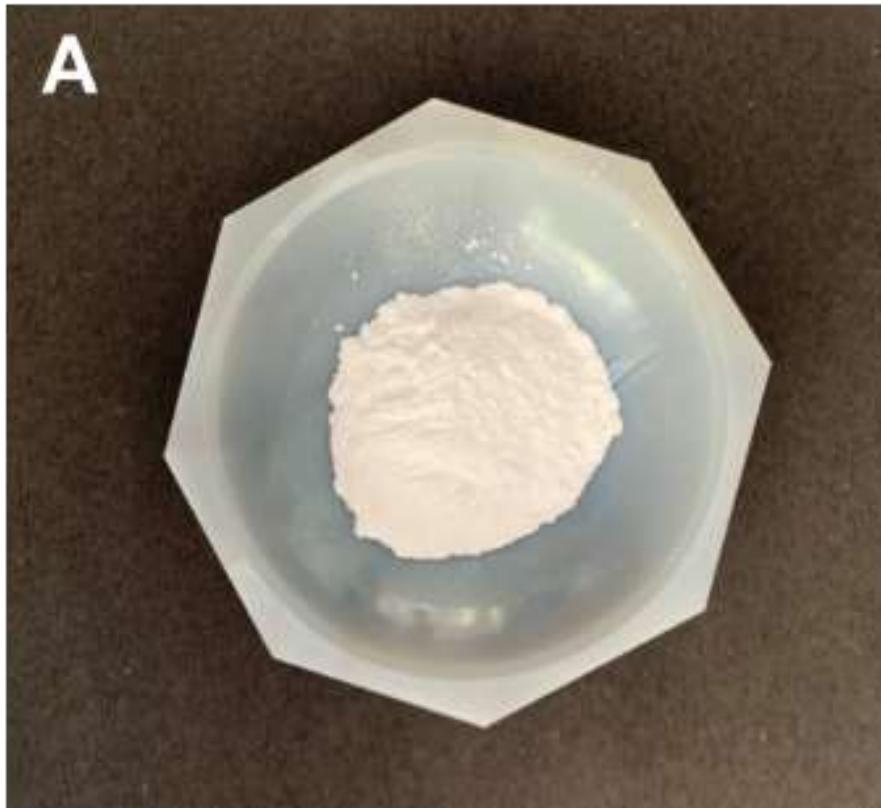


Sand, the Ubiquitous Material

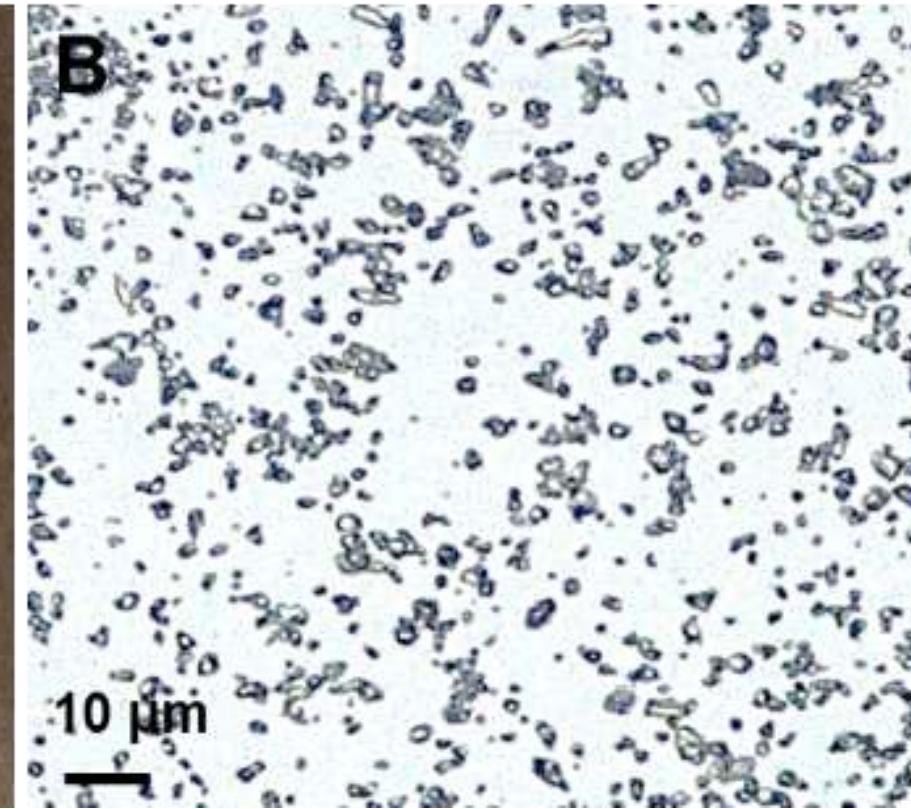


Images from Wikipedia



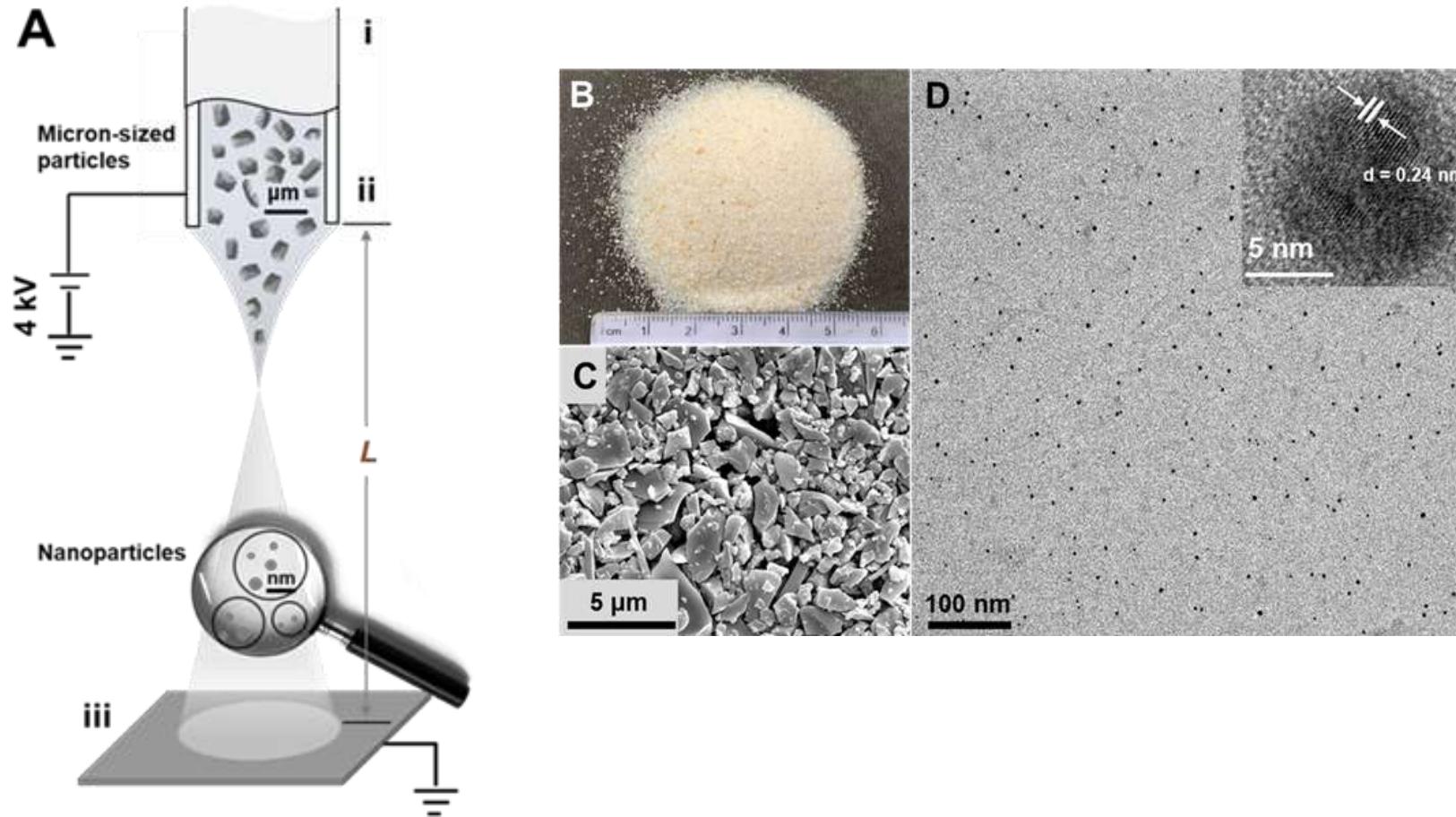


Ground silica

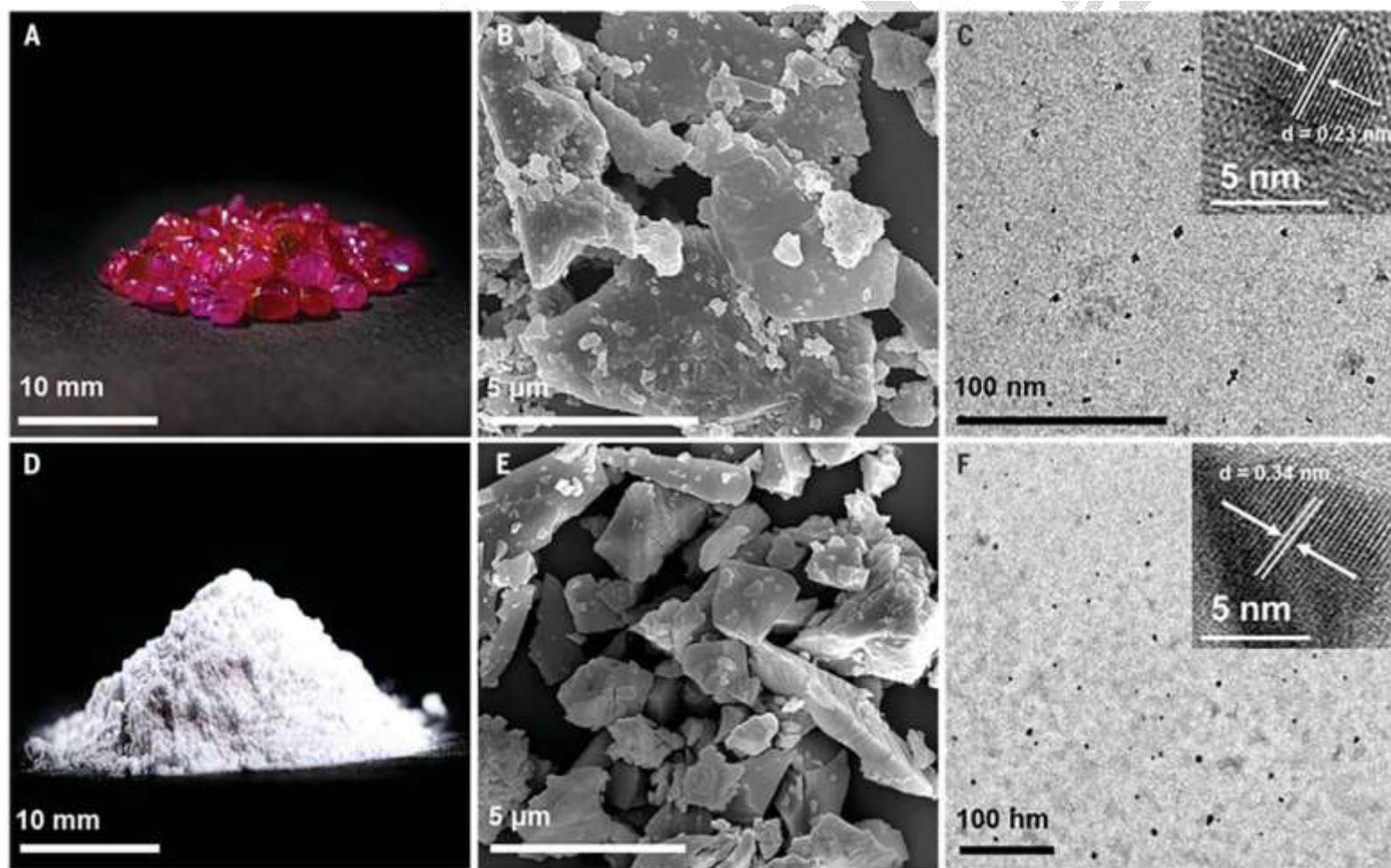


Optical image of silica

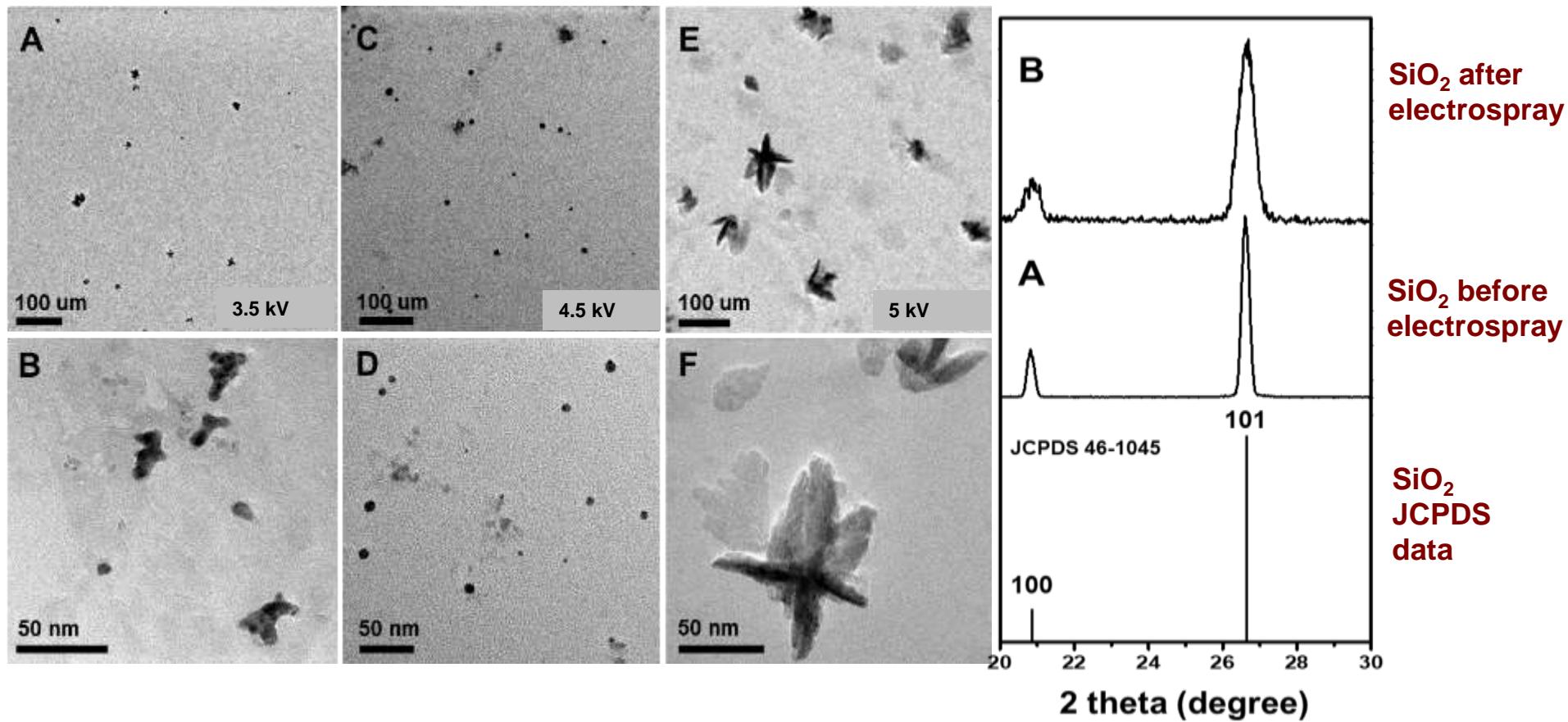
Weathering of Minerals in Microdroplets



Ruby, Fused Alumina

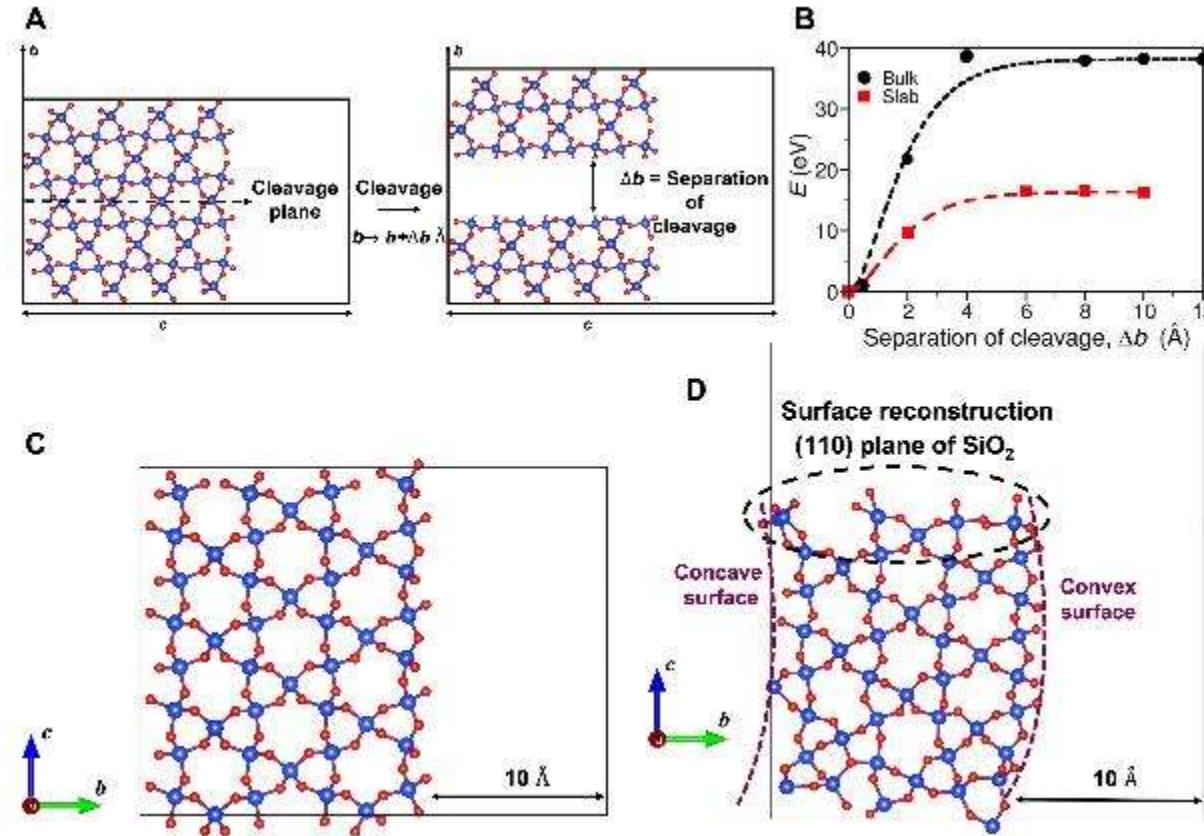
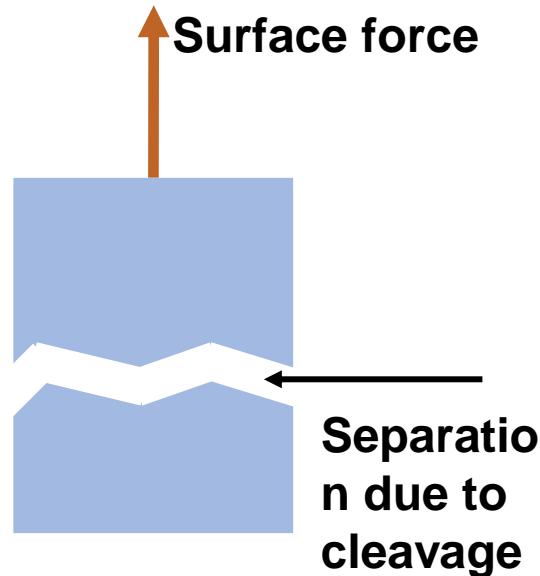


Fragmentation of Silica – Varying Conditions

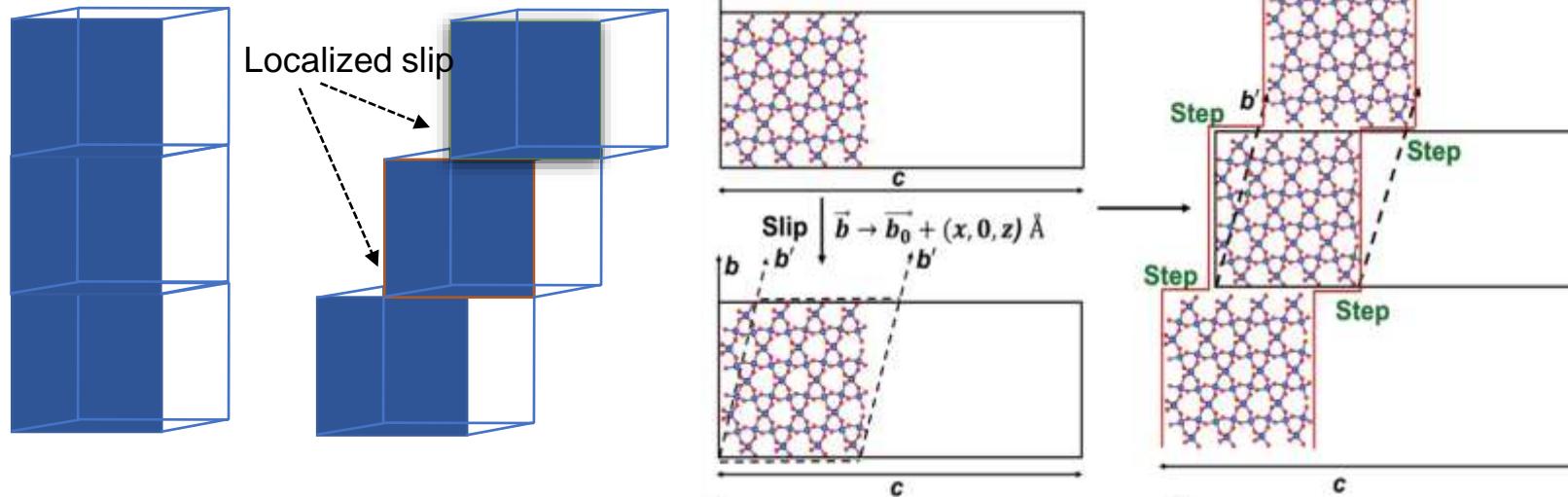


Mechanism: Cleavage

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

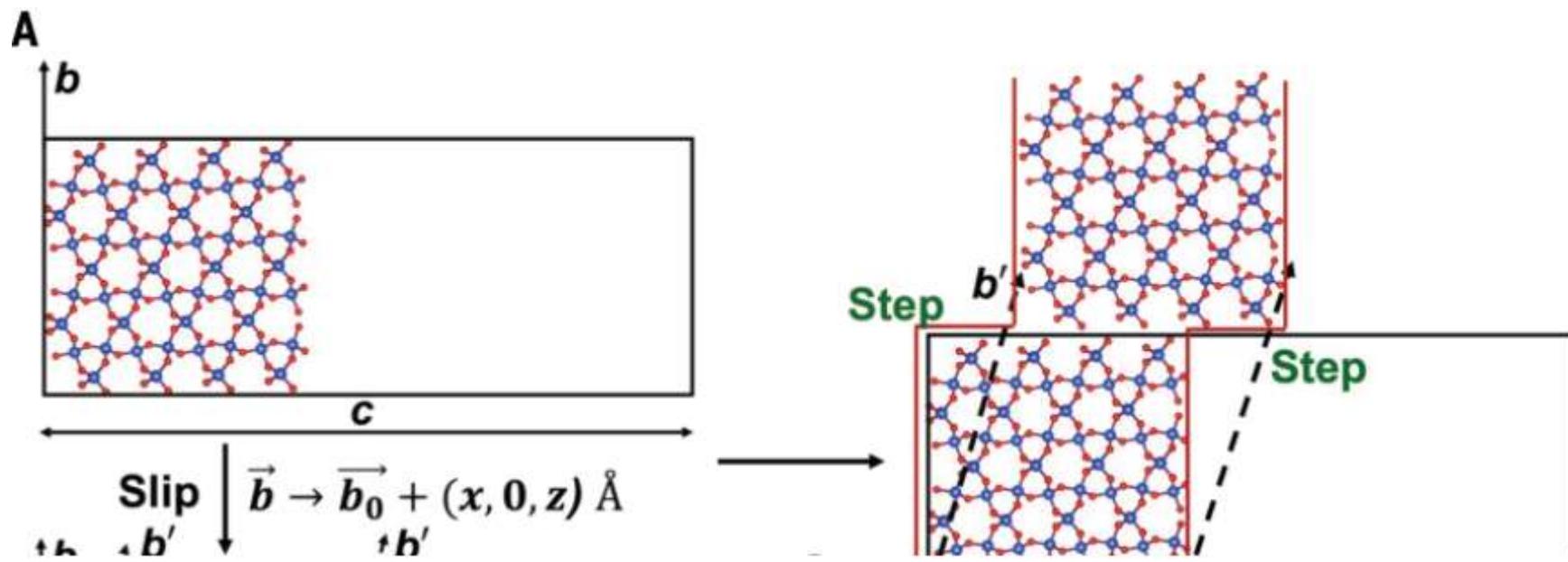
Stacking fault

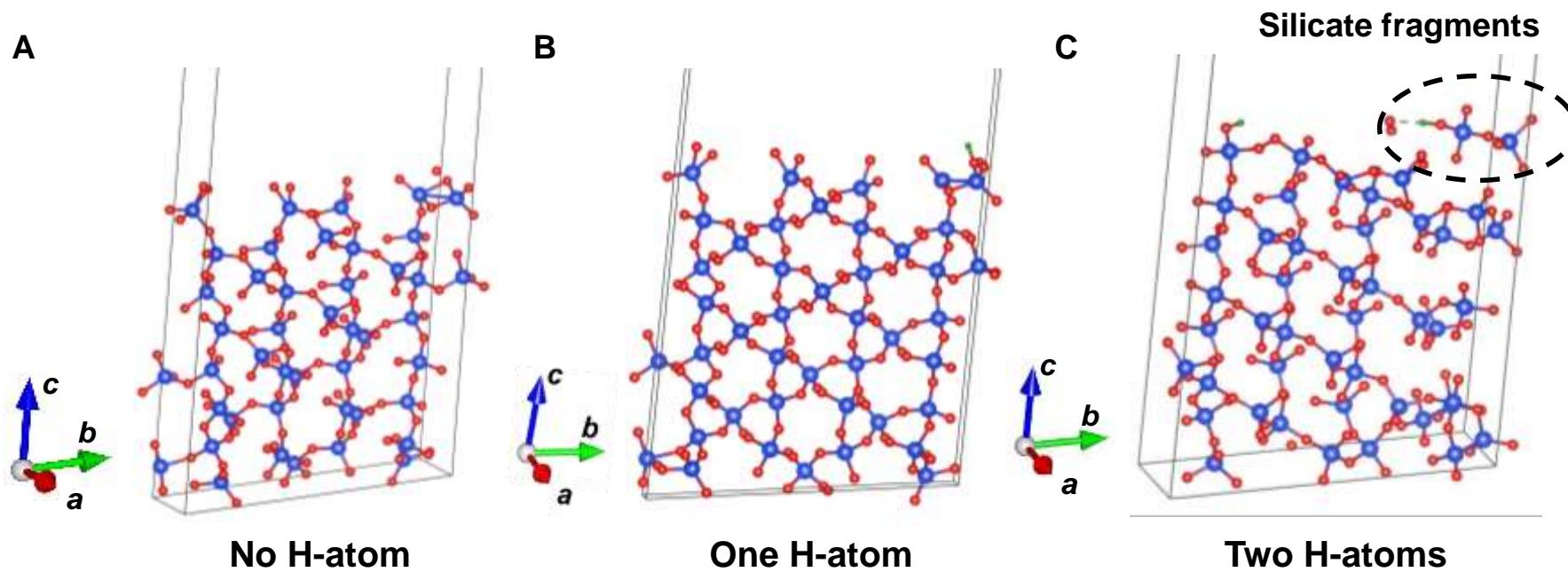
$$\vec{b} \rightarrow \vec{b}_0 + (x, 0, z),$$

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

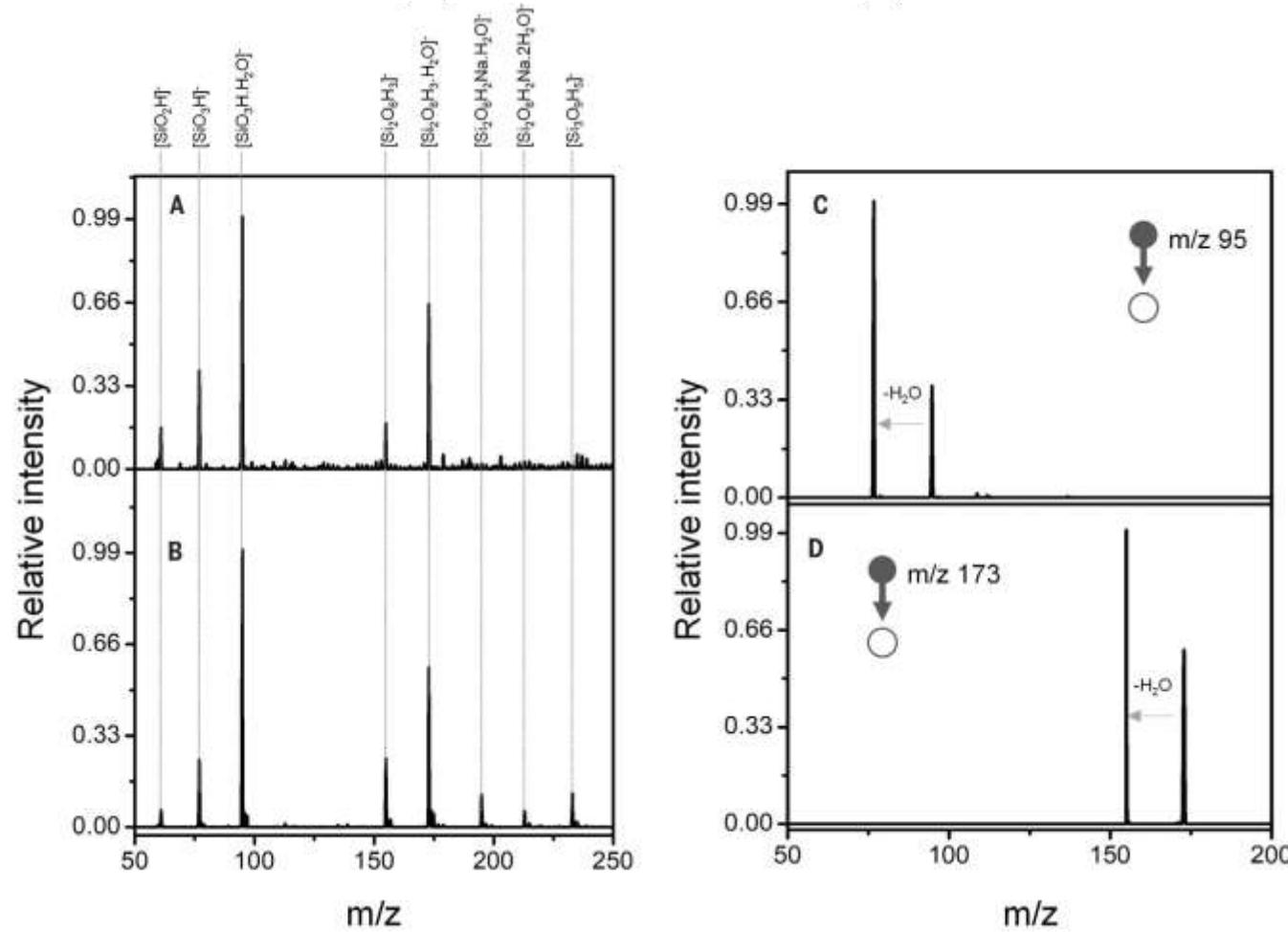
SFEs of (010) direction with (0, 0), (0, 0.5), (0.5, 0) and (0.5, 0.5) slip configurations on the (110) plane of SiO_2

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	0
0.5	0.5		-1.21	-0.93	-0.88	-1.20
0.5	0.0	0.0	1.20	1.18	0.90	1.12
0.0	0.5		-0.07	0.89	-0.83	-0.09

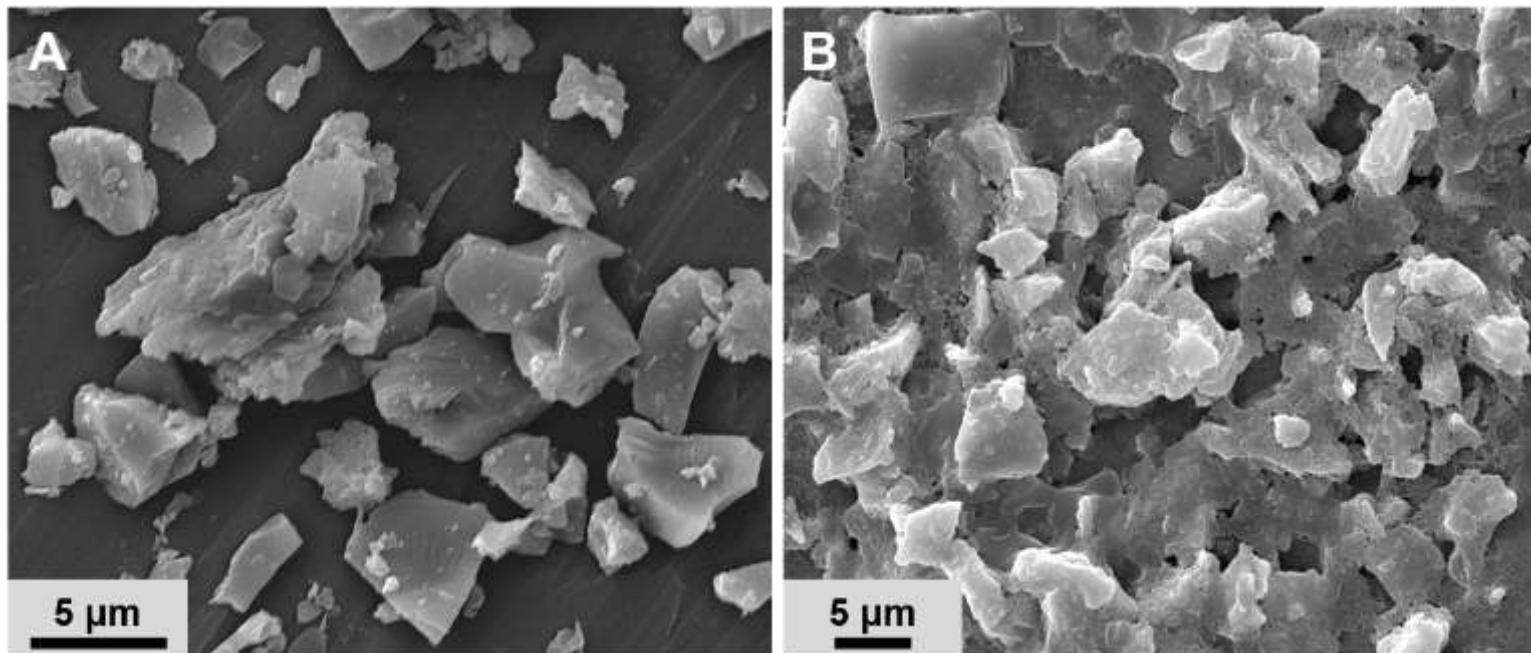




Mass Spectrometry of the Fragments

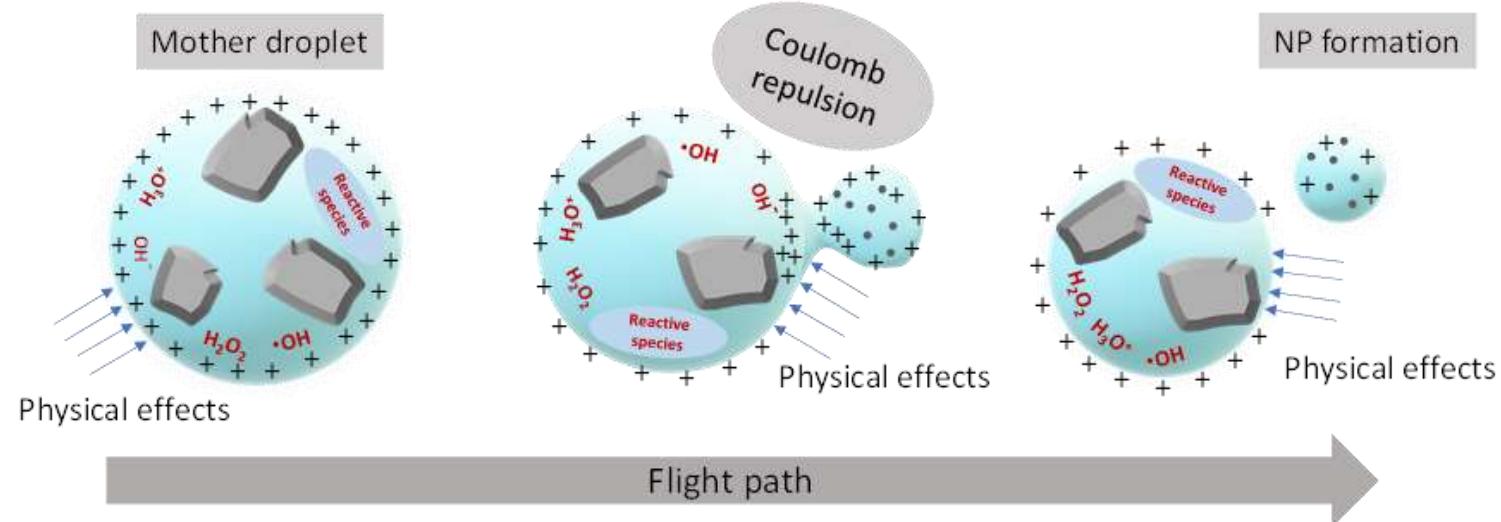


Effect of charged microdroplets on quartz



Increased surface roughness after the spray

Mechanism of nanoparticle formation



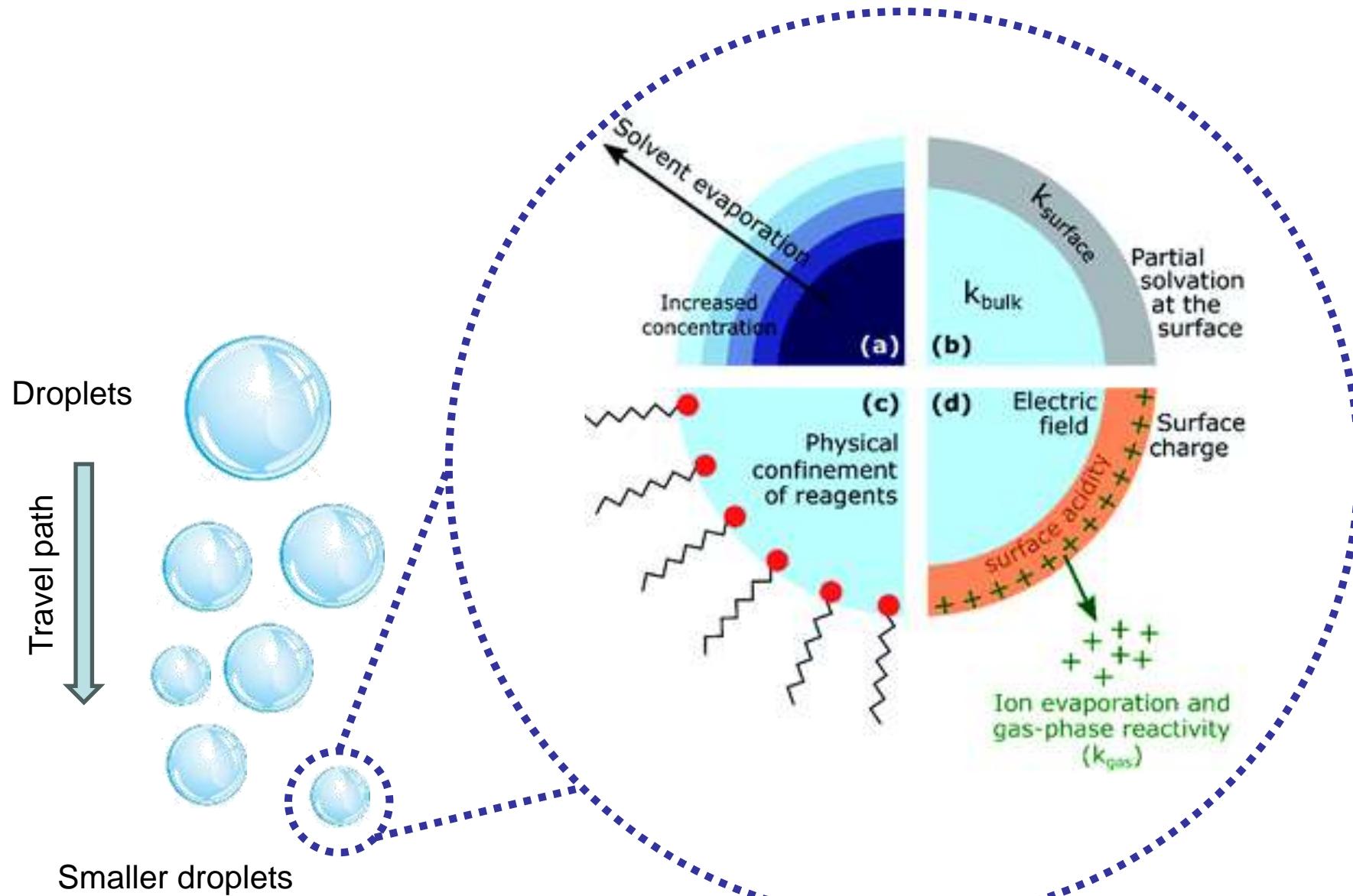
Rayleigh, On the
equilibrium of liquid
conducting masses
charged with electricity,
Philosophical Magazine,
1882

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



Image from Wikipedia

Understanding Microdroplets



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, Spoothi *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, Spoothi *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, Spoothi *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 ($\text{H}_2\text{O}^+/\text{H}_3\text{O}^+$) coexists with oxidative species such as hydrogen peroxide (H_2O_2) and OH^+ . 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).

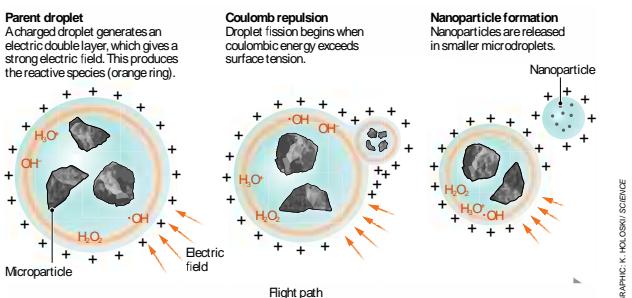
Through their study, Spoothi *et al.* have added natural weathering to a list of processes in which accelerated interfacial microdroplet reactions play an important role. Other processes include those in the atmosphere, both natural and anthropogenic, the latter typified by pollution that involves nitrate 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 Spoothi *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

Downloaded from https://www.science.org on May 30, 2024

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

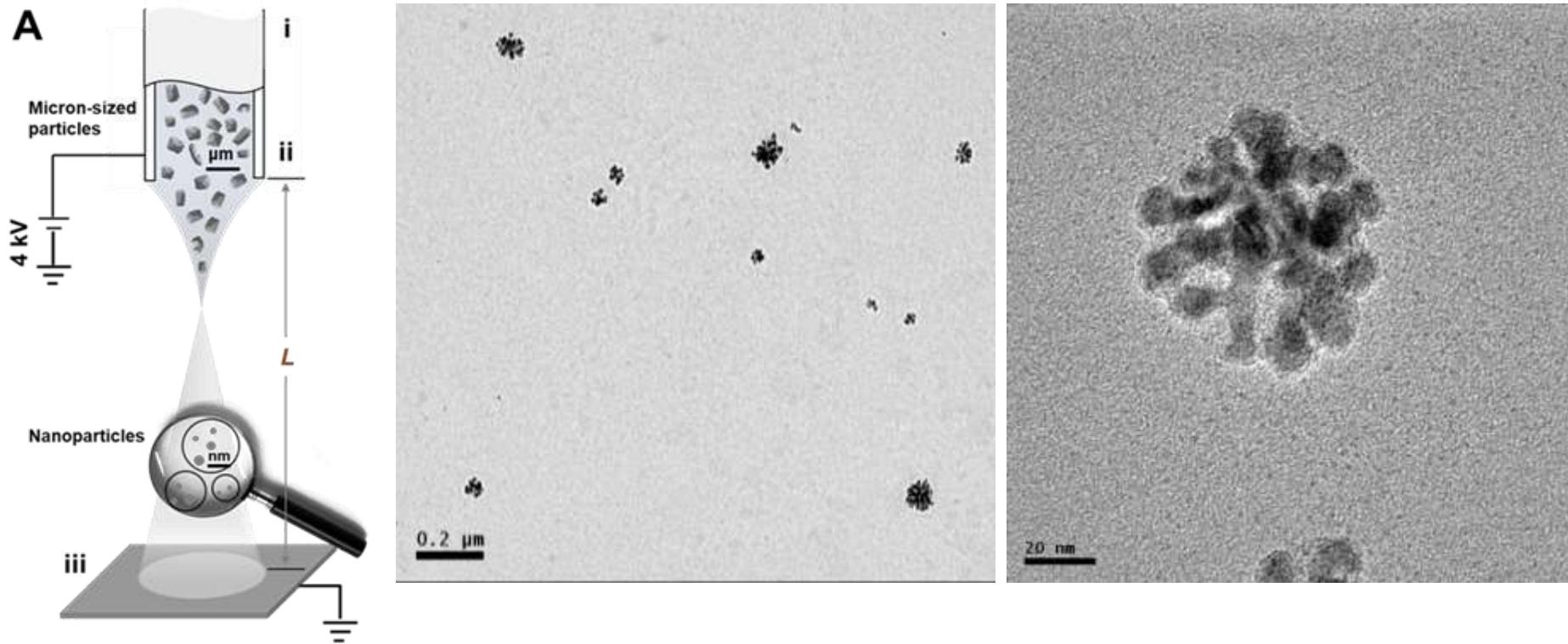
Reactions that promote mineral disintegration are accelerated at the air-water interface of microdroplets. Key reactive species are the result of the effects of a high electric field at the surface of the water droplets.



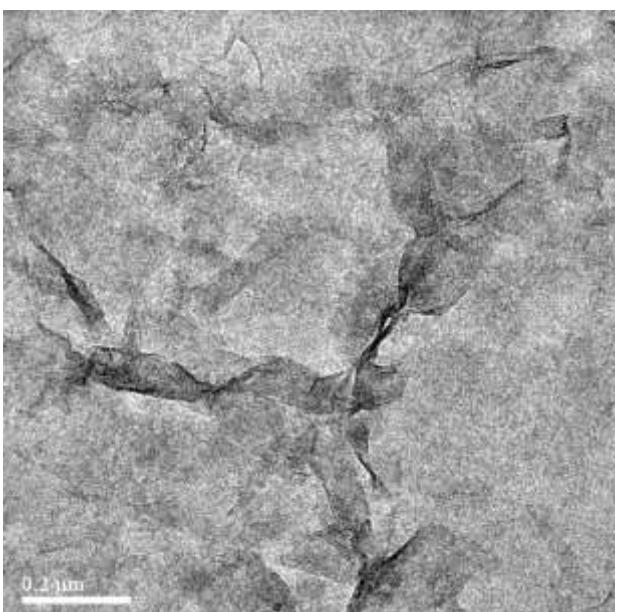
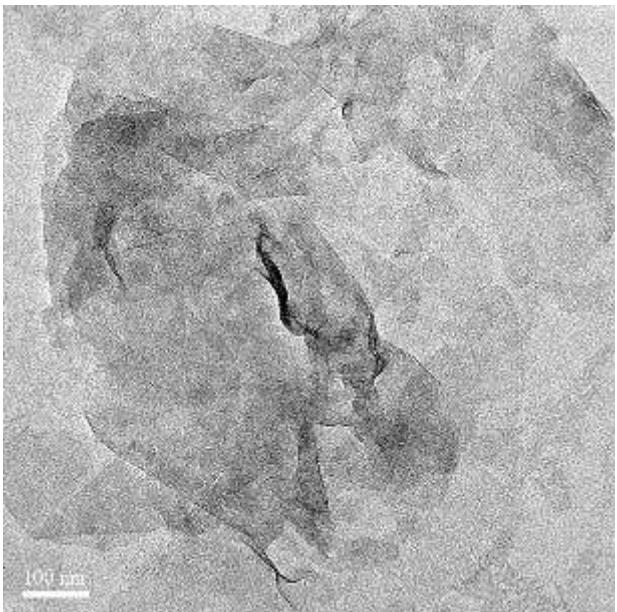
GRAPHIC: K. HOLDEN/SCIENCE

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

How do they form?



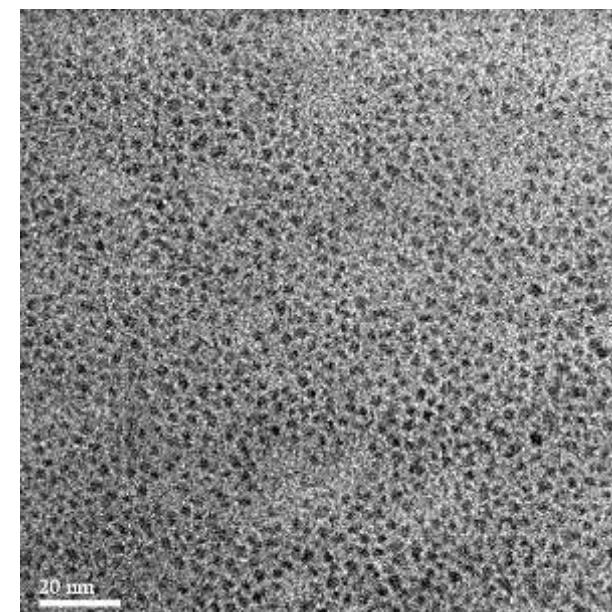
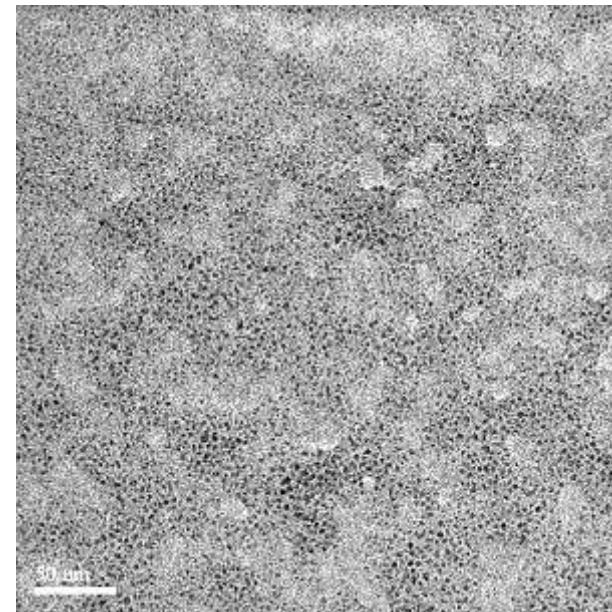
MoS₂ Nanosheets



MoS₂ Nanosheet

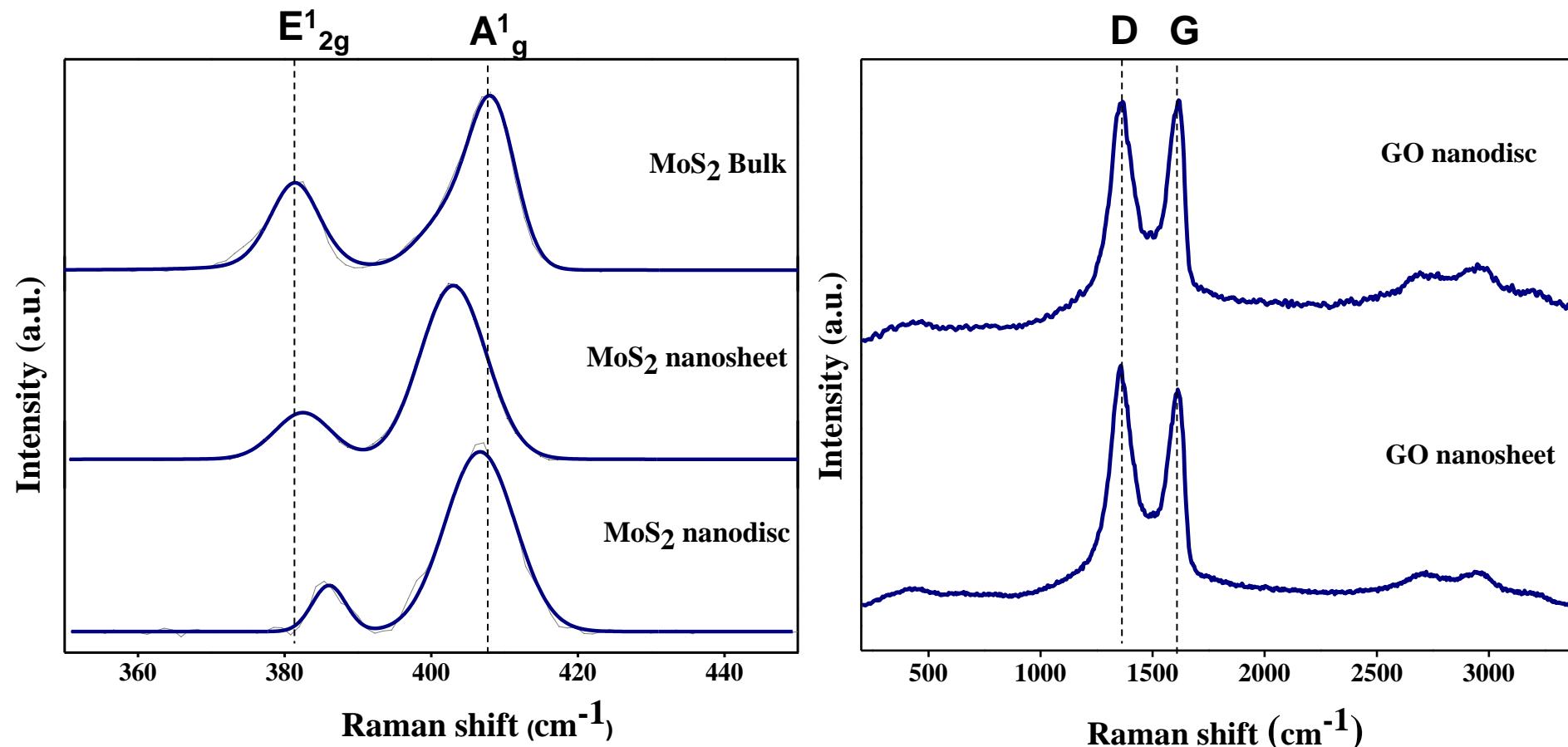
Ambient electrospray

Solvent: Water
Potential: 3.0 kV



MoS₂ Nanoparticles

Raman Spectra of MoS_2 and Graphene Oxide Nanosheets



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

Relative peak intensity
Spoorthi et al. Chem. Comm. 2025

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

Mohan Udhaya Sankar¹, Sahaja Aigal¹, Shihabudheen M. Maliyekkal¹, Amrita Chaudhary, Anshup, Avula Anil Kumar, Kamalesh Chaudhari, and Thalappil Pradeep²

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 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 problem synthesis of stable materials that can ously in the presence of complex s drinking water that deposit and caus surfaces. Here we show that such co 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 lily. The ability to prepare nanostruct ambient temperature has wide releva water purification.



Madras, Chennai 600 036, India

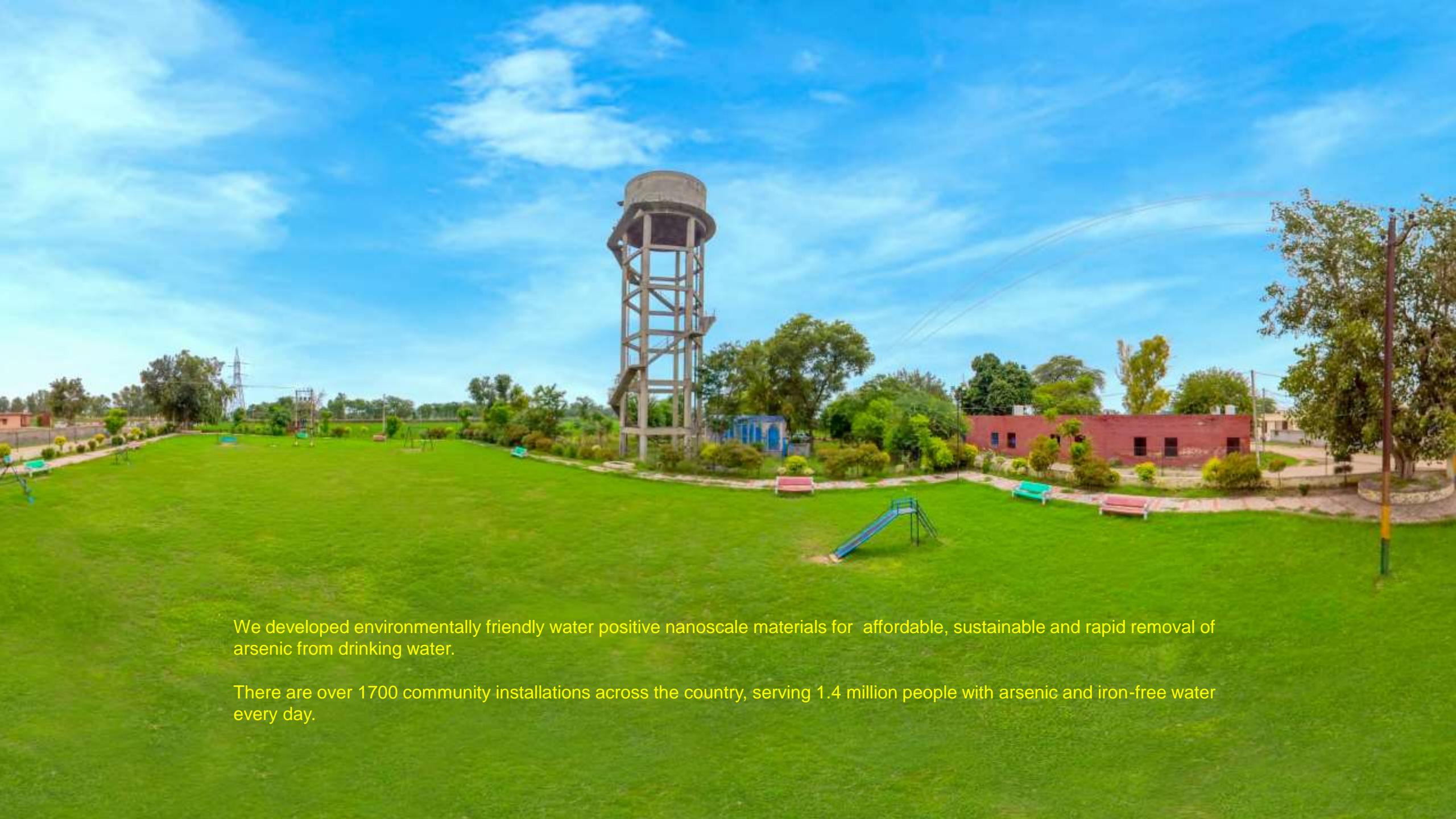
(received for review November 21, 2012)

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 al antimicrobial activity in drinking osites have been developed that can ts in water. We demonstrate an af device based on such composites de undergoing field trials in India, as spread eradication of the waterborne

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

RESULTS

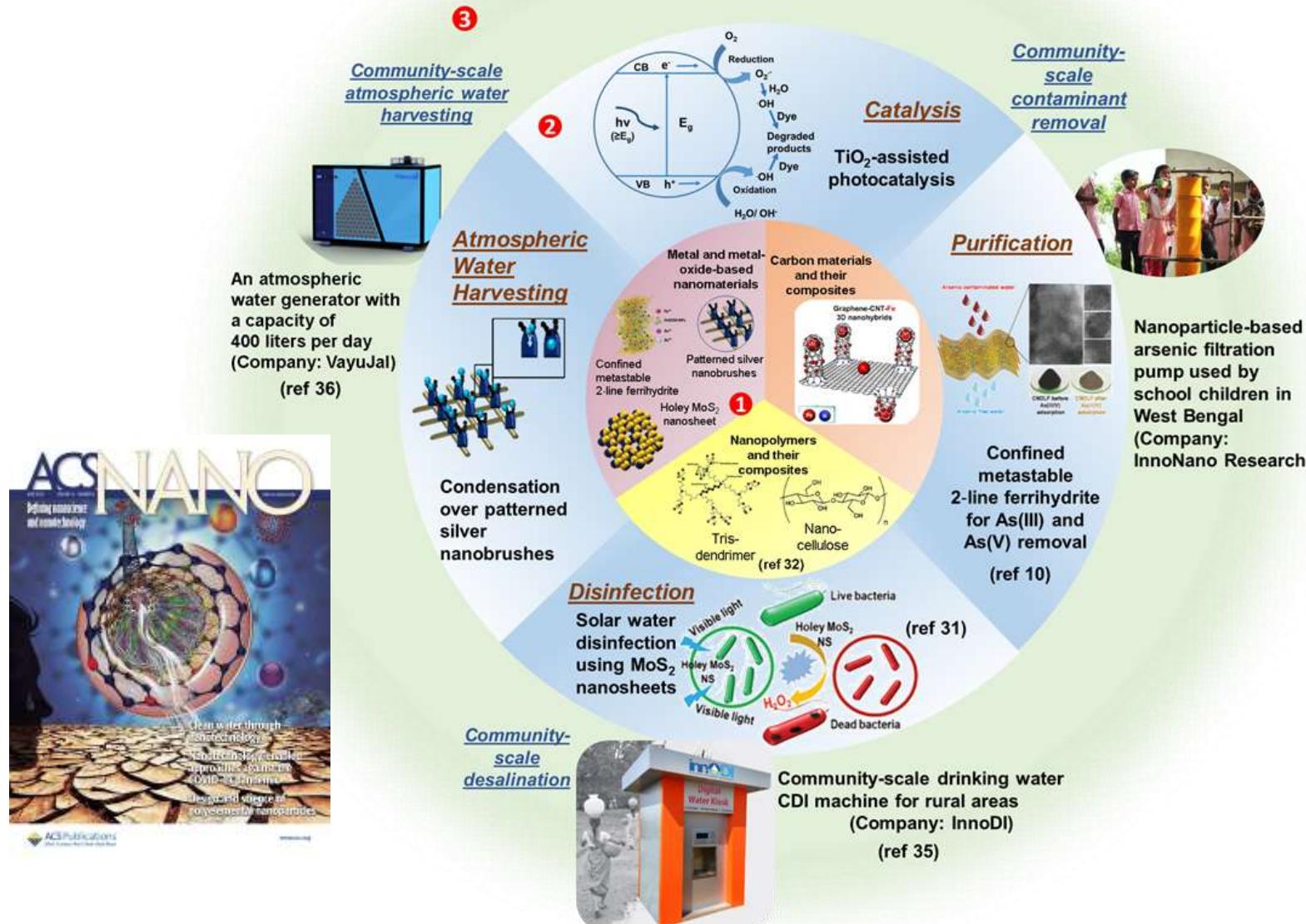
Results and Discussion



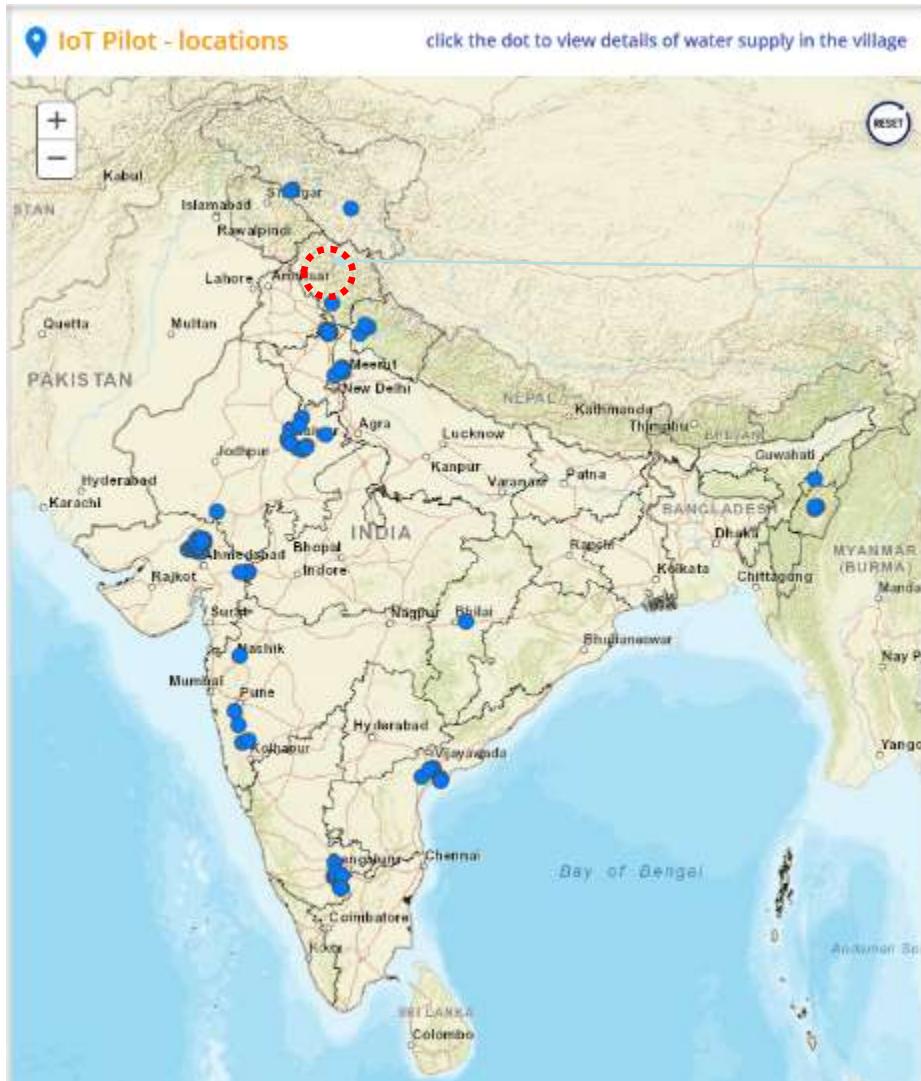
We developed environmentally friendly water positive nanoscale materials for affordable, sustainable and rapid removal of arsenic from drinking water.

There are over 1700 community installations across the country, serving 1.4 million people with arsenic and iron-free water every day.

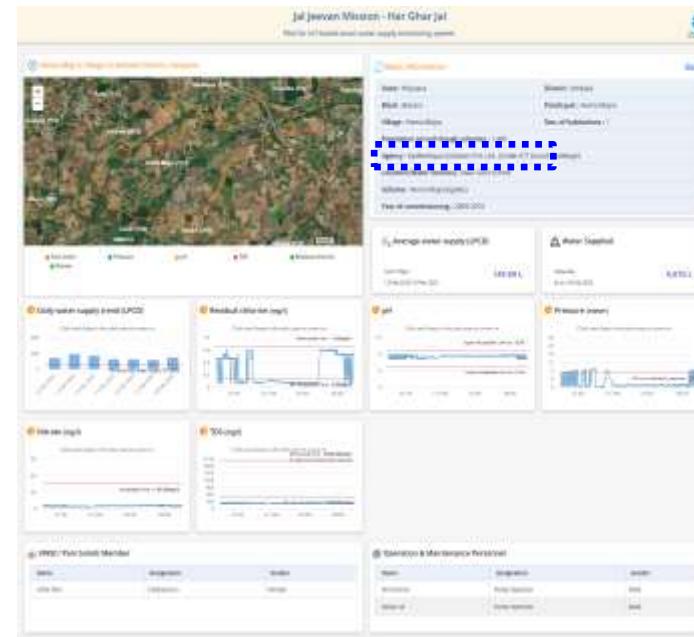
Evolution of materials to products



India's water is being monitored



IITM/IISc
Installations made by four companies

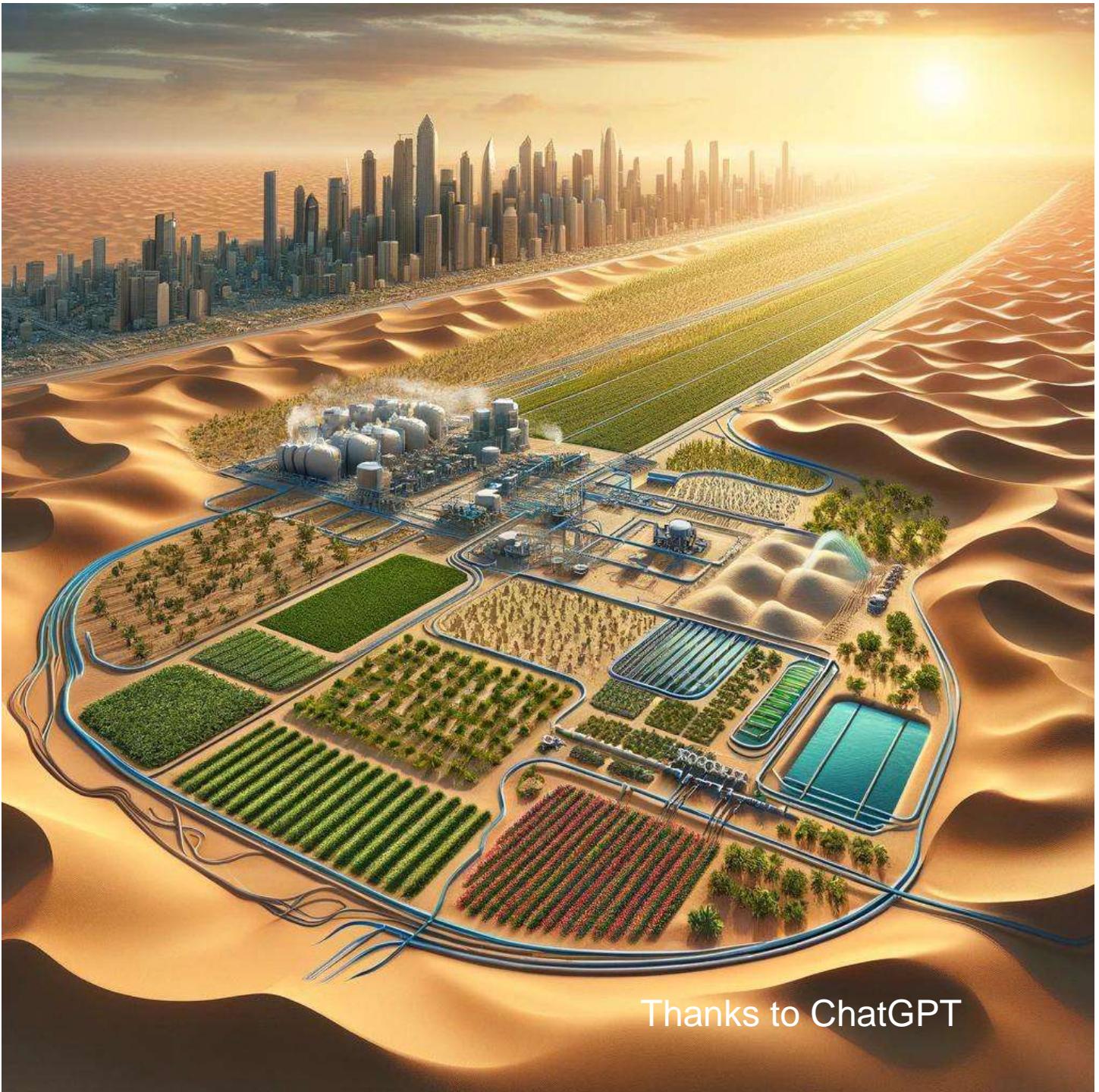




Thanks to ChatGPT

Vision

Make soil using processed wastewater and make deserts bloom.



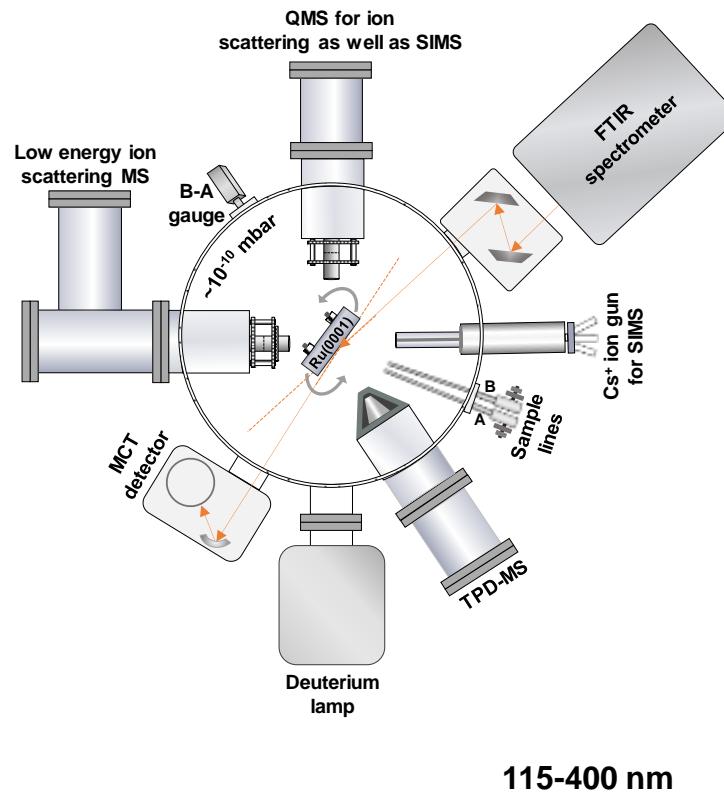
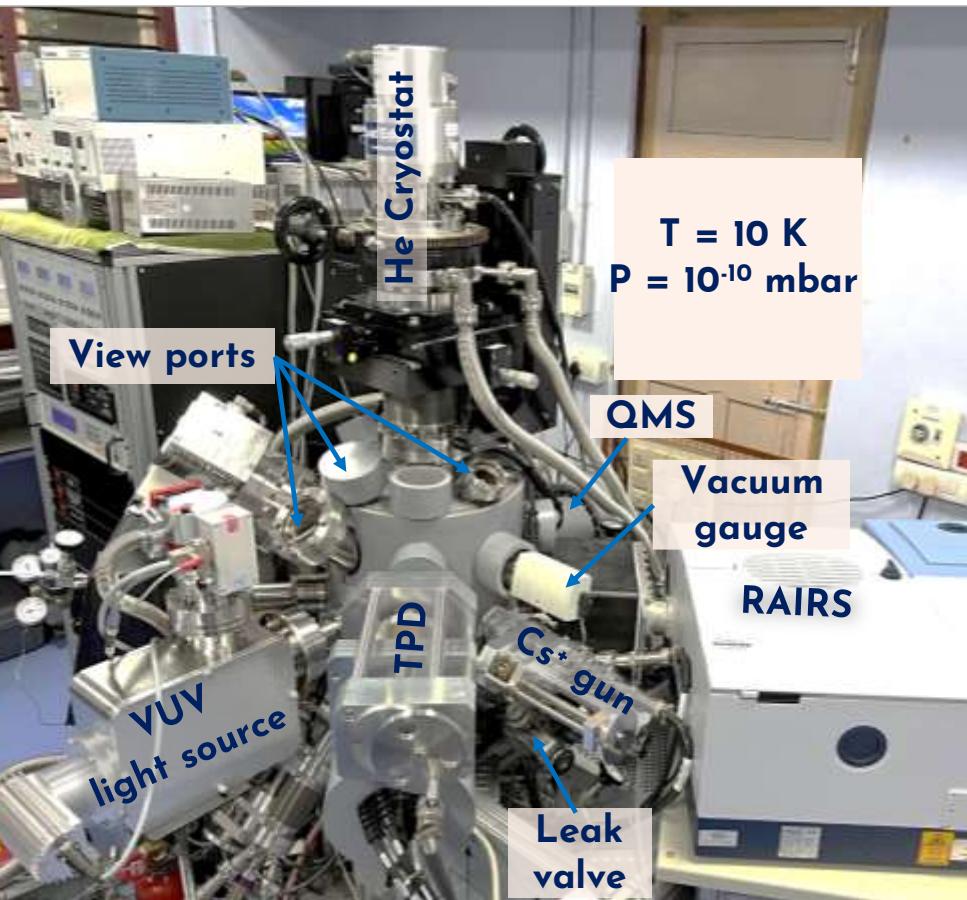
Thanks to ChatGPT



Can Clathrate Hydrates Exist in Space?

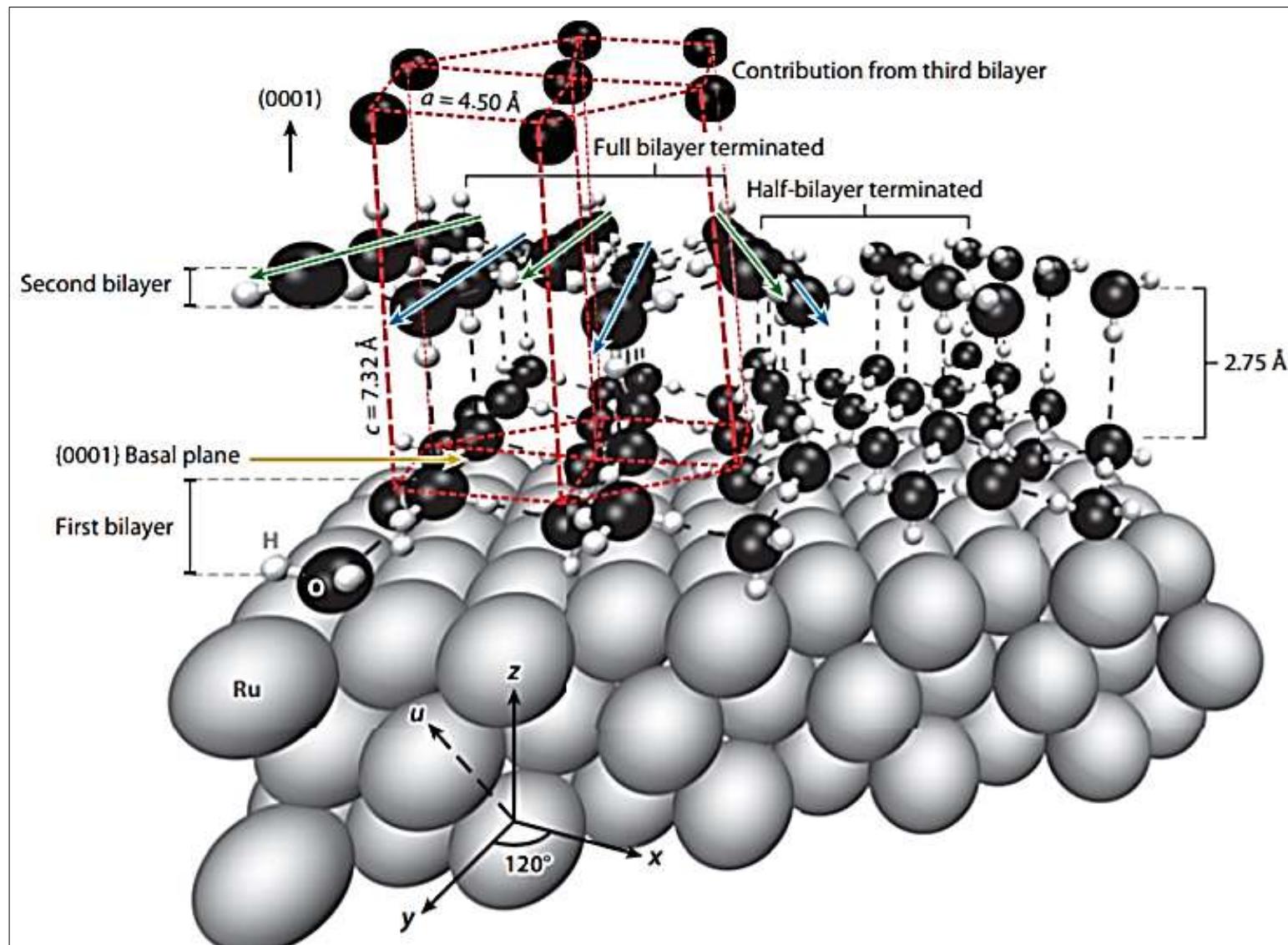
Exploring astrobiology

Instrumentation



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

Viswakarma, G. et al., *J. Phys. Chem. Lett.*, **2023**, *14*, 2823–2829

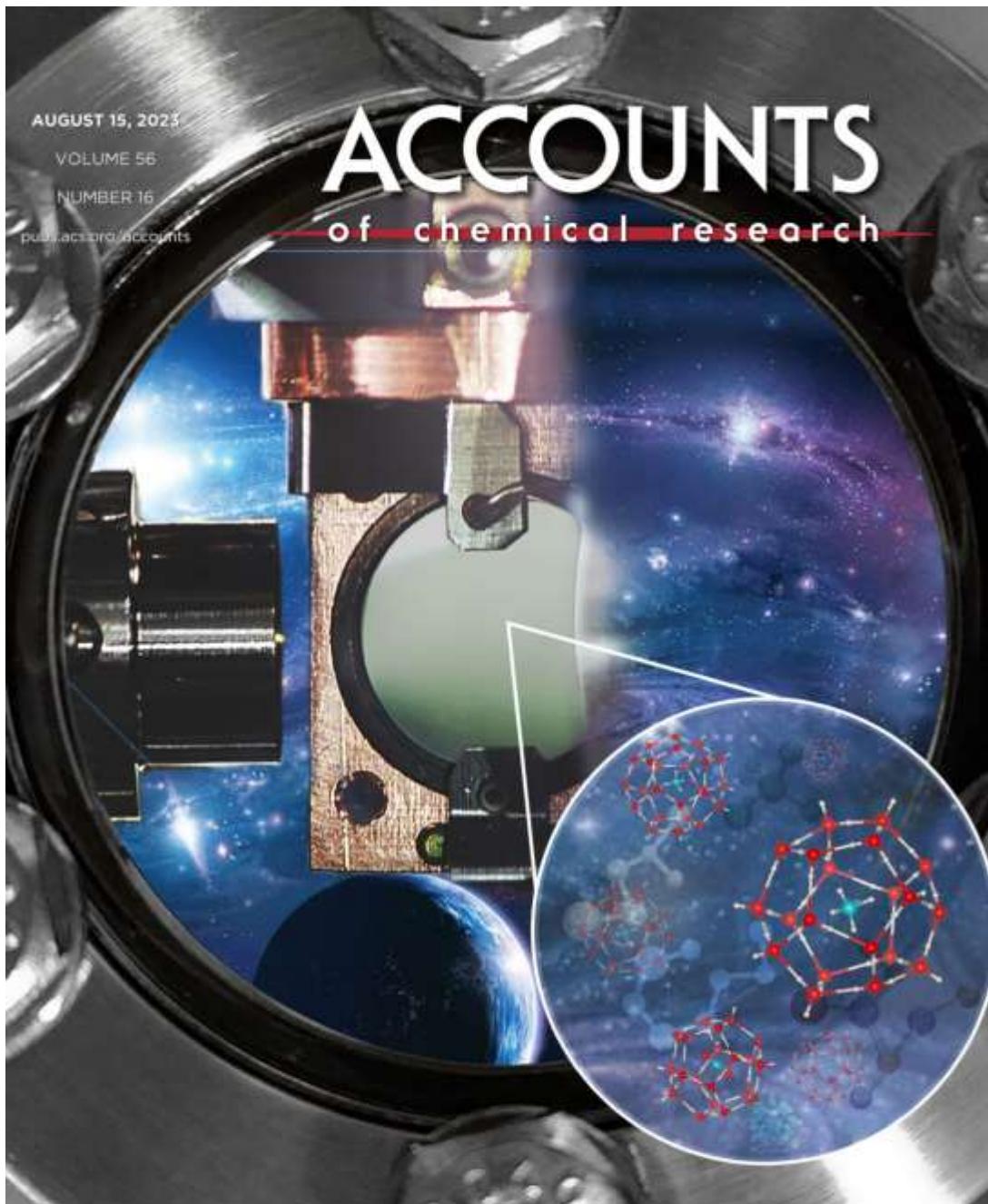


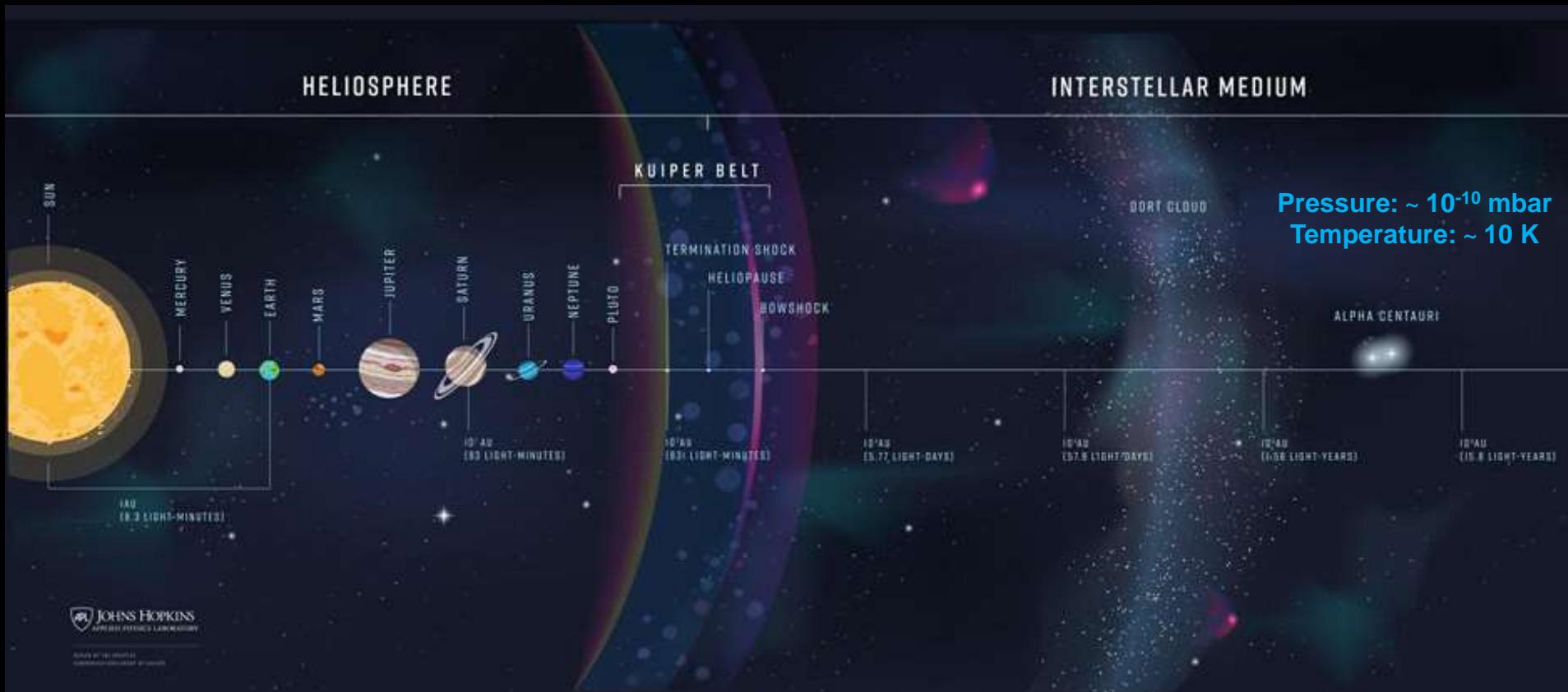
Formation and Transformation of Clathrate Hydrates under Interstellar Conditions

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

 Cite This: <https://doi.org/10.1021/acs.accounts.3c00317>

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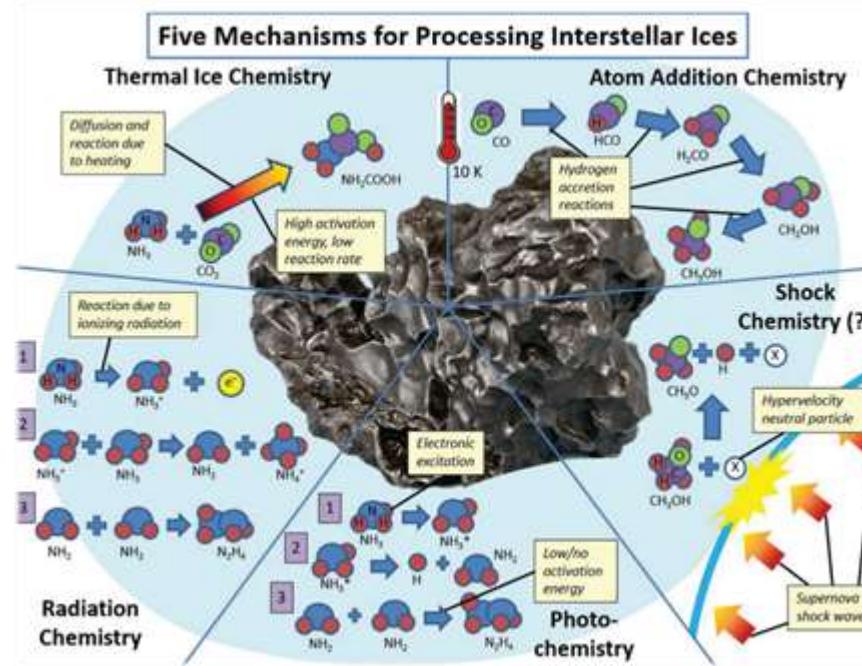
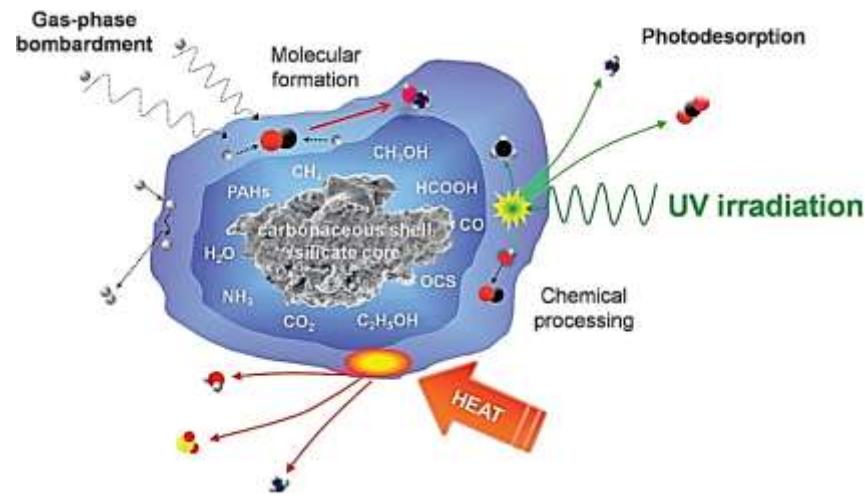


Diffuse clouds: $T \sim 100$ K, $n \sim 100$ molecules per cm^3

Dense clouds: $T \sim 10\text{-}100 \text{ K}$, $n \sim 10^4\text{-}10^8 \text{ molecules per cm}^3$

On Earth sea level: $T \sim 300 \text{ K}$, $n \sim 3 \times 10^{19} \text{ molecules per cm}^3$

Interstellar ices

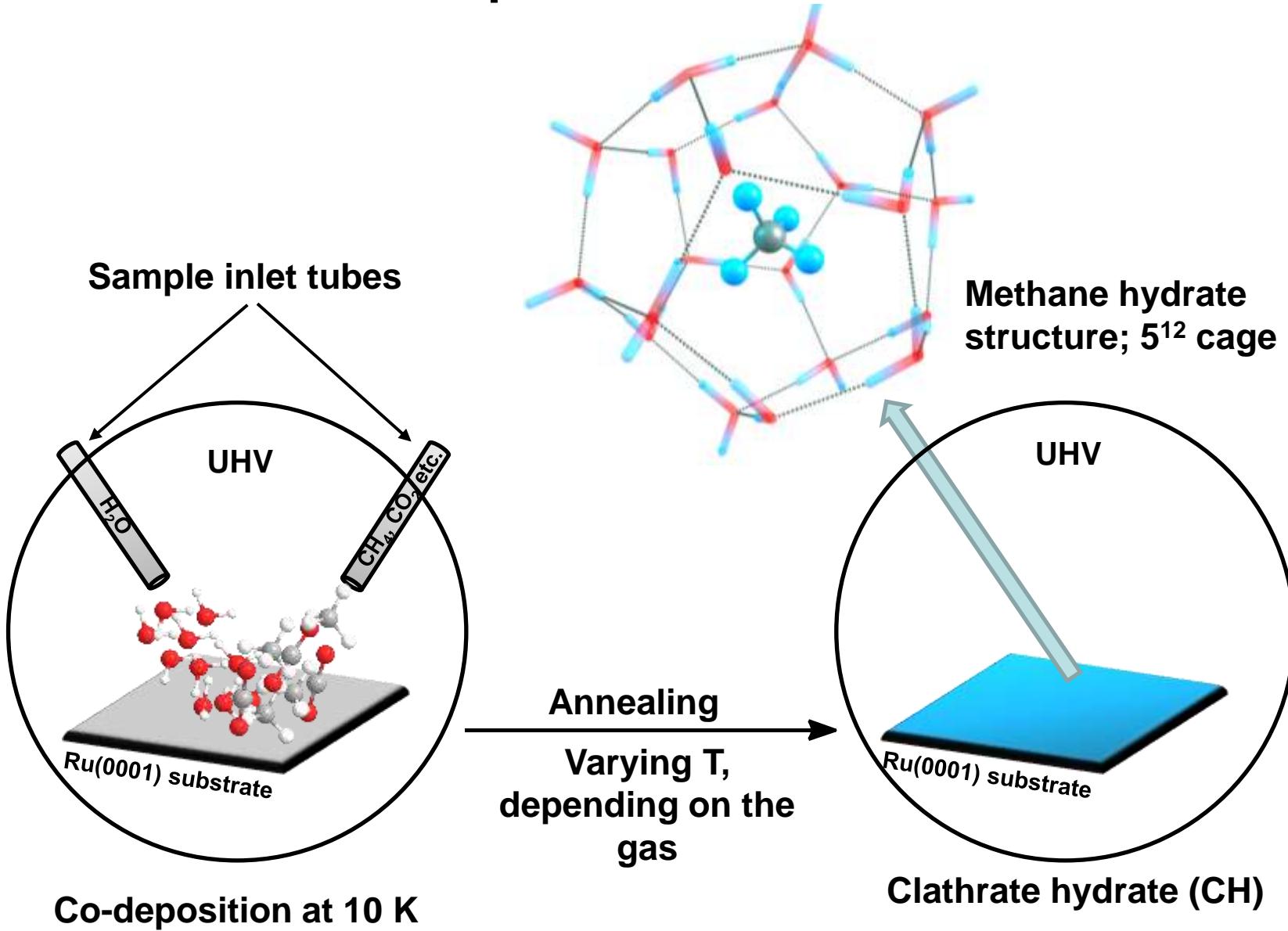


Silicates and carbonaceous material – 0.01-0.5 μm

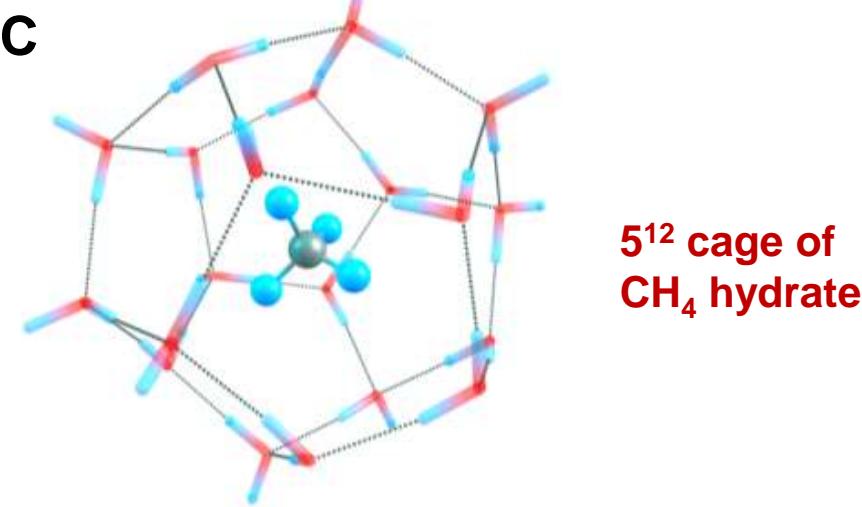
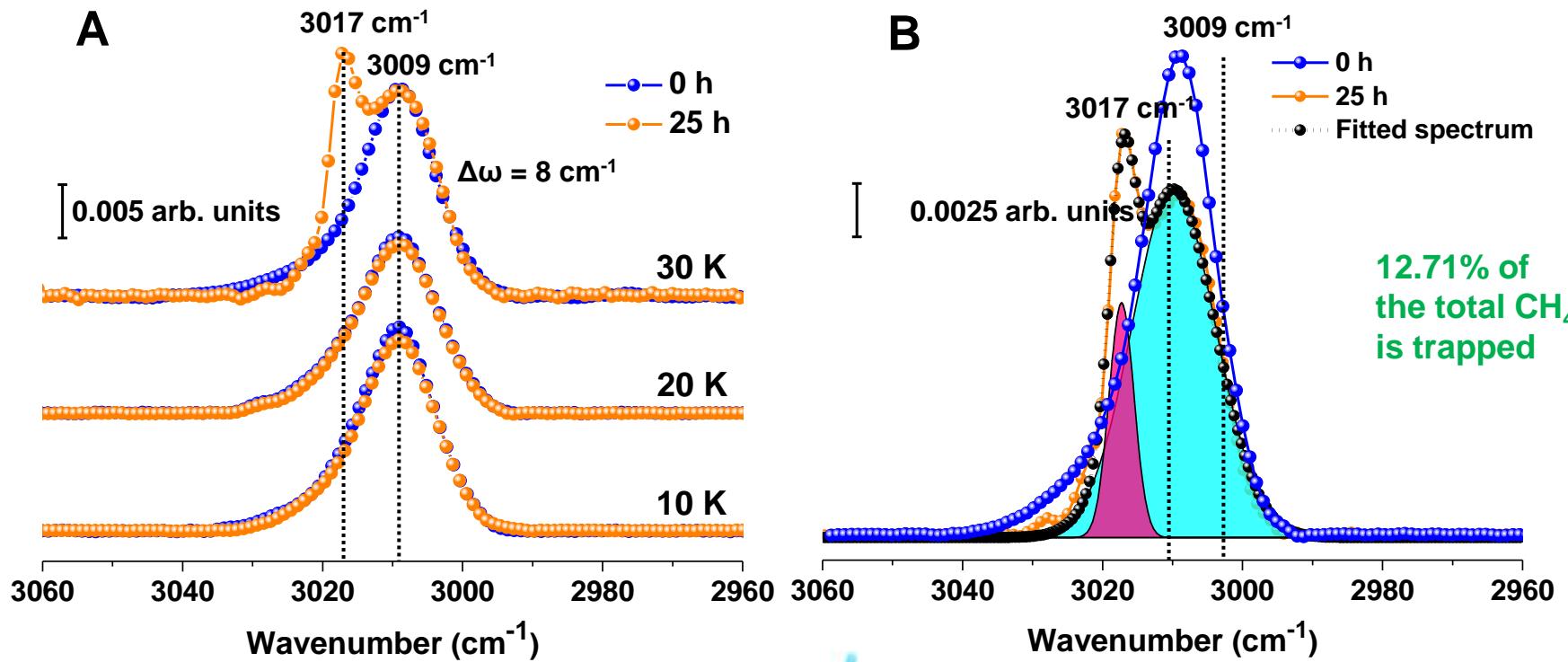
Clathrate hydrates in interstellar environment

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

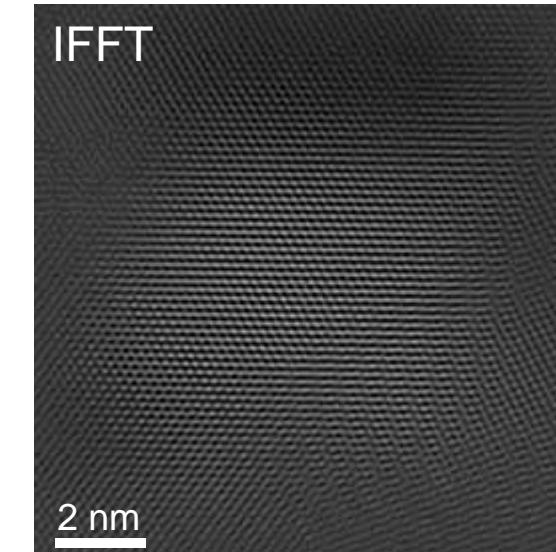
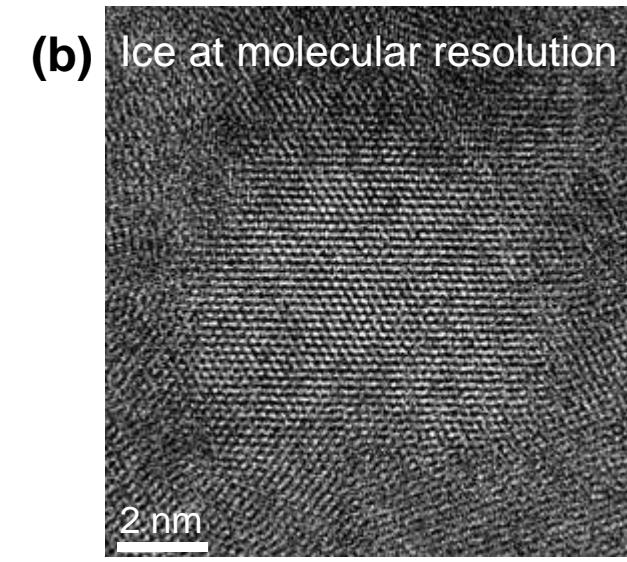
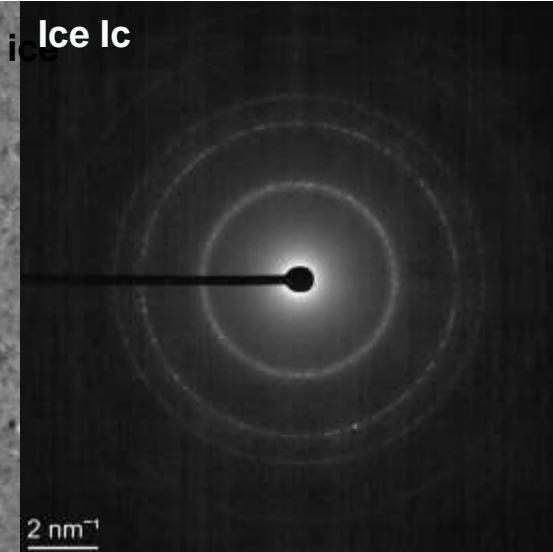
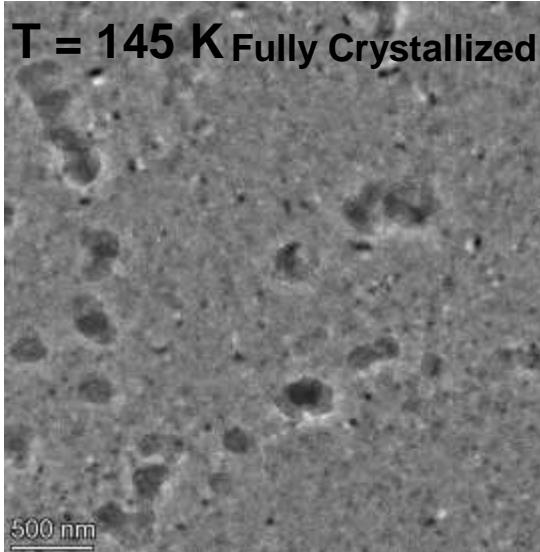
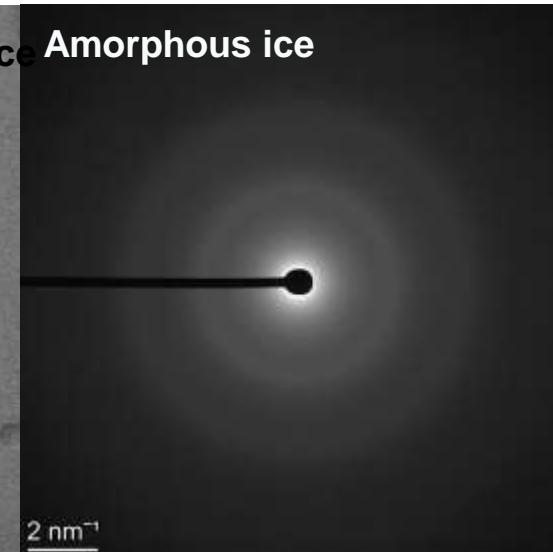
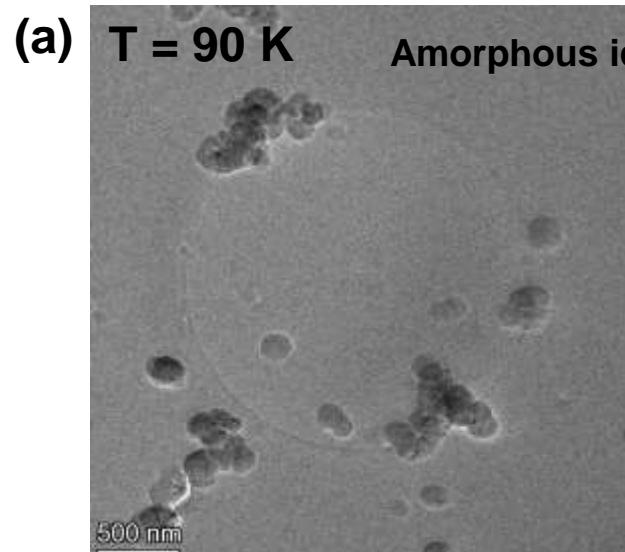
Experimental method



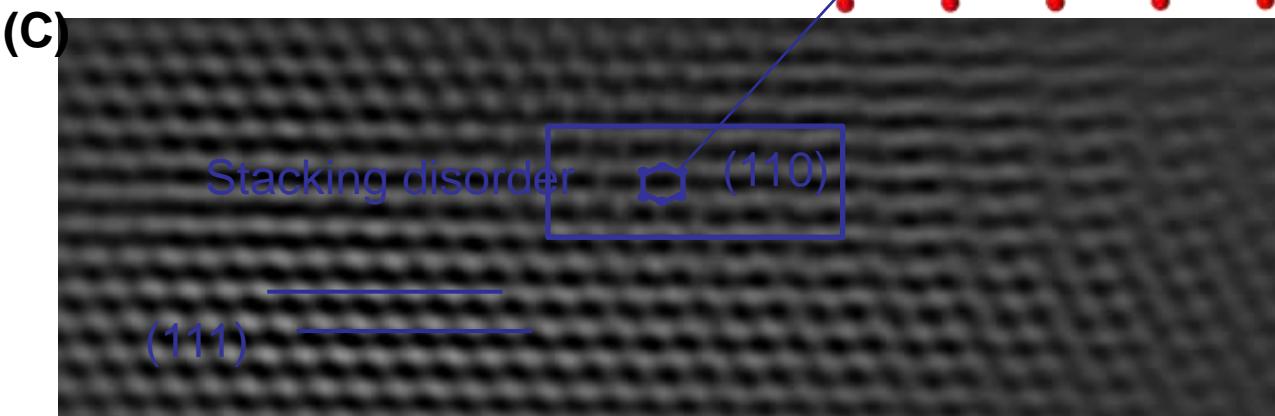
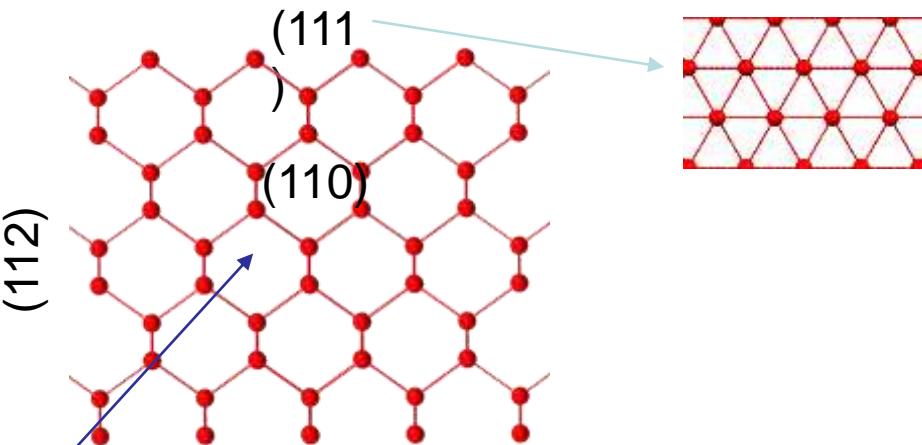
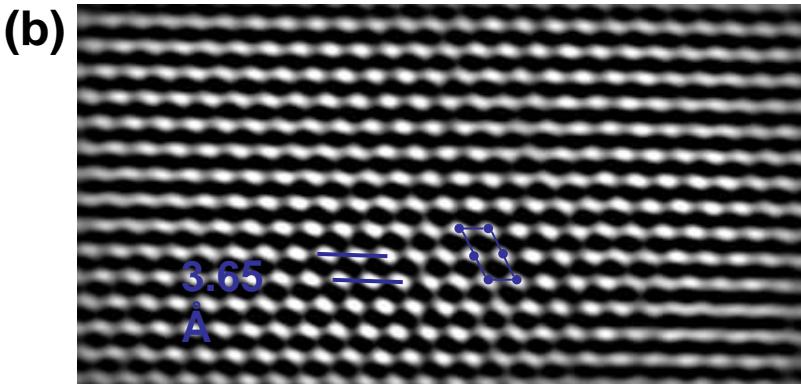
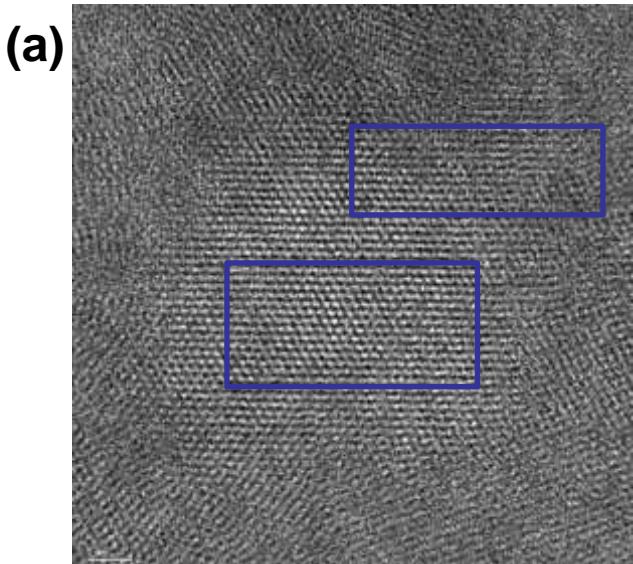
Clathrate hydrates in interstellar environment



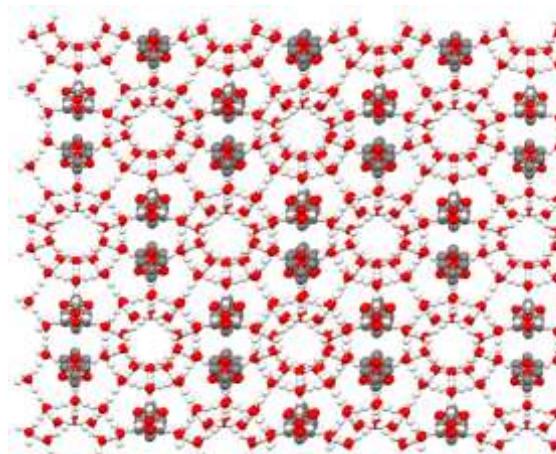
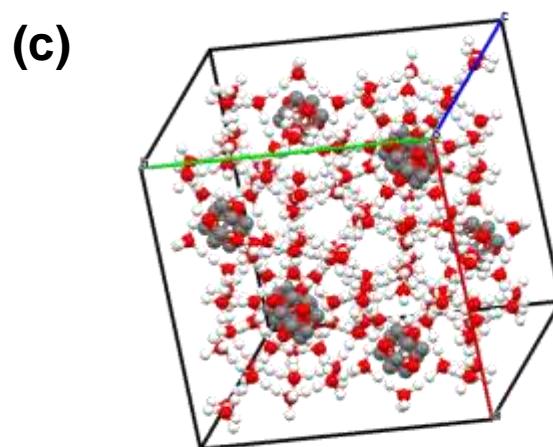
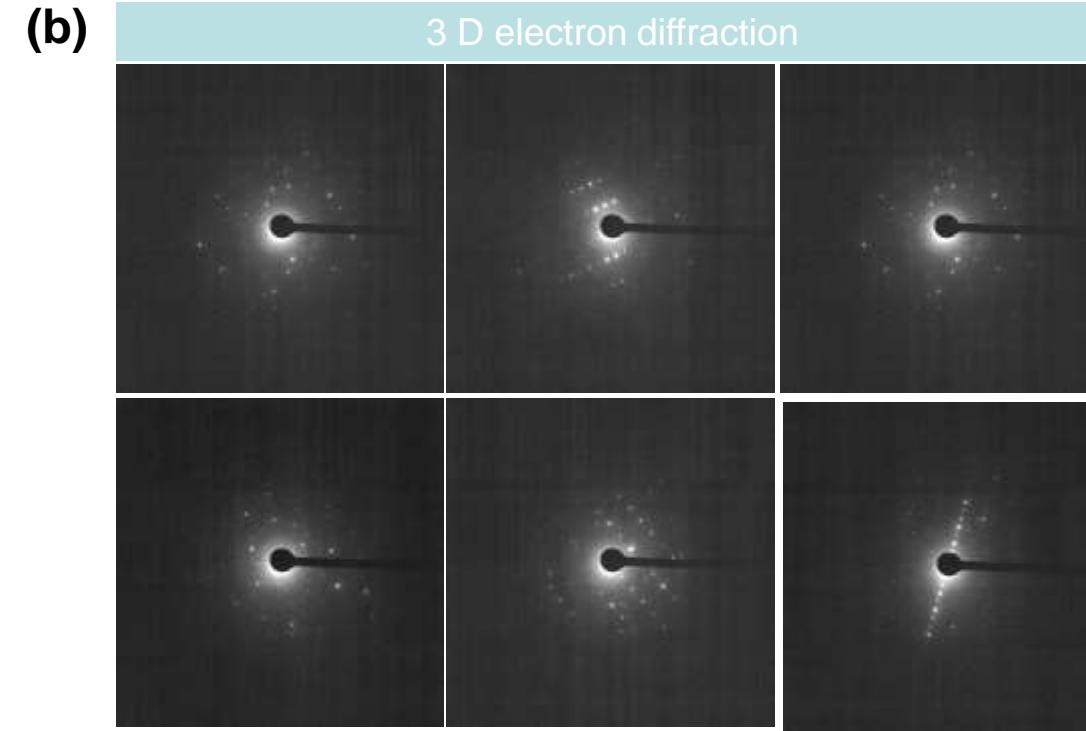
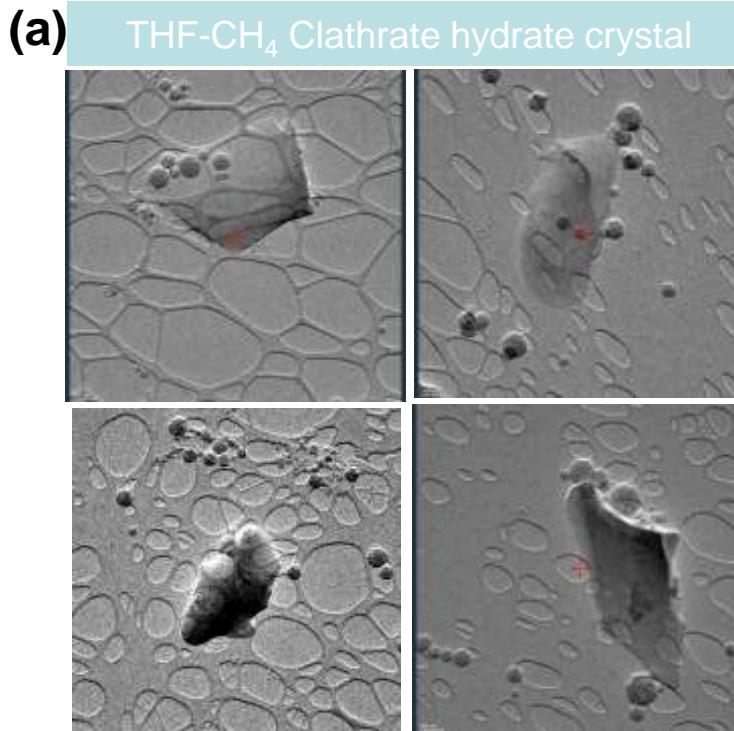
Observing growth of crystalline ice from amorphous ice



Imaging cubic ice at molecular resolution



Electron diffraction of nanometer-scale crystals of clathrate hydrate



Crystal structure



International Centre for Clean Water

People's Water Data

Visit Course

Sample ID
HA09041000

Source
Household water sample

Date
25/4/2024

Parameters Overview

TDS
ORP
Turbidity
pH
Alkalinity
Coliform
Conductivity
Hardness
TotalChlorine
EColi
FreeChlorine

PEOPLES WATER DATA

PEOPLES WATER DATA

Visit Course

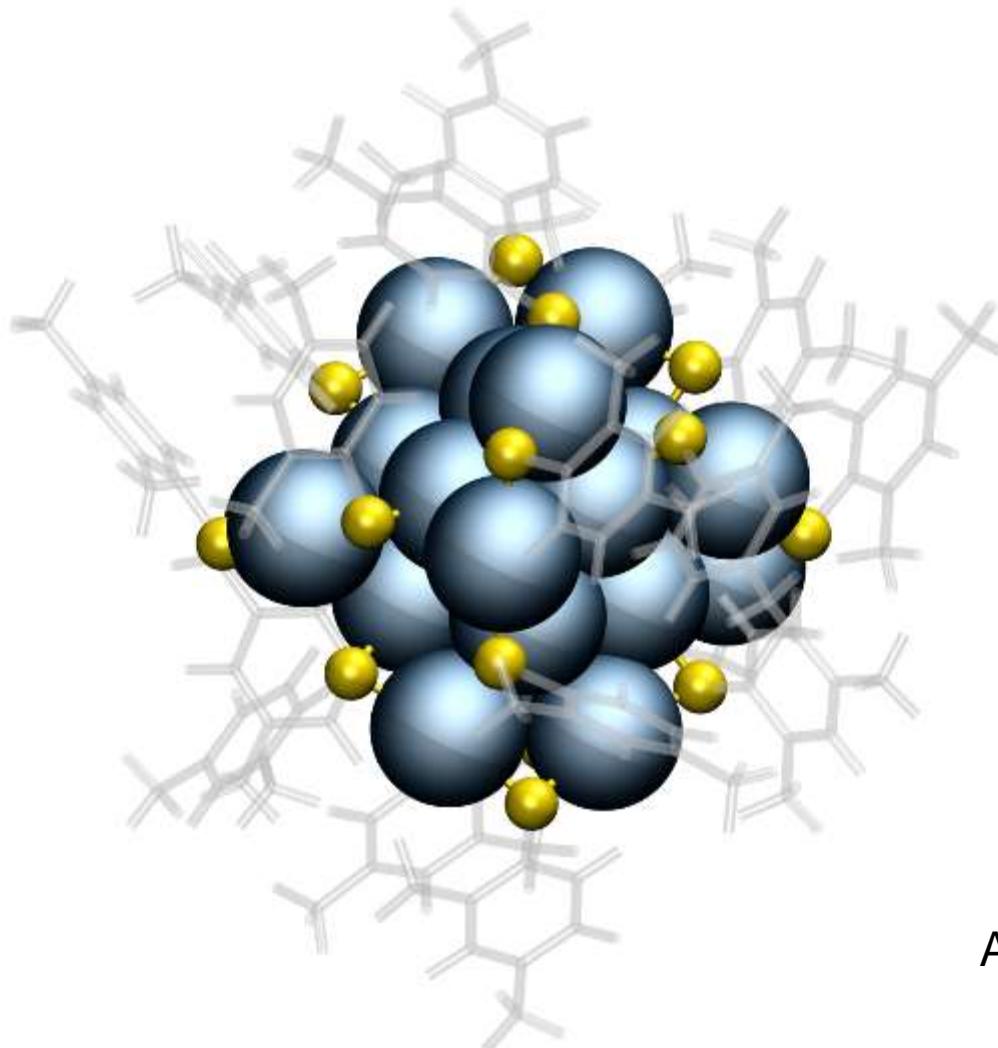
Go To Home

Go To Home

A course by IITM

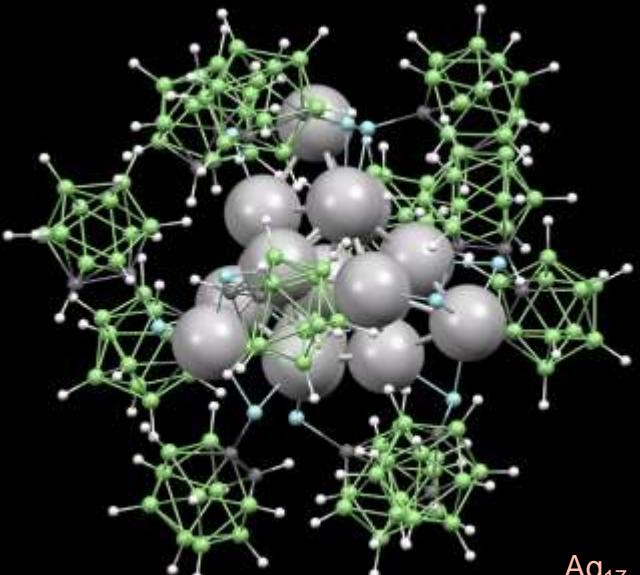
51

New molecules

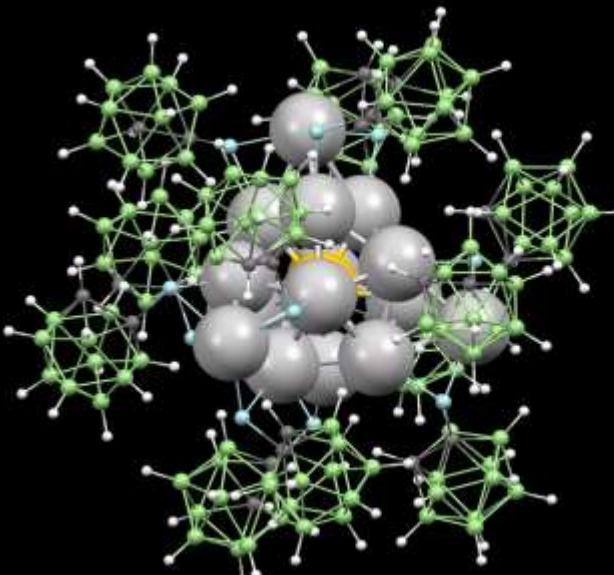


$\text{Au}_{25}, \text{Ag}_{25}, \text{Ag}_{29}$

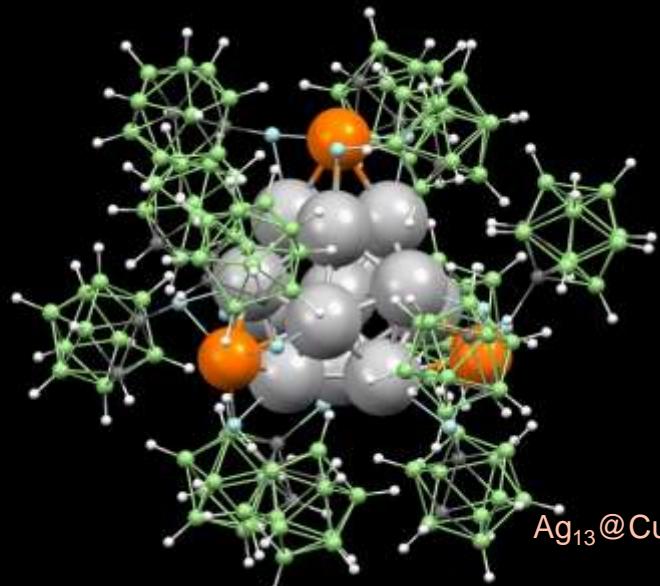
Structure of M_{17} Nanoclusters



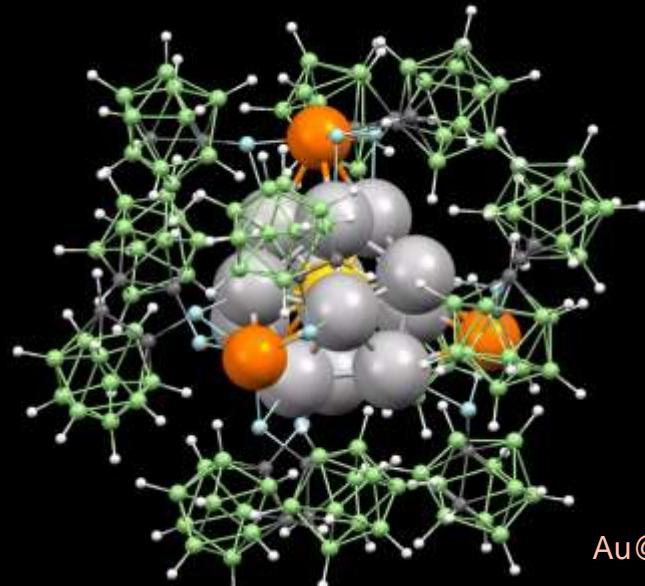
Ag_{17}



$Au@Ag_{16}$



$Ag_{13} @ Cu_4$



$Au @ Ag_{12} @ Cu_4$

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

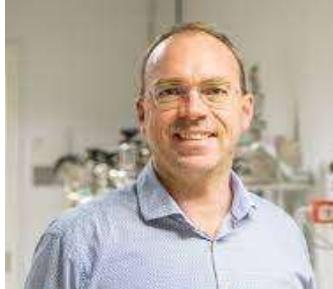
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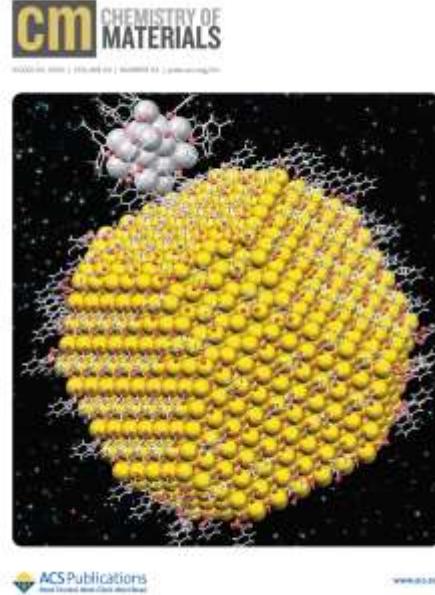
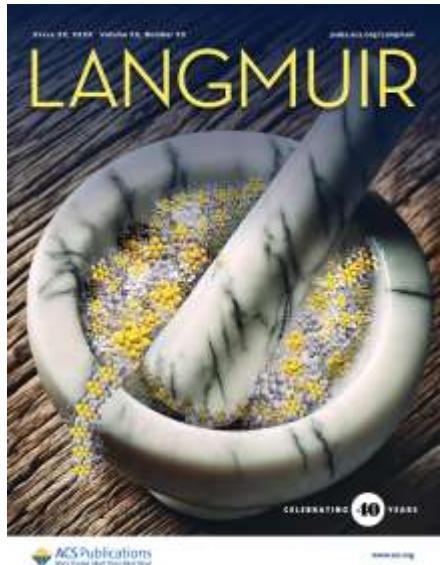


Vivek Polshettiwar

Department of Science and Technology

Institute of Eminence

Many Outstanding Individuals







Indian Institute of Technology Madras



Bhaskar Ramamurthi/V. Kamakoti

Thank you all

