Since 1959

Can Microdroplets Make Soil?

A path to sustainable nanotechnology

Matter in confinement for sustainability

Thalappil Pradeep

Institute Professor, IIT Madras

https://pradeepresearch.org/

pradeep@iitm.ac.in

Co-founder

InnoNano Research Pvt. Ltd.
InnoDI Water Technologies Pvt. Ltd.
VayuJAL Technologies Pvt. Ltd.
Aqueasy Innovations Pvt. Ltd.
Hydromaterials Pvt. Ltd.
EyeNetAqua Pvt. Ltd.
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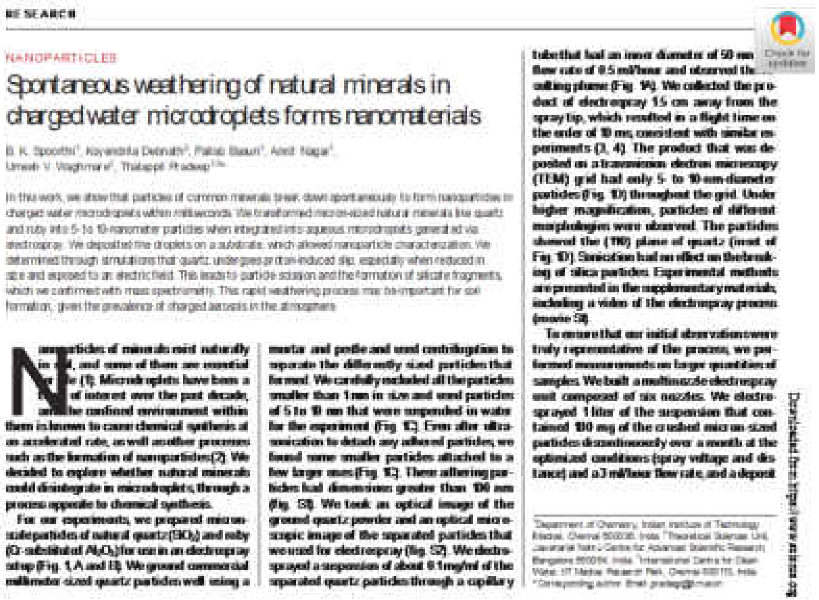
Professor-in-charge

International Centre for Clean Water

Institute Colloquium, IIT Madras, August 7, 2024

Science



RESEARCH

NANOPARTICLES

Spontaneous weathering of natural minerals in charged water microdroplets forms nanomaterials

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

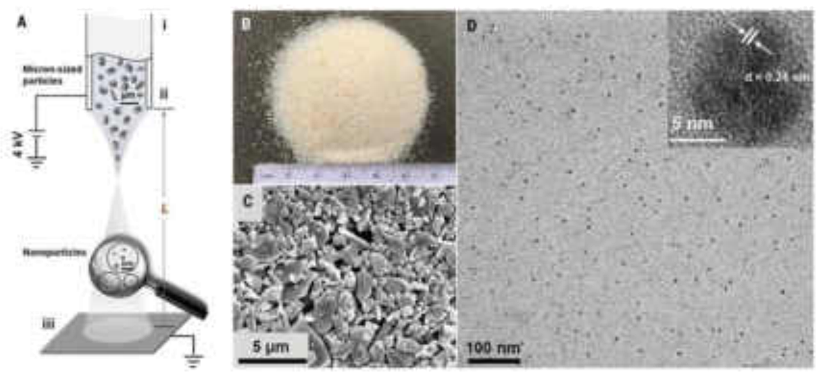
In this work, we show that particles of common minerals break down spontaneously to form nanoparticles in charged water microdroplets within milliseconds. We transformed micron-sized natural minerals like quartz and ruby into 5- to 10-nanometer particles when integrated into aqueous microdroplets generated 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 for life (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. S3). 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 flow rate of 0.5 ml/hour and observed the 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

[1]Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India. [2]Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India. [3]International Centre for Clean Water, IIT Madras Research Park, Chennai 600113, India.
*Corresponding author. Email: pradeep@iitm.ac.in



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

A scale of 1000

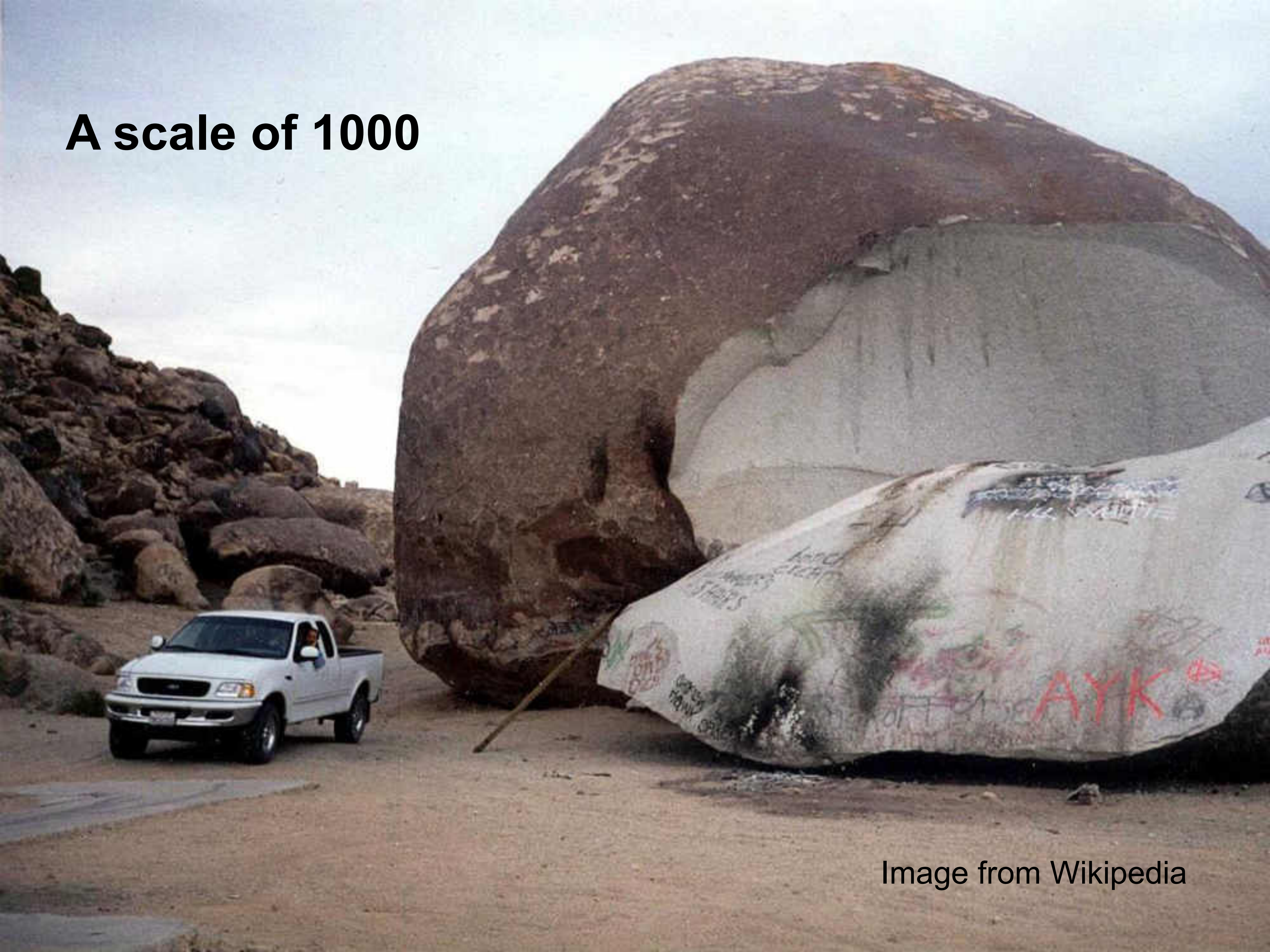
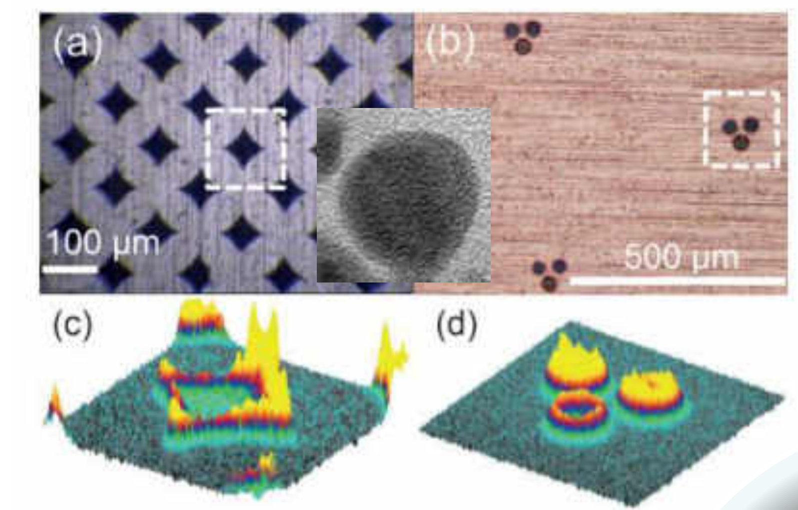
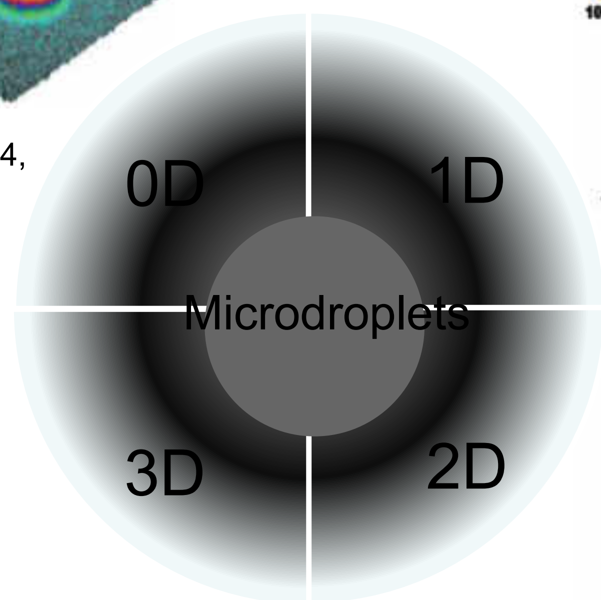


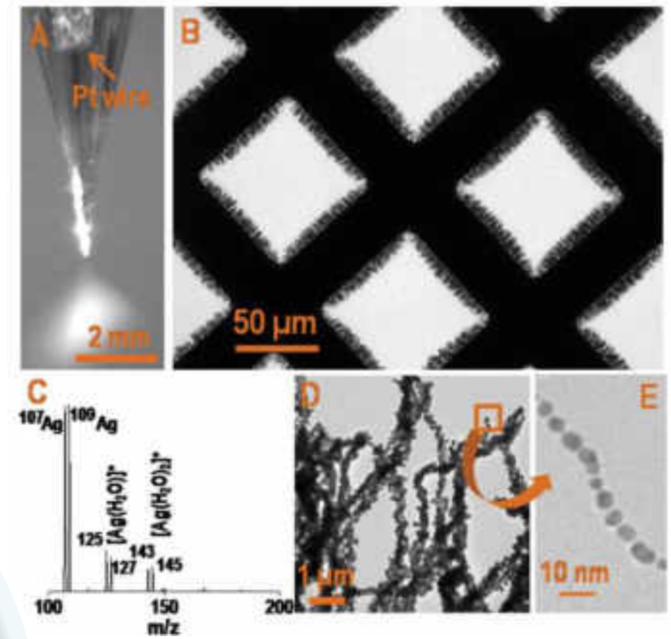
Image from Wikipedia

Functional Nanomaterials

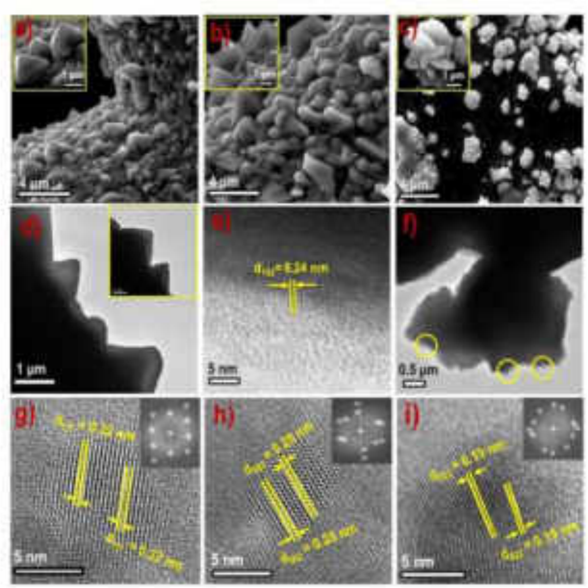


Anyin Li, et. al., Angew. Chem. Int. Ed. 2014, 53, 12528 –12531.

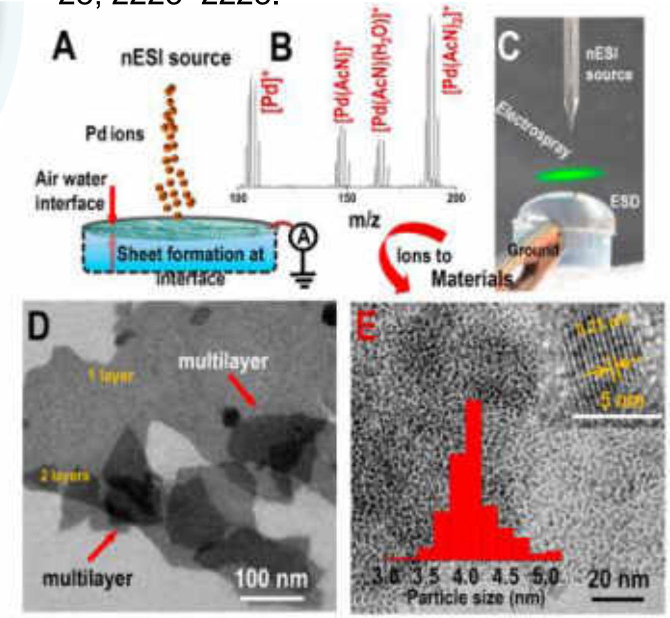




Depanjan Sarkar et. al., *Adv. Mater.* 2016, 28, 2223–2228.



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



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

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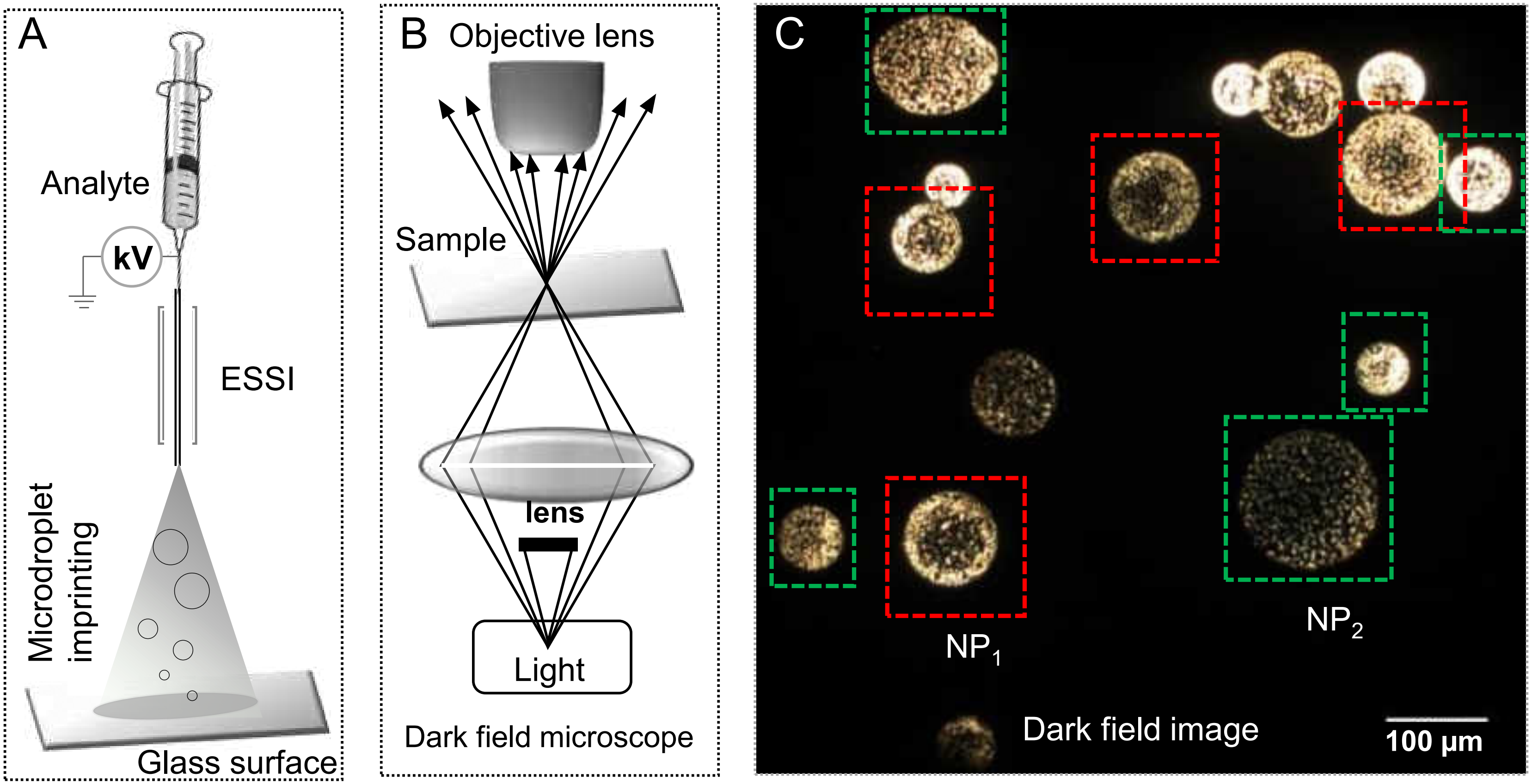
ROYAL SOCIETY OF CHEMISTRY

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

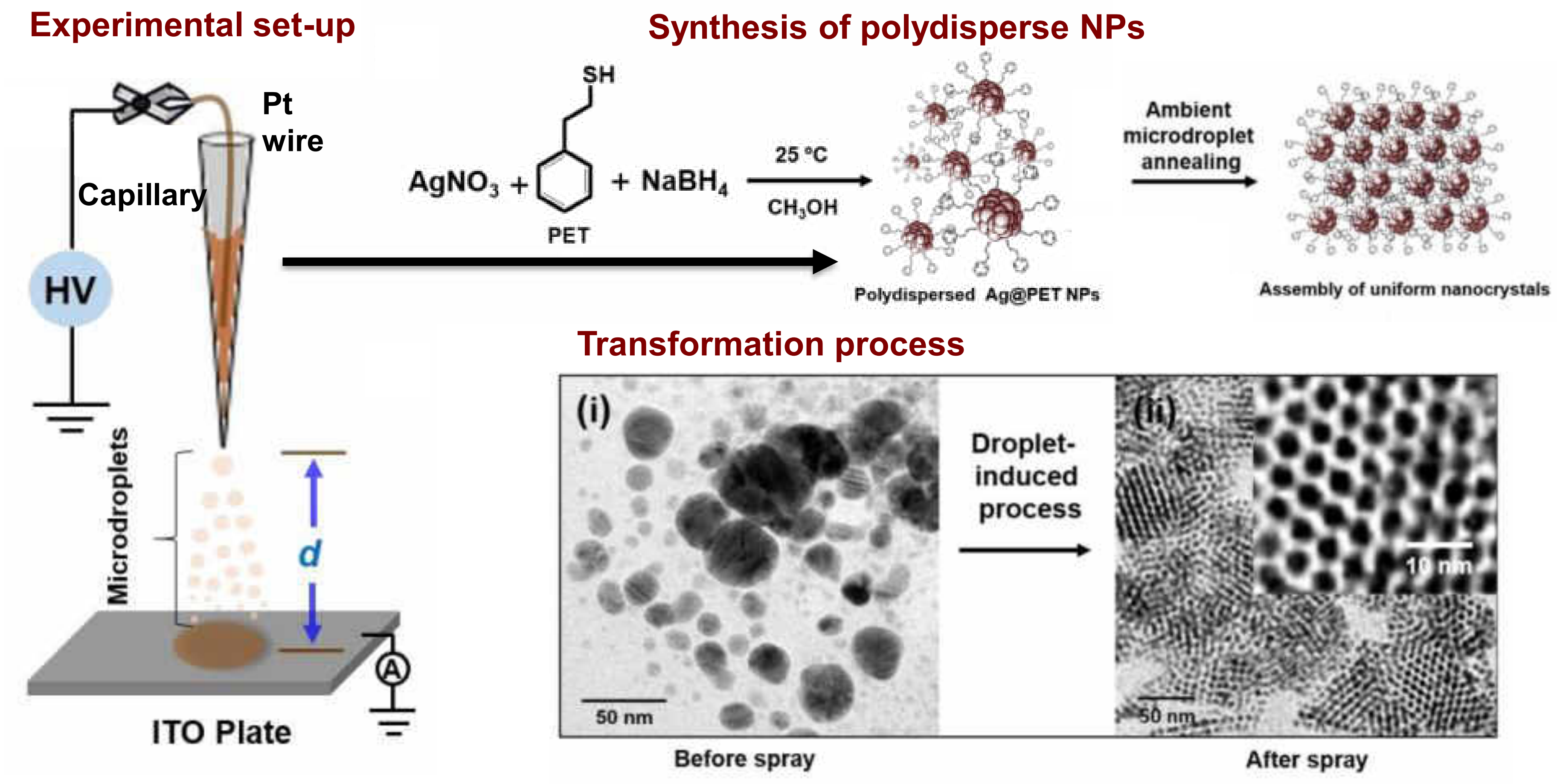
Understanding Microdroplets



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

Transformation of Materials in Microdroplets

Ambient Microdroplet Annealing of Nanoparticles



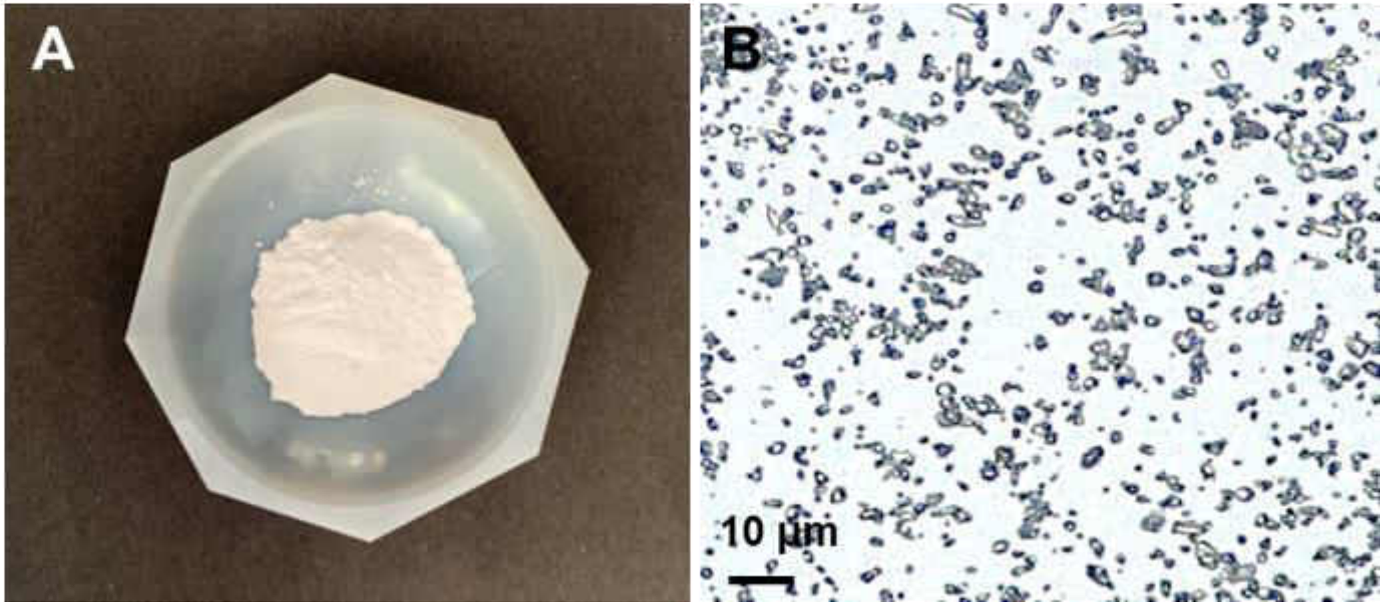
Angshuman Ray Chowdhuri et. al., *Chem. Sci.*, 2021, 12, 6370–6377.


Thanks to ChatGPT

Weathering in Nature

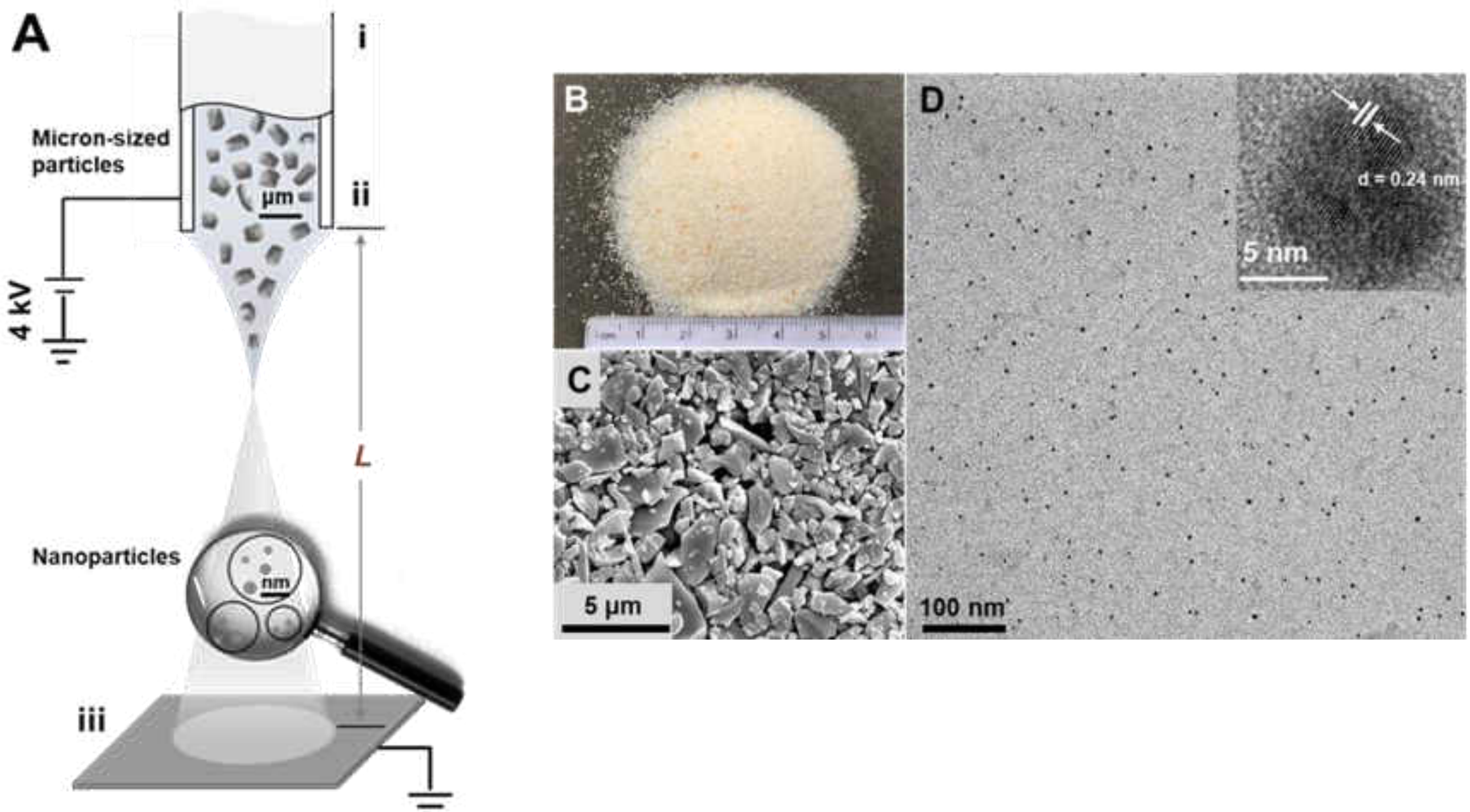
Sand, the Ubiquitous Material

Images from Wikipedia



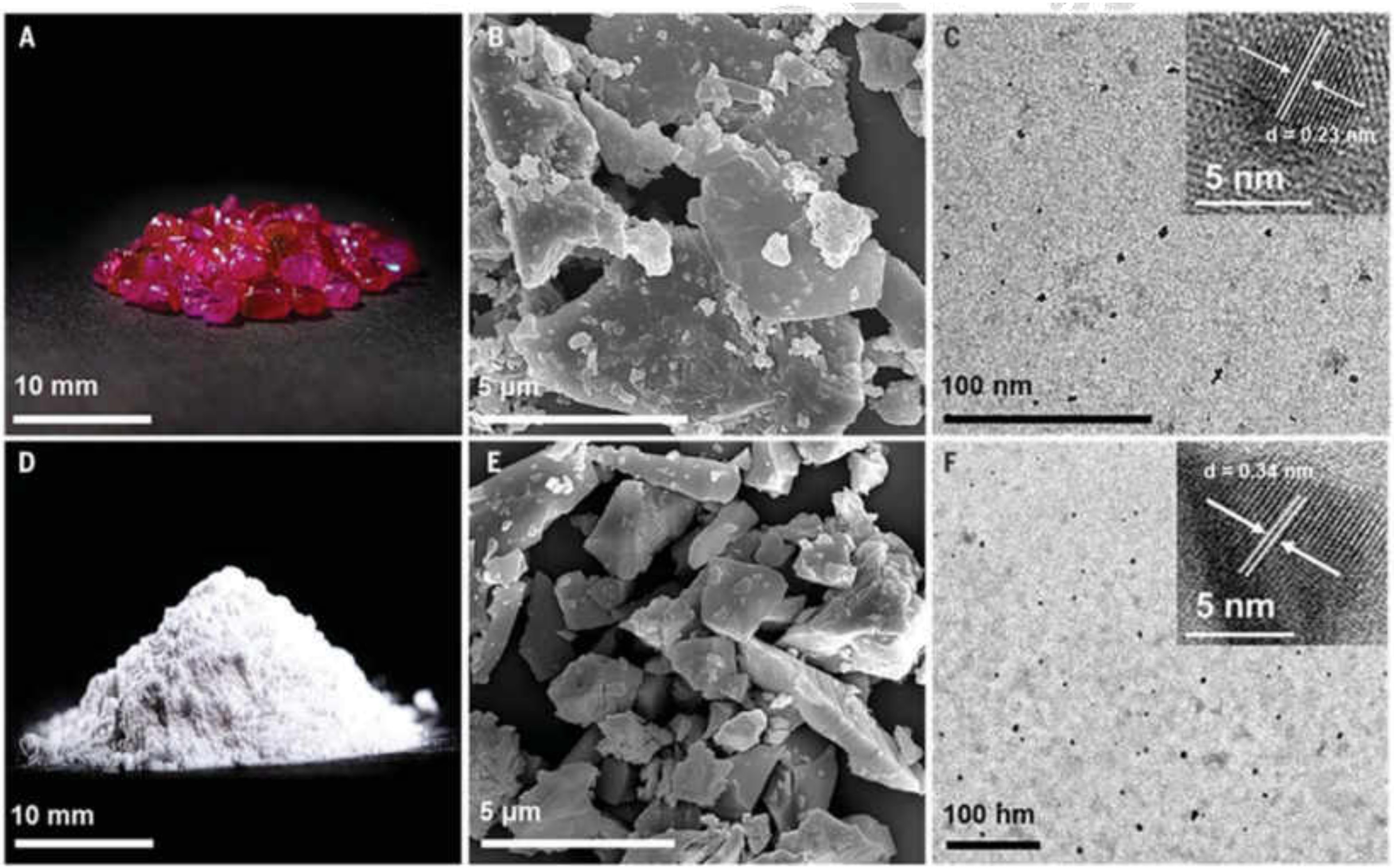
Ground silica **Optical image of silica**

Weathering of Minerals in Microdroplets

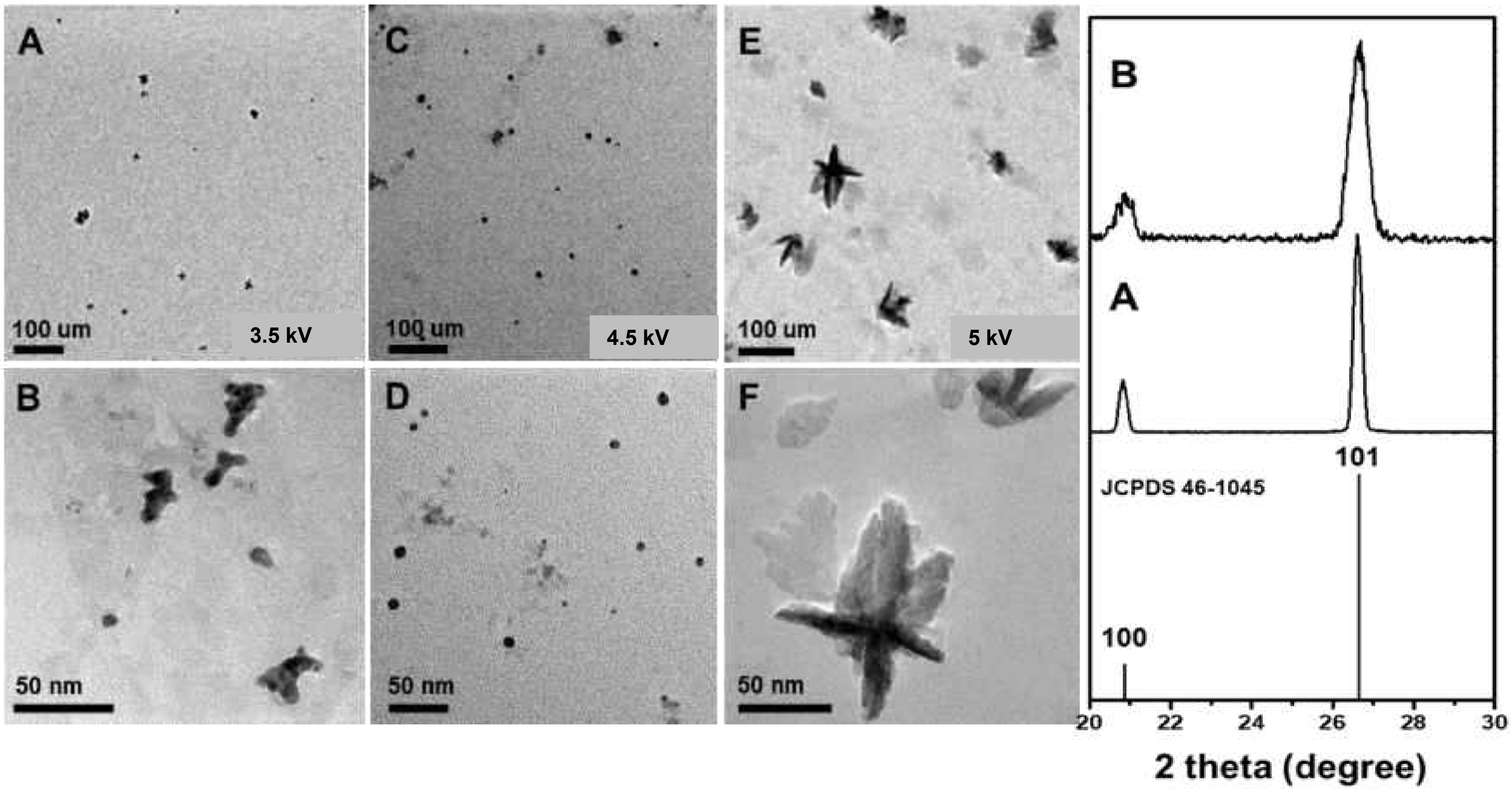


Spoorthi, et. al., *Science*, 2024

Ruby, Fused Alumina



Fragmentation of Silica – Varying Conditions



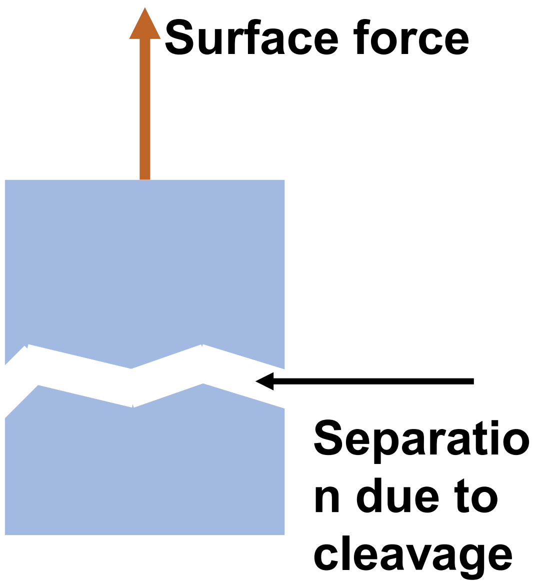
SiO_2 after electrospray

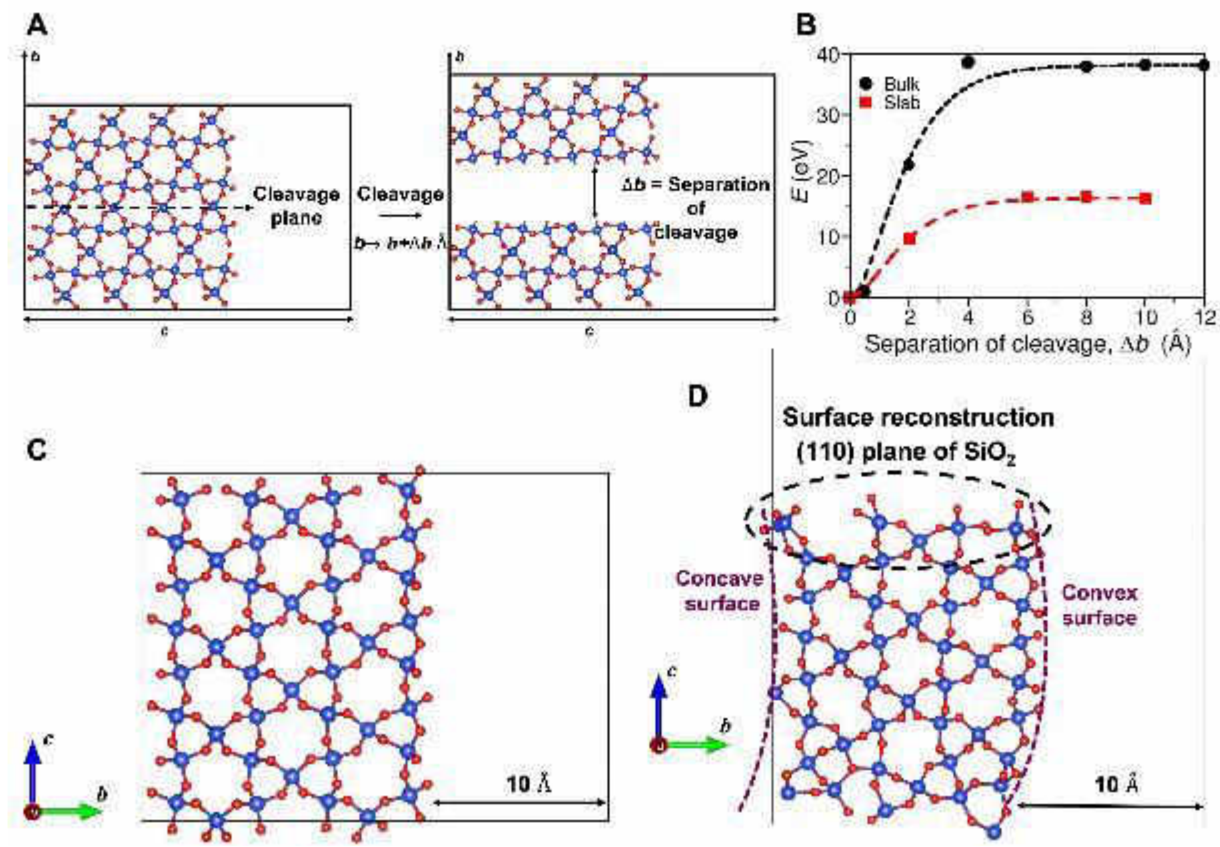
SiO_2 before electrospray

SiO_2 JCPDS data

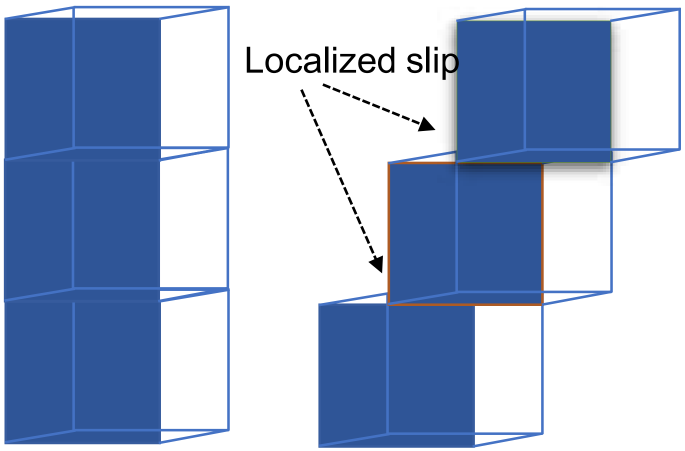
Mechanism: Cleavage

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

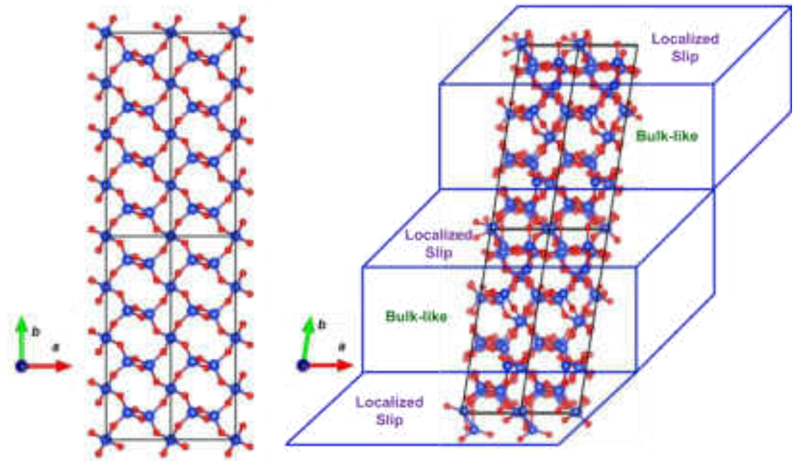




Mechanism: Slip



No slip | Slip

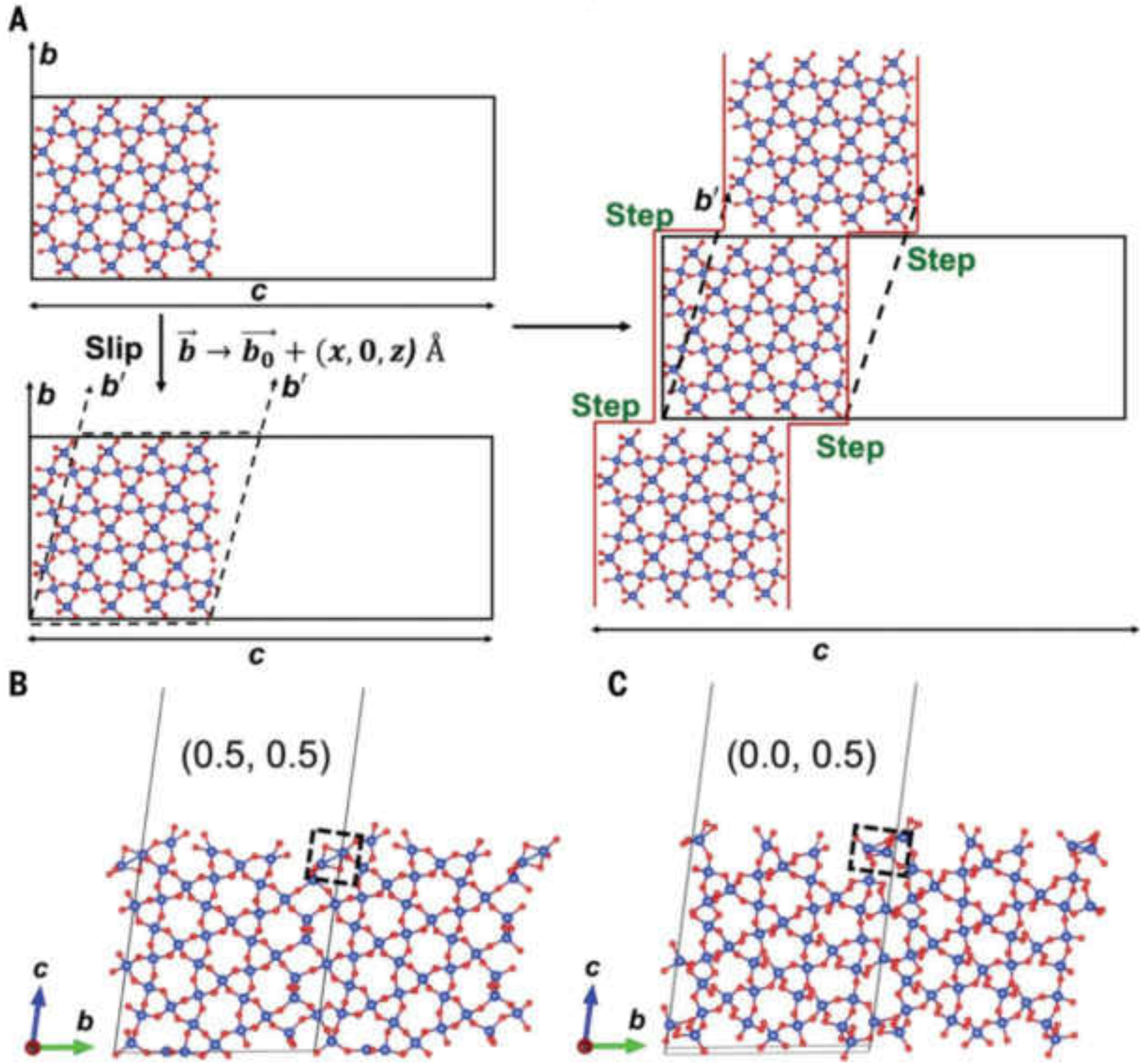


This instability leads to the formation of a stacking fault on the (010) plane, achieved with slip localized at (010) plane

Stacking fault

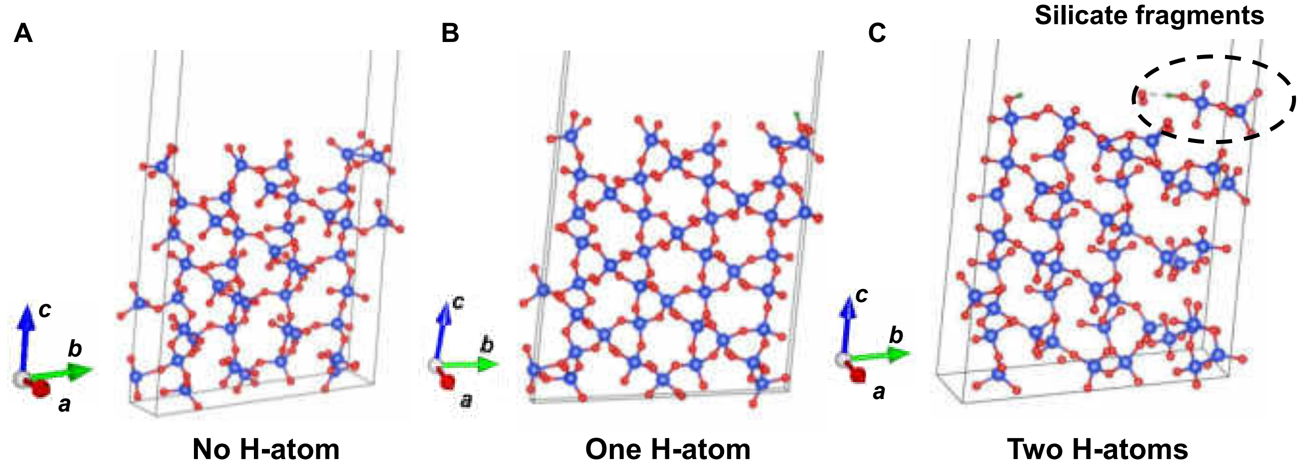
$$\vec{b} \rightarrow \overrightarrow{b_0} + (x, 0, z).$$

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

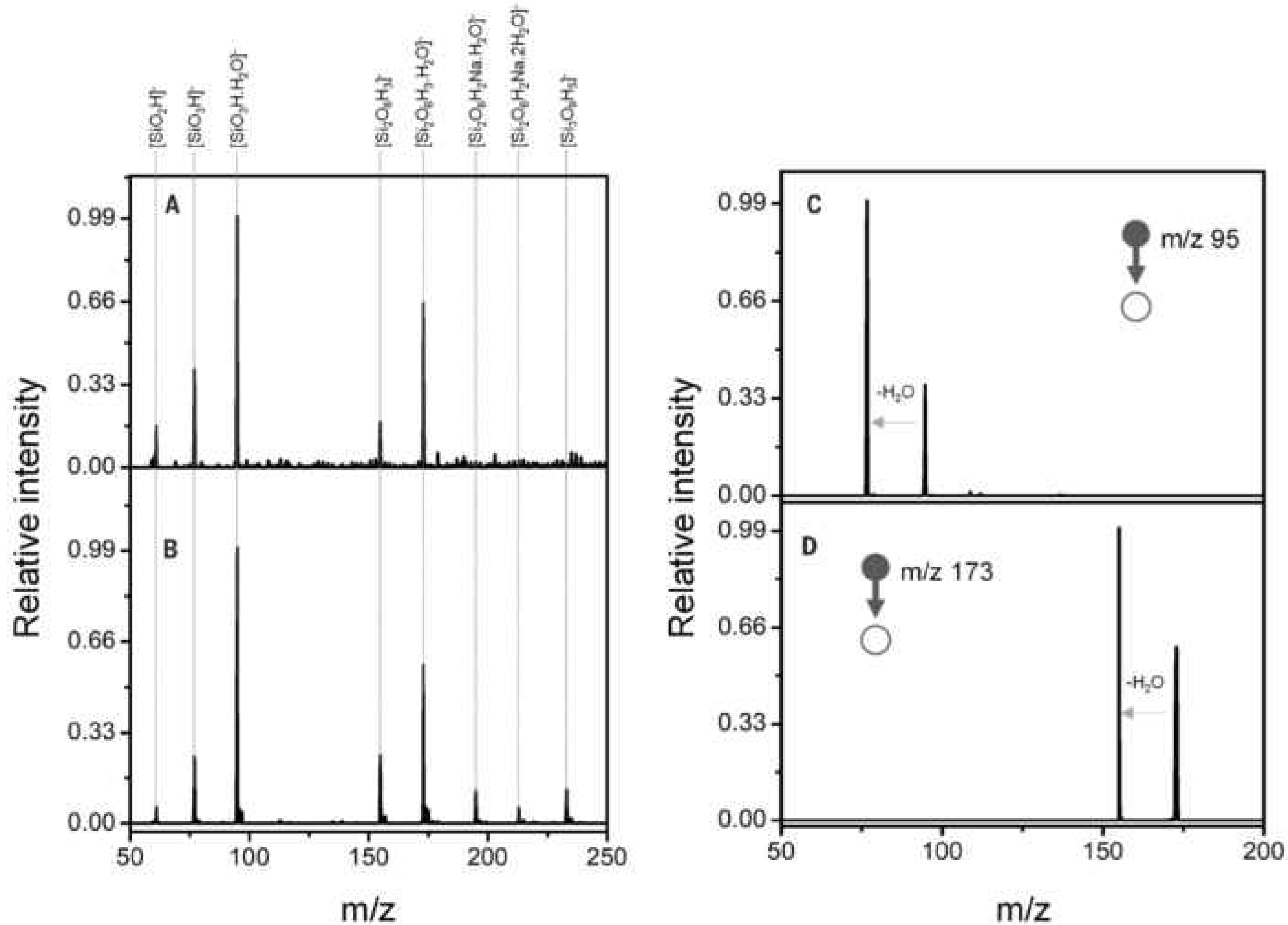

A
b
c
Slip
$\vec{b} \rightarrow \vec{b_0} + (x, 0, z)$ Å
b′
b′
b
c
Step
b′
Step
Step
Step
c
B
(0.5, 0.5)
c
b
C
(0.0, 0.5)
c
b

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

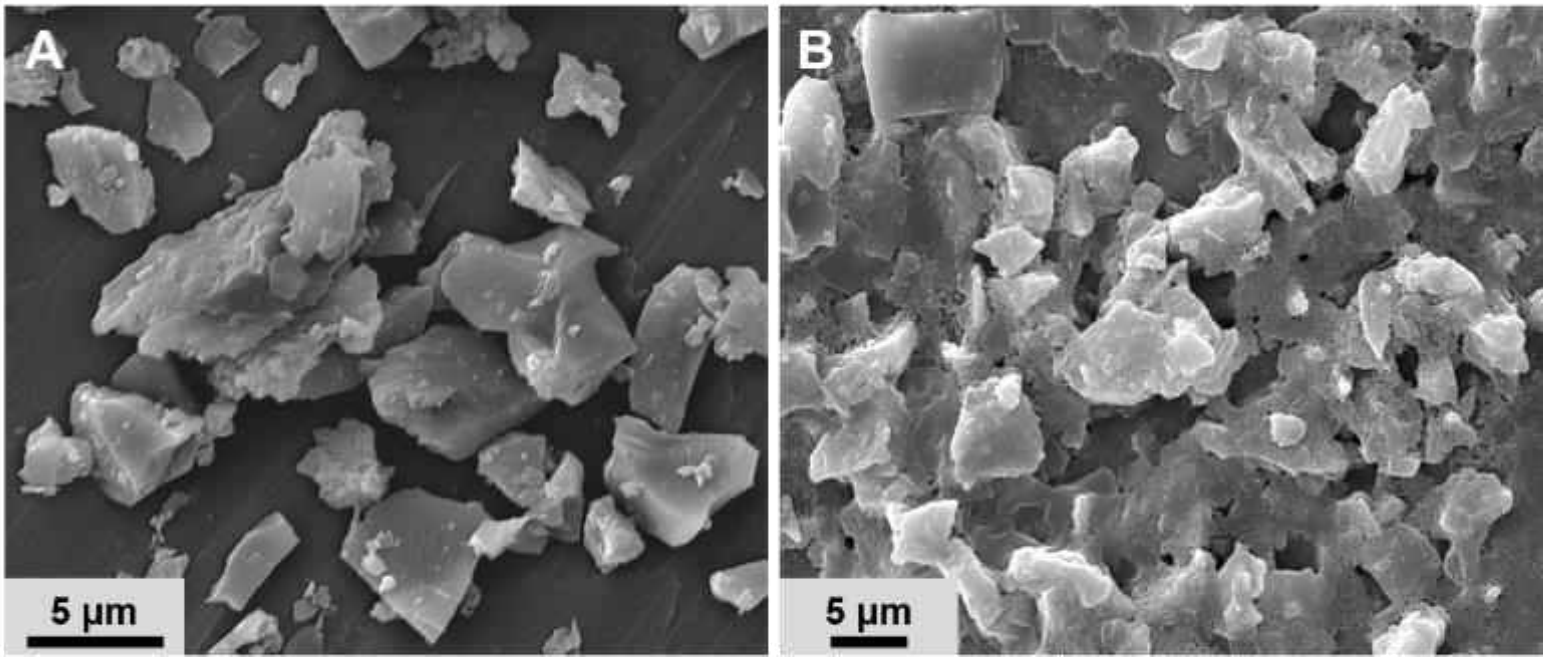
SFE (J/m^2)	Slab					
	x	z	w/o H-atom	1 H-atom	2 H-atoms	E
	0.0	0.0	0	0	0	0
	0.5	**0.5**	**-1.21**	**-0.93**	**-0.88**	**-1.20**
	0.5	0.0	1.20	1.18	0.90	1.12
	0.0	**0.5**	**-0.07**	**0.89**	**-0.83**	**-0.09**



Mass Spectrometry of the Fragments

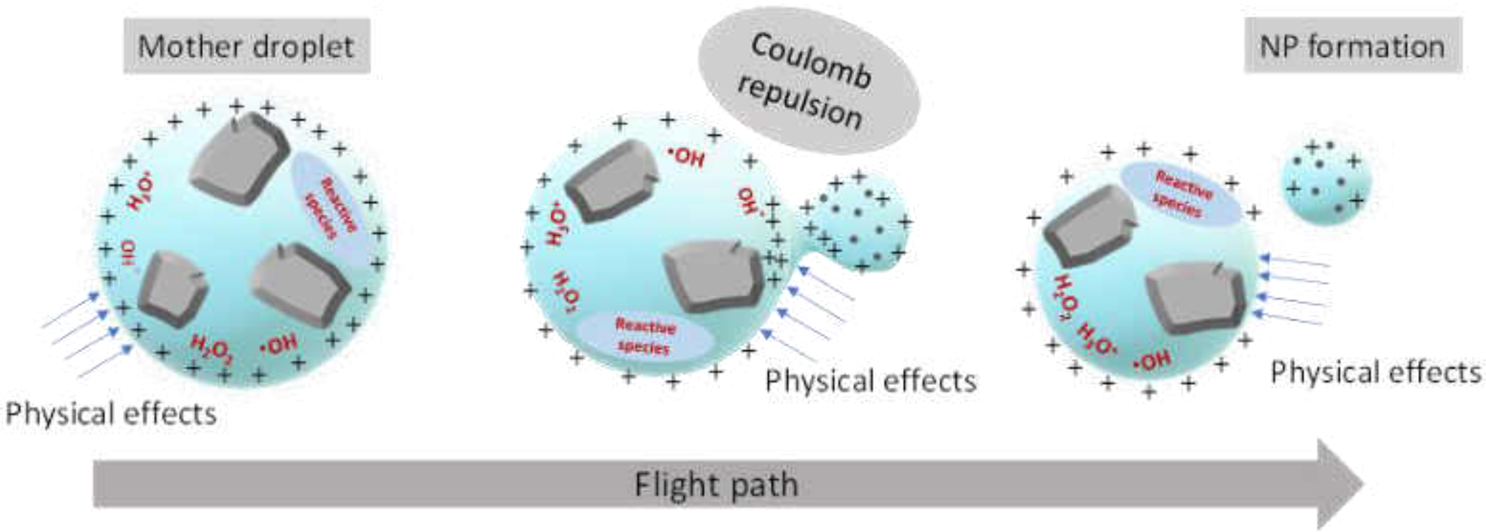


Effect of charged microdroplets on quartz



Increased surface roughness after the spray

Mechanism of nanoparticle formation



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

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

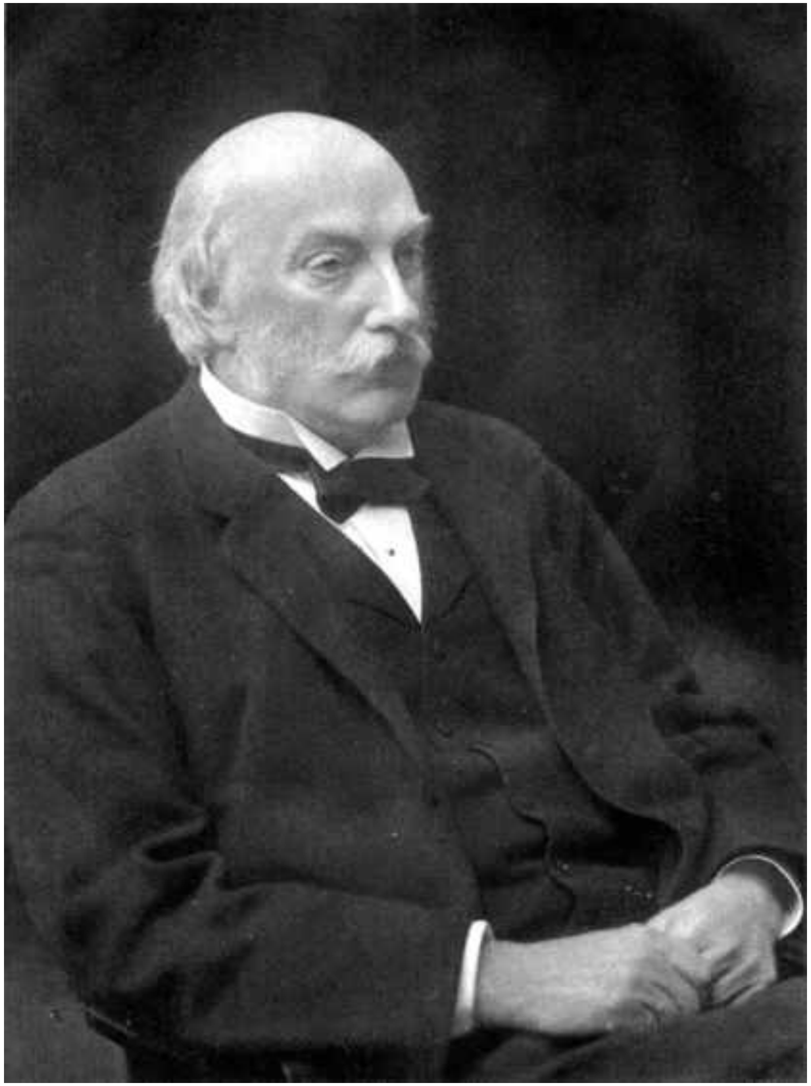
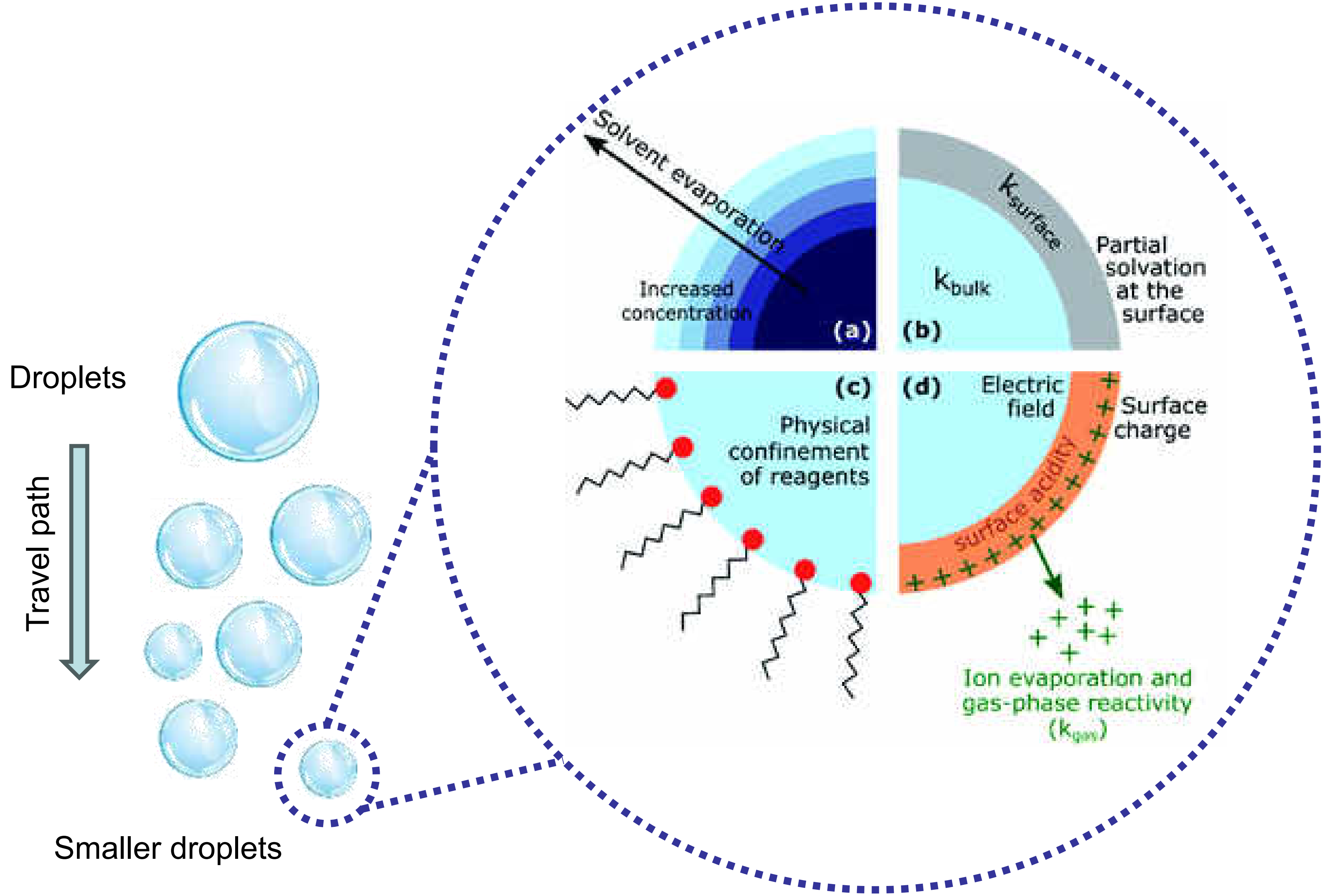


Image from Wikipedia

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.

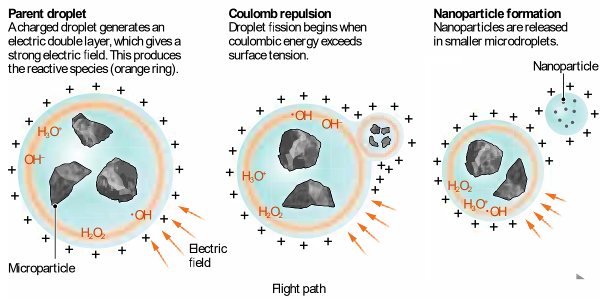
The unusual chemical nature of the air-water interface results in much remarkable chemistry. For example, amino acids in water undergo dehydration to form peptides in this environment (*6*), whereas bulk water simply solvates amino acids. The superacidic interface activates amino acids and removes water 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 (C–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

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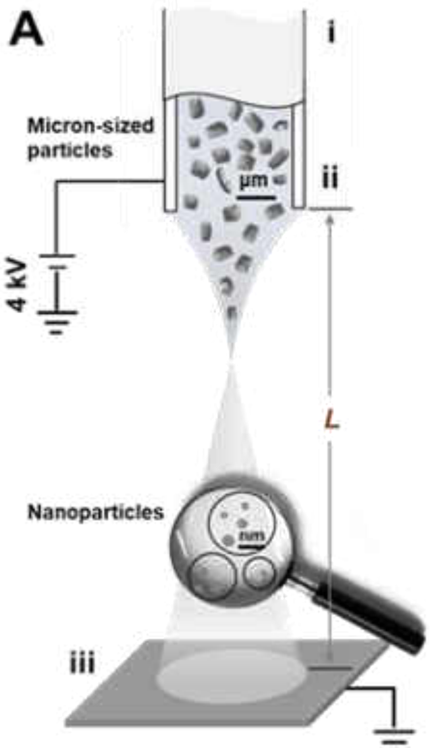
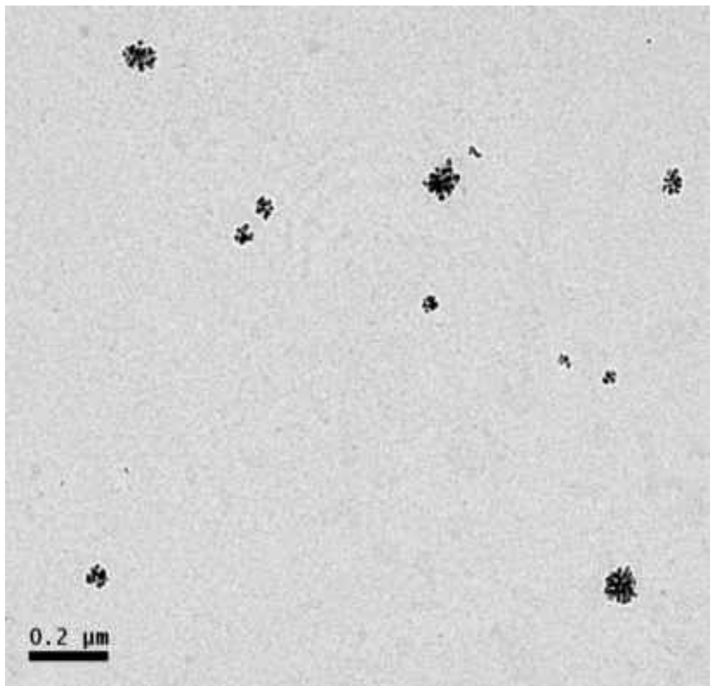
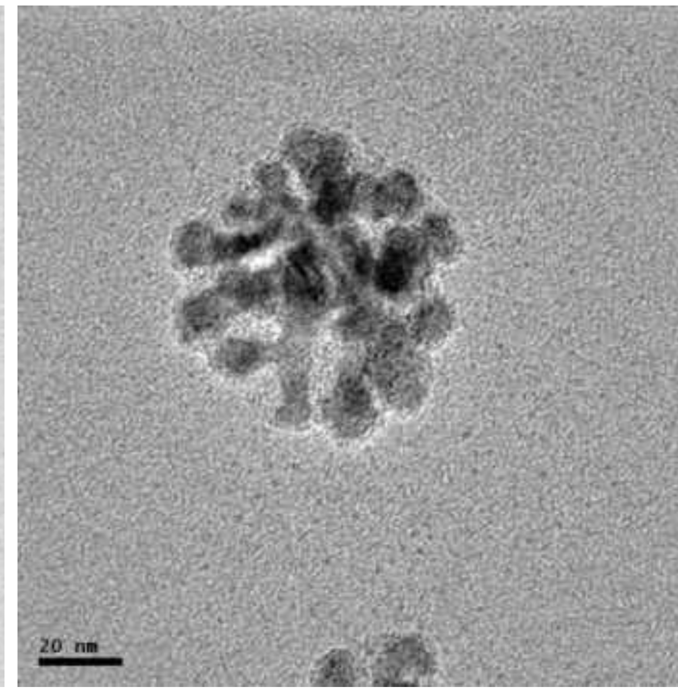
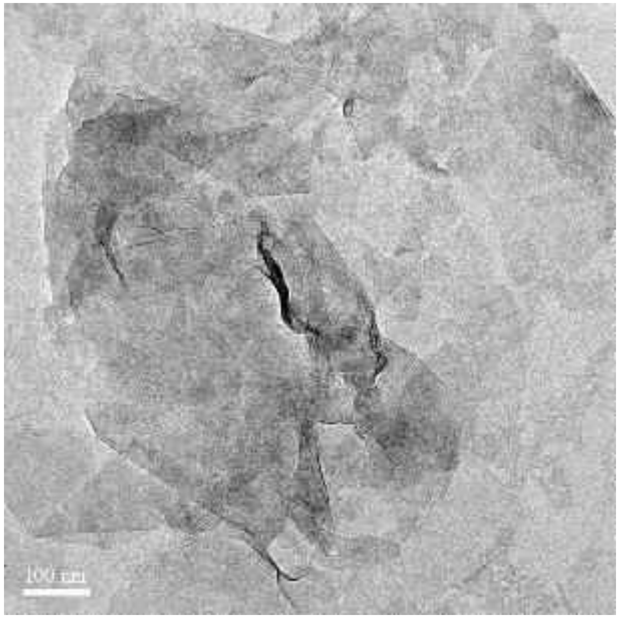
How do they form?

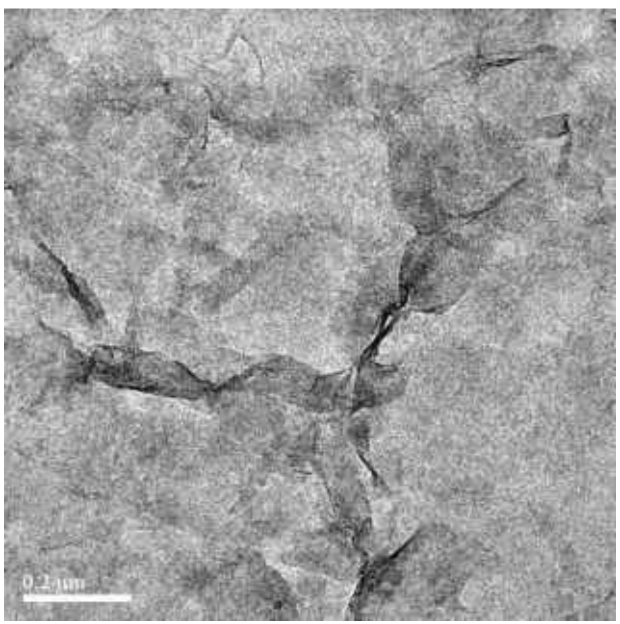






MoS_2 Nanosheets

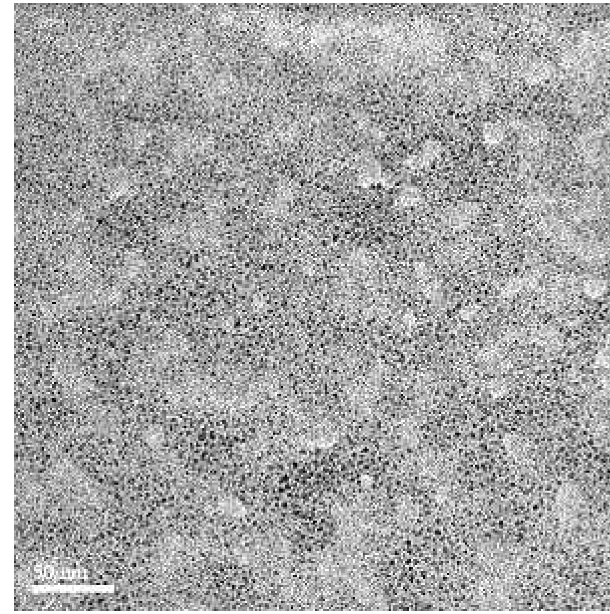


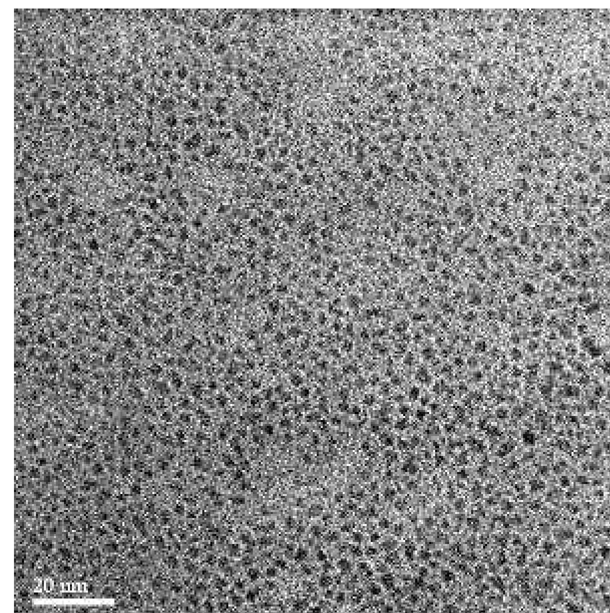


MoS_2 Nanosheet

Ambient electrospray

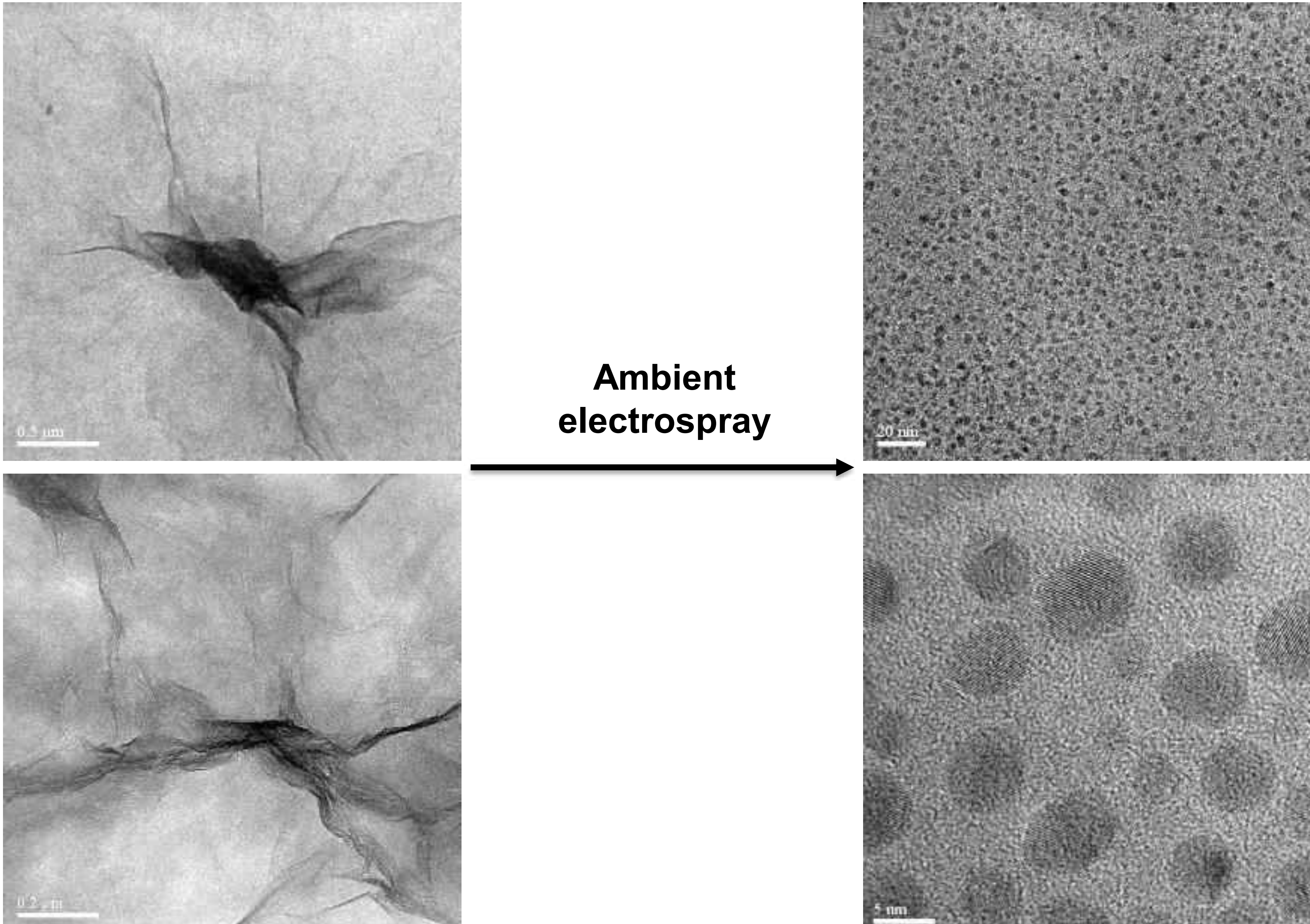
Solvent: Water
Potential: 3.0 kV





MoS_2 Nanoparticles

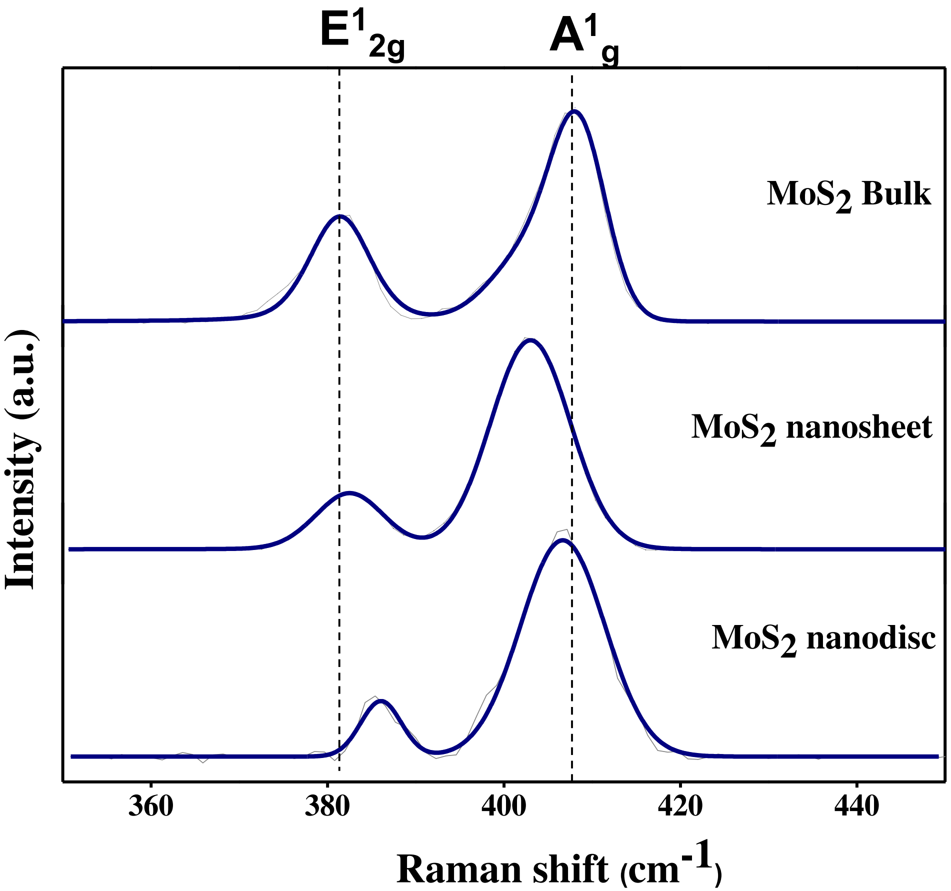
Graphene Oxide

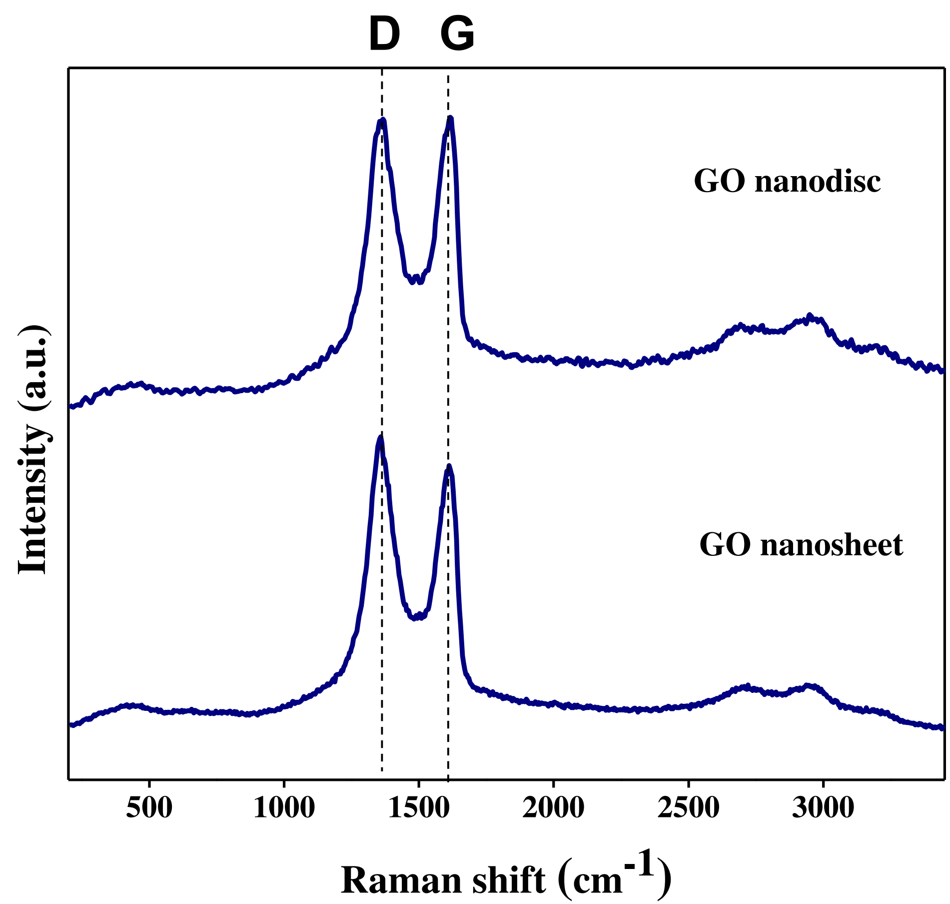


Graphene oxide nanosheet

Graphene oxide nanodiscs

Raman Spectra of MoS_2 and Graphene Oxide Nanosheets



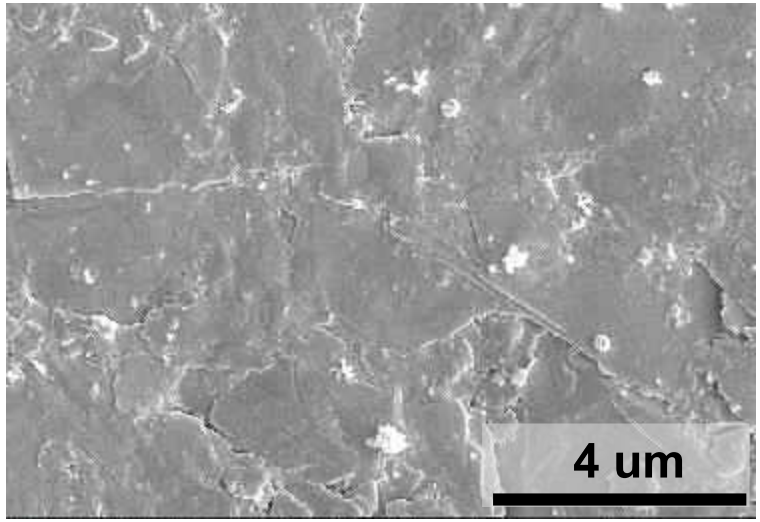


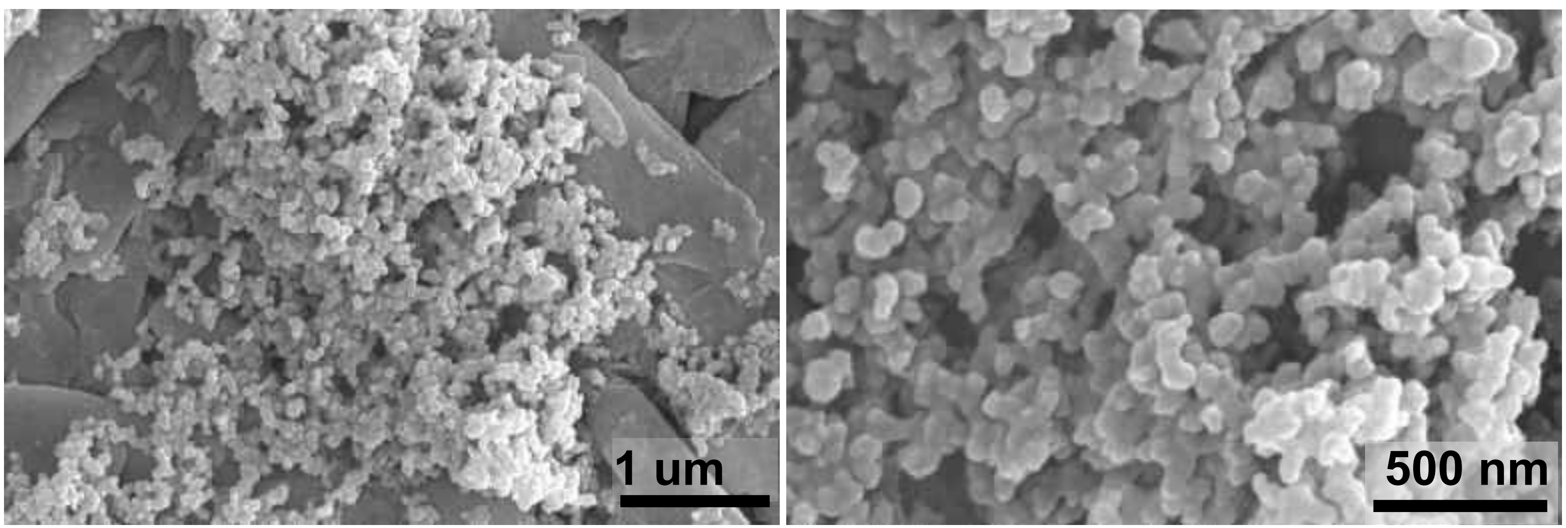
	E^1_{2g} (cm^{-1})	A^1_g (cm^{-1})
Bulk	381.34	407.67
NS	382.88	402.95
ND	386.01	406.67

Relative peak intensity

Charged Droplets on MoS_2 Bulk

Bulk MoS_2 surface before the spray



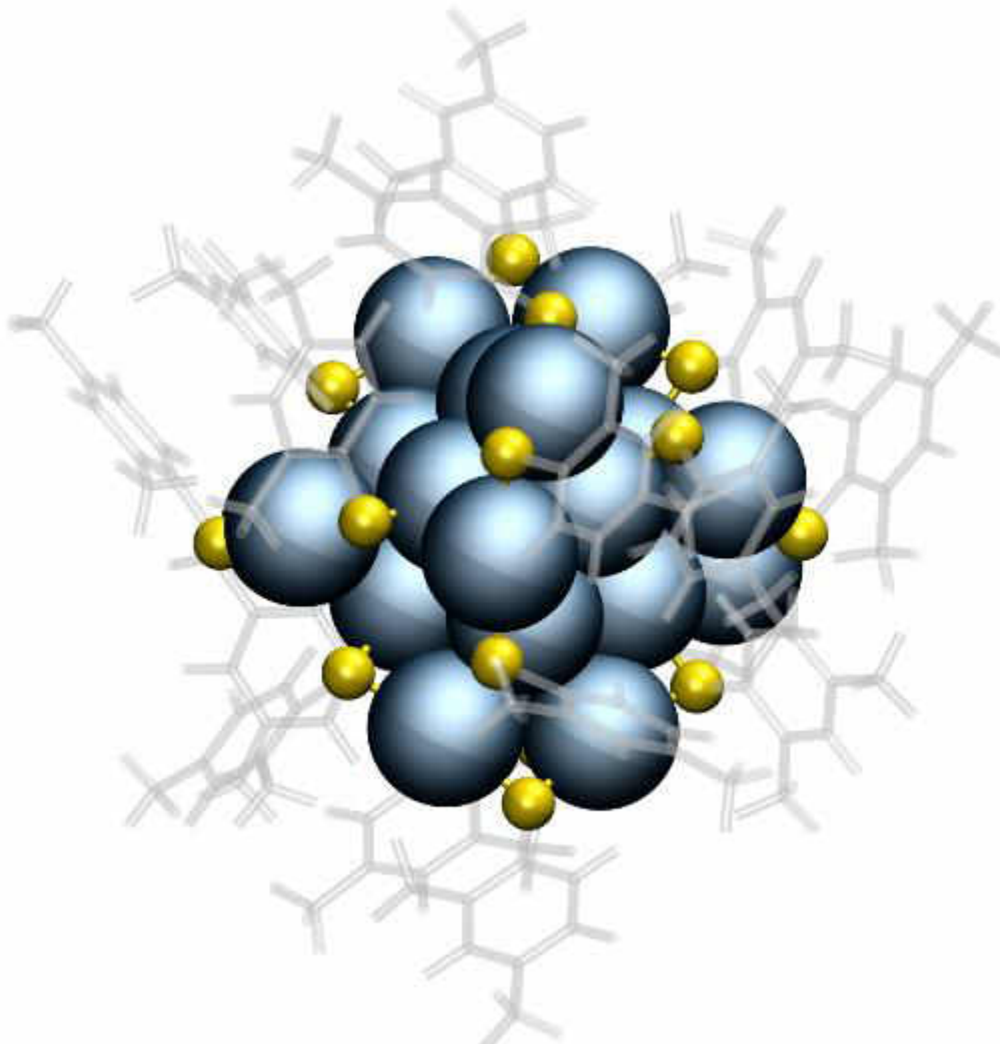


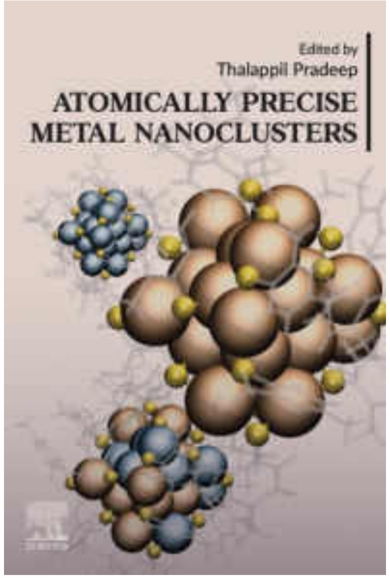
Appearance of microspheres after the water spray on MoS_2

Marcasite, FeS_2

Image from Wikipedia

New molecules





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

PNAS PNAS PNAS PNAS

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

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

Unit of Nanoscience and Thematic Unit of Ex

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

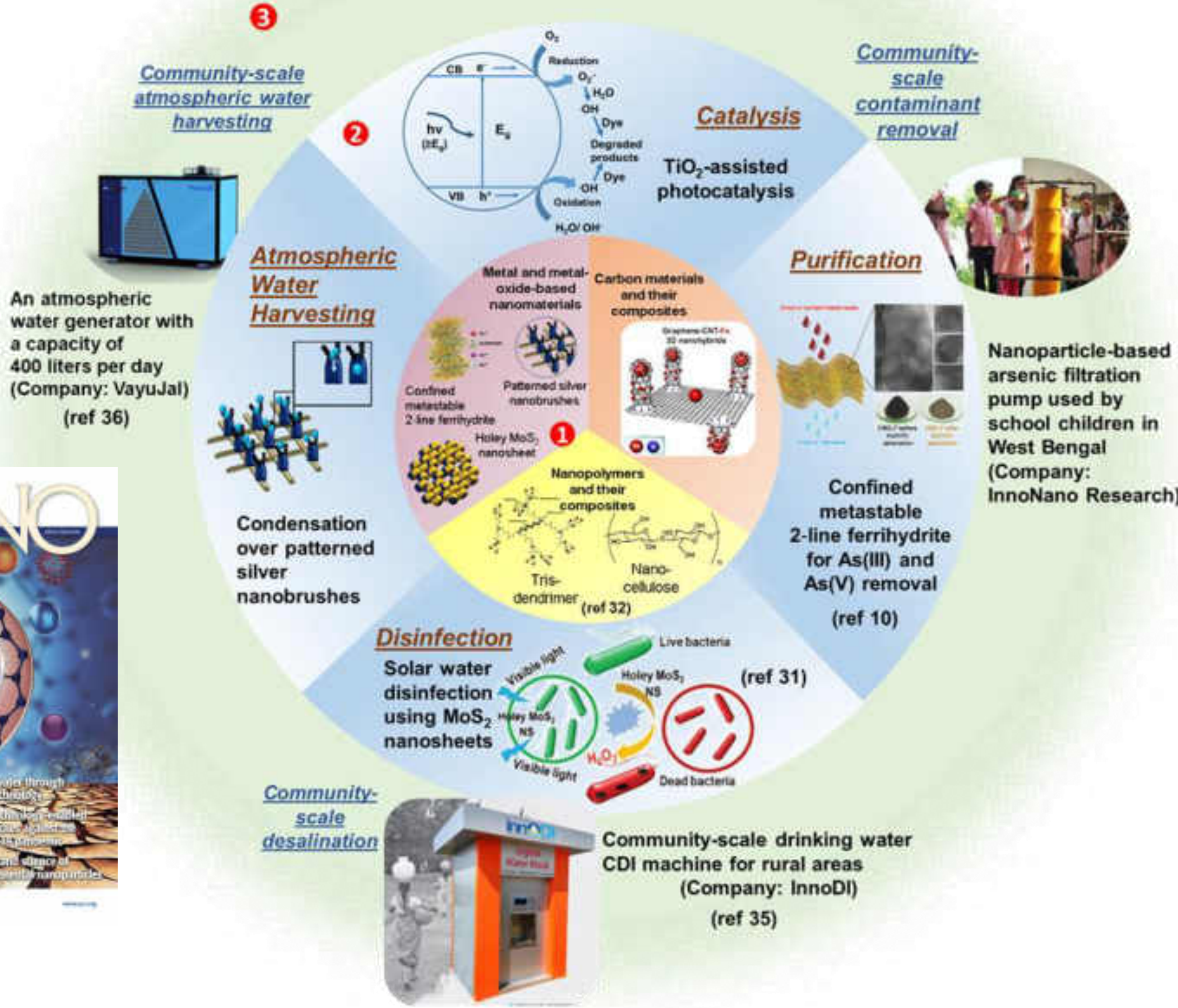
Results and Discussion

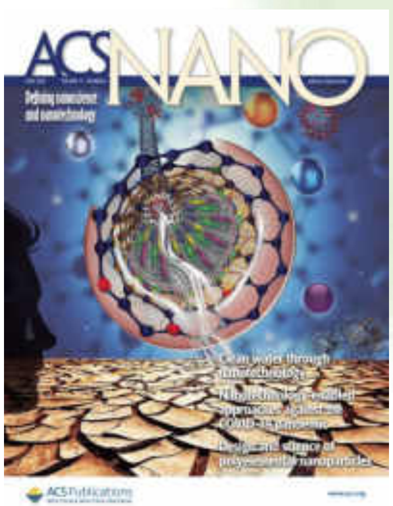
M. Udhaya Sankar, et. al. *Proc. Natl. Acad. Sci.,* 110 (2013) 8459-8464.

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.

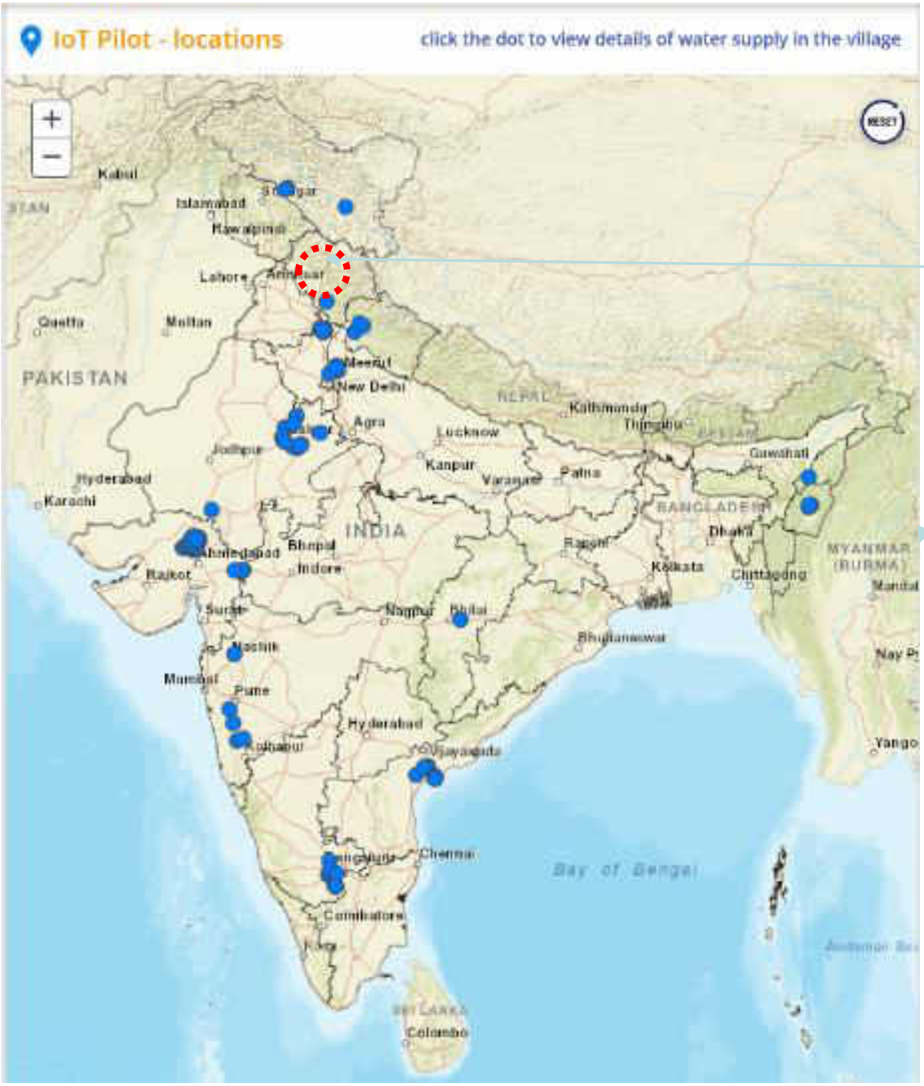
Evolution of materials to products





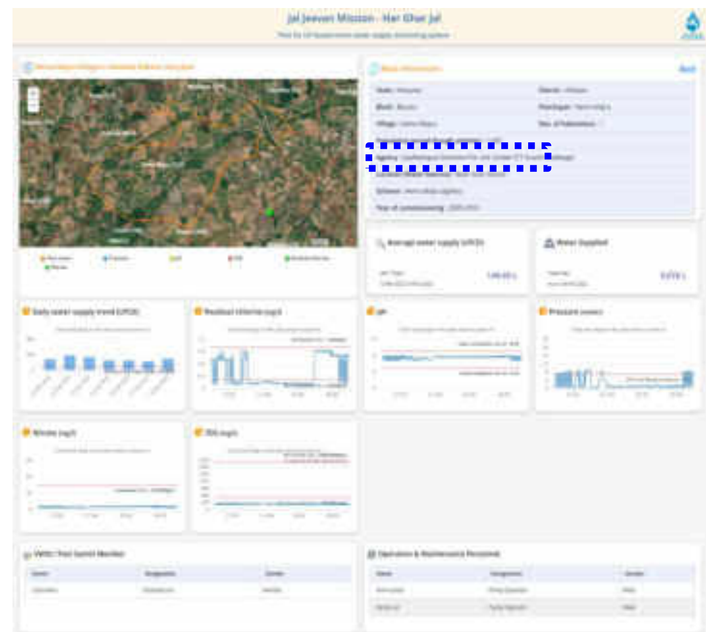
Ankit Nagar and T. Pradeep, *ACS Nano* 14 (2020) 6420-6435.

India’s water is being monitored



IITM/IISc

Installations made by four companies



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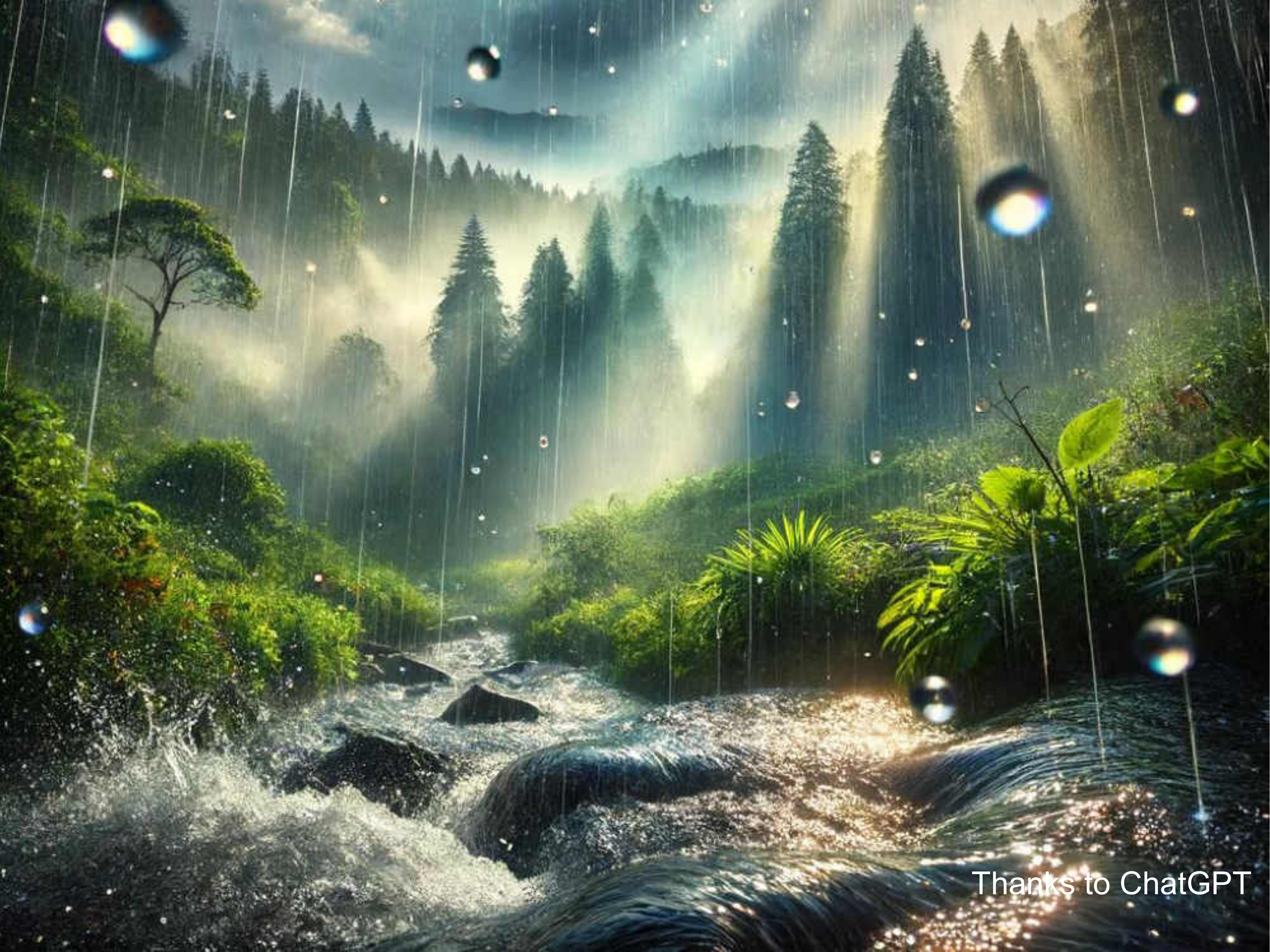

Thanks to ChatGPT

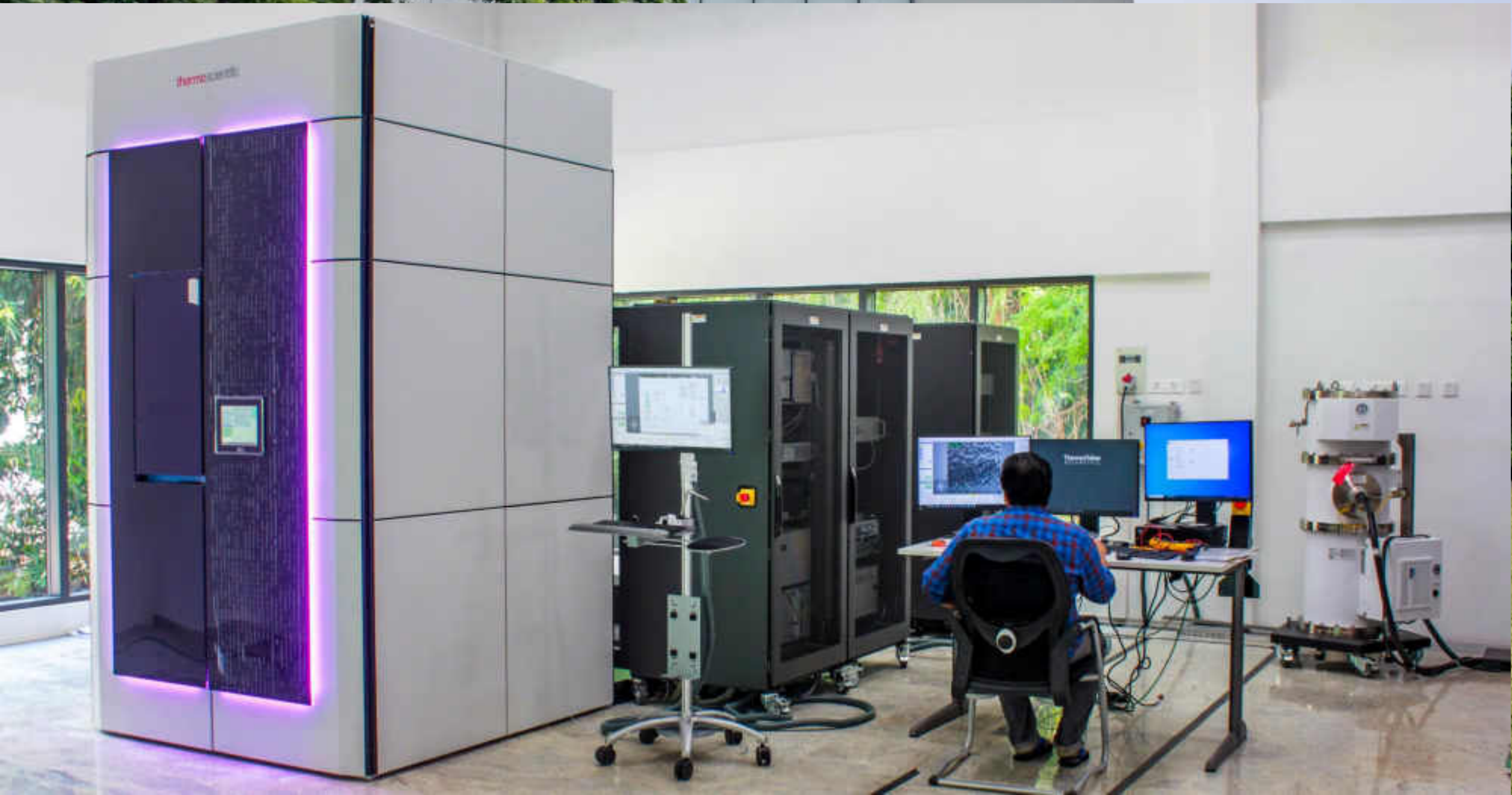
Vision

Make soil using processed wastewater and make deserts bloom.

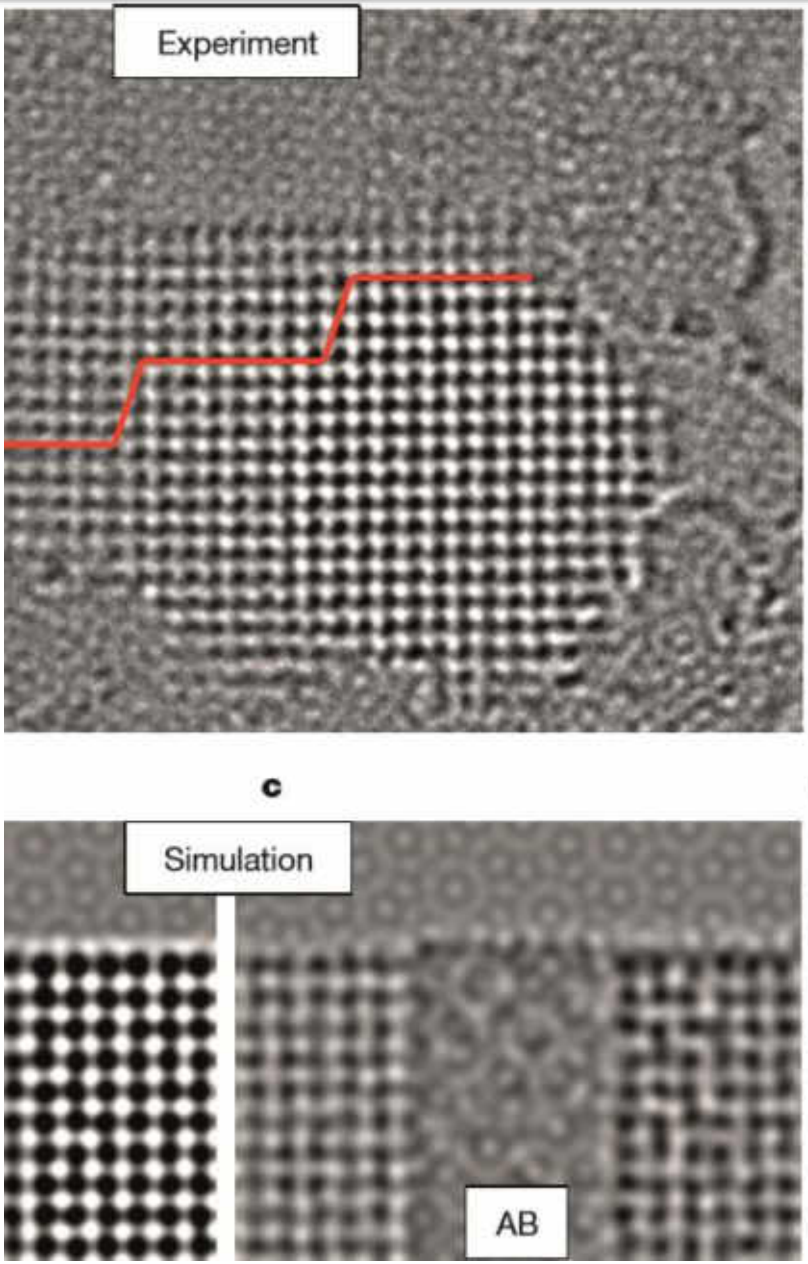
Thanks to ChatGPT

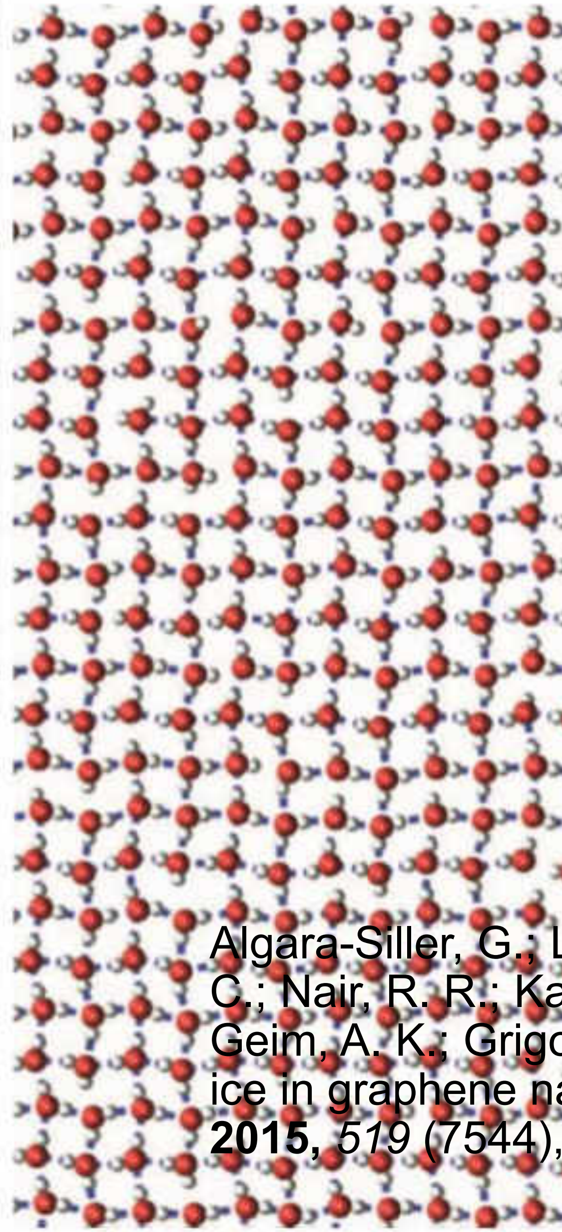
Conclusions

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



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.

International Centre for Clean Water


IIT Madras Research Park


Indian Institute of Technology Madras

Bhaskar Ramamurthi/V. Kamakoti

Department of Science and Technology

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Thank you all