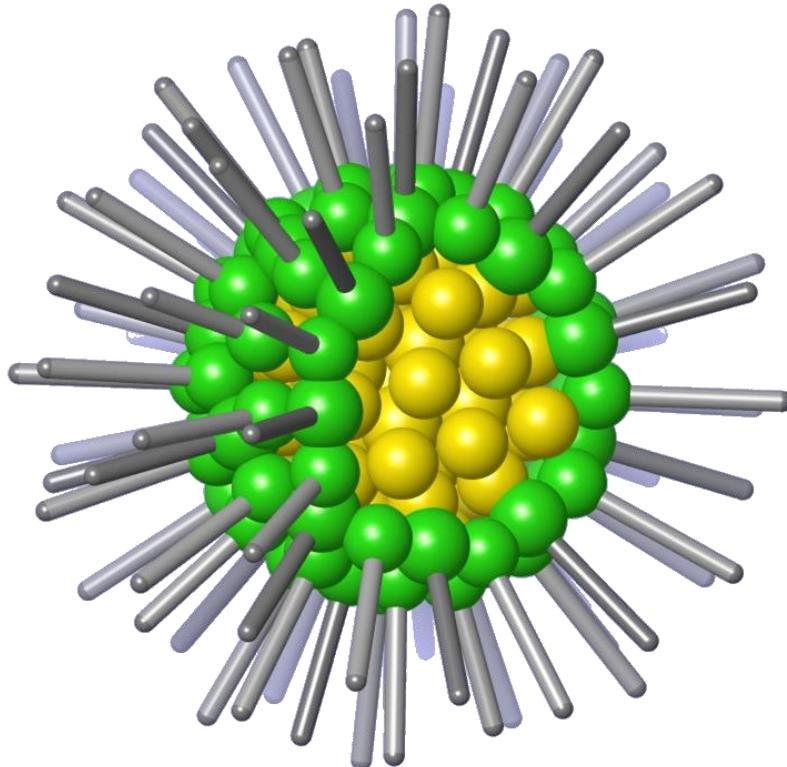


drinking Affordable point-of-use water purification using nanomaterials



T. Pradeep

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

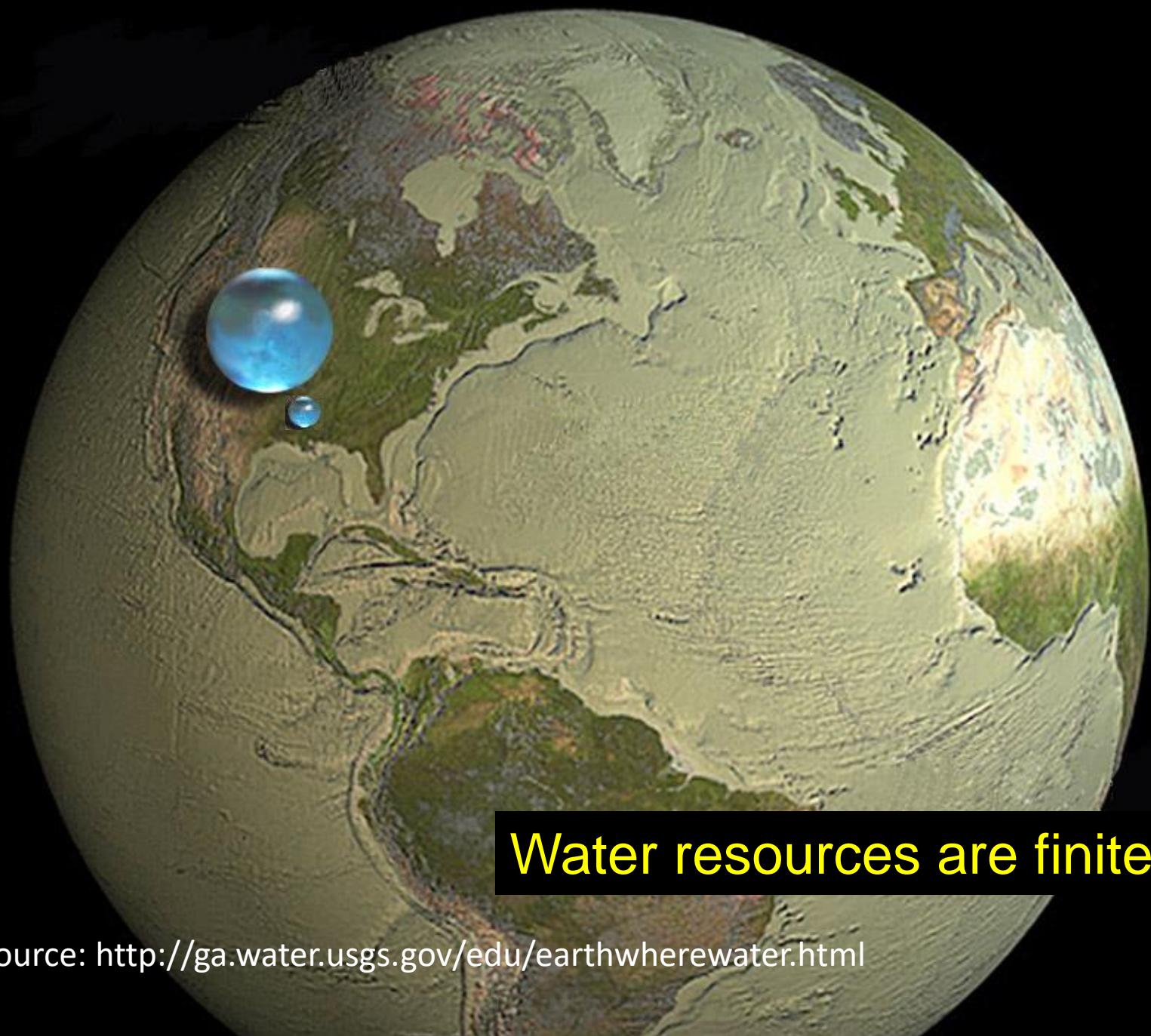
AsiaNANO 2014, October 26-28, 2014

Indian Institute of Technology Madras



Bhaskar Ramamurthi
Director





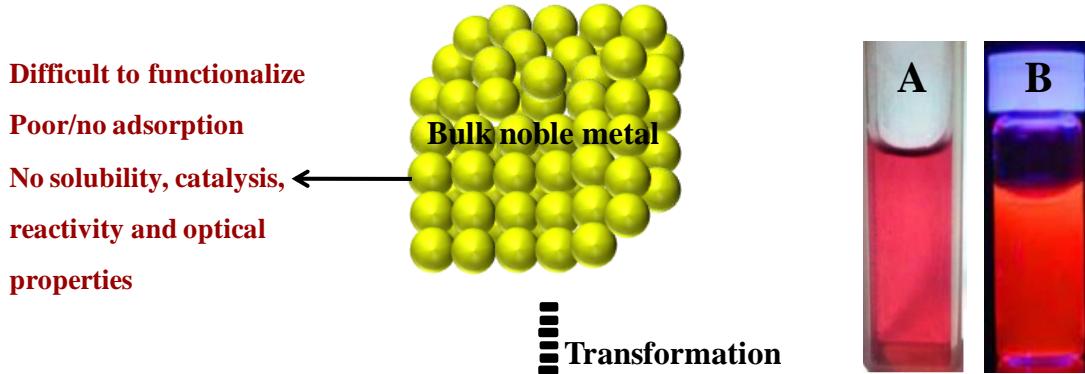
Water resources are finite

Source: <http://ga.water.usgs.gov/edu/earthwherewater.html>

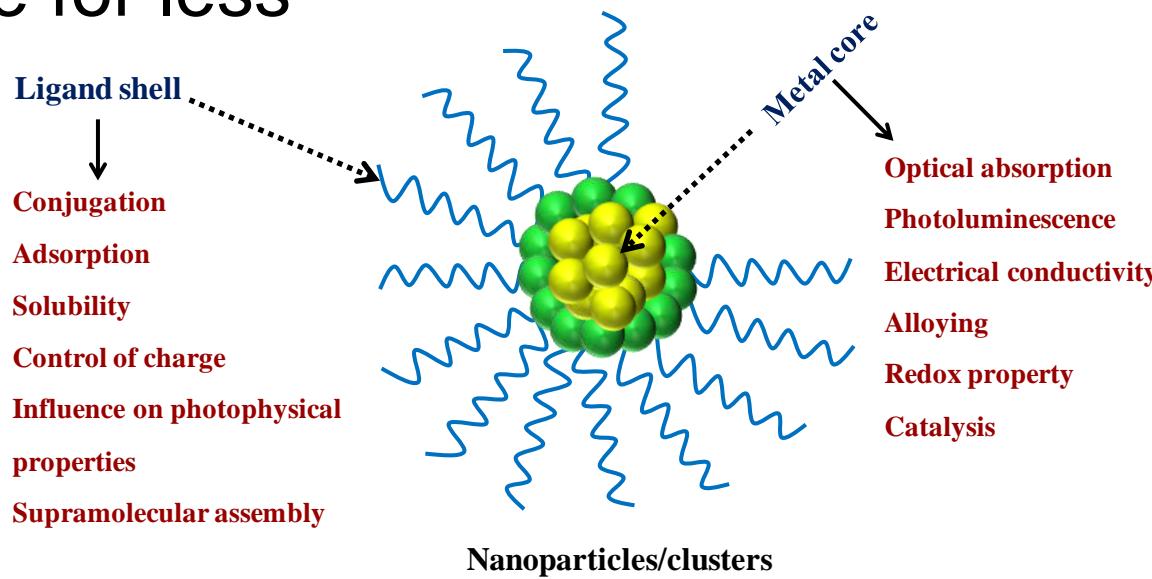
Why nanotechnology?

10^{-9}

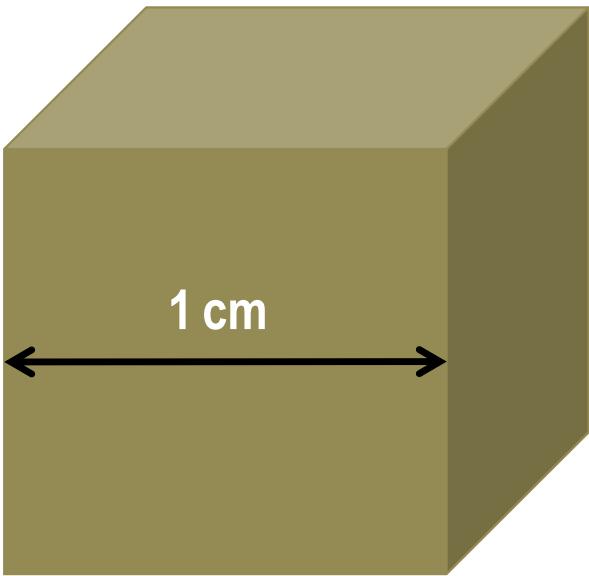
T. Pradeep, Env. Sci. Technol. 2014, Feature



1. More for less

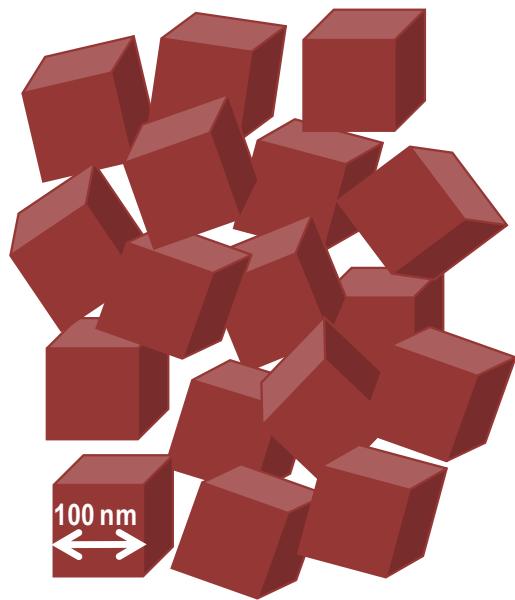


Variation in properties originating from ligand shell and metal core as bulk noble metals transform to nanoparticles/clusters. Sizes are not to scale. New properties such as color and photoluminescence arise in such size regime. Photographs of Au@citrate nanoparticles (inset A) showing intense absorption of visible light and Au@SG (SG corresponds to glutathione thiolate) clusters (inset B) showing intense photoluminescence upon ultraviolet irradiation (from the author's work).

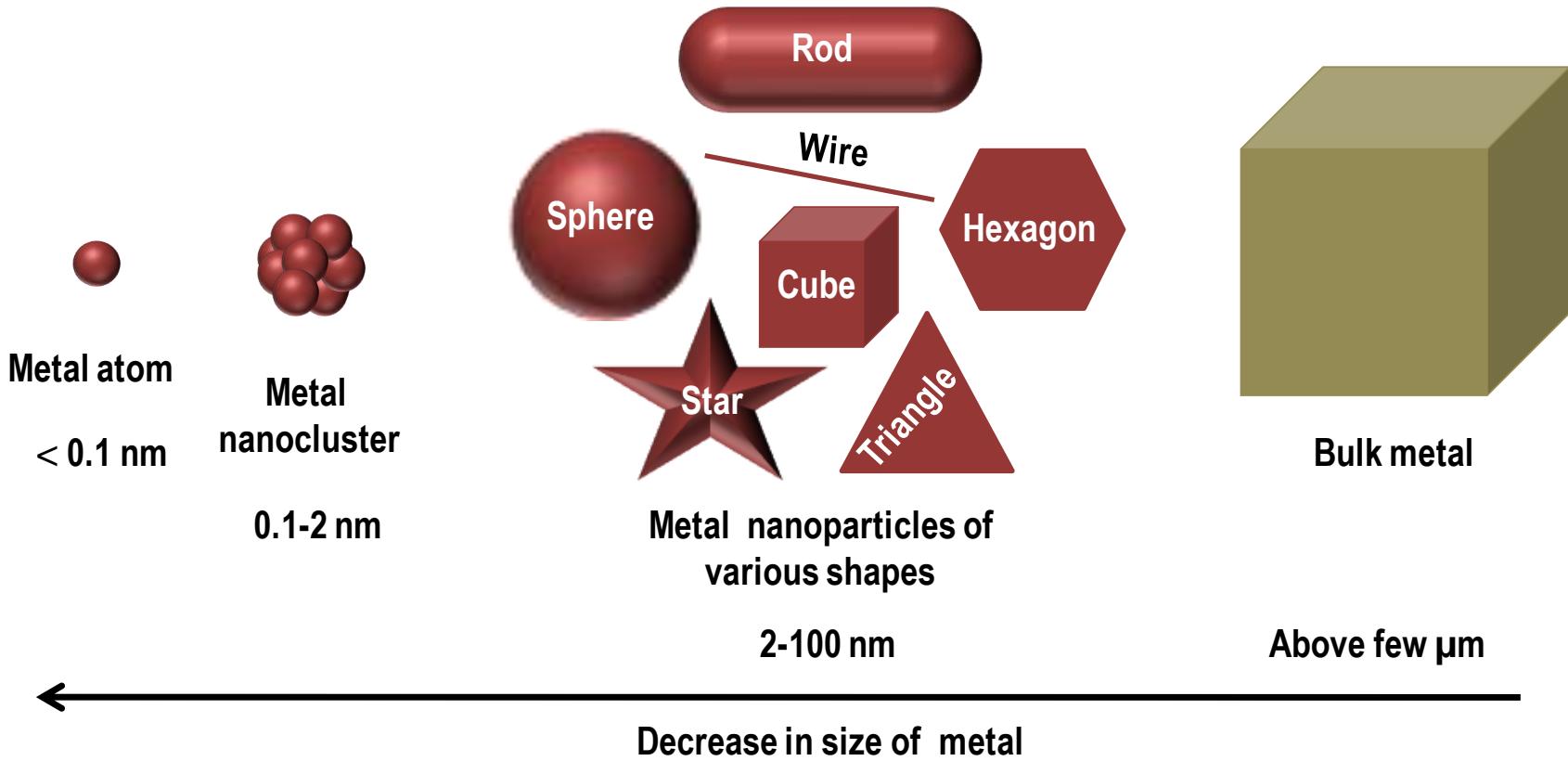


Bulk noble metal

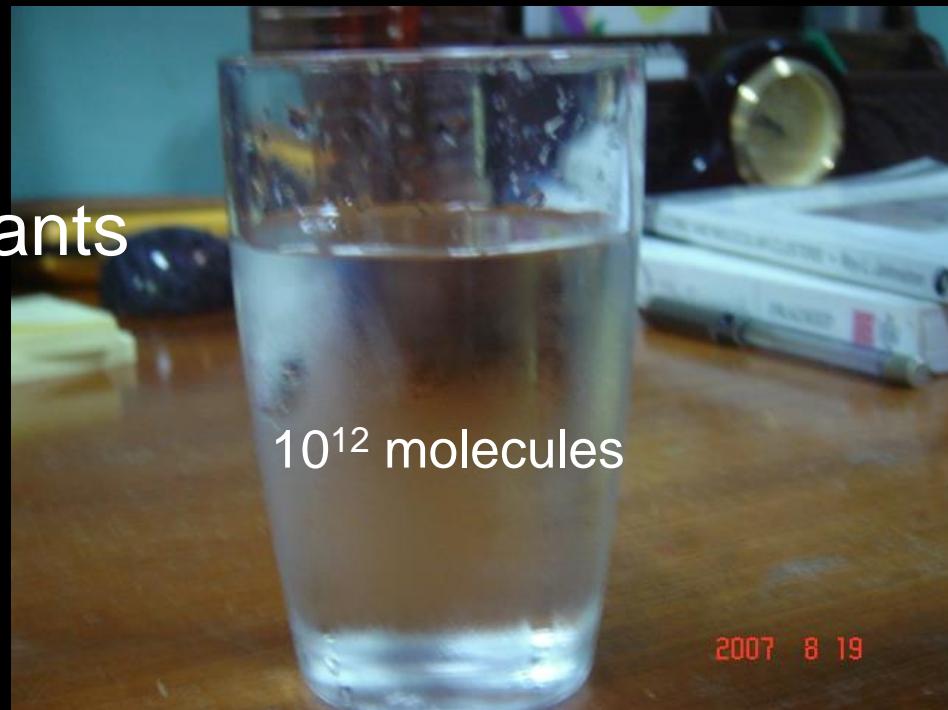
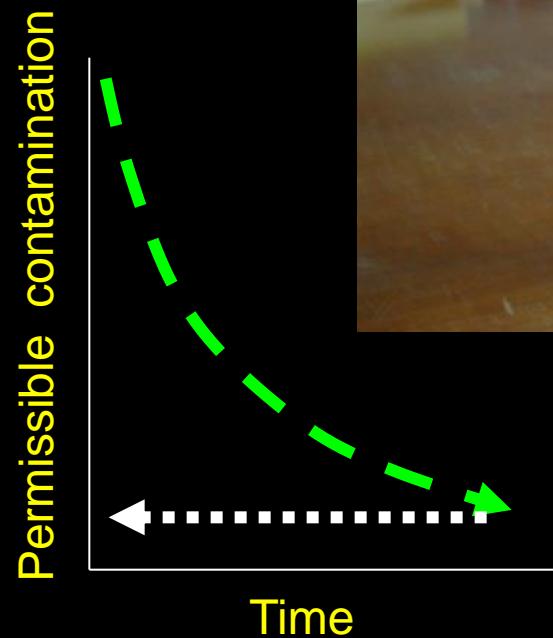
Reduction of size →
Surface area
increases by 10^5



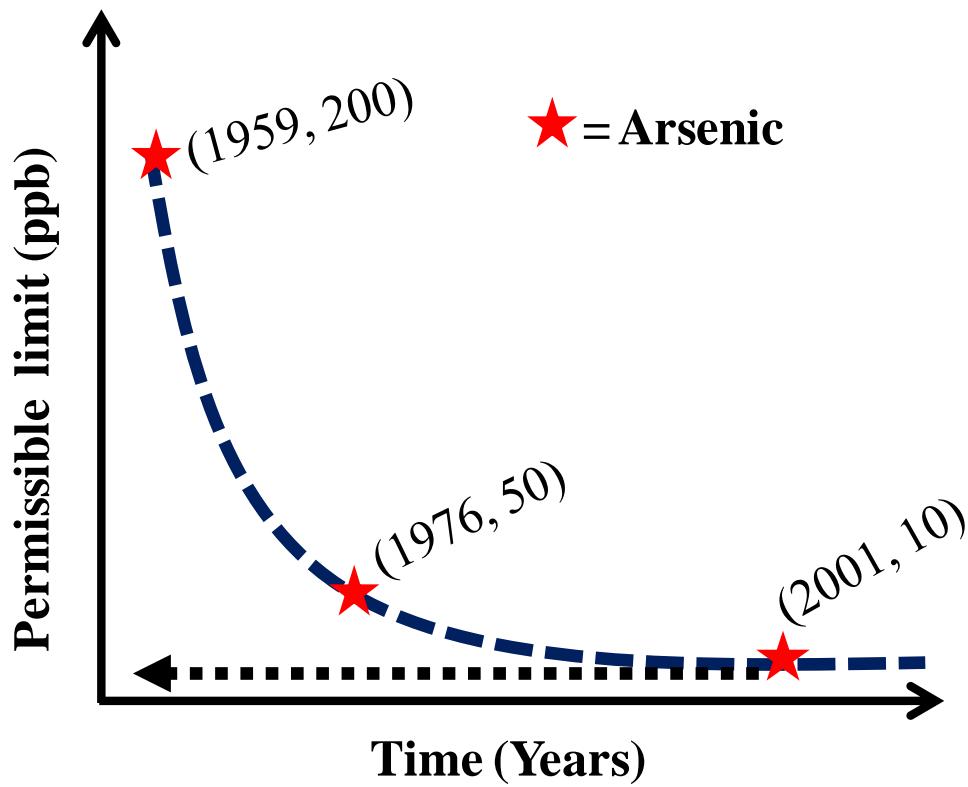
Noble metal of smaller size



2. Limits of contaminants

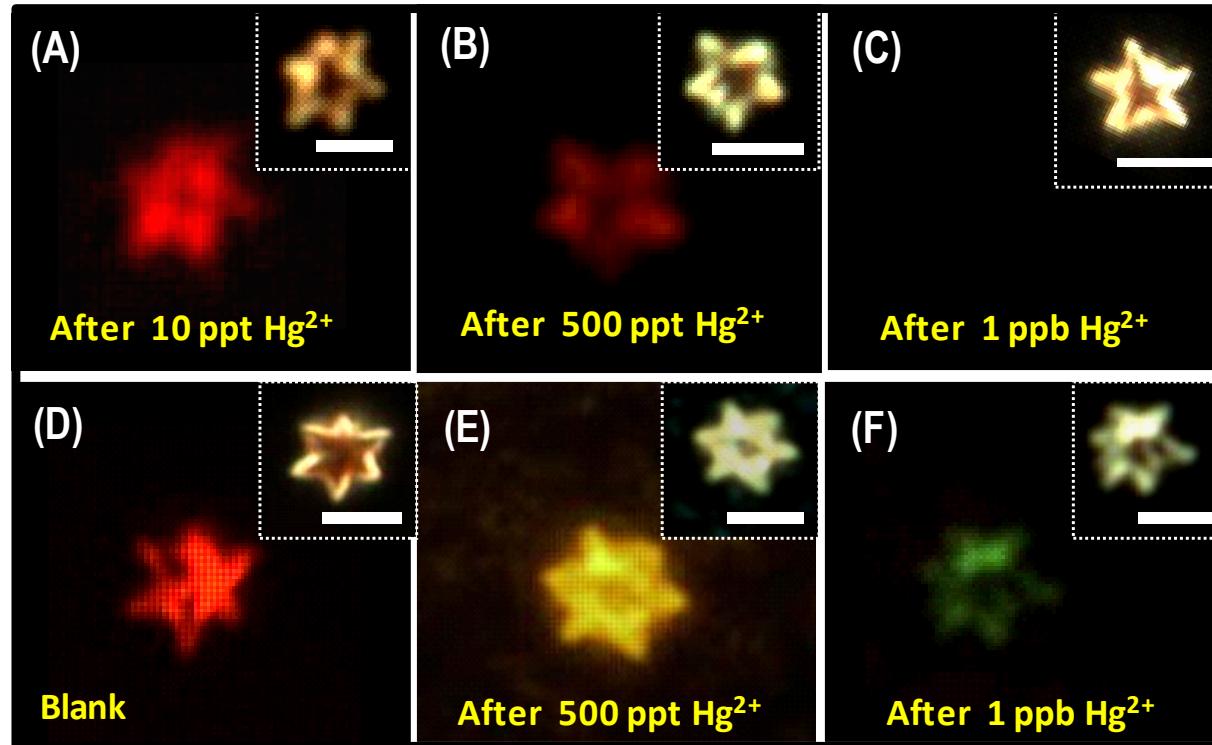


Permissible contamination reaches limits of detection



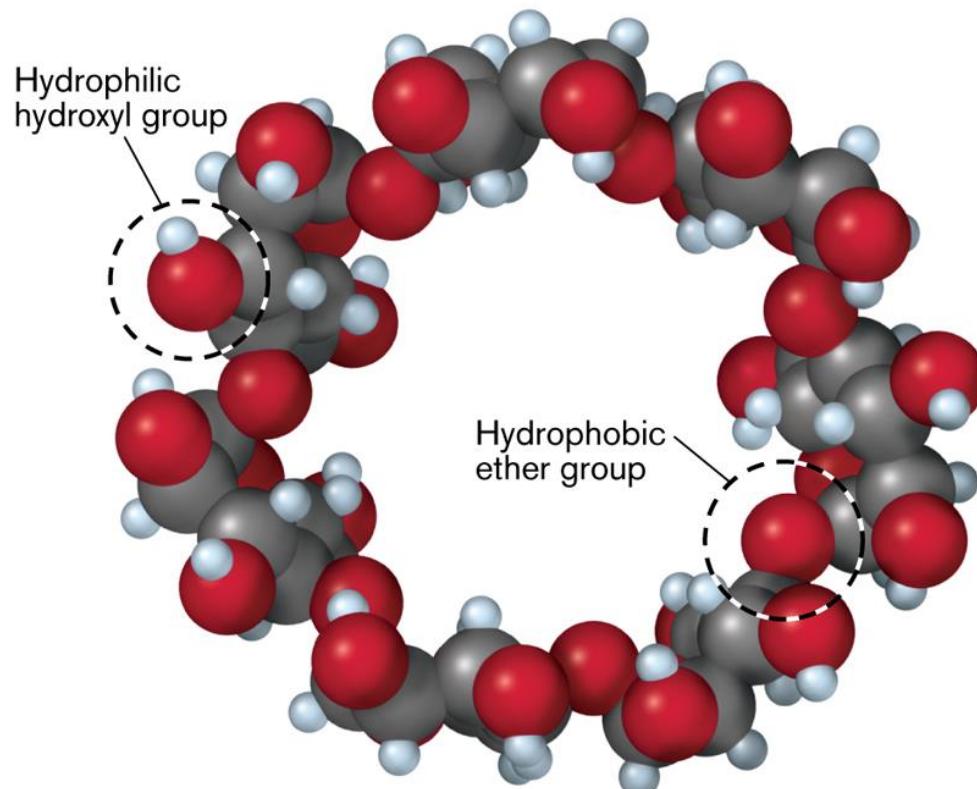
Decrease in the permissible limit of arsenic in drinking water, according to US EPA, with time. The graph indicates a general trend.

3. Can we reach limits?

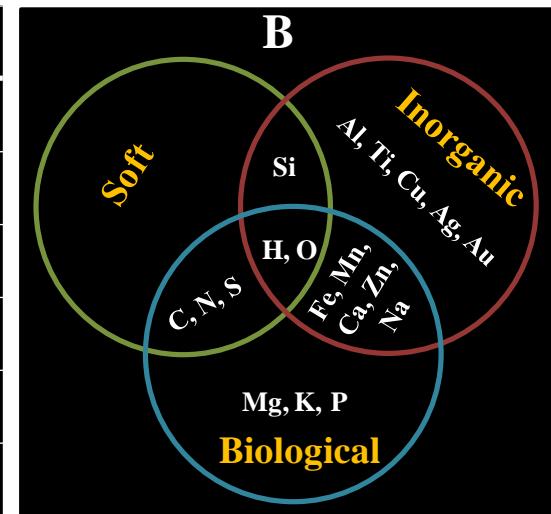
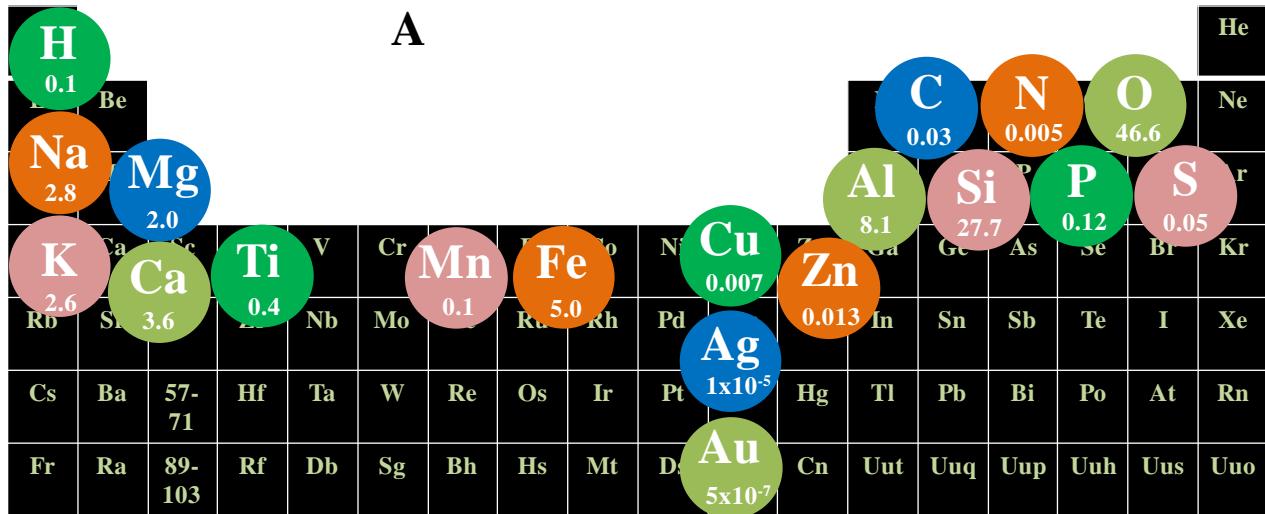


(A)–(C) Dark field fluorescence images of Au@SiO₂@Ag₁₅ MFs showing the gradual disappearance of luminescence with increasing Hg²⁺. (D)–(F) Fluorescence images showing variation in color during the addition of Hg²⁺ of different concentrations to Au@SiO₂-FITC@Ag₁₅ MFs. Insets in all images show the corresponding optical images of the MFs; scale bars are 3 μm.

Cavities, channels, imprints, assemblies, fibres,

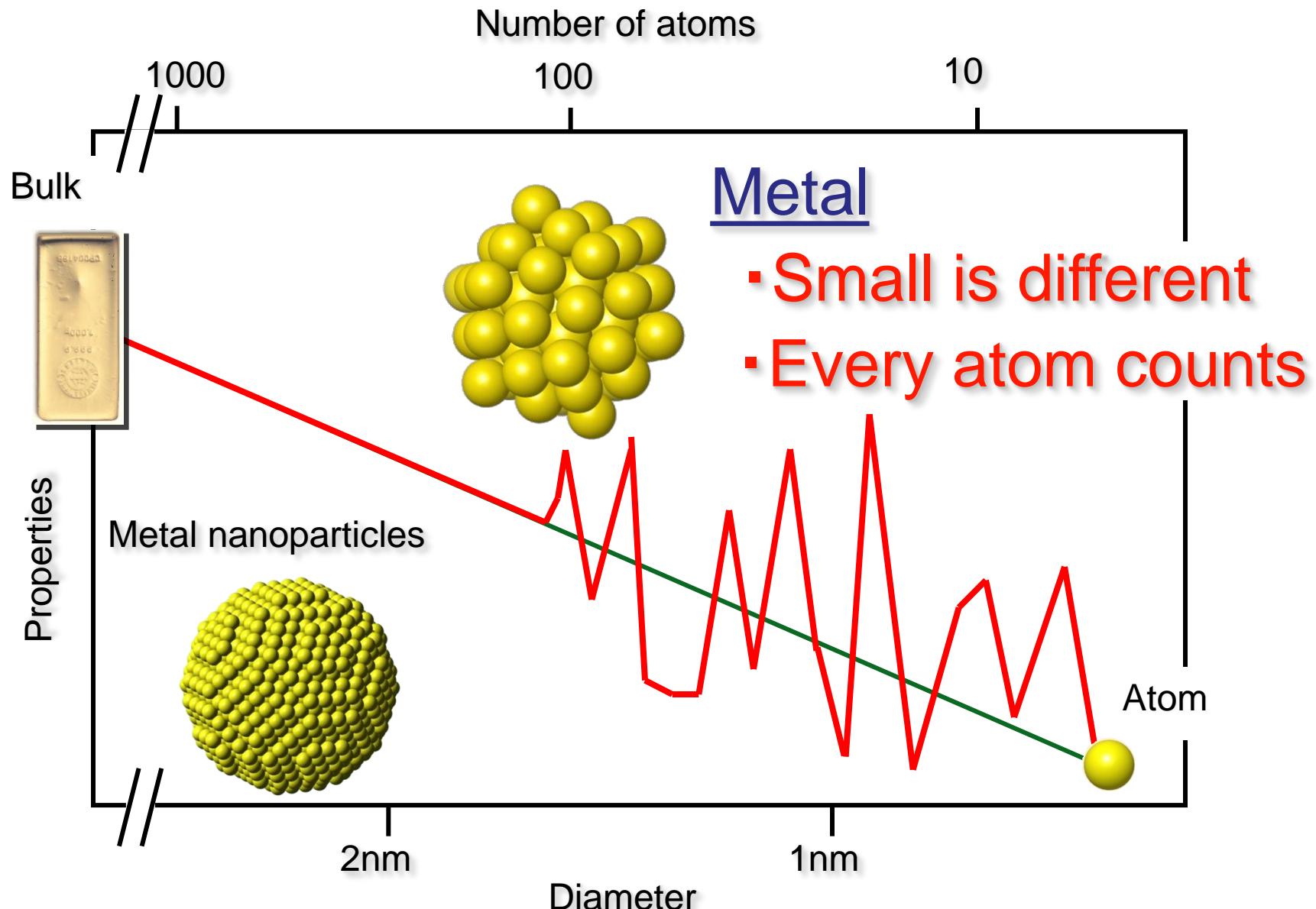


Materials in water – A simple view



(A) Periodic table of elements and those used for water purification (highlighted). Abundances (in wt %)² of the highlighted elements in earth's crust are also mentioned. Note: The highlighted elements are not exactly in their original positions of the periodic table for clarity. (B) Elements that can be grouped to create diverse materials used for water purification.

Metal Clusters



Magic clusters

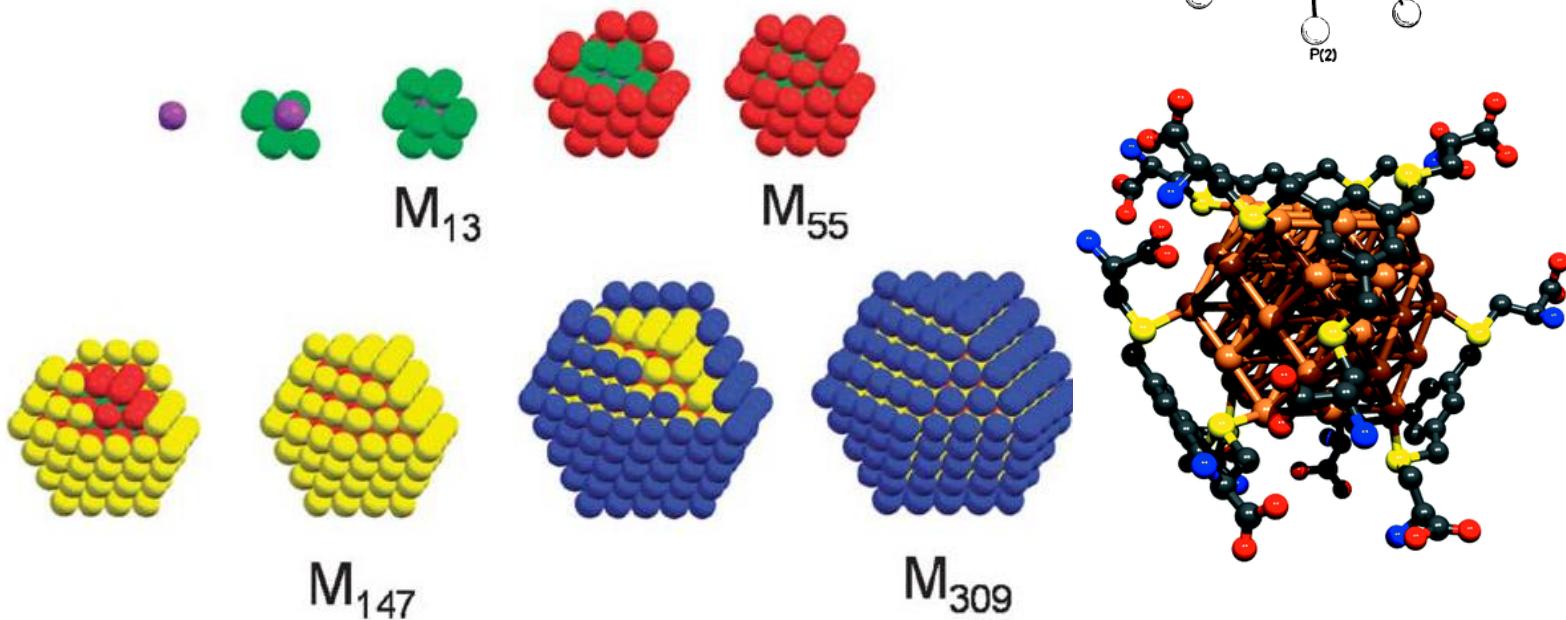
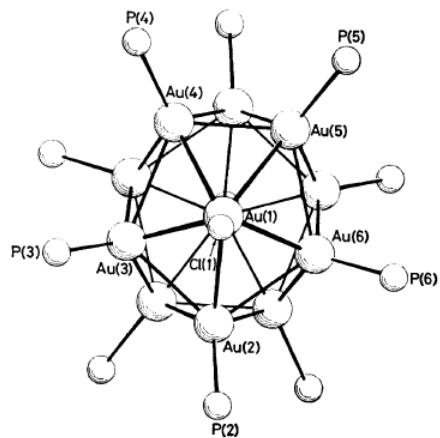
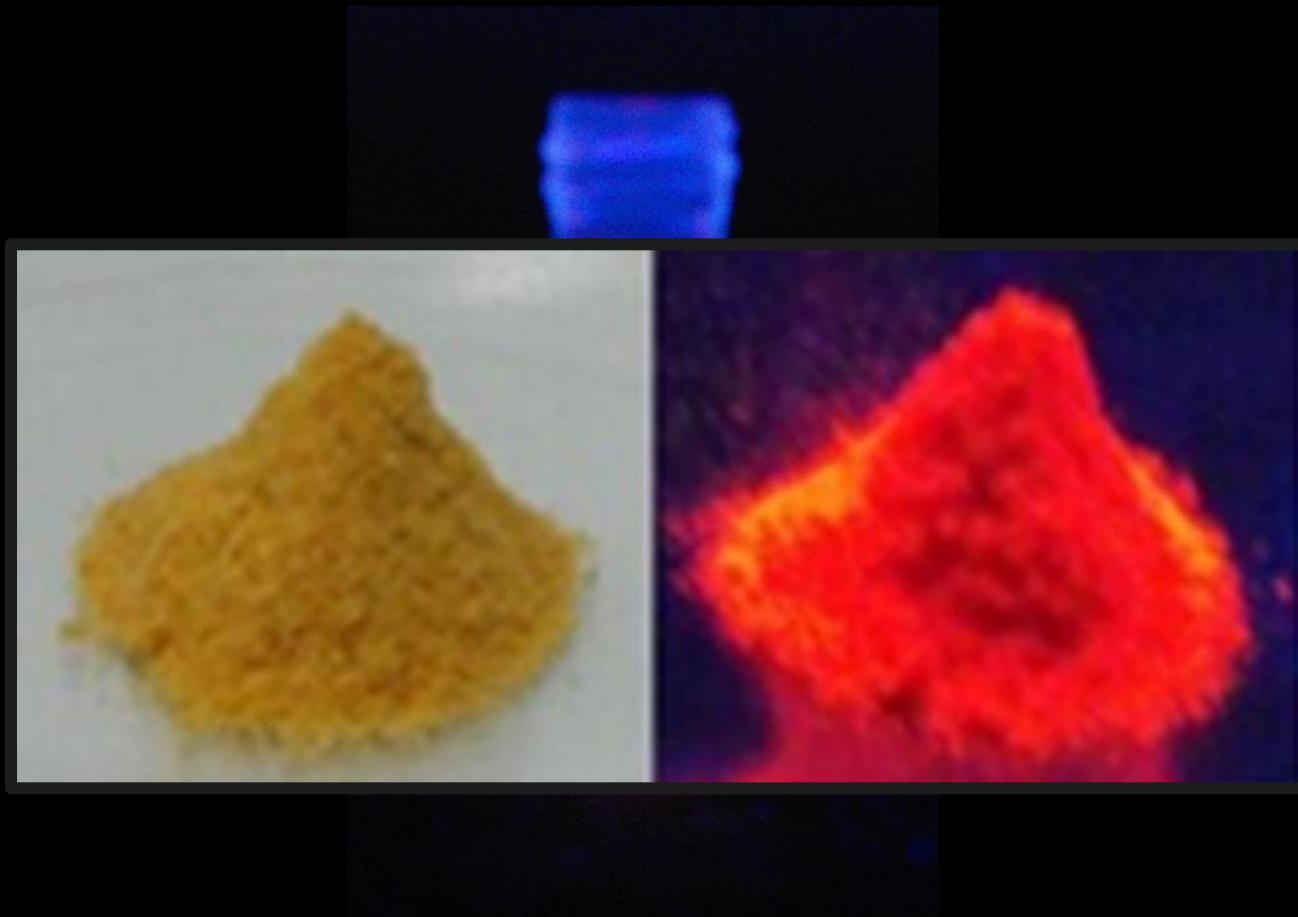


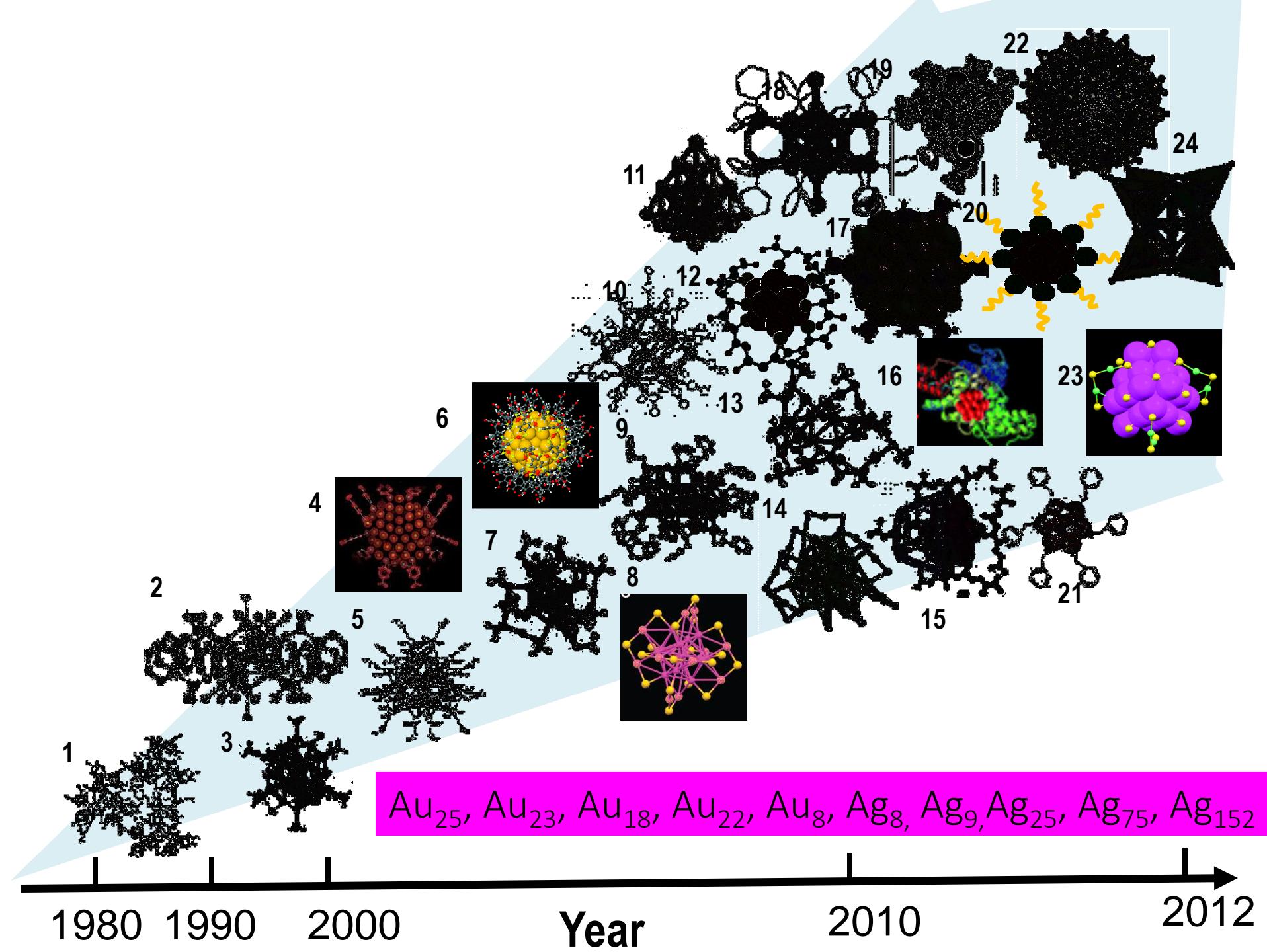
Fig. 1 Organization of full-shell clusters: a first single atom (purple) is surrounded by 12 others (green) to give a one-shell cluster M_{13} . 42 atoms (red) can be densely packed on the 12 green atoms ending with the M_{55} two-shell cluster, followed by 92 atoms (yellow) and 162 atoms (blue) to give M_{147} and M_{309} , respectively.

From Gunter Schmidt, *Chem. Soc. Rev.* **2008**, 37, 1909–1930





Shibhu, Habeeb, Uday, Kamalesh, Lourdu, Ammu, Ananya, Indranath, Atanu,....



New Protocols for the Synthesis of Stable Ag and Au Nanocluster Molecules

T. Udayabhaskararao and T. Pradeep*

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

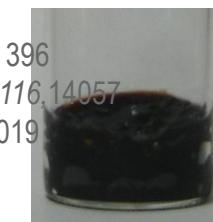
ABSTRACT: “Catching” metals in the nonmetallic form in solution, as they grow to bulk, is one of the most exciting areas of contemporary materials research. A new kind of stabilization to catch the nonmetallic form of noble metals with small thiols has evolved as an exciting area of synthesis during the past decade. Gold clusters stay in the frontline of this research, yielding new “molecules” composed of a few to several hundreds of atoms. By taking guidelines from gold cluster research, various new protocols for silver nanoclusters were developed. In this Perspective, we highlight the recent advances on the synthesis of atomically precise silver, gold, and their alloy clusters with a special emphasis on silver. As a result of intense efforts of the recent past, clusters such as $\text{Ag}_{7,8}(\text{SR})_{7,8}$, $\text{Ag}_7(-\text{S}-\text{R}-\text{S}-)_4$, $\text{Ag}_9(\text{SR})_7$, $\text{Ag}_{32}(\text{SR})_{19}$, $\text{Ag}_{44}(\text{SR})_{30}$, $\text{Ag}_{140}(\text{SR})_{53}$, $\text{Ag}_{280}(\text{SR})_{140}$ and $\text{Ag}_{152}(\text{SR})_{60}$ (SR and $\text{S}-\text{R}-\text{S}$ refer to thiolate and dithiolate ligands, respectively) were added to the literature. Moreover, “silver-covered” and “gold-covered” alloy clusters have also been synthesized. Early reports of the crystallization of such clusters are available. Several of these clusters are shown to act as sensors, catalysts, and pesticide degradation agents, which suggests that these materials may find applications in daily life in the foreseeable future.



Diverse methods of synthesis

Udayabhaskararao et al. J. Am. Chem. Soc. 2010, 132, 16804
 Indranath et al. Nano Lett. 2012, 12, 5861
 Anindya et al. J. Nanoparticle Res. (In Press)
 Udayabhaskararao et al. J. Phys. Chem. C 2012 (Revision)
 Udayabhaskararao et al. J. Nanoparticle Res. 2013 (Preparation)

Indranath et al. J. Haz. Mater. 2012, 211-212, 396
 Aditi and T. Pradeep J. Phys. Chem. C 2012, 116, 14057
 Remya et al. J. Phys. Chem. C, 2012, 116, 26019



Inside gels



Indranath et al. Chem. Commun. 2012, 48, 859
 Dhanalakshmi et al. Chem. Commun. 2012, 48, 6788
 Shibu and T. Pradeep, Chem. Mater. 2011, 23, 989
 Shibu et al. J. Phys. Chem C 2008 112, 12168
 Shibu et al. ACS Appl. Mater. Interfaces, 2009, 1, 2199
 Habeeb et al. Nano Res. 2008, 1, 333

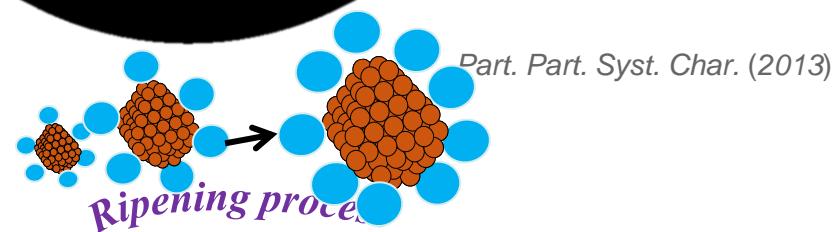
T. Udayabhaskararao and T. Pradeep, J. Phys. Chem. Lett. 4 (2013) 1553–1564



Habeeb et al. Chem. Eur. J. 2009, 15, 10110
 Udayabhaskararao et al. Angew. Chem. Int. Ed. 2010, 49, 392
 Mrudula et al. J. Mater. Chem. 2009, 19, 4335



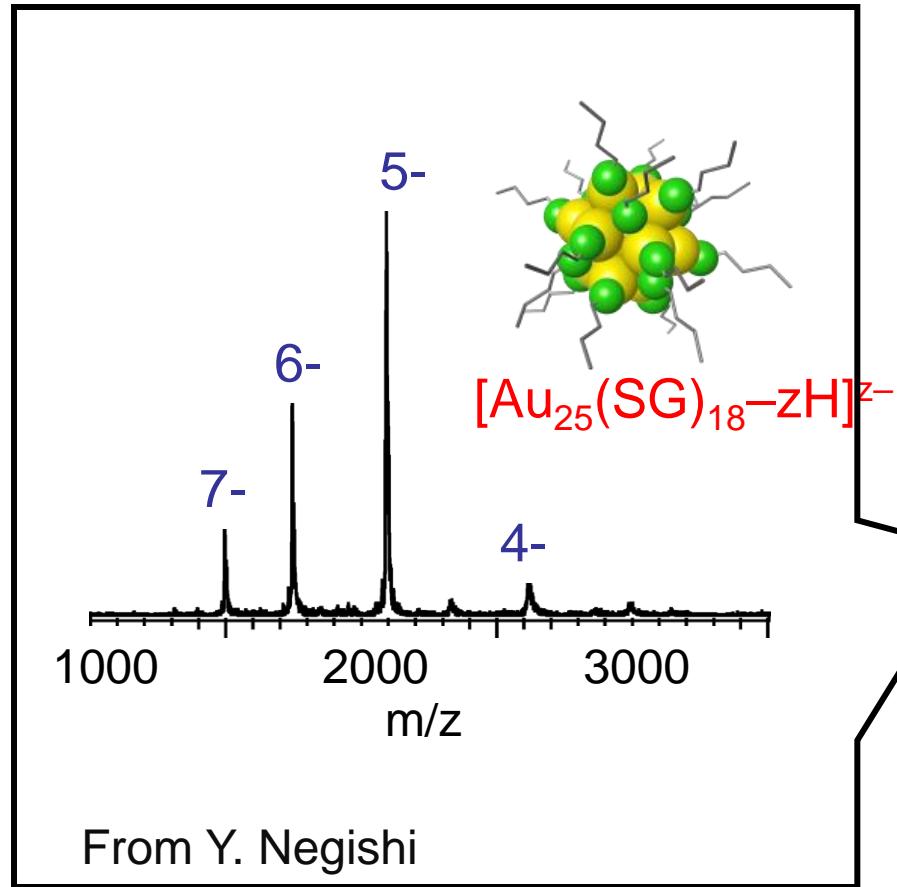
Interfacial etching



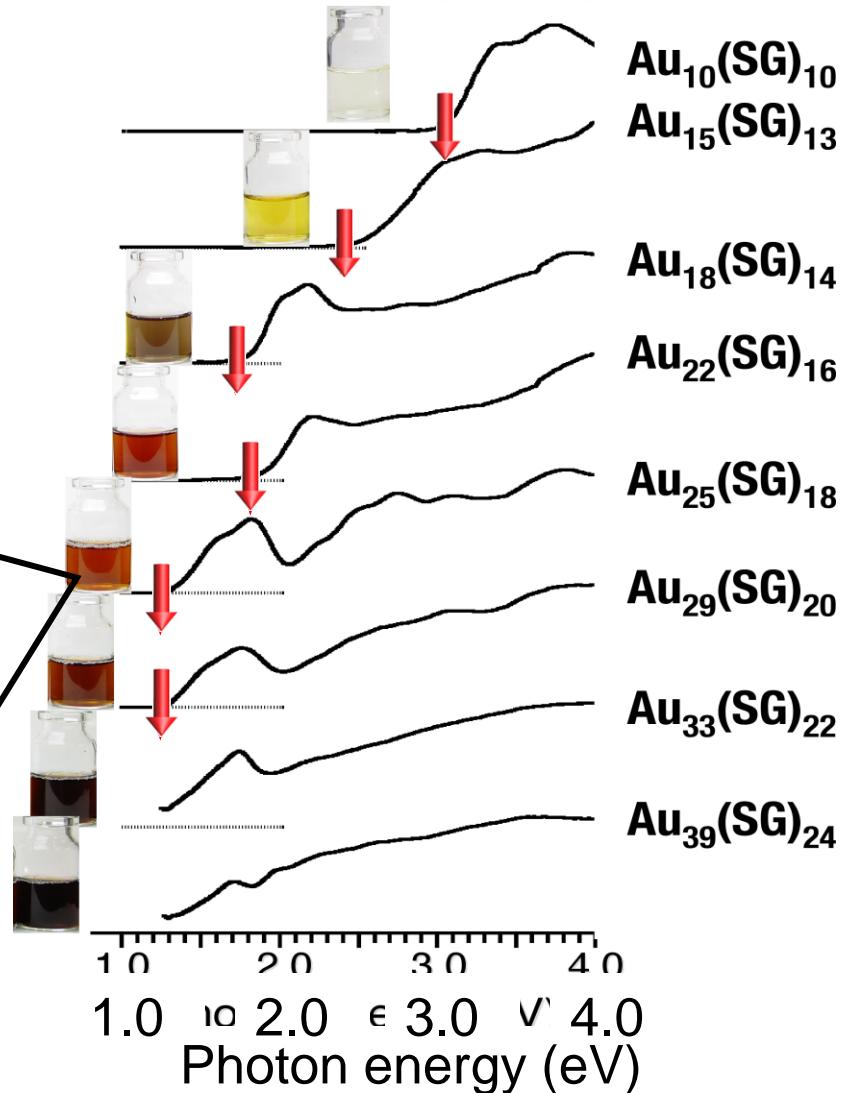
Part. Part. Syst. Char. (2013)

Systematic Isolation of Glutathione-Protected Gold clusters

Negative ESI mass spectrum



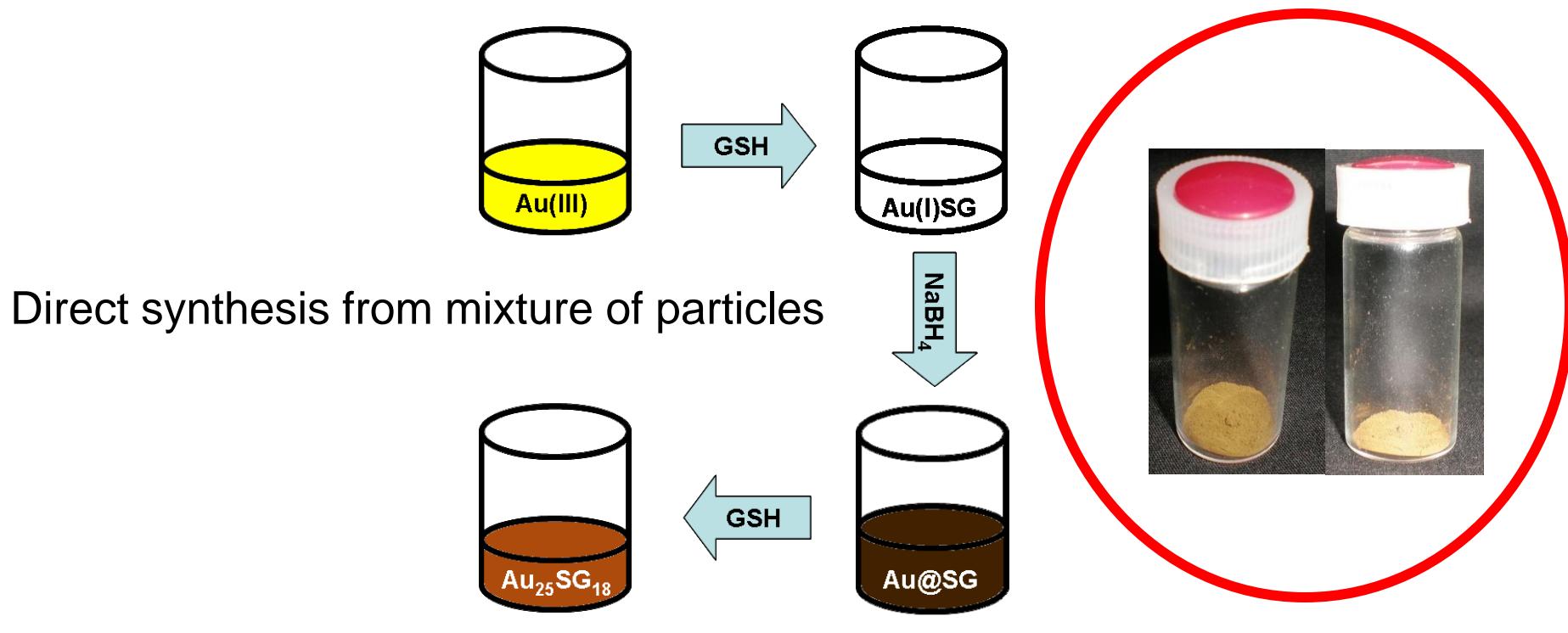
UV-vis absorption spectra



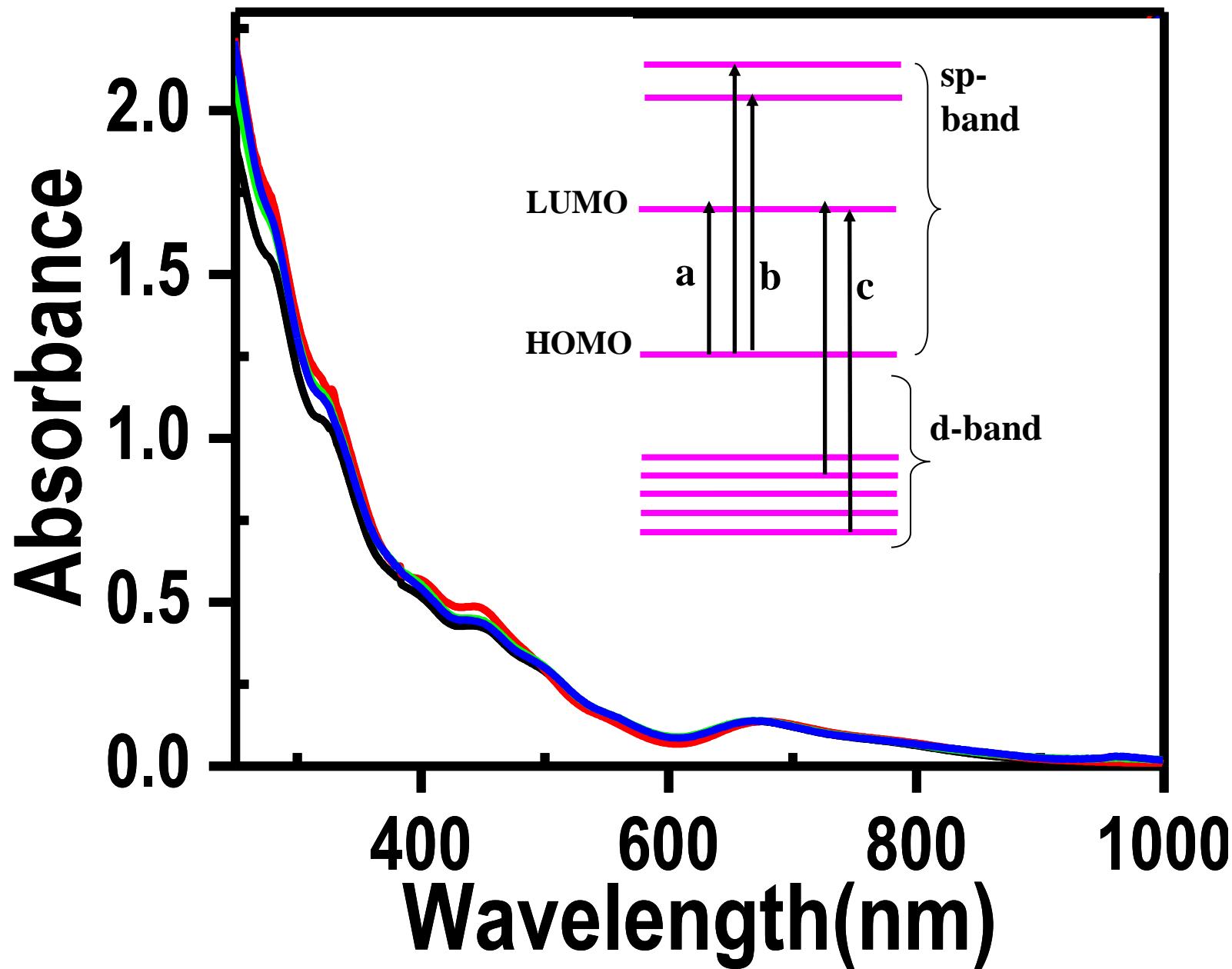
Negishi, Y.; Nobusada, K.; and Tsukuda, T.
J. Am. Chem. Soc. **2005**, 127, 5261-70.

$\text{Au}_{25}\text{SG}_{18}$

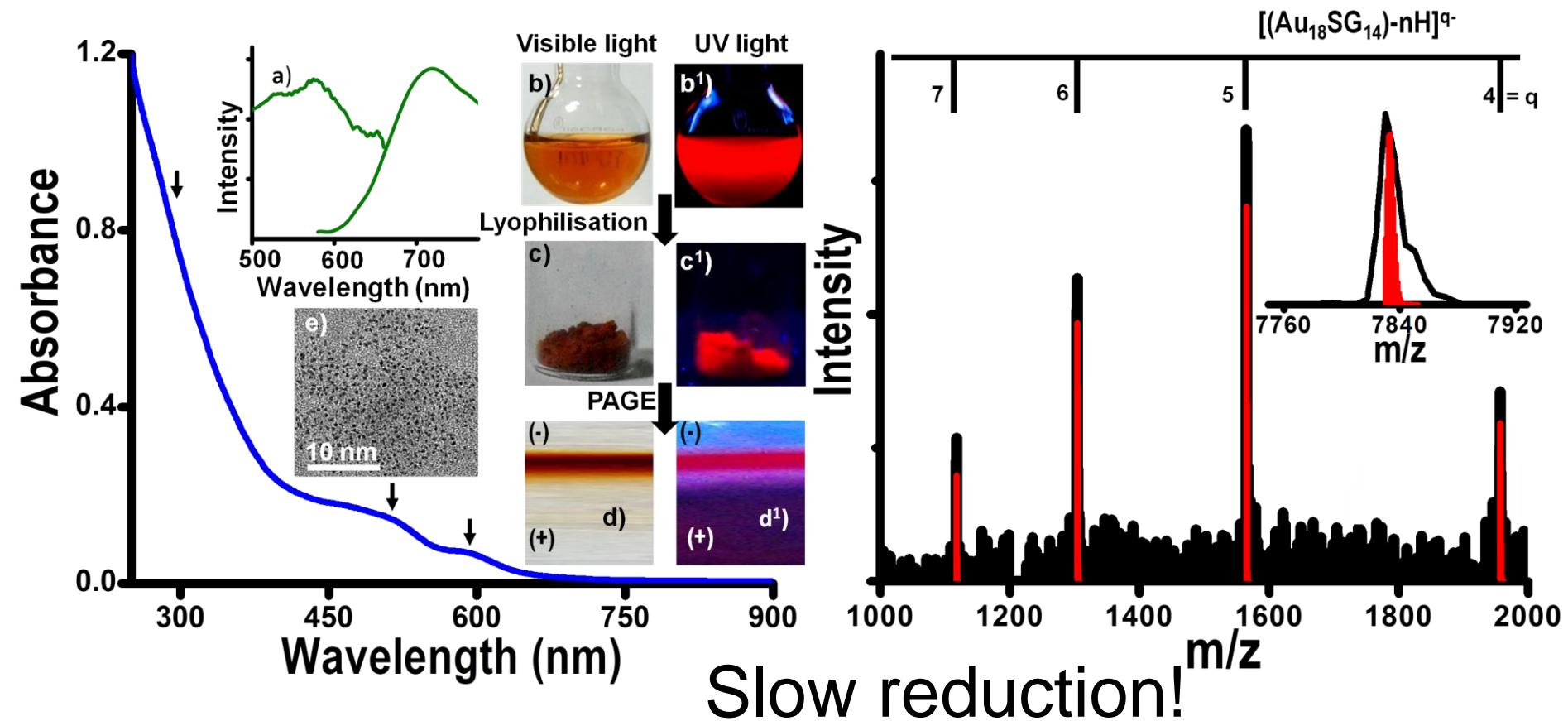
Synthesis: Au_{25} clusters can be preferentially populated by dissociative excitation of larger precursors



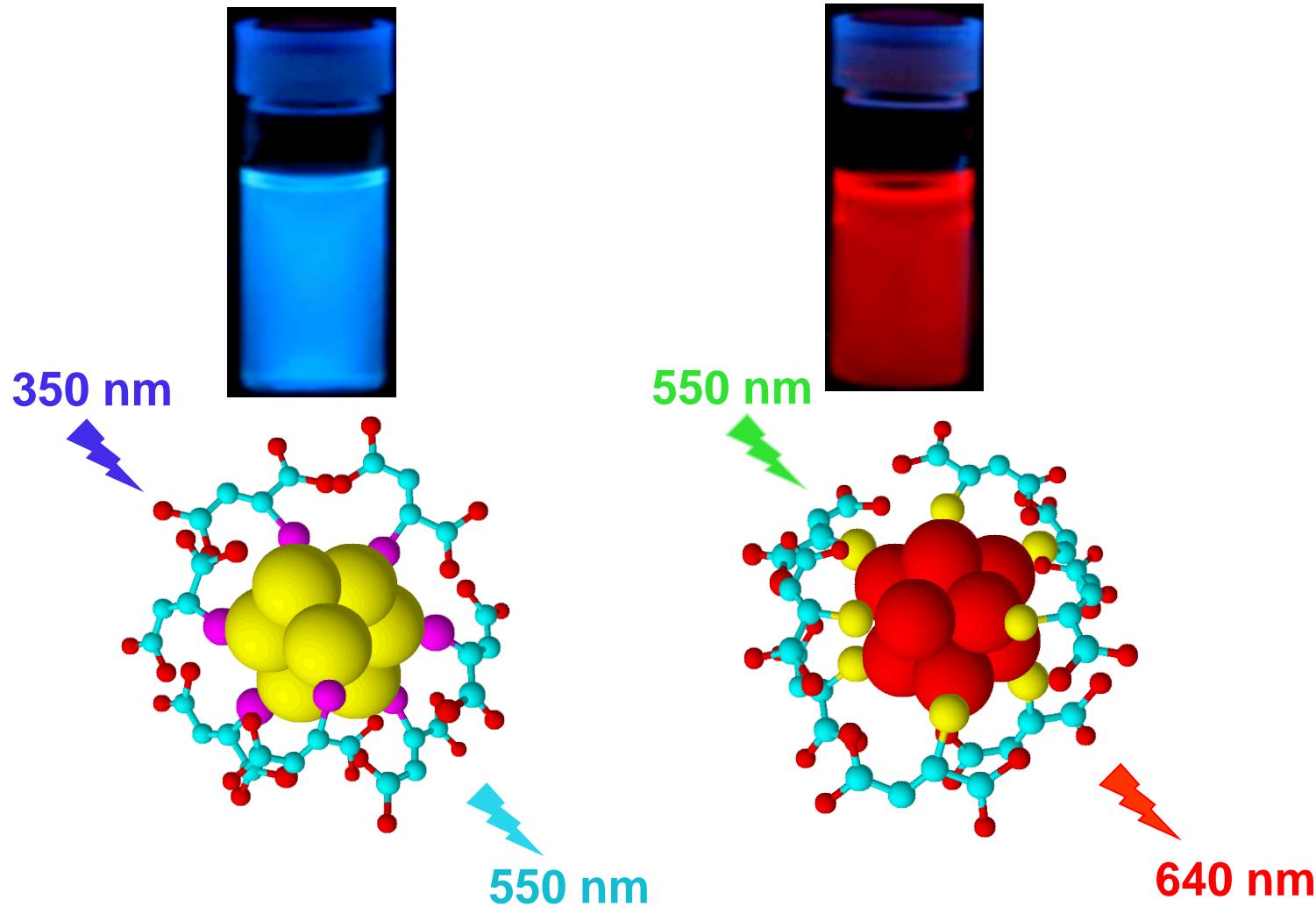
Scheme showing the synthesis of $\text{Au}_{25}\text{SG}_{18}$ clusters



One step methods - $\text{Au}_{18}\text{SG}_{14}$



Silver clusters - interfacial etching



TUB Rao and T Pradeep, Angew. Chem. Int. Ed. 49 (2010) 3925-3929(2010).

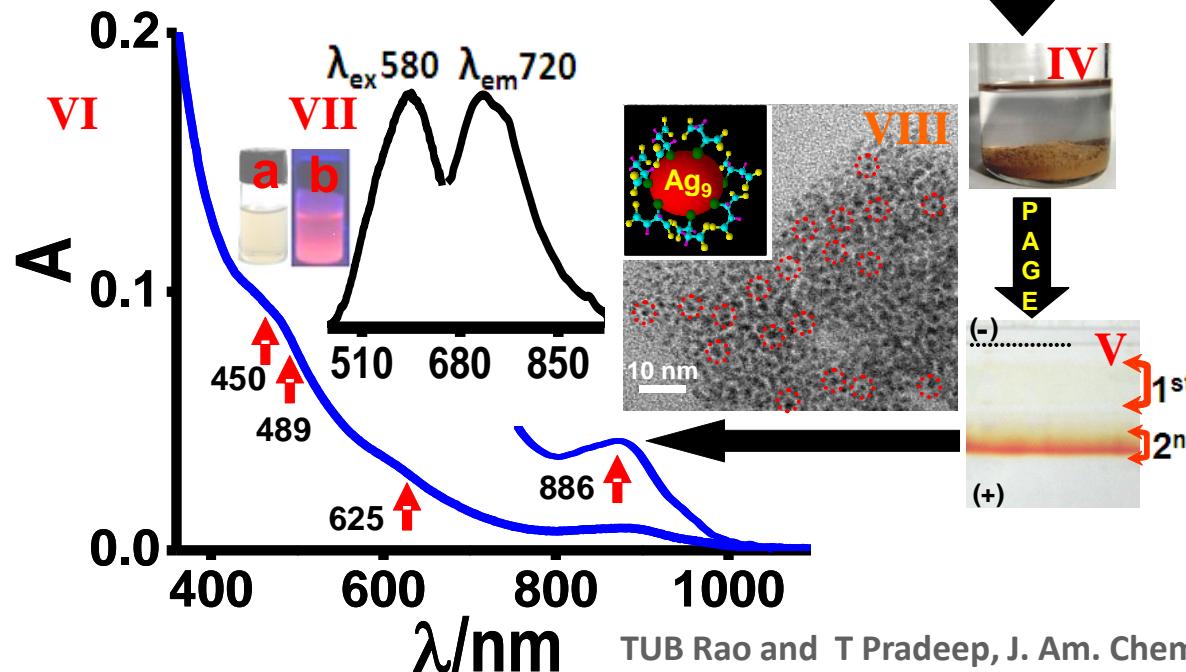
Ag₉MSA₇ - solid state synthesis



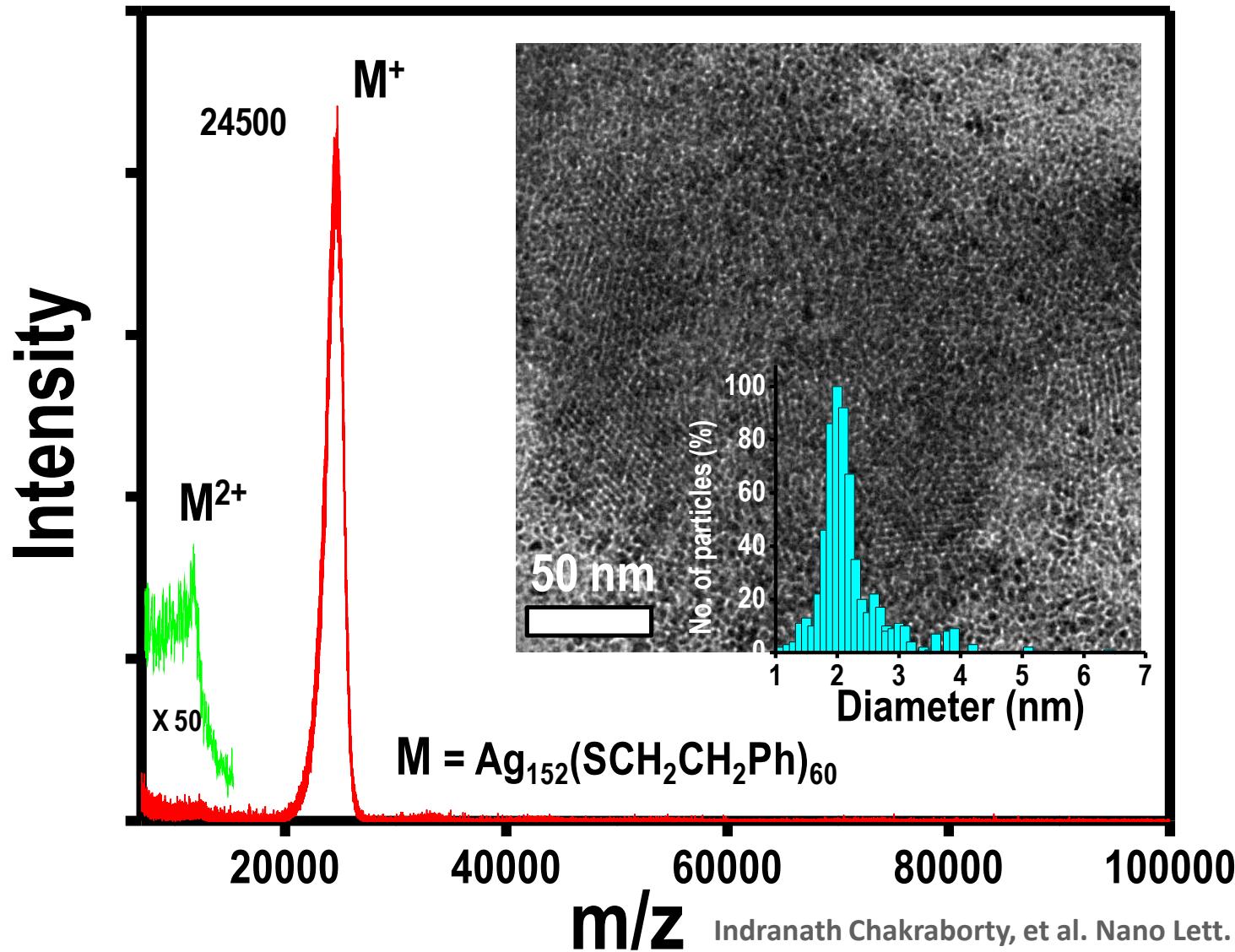
AgNO₃ + H₂MSA
(Initially both
are colorless)

Became orange
color

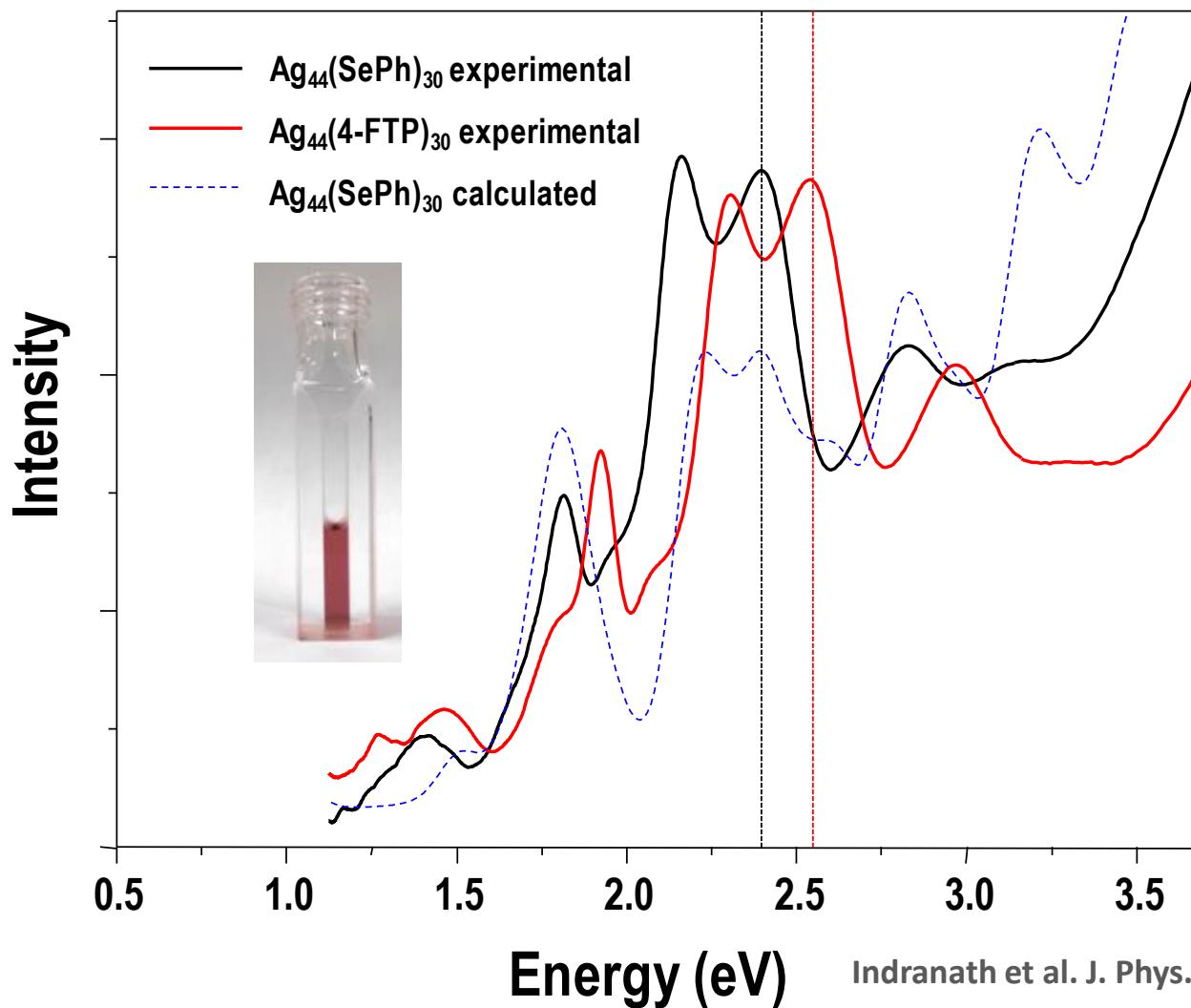
Water +
[Ethanol
(excess)]

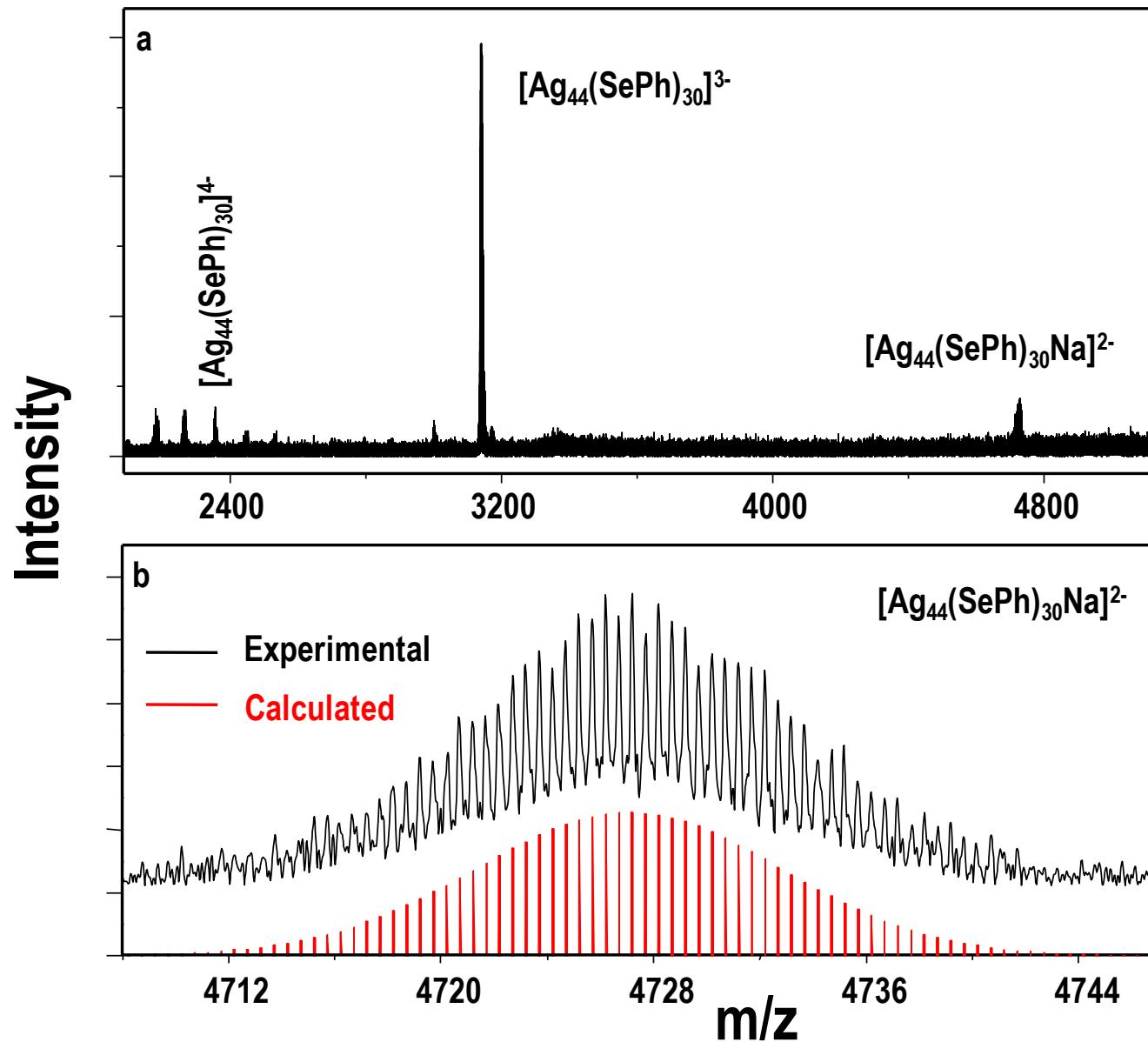


$\text{Ag}_{152}\text{PET}_{60}$

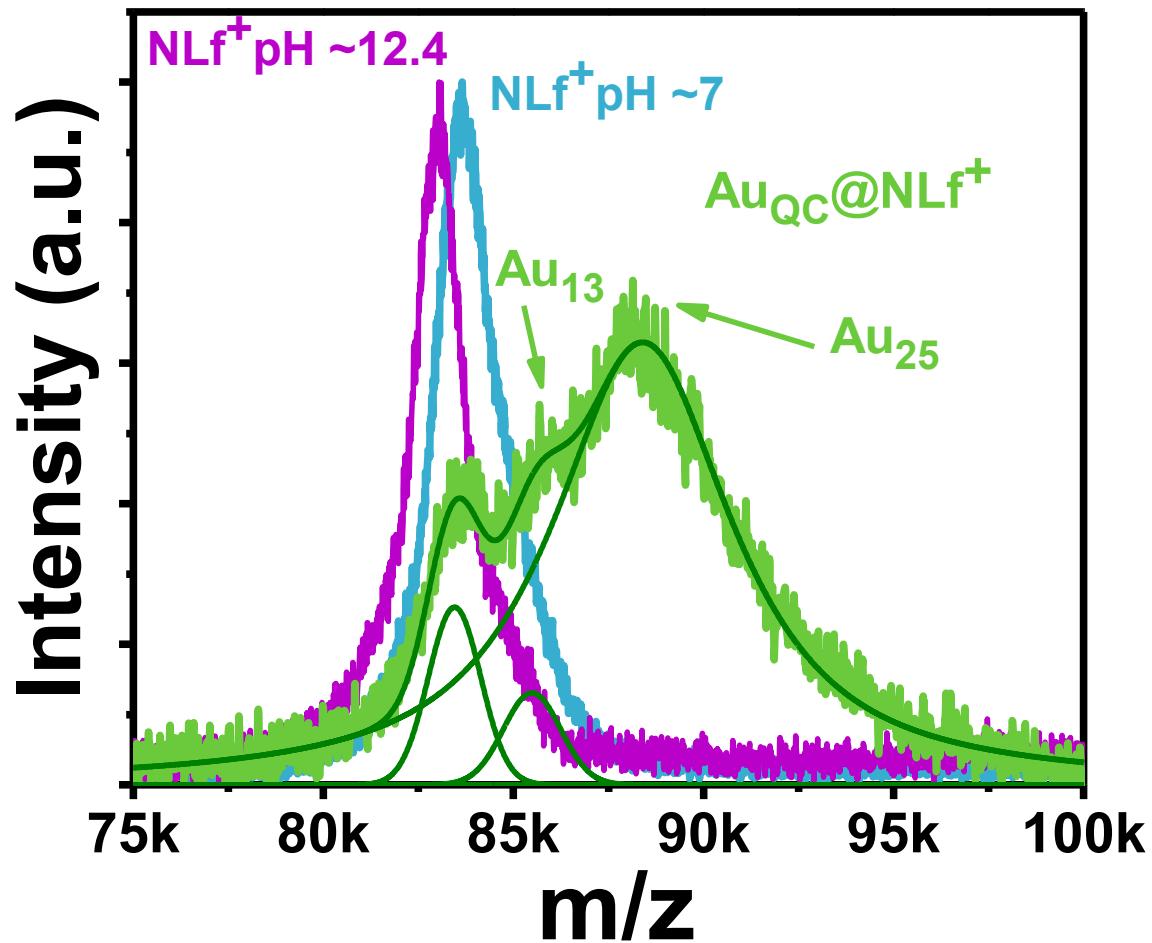


$\text{Ag}_{44}\text{SePh}_{30}$





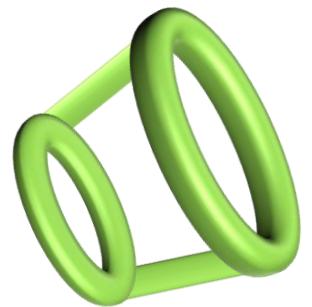
Cluster nucleation in proteins



Kamalesh Choudhari et al. ACS Nano (2011)

Clusters in cavities

Cluster assemblies and host-guest complexes



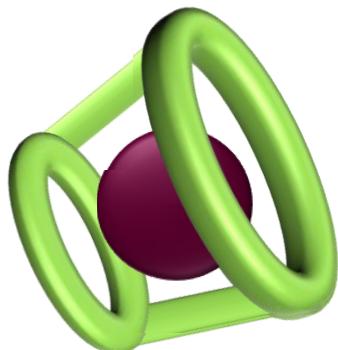
+



Host

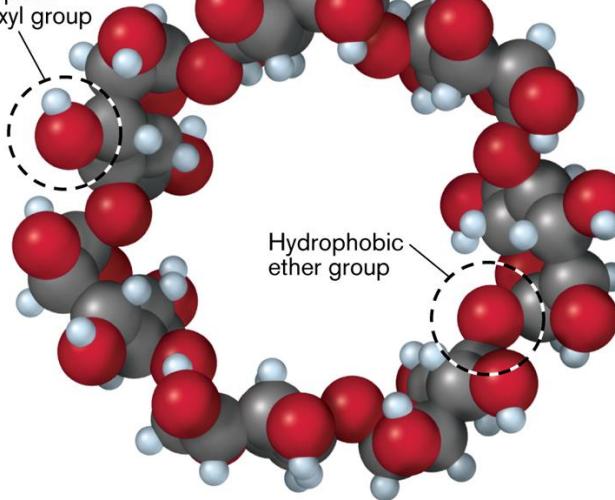
Guest

K_s

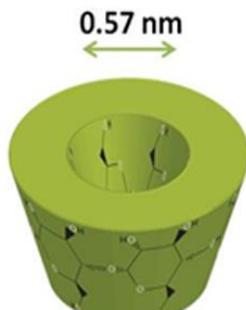


Inclusion complex

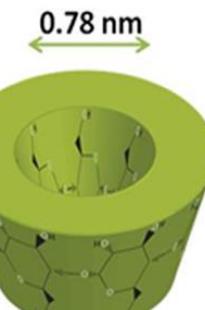
Hydrophilic hydroxyl group



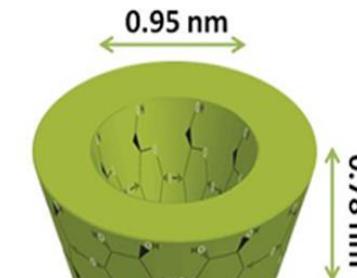
Hydrophobic ether group



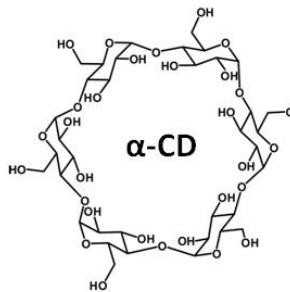
α -CD



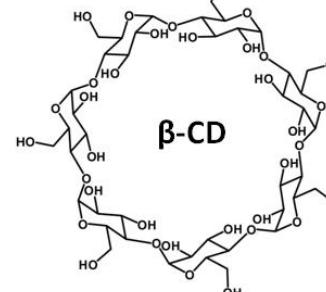
β -CD



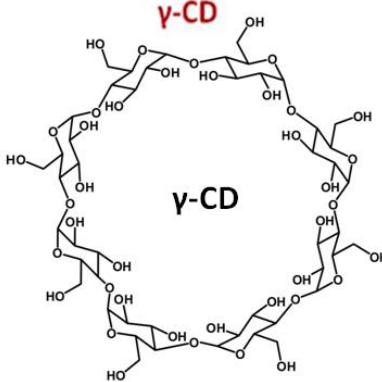
γ -CD



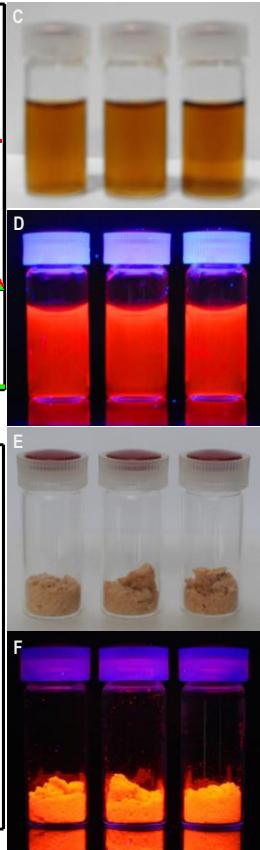
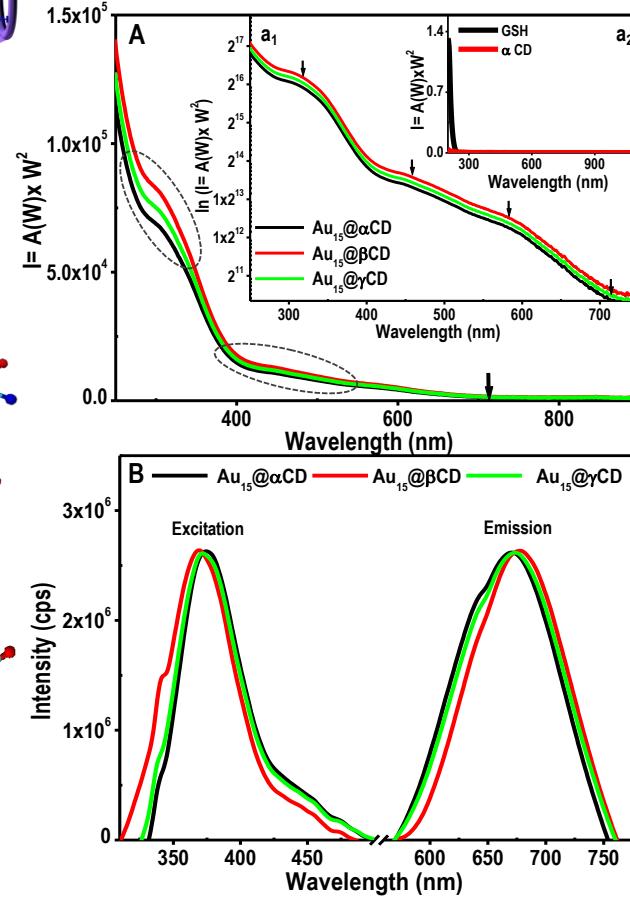
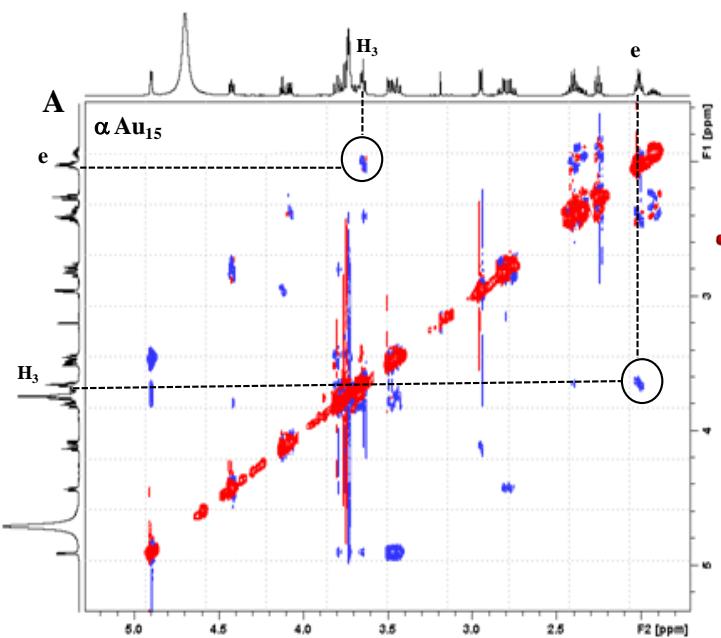
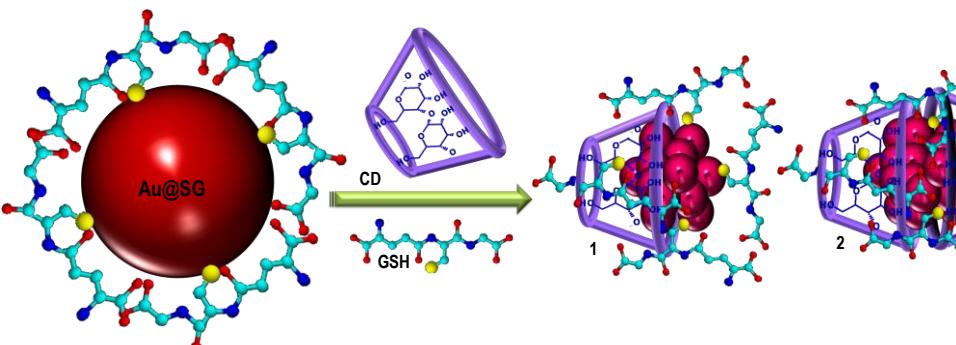
α -CD



β -CD



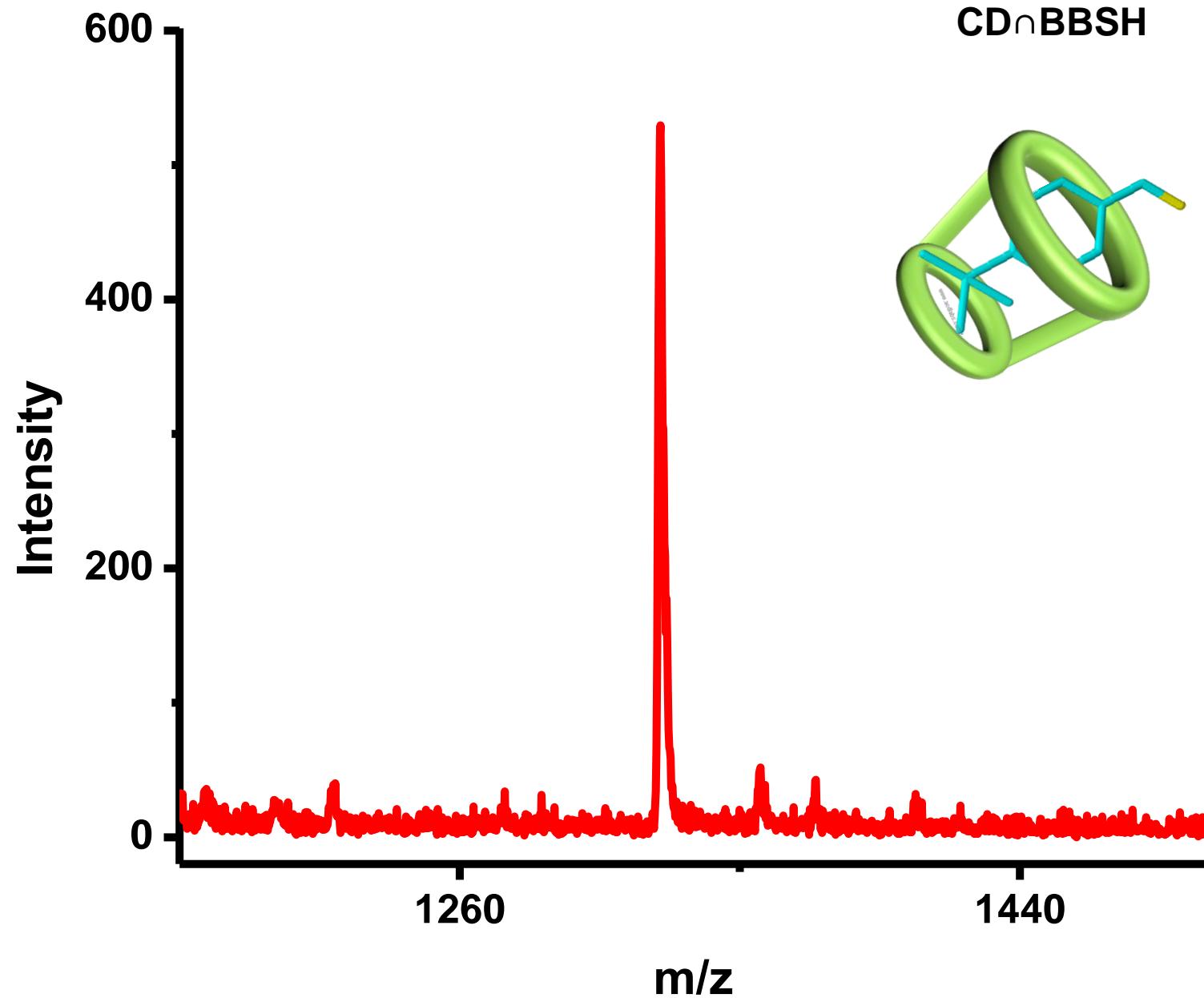
γ -CD



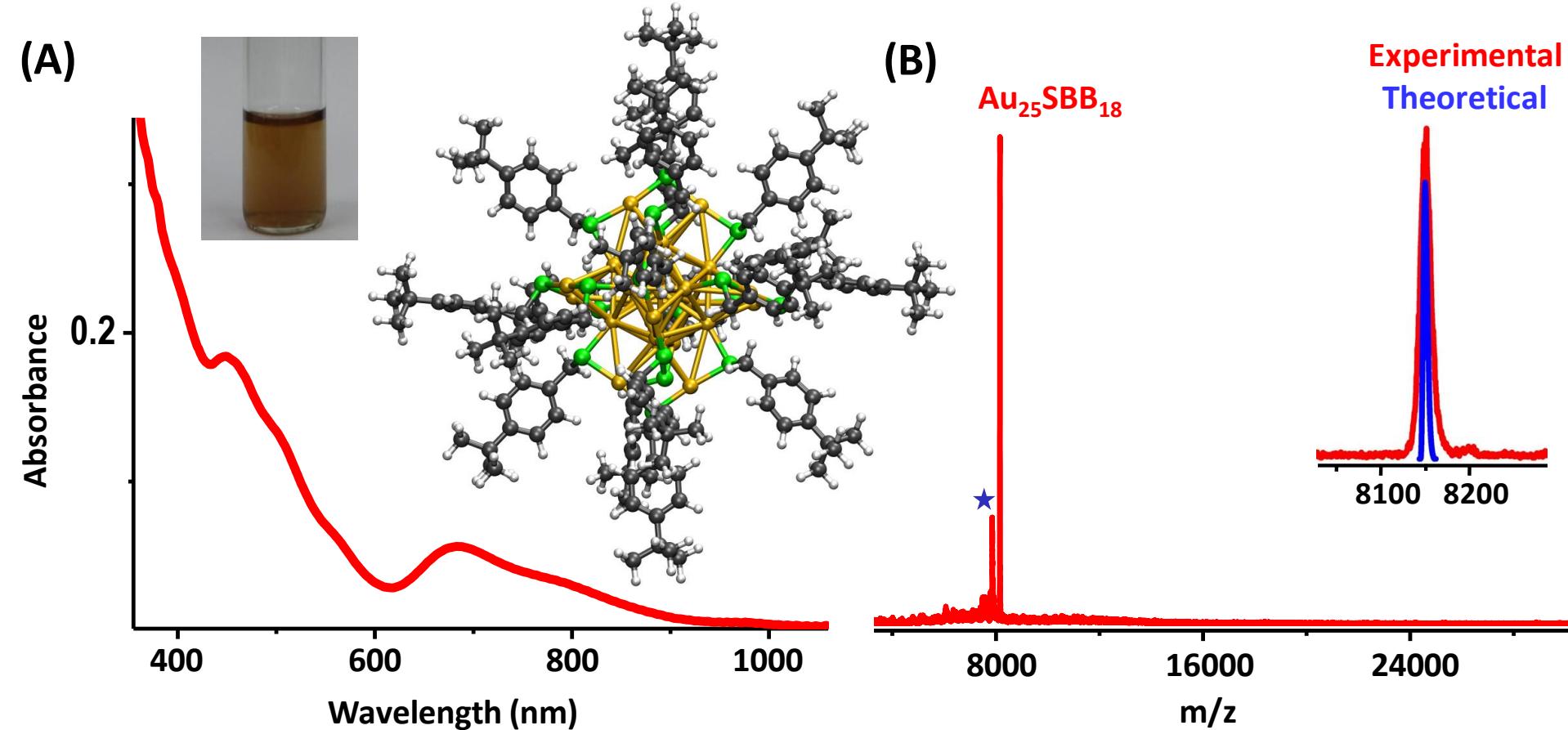
Indian patent, 4036/CHE/2010, filed on December 30, 2010.

E. S. Shibu and T. Pradeep, Chem. Mater. 23 (2011) 989–999.

Positive mode MALDI of BBSH \cap CD complex

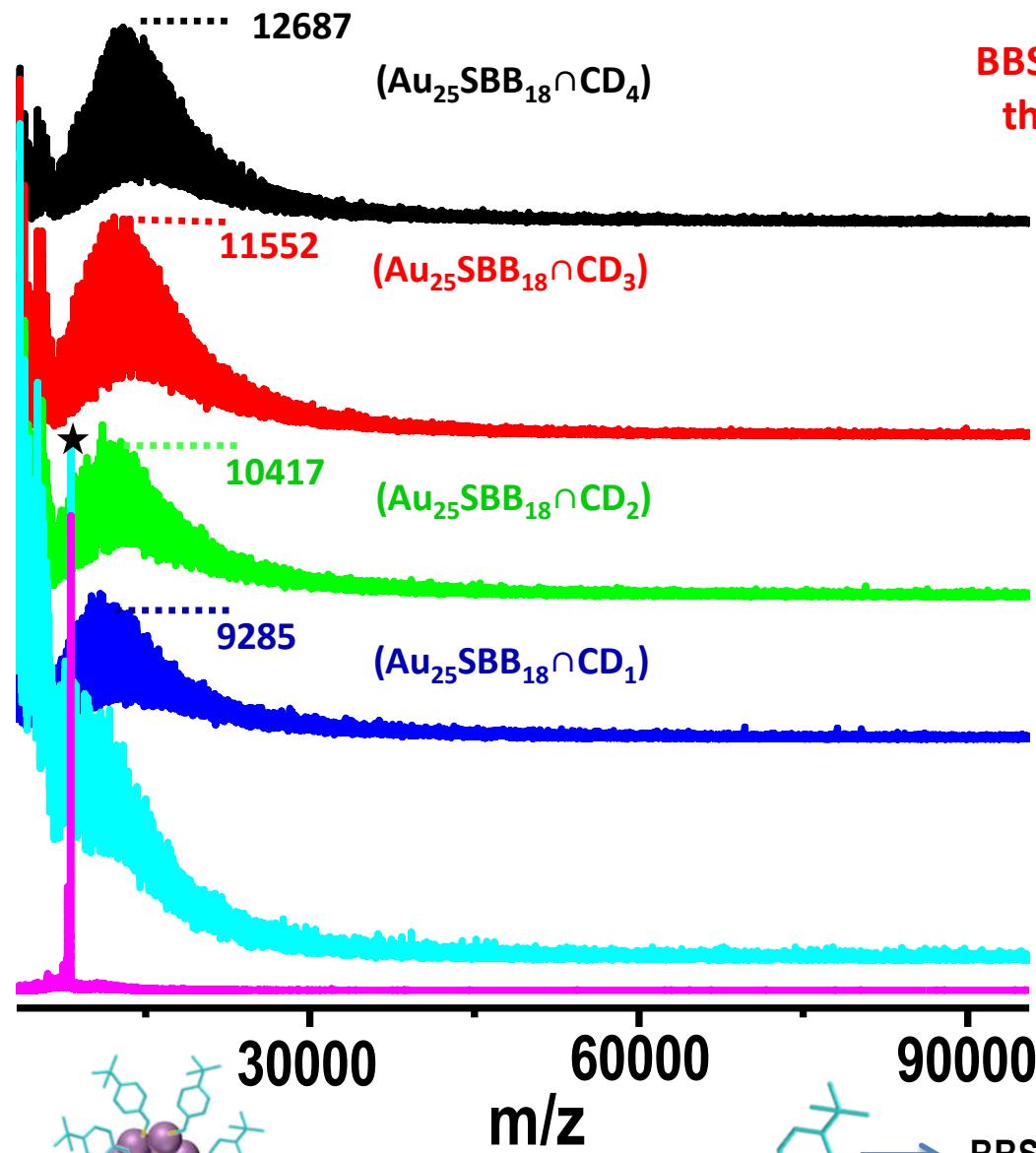


$\text{Au}_{25}\text{SBB}_{18}$



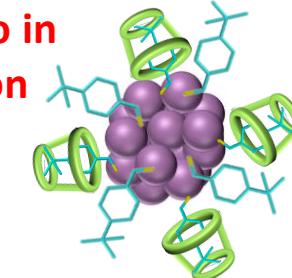
Ammu Mathew et al. ACS Nano 2014.

$\text{Au}_{25}\text{BBS}_{18} \cap \text{CD}$

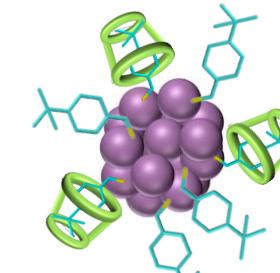


BBS:CD ratio in
the solution

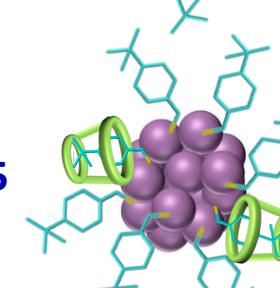
1: 1.2



1: 1



1: 0.8



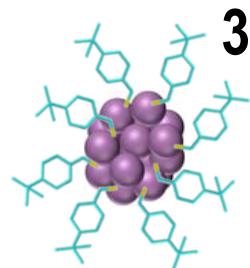
1: 0.05



1: 0.03



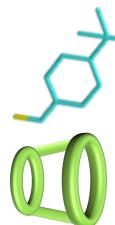
$\text{Au}_{25}\text{SBB}_{18}$



300000

m/z

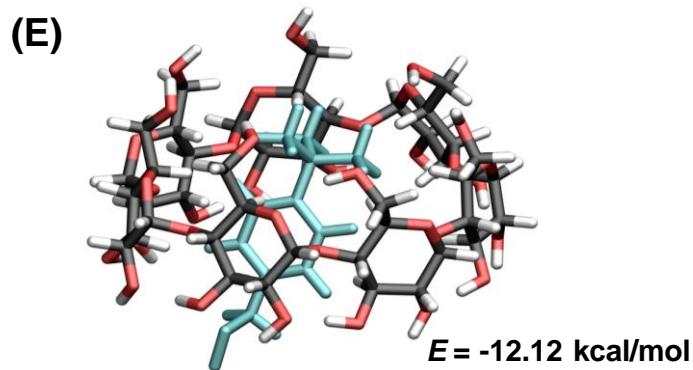
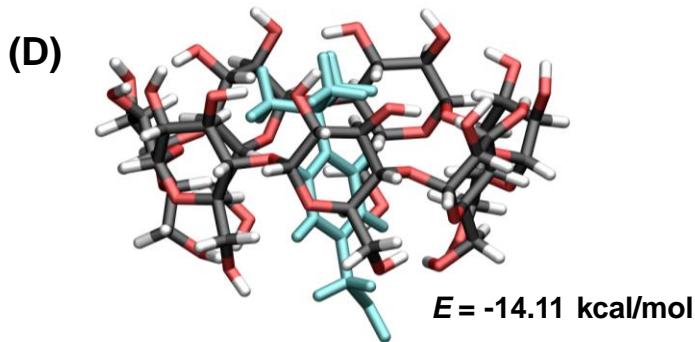
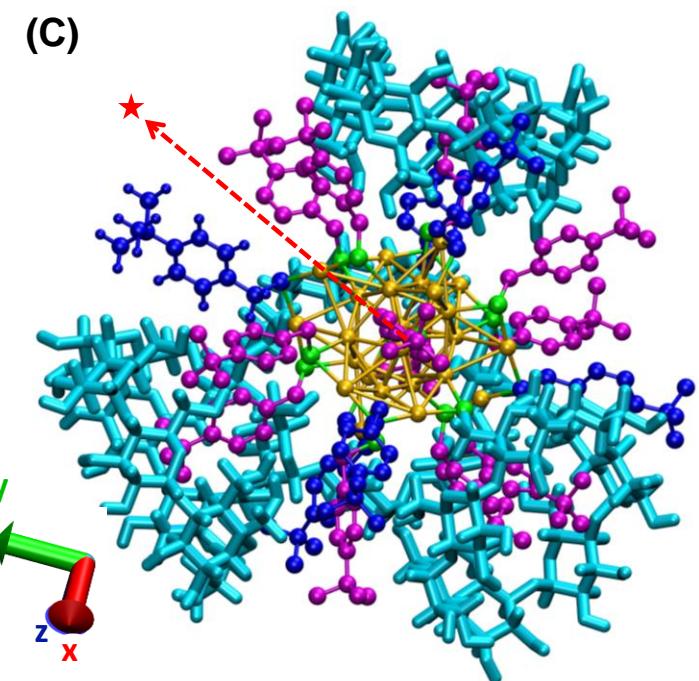
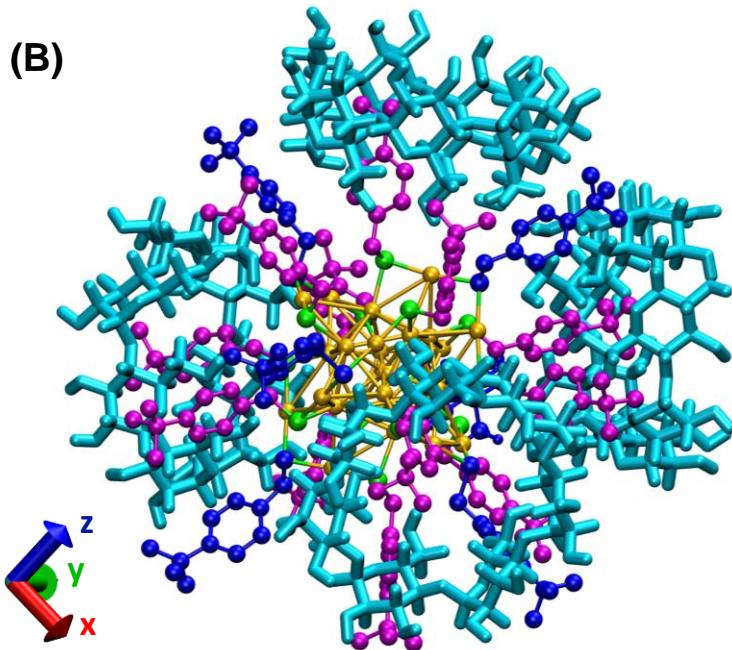
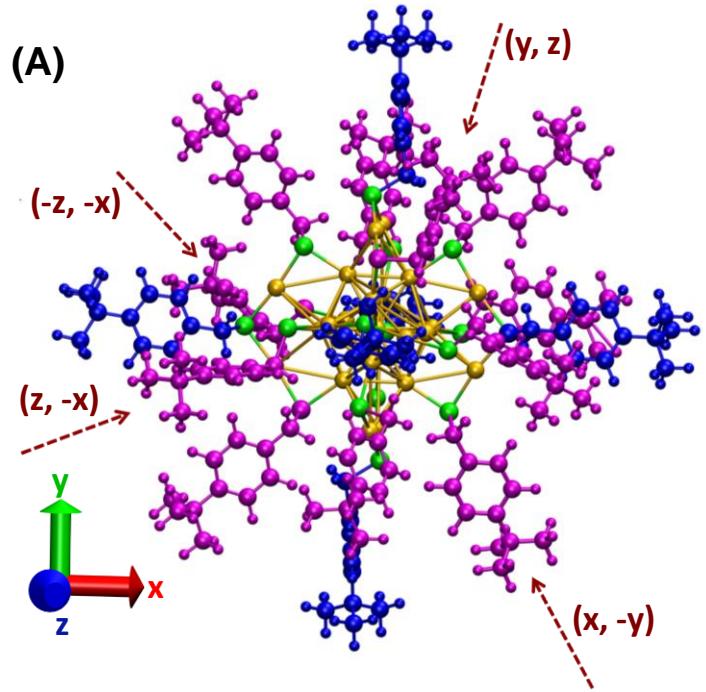
$\text{Au}_{25}\text{SBB}_{18}$

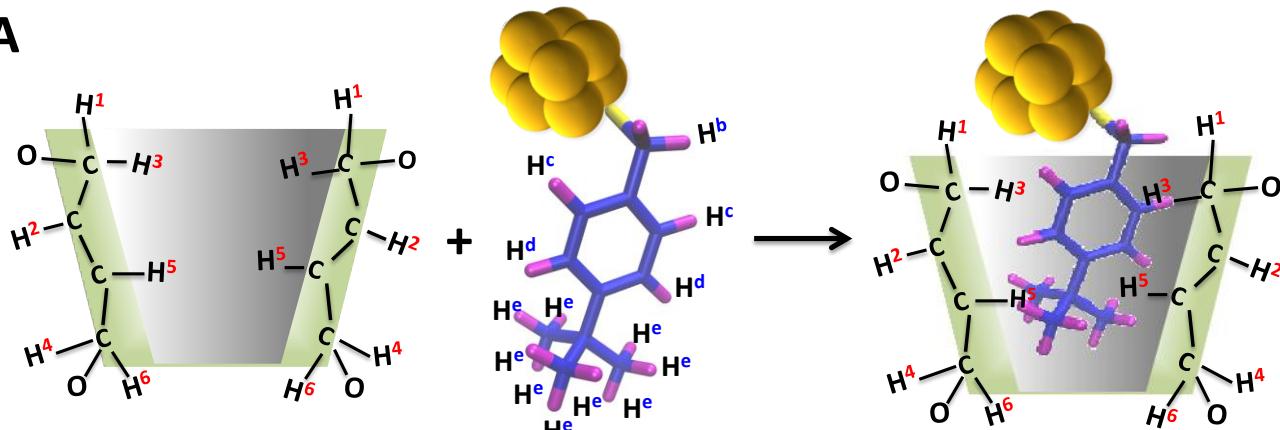
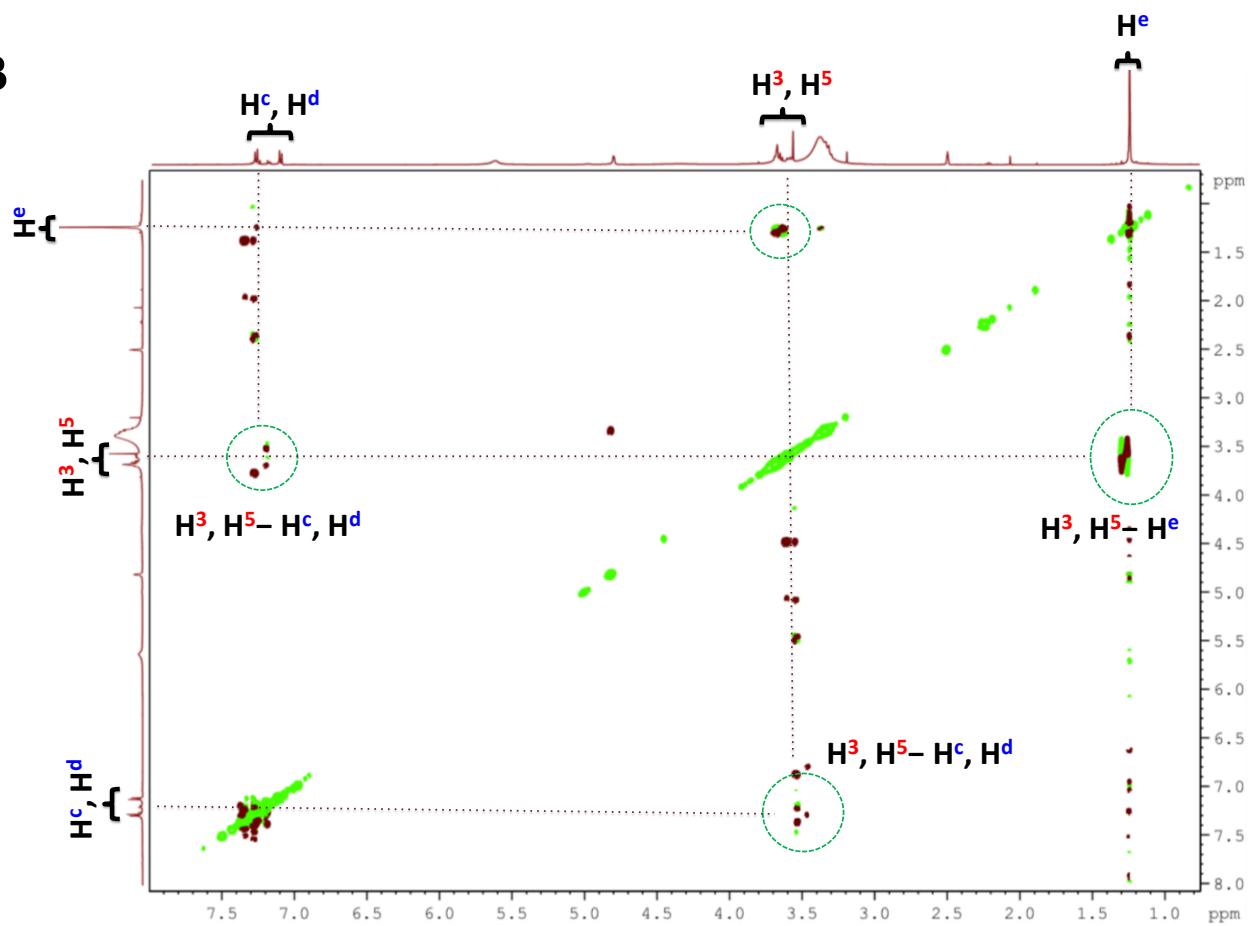


BBS

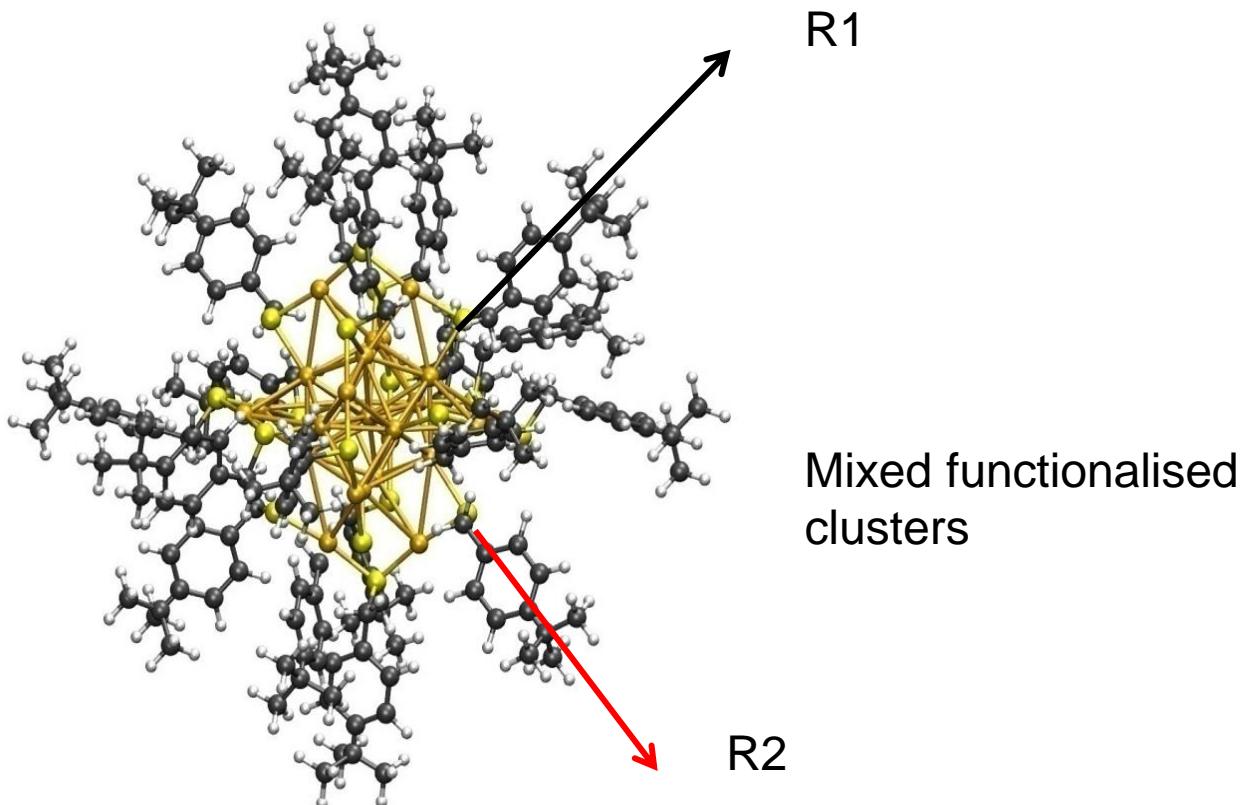


$\beta\text{-CD}$



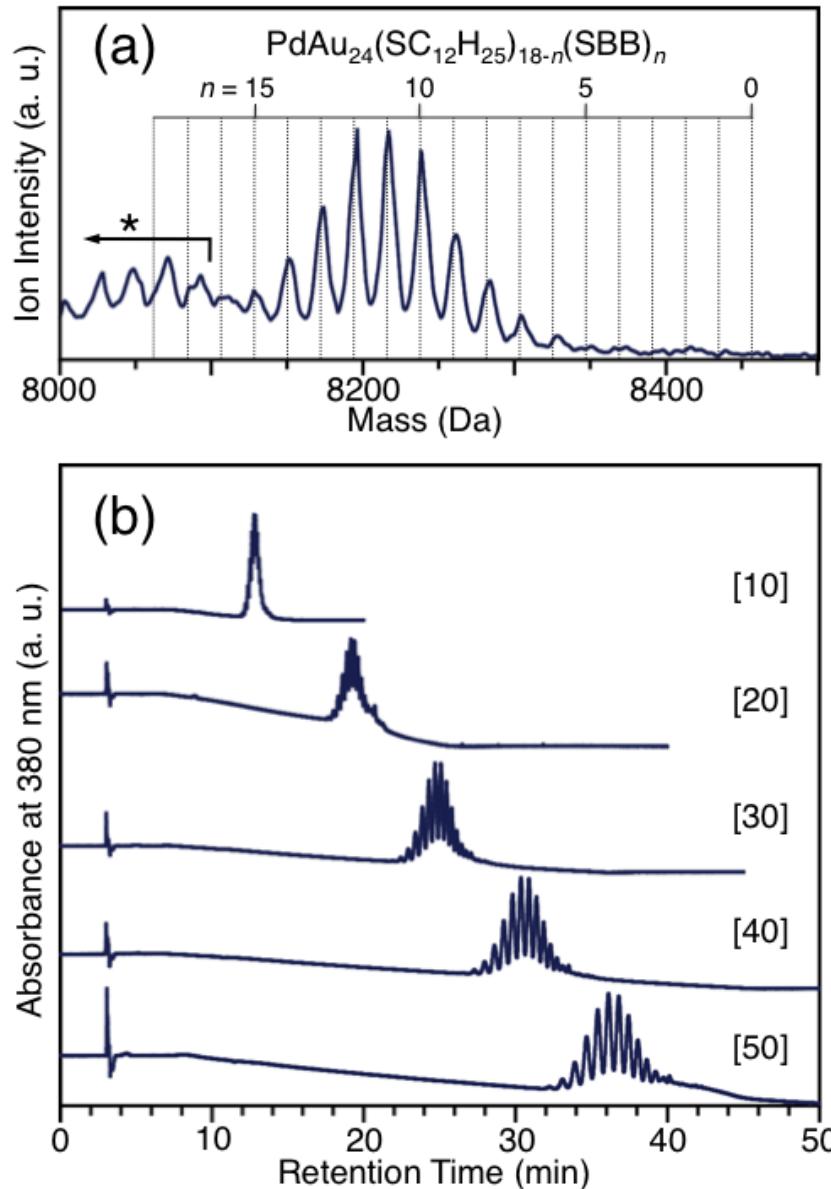
A**B**

Substitution chemistry of clusters

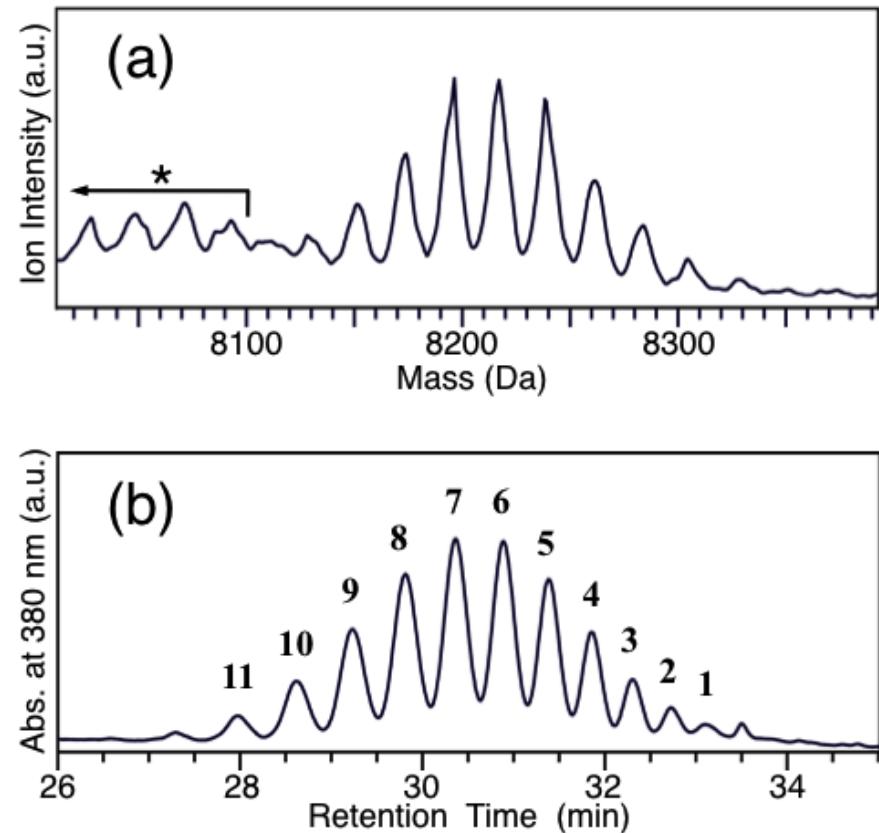


Yoshiki Niihori, Miku Matsuzaki, T. Pradeep and Yuichi Negishi, J. Am. Chem. Soc., 135 (2013) 4946-4949

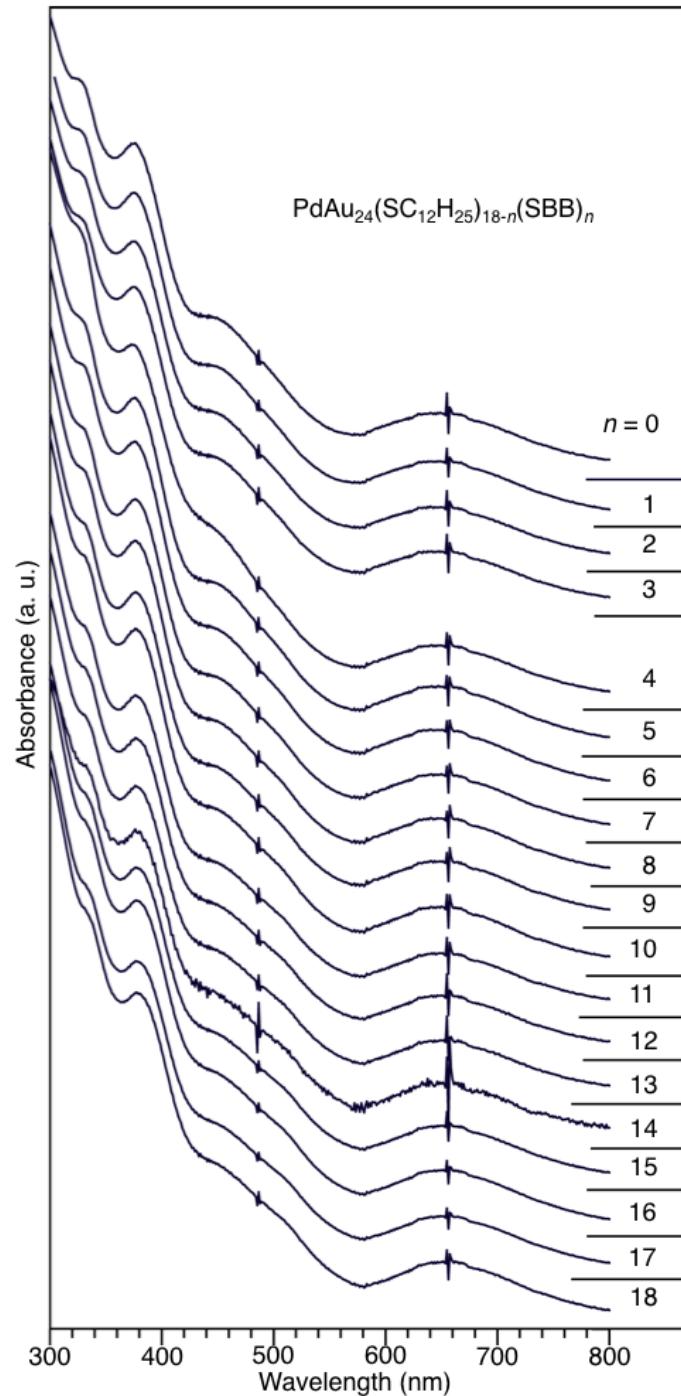
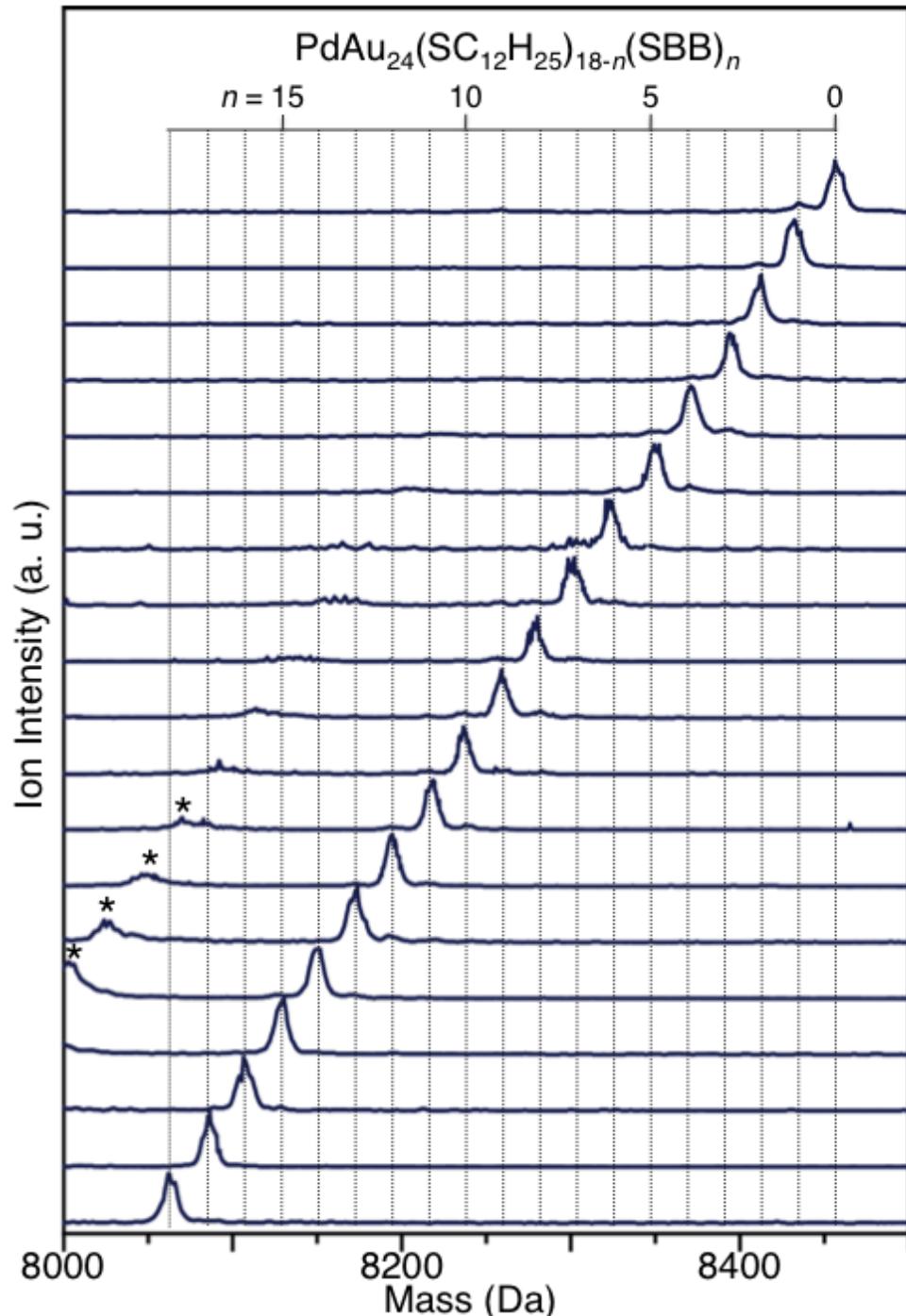
Separation of precise compositions of noble metal clusters protected with mixed ligands

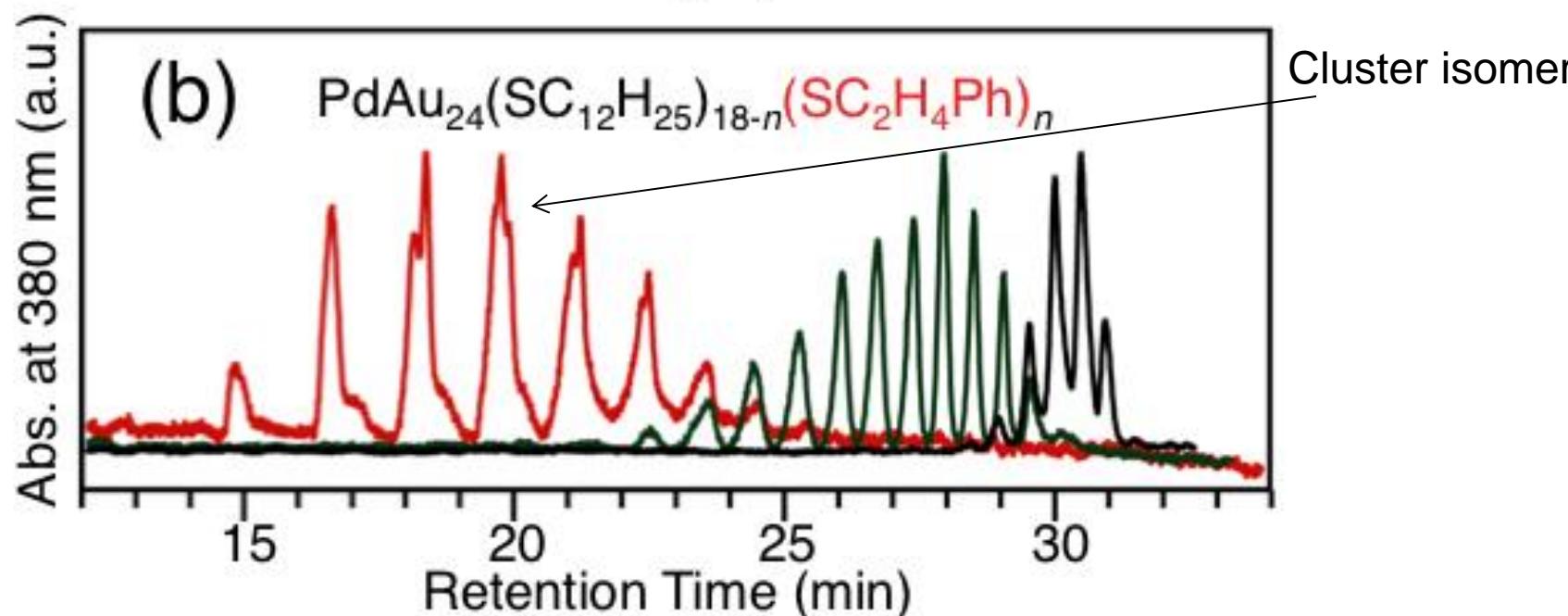
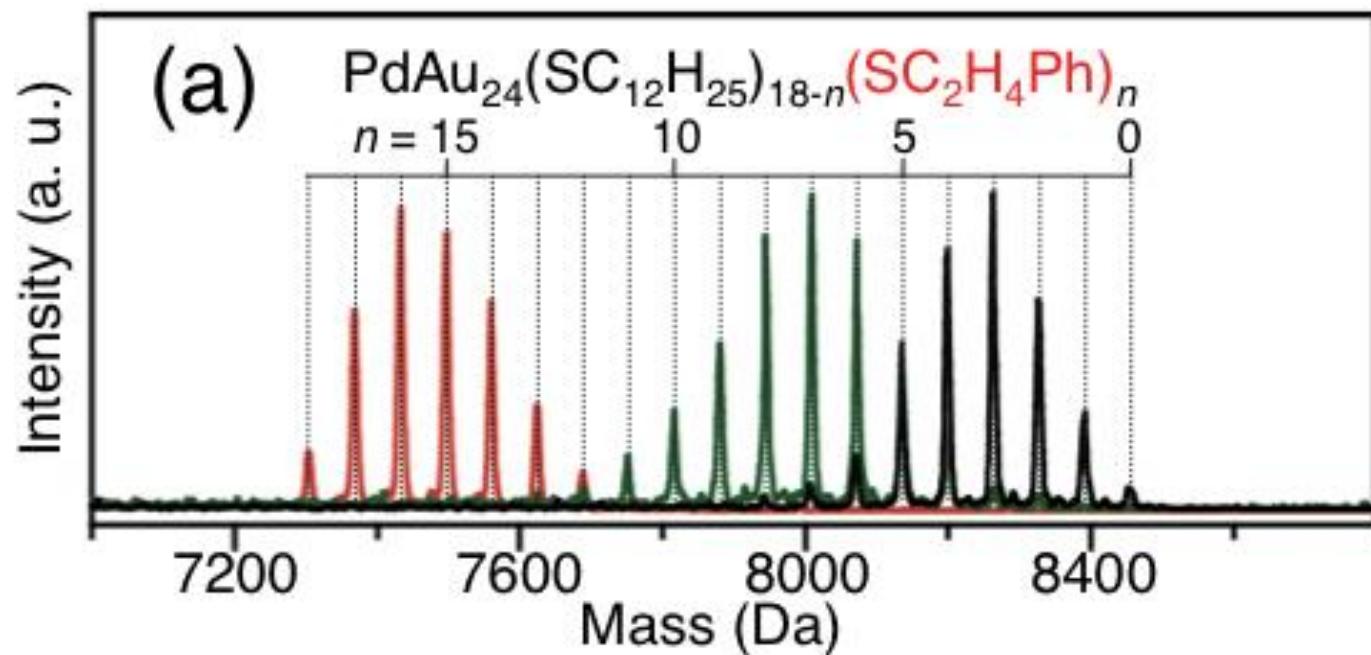


Ligand exchange chemistry –
Substitution chemistry

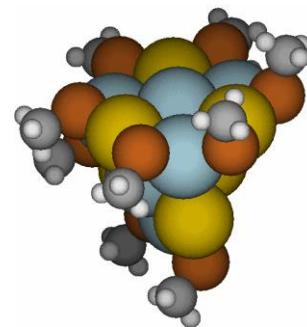


With Niihori and Negishi, Tokyo University of
Science

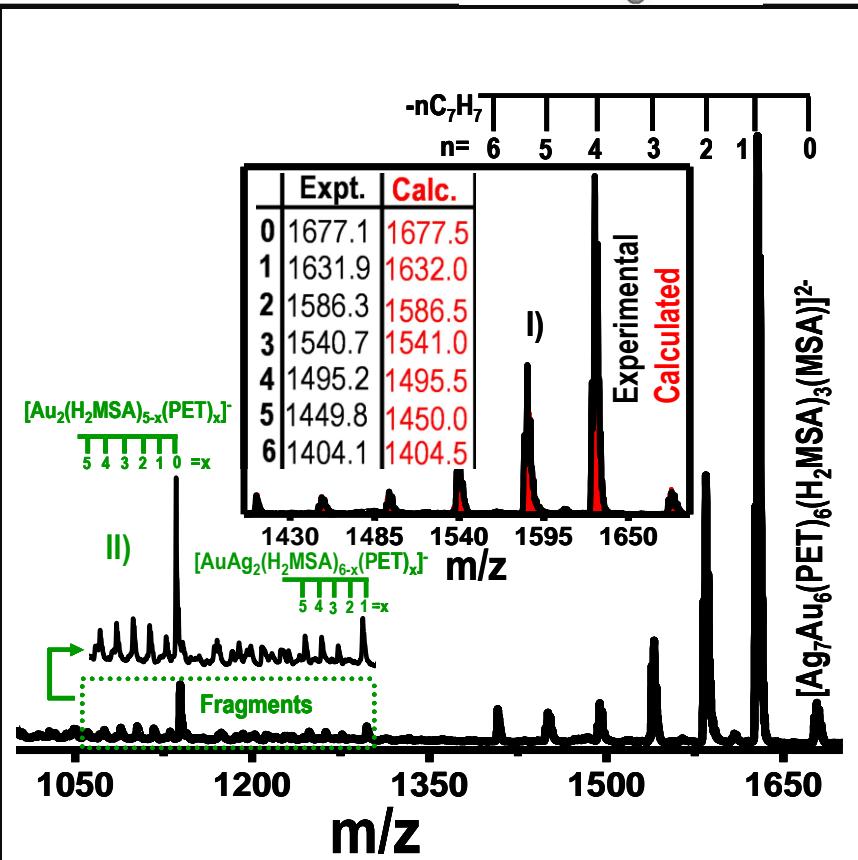
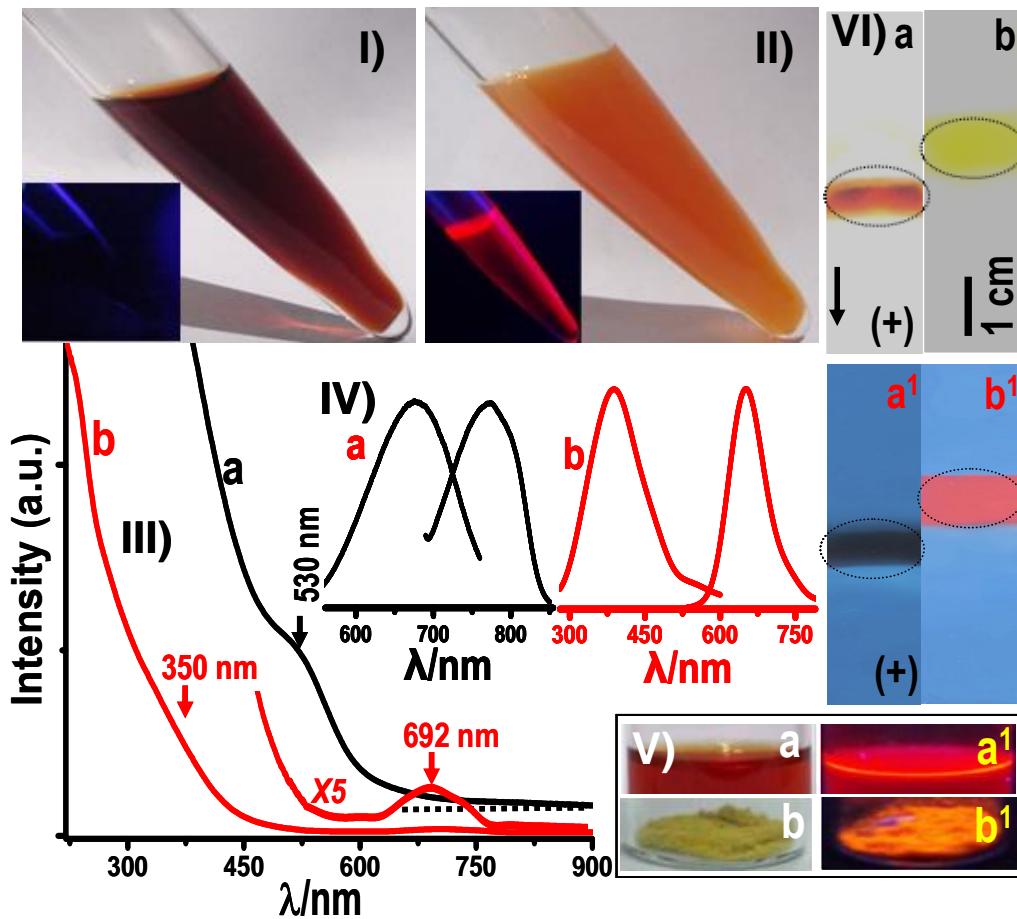




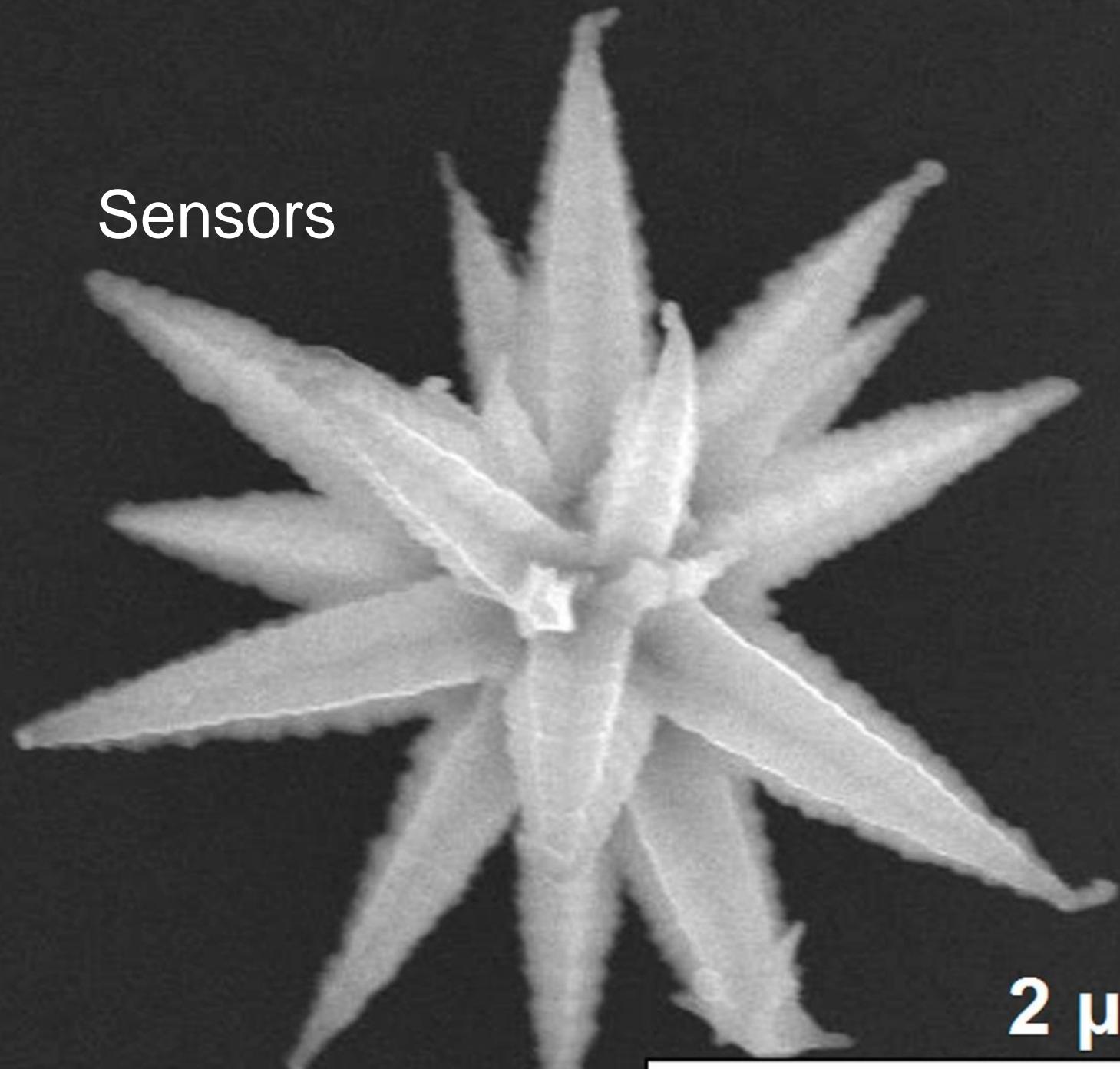
Cluster alloys



Ag_7Au_6 – 13 atom alloy cluster



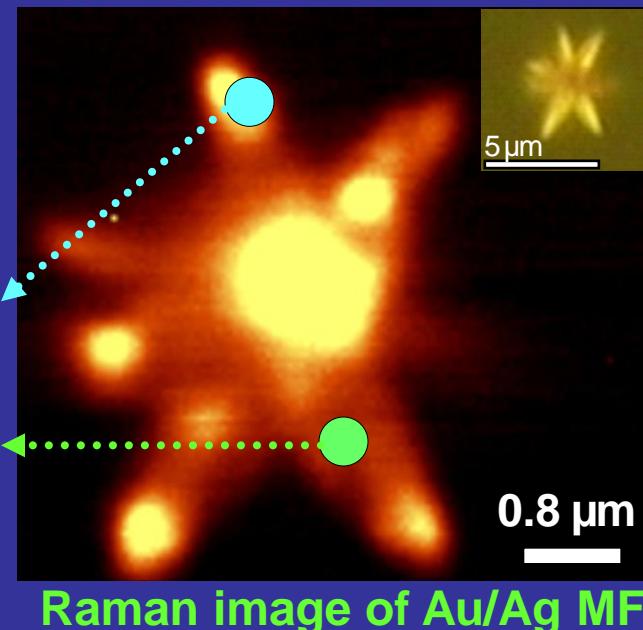
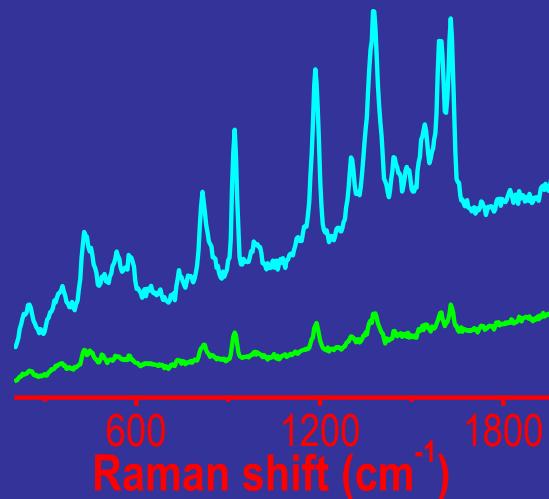
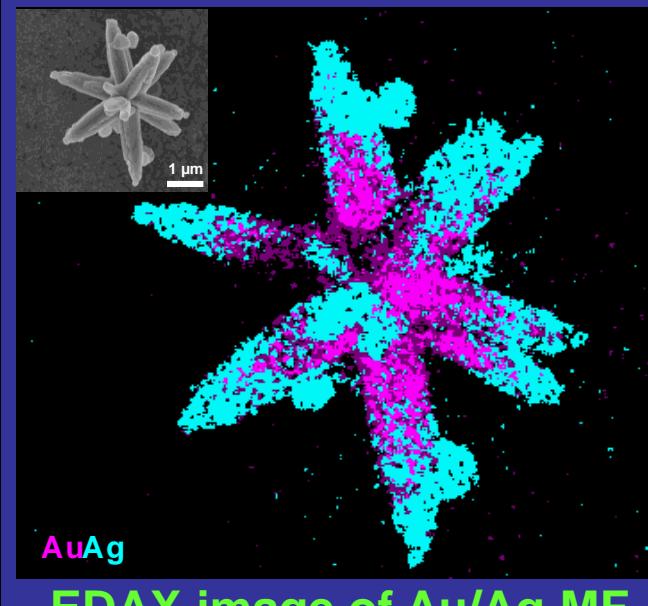
Sensors



2 μ m

Region-specific SERS activity

Decreasing order of SERS activity → Au/Ag MFs > Au MFs > Au/Pt MFs

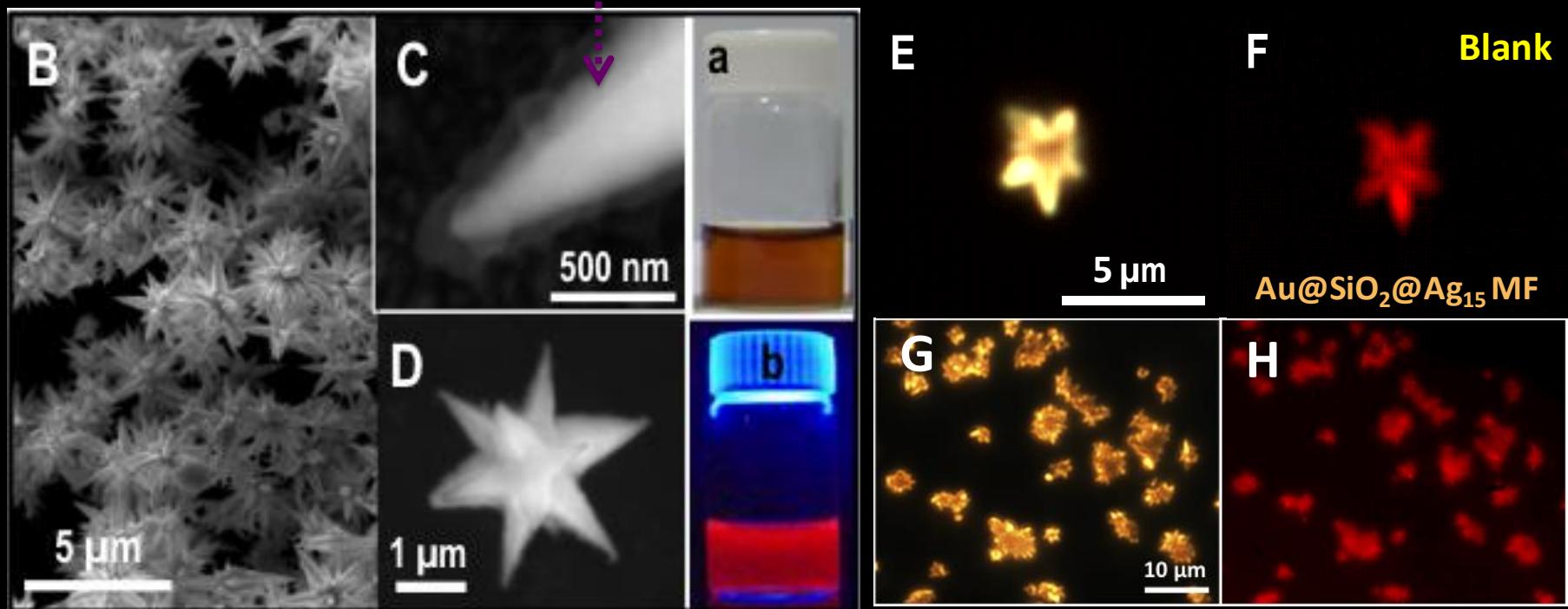
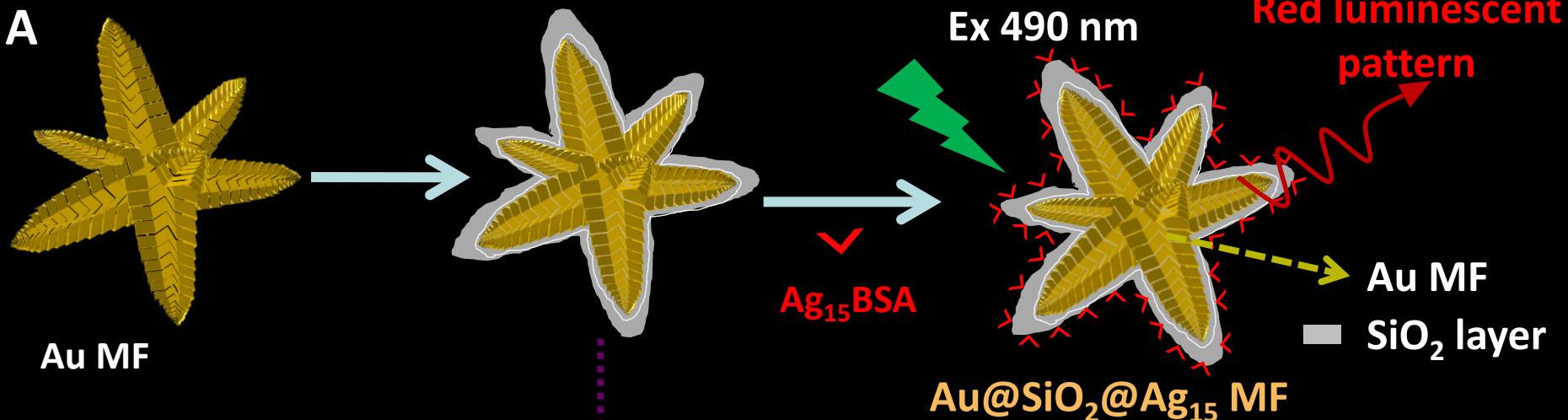


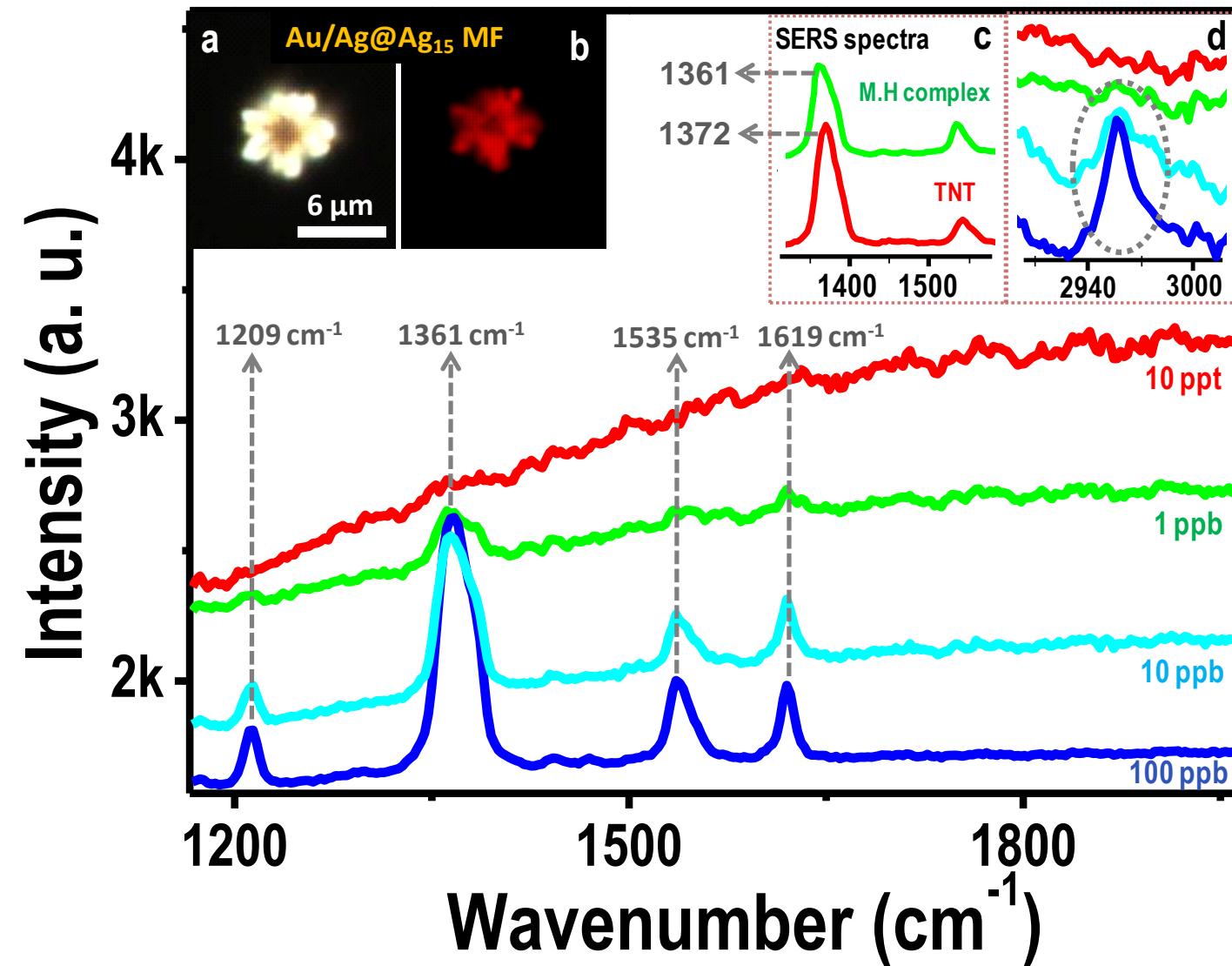
SERS intensity is higher at the tip compared to the body of the stem.

Au/Ag mesoflowers

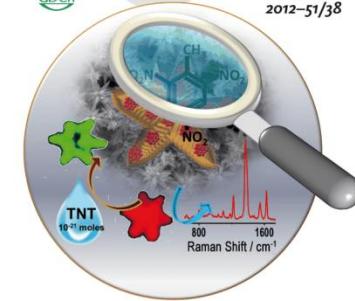
- show high SERS activity than Au mesoflowers.
- show ten-fold increase in the SERS enhancement factor than Au mesoflowers.
- capable of detecting biomolecules and explosives at very low concentrations.

Designing a sensor



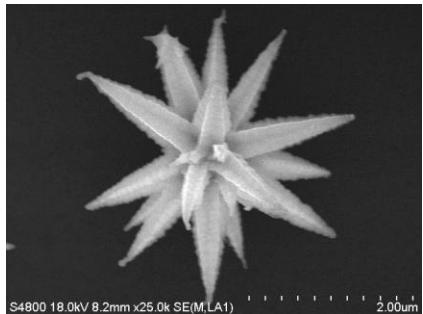
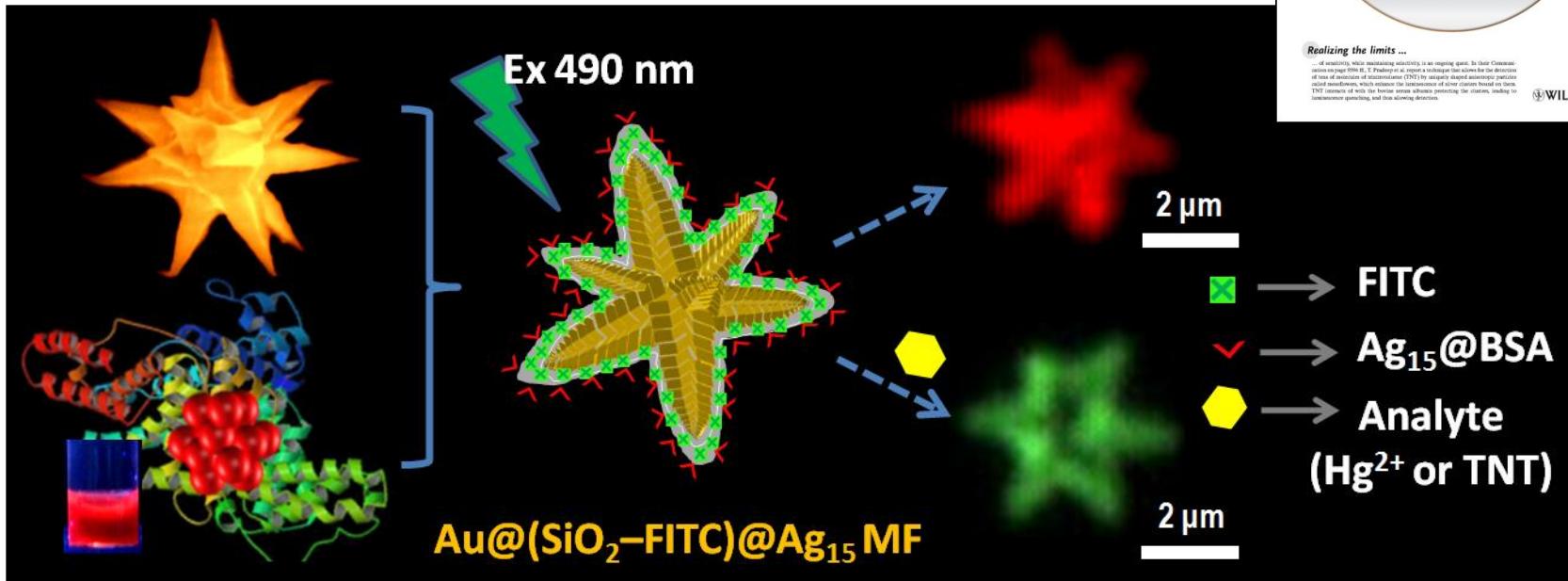


Raman spectra showing the gradual evolution of TNT features as the concentration of TNT added to Au/Ag@Ag₁₅ MFs (a and b) increases. (c) Comparison of the symmetric and asymmetric NO₂ stretching bands in the SERS spectra of TNT before (black) and after Meisenheimer complex formation (gray). (d) The gradual appearance of a Raman band at 2960 cm⁻¹.



Realizing the limits ...
of sensitivity while maintaining selectivity is an ongoing quest. In their Communication on page 8996 H.-T. Frieden et al. report a technique that allows for the detection of very small amounts of analytes by using star-shaped gold nanoclusters functionalized with conjugated monolayers, which enhance the luminescence of other clusters bound on them. TNT (orange) or with the boron neutron affinity pentagonal cluster, leading to luminescence quenching and thus allowing detection.

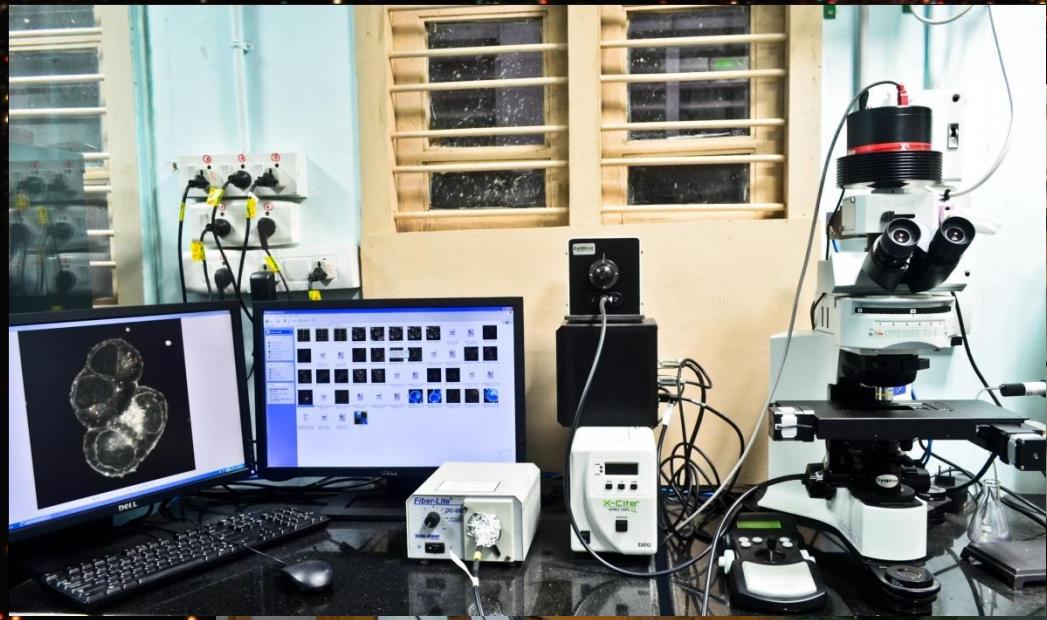
WILEY-VCH



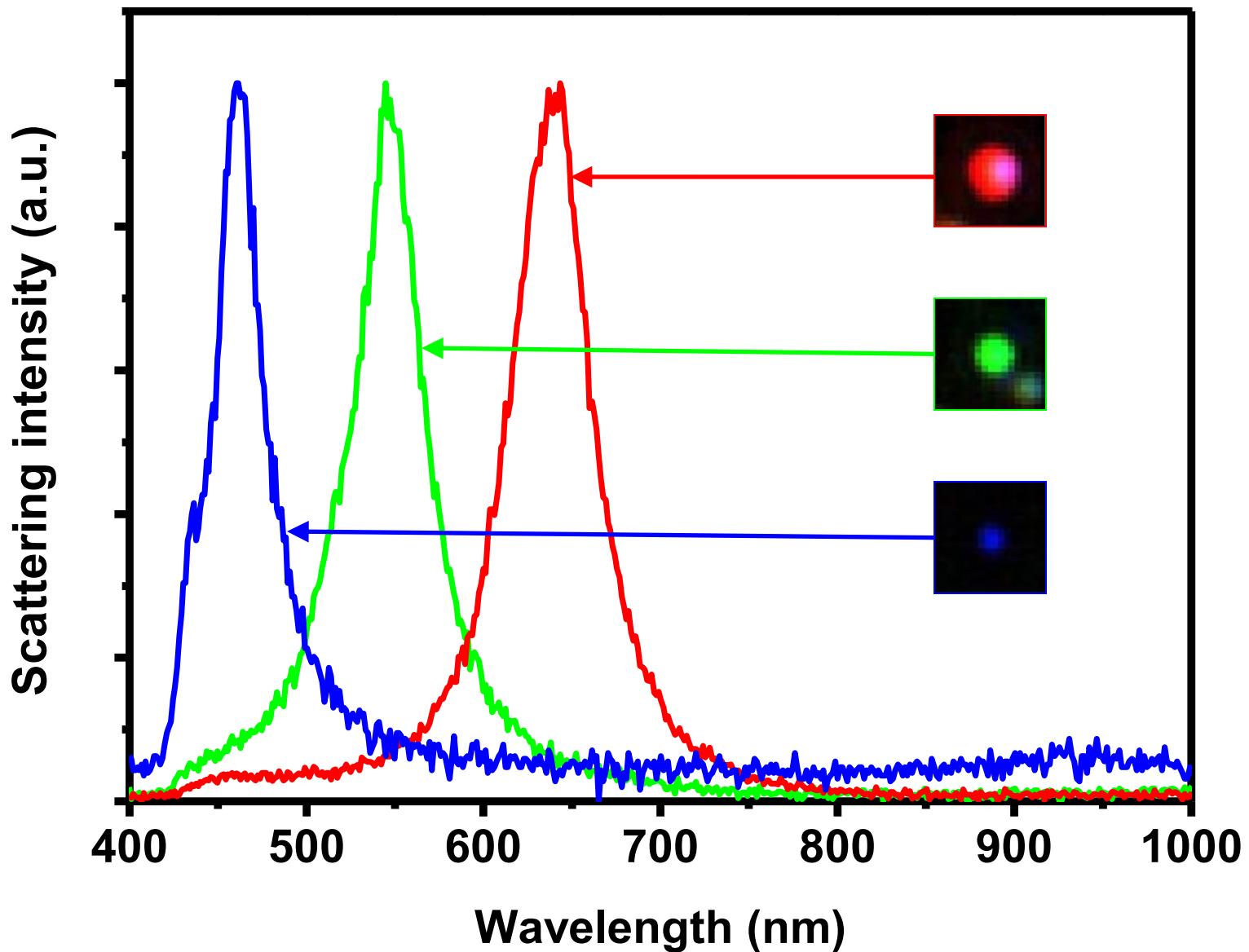
Featured in:
The Hindu, Telegraph, Times of India, etc.
C&E News
and many others

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

Observing nanochemistry in real time

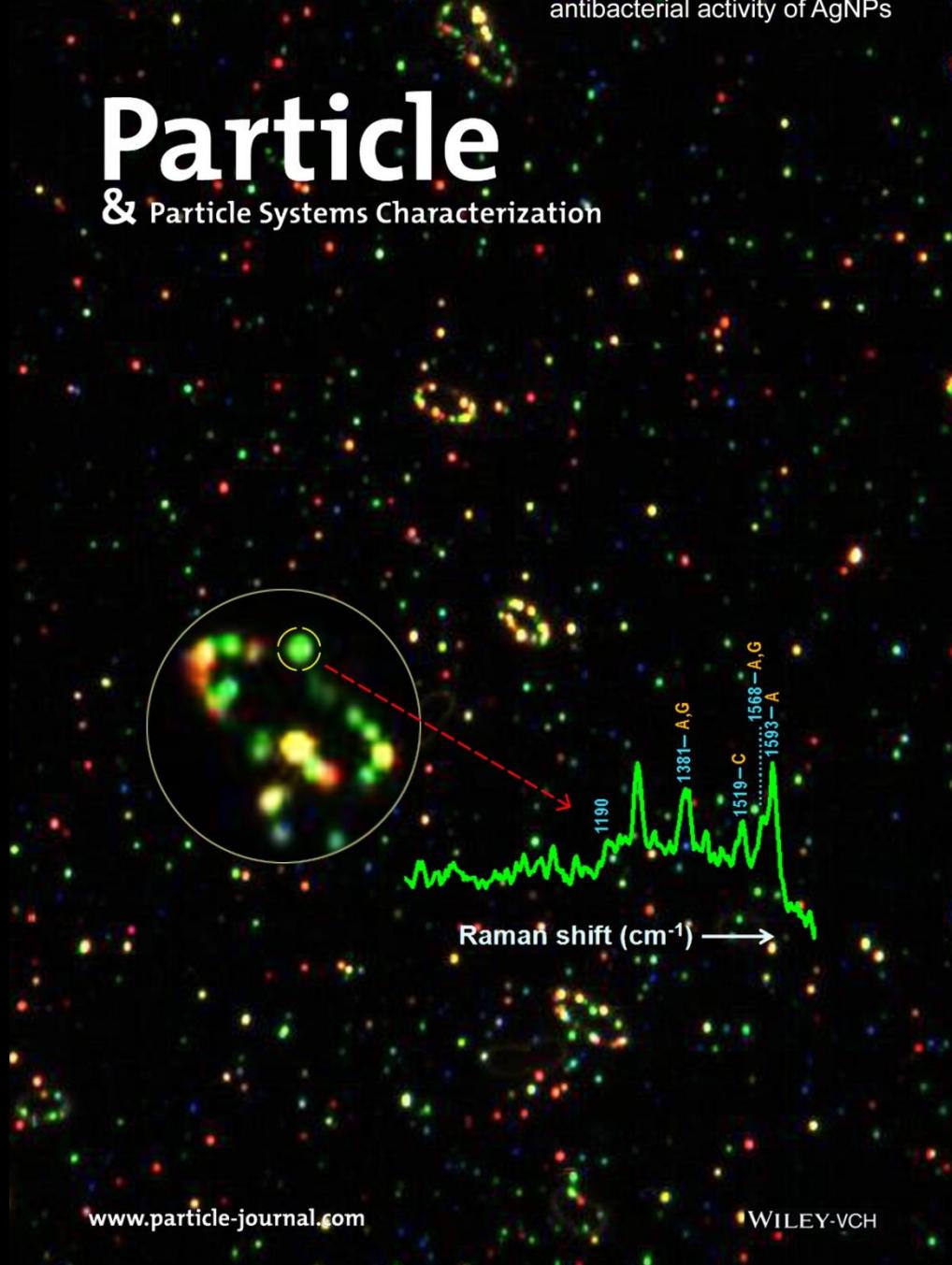


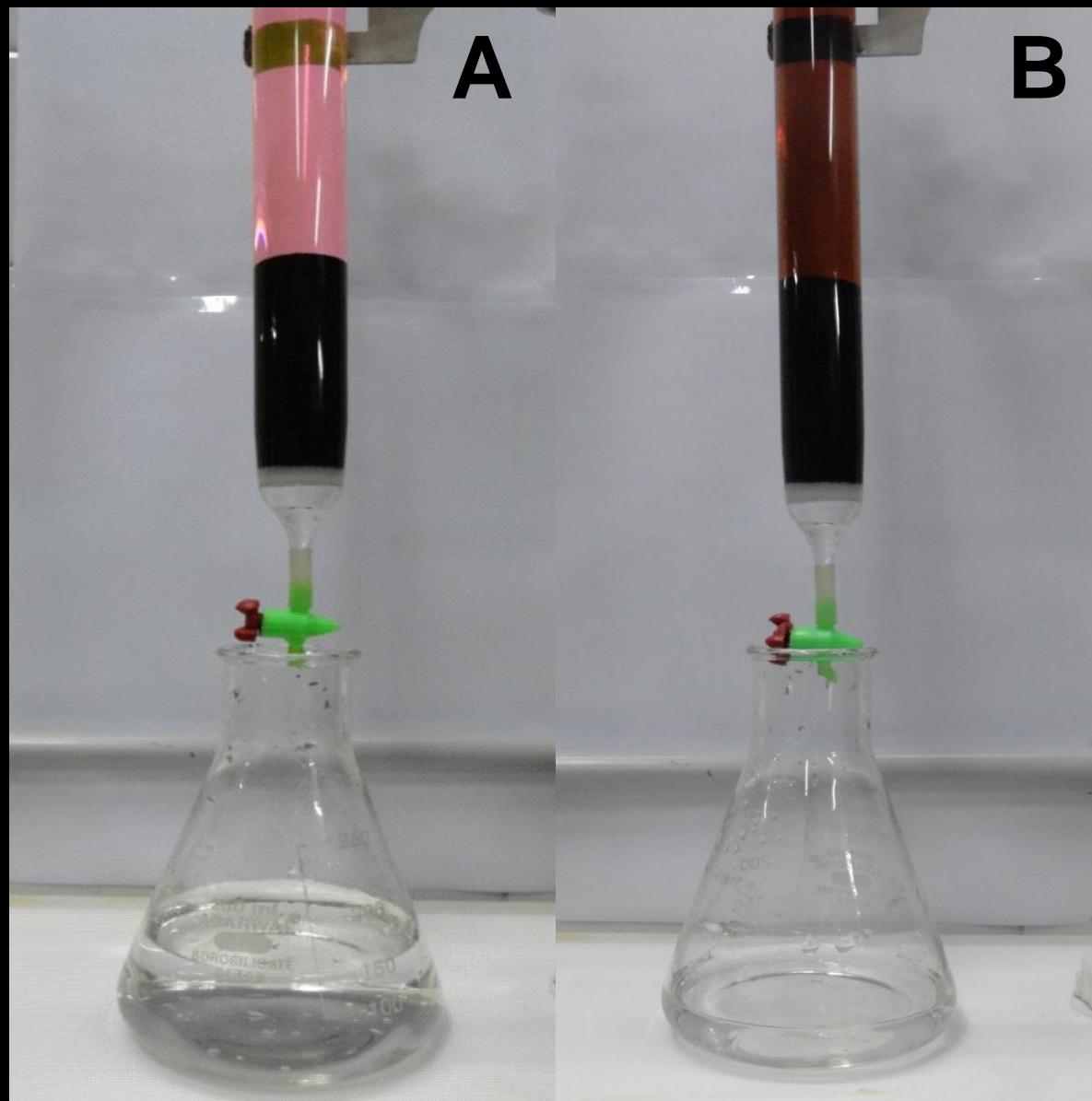
Mechanism of action

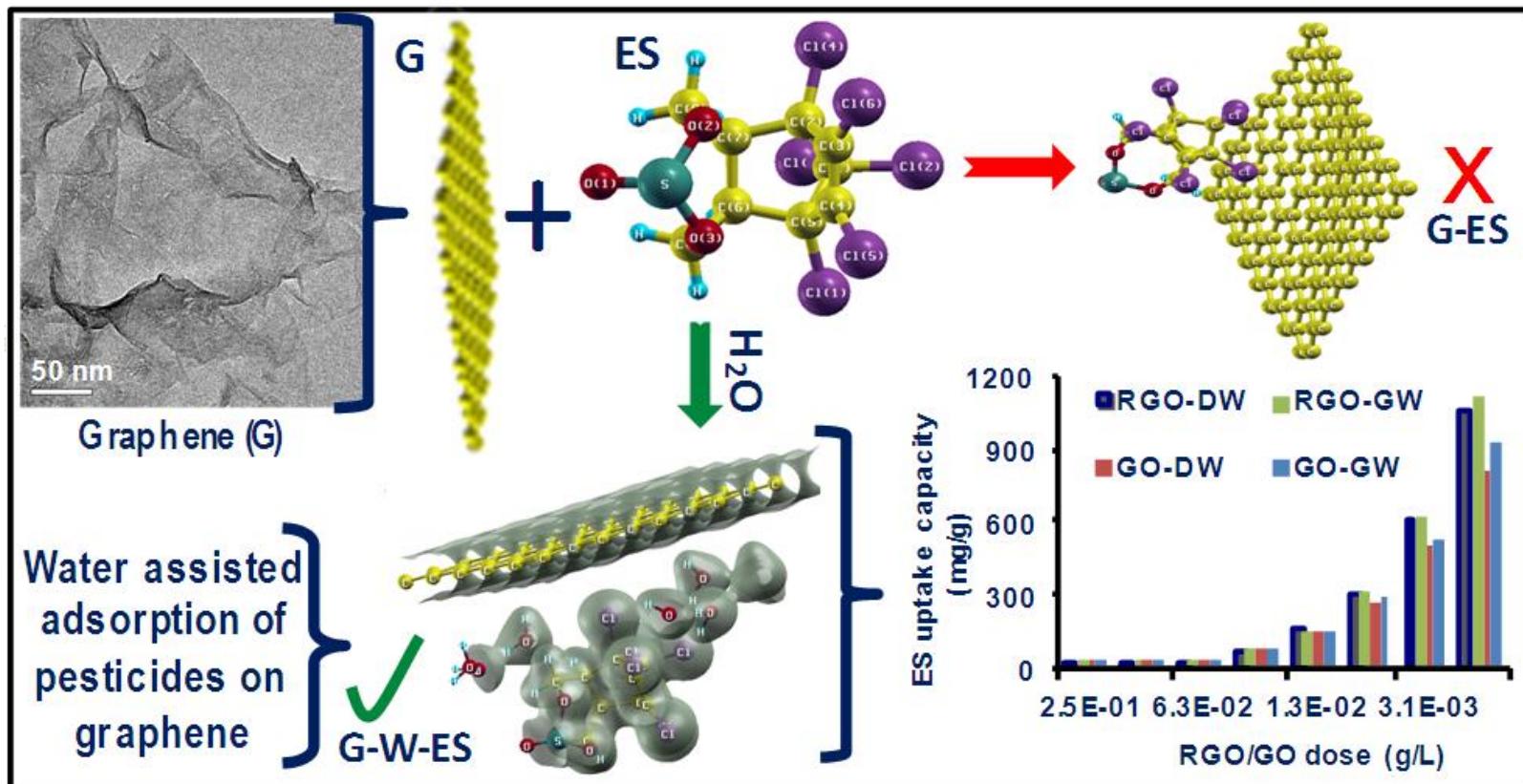


Particle

& Particle Systems Characterization







Graphene adsorbs pesticides more than its self weight!

Biopolymer-reinforced nanocomposite water purifier

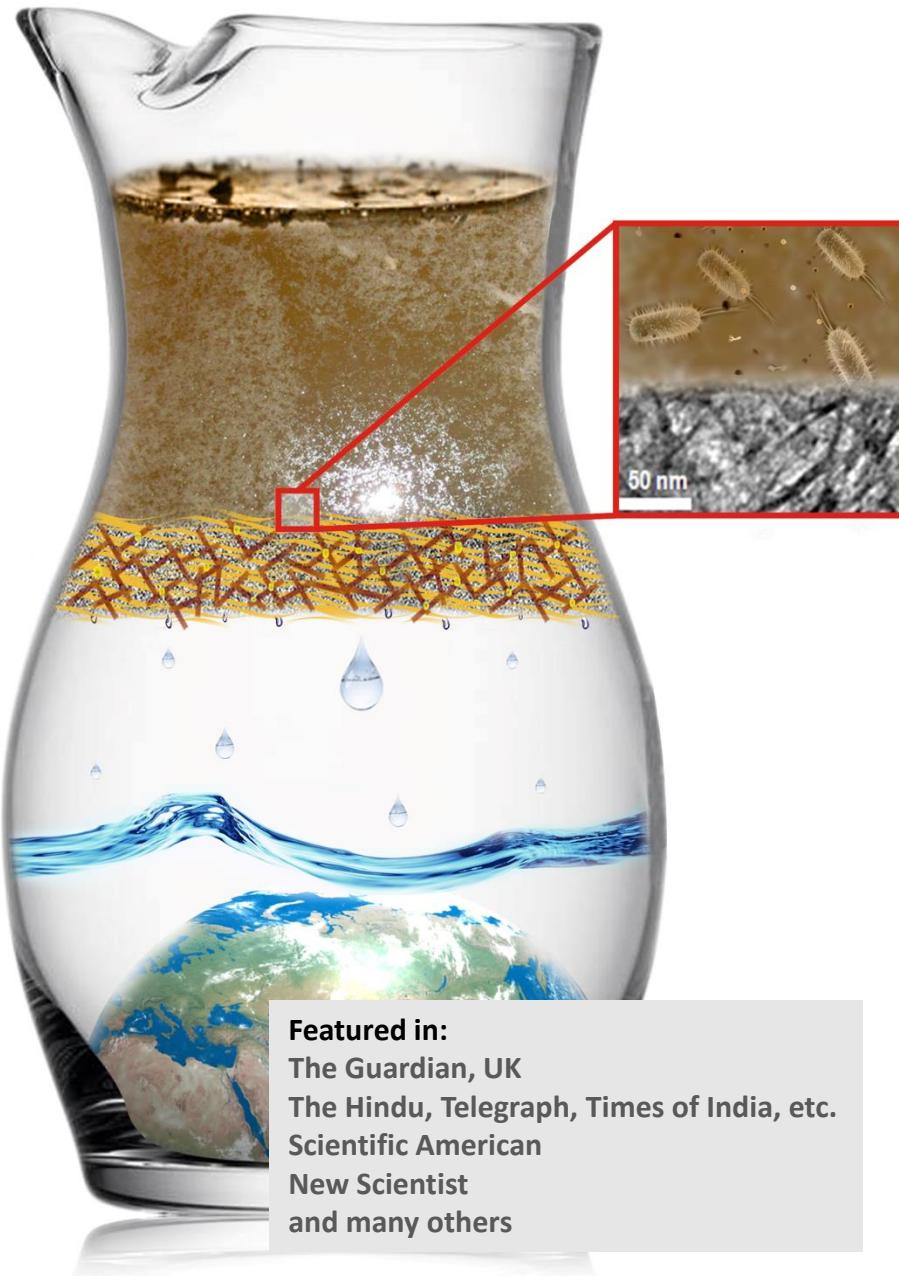
Mohan Udhaya Sankar¹, Sahil Kamalesh Chaudhari, and Thushar

Unit of Nanoscience and Thematic Ur

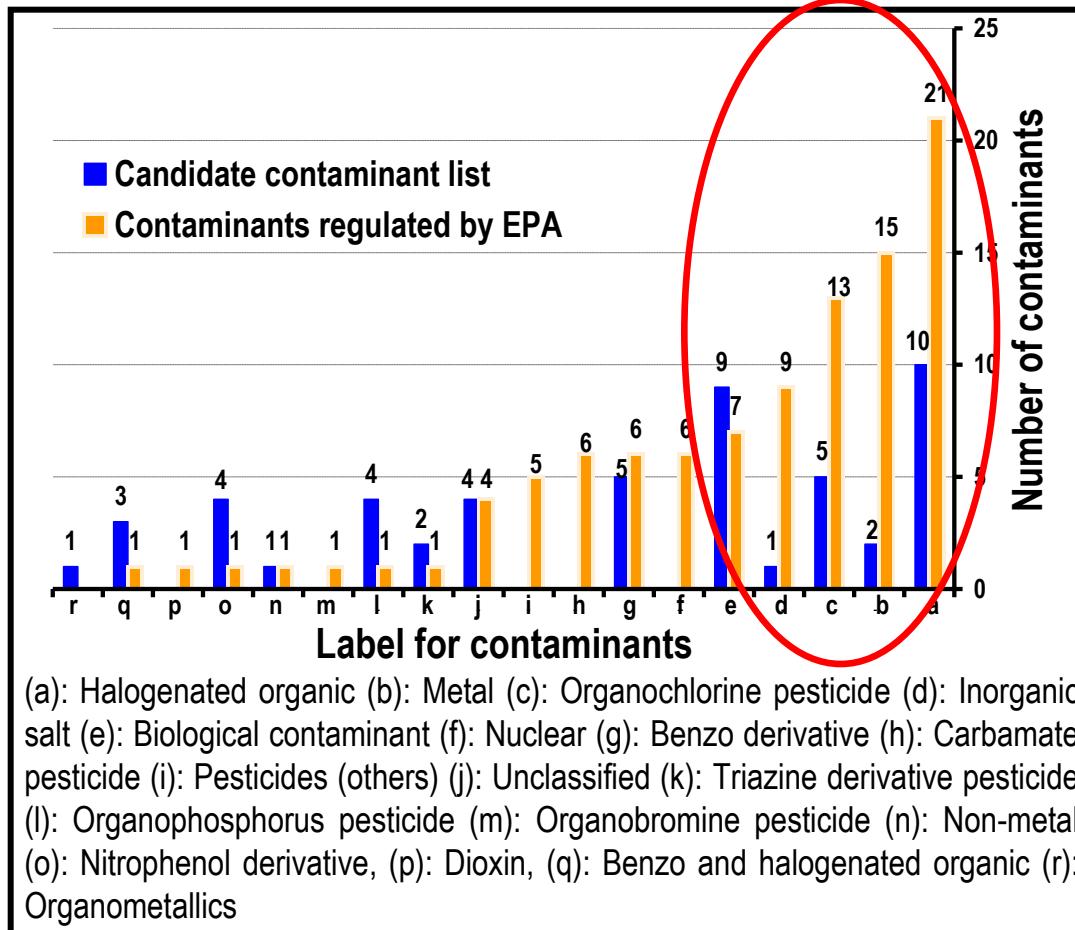
Edited by Eric Hoek, University of Cal

Creation of affordable materials for water is one of the most promising ways to provide drinking water for all. Combining nanocomposites to scavenge toxic species and other contaminants along with creating an affordable, all-inclusive drinking water purifier without electricity. The critical synthesis of stable materials that can be used in the presence of common drinking water that deposit and remove surfaces. Here we show that such materials can be synthesized in a simple and effective way without the use of electrical power. These materials have sand-like properties, such as high porosity and low density. These materials have been used as a water purifier to deliver clean drinking water. The ability to prepare nanocomposites at ambient temperature has wide applications in water purification.

hybrid | green | appropriate technology



Future of water purification: An enigma with some pointers



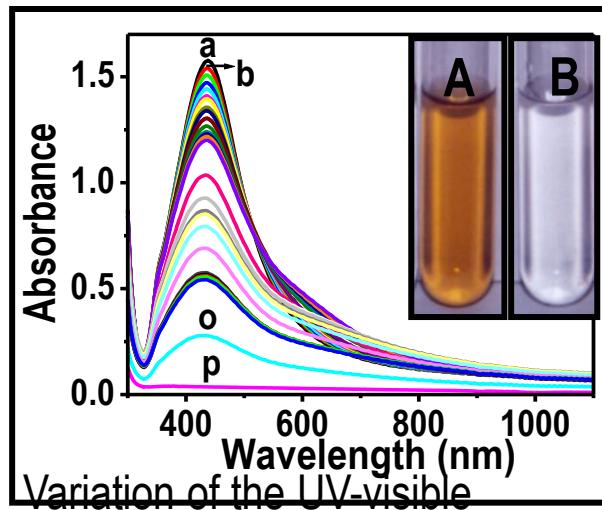
Category-wise distribution of contaminants regulated by USEPA and future contaminants

Noble metal nanoparticles for water purification: A critical review, T. Pradeep and Anshup, Invited critical review, Thin Solid Films, 517 (2009) 6441-6478 (DOI: 10.1016/j.tsf.2009.03.195).

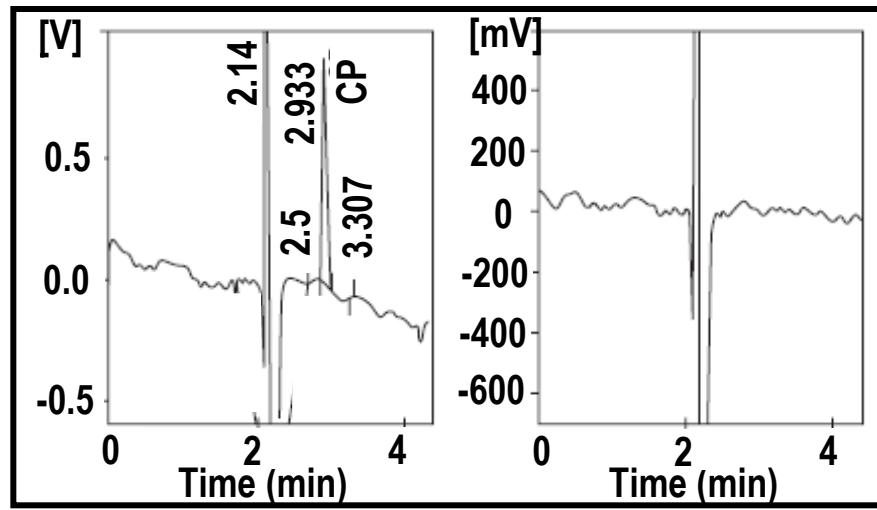
Noble metal nanoparticles: removal of pesticides from water

A.S. Nair, T. Pradeep, Curr. Sci. 84 (2003) 1560

A.S. Nair, R.T. Tom, V.R. Rajeev Kumar,
C. Subramanian, T. Pradeep, Cosmos
3, (2007) 103



Variation of the UV-visible absorption spectrum of silver nanoparticles upon the addition of CCl_4



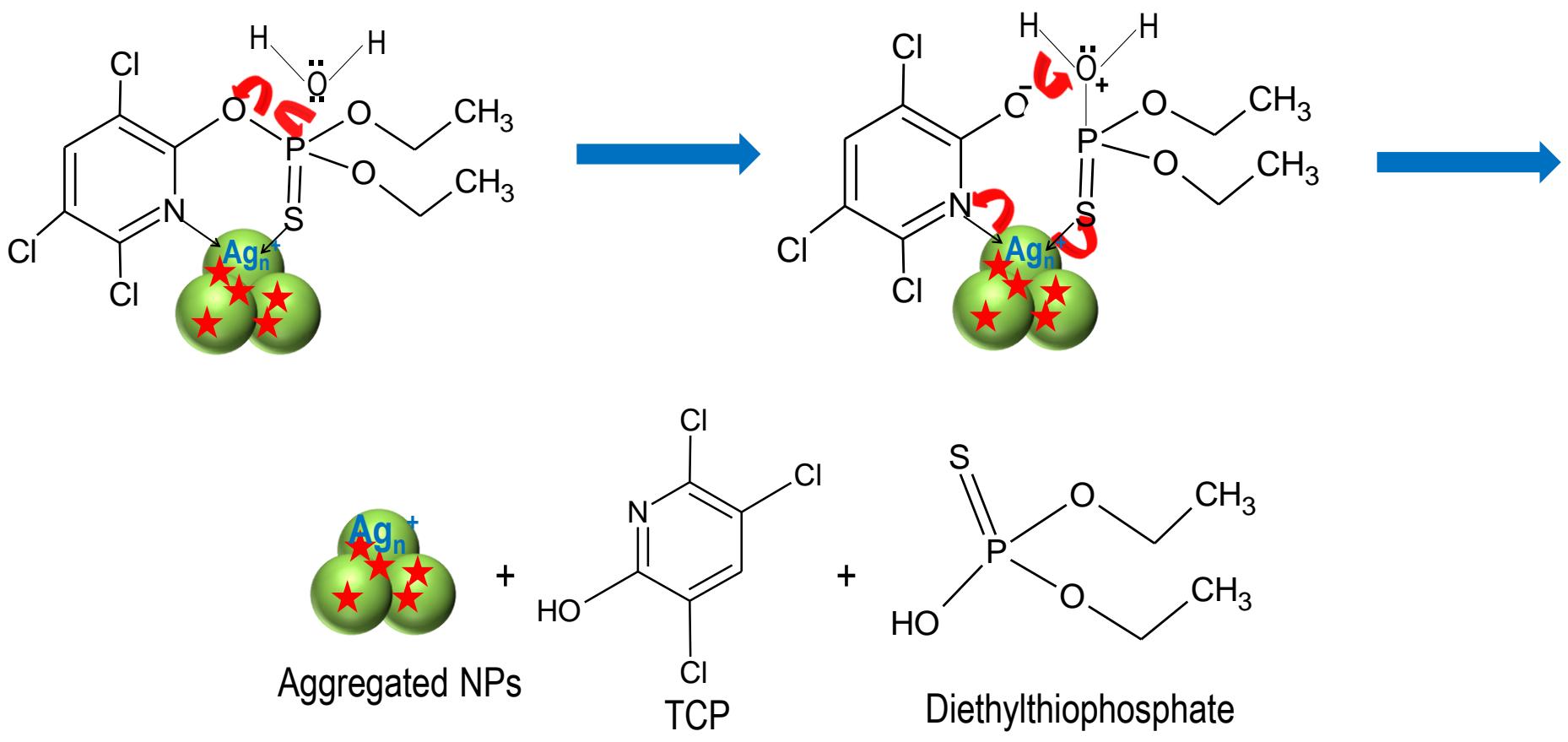
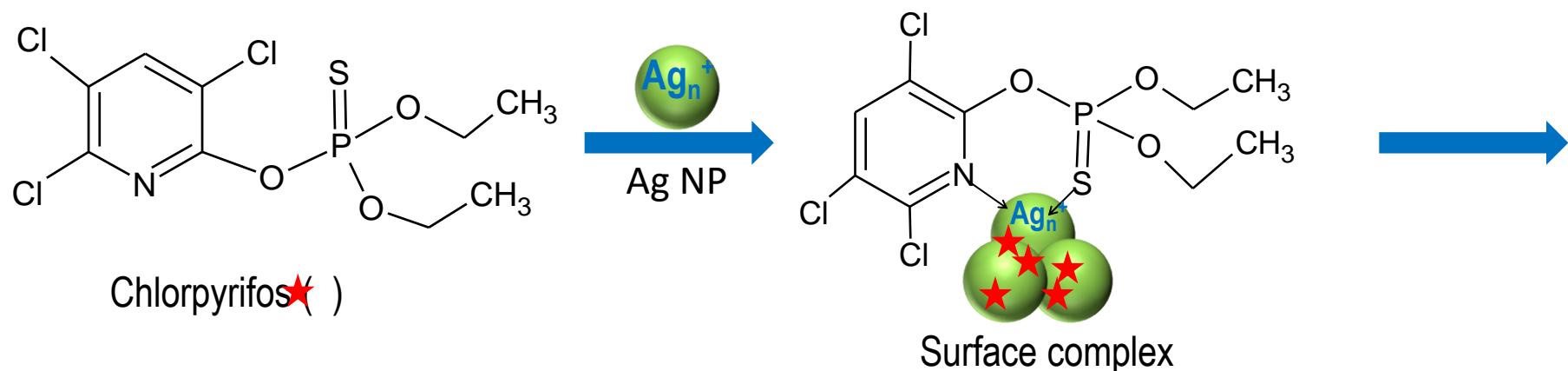
Gas chromatogram of chlorpyrifos solution (L) and after treatment with silver nanoparticles (R)



Indian patent 2006
PCT 2011 – US, Europe, Asia

June 2007

(L) Silver nanoparticles coated on activated alumina (R) Photograph of a pesticide filter device using supported nanoparticles (WQA certified)



Bootharaju and Pradeep, *Langmuir* 2012

World's first nanochemistry-based water purifier

RSC Advancing the
Chemical Sciences
Chemistry World

Pesticide filter debuts in India

20 April 2007

Killugudi Jayaraman Bangalore, India

A domestic water filter that uses metal nanoparticles to remove dissolved pesticide residues is about to enter the Indian market. Its developers at the Indian Institute of Technology (IIT) in Chennai (formerly Madras) believe it is the first product of its kind in the world to be commercialised.

Mumbai-based Eureka Forbes Limited, a company that sells water purification systems, is collaborating with IIT and has tested the device in the field for over six months. Jayachandra Reddy, a technical consultant to the company, expects the first 1000 units to be sold door-to-door from late May.

'Our pesticide filter is an offshoot of basic research on the chemistry of nanoparticles,' Thalapillil Pradeep who led the team at IIT Chennai told *Chemistry World*. He and his student Sreekumaran Nair discovered in 2003 that halocarbons such as carbon tetrachloride (CCl₄) completely break down into metal halides and amorphous carbon upon reaction with gold and silver nanoparticles¹.

Pradeep said this prompted them to extend their study to include organochlorine and organophosphorus pesticides, whose presence in water is posing a health risk in rural India. In research funded by the Department of Science and Technology in New Delhi, his team found^{2,3} that gold and silver nanoparticles loaded on alumina were indeed able to completely remove endosulfan, malathion and chlorypyrphos - three pesticides that have been found at elevated levels in Indian water supplies.

Use and recycle

The mechanism of removal is not clear, but Pradeep explained, 'environmental filters are a new concept.'

Chemistry world First ever nanotechnology product for clean water



A plant to make supported nanomaterials for water purification; with capacity of 4.5 tons per month, 2007



1. Patents: A method of preparing purified water from water containing pesticides, **Indian patent 200767**
2. Extraction of malathion and chlorpyrphos from drinking water by nanoparticles , **US 7,968,493** A method for decontaminating water containing pesticides, **EP 17,15,947**
Product is marketed now by a Eureka Forbes Ltd.
Several new technologies are now available

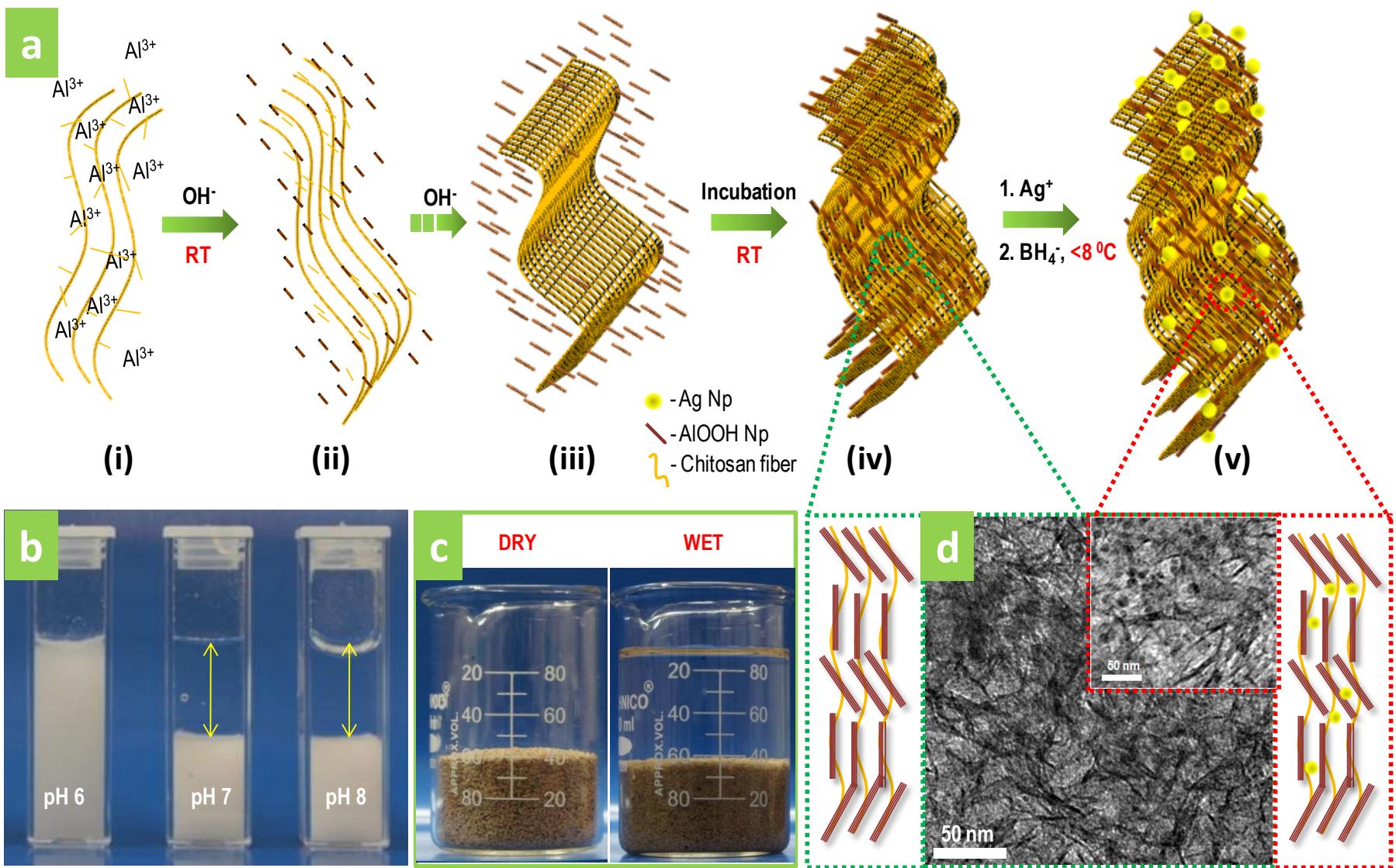
Affordable materials for water purification - Bioinspired

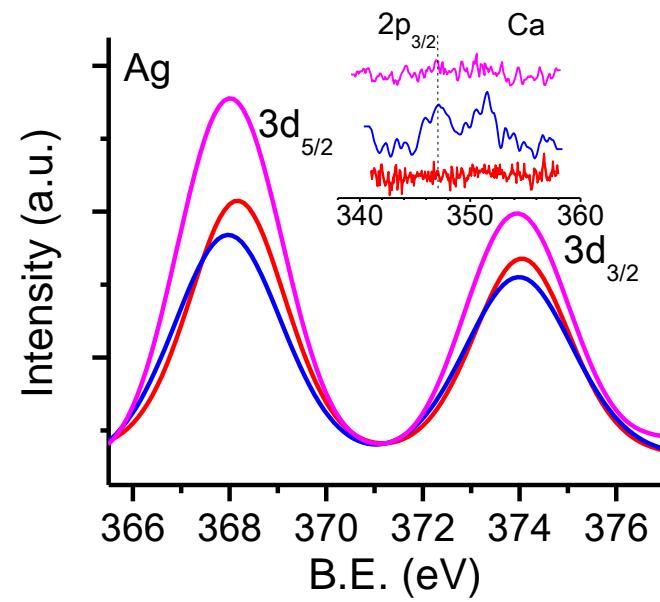
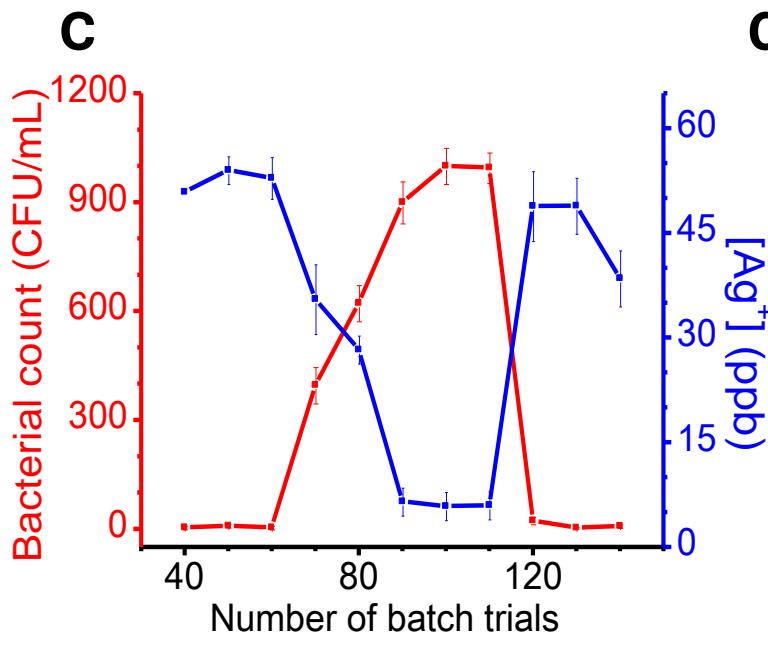
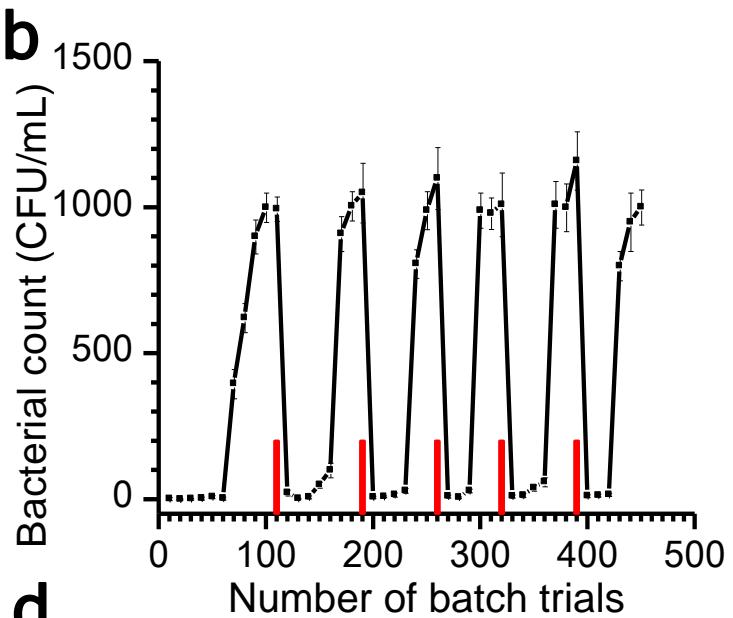
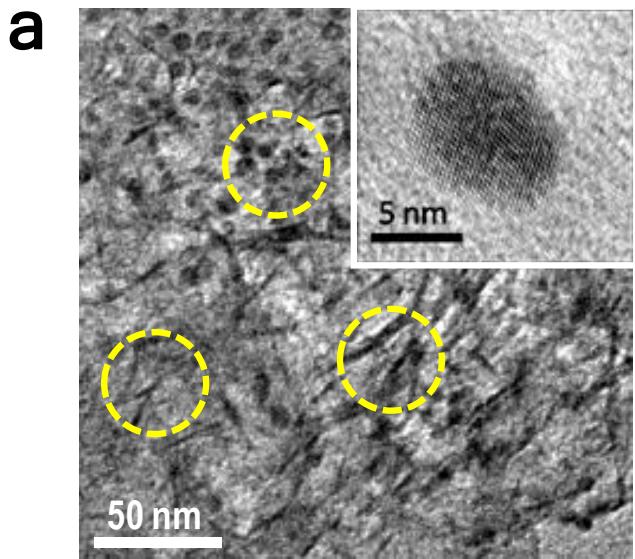
Water positive

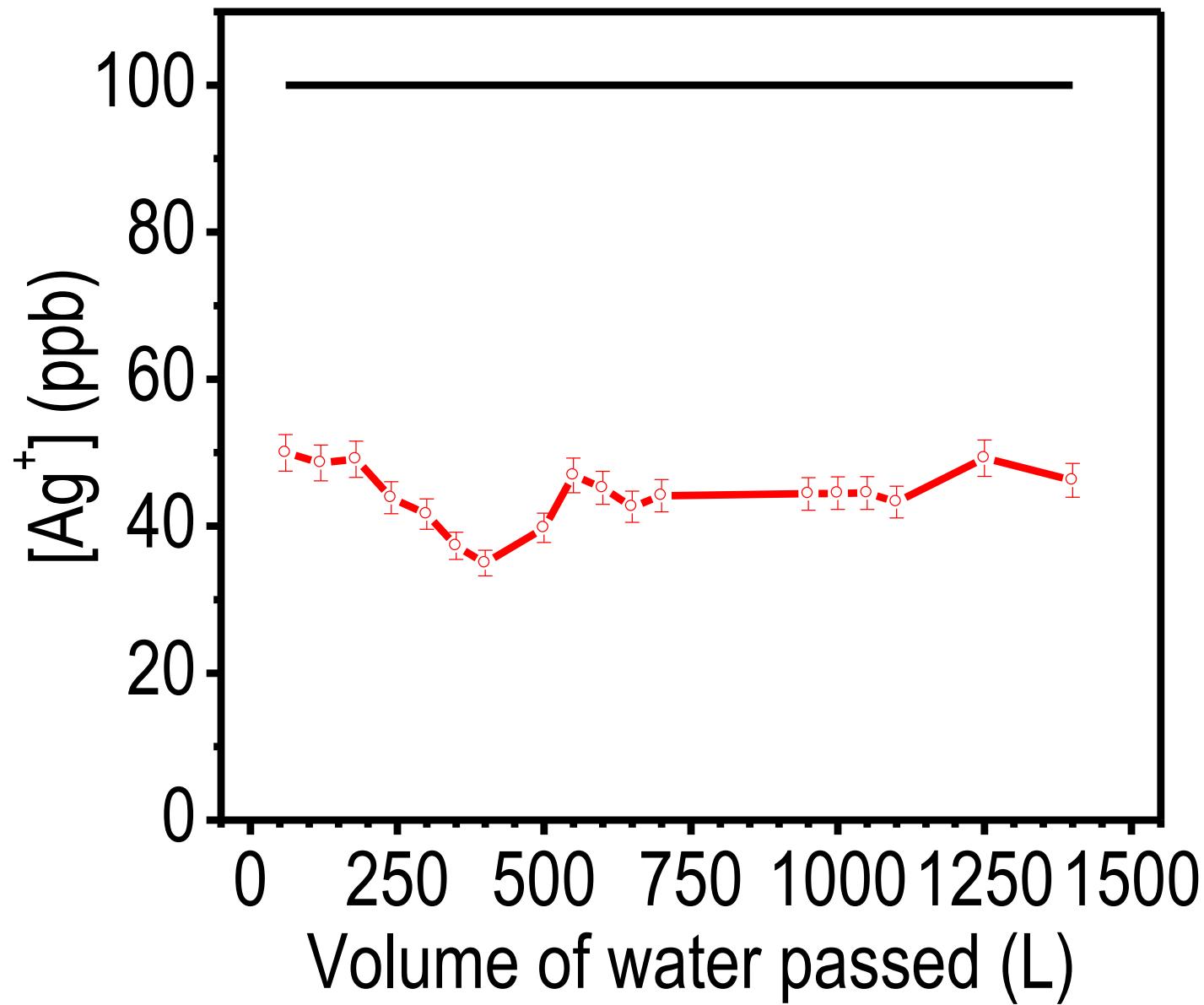
Water-based, room temperature, water stable

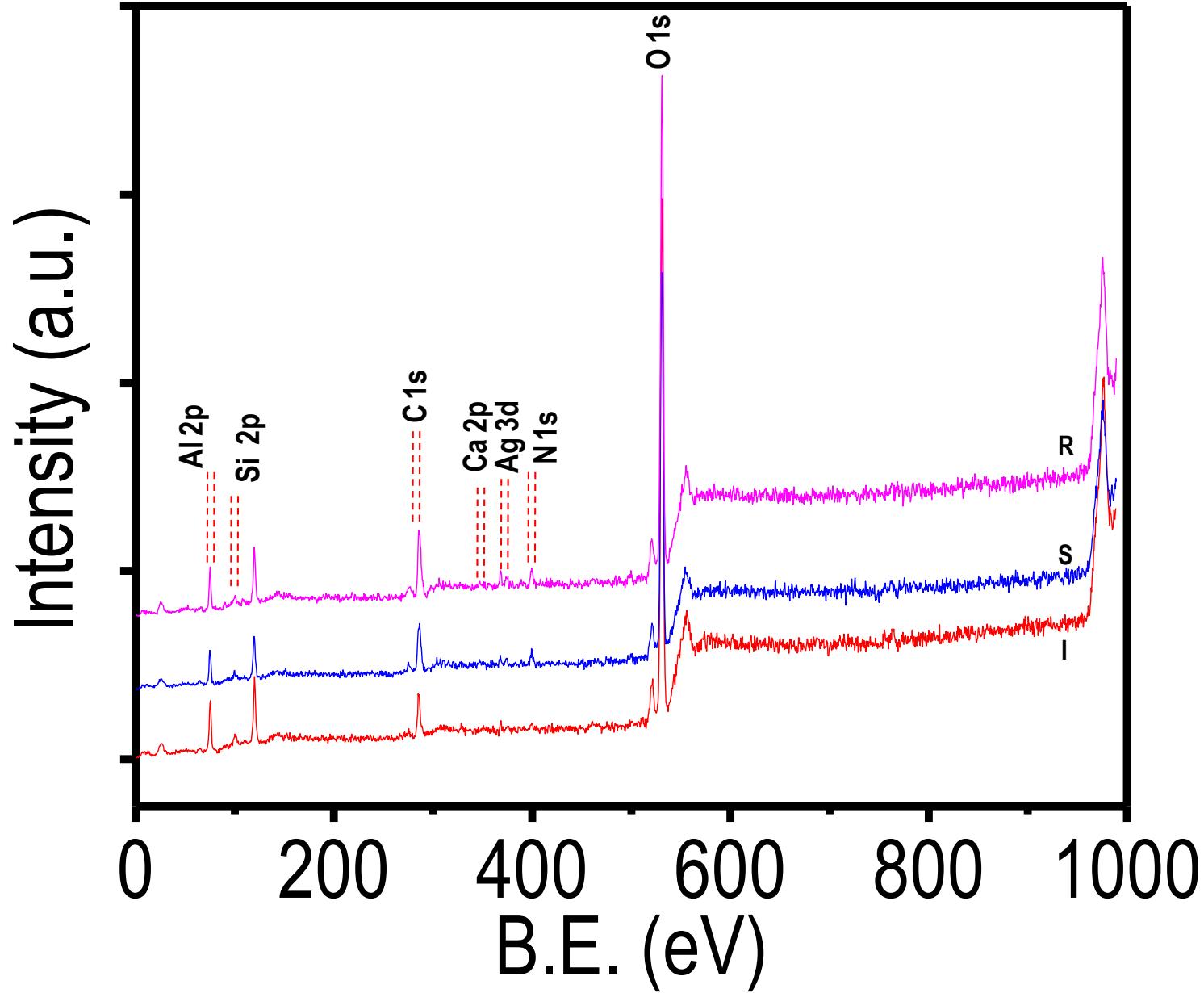
Green

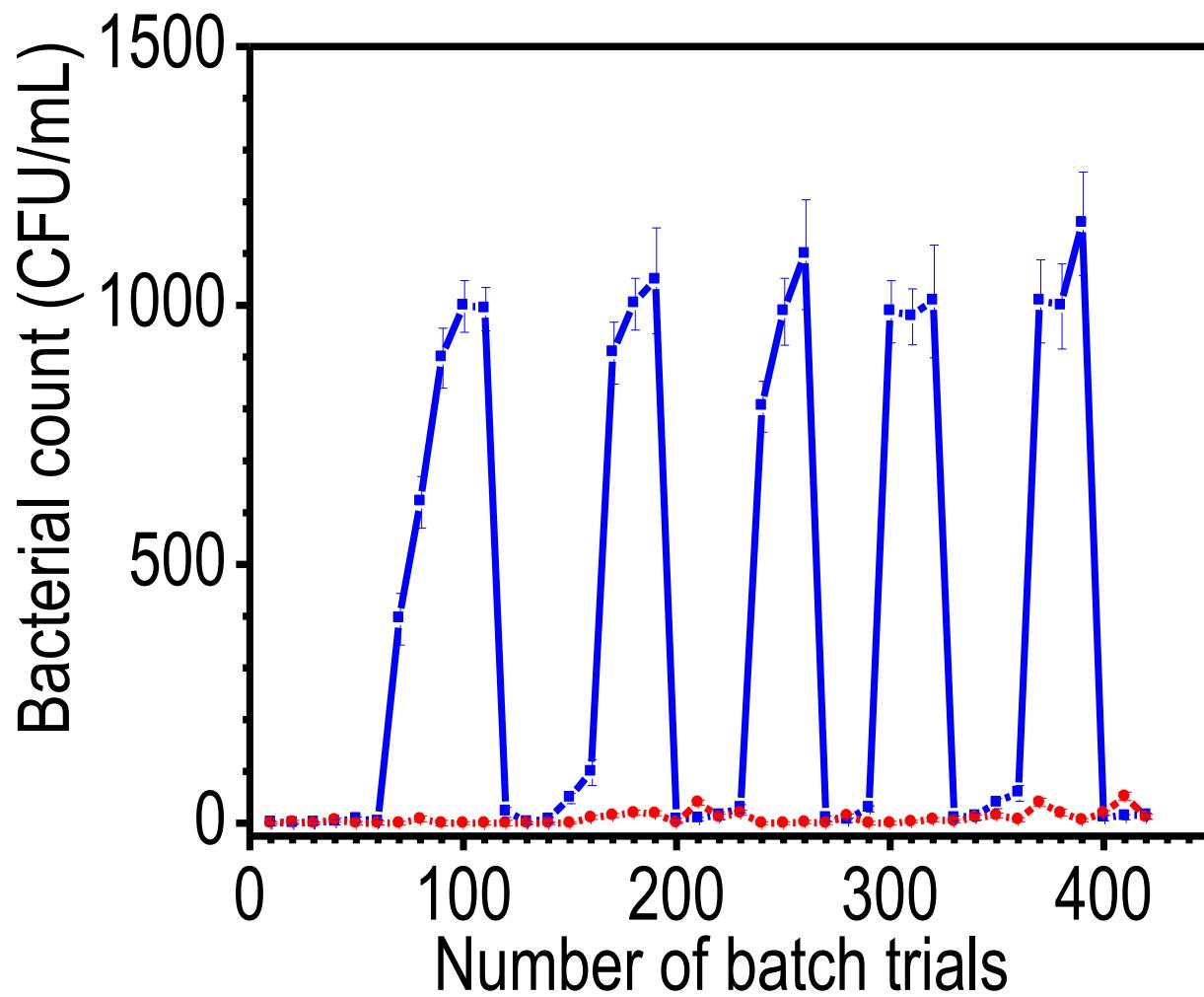
M. U. Sankar et al, PNAS 2013

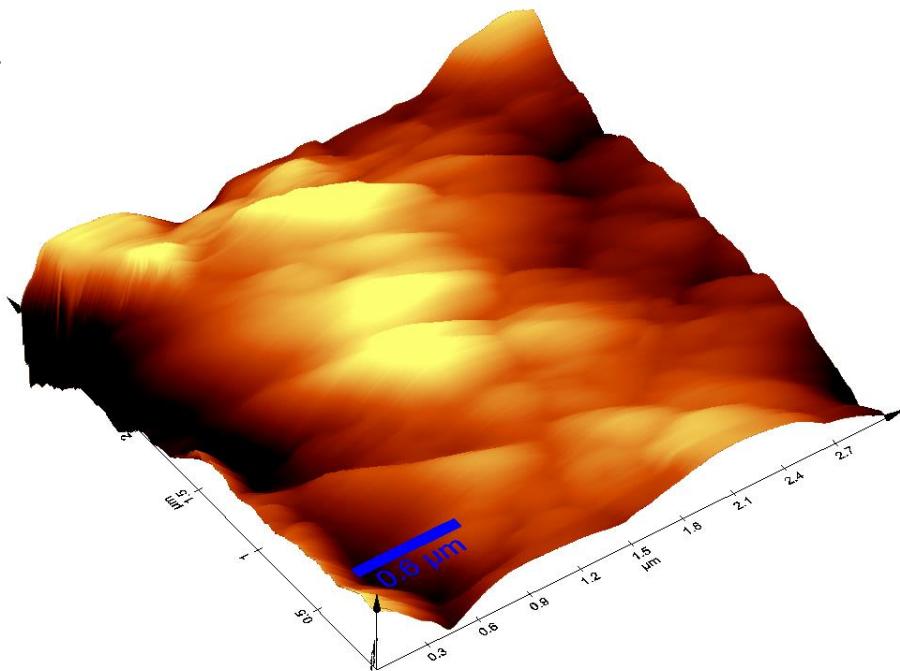








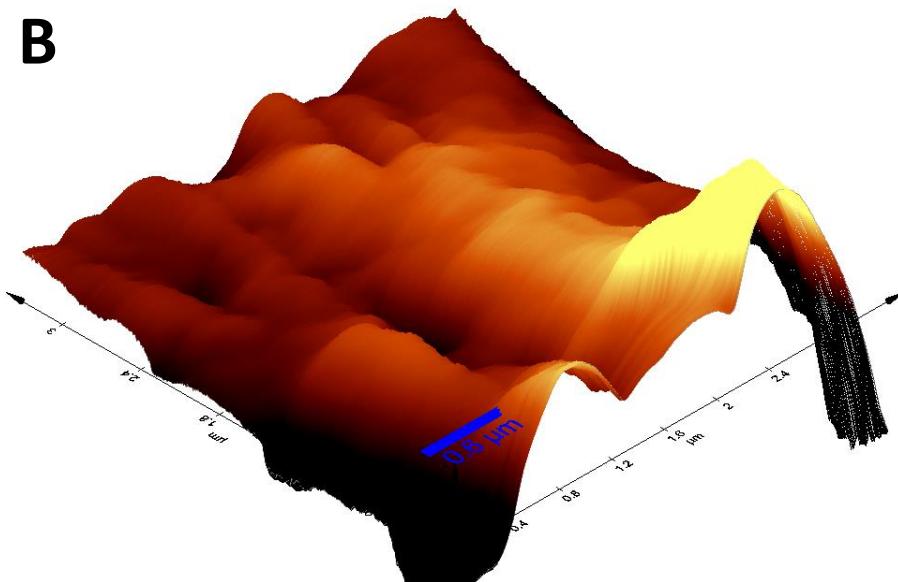


A

451.5 nm



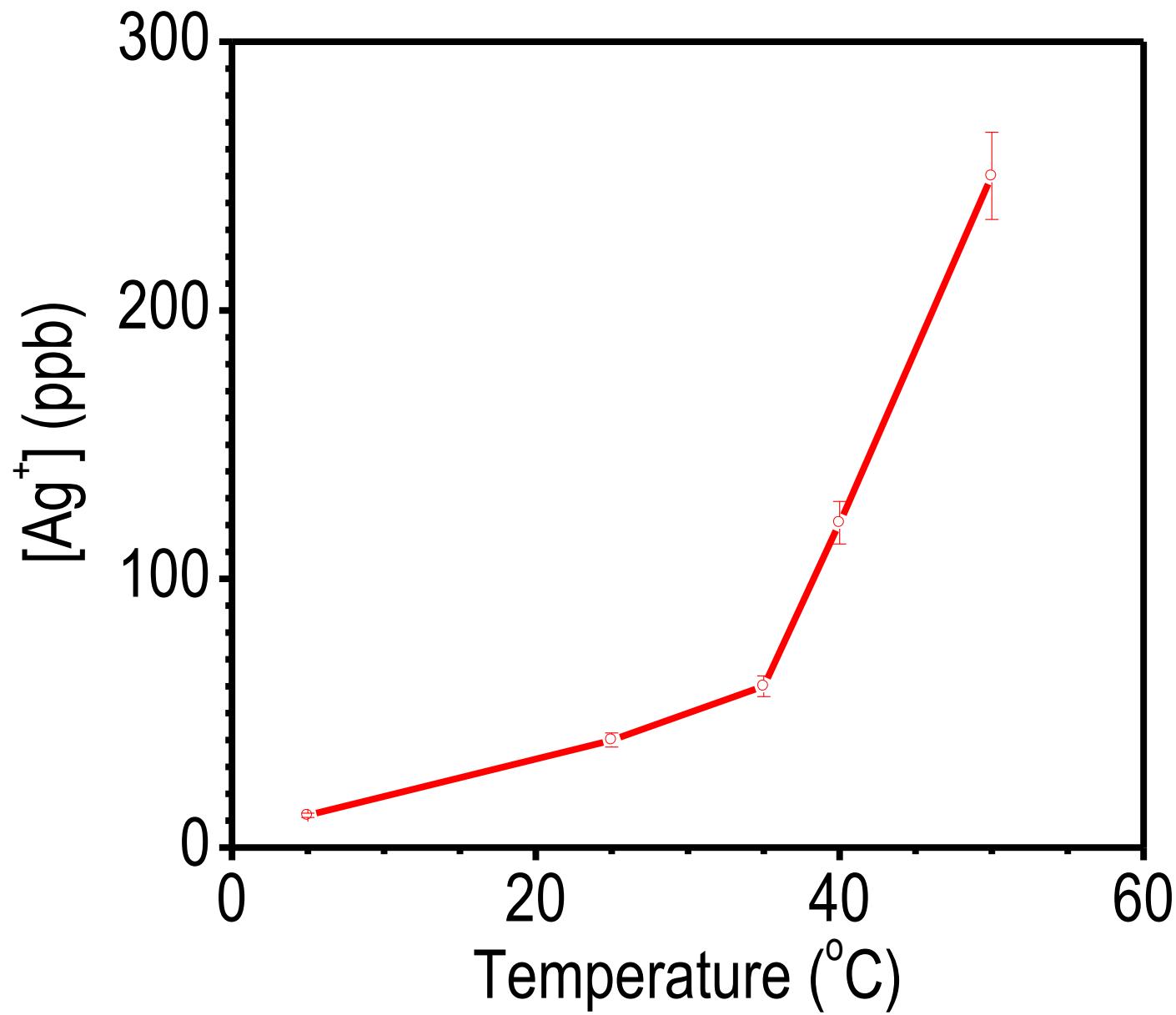
0 nm

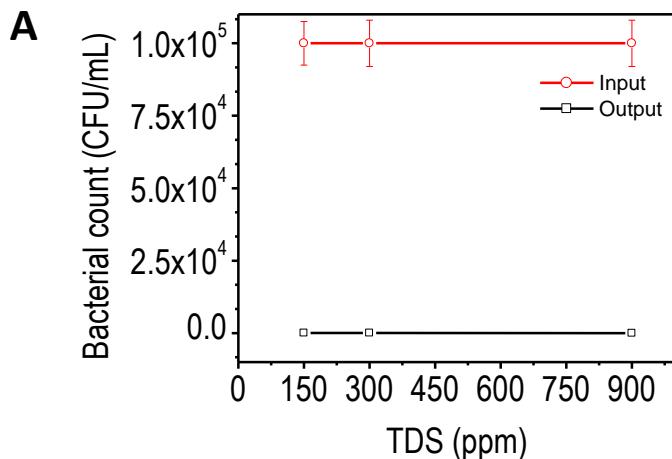
B

149.3 nm

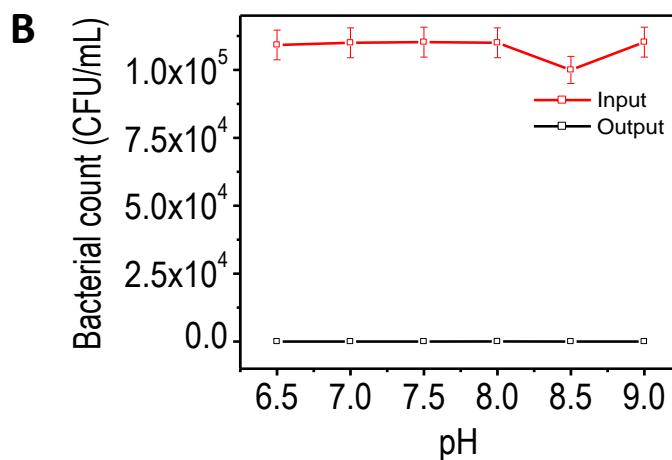


0 nm



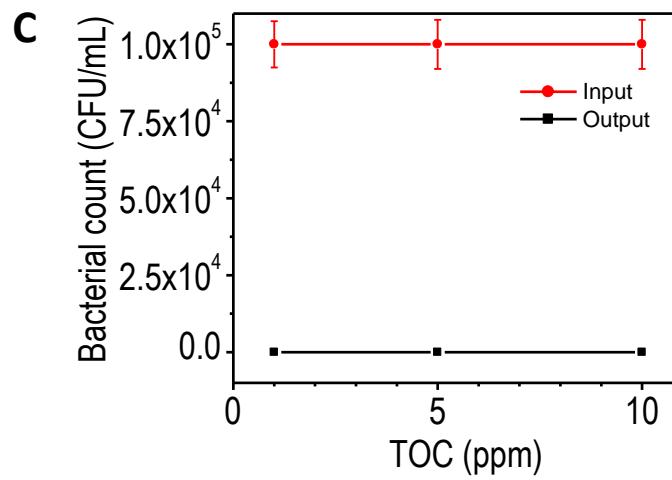


TDS



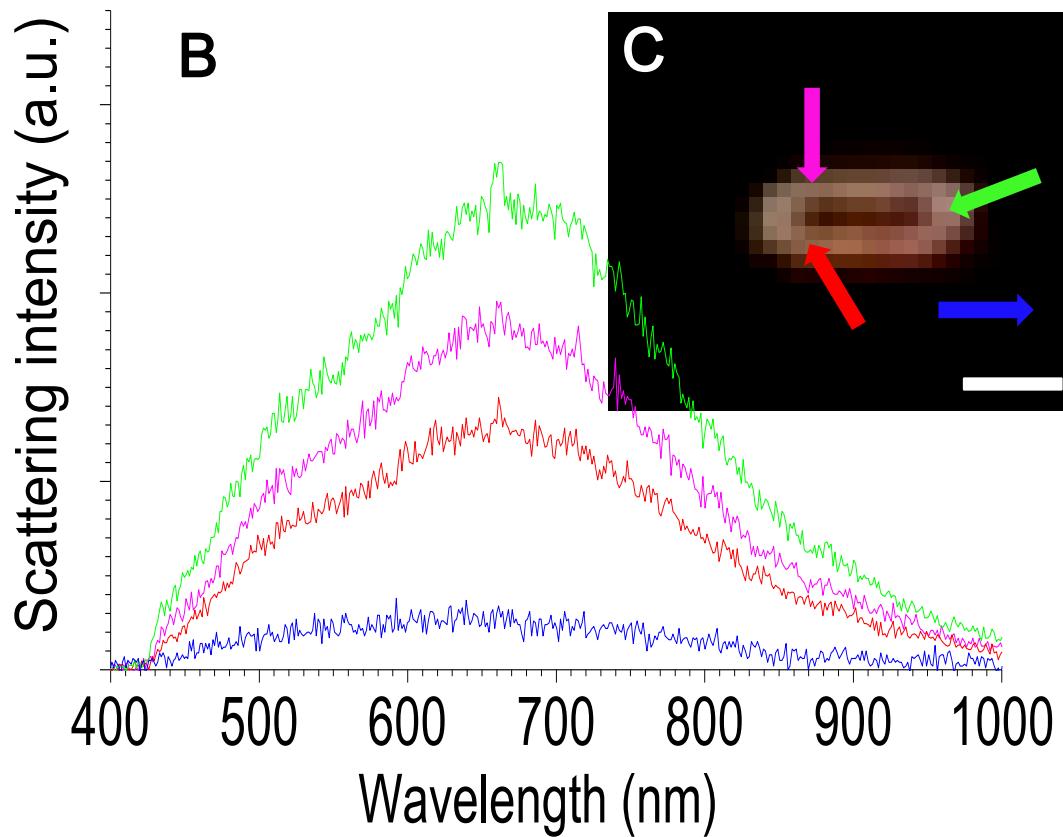
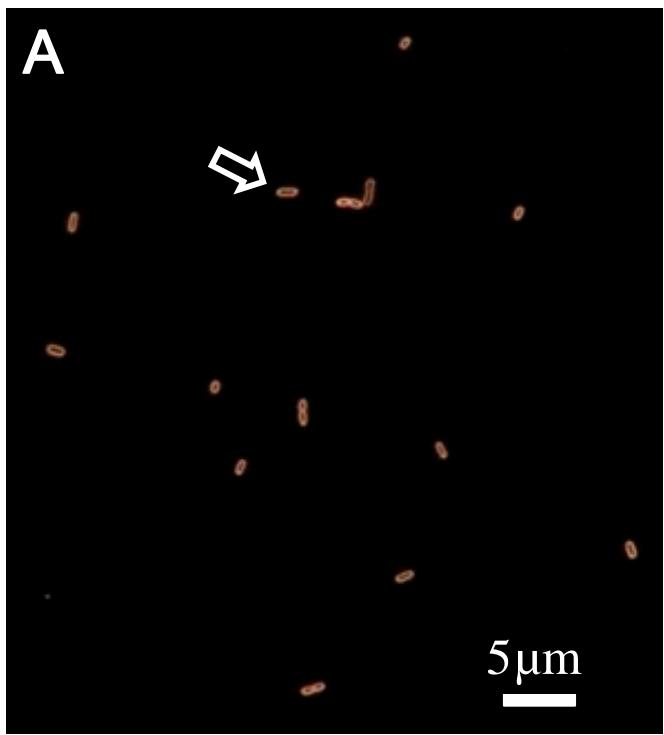
pH

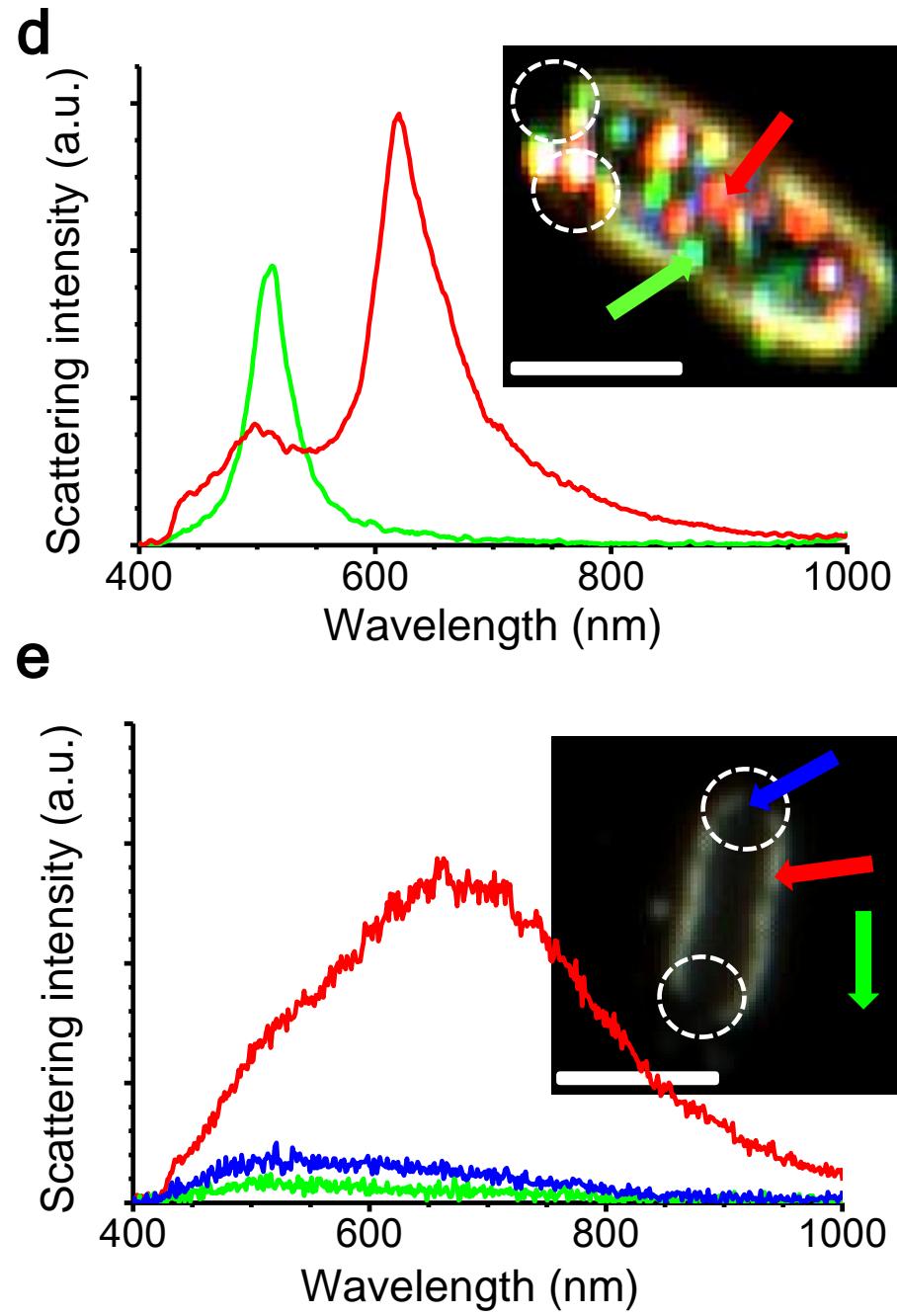
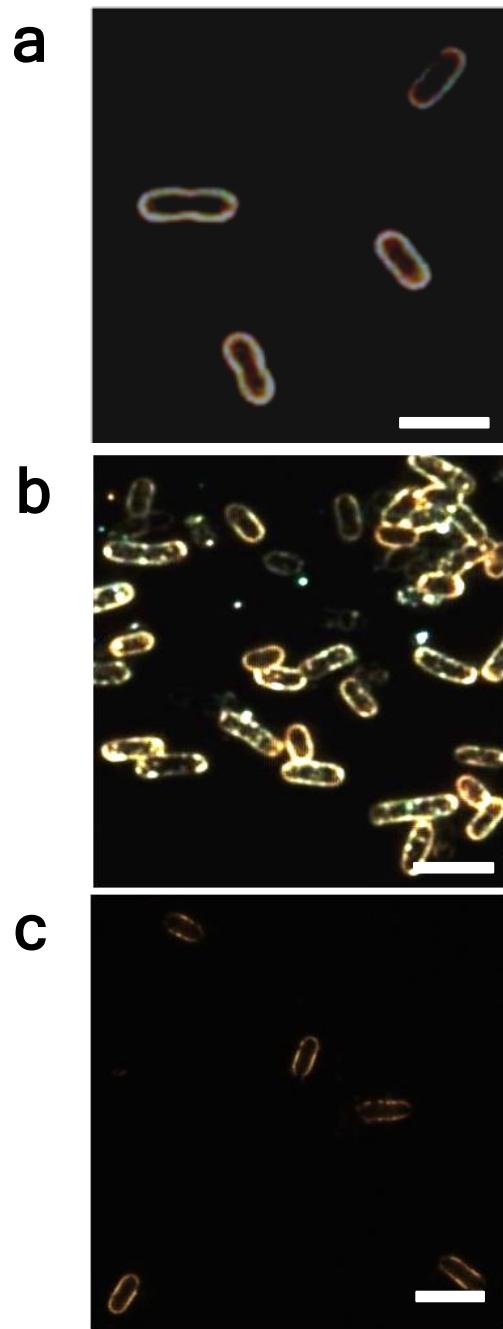
Real water experiments



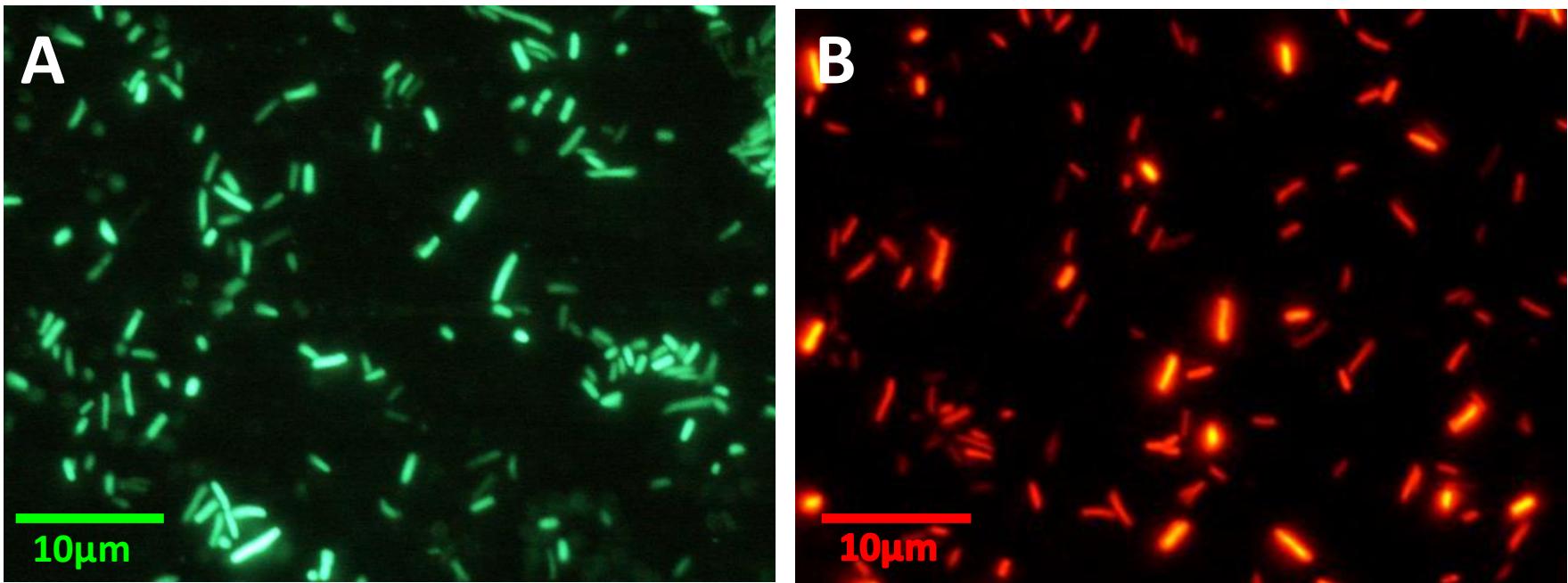
TOC – Humic acid

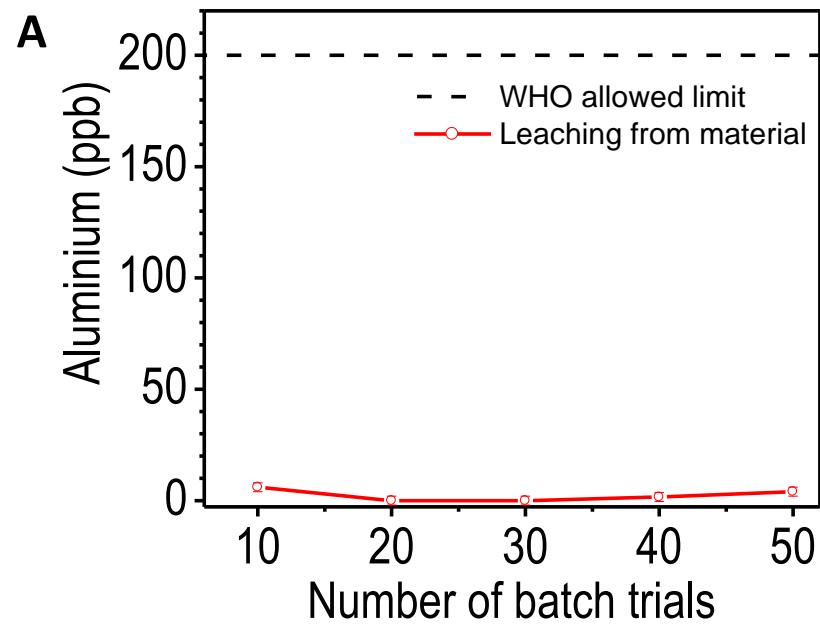
Nanotoxicity?



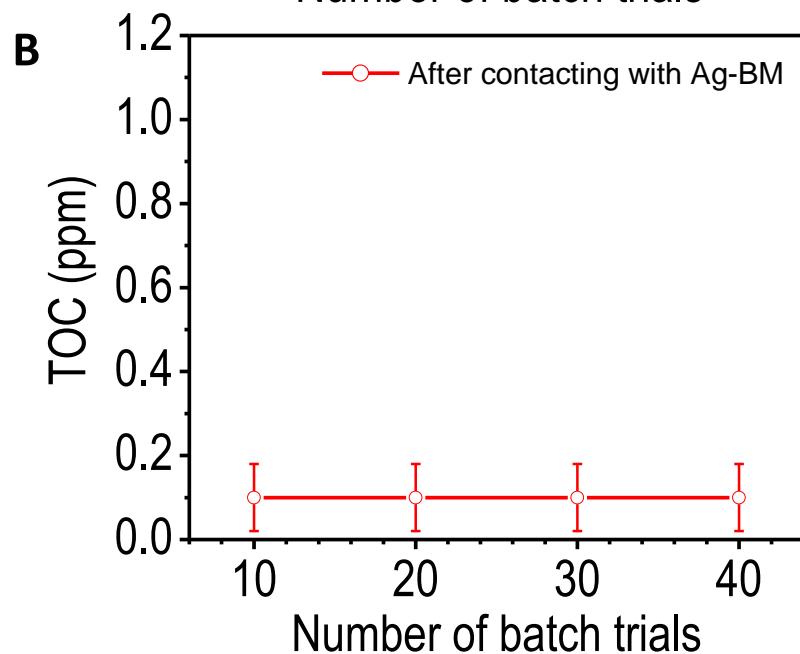


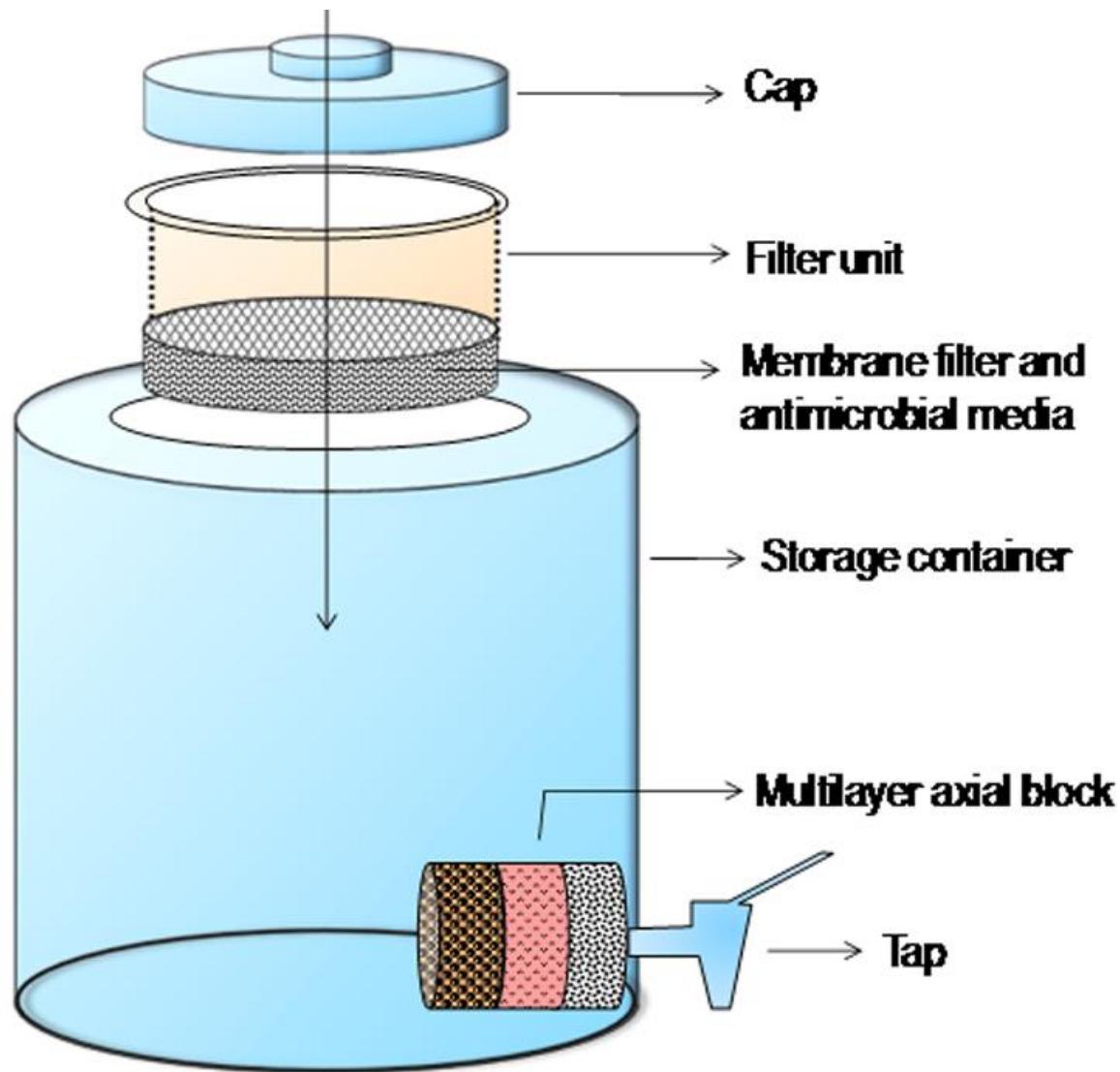
Live/dead staining experiments





Leaching experiments





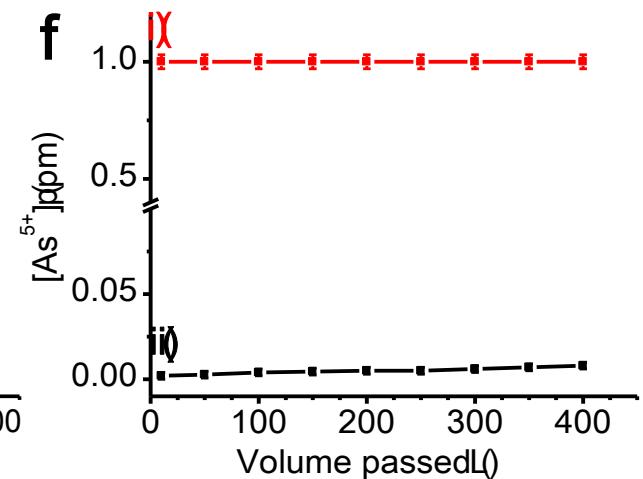
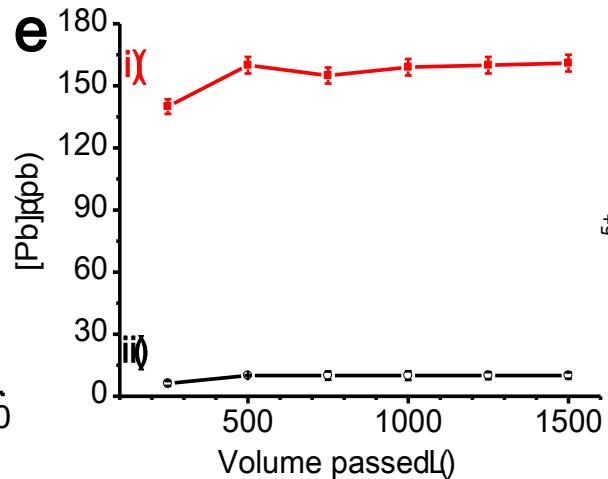
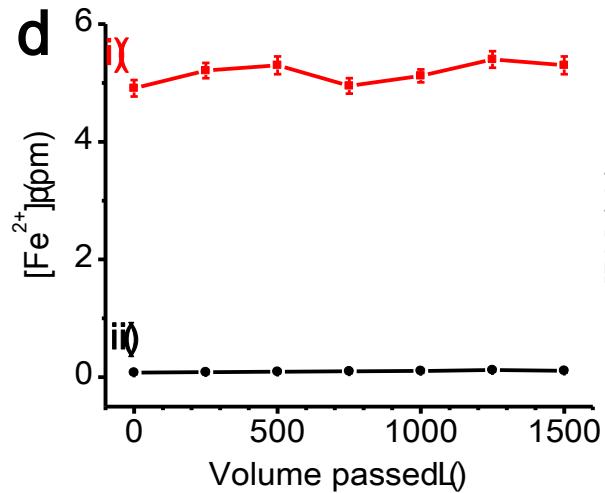
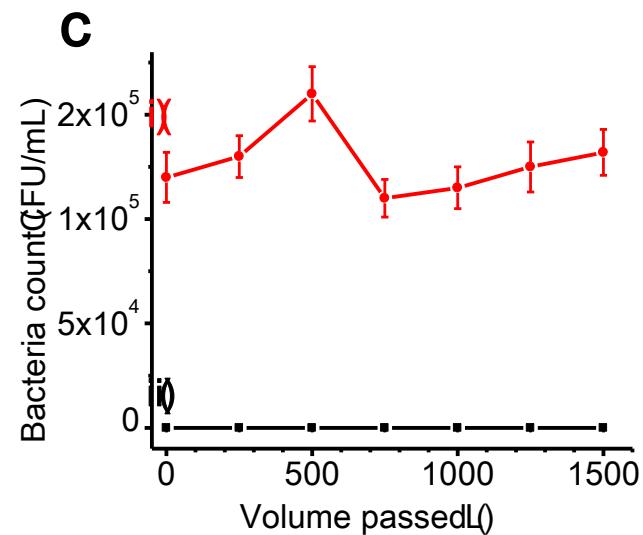
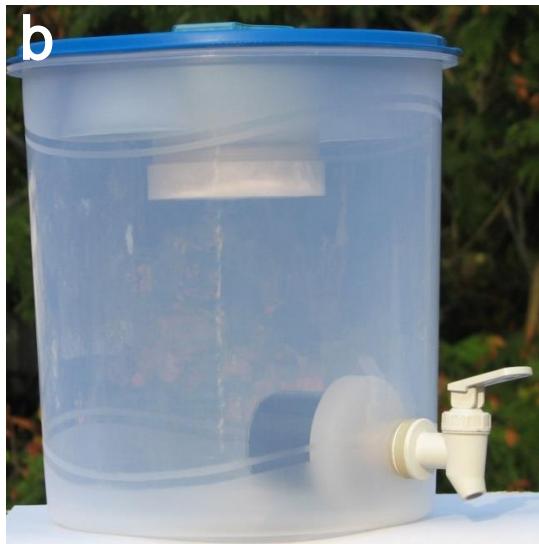
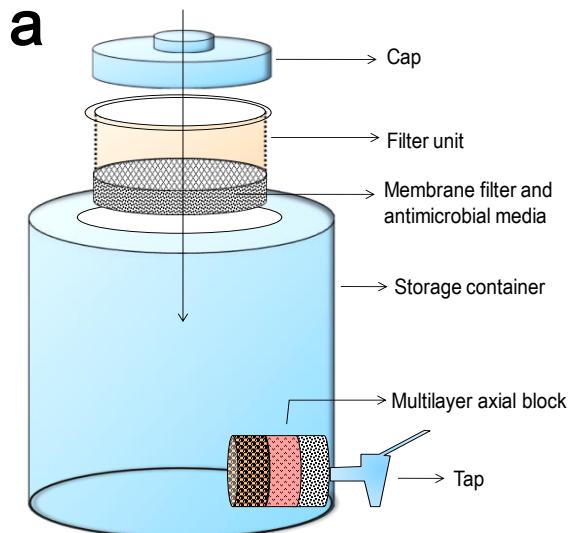
Physicochemical characteristics of influent natural drinking water

(Note: All parameters are expressed in mg L⁻¹, except for pH and conductivity)

ND-not detected

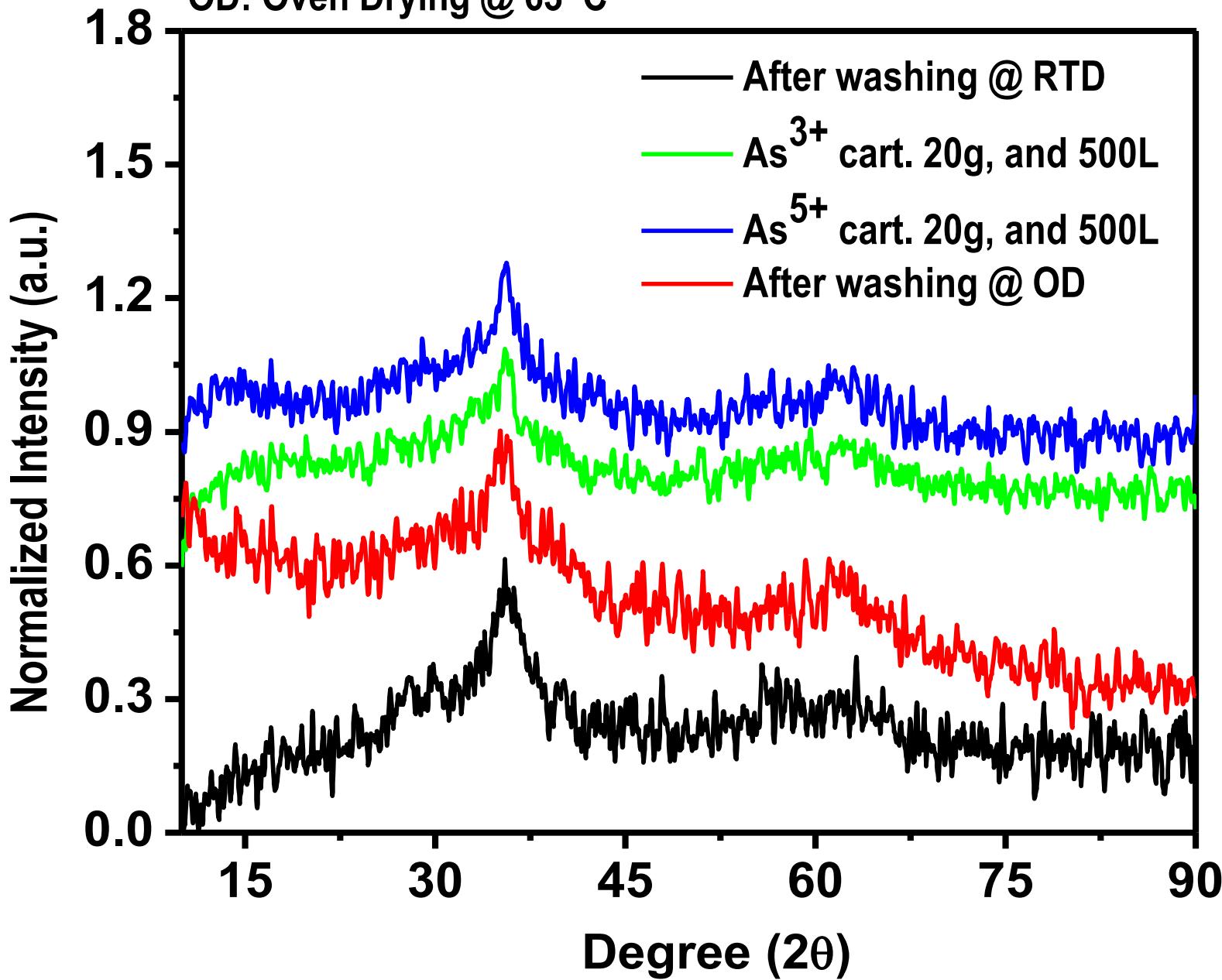
Natural drinking water (without treatment so that there is a residual bacterial count in it) was used for testing to ensure that that the material functions in the field.

Parameters	Value
Total coliforms (CFU/mL)	1-2 x 10 ³
p H @25°C	7.8
Conductivity (µS/cm)	640.000
Fluoride	0.573
Chloride	86.340
Nitrate	1.837
Sulphate	32.410
Silicate	15.870
Lithium	ND
Sodium	53.740
Ammonium	ND
Potassium	2.330
Magnesium	14.340
Calcium	28.720

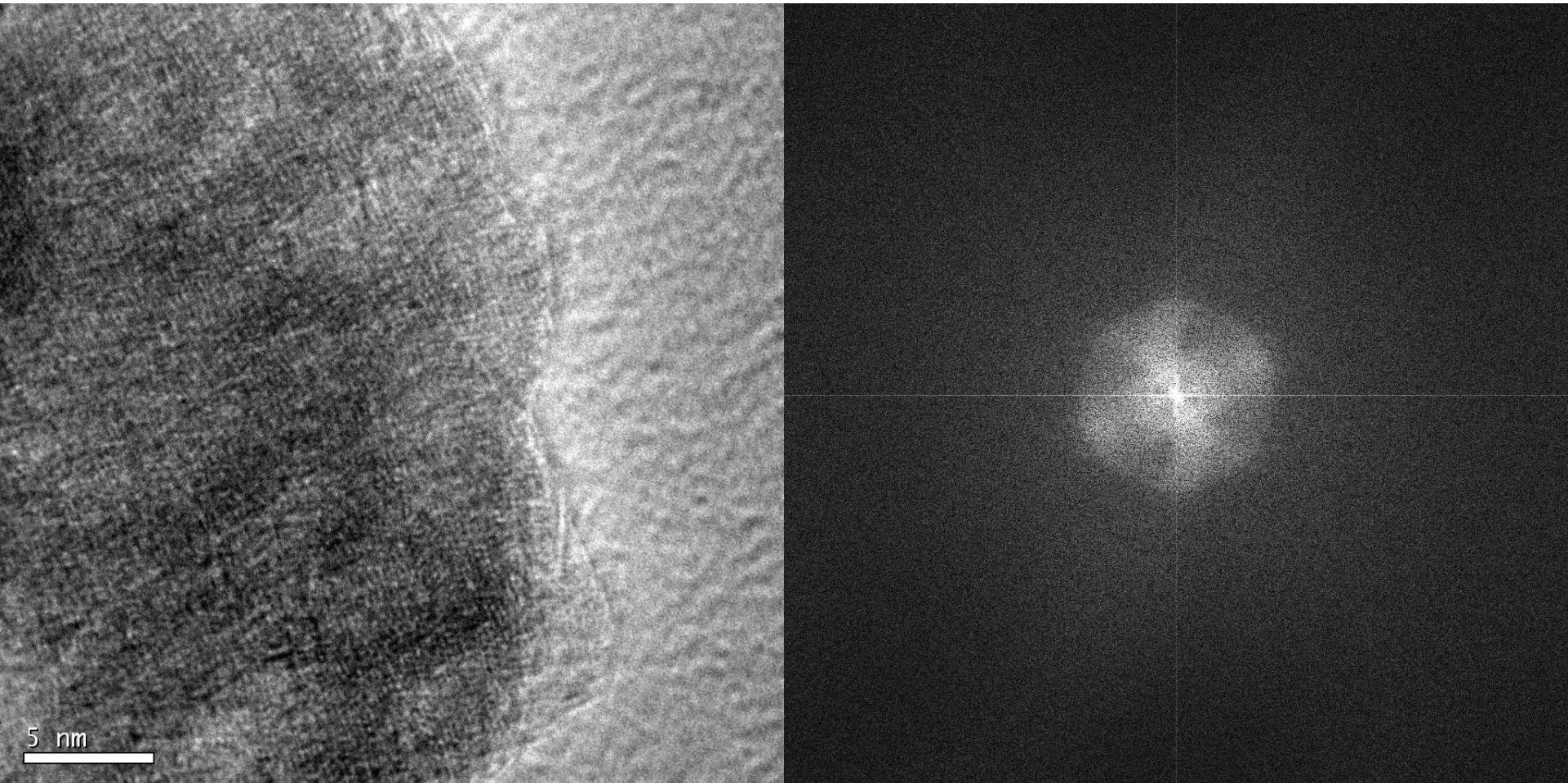


RTD: Room Temperature Drying

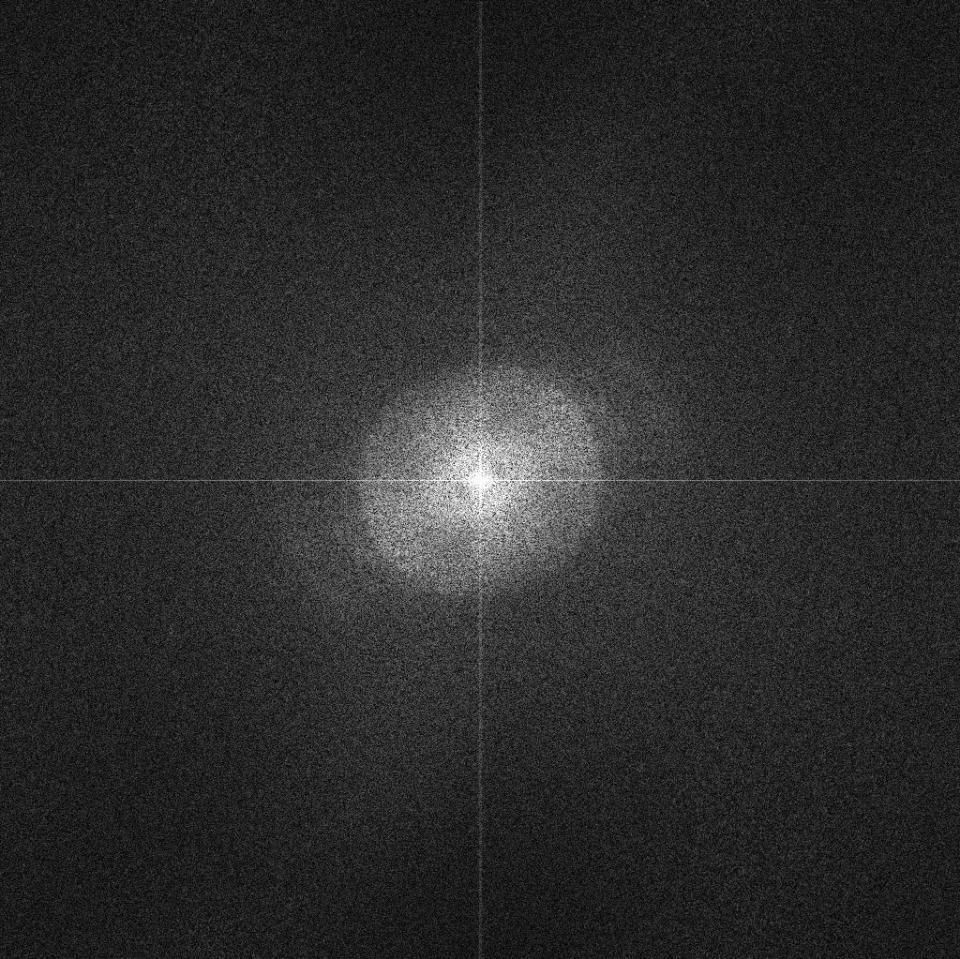
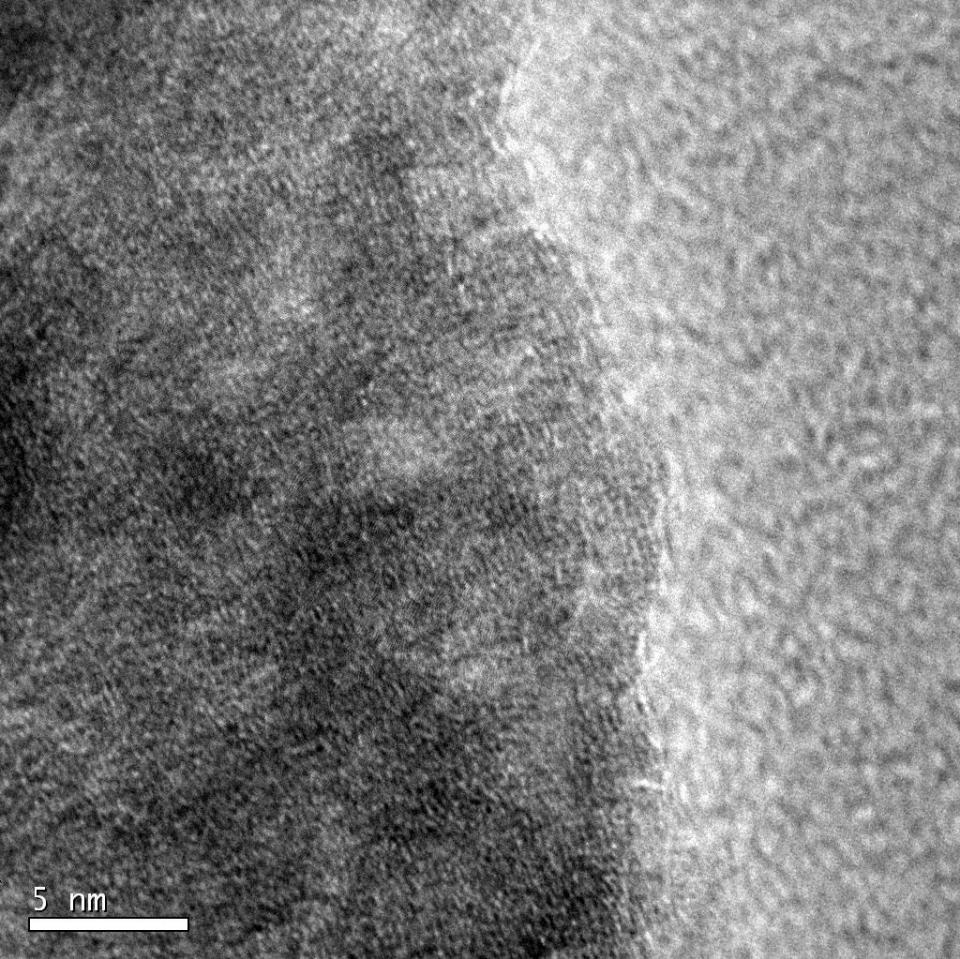
OD: Oven Drying @ 63°C



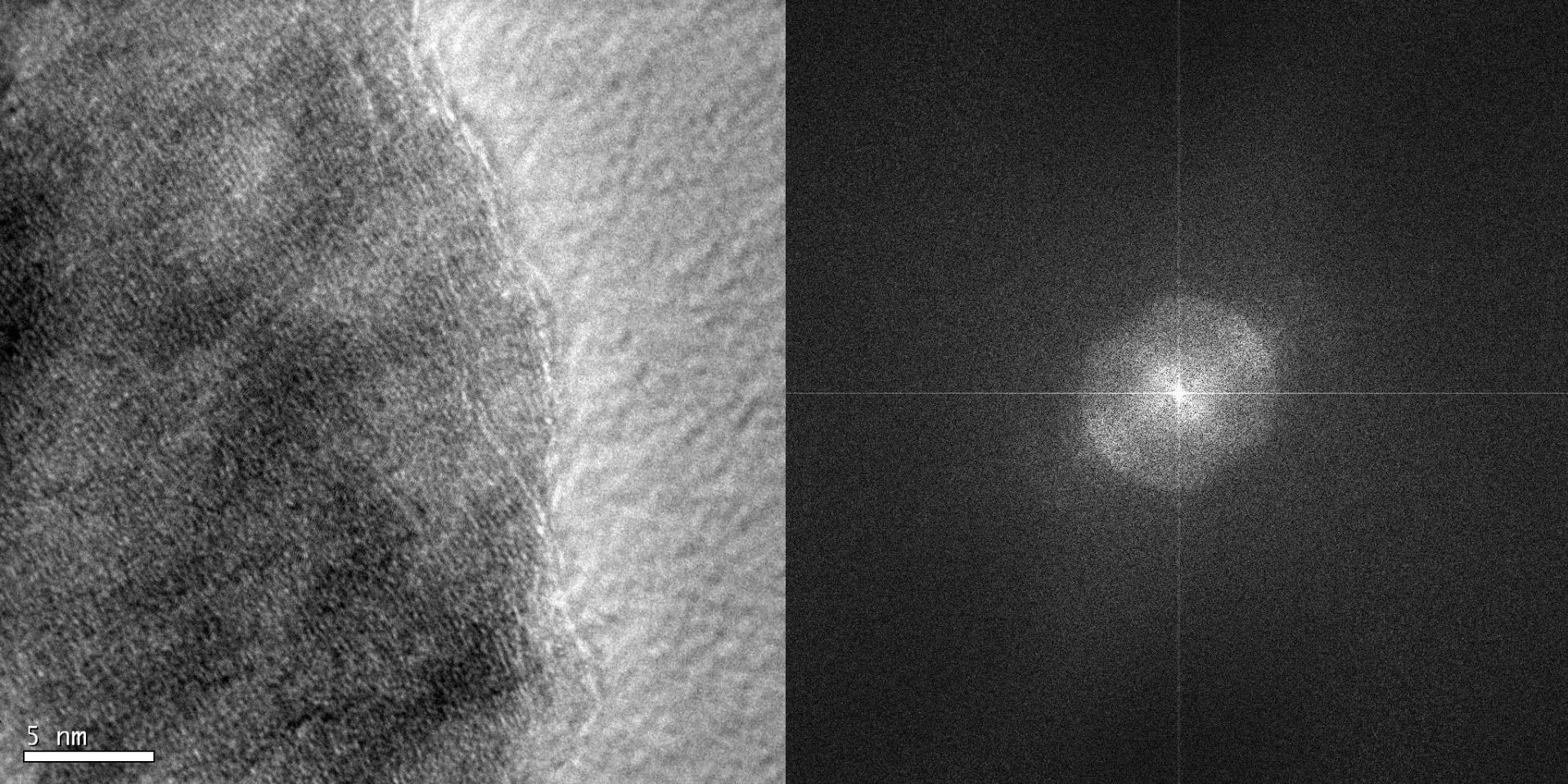
Metastable phase



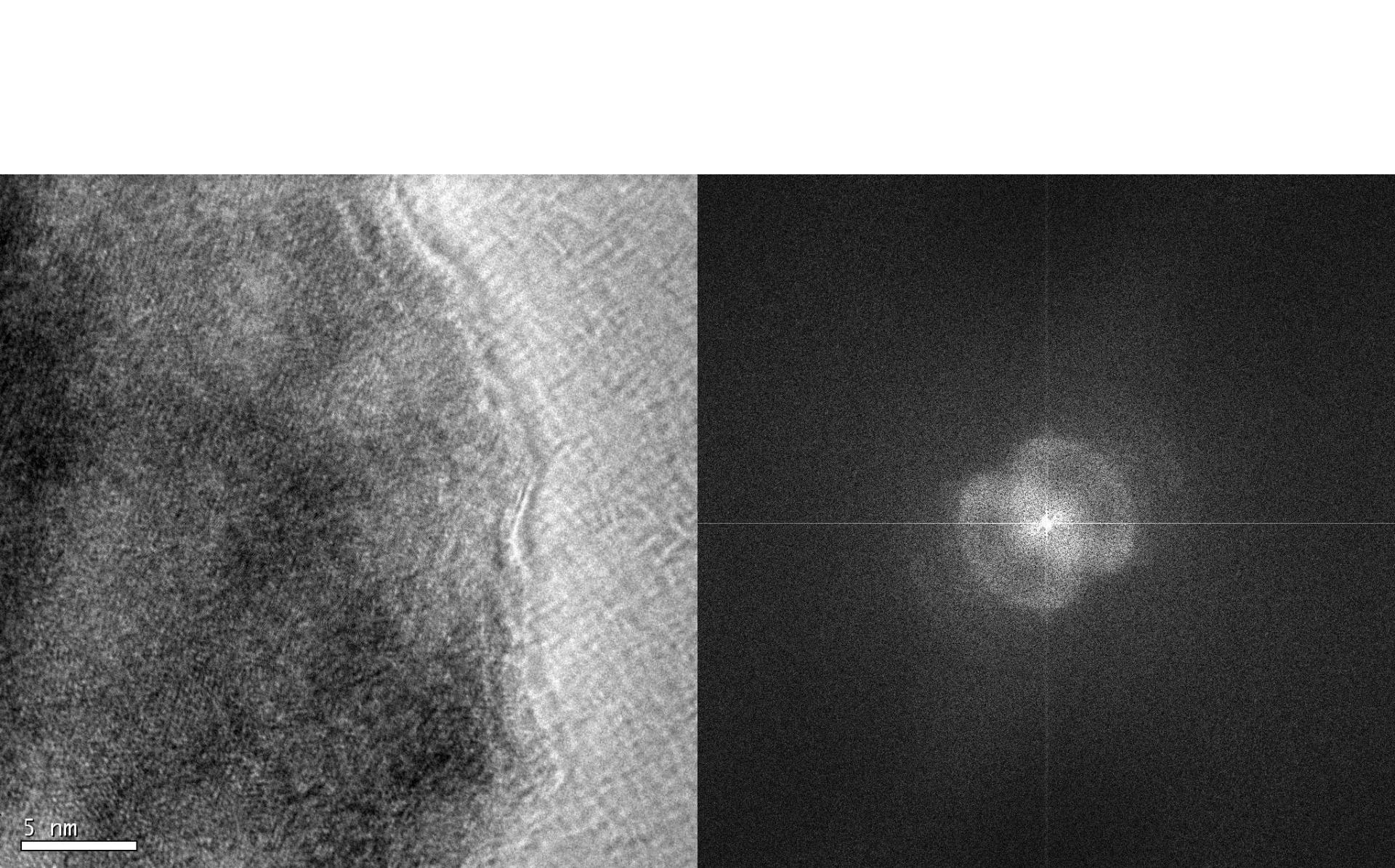
Time dependent TEM



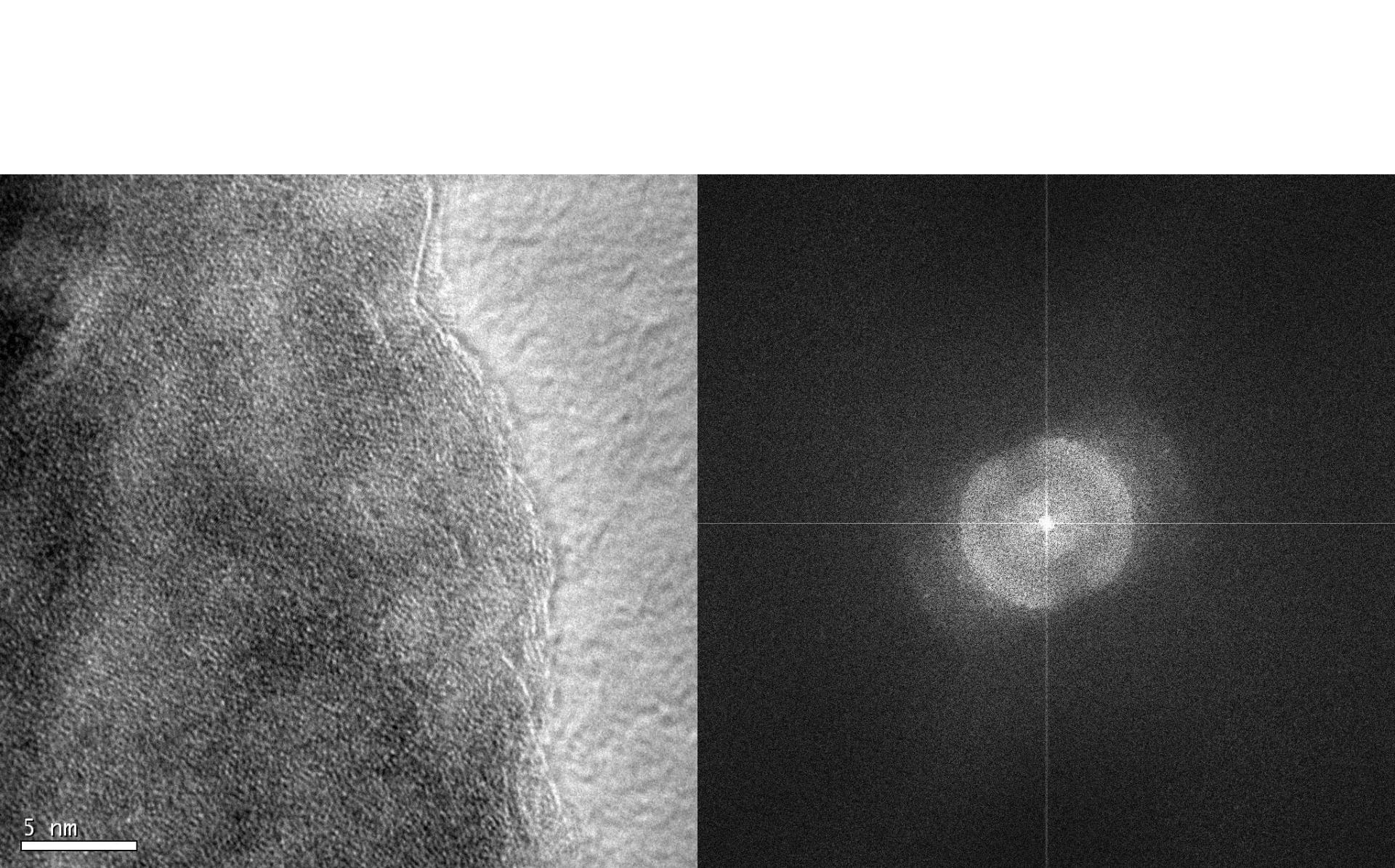
5 nm



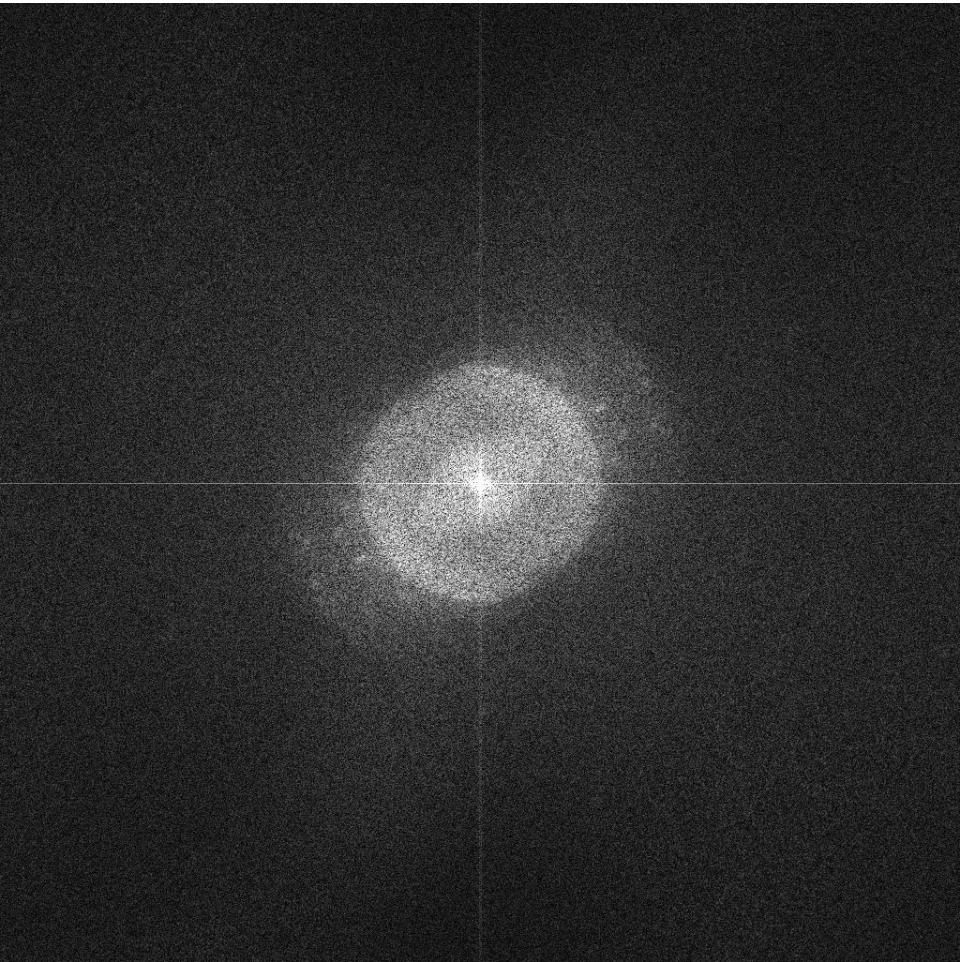
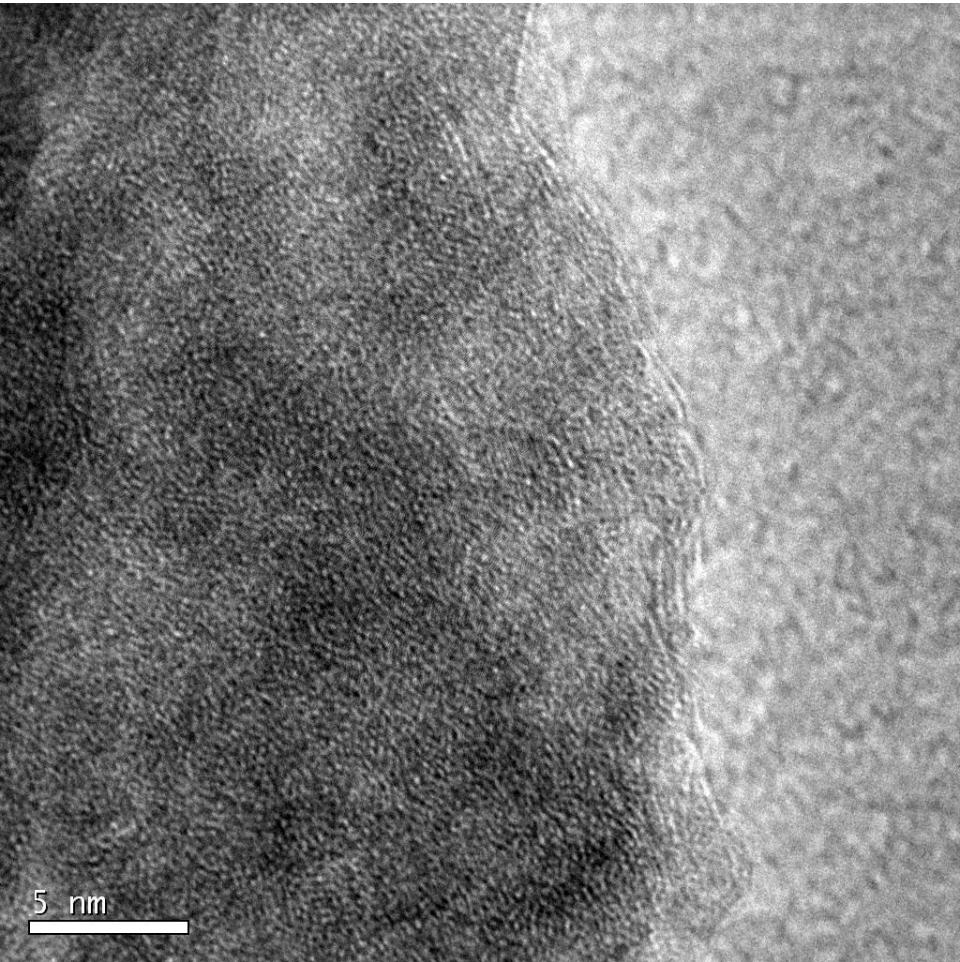
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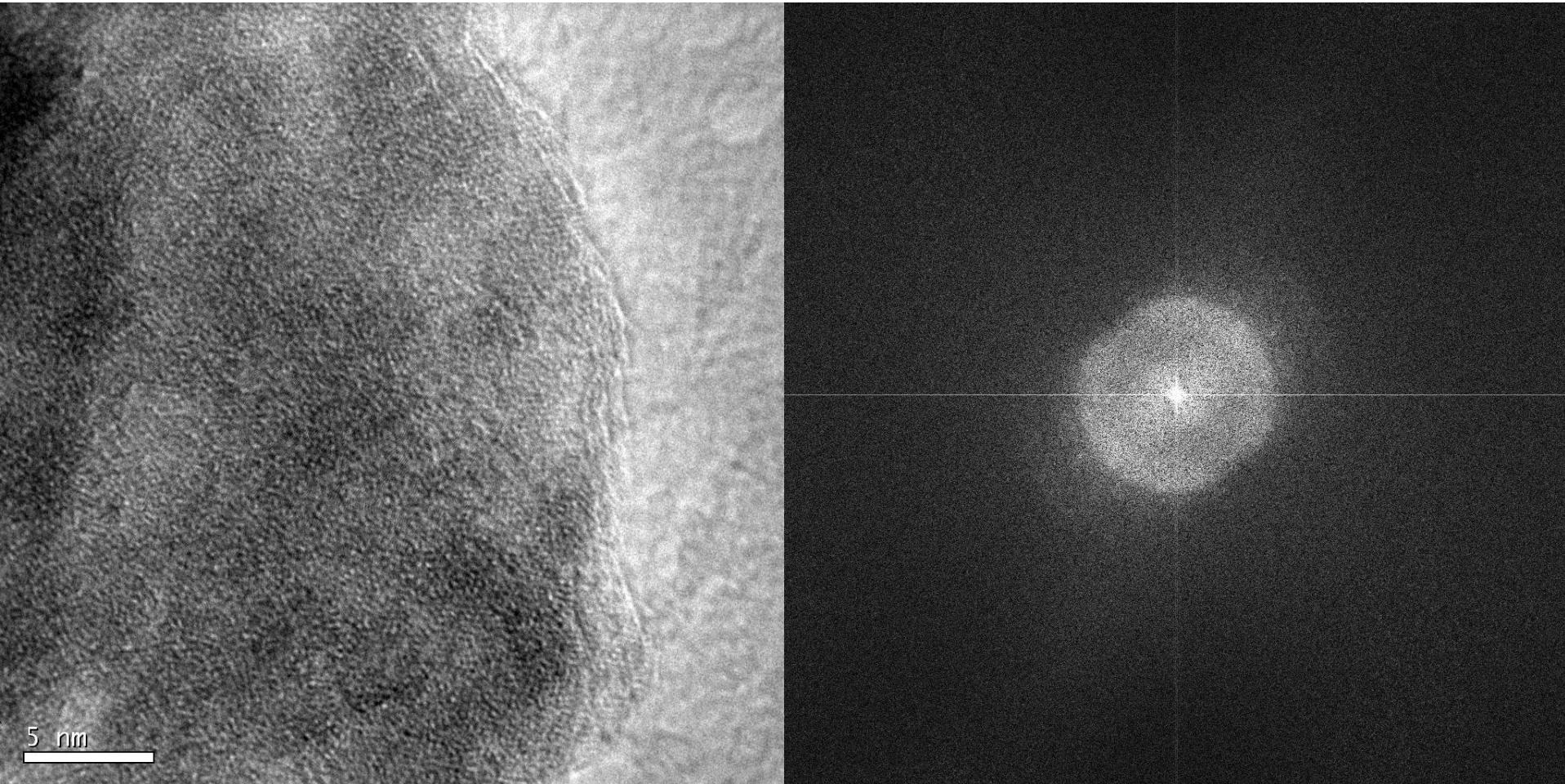


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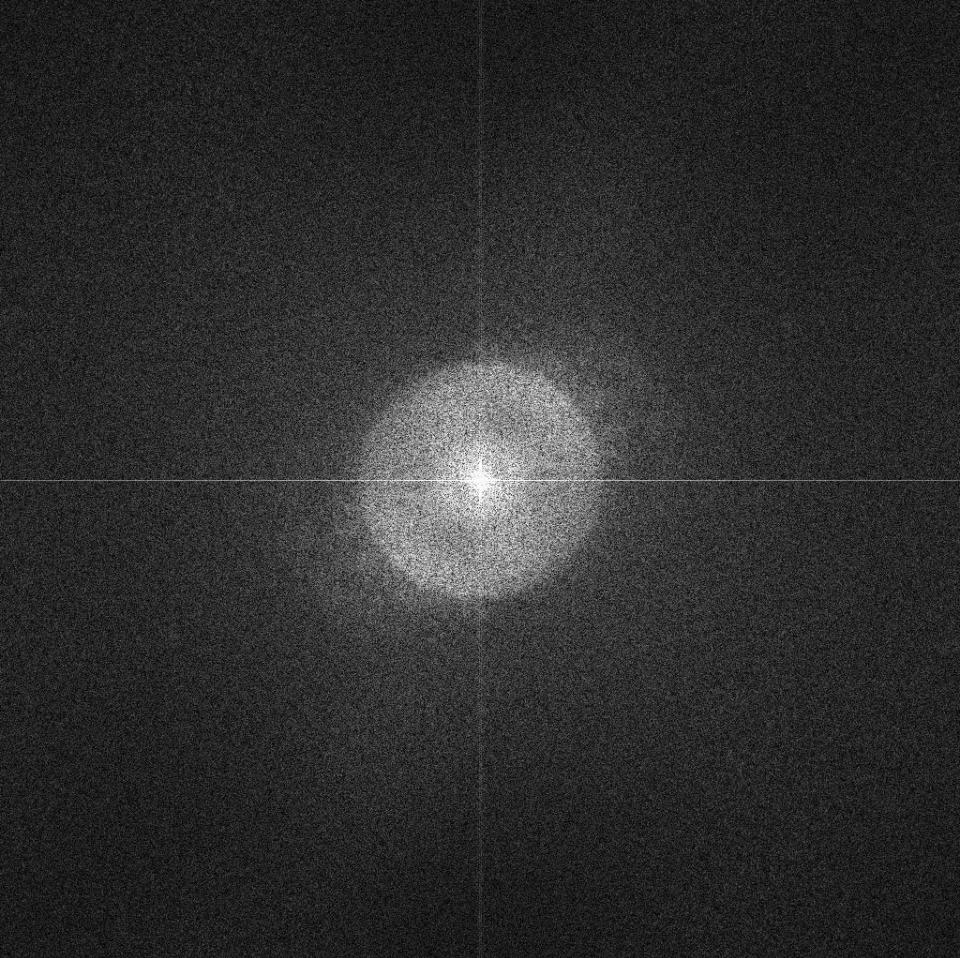
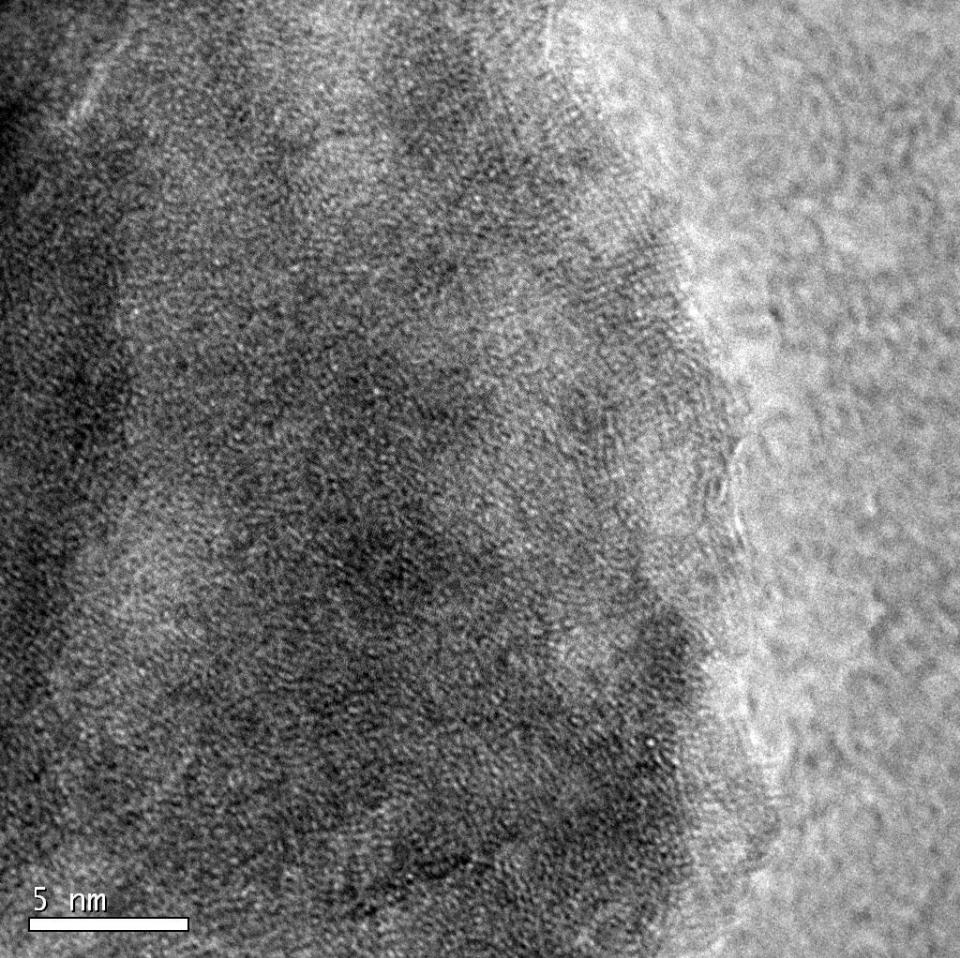


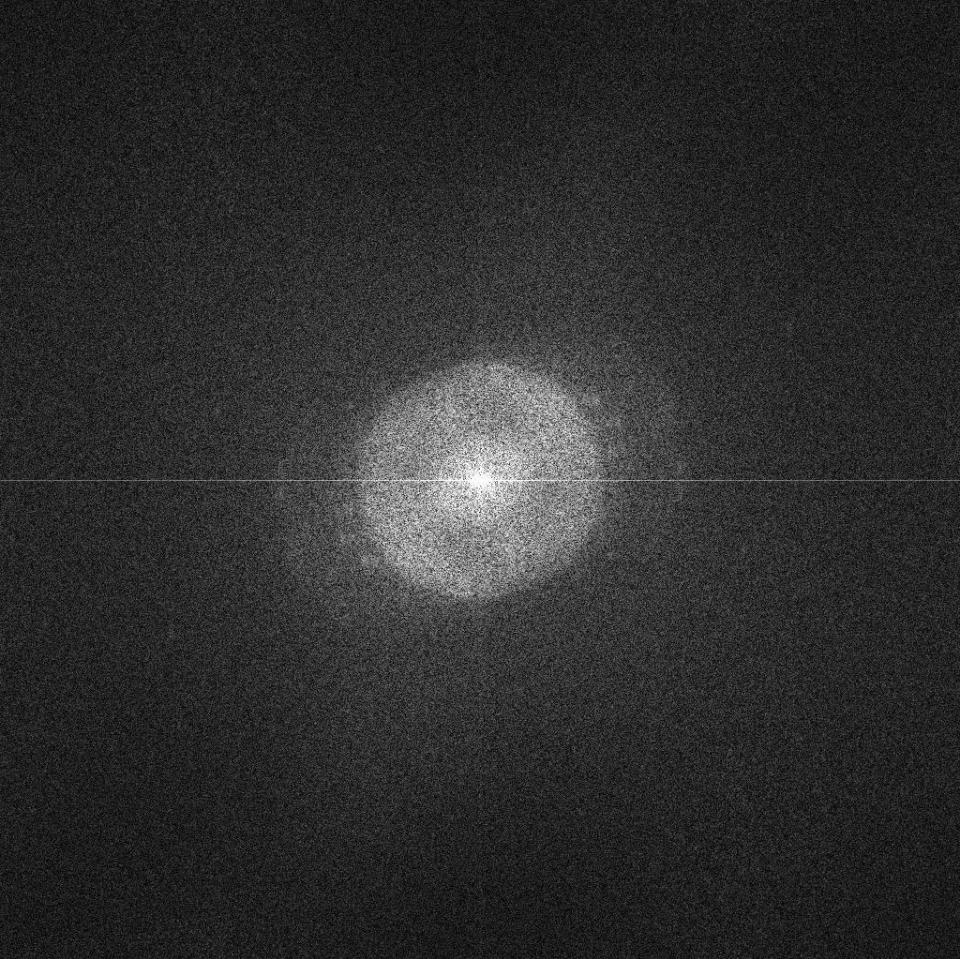
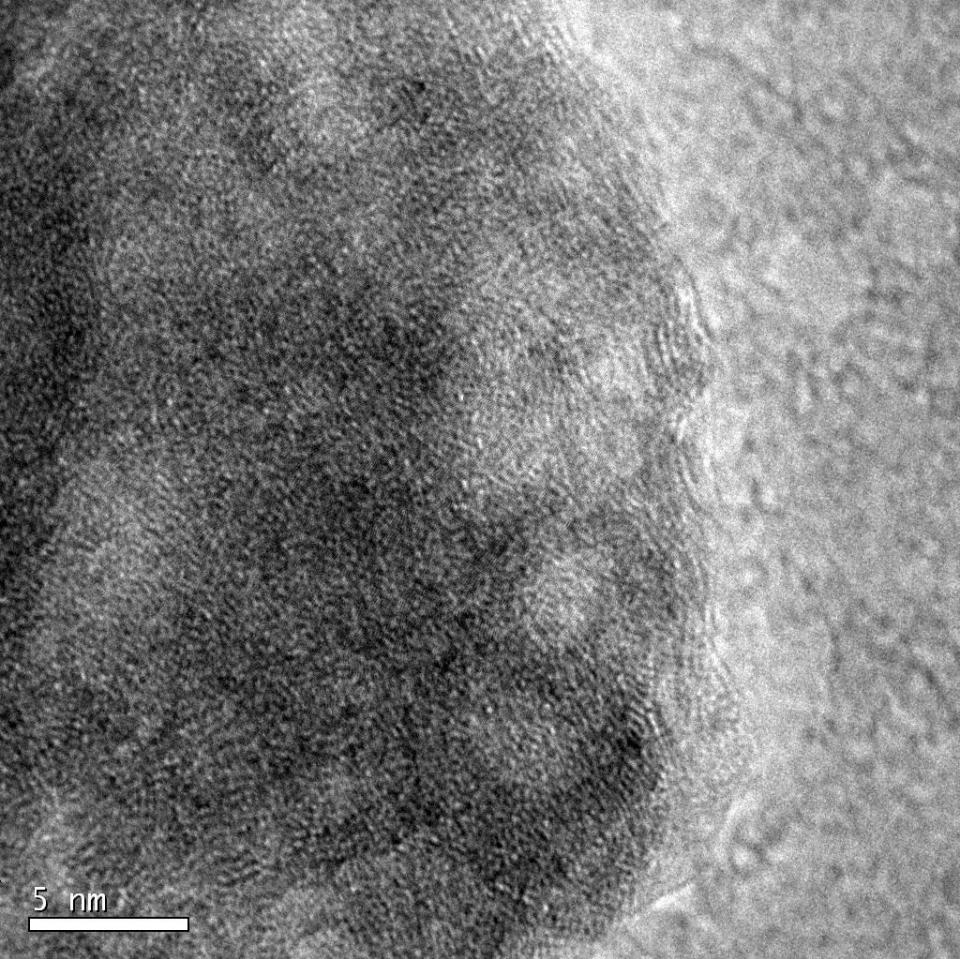
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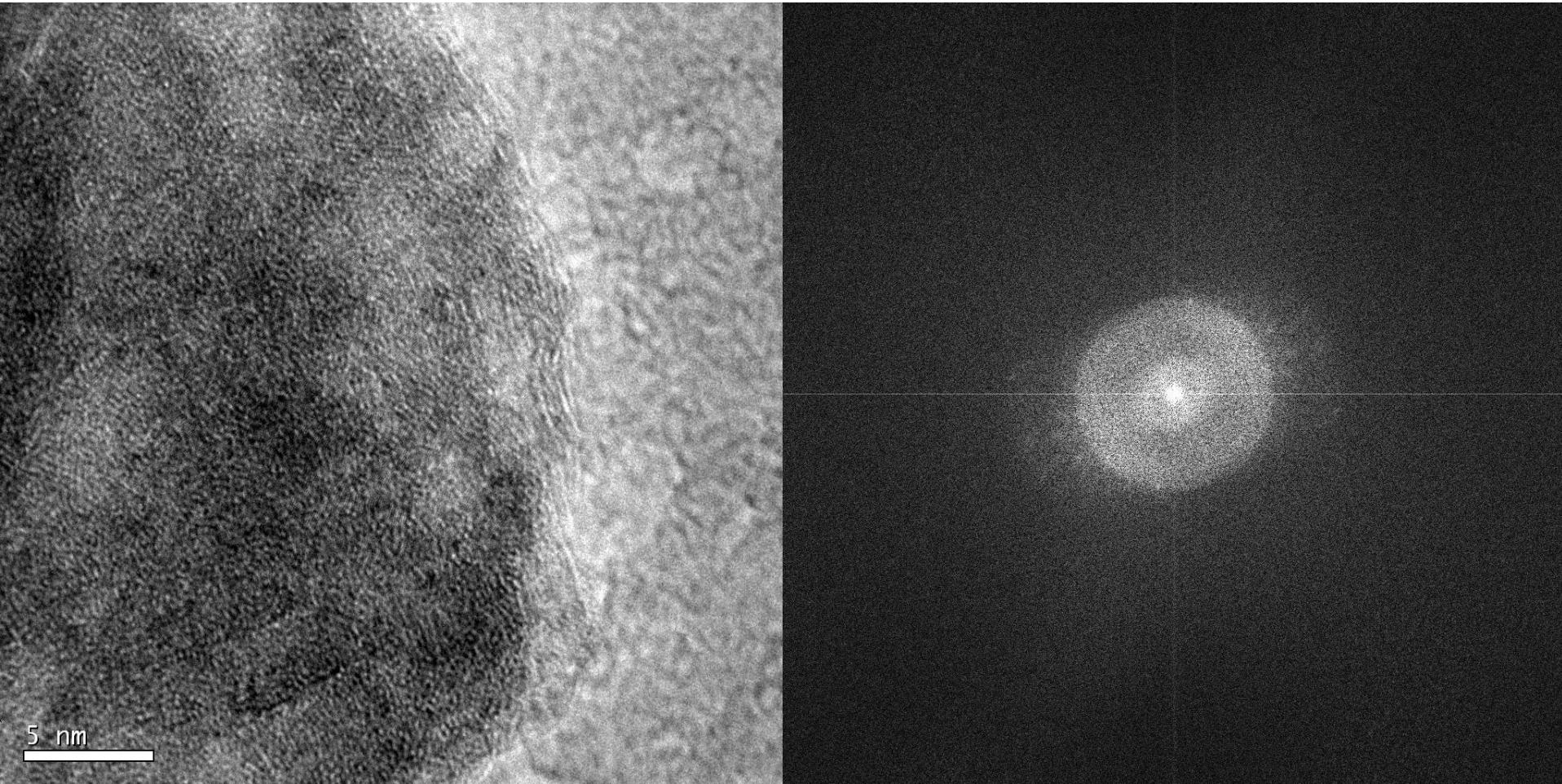




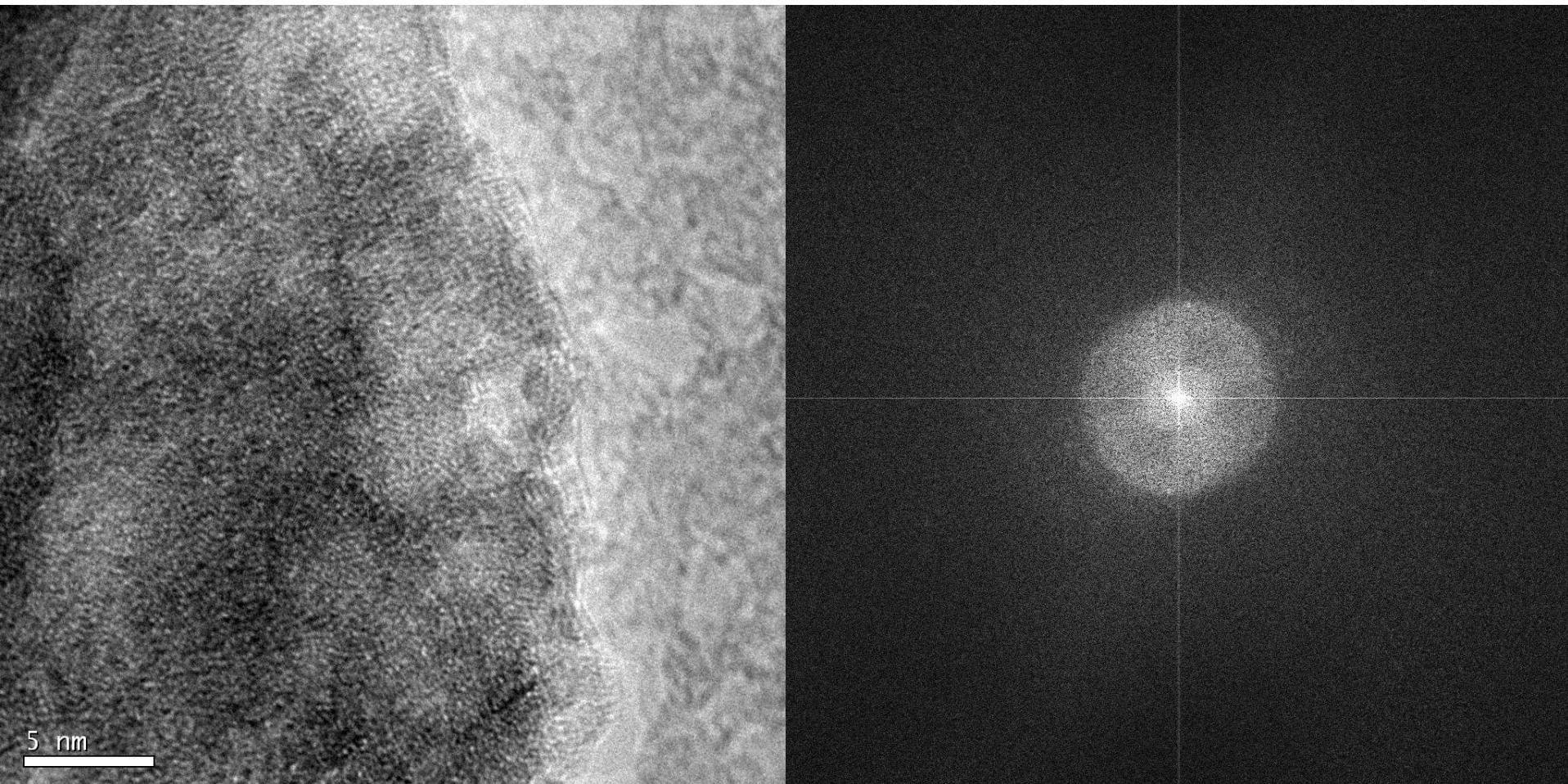
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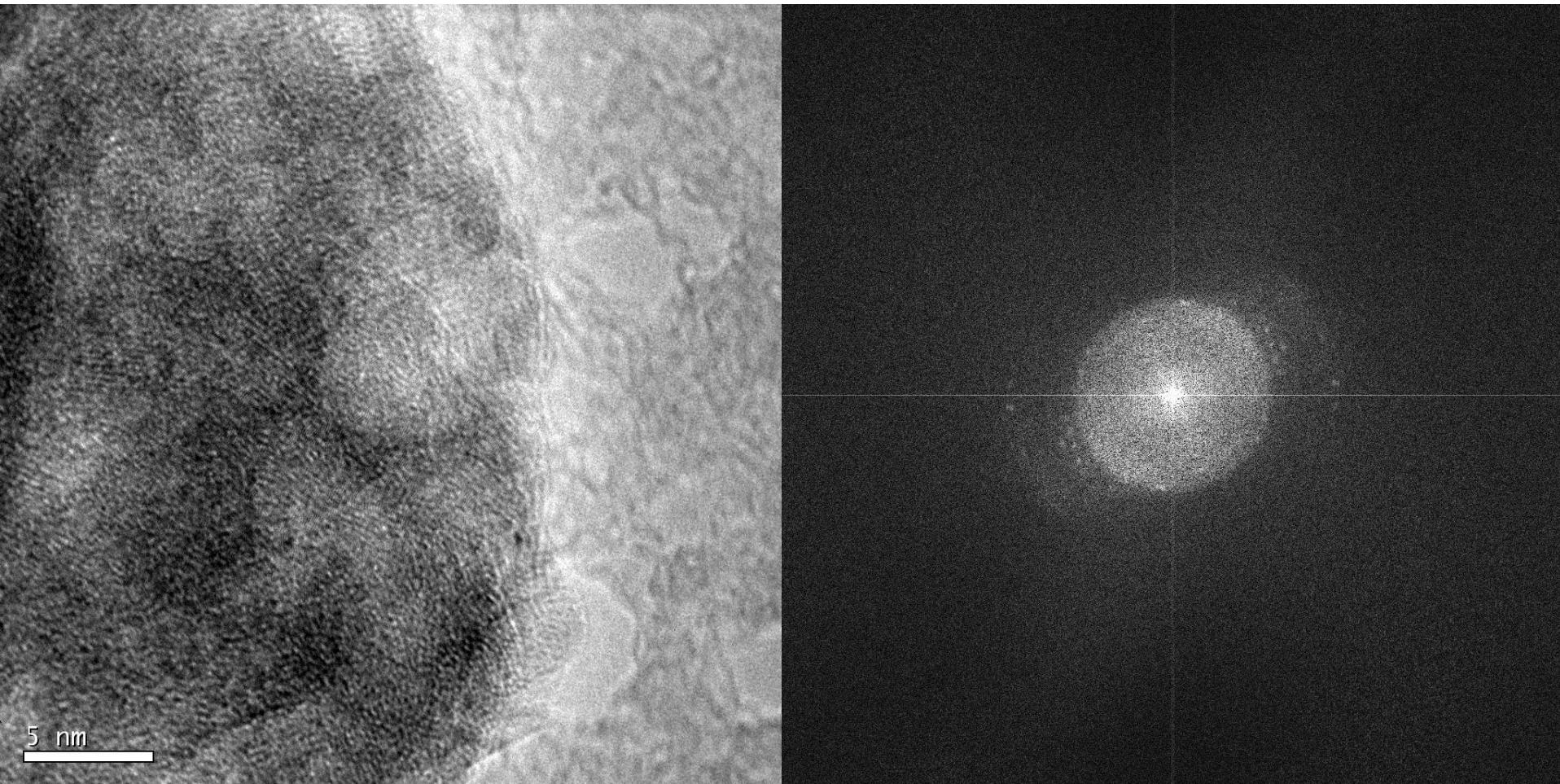




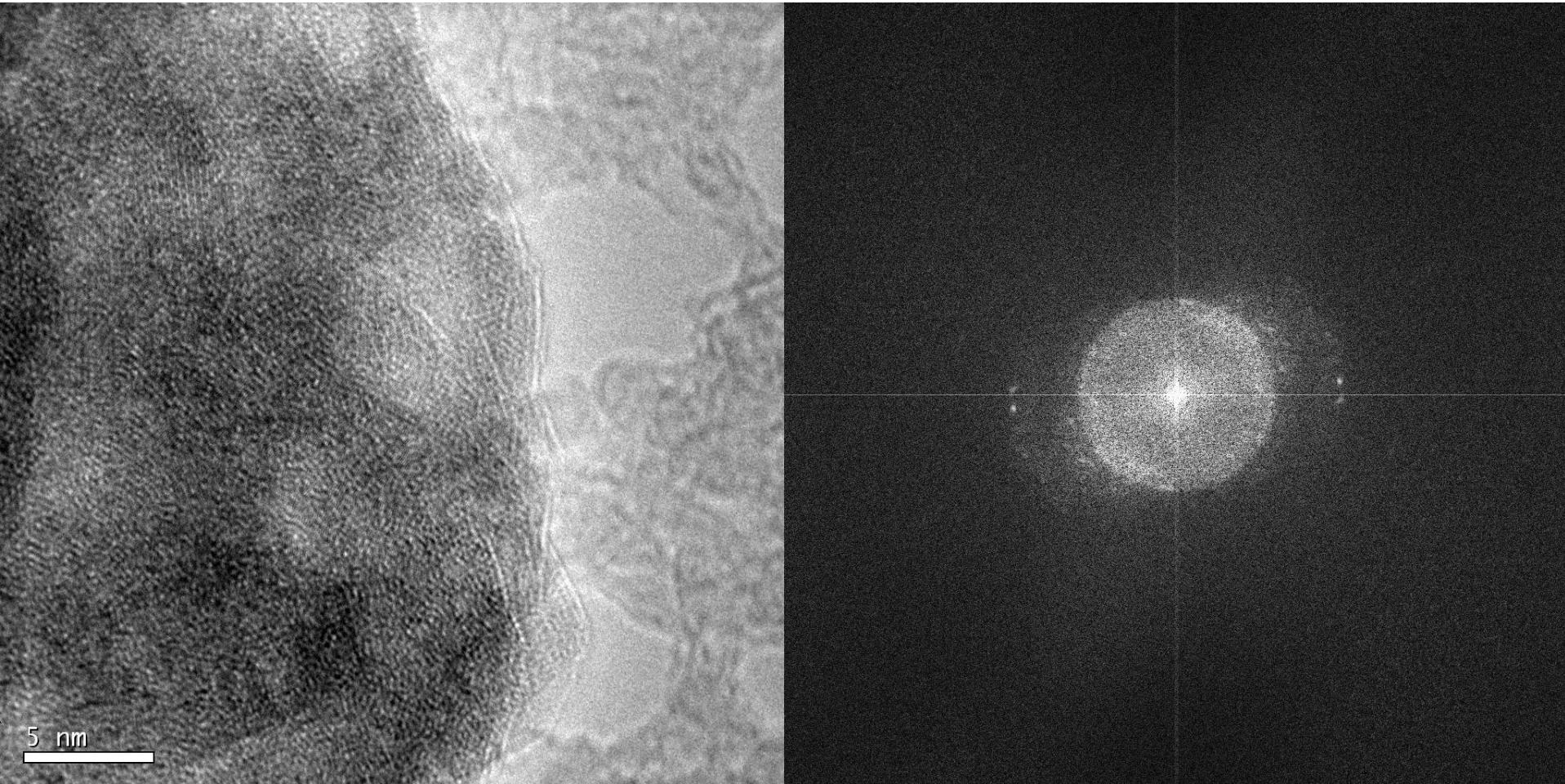
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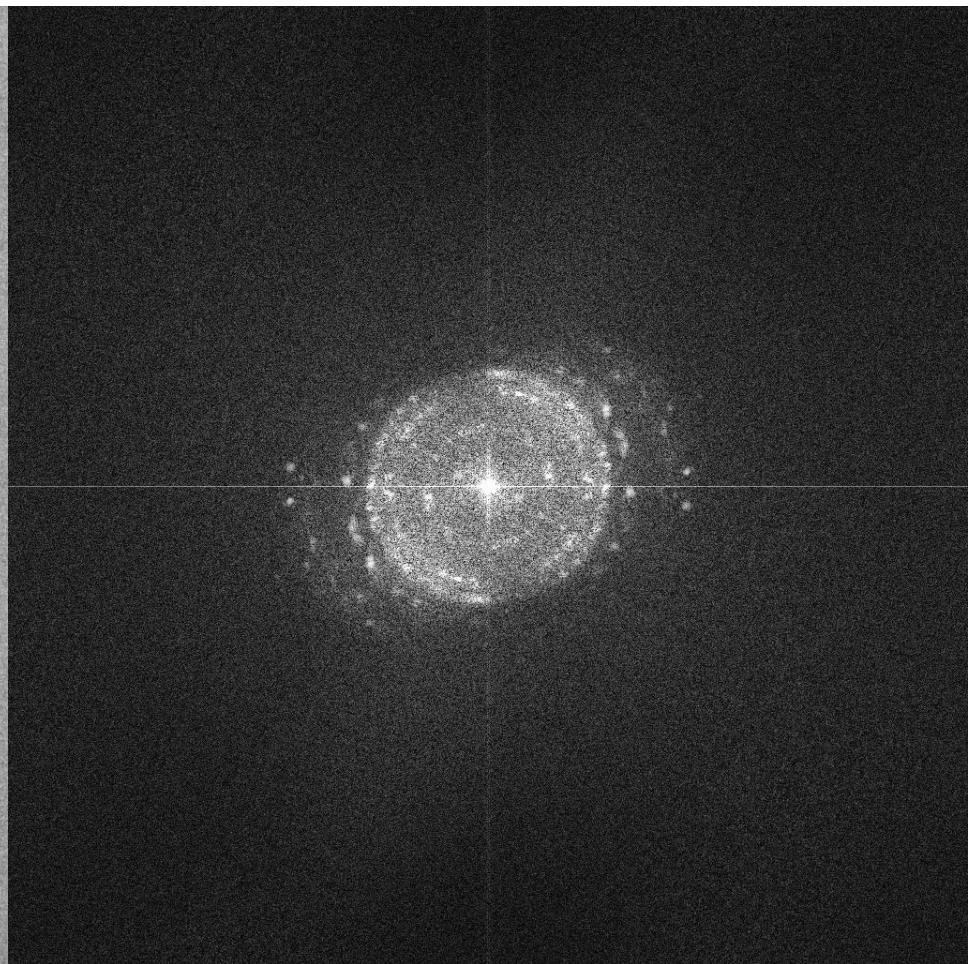
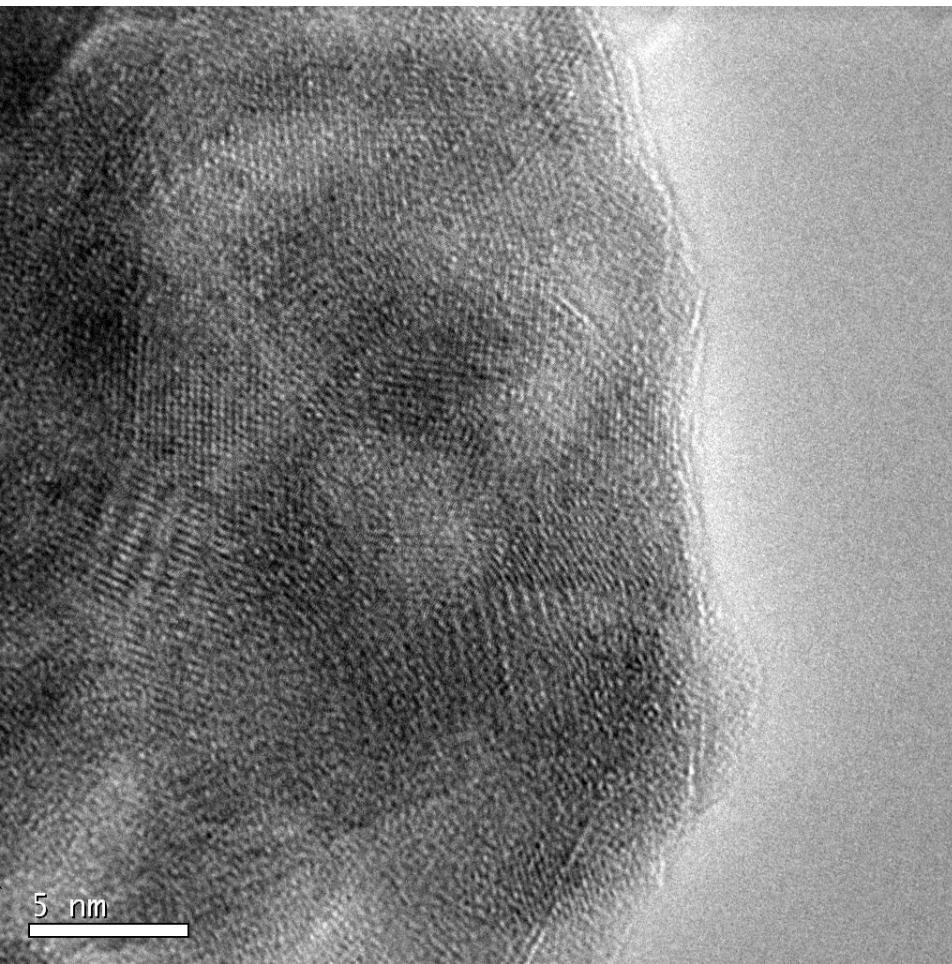
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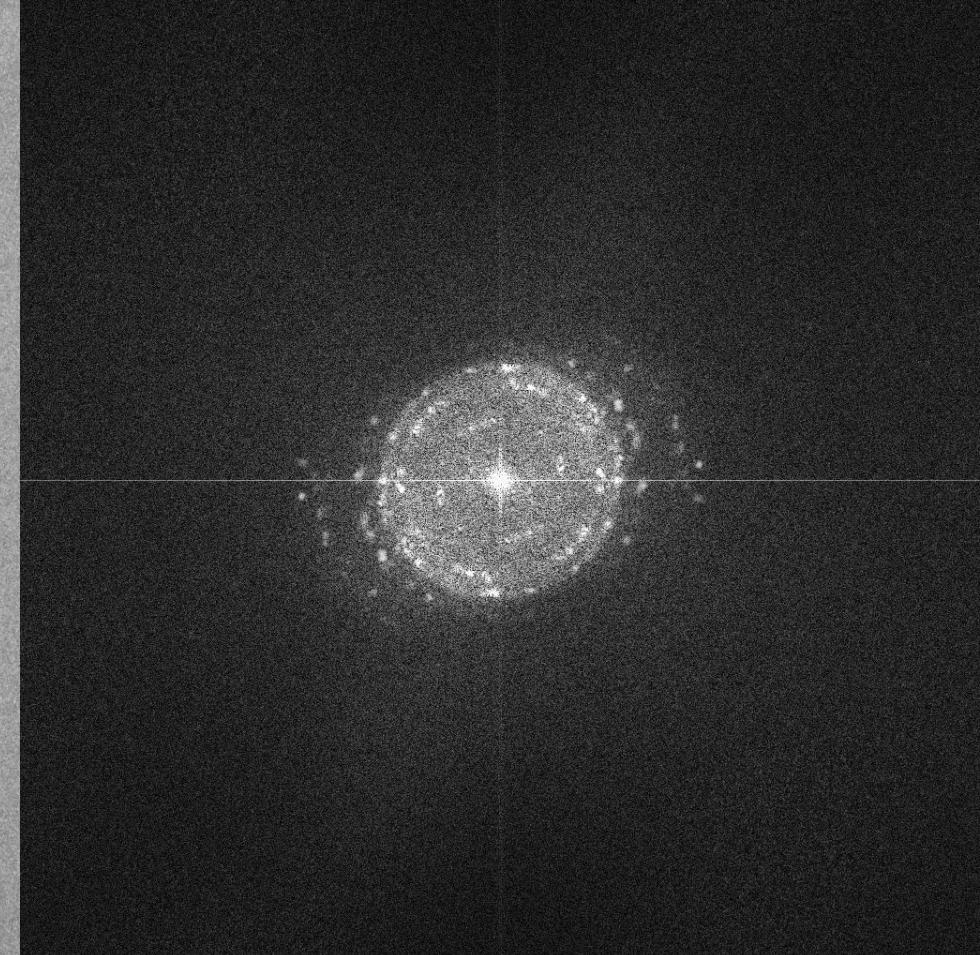
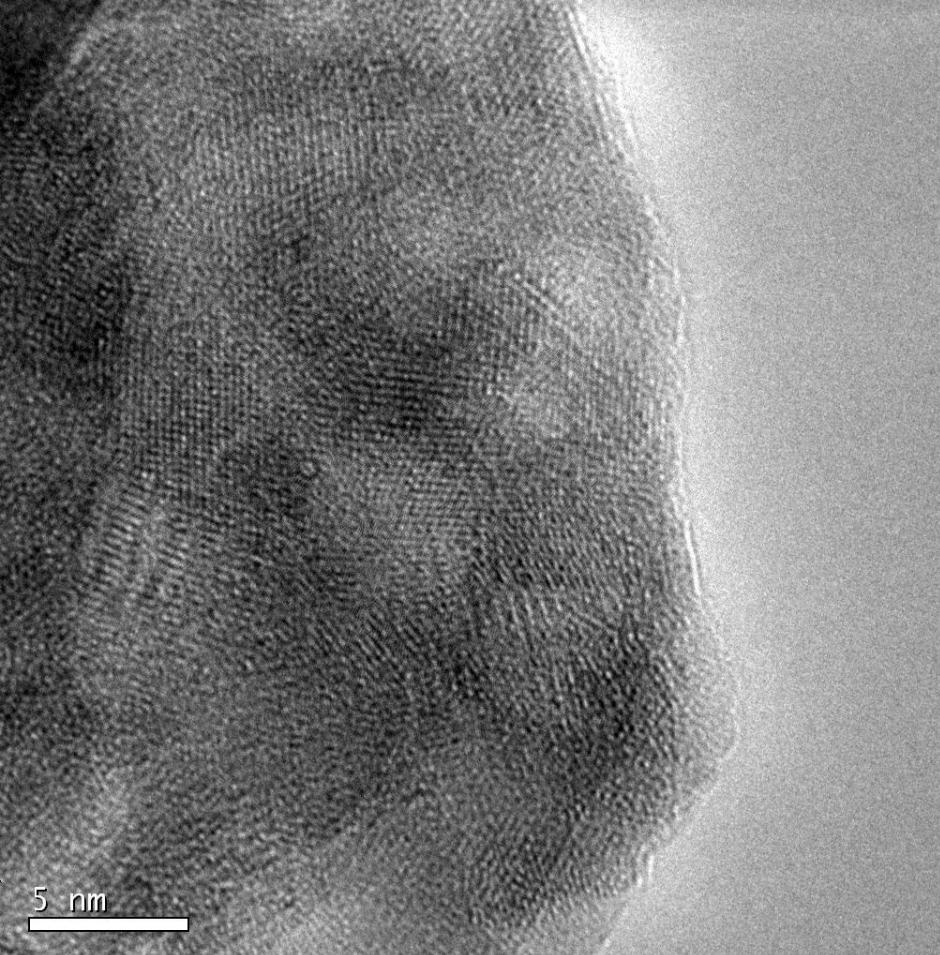


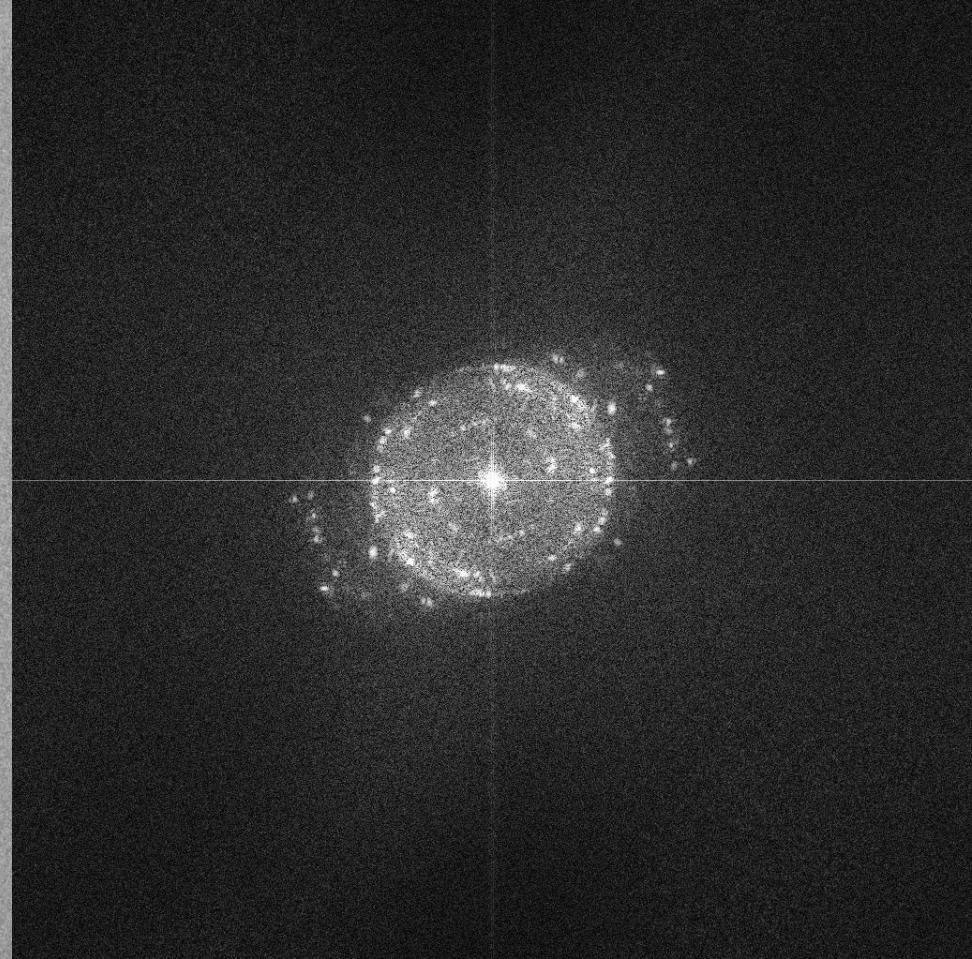
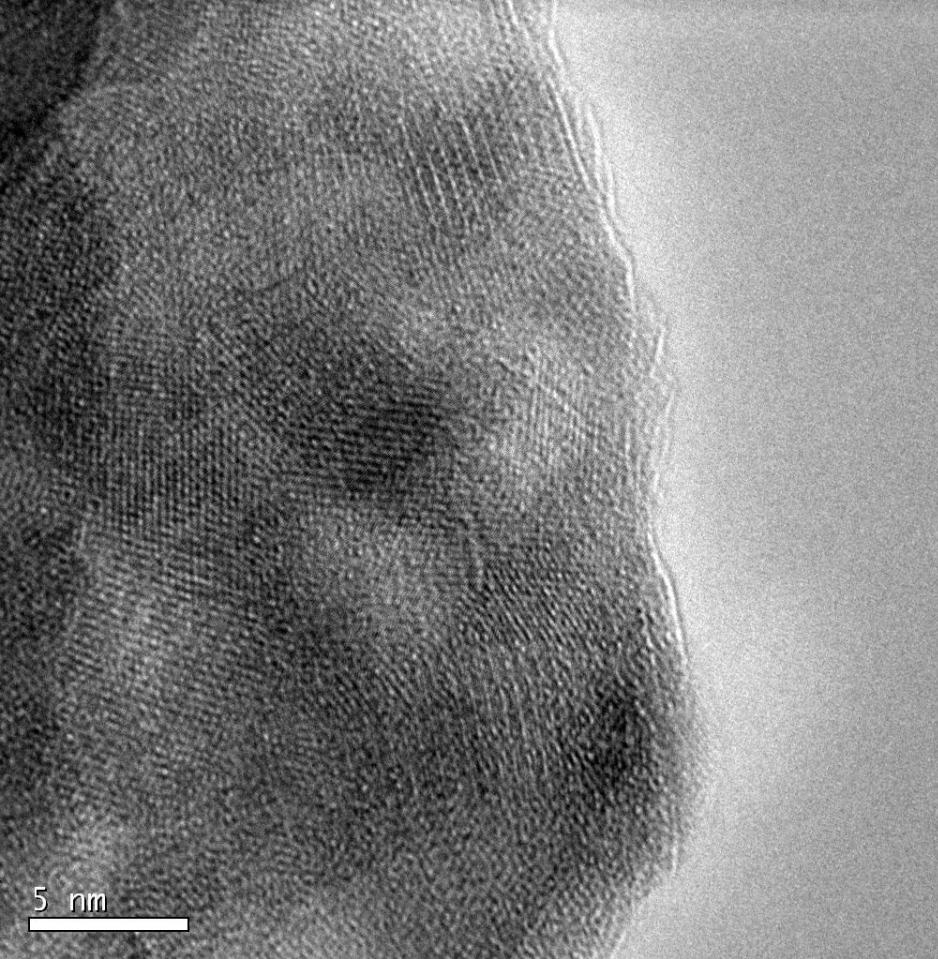
5 nm

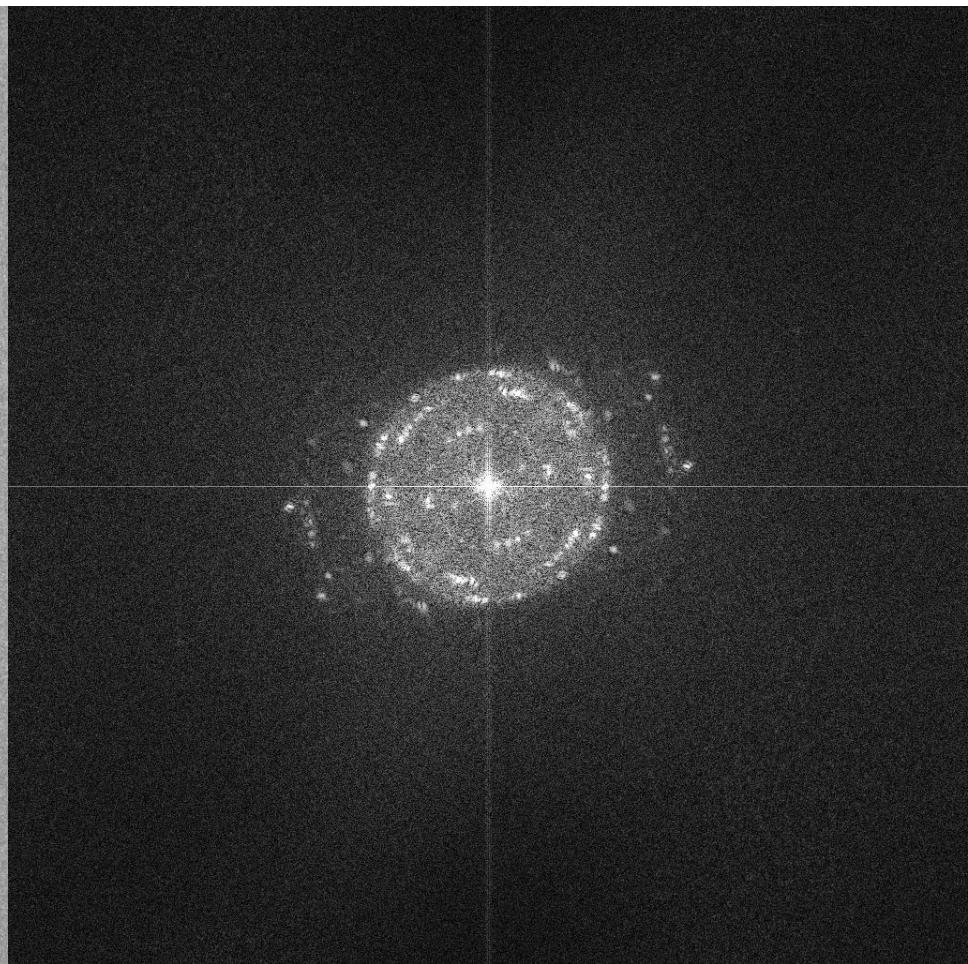
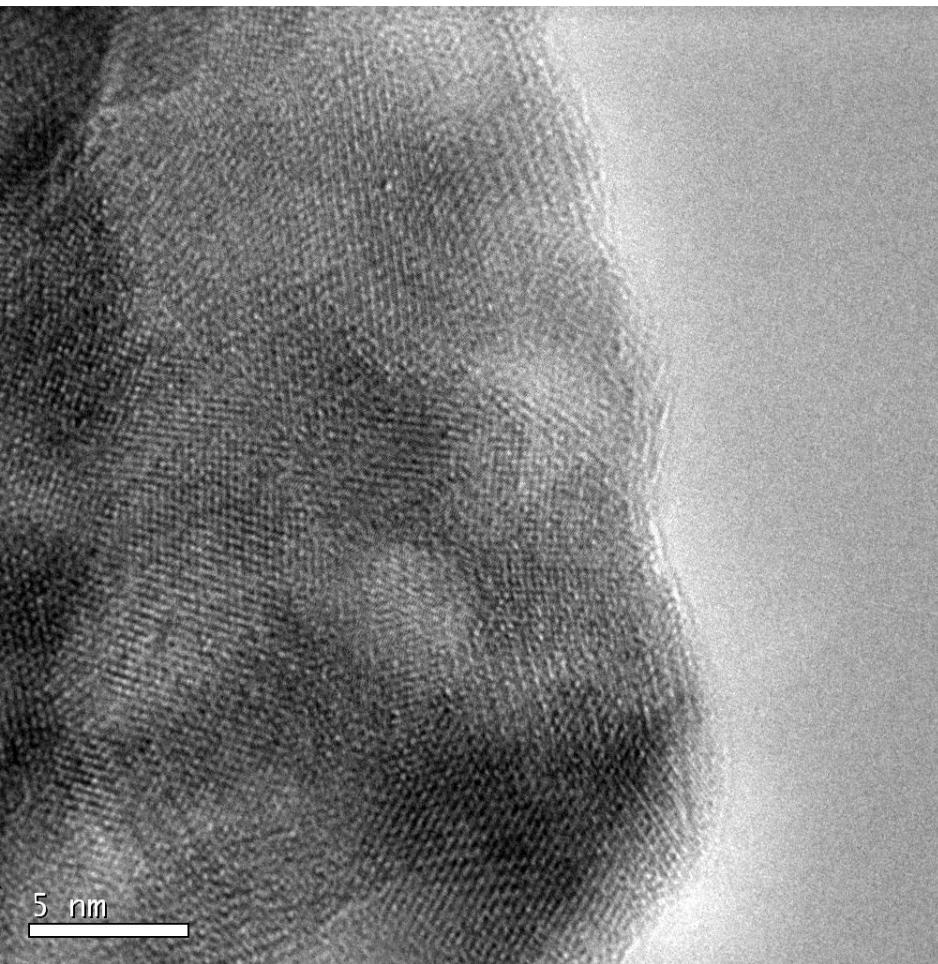


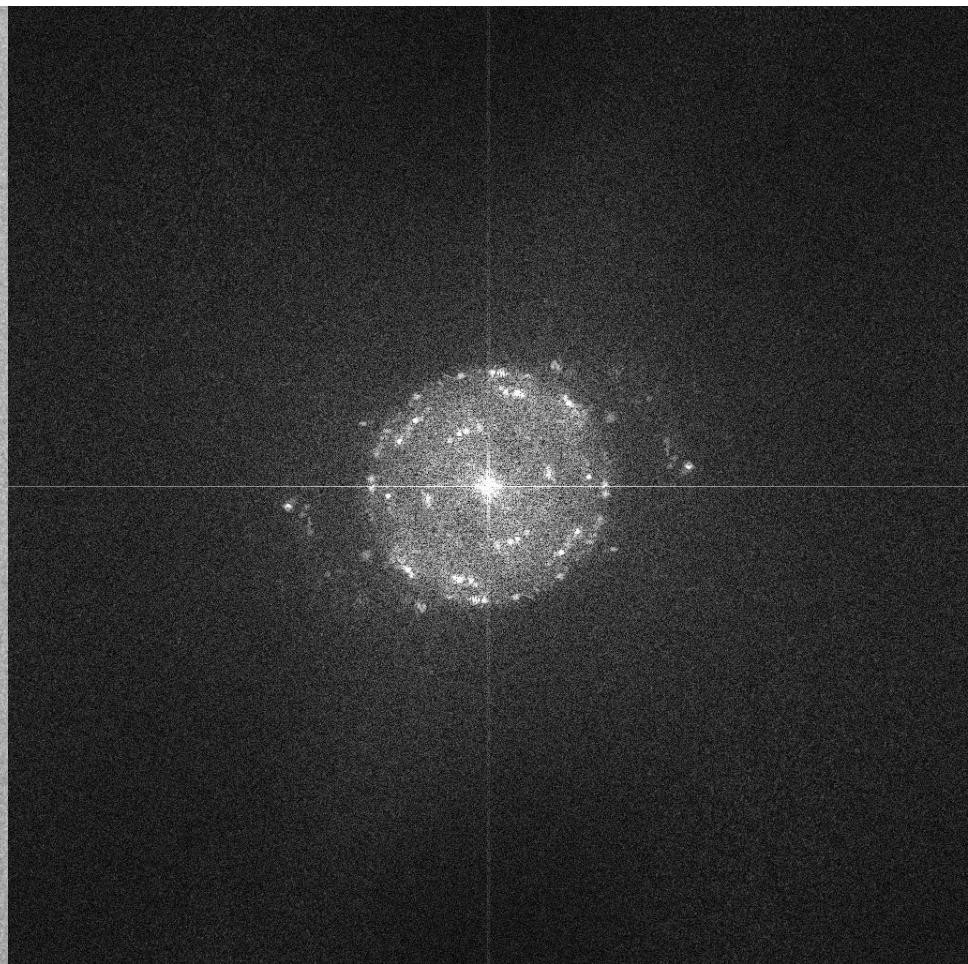
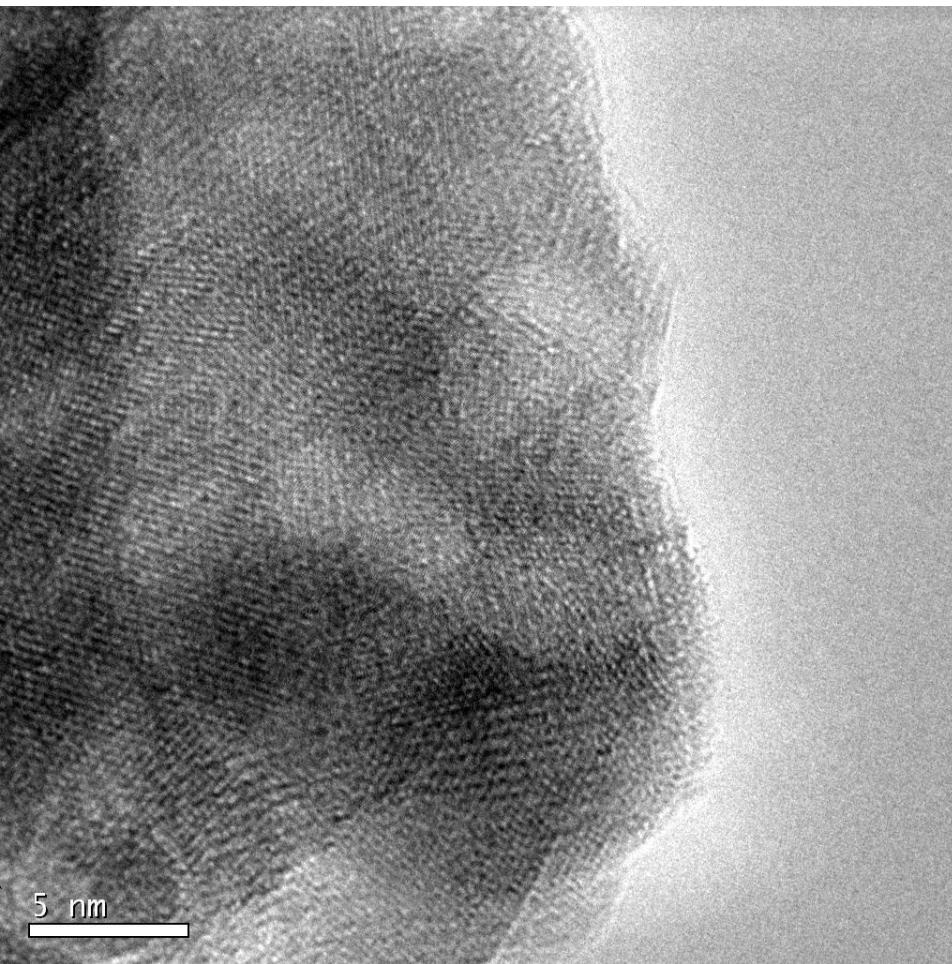
5 nm

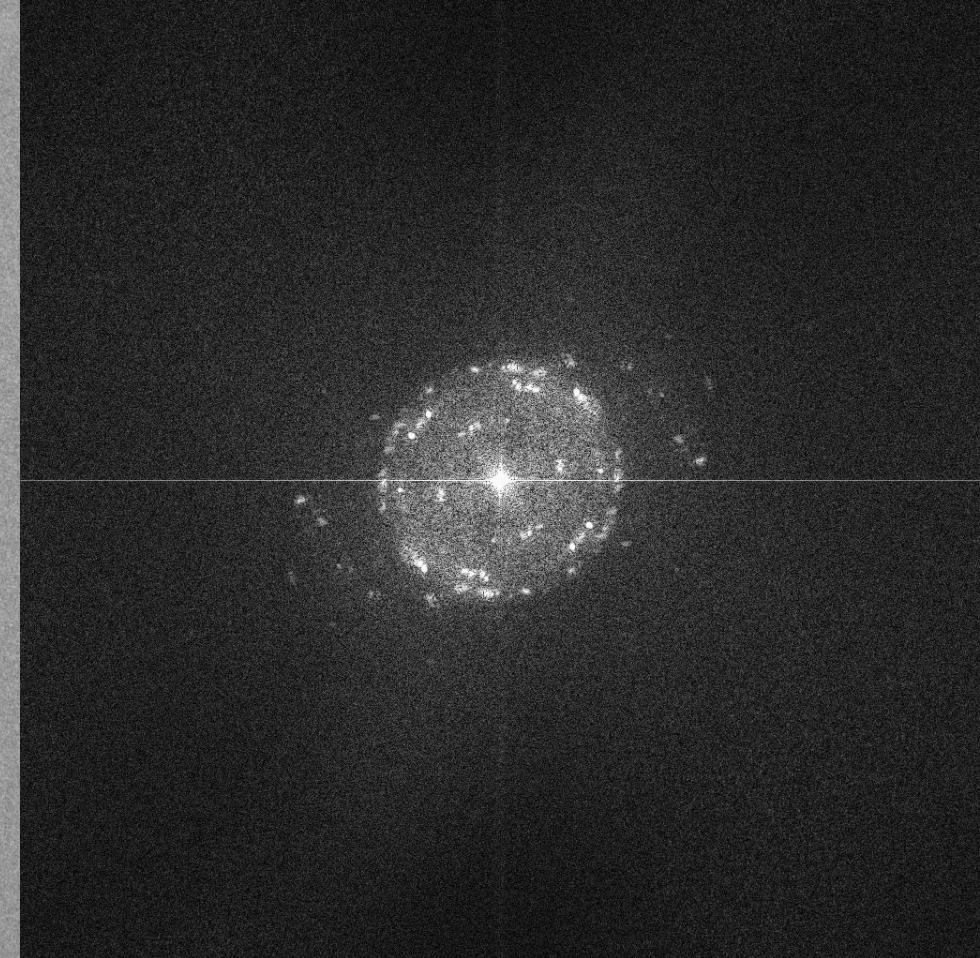
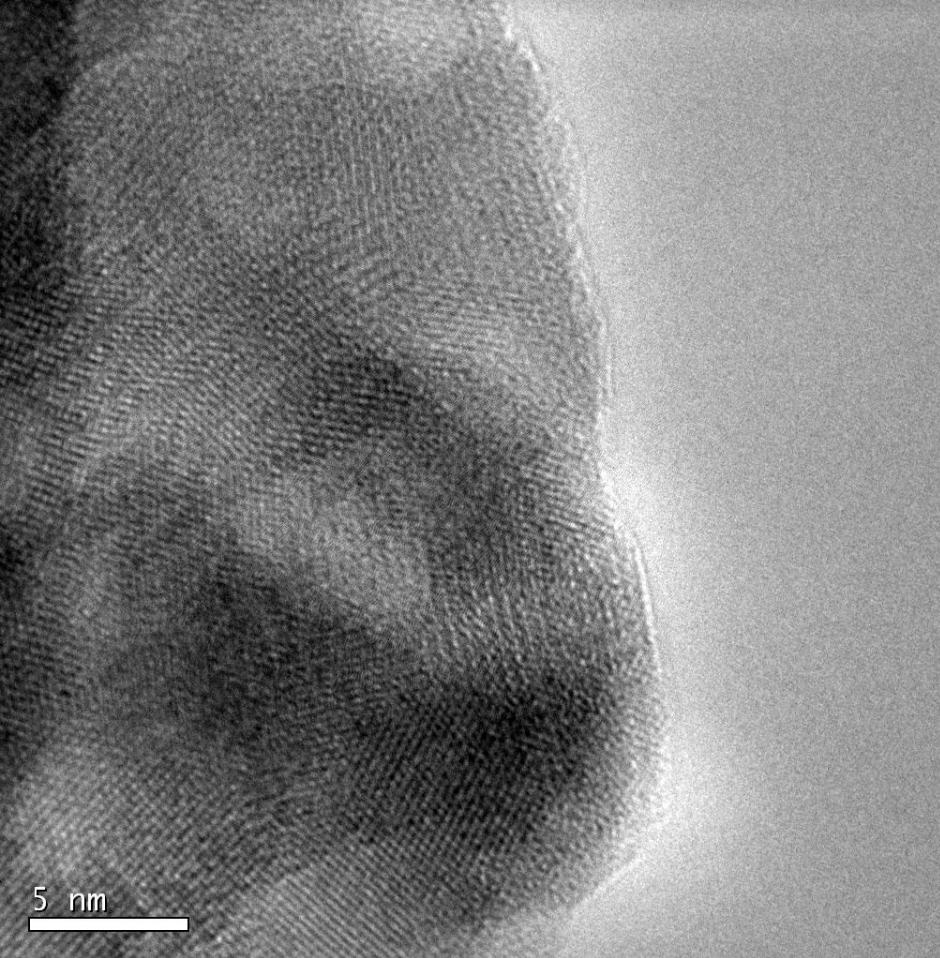


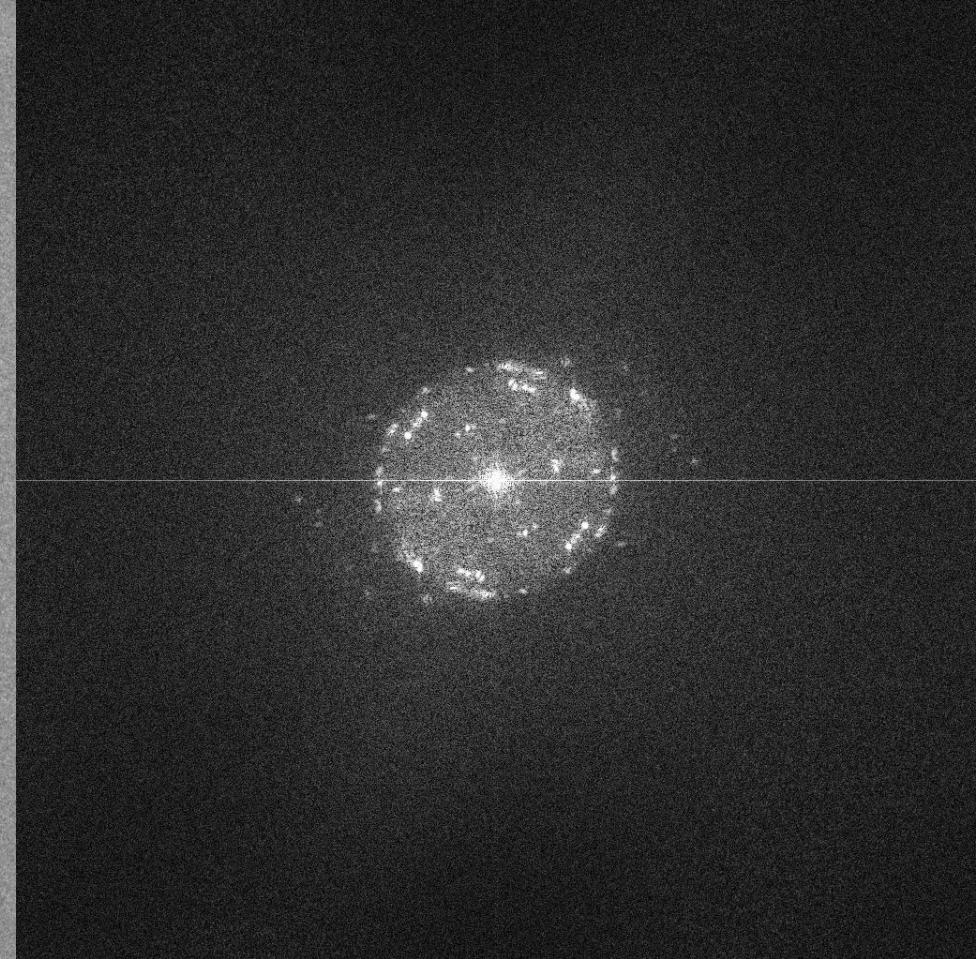
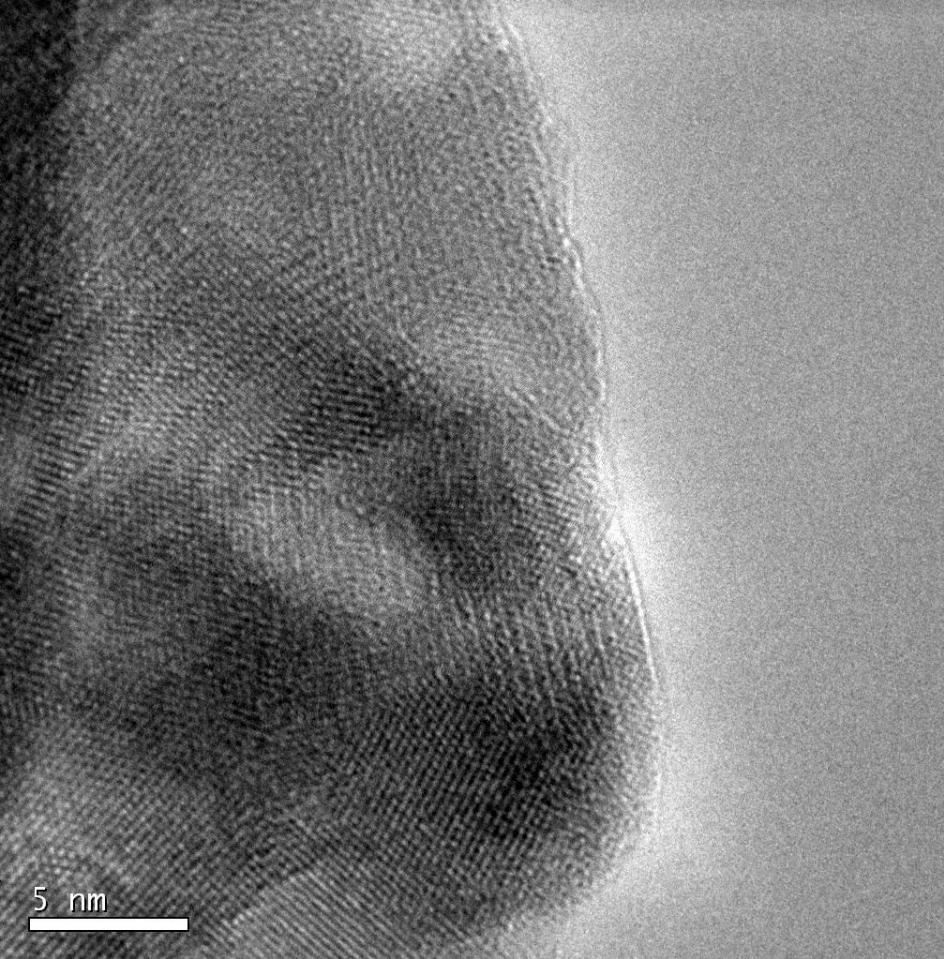












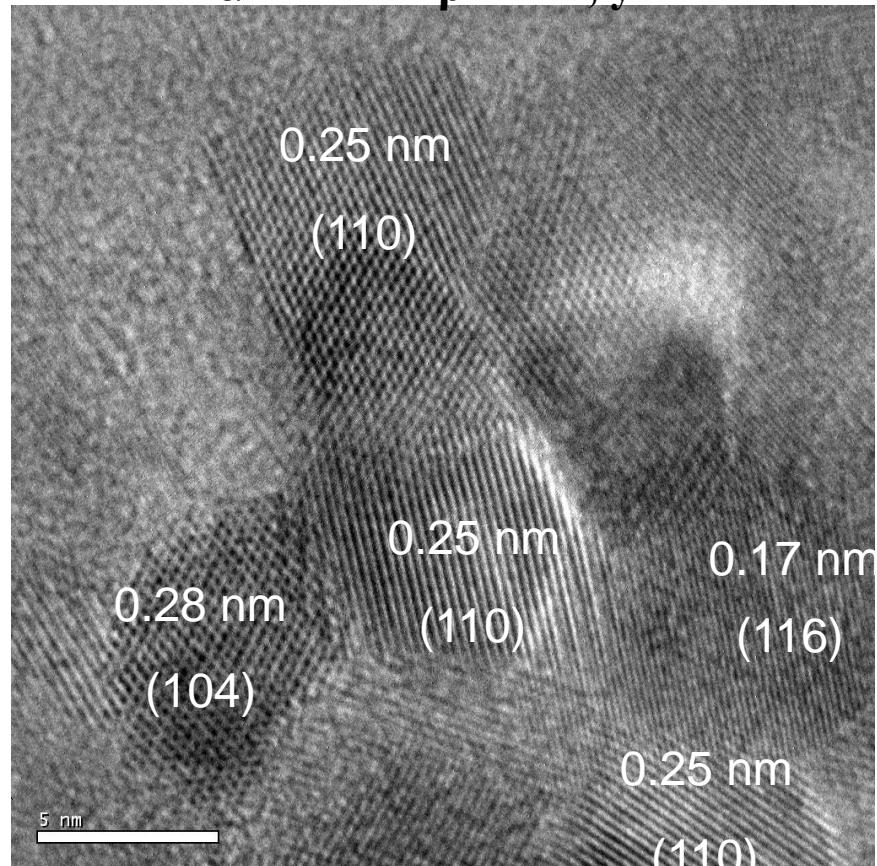
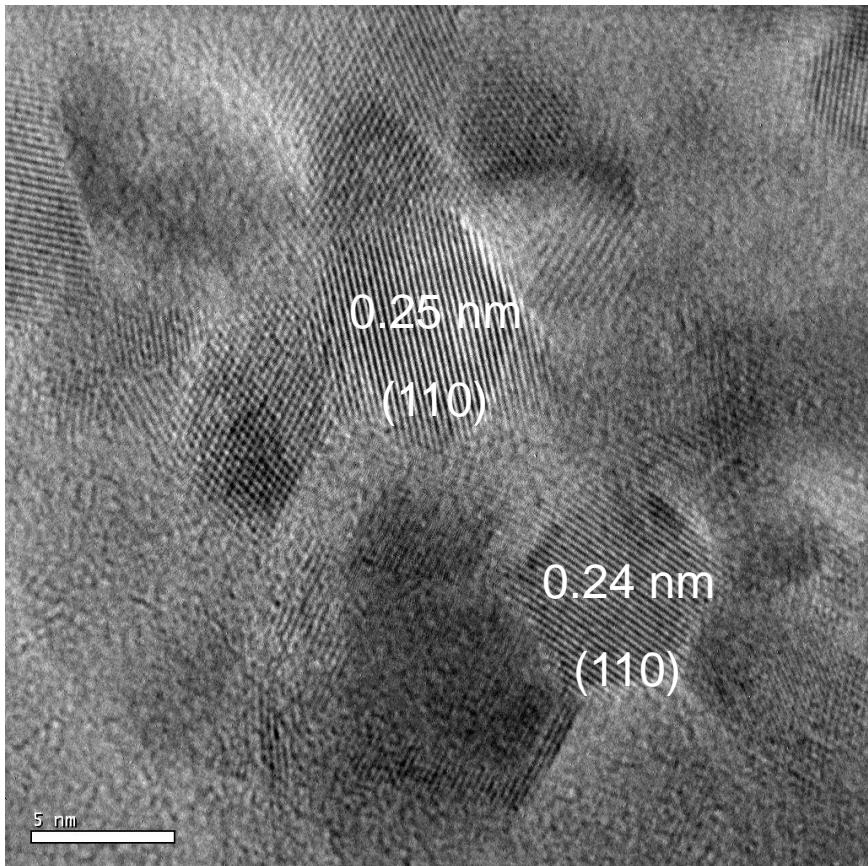
Ferrihydrite: 0.22 nm, 0.25 nm

HRTEM images of initial material

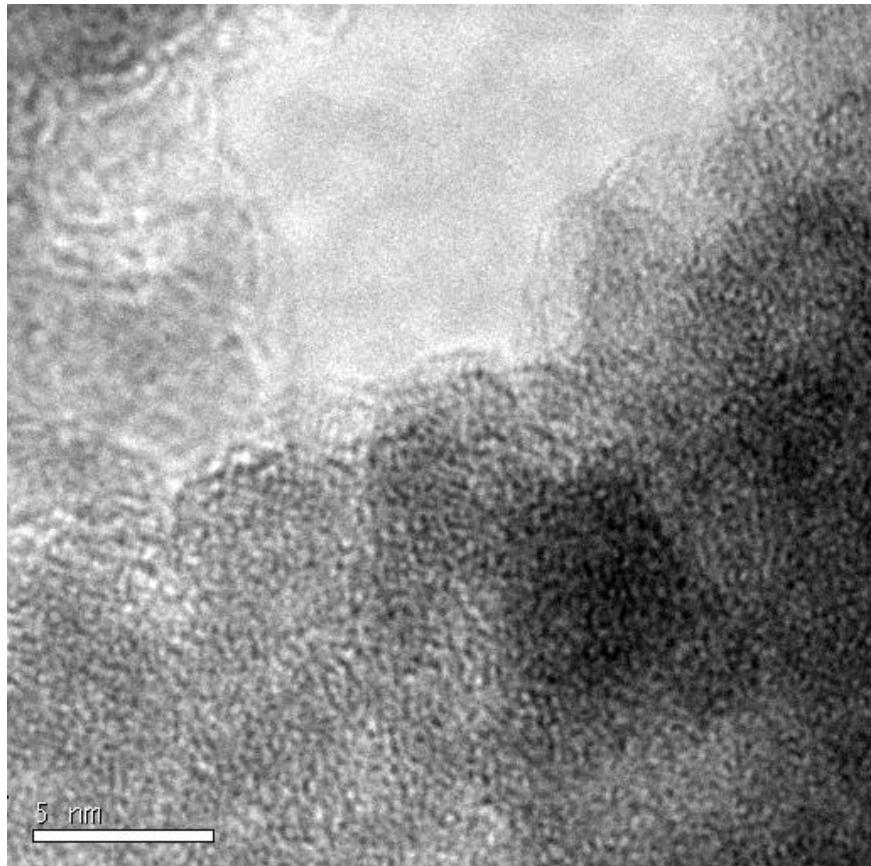
PCPDF No. 29-0712 (Hexagonal)

$a = 5.08$, $b =$, $c = 9.4$

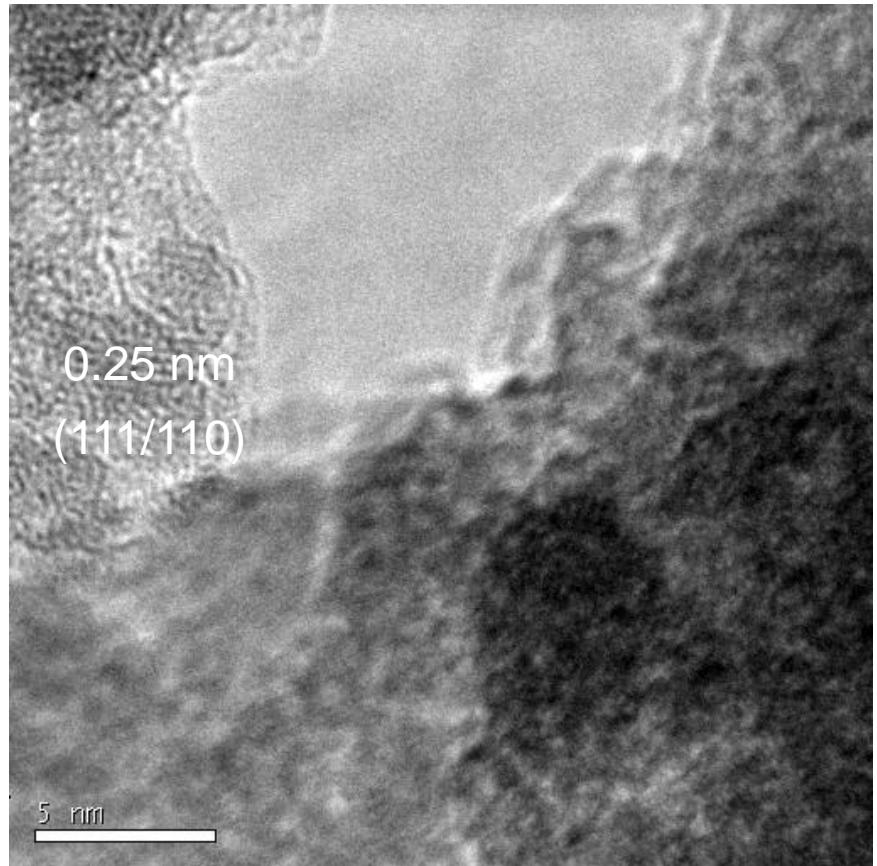
$\alpha =$, $\beta =$, $\gamma =$



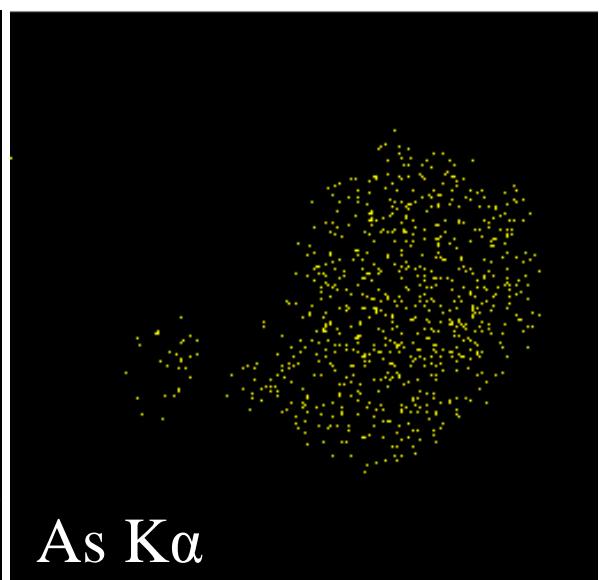
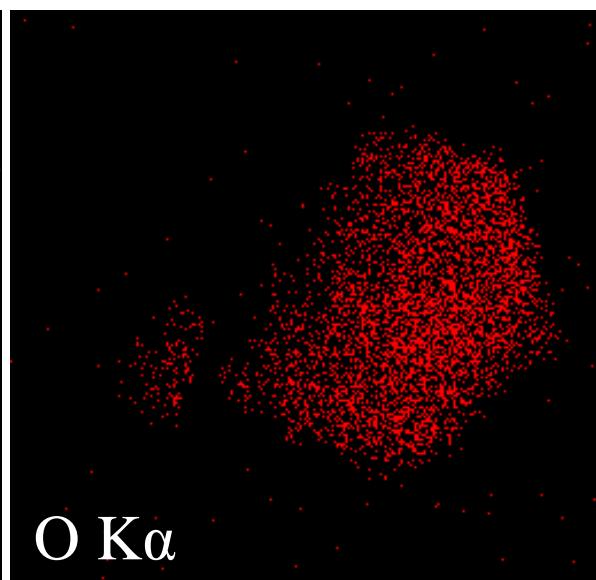
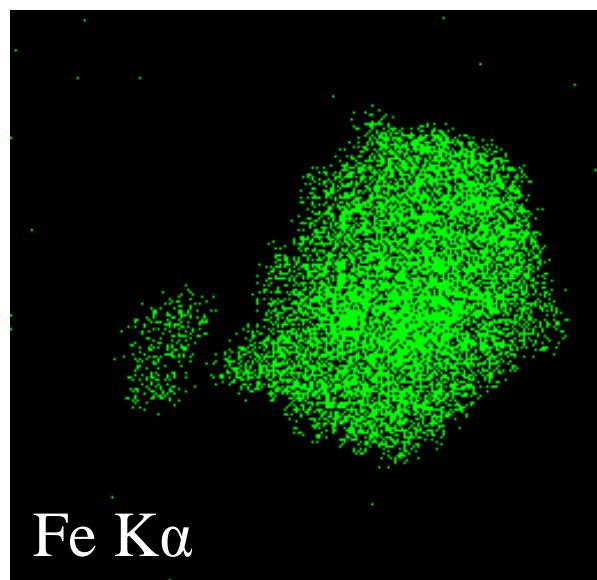
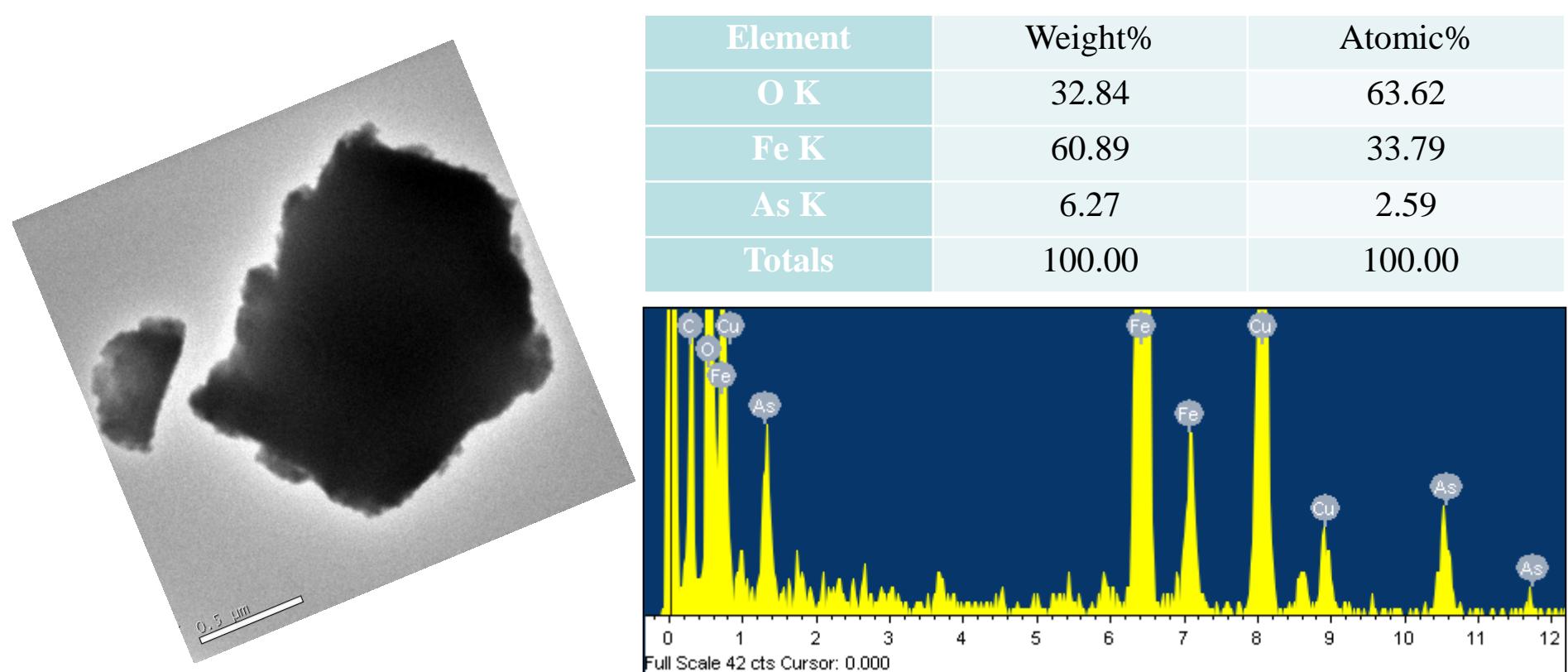
HRTEM images of As(V) adsorbed (or reacted) material [image from the same area at different depth of focus]

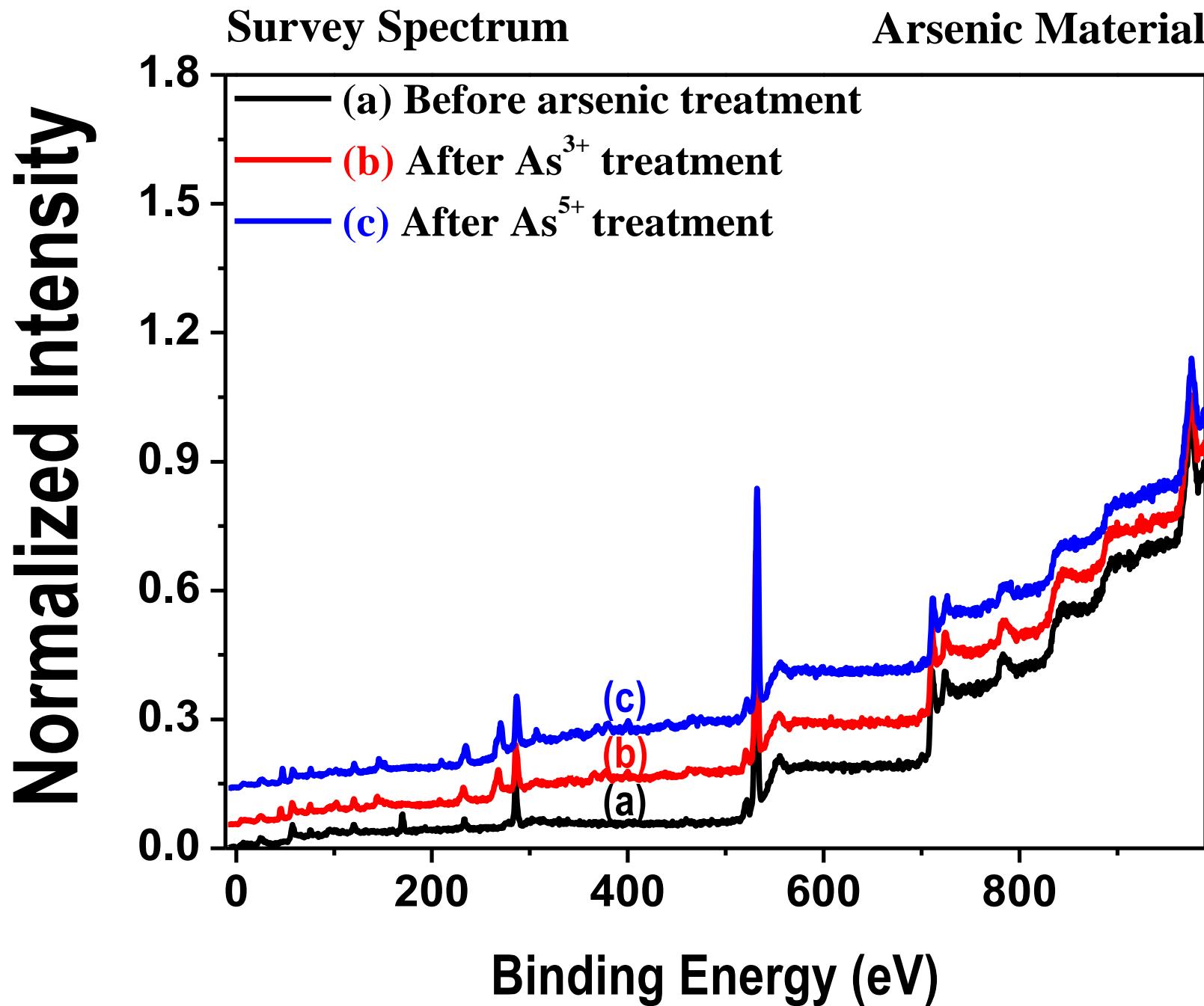


Goethite: α -FeOOH (0.25 nm)
PCPDF No. **81-0464 (Orthorhombic)**
 $a = 4.604$, $b = 9.959$, $c = 3.023$
 $\alpha = \quad$ $\beta = \quad$, $\gamma = \quad$

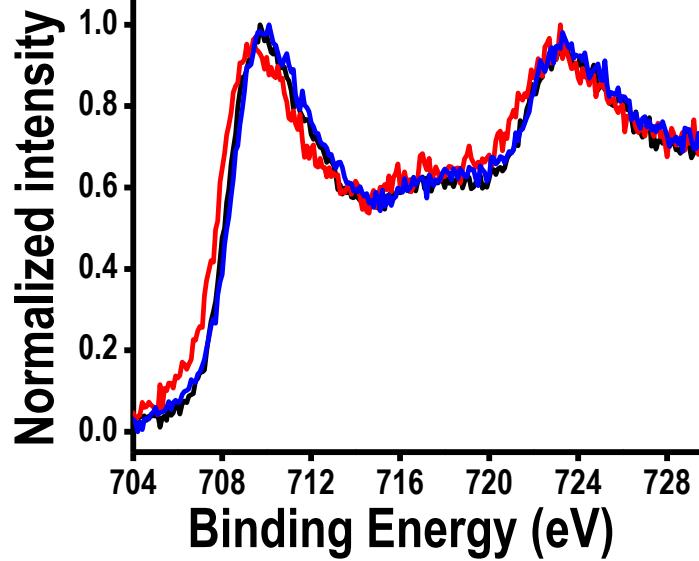
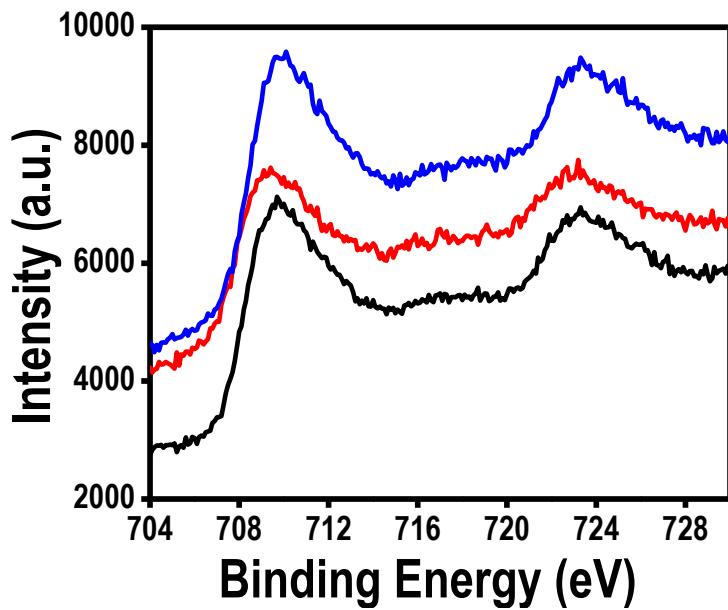


Ferrihydrite: 0.22 nm, 0.25 nm
PCPDF No. **29-0712 (Hexagonal)**
 $a = 5.08$, $b = \quad$, $c = 9.4$
 $\alpha = \quad$ $\beta = \quad$, $\gamma = \quad$

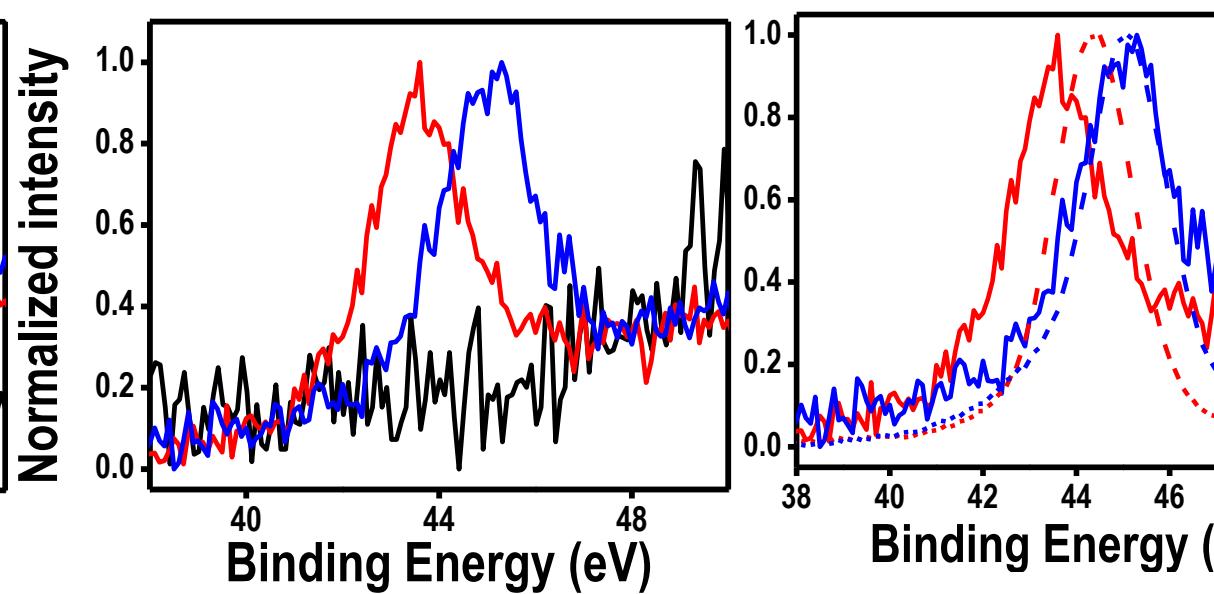
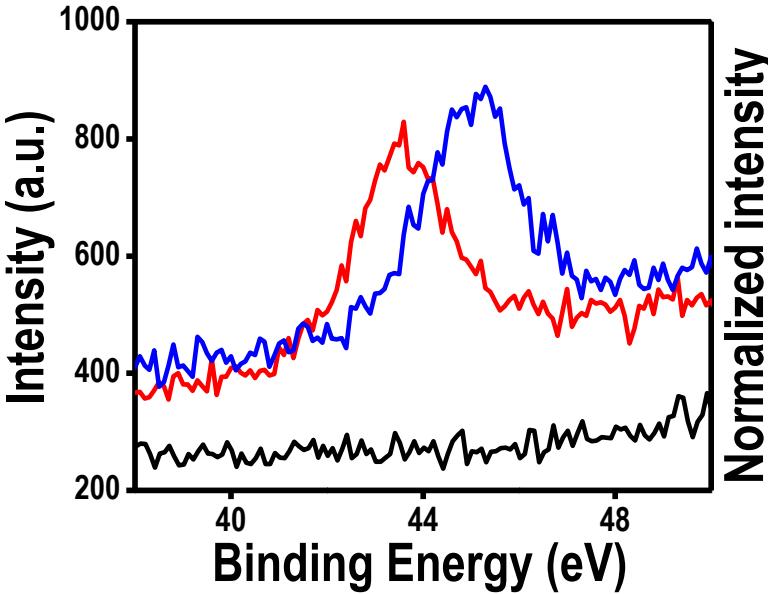




Iron 2p



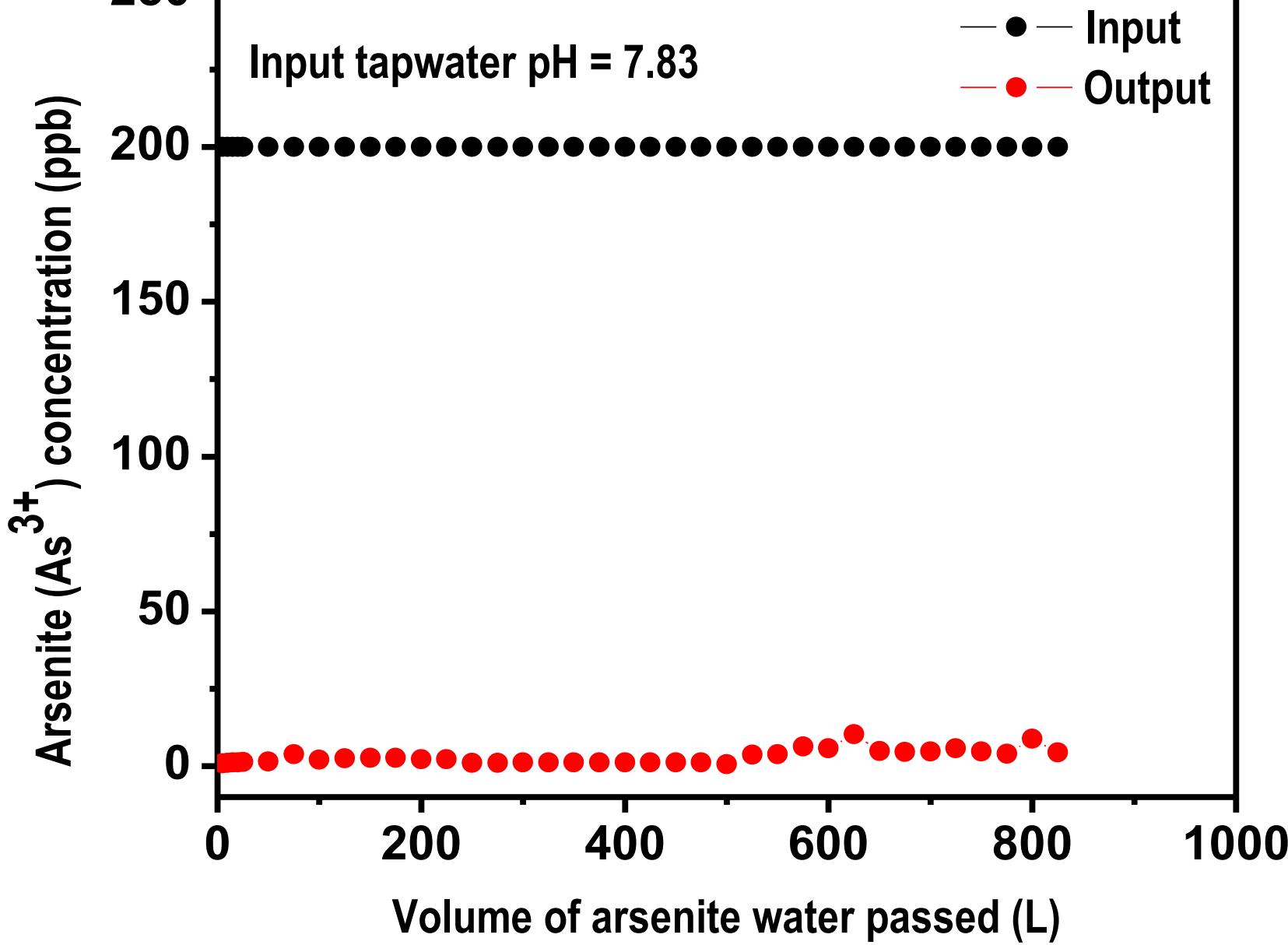
Arsenic 3d_{5/2}



*As*³⁺

As^{3+}

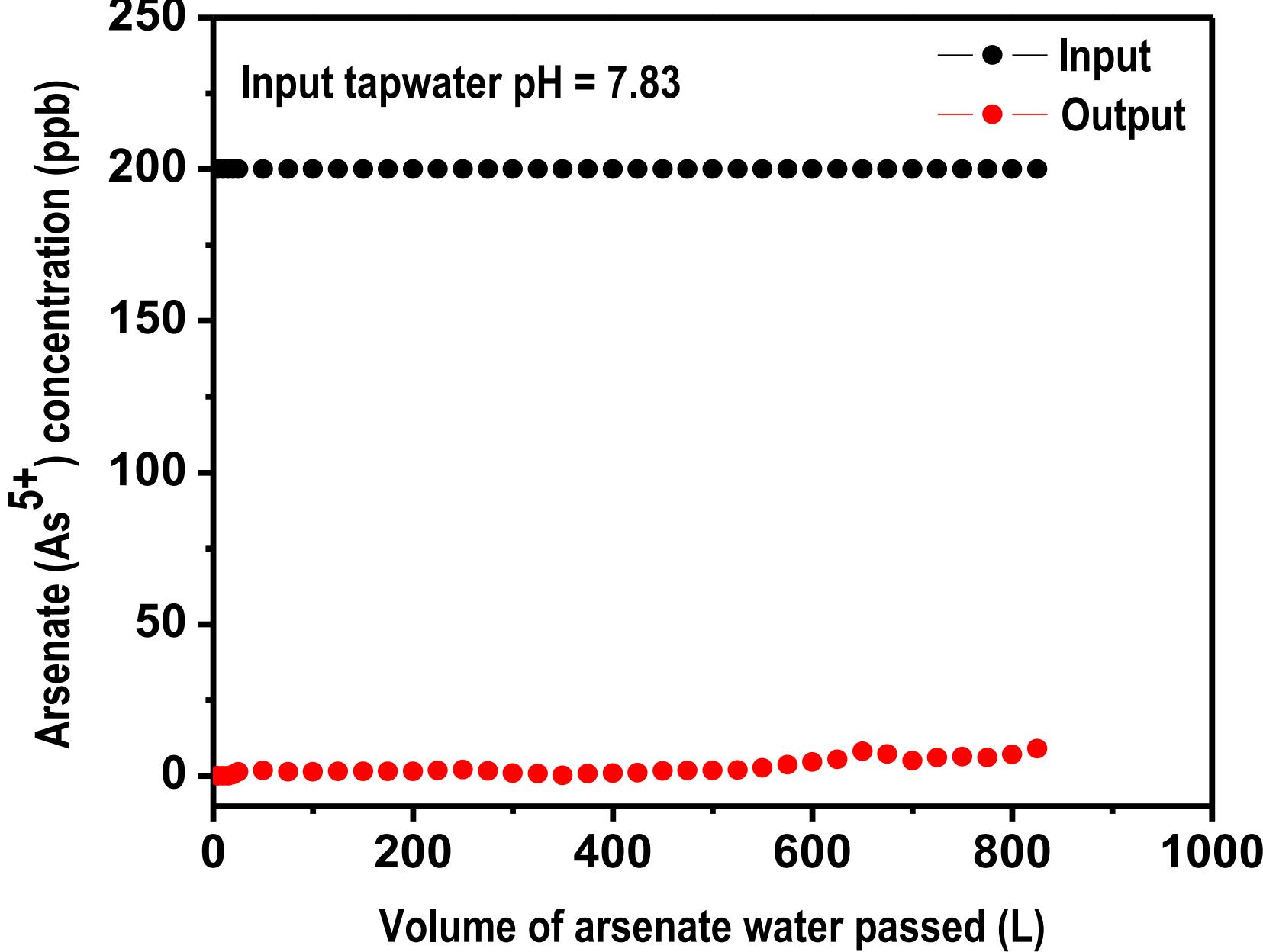
60g, 72 mesh and flow rate: 12-15 mL/min.



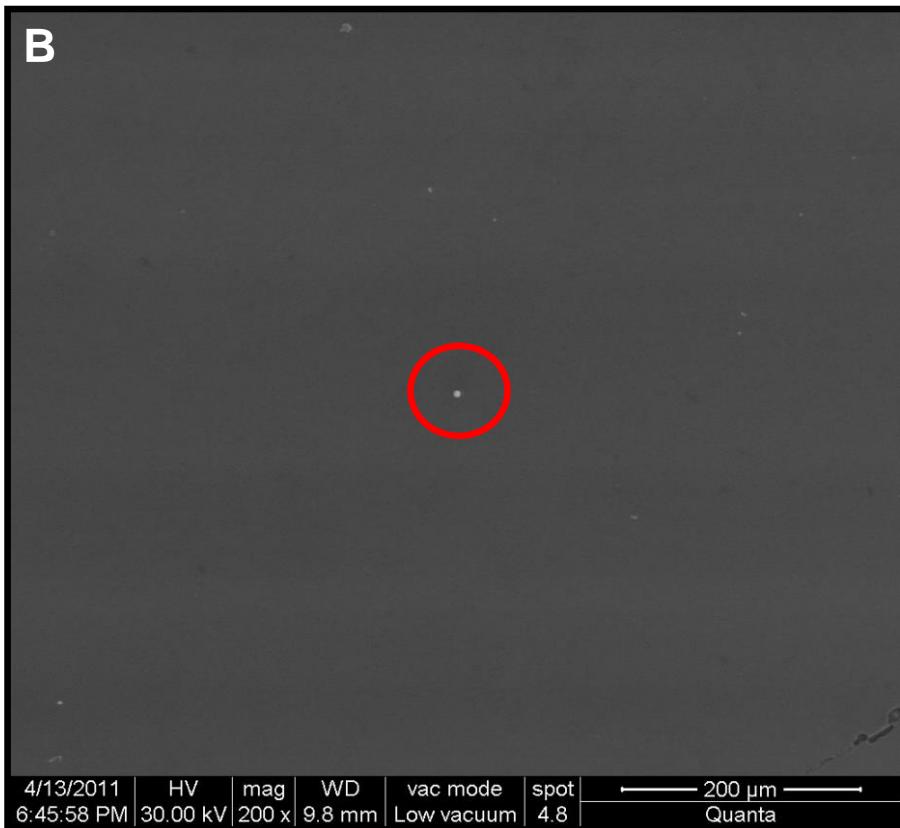
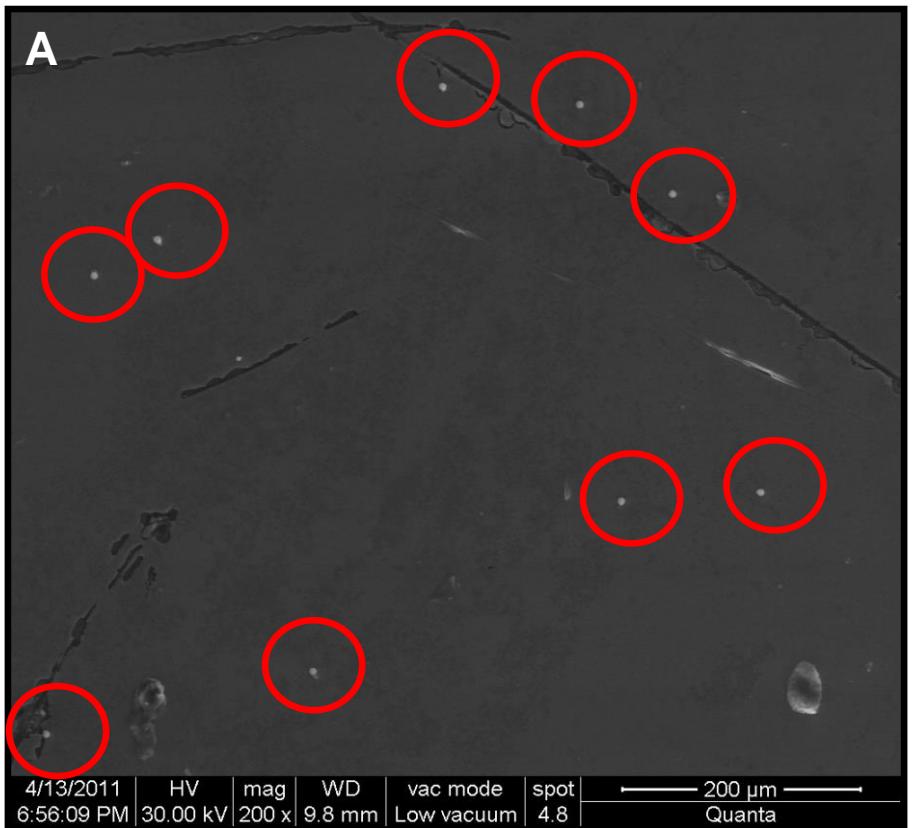
*As*⁵⁺

As^{5+}

60g, 72 mesh and flow rate: 12-15 mL/min.



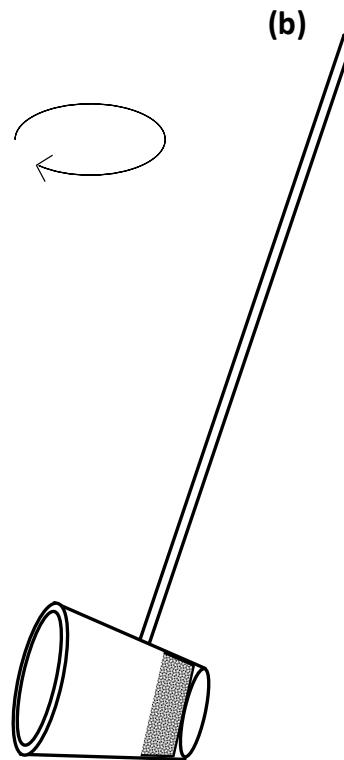
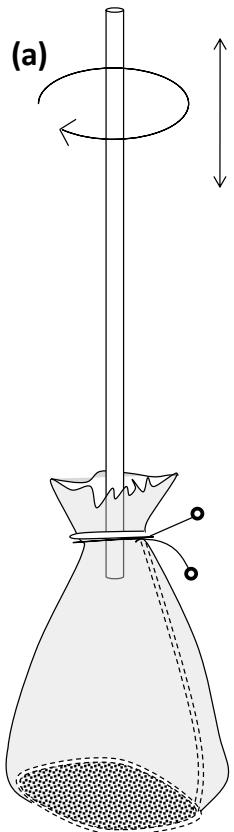
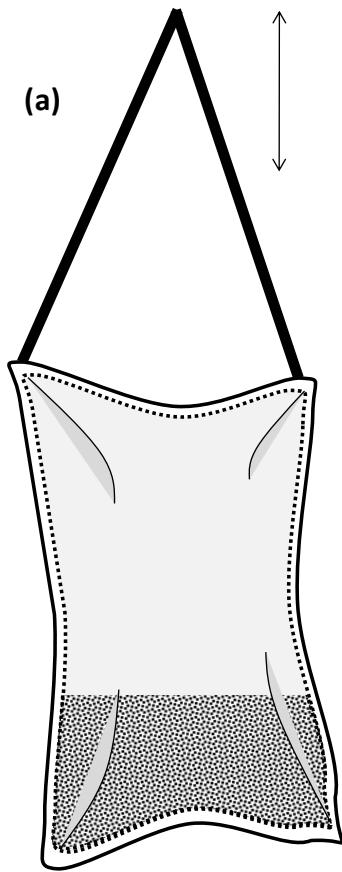
Cyst removal



Performance summary

Functional Parameters	NSF norms	NSF Standard	InnoNano's Product
Functional Parameters	Sand & Sediment Turbidity: 11 NTU to <0.5 NT	NSF/ANSI 53	✓
	Chlorine 2 ppm to <0.5 ppm	NSF/ANSI 42	✓
	Bacteria 105 CFU/ml to absent	NSF/ANSI 55	✓
	Virus 103 PFU/ml to absent	NSF/ANSI 55	✓
	Cyst 50000/ml to <2/ml	NSF/ANSI 53	✓
	Pesticides Chloroform: 300 ppb to <15	NSF/ANSI 53	✓
	Iron 2 ppm to <0.2 ppm		✓
	Lead 150 ppb to 10 ppb	NSF/ANSI 53	✓
	Arsenic 300 ppb to 10 ppb	NSF/ANSI 53	✓
	Mercury 6 ppb to 2 ppb	NSF/ANSI 53	✓
TDS		Not applicable	X
Nitrate		Not applicable	X

Implementing technologies





AMRIT



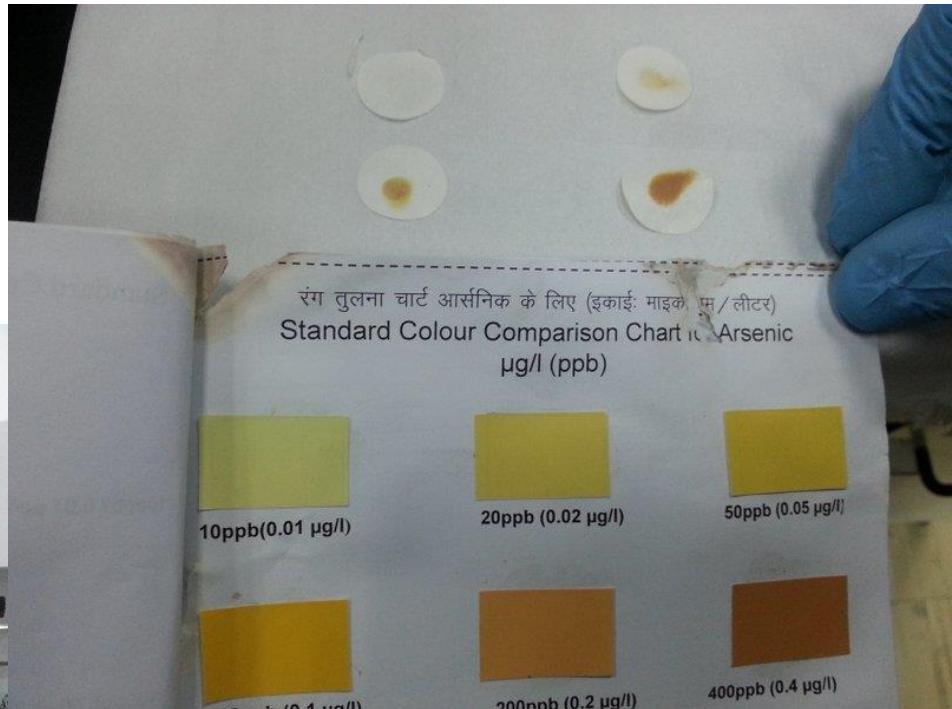
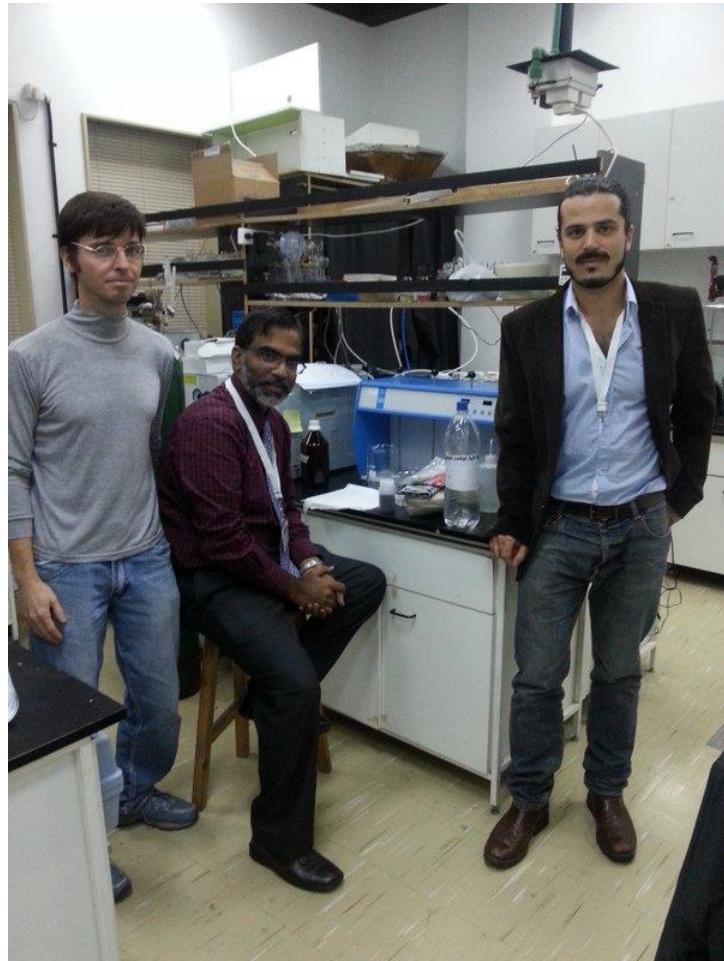


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DST Nano Mission









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Thank you

Department of Science and Technology

New Book

