



Kaifu Bian
2019 MRS Postdoc Award



Casey Karler



Brian Billstrand



Dr. Zaicheng Sun
UNM postdoc



Dr. Feng Bai
UNM postdoc



Dr. Huimeng Wu
SNL postdoc



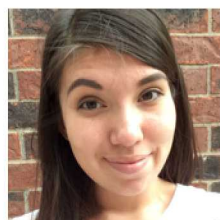
Dr. Bruce Burckel
SNL postdoc



Raid Haddad



Hattie Schunk



Leanne Alarid



Adrian Rodriguez
UNM student



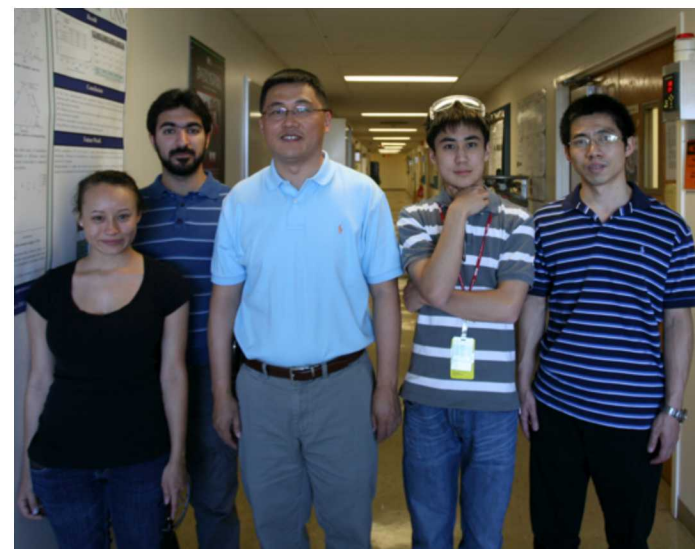
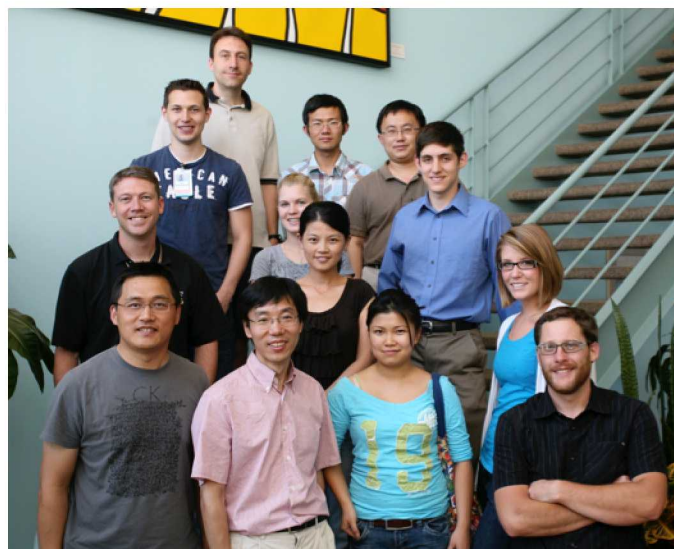
Adam Wright
UNM student



Eric Leve
UNM student



Samantha Schmitt
UNM student



Mentors and Collaborators



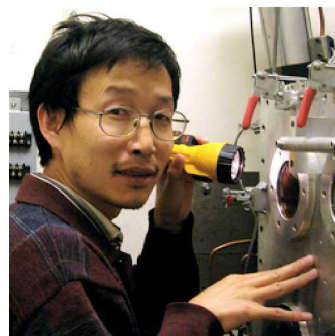
Gabriel Lopez

Univ. New Mexico



Jeff Brinker

Univ. New Mexico



Zhongwu Wang

Cornell Univ.



Prof. Dan Boye

Davidson College



Quanxi Jia

University at Buffalo

Sandia National Labs: Gary Grest, Matthew Lane, Sheng Liu, Willie Luk, Igor Brener, Dale Huber, Mike Sinclair, Ping Lu, Eric Coker, Paul Clem, David Rosenberg, Jack Wise, Tommy Ao, Randy Hickman, Xiaowang Zhou, Chris Forsyth, Terry Aselage, Mike Valley, Randy Schunk, Sean Hearne, Bill Hammetter Alan Hurd, Julia Philips

Cornell Univ.: Road Hoffman, Xin Huang

Univ. Texas, Arlington: Jeffrey P. Liu, Weidong Zhou, Dune Dimos

MIT: Ju Li, Wenbin Li

Georgia Tech.: Younan Xia, Dong Qin

Univ. Akron: Yu Zhu

Argonne National Lab: Zhang Jiang, Jin Wang

Lockheed Martin Co.: Earl Stromberg

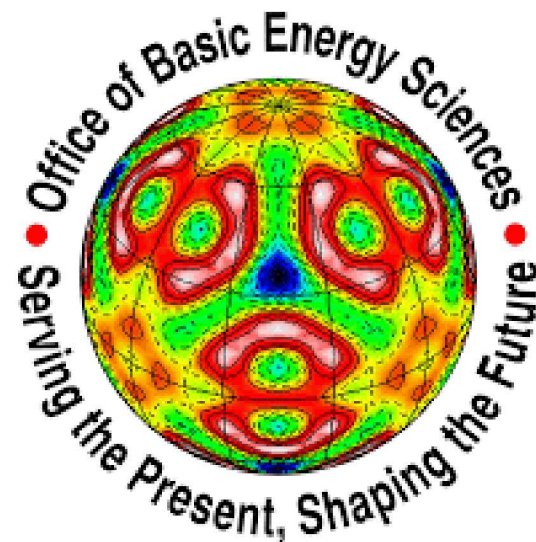
Univ. New Mexico: Michael Wilson, Ying-Bing Jiang, Wei Wang, Kevin Malloy

Brookhaven National Lab: Ruipeng Li



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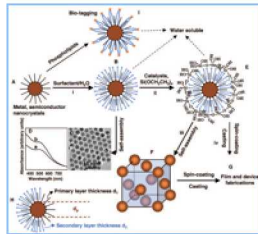
Self-Assembly of Functional Nanoscale Materials

Hongyou Fan

Distinguished Member of Technical Staff, Sandia National Laboratories

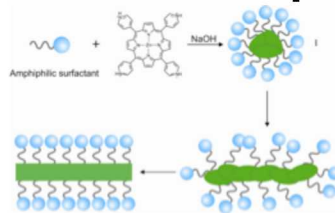
National Laboratory Professor, University of New Mexico

1. Surfactant-assisted nanoparticle self-assembly and optical coatings



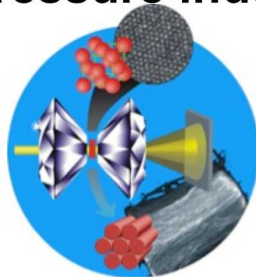
- Synthesis of water-soluble and biocompatible nanoparticles
- Fabrication of robust ordered nanoparticle films
- Applications: optical coatings and bio-applications

2. Confined cooperative self-assembly of photoactive nanostructures

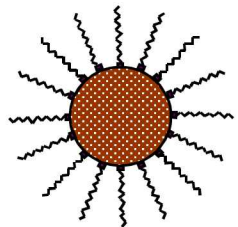


- Formation of 1-3D well-defined porphyrin nanocrystals
- Unique optical and electronic properties
- Photocatalytic synthesis

3. Pressure induced nanoparticle assembly

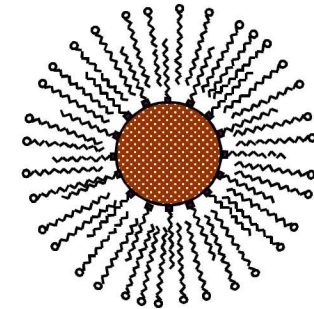


- Pressure induced phase separation in atomic and meso
- Pressure induced nanoparticle coalescence and fabrication
- Pressure induced nanoparticle optical coupling

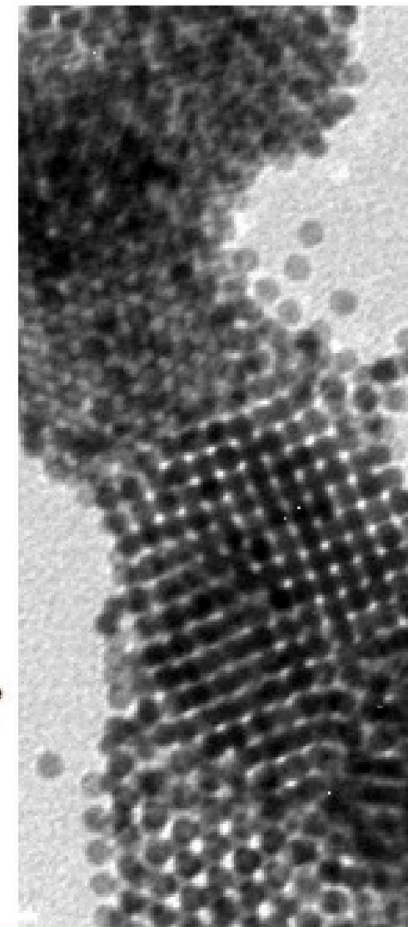
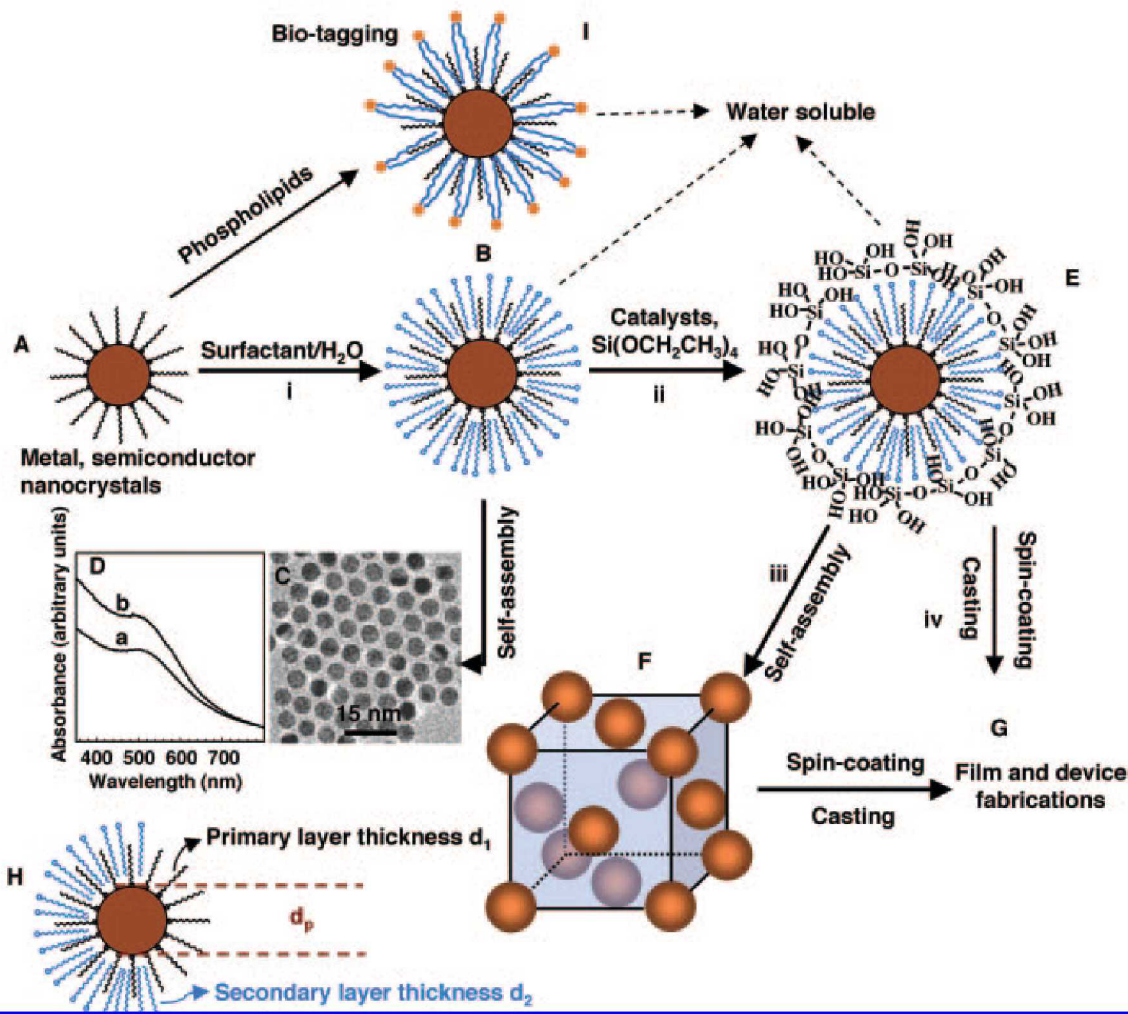
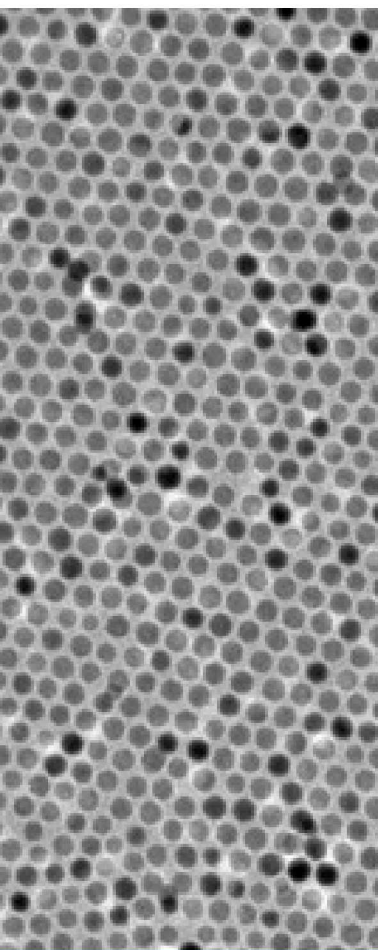


Hydrophobic

1. Surfactant-Assisted Nanoparticle Self-Assembly and Optical Coatings



Water soluble



Optical Coatings: Opportunities and Challenges

Sputtering and CVD has produced high performance of optical and semiconductor applications, but this performance comes at a significant cost, impacting budget, logistics, and environmental, safety, and health areas.

Disadvantages:

- High temperature
- High vacuum
- Capital equipment
- Toxic precursors
- Limited work place



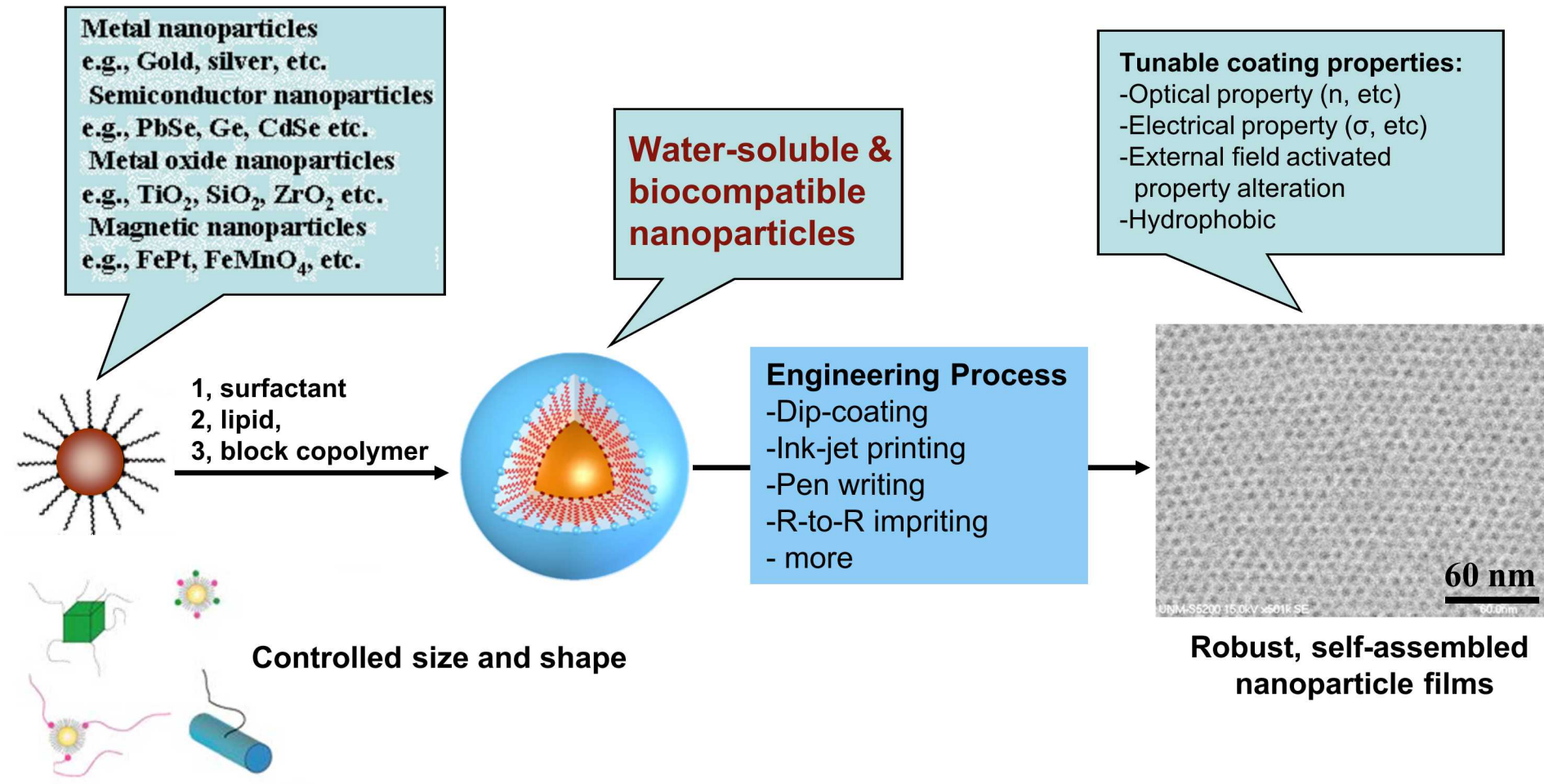
Challenges:

- Low temperature
- Ambient conditions
- Simple process
- Green chemistry
- In-field application

Motivation: A simple and mild coatings process is needed for applications for delicate, large foot print, in-field coatings.

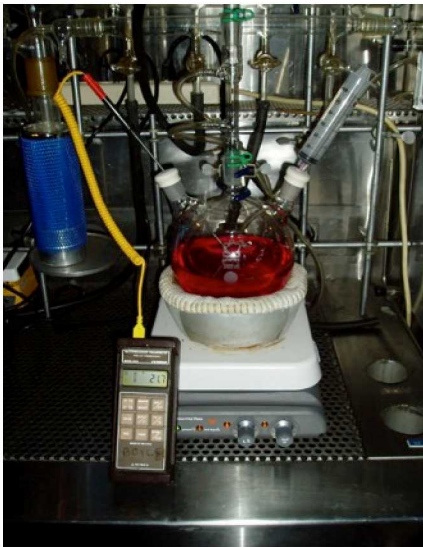
Soft Self-Assembly to Functionalize Nanoparticles to Fabricate Robust Nanoparticle Coatings

Soft self-assembly is a simple, economical process, enables the development of unique optical, electronic, and magnetic nanoparticle thin films in mild conditions, with architectures and properties unattainable by any other processing methods (CVD, sputtering, etc).



Synthesis of Nanoparticles

(1) Nucleation and growth at high temperature



Semiconductor nanocrystals:

- CdSe, CdS, etc.
- PbS, PbSe, etc.

Magnetic nanocrystals

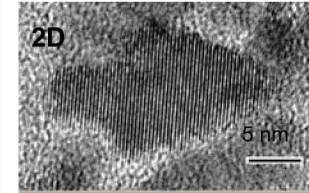
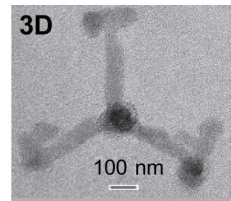
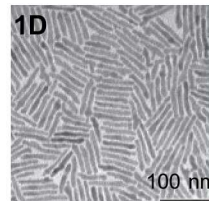
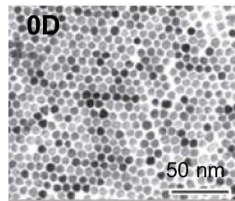
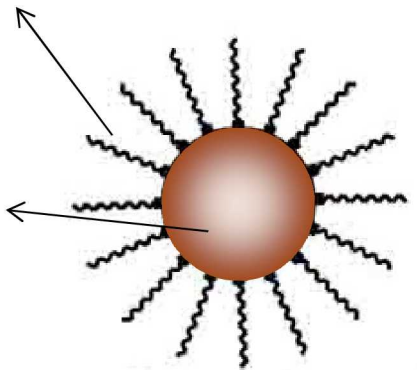
- FePt, FeMnO₄, Fe₃O₄

Perovskite nanocrystals:

- Cs₄PbBr₆

Organic ligand
hydrophobic

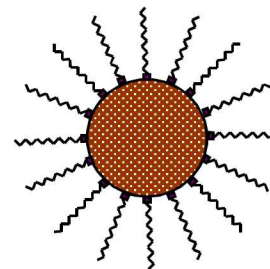
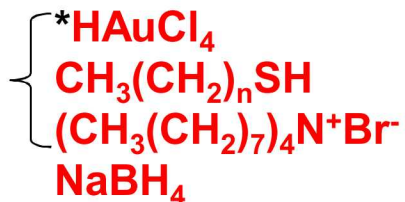
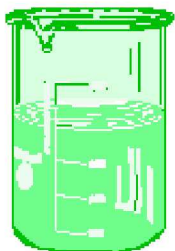
Core



Murray, CB et al. *Annu. Rev. Mater. Sci.* **2000**, 30, 545-610.

Yin, Y., et al., *Nature*, v.437, 664-670, 2005.

(2) Synthesis of metal nanocrystals

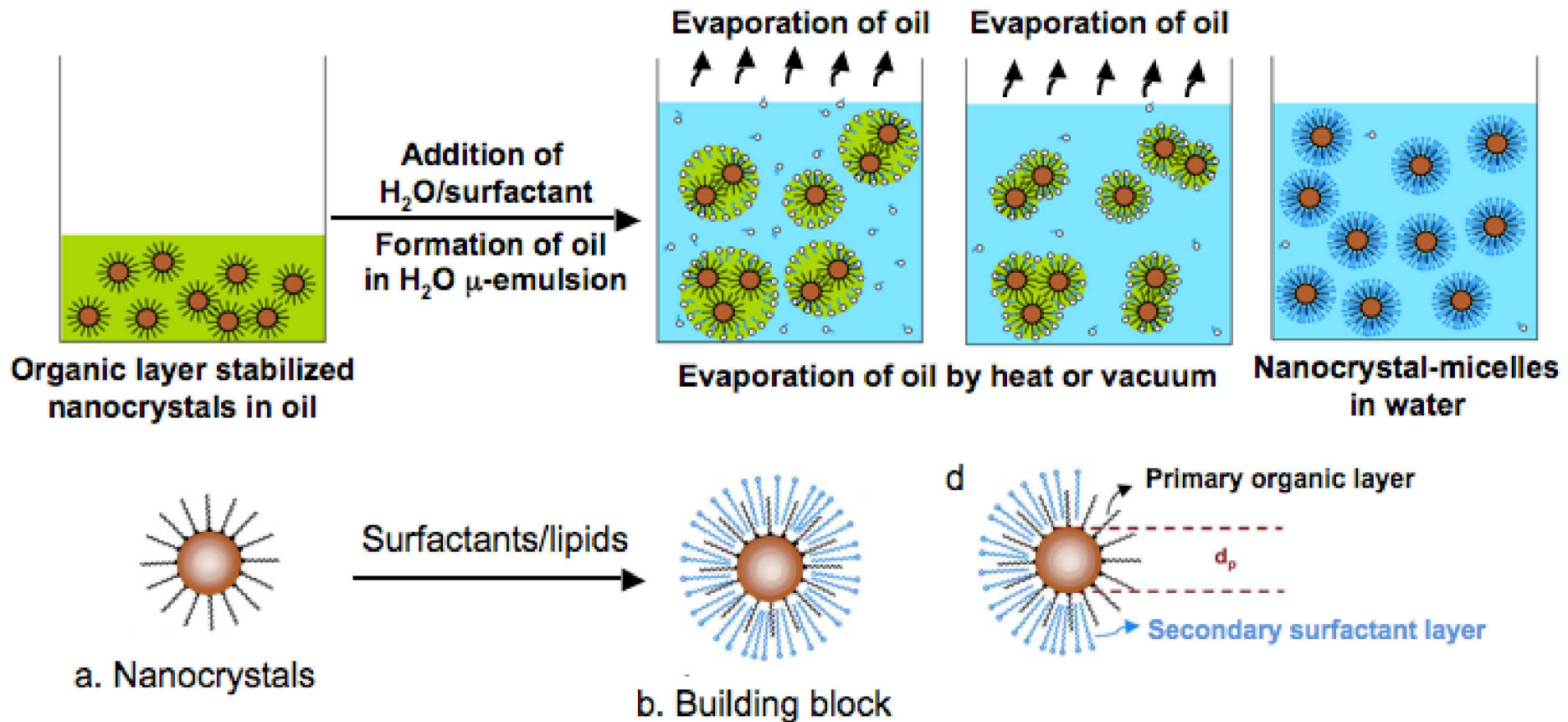


Metal nanoparticles

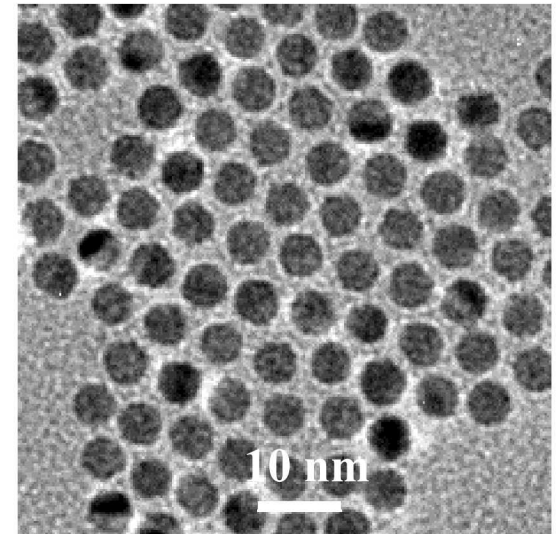
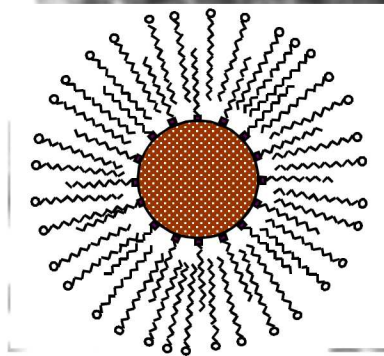
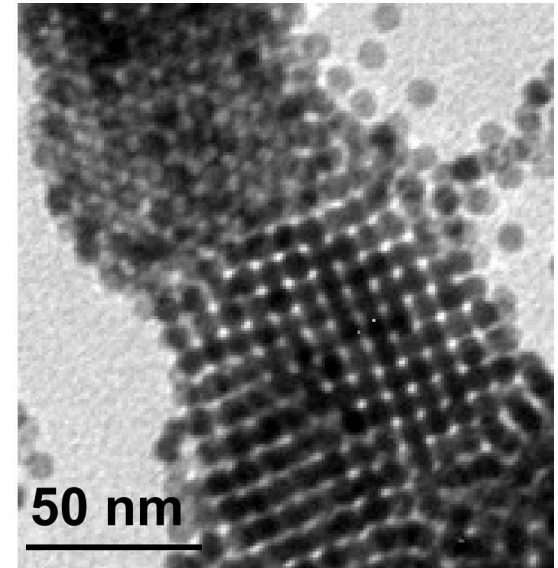
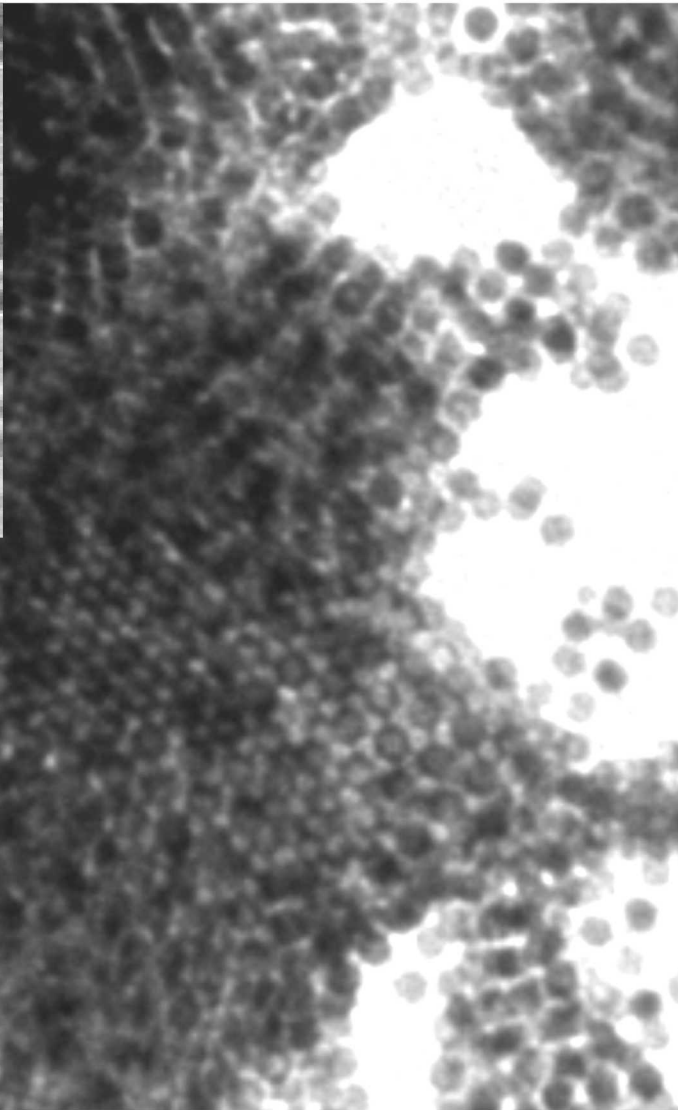
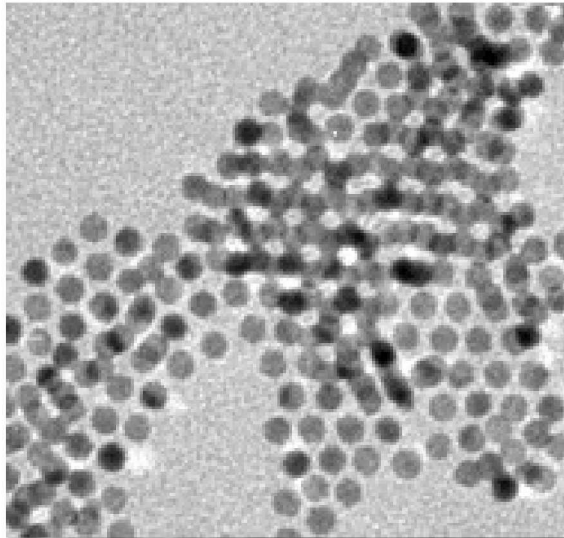
- Au, Ag, Pt, etc.

* Brust, M., et al. *J. Chem. Soc.-Chem. Comm.* 7, 801 - 802 (1994).

Formation of Self-Assembled Nanoparticle Micelles

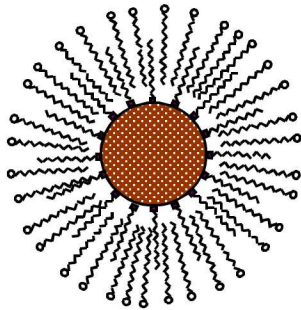


Self-Assembly of Gold Nanoparticle-Micelles from Water Phase

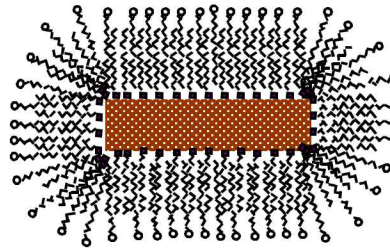


Nanoparticle Micelles with Different Shapes

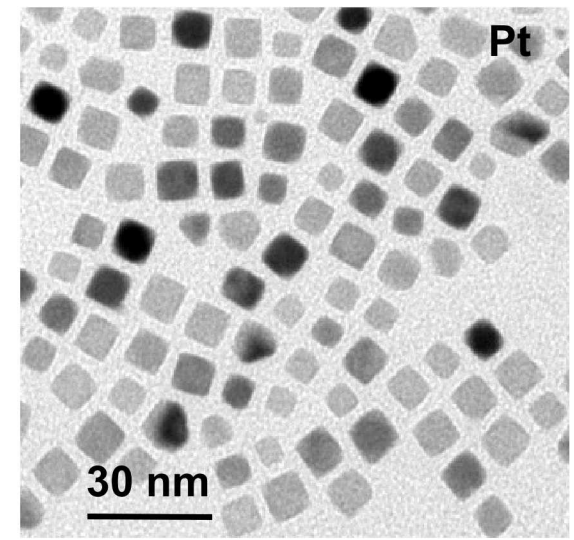
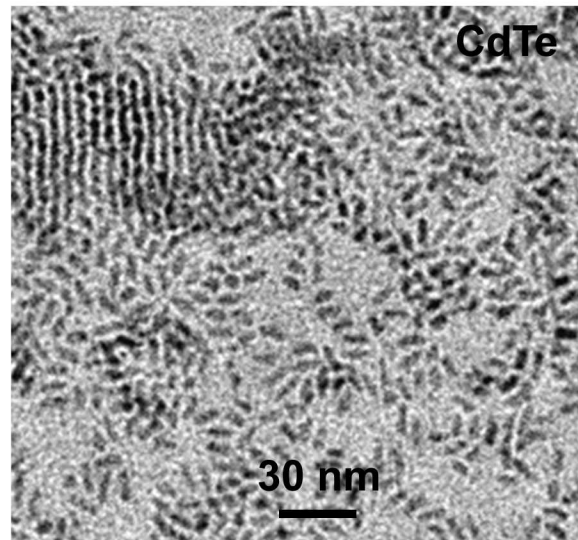
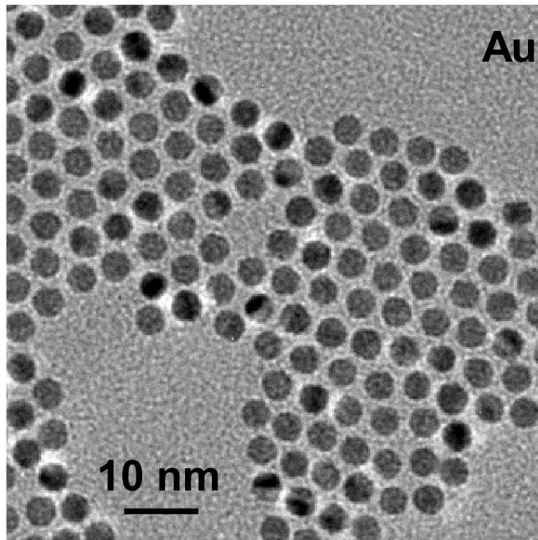
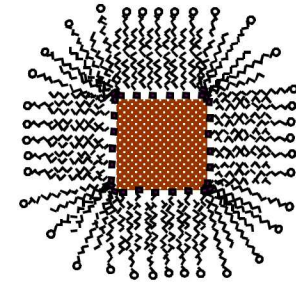
Sphere



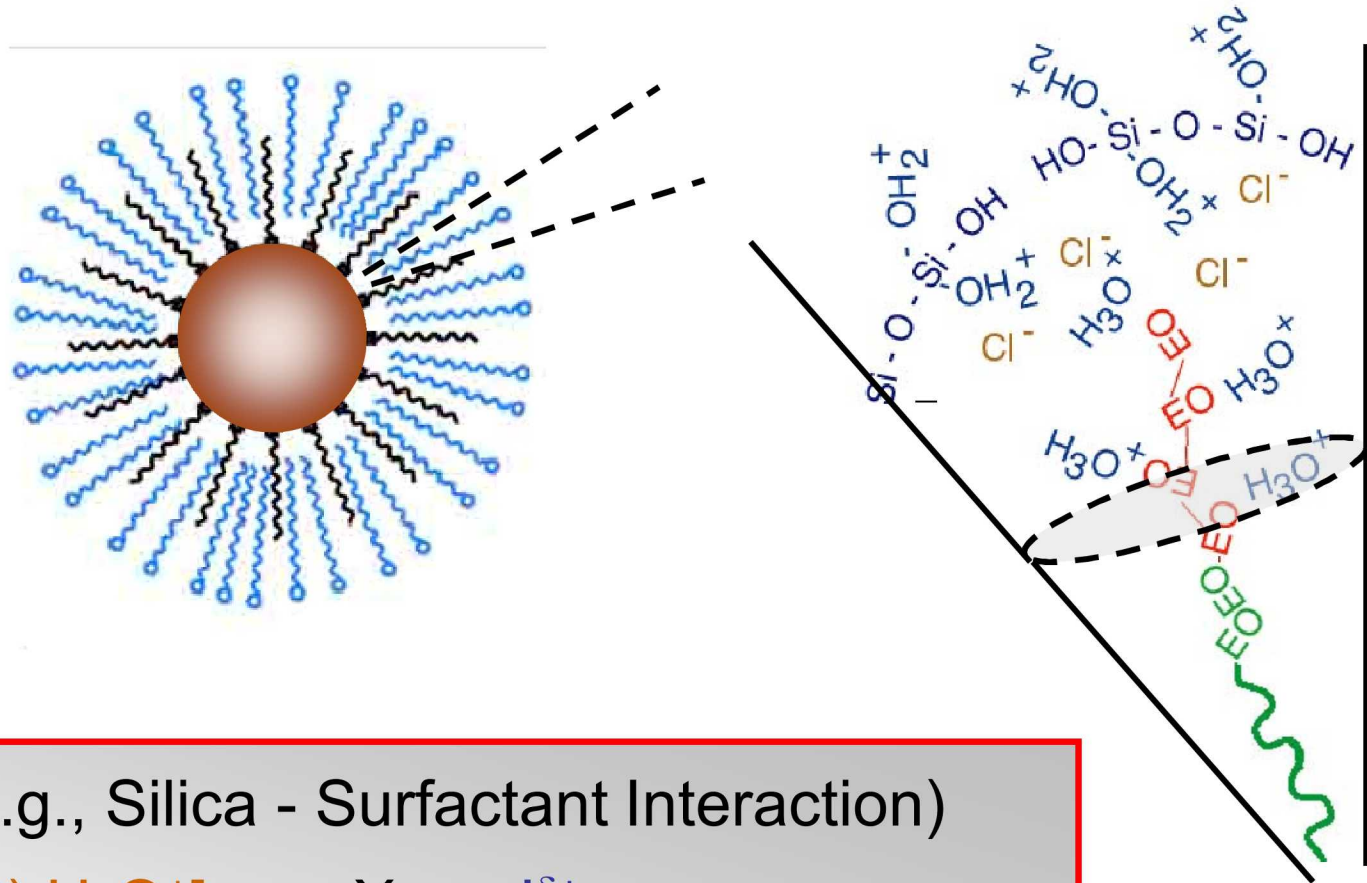
Rod



Cube



Nanoparticle-micelles Provide Flexible Surface Chemistry for further Self-assembly.



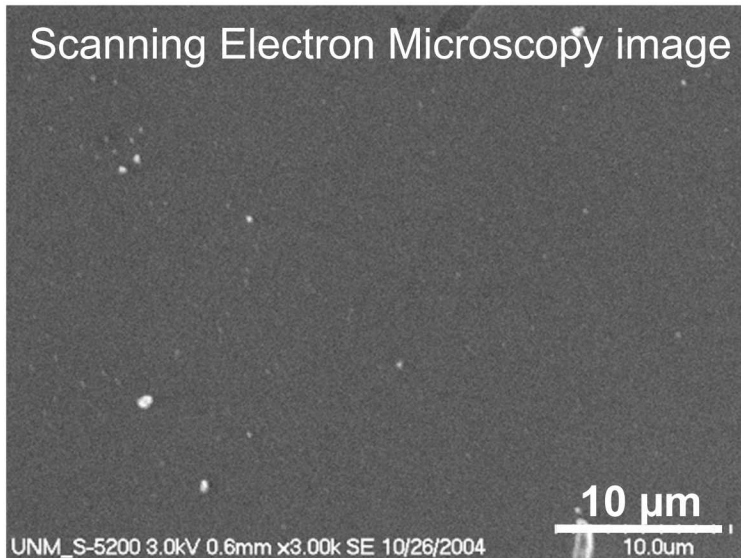
Precursor (e.g., Silica - Surfactant Interaction)



where (I = hydrophilic precursors (e.g., silicate; δ = framework charge, surfactant head groups = charge groups, EO = ethylene oxide, R = alkyl chain)

Highly Order Nanoparticle/Silica Films

Scanning Electron Microscopy image



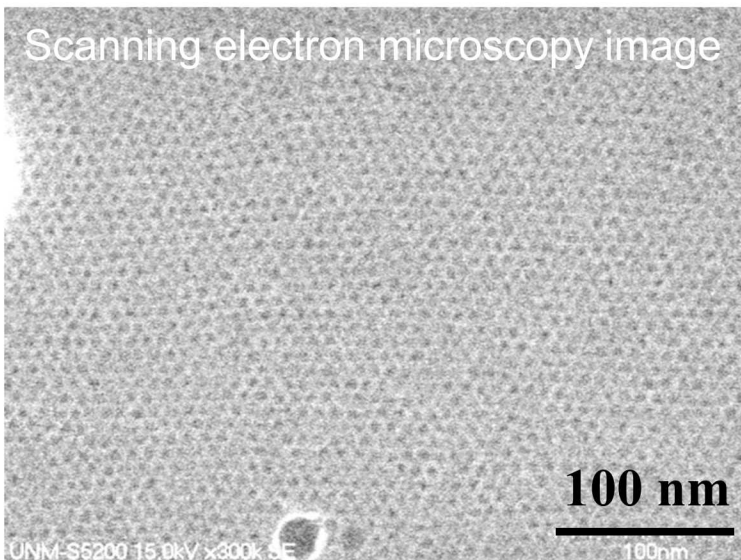
Advantages:

- Mild conditions.
- More stable in inorganic framework. ($>200^{\circ}\text{C}$)
- Uniform and continuous without cracking.
- Compatible with standard fabrication process.
- Robust material: metal, semiconducting, magnetic, etc

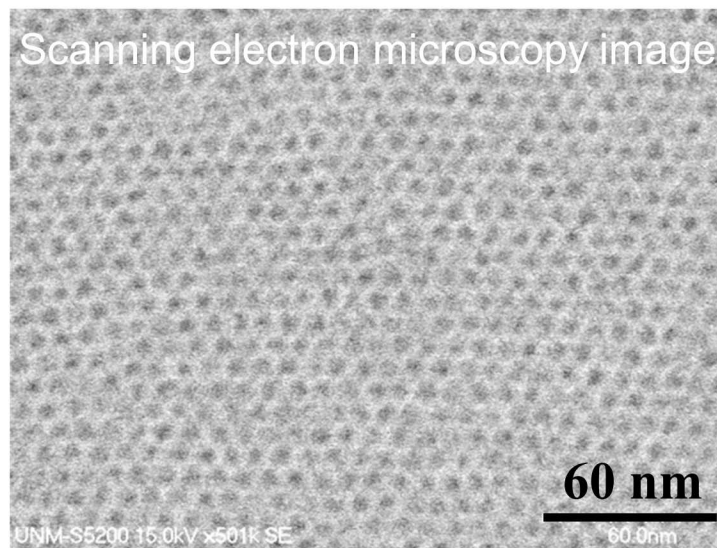


Optical picture

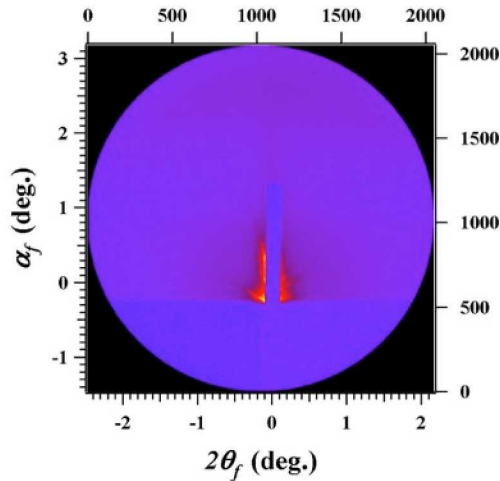
Scanning electron microscopy image



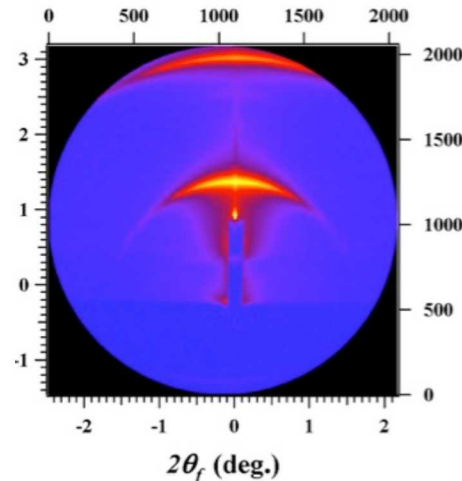
Scanning electron microscopy image



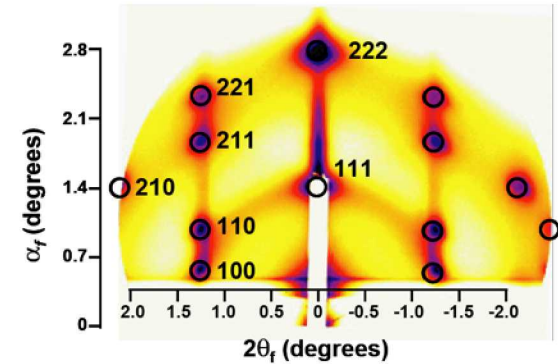
In-situ Grazing Incidence Small-Angle X-ray Scattering Ensure Long Range Order



Drying time: $t = 18$ minutes

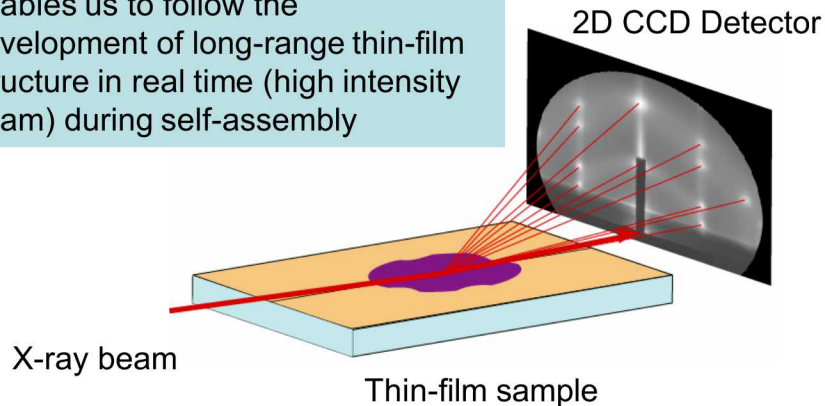


$t = 28$ minutes

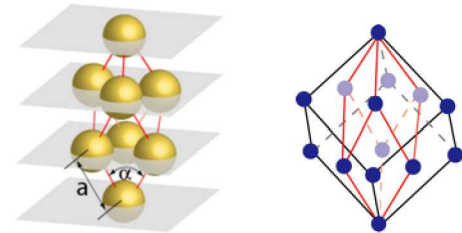


$t = 50$ minutes

GISAXS at a synchrotron source enables us to follow the development of long-range thin-film structure in real time (high intensity beam) during self-assembly



Unit cell of rhombohedral space group $R3m$ showing 111 planes



Relationship between rhombohedral and fcc structures ($\alpha = 60^\circ$)

Nanoparticle Coatings with Tunable Optical Property

Self-assembly method was extended to different nanoparticles to tune film property.

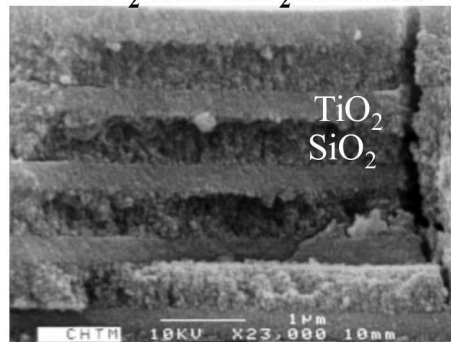
	Material	Measured Index n	Measured Absorption k
Low Index	Porous Silica (Acid Catalyzed)	1.18-1.25	<0.15 (out to 10 μm)
	Porous Silica (Base Catalyzed)	1.19-1.25	<.01 (out to 10 μm)
	Dense Silica	1.4	To Be Measured
Medium Index	TiO ₂ (Acid Catalyzed)	1.4-2.4	<0.15 (out to 10 μm)
	TiO ₂ (Base Catalyzed)	1.7-1.8	<.01 (out to 7 μm)
	CdSe	1.7-1.8+	<0.15 (out to 10 μm)
High Index	Gold	1.8-1.9+	<0.15 (out to 10 μm)
	Ge	2-4 *	Under Development
	FePt	~2.2+	~.1
	PbSe	~2.2+	~.1

* Theoretical Values

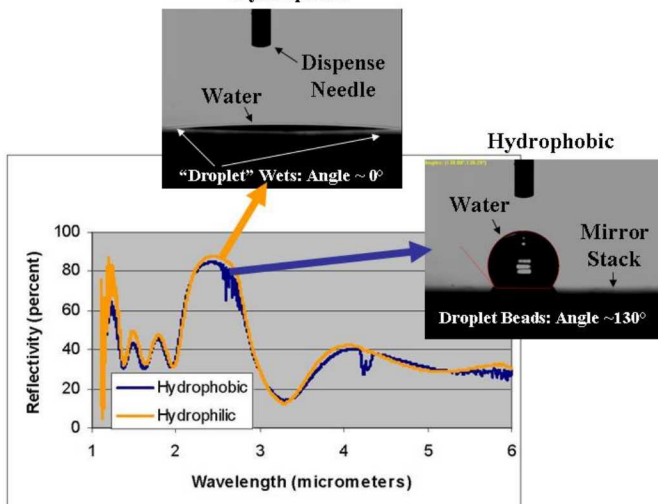
Nanoparticle Coatings for Near Infrared Reflectors

Quarter wave stacking of self-assembled nanoparticle films for near infrared reflectors, overcomes the harsh conditions from conventional processing (CVD, sputtering, etc) with improved functionality.

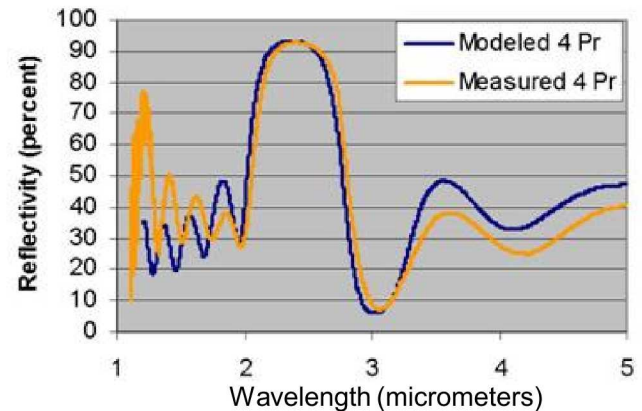
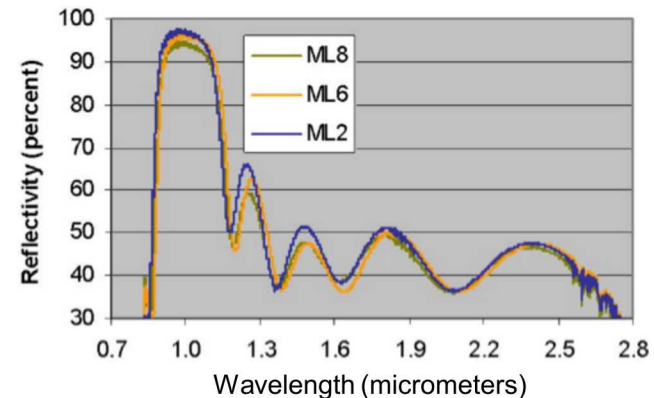
SEM image of quarter wave stacking of TiO_2 and SiO_2 reflector



Functionalization of optical coatings



Reflectivity studies show high and reproducible reflectivity over controlled wavelength windows (1-2 μm , 2-3 μm , 8-12 μm , etc)

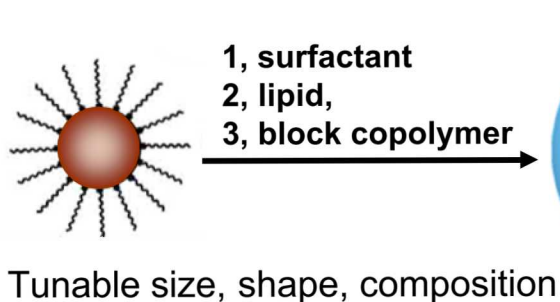
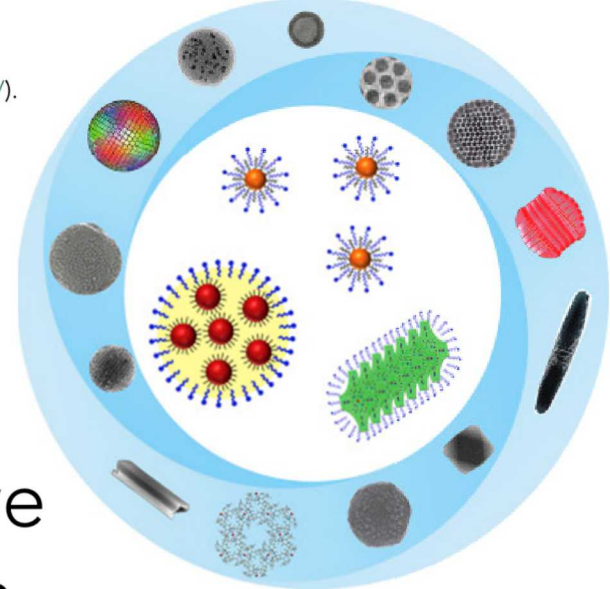


Model design show 99.9% and address key manufacturing issue.

Review

Surfactant-Assisted Cooperative Self-Assembly of Nanoparticles into Active Nanostructures

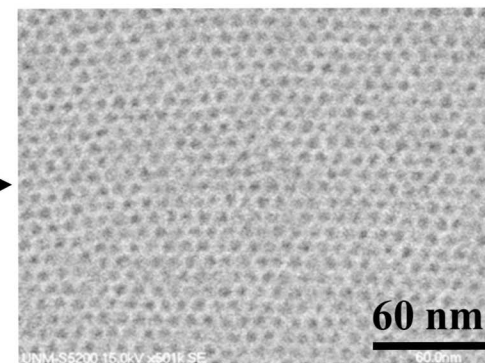
Wenbo Wei,¹ Feng Bai,^{1,*} and Hongyou Fan^{2,3,4,*}



Tunable size, shape, composition

Engineering Process

- Dip-coating
- Ink-jet printing
- Pen writing
- R-to-R imprinting
- more

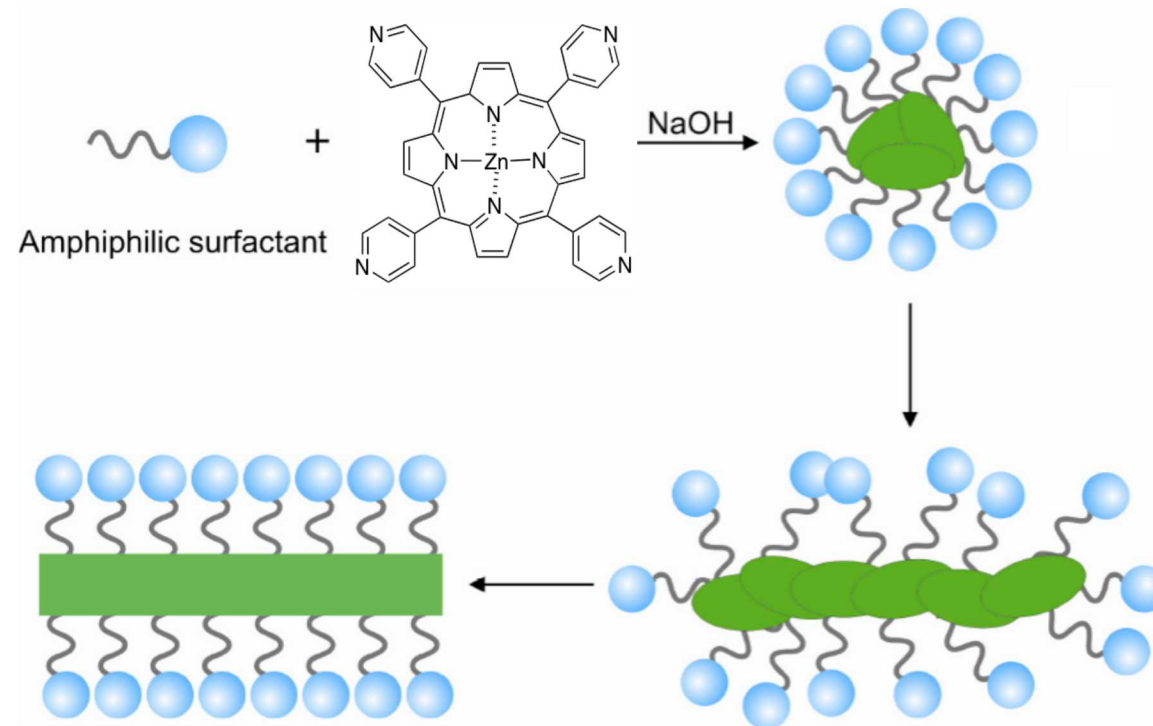


Tunable property

2. Confined Cooperative Self-Assembly of Photoactive Nanostructures

Surfactant assisted micelle confinement of non-covalent interactions:

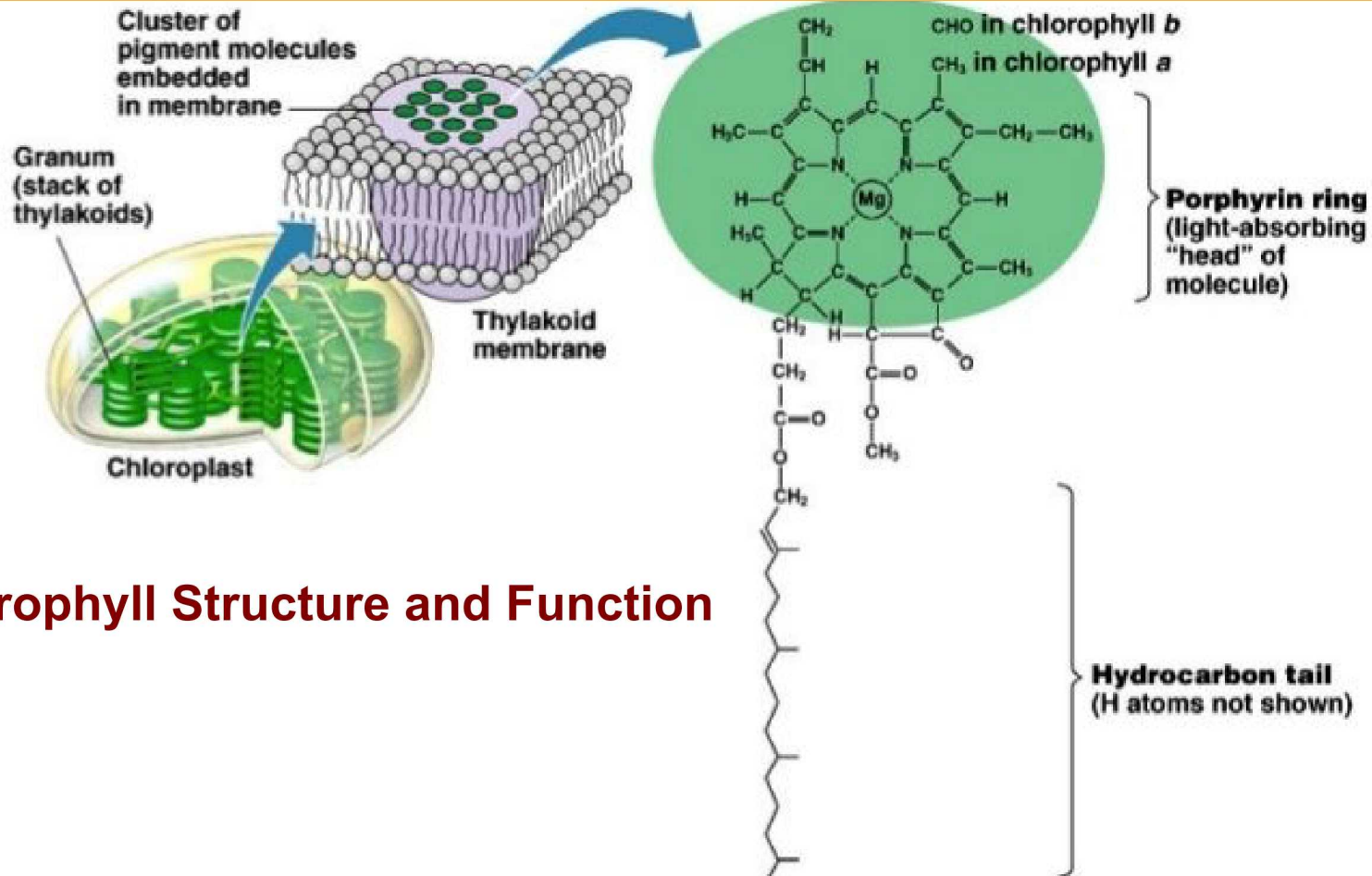
- Hydrophobic-hydrophobic interactions,
- π - π stacking,
- Metal-ligand coordination.



Y. Liu, et al. *Nano Lett.*, **2019**.
K. Bian et al. *Nature Communicitons*, **2018**.
K. Bian et al. *MRS Adv.*, **2018**, 3 (45), 2757-2762.
N. Zhang, et al. *Nano Lett.*, **2018**, 18 (1), 560-566.
D. Wang, et al. *ACS Nano*, **2018**, 12 (4), 3796-3803.
J. Wang, et al. *Nano Lett.*, **2017**, 17 (11), 6916-6921.
J. Wang, et al. *Nano Lett.* **2016**, 16, 6523-6528.
F. Bai, et al. *Adv. Mater.* **2016**, 28, 1989-1993.
Y. Zhong, et al. *Nano Lett.*, **2014**, 14, 7175-7179.
Y. Zhong, et al. *ACS Nano*, **2014**, 8 (1), 827-833.
F. Bai, et al. *Nano Lett.*, **2011**, 11, 3759-3762.
F. Bai, et al. *Nano Lett.*, **2011**, 11, 5196-5200.
F. Bai, et al. *Chem. Commun.*, **2010**, 46, 4941-4943.

Why Porphyrins?

Biomacromolecules (e.g., chlorophyll, heme, etc.) with well-defined size and chemistry are essential pigments in many biological energy transduction processes in plants, algae, and bacteria including photosynthesis (absorb light, transfer energy, etc), water splitting, etc.



Chlorophyll Structure and Function

Why Porphyrins?

Inspired by biological nature, many synthetic molecular building blocks such as porphyrins, organic dyes, etc have been demonstrated for new optical and electronic applications in areas of molecule electronics, photovoltaics, and sensors.

Well-defined size and chemistry:

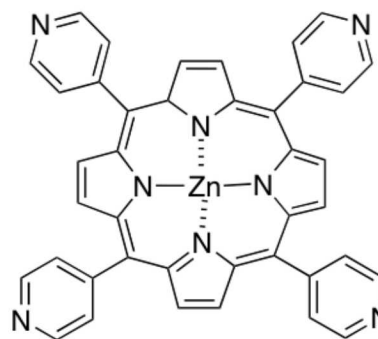
- Well-defined size and surface chemistry,
- Optical and electrical activity due to the conjugated aromatic π system,
- Covering wide range of visible spectrum.

Driving forces for self-assembly:

- Hydrophobic-hydrophobic,
- π - π stacking,
- Metal-ligand coordination,
- Ionic interactions.

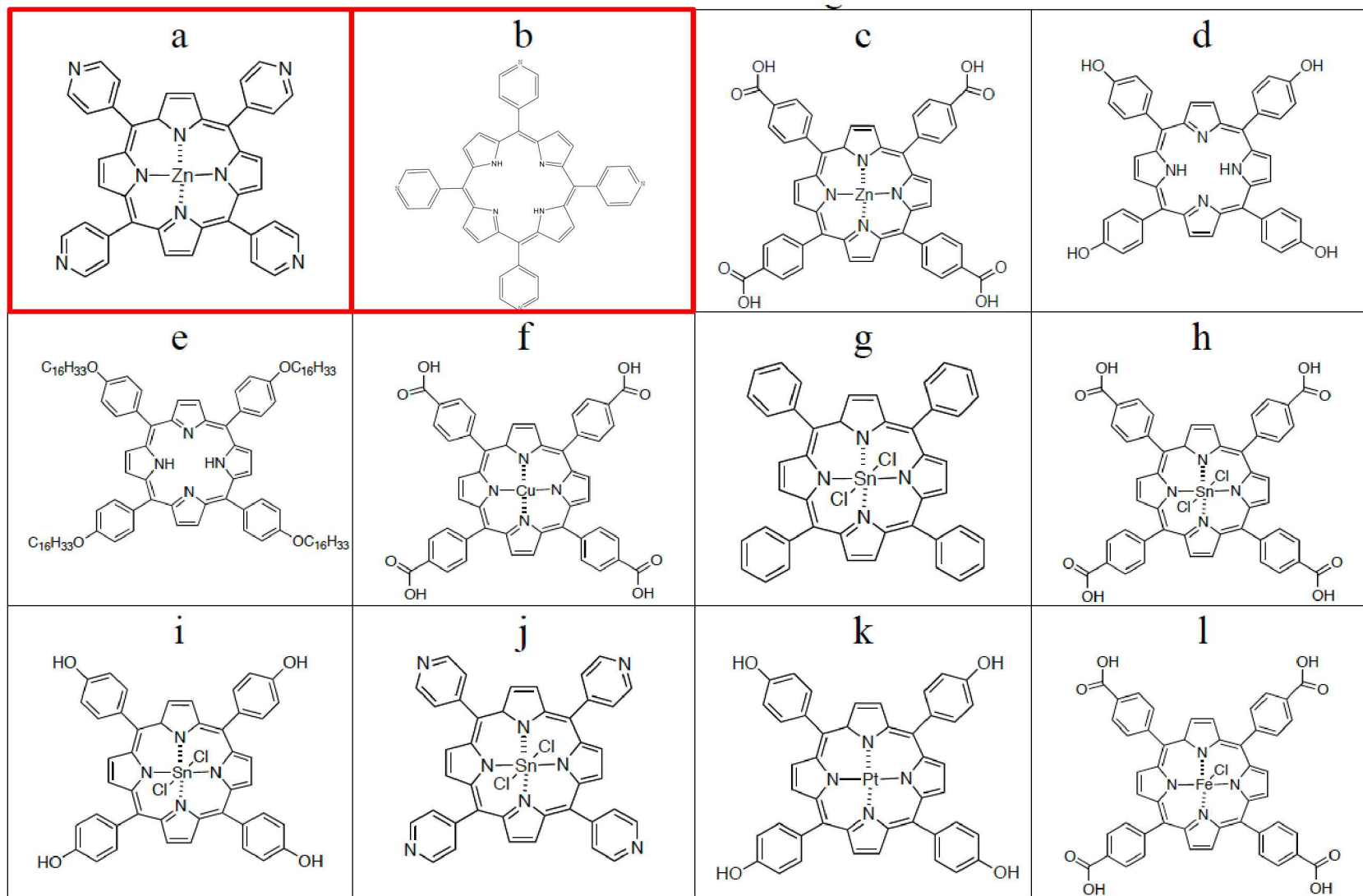
Applications in energy conversion/storage and sensors:

- Photocatalysts,
- Sensors,
- Phototherapy,
- Dye sensitized solar cells.

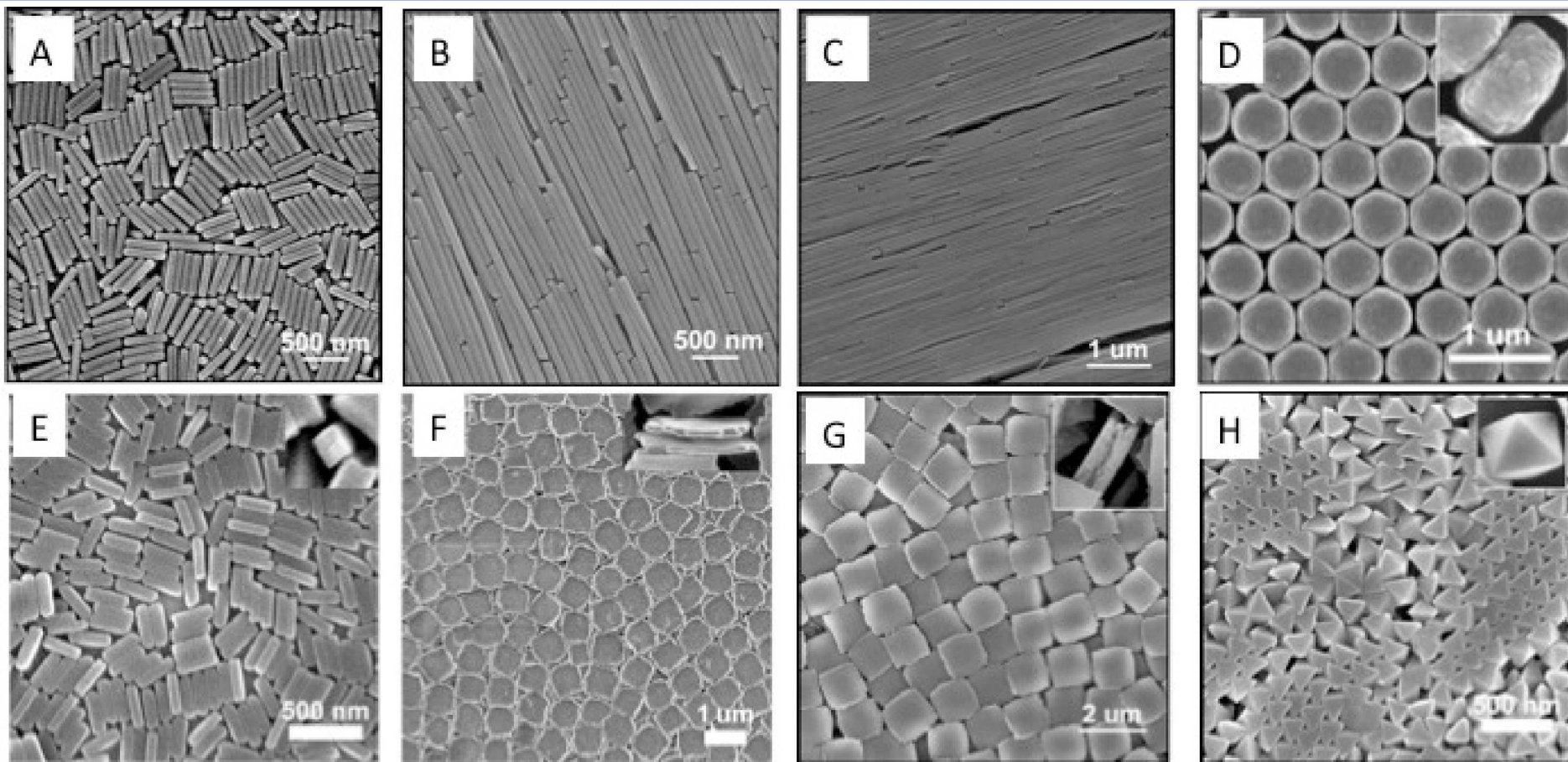


ZnTPyP

Porphyrin Used in Our Research



Hierarchically Structured Porphyrin Nanocrystals



K. Bian et al. *Nature Communicitons*, **2018**.

K. Bian et al. *MRS Adv.*, **2018**, 3 (45), 2757-2762.

D. Wang, et al. *ACS Nano*, **2018**, 12 (4), 3796-3803.

N. Zhang, et al. *Nano Lett.*, **2018**, 18 (1), 560-566.

J. Wang, et al. *Nano Lett.*, **2017**, 17 (11), 6916-6921.

J. Wang, et al. *Nano Lett.* **2016**, 16, 6523-6528.

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Y. Zhong, et al. *Nano Lett.* **2014**, 14, 7175-7179.

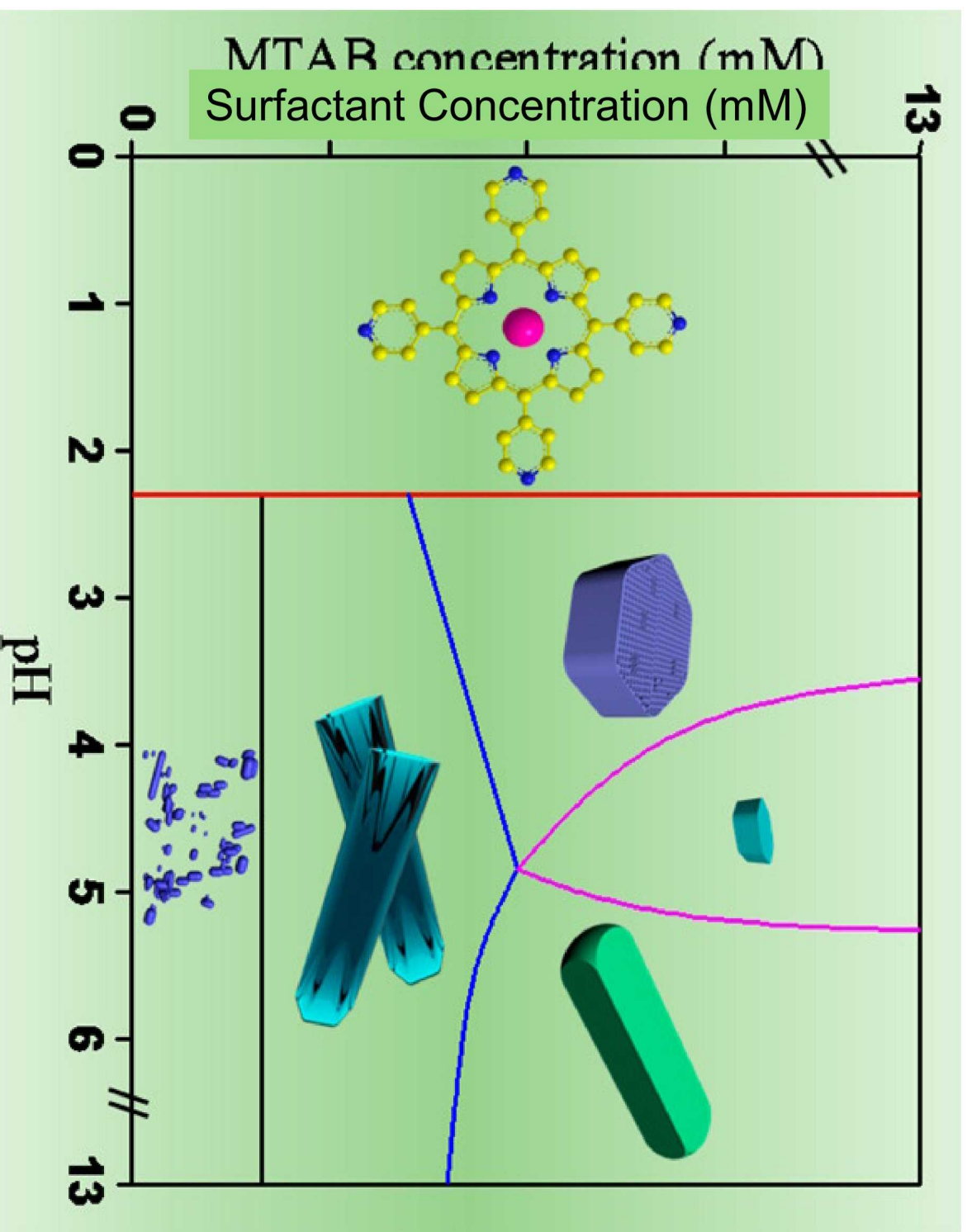
Y. Zhong, et al. *ACS Nano*, **2014**, 8 (1), 827-833.

F. Bai, et al. *Nano Lett.* **2011**, 11, 3759-3762.

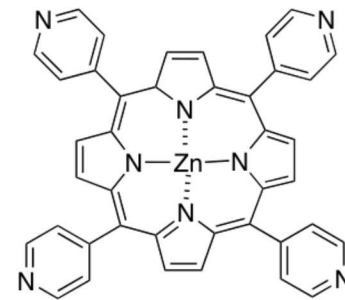
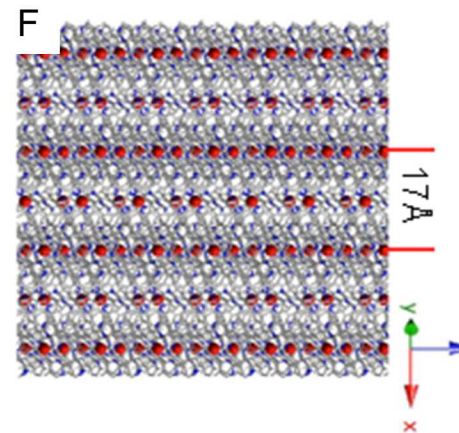
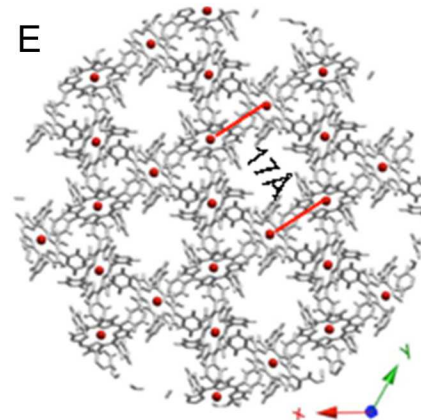
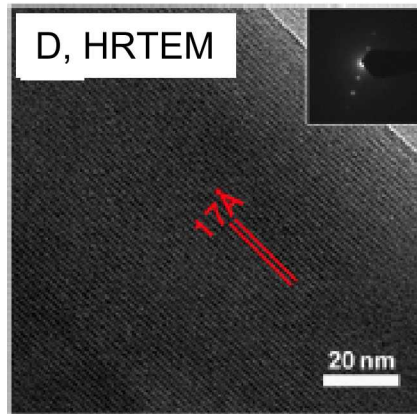
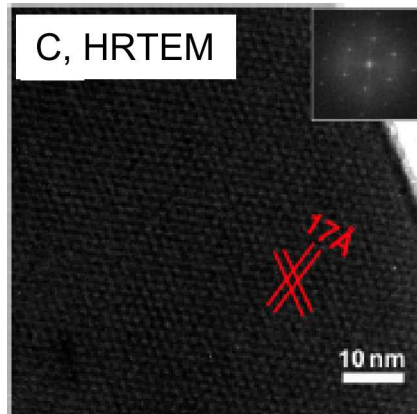
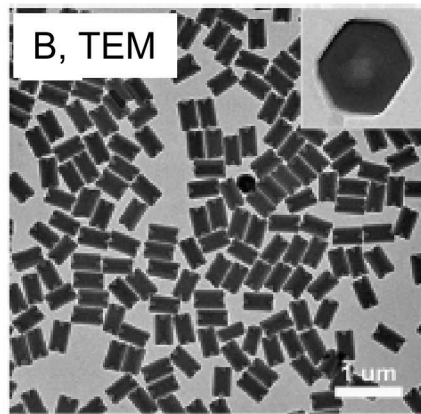
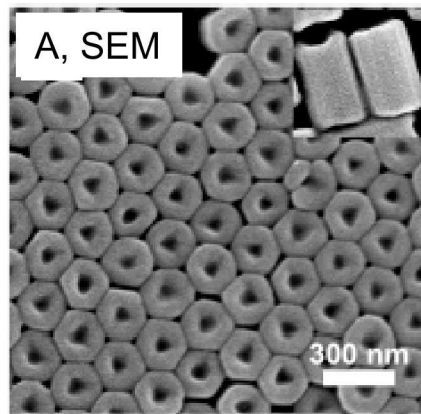
F. Bai, et al. *Nano Lett.* **2011**, 11, 5196-5200.

F. Bai, et al. *Chem. Commun.*, **2010**, 46, 4941-4943.

Phase Diagram of Self-Assembled Porphyrins



Hierarchically Structured Porphyrin Nanorods

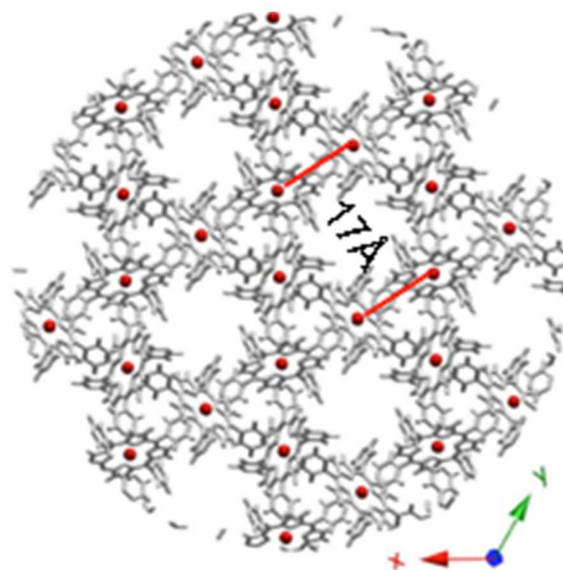
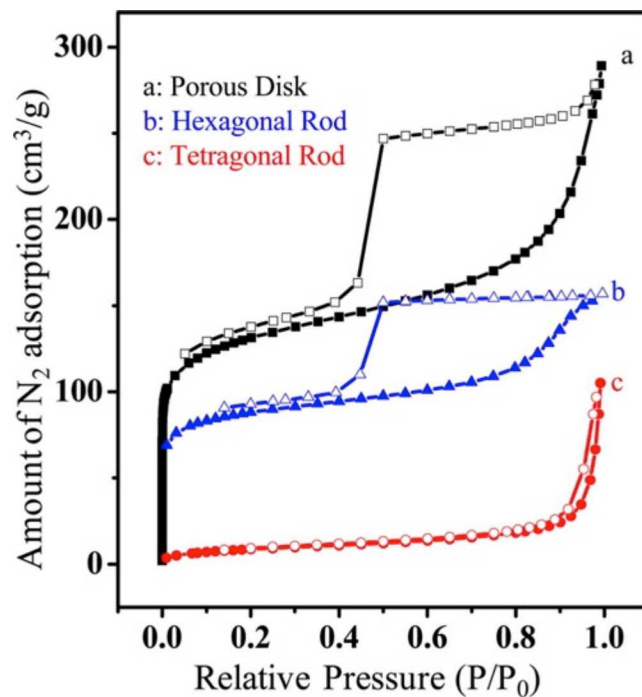


E, simulated crystal structure, viewed along the crystallographic z axis, Zn (red).

F, simulated crystal structure, viewed along the nanowire.

Crystal structure: Hexagonal R-3 (148) $a=b=33.110$, $c=9.273$; $\alpha=\beta=\gamma=120$

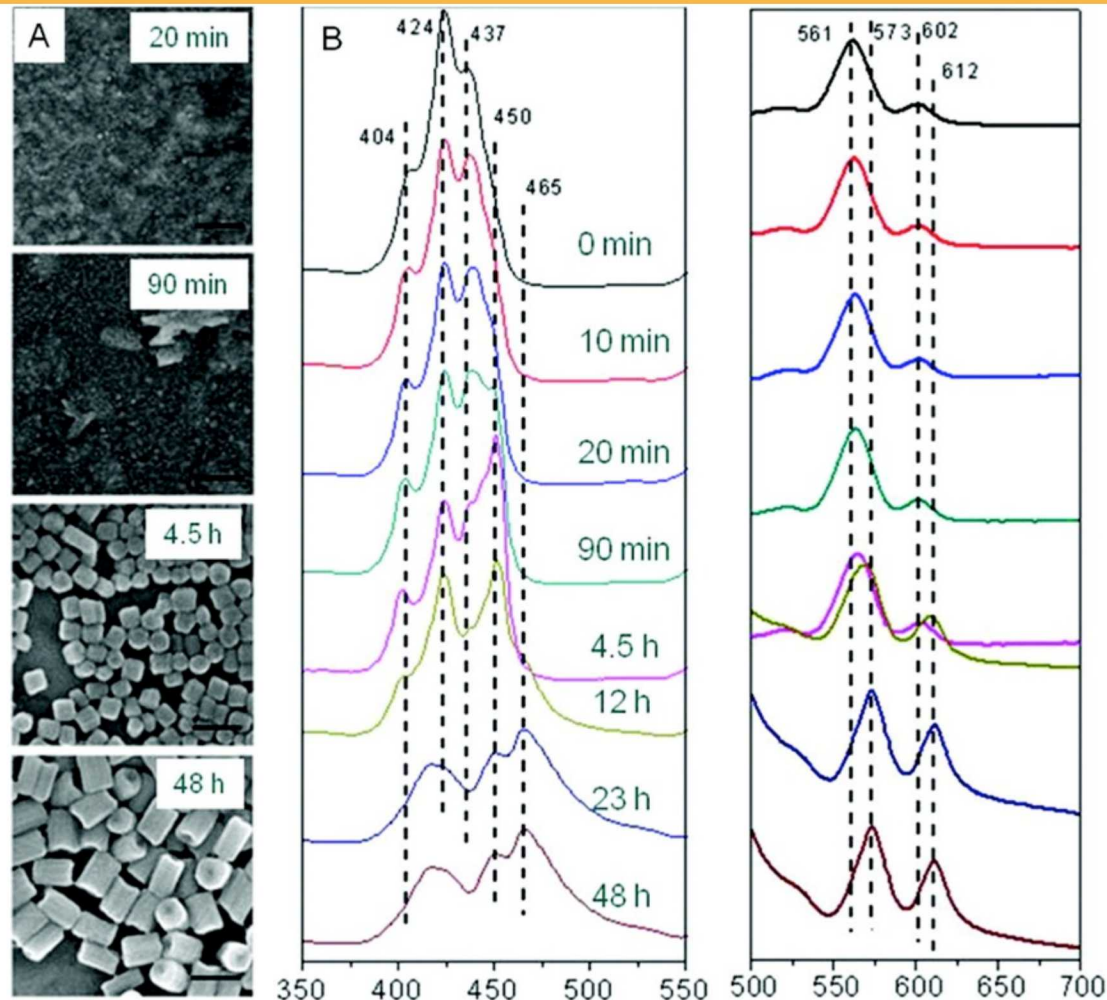
Nitrogen Sorption Isotherms of Porphyrin Nanocrystals



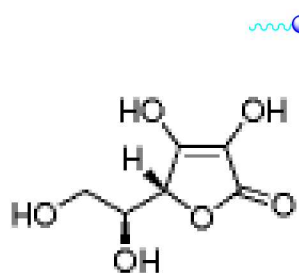
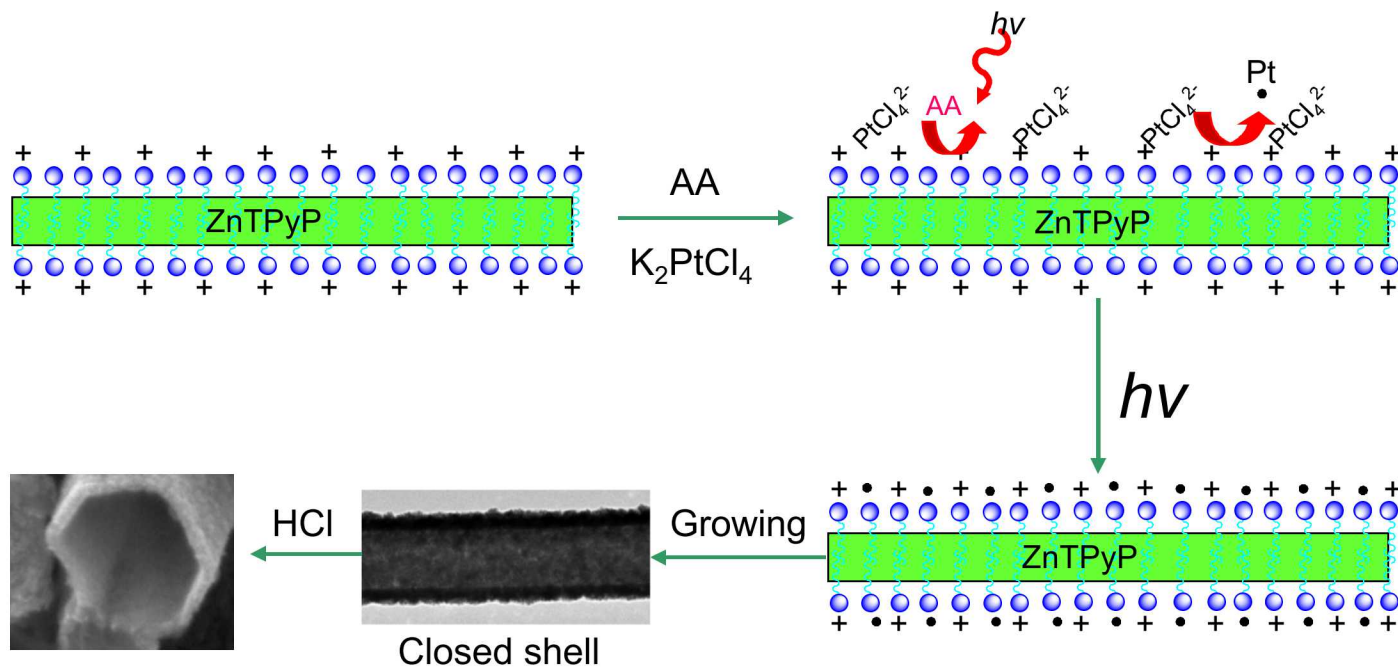
	Porosity (%)	Surface area (m^2/g)	Pore size (nm)
Tetragonal rod	34.3	371	0.81
Hexagonal rod	20.1	327	0.79
Long wire	16.1	294	0.78

Structural Evolution during Self-Assembly

SEM images of hexagonal nanorods and UV-spectra of the reaction solution at different reaction times.

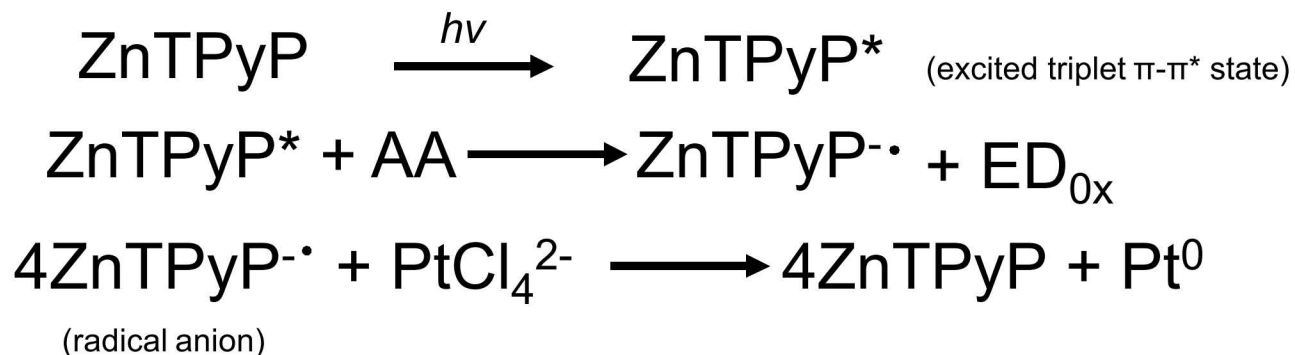


Photocatalytic Synthesis of Hollow Pt Nanostructures

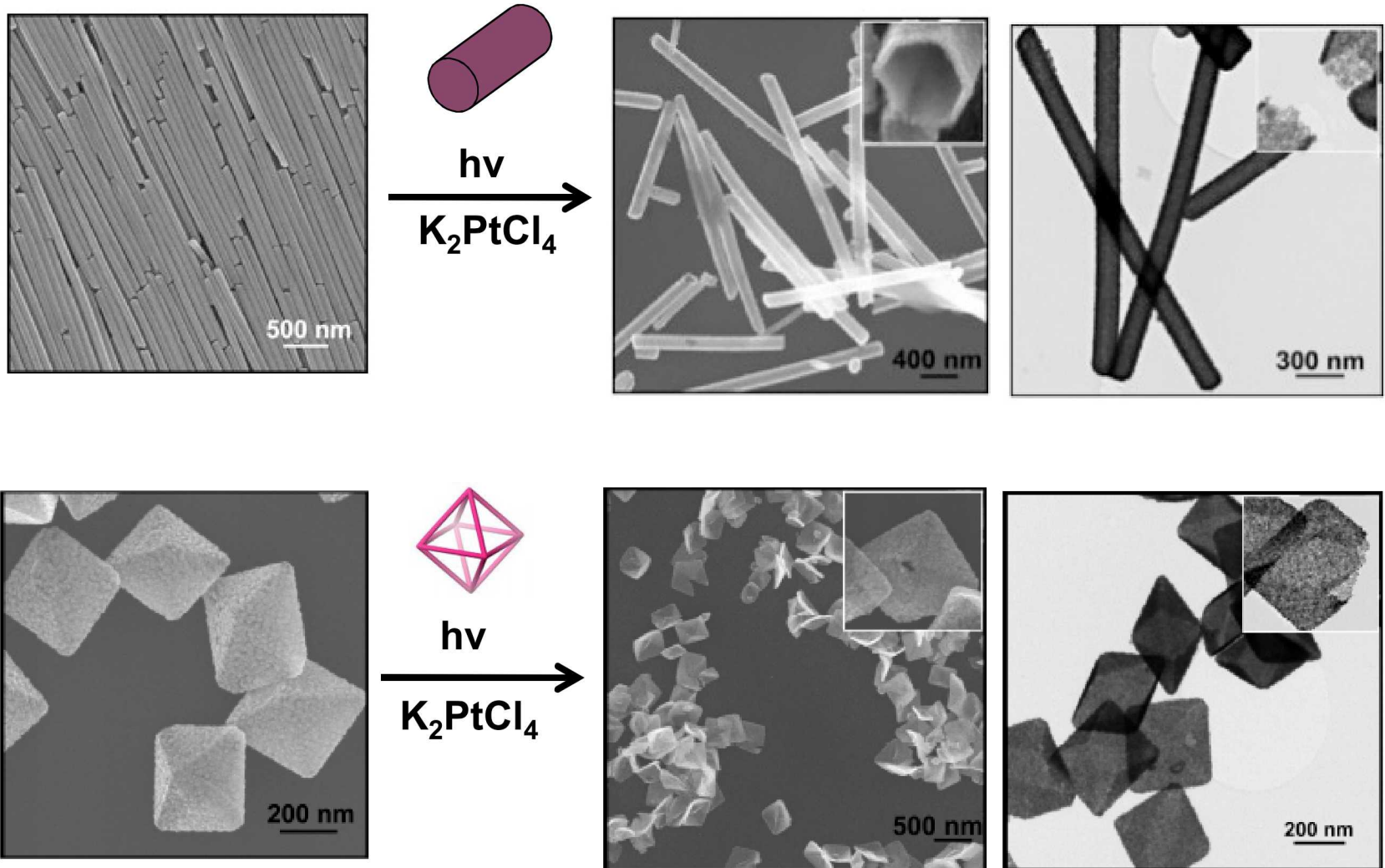


CTAB

Ascorbic Acid: AA **E**lectron **D**onor



Photocatalytic Synthesis of Hollow Pt Nanostructures through Porphyrin Nanocrystals

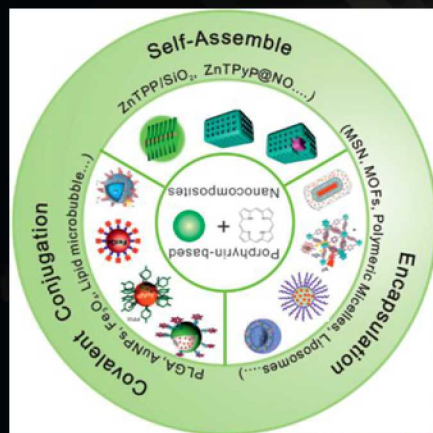


MRS Bulletin

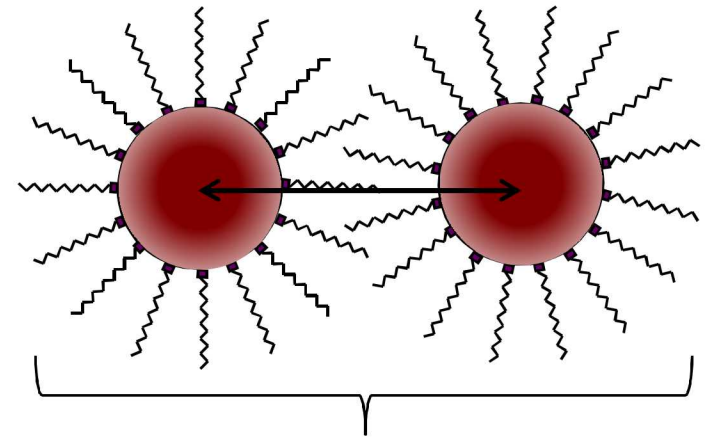
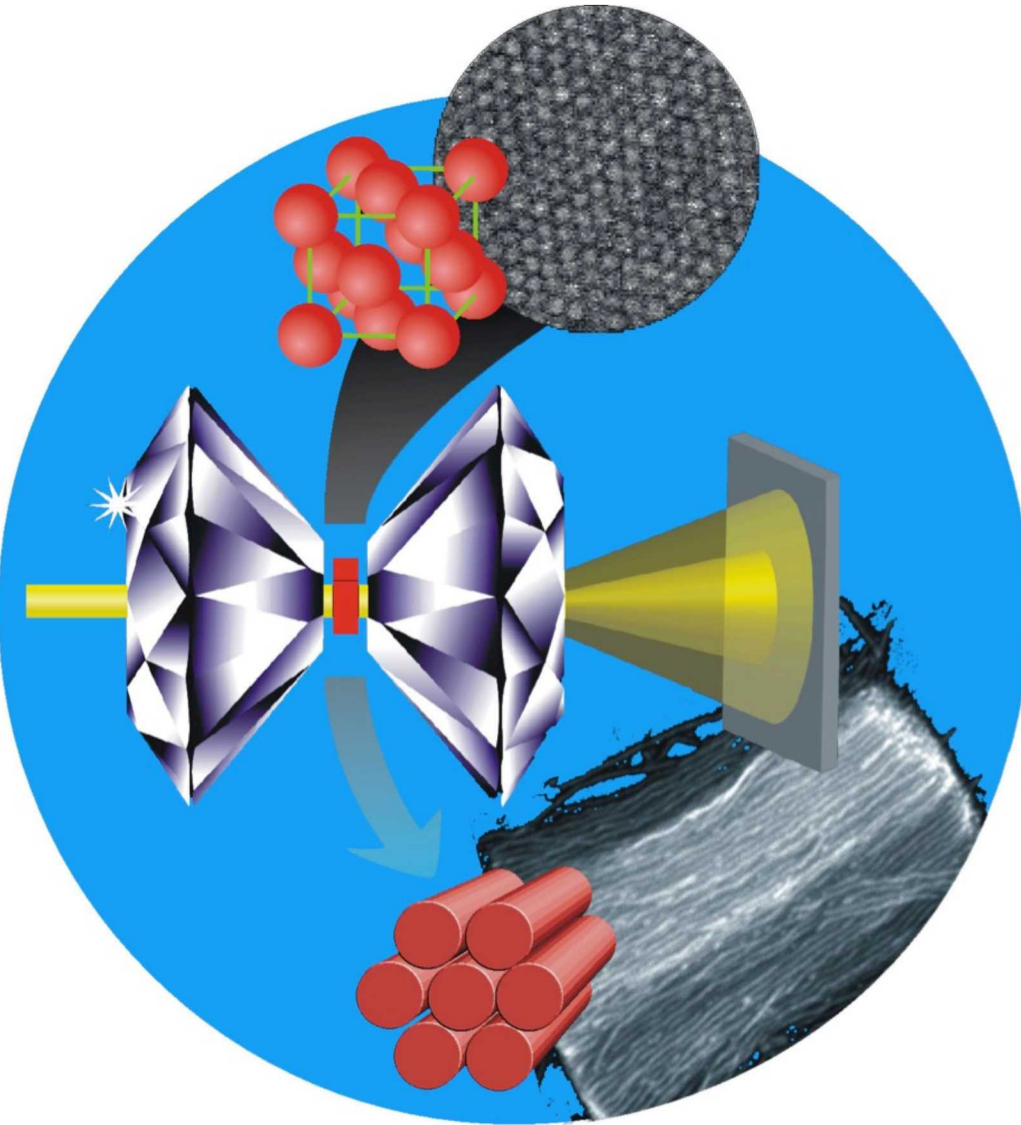
March 2019 Vol. 44 No. 3
www.mrs.org/bulletin

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Self-assembled porphyrin and macrocycle derivatives

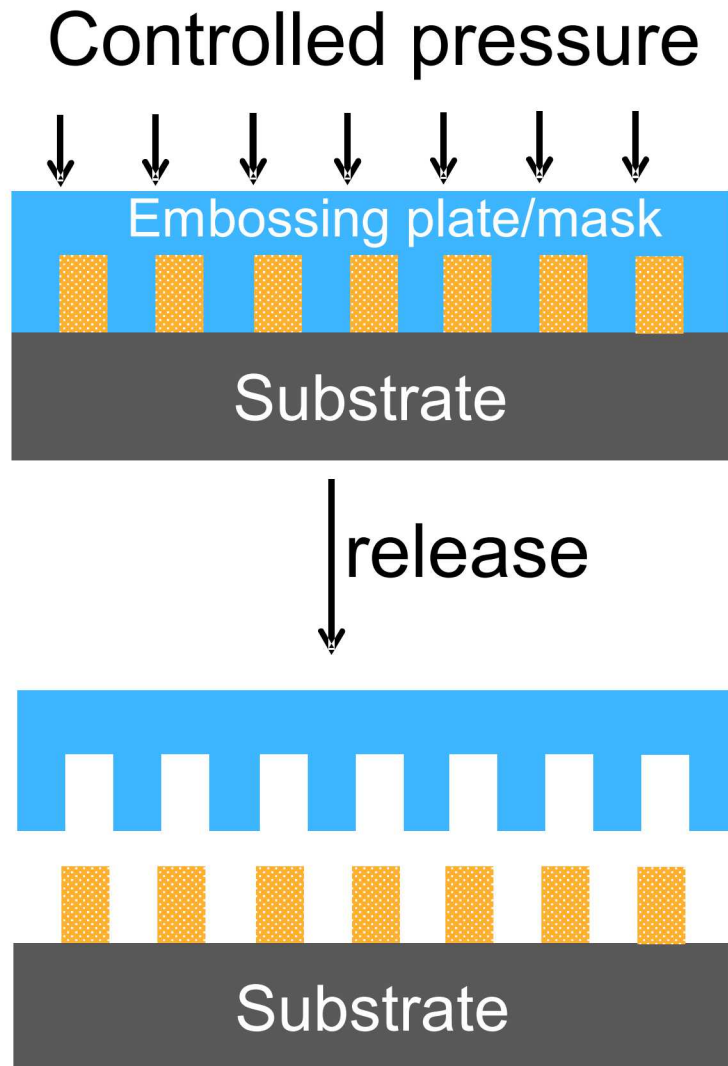


3. Pressure Induced Nanoparticle Assembly



Nanoparticle interactions and coupling

Our Research - Nanoparticle Assembly under Pressure: *Mimic Manufacturing Processes - Embossing or Imprinting*

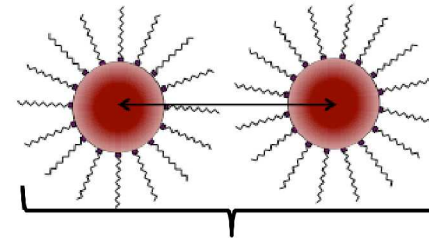
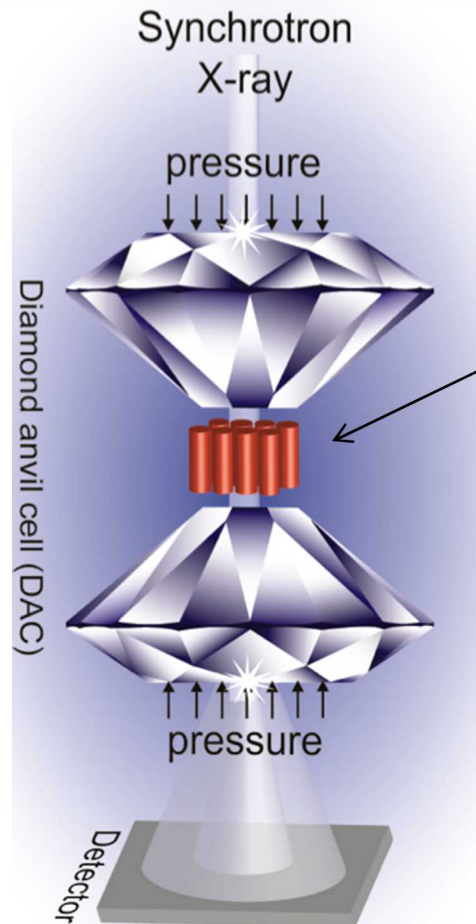


Features:

- Rapid
- Cost effective
- High throughput
- High fidelity

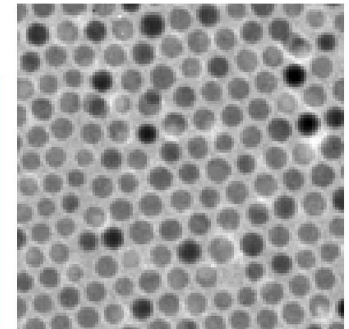
Pressure-Induced Assembly and Fabrication

An external pressure overcomes balanced interparticle interactions, enables engineering of nanoparticle assembly, allowing fine-tuning of lattice structure and interparticle separation distance, and to fabricate new nanoparticle architectures.



Balanced Nanoparticle interactions:

- Attraction
- Van der Waals
- Charge interactions
- Dipole-dipole
- ...

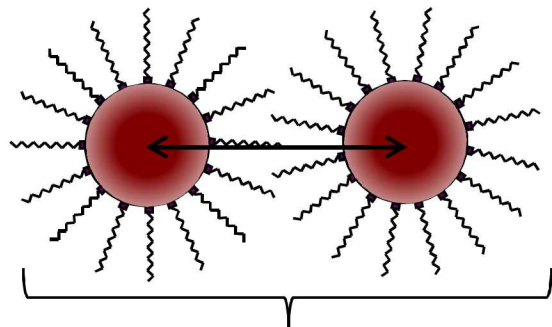


- Provide controlled pressure fields:
 - Hydrostatic & uniaxial
 - Controlled pressure range
- Allow in-situ structural and property characterizations
 - Absorption, emission, etc.
 - Crystal structure, phase transition, etc.
 - Structural evolution with pressure

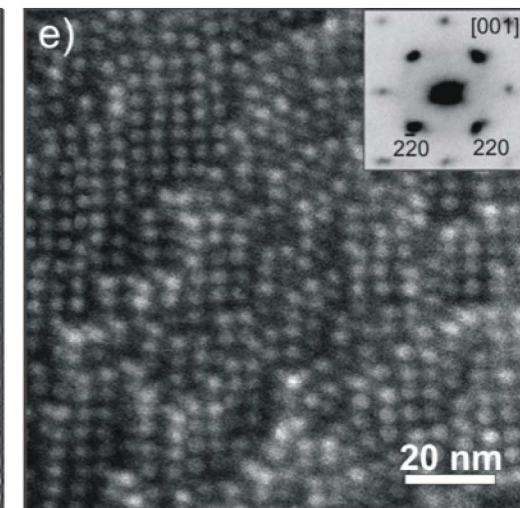
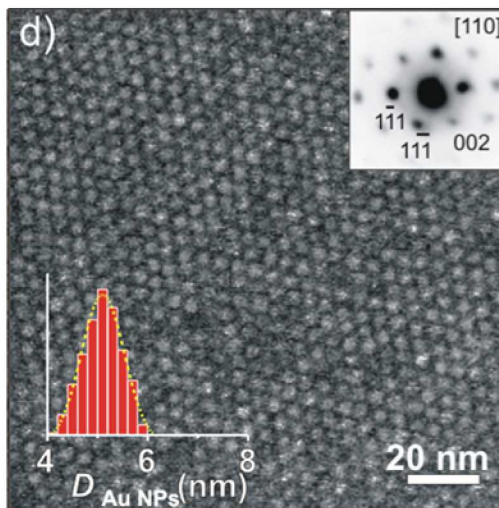
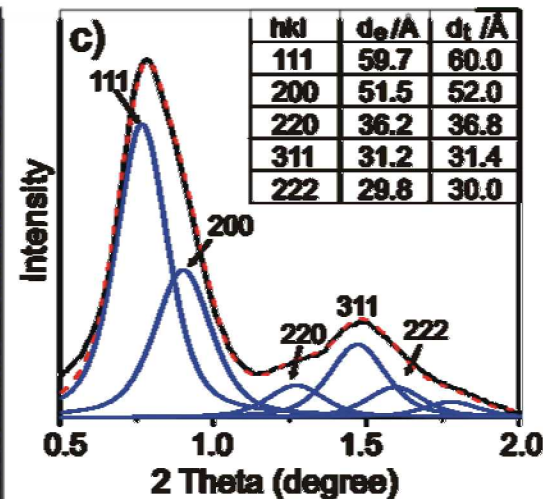
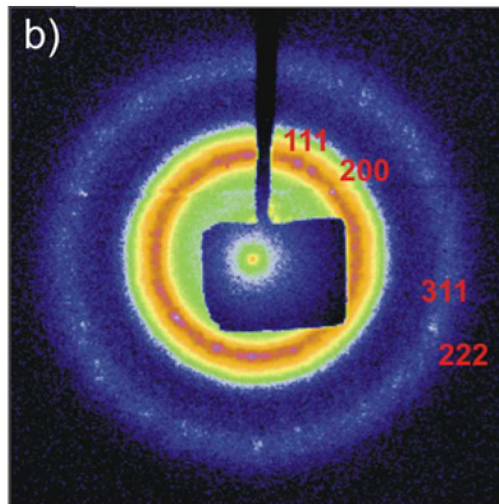
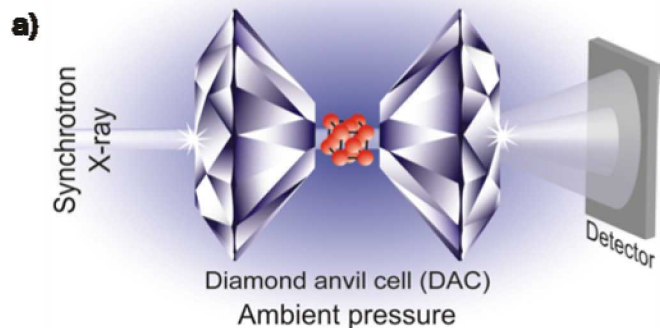
Diamond Anvil Cell (DAC)

Before Compression – Starting Materials: Ordered Spherical Gold Nanoparticle Arrays

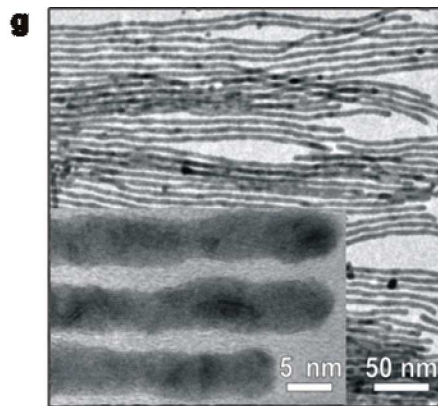
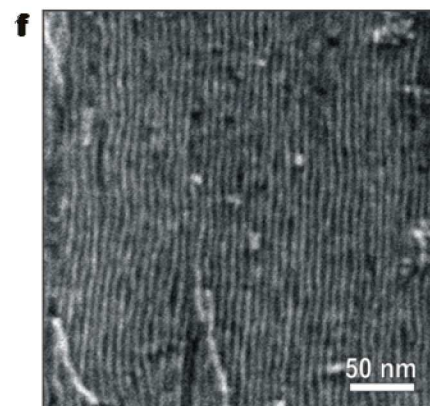
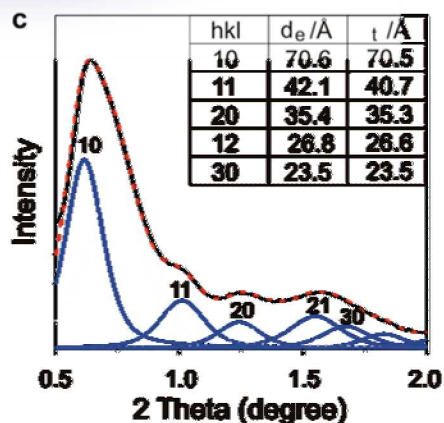
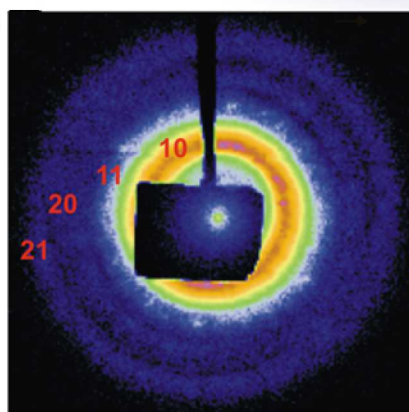
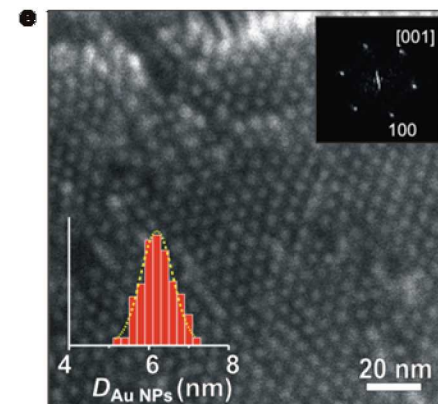
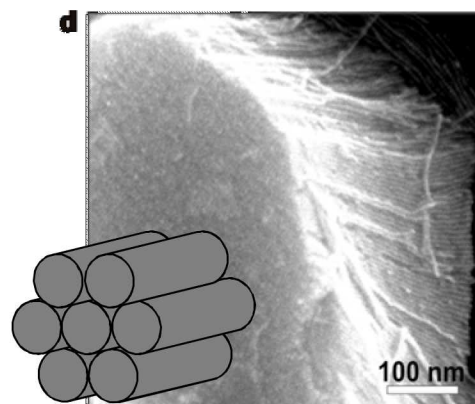
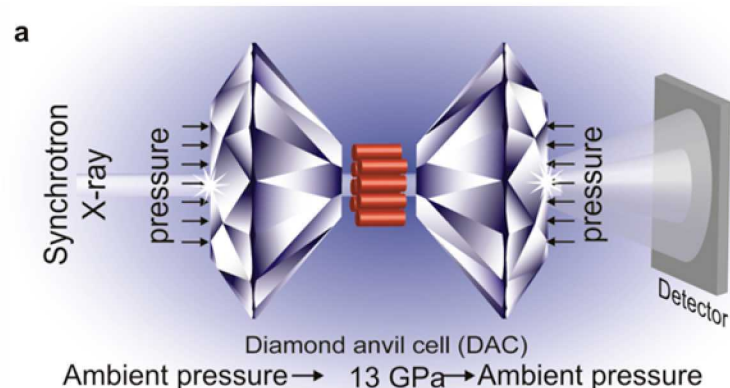
5 nm gold nanoparticles and *fcc* lattice ($a = 0.357$ nm)



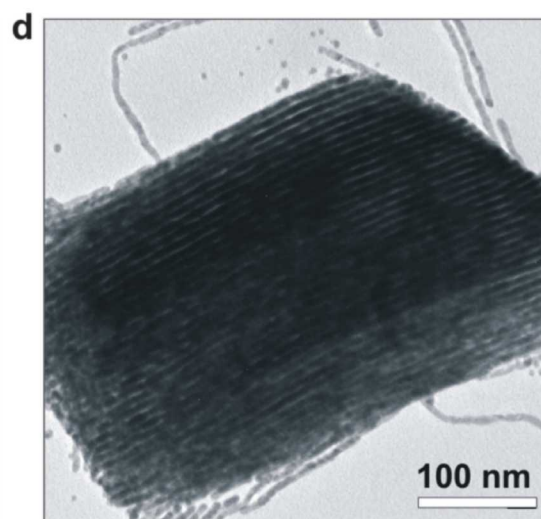
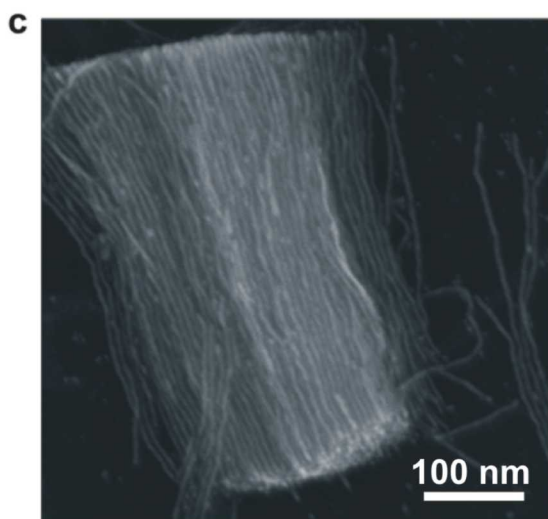
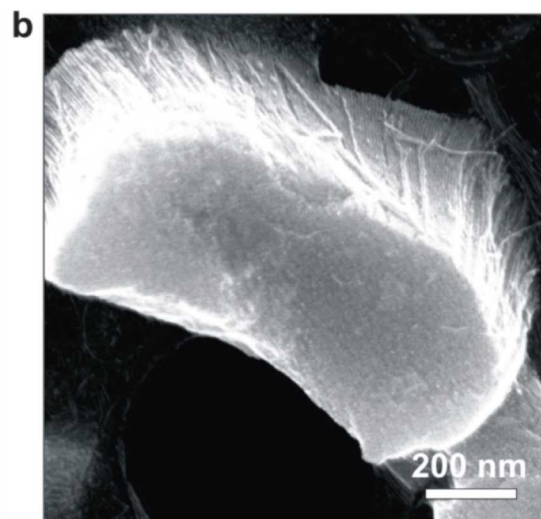
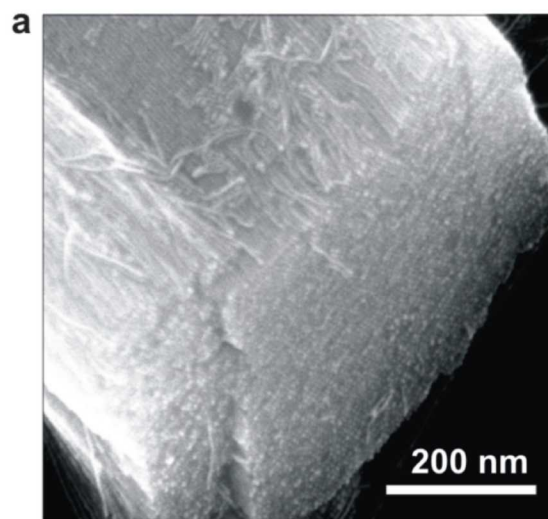
Balanced particle interactions



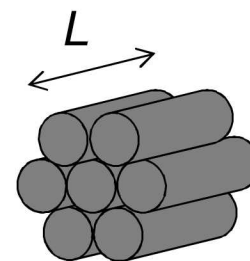
After Compression – Formation of 1D Nanowires



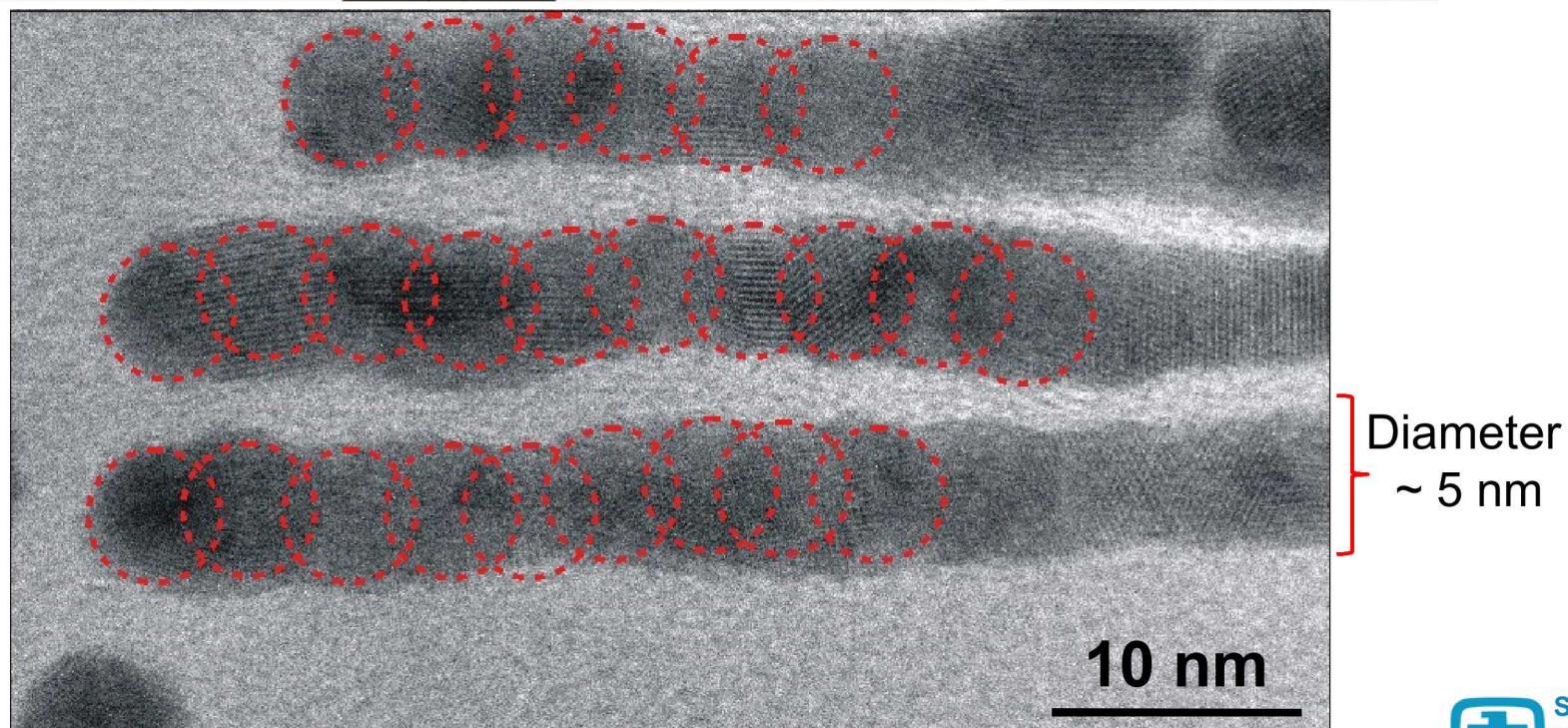
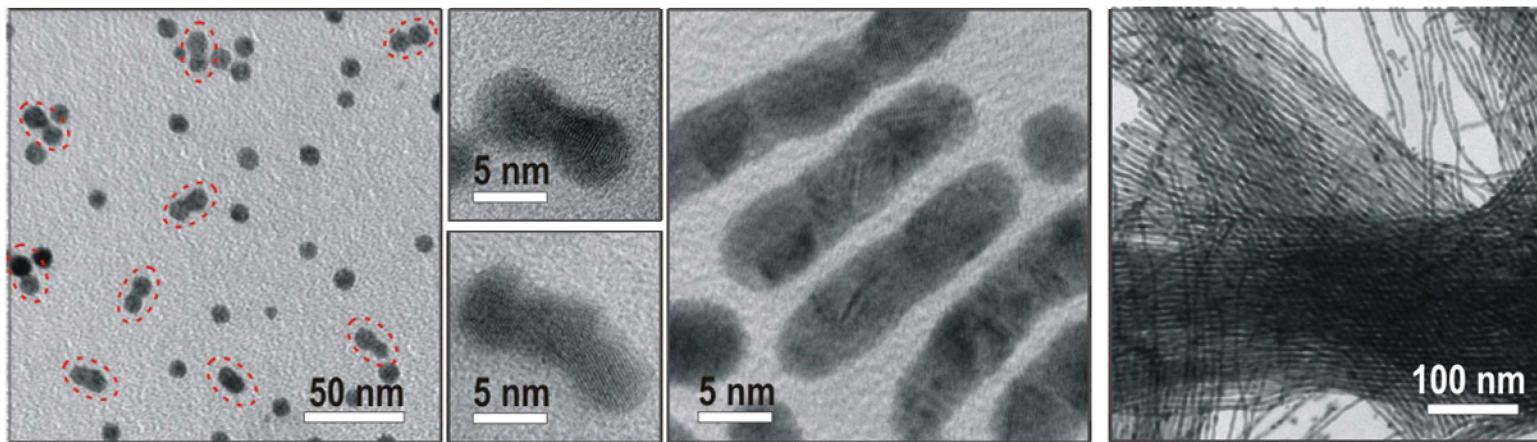
Bundles of 1D Nanowire Arrays



Uniform length



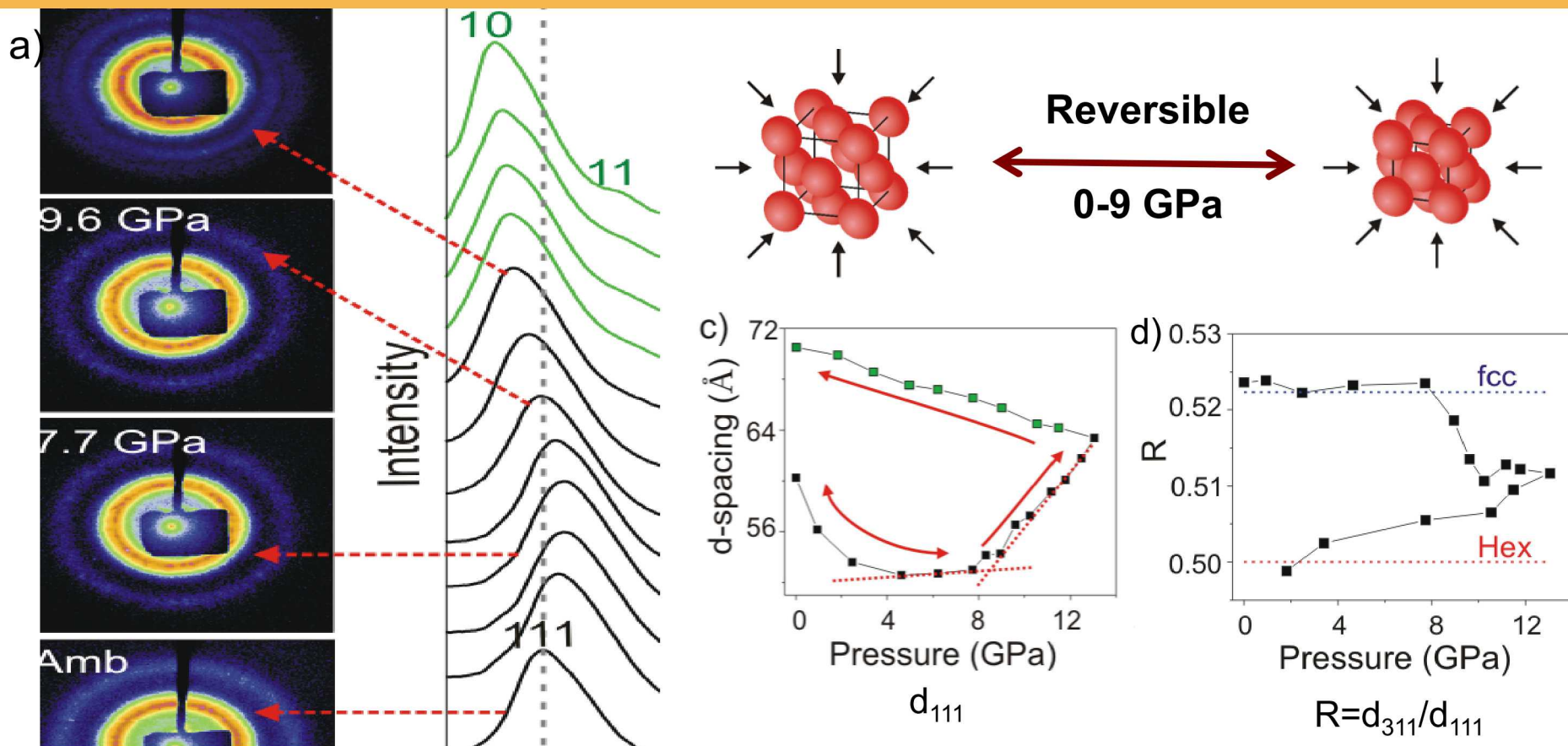
Pressure Tuned 1D Nanostructures



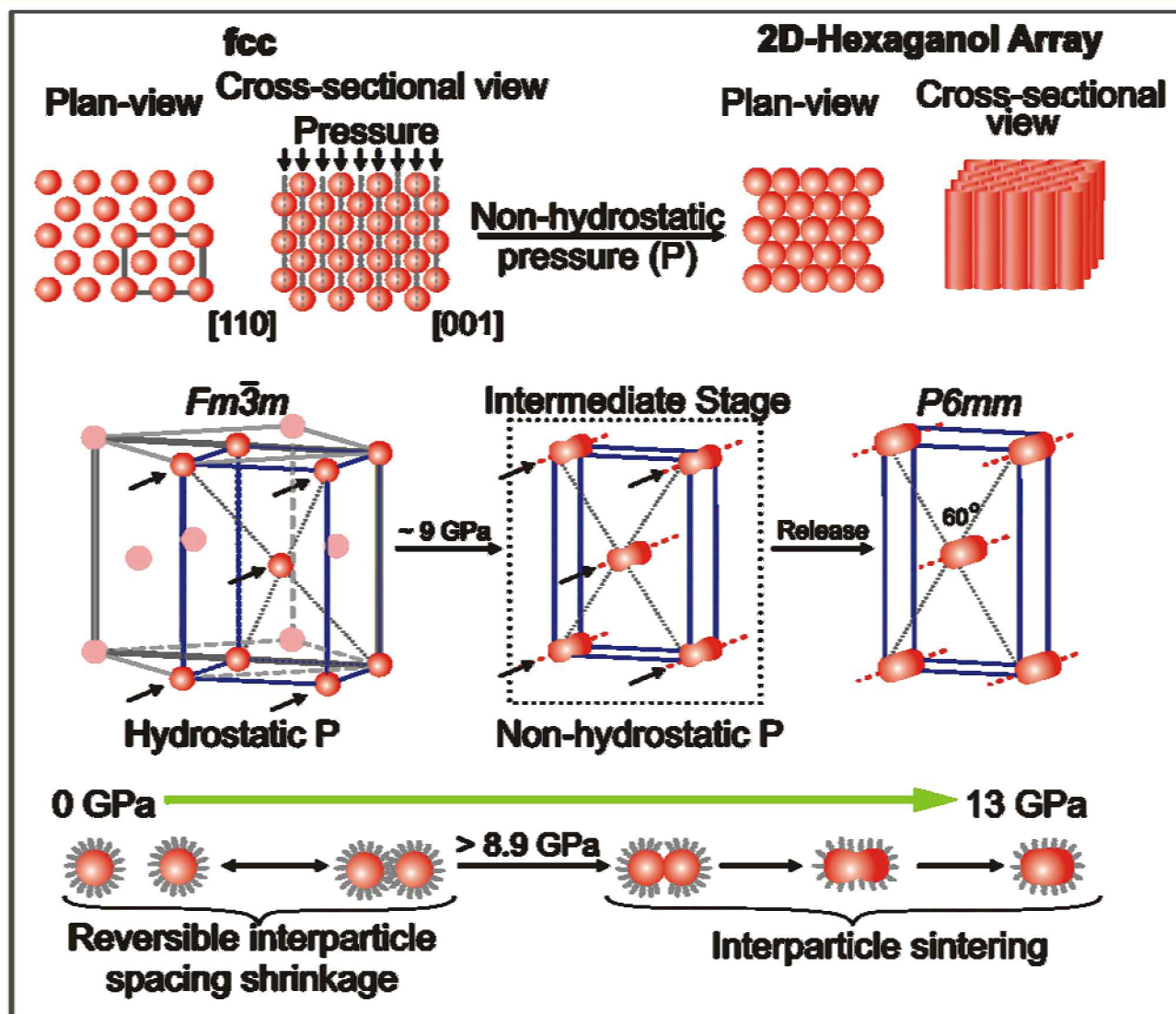
Wu H., et al. *Angew. Chem. Int. Ed.*, 49, 8431-8434, 2010.

In-situ Synchrotron X-ray Studies of Nanoparticle Assembly under Pressure

An external pressure overcomes specific interparticle interactions, enables engineering of nanoparticle assembly, allowing fine-tuning of lattice structure and interparticle separation distance, and to fabricate new nanoparticle architectures.

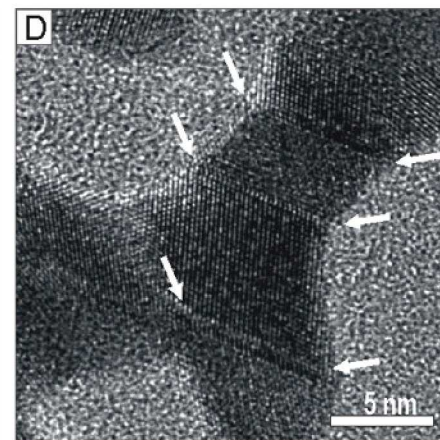
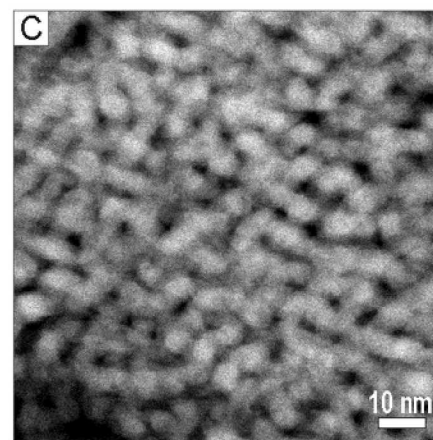
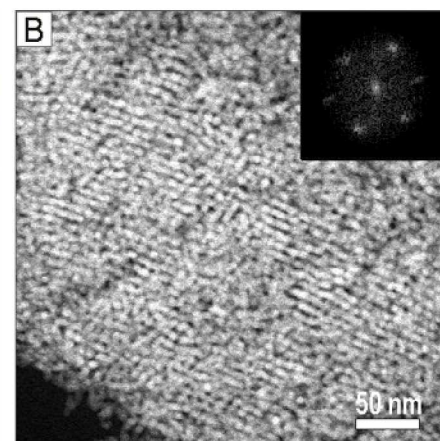
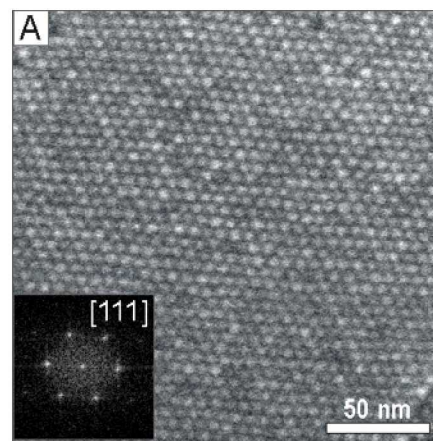
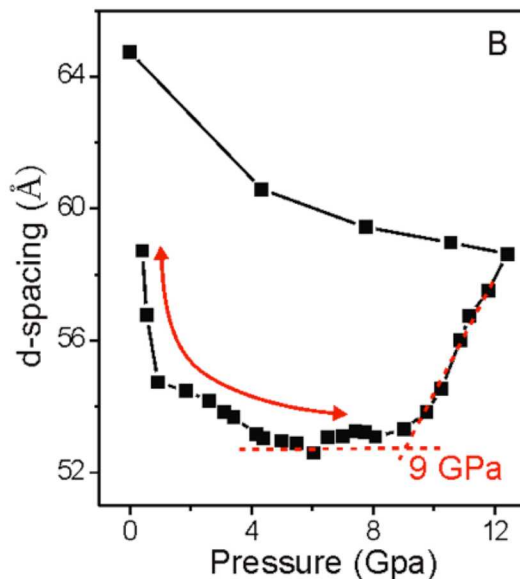
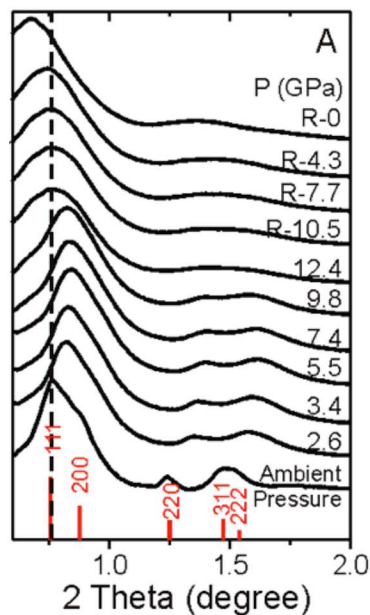
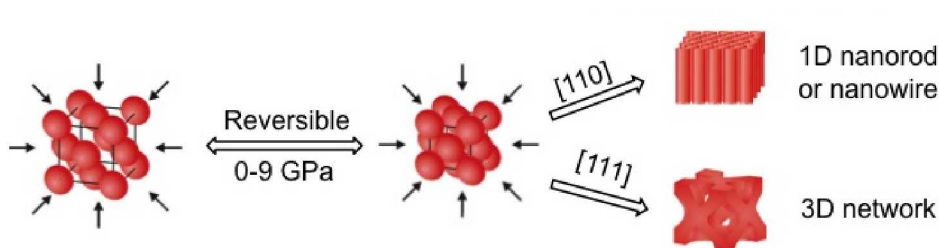


Pressure-Induced Nanoparticle Assembly Processes



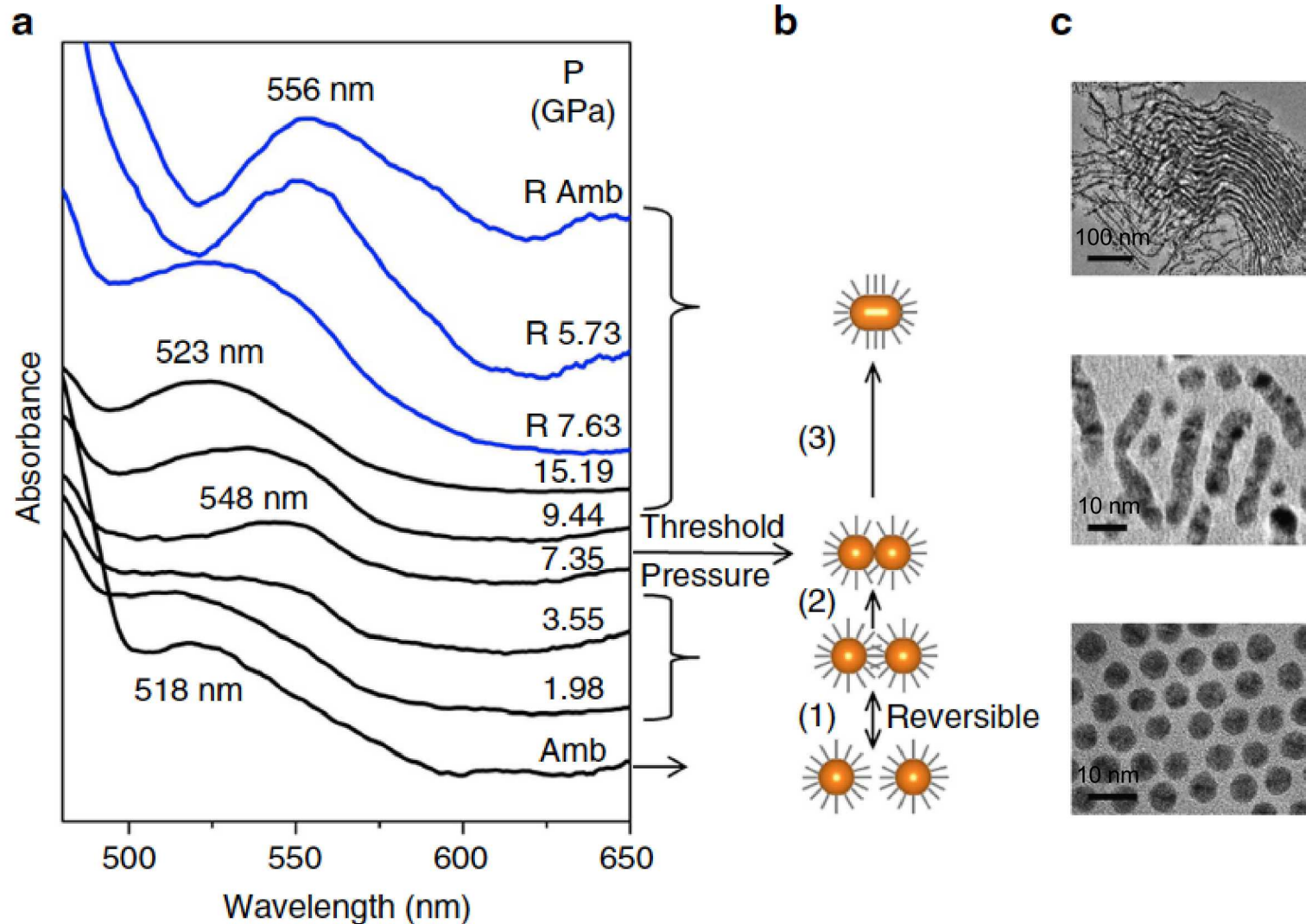
Pressure-Induced Formation of 3D Nanostructures

Interconnected 3D gold networks are formed depending on initial nanoparticle packing

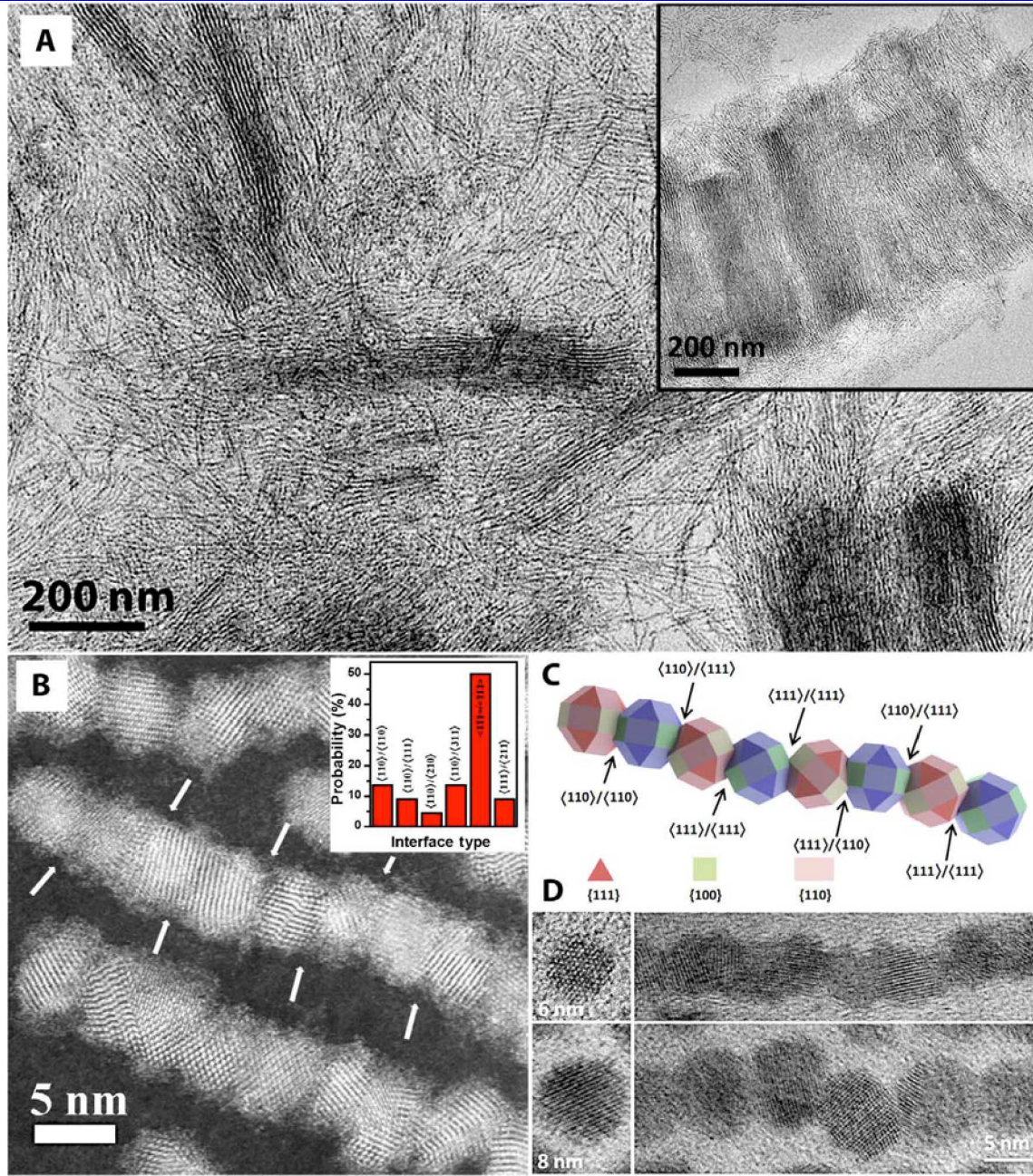


Pressure-Tuned Nanoparticle Interactions and Coupling

Structure - optical property correlation of Ag nanoparticle arrays

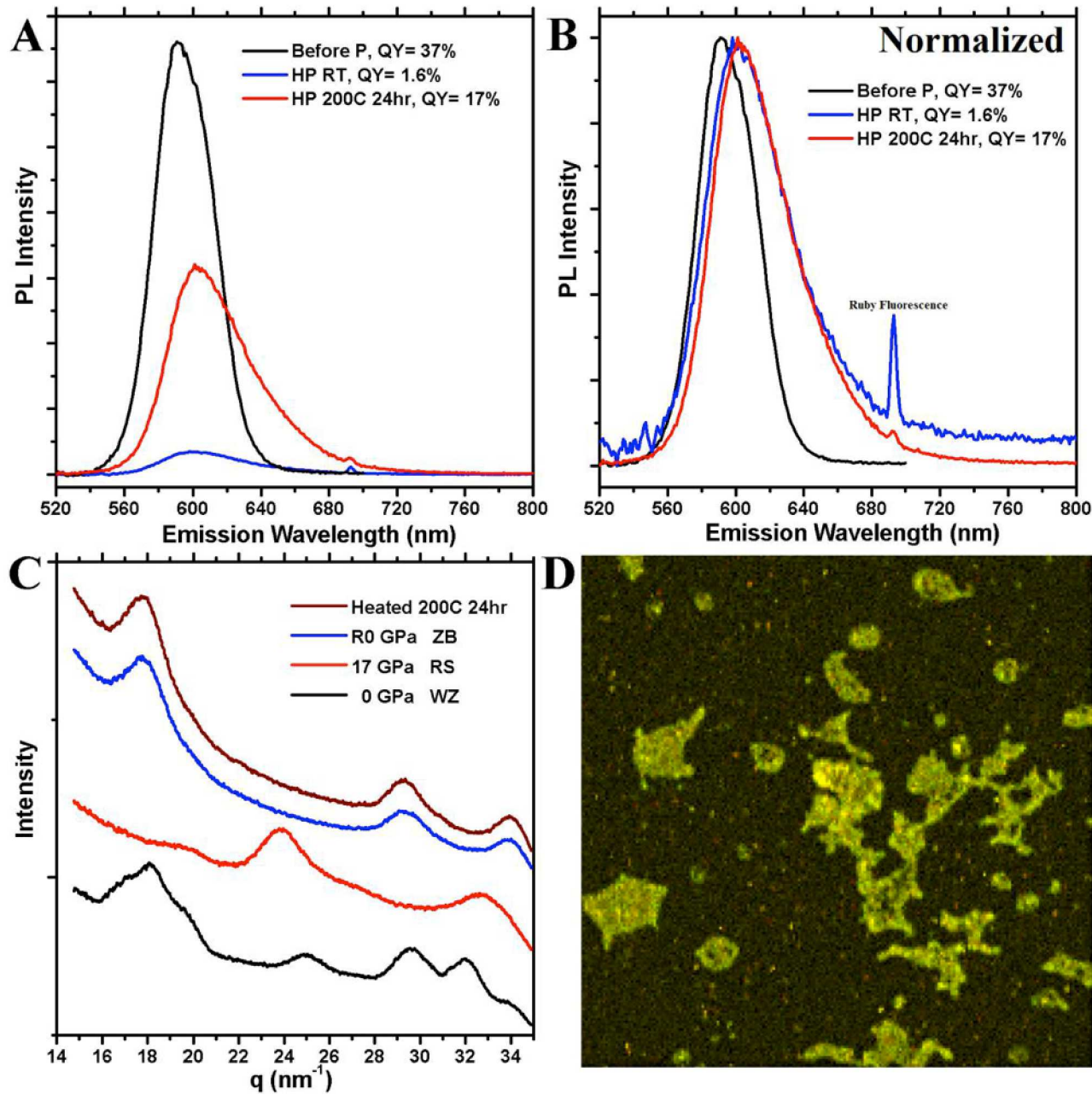


Transmission Electron Microscopy Image of CdSe Nanowires



B. Li, K. Bian, et al,
Science Advances
3, e1602916 (2017).

Optical Property of CdSe Nanowires



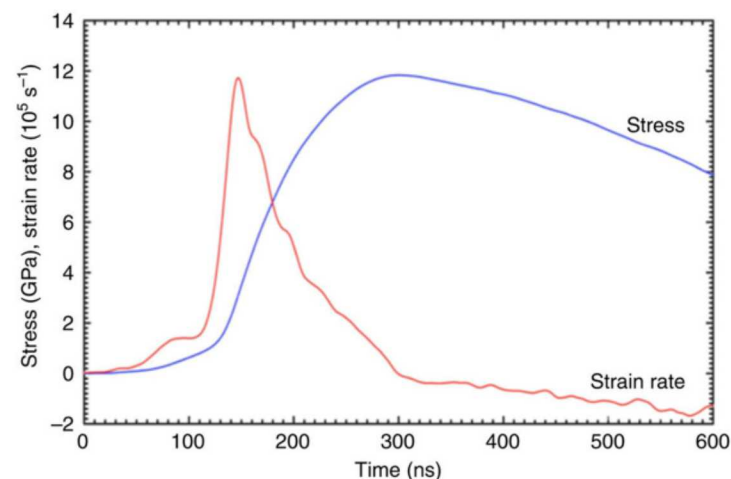
B. Li, K. Bian, et al,
Science Advances
3, e1602916 (2017).

Received 17 Nov 2016 | Accepted 31 Jan 2017 | Published 16 Mar 2017

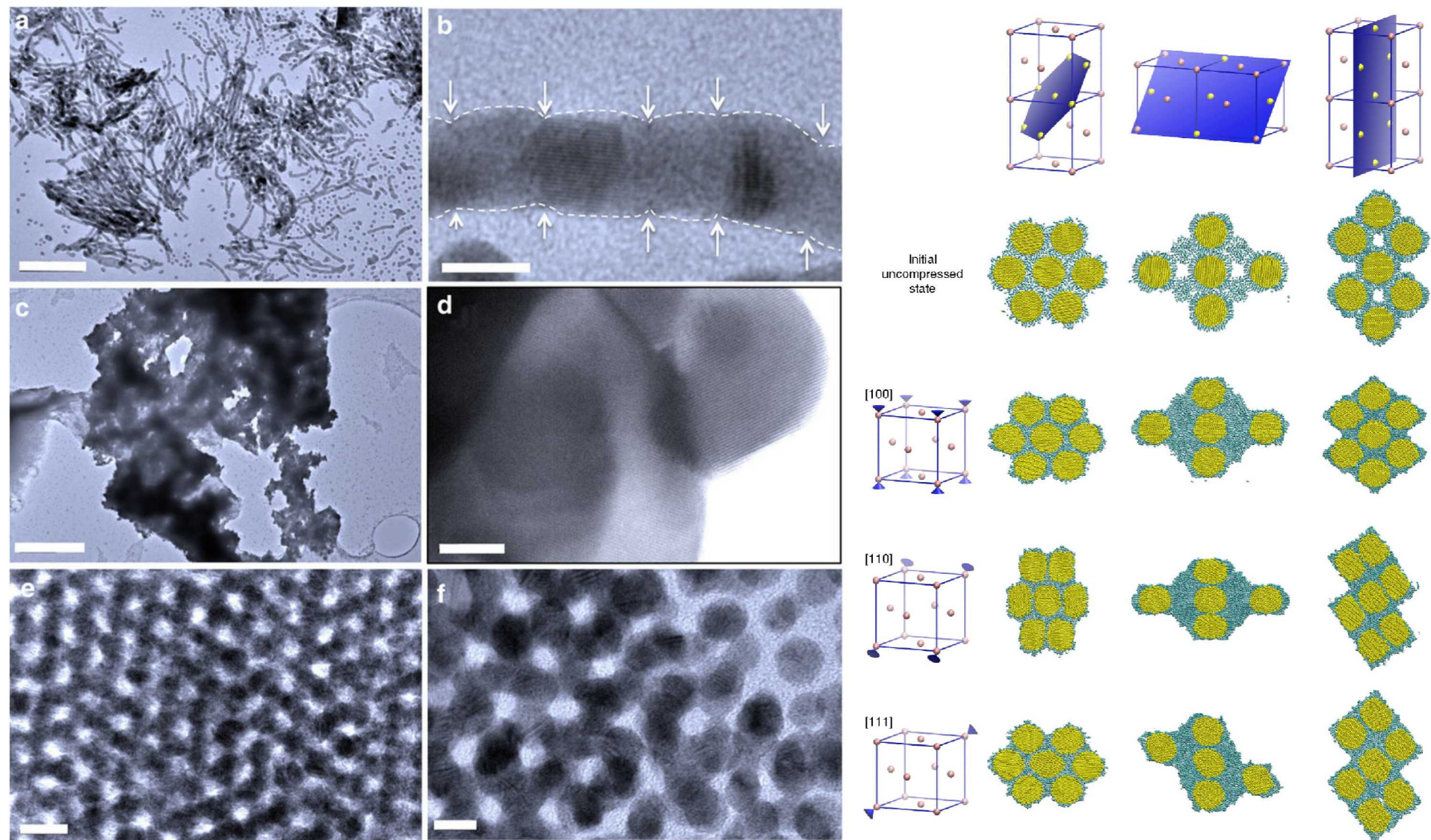
OPEN

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Ultrafast Assembly and Synthesis of 1-3D Nanostructures within Nanoseconds via Pulsed Power



Summary: Pressure-Induced Nanoparticle Engineering

Pressure-Induced Assembly presents a paradigm shift in engineering nanoparticle arrays:

- Allow precise, systematic, and reversible tuning of interparticle distance for interrogation of new chemical and physical properties.
- Produce new chemically and mechanically stable 1-3D nanostructures, which is not possible for current top-down and bottom up methods.

