Self-Asse… Materials

This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND2019-5440C

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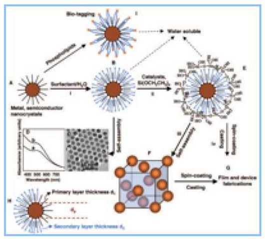
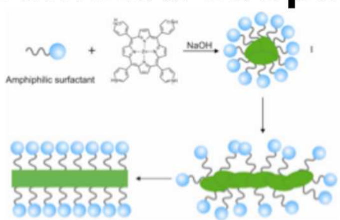
National Laboratory Professor, University of New Mexico

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



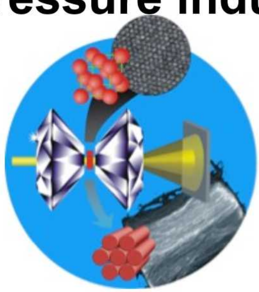
- Synthesis of water-soluble nanoparticles
- Fabrication of robust ordered nanoparticle films
- Applications: optical coatings

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 mesoscales
- Pressure induced nanoparticle coalescence and fabrication
- Pressure induced nanoparticle optical coupling

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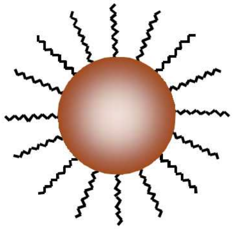
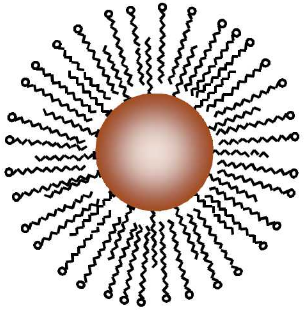
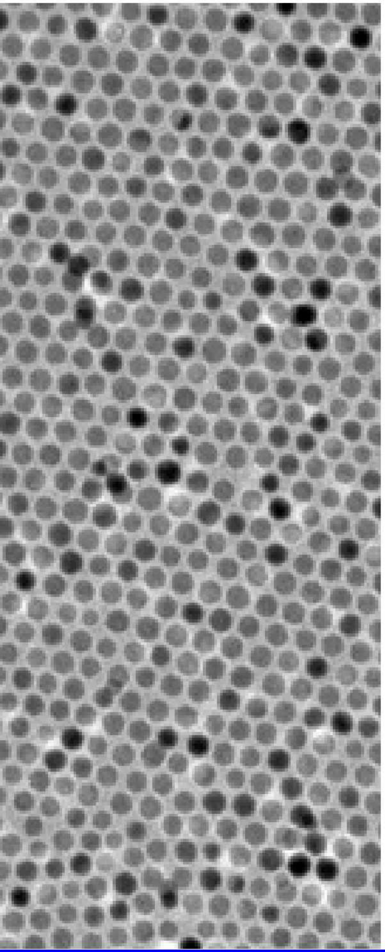
1. Surfactant-Assisted Nanoparticle Self-Assembly and Optical Coatings

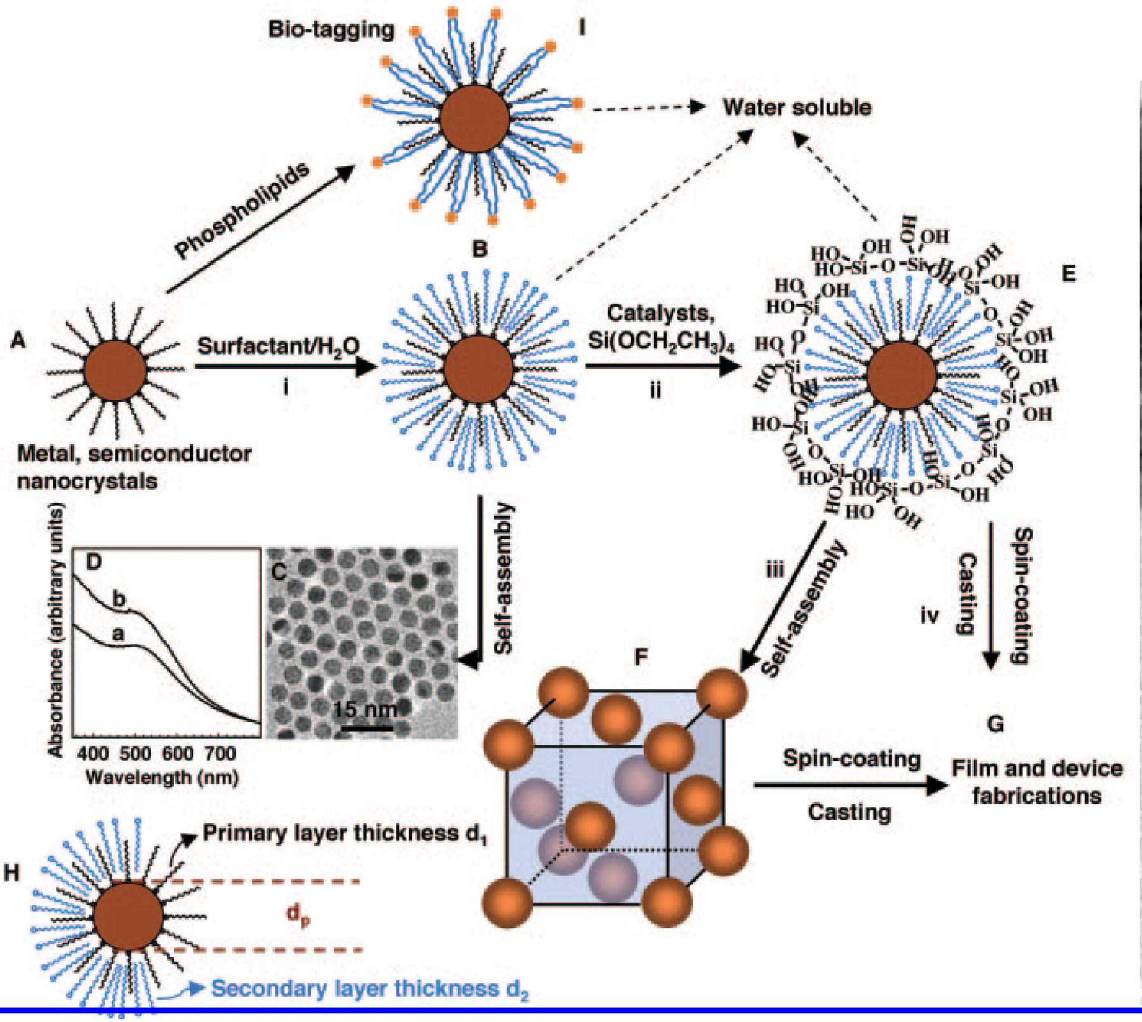


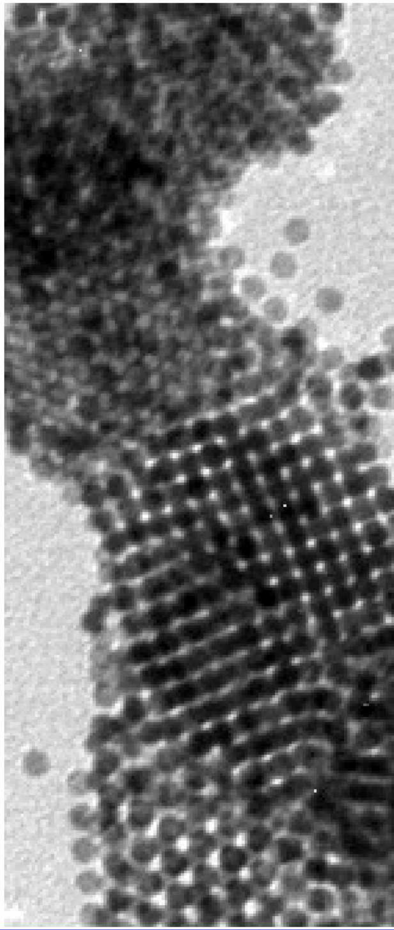
Hydrophobic



Water soluble







Fan et al. patent application (2003), *Science* 304, 567, 2004 & 2006, *Nano Lett.*, 2005, *J. Am. Chem. Soc*, 2005 & 2006, *Adv. Mater.*, 2005, *Chem. Commun.*, 2006 & 2008, *Adv Funct. Mater.*, 2006, *Chem. Mater.*, 2006, *J. Nanomater.* 2009.

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

→

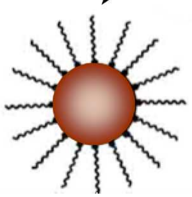
Challenges:
- Low temperature
- Ambient conditions
- Simple process
- Green chemistry
- In-field application

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

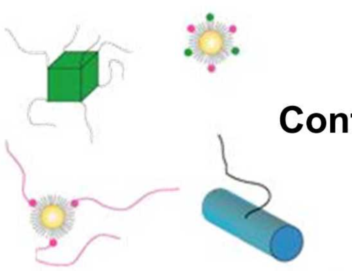
Soft Self-Assembly to Functionalize Nanoparticles to Fabricate Robust Nanoparticle Coatings

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).

Metal nanoparticles
e.g., Gold, silver, etc.
Semiconductor nanoparticles
e.g., PbSe, Ge, CdSe etc.
Metal oxide nanoparticles
e.g., TiO_2, SiO_2, ZrO_2 etc.
Magnetic nanoparticles
e.g., FePt, $FeMnO_4$, etc.

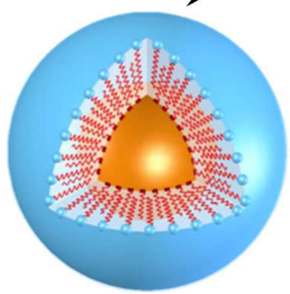


1, surfactant
2, lipid,
3, block copolymer



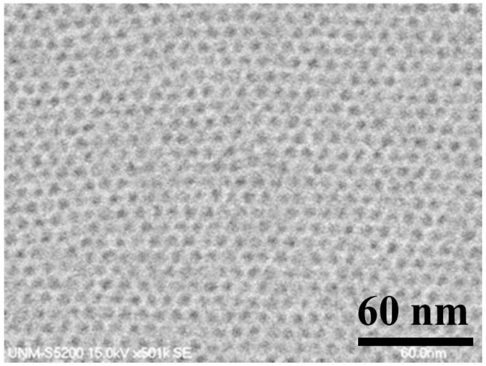
Controlled size and shape

Water-soluble & biocompatible nanoparticles



Engineering Process
-Dip-coating
-Ink-jet printing
-Pen writing
-R-to-R impriting
- more

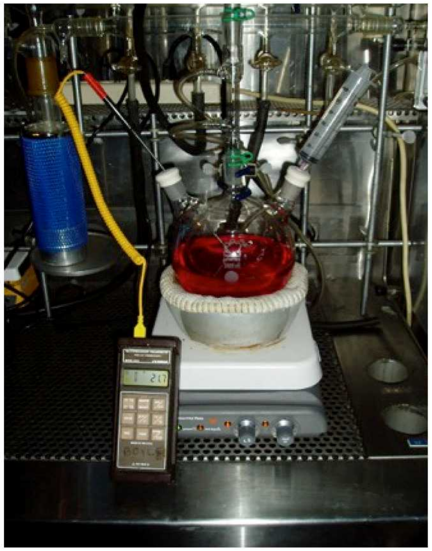
Tunable coating properties:
-Optical property (n, etc)
-Electroni property (σ, etc)
-External field activated
property alteration
-Hydrophobic



Robust, self-assembled nanoparticle films

Synthesis of Nanoparticles

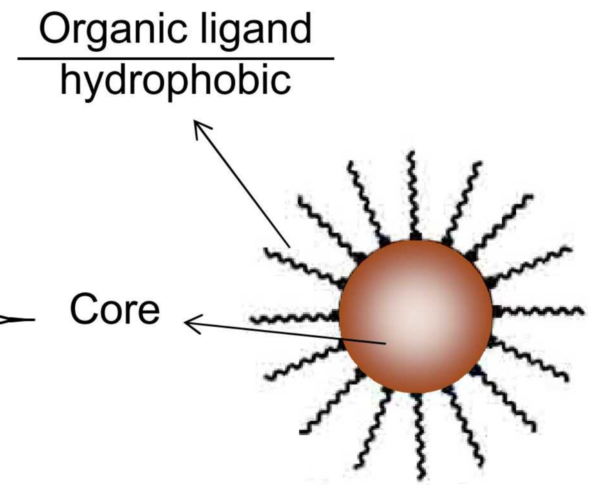
(1) Nucleation and growth at high temperature

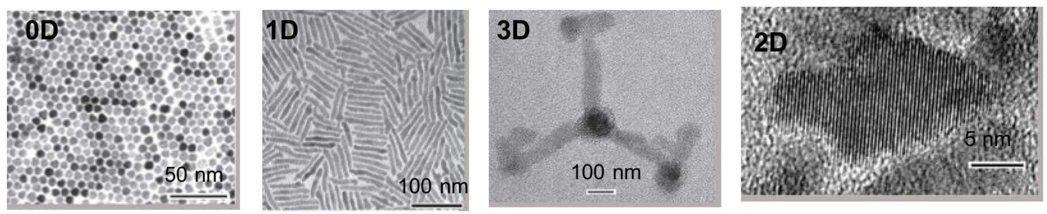


Semiconductor nanocrystals:
- **CdSe, CdS, etc.**
- **PbS, PbSe, etc.**

Magnetic nanocrystals
- **FePt, $FeMnO_4$, Fe_3O_4**

Perovskite nanocrystals:
- **Cs_4PbBr_6**

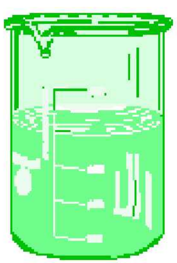




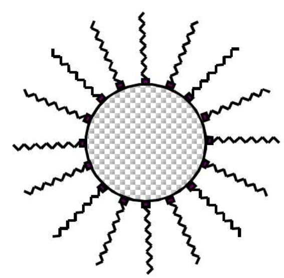
Murray, CB *et al. Annu. Rev. Mater. Sci.* **2000,** *30,* 545-610.

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

(2) Synthesis of metal nanocrystals



***$HAuCl_4$**
$CH_3(CH_2)_nSH$
$(CH_3(CH_2)_7)_4N^+Br^-$
$NaBH_4$



Metal nanoparticles
- **Au, Ag, Pt, etc.**

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

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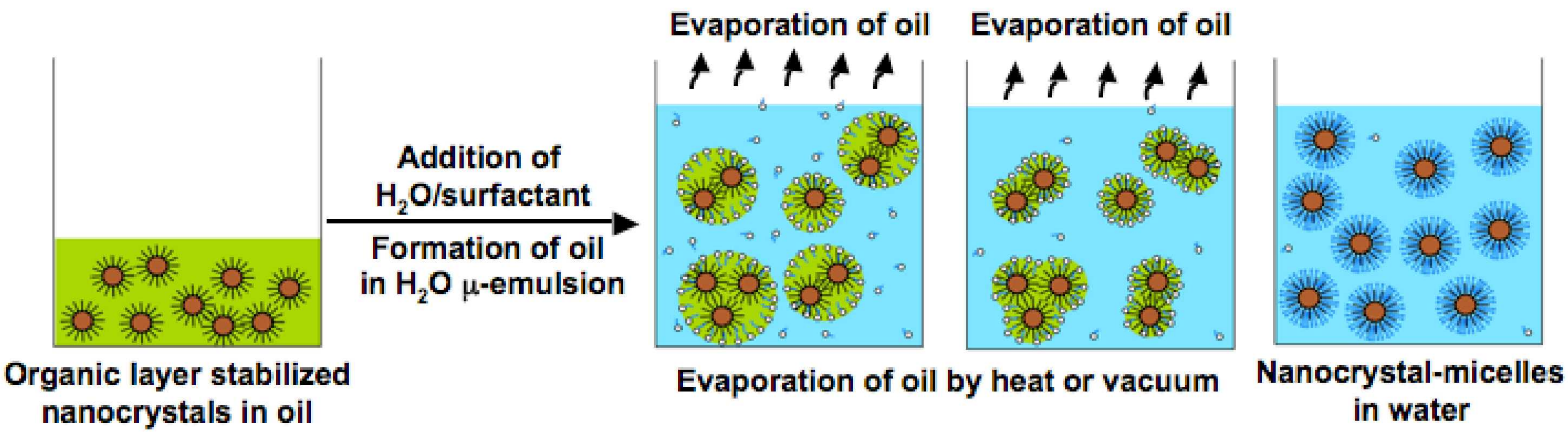
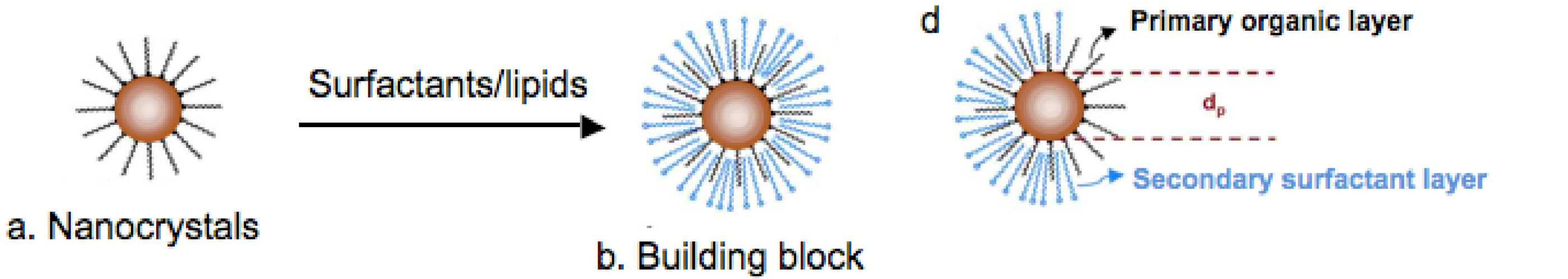
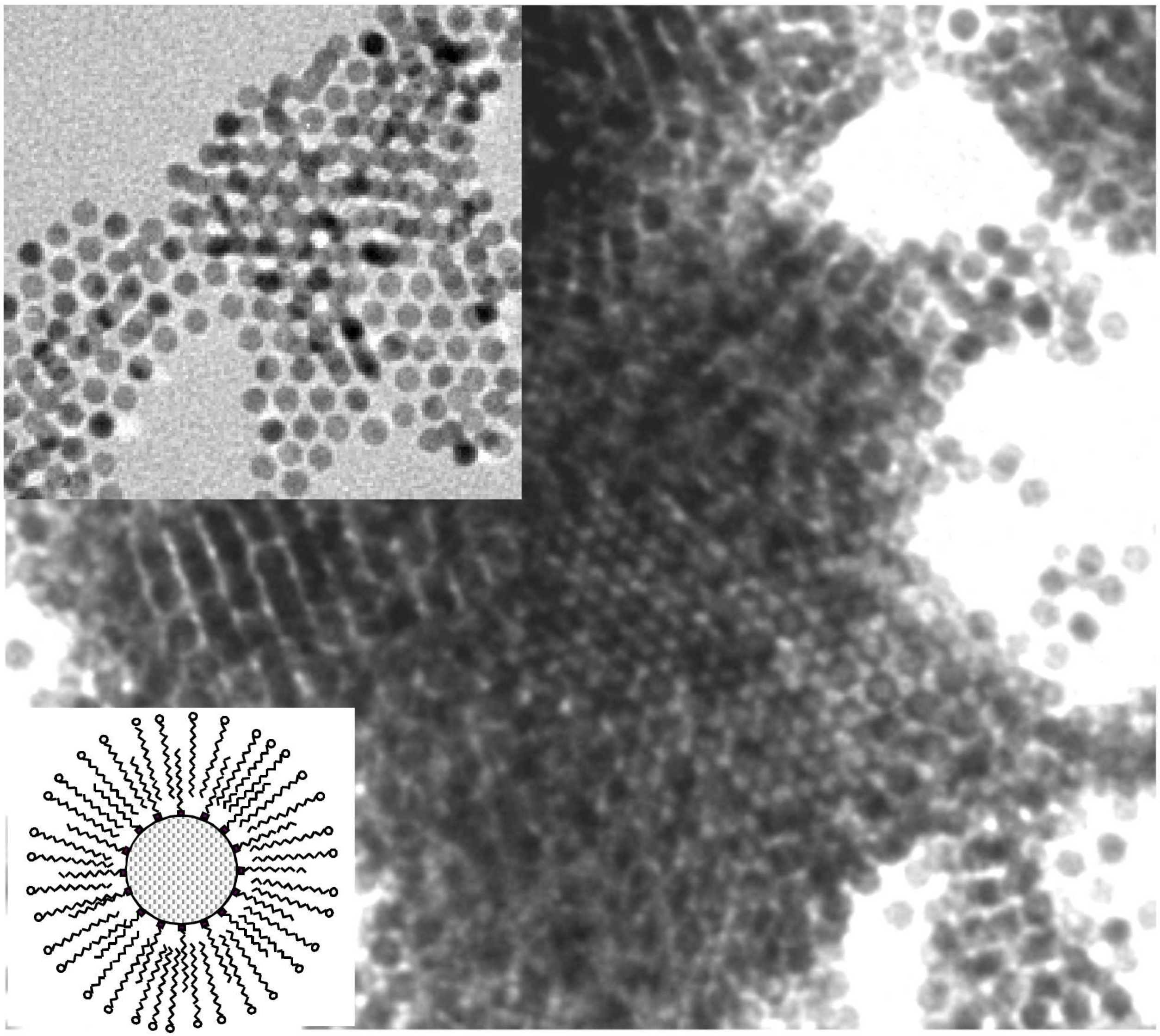
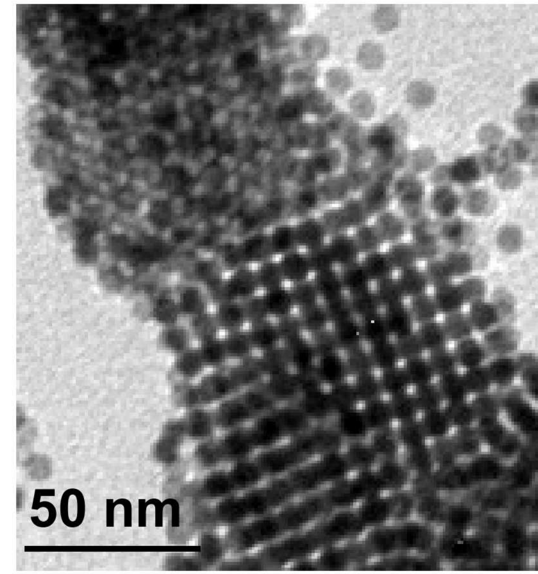
Formation of Self-Assembled Nanoparticle Micelles

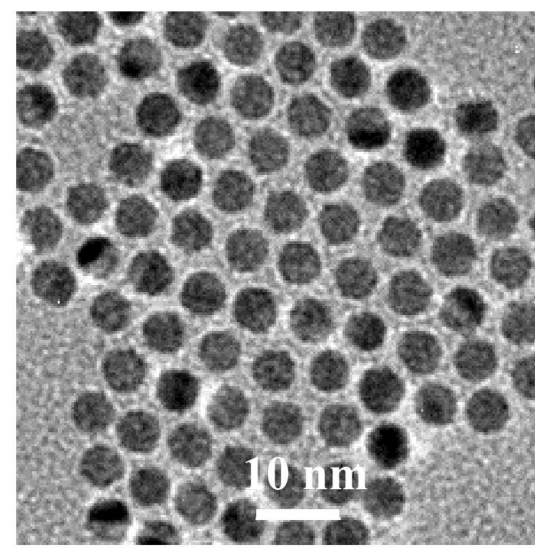




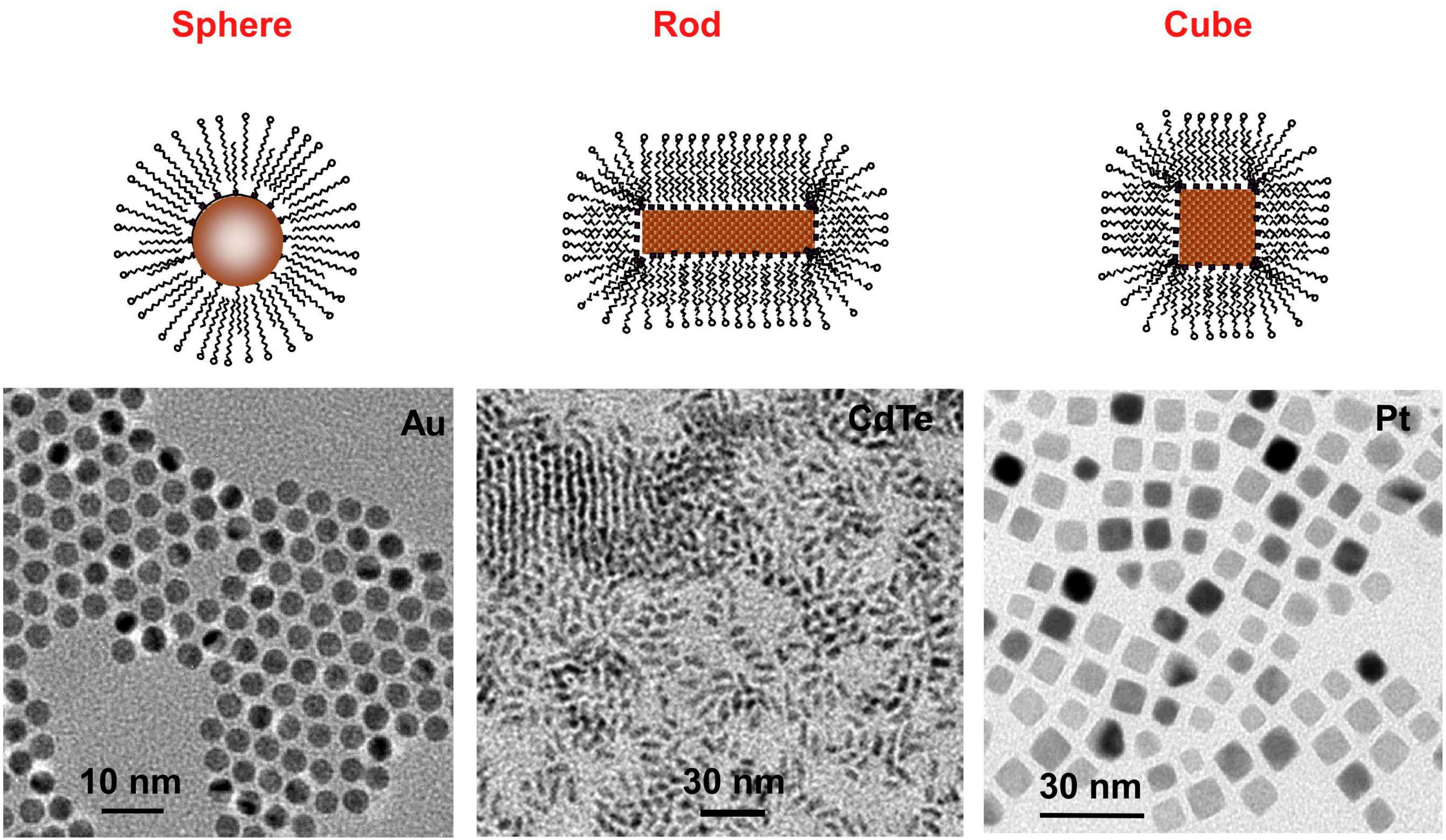
Self-Assembly of Gold Nanoparticle-Micelles from Water Phase



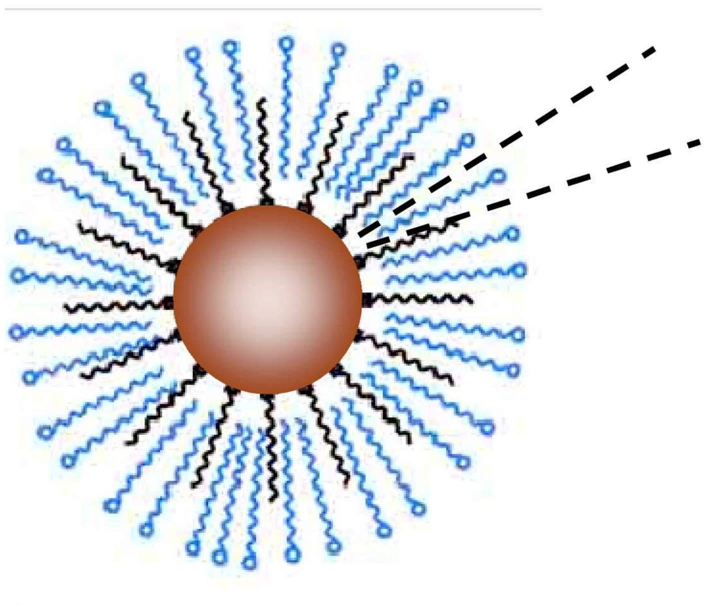


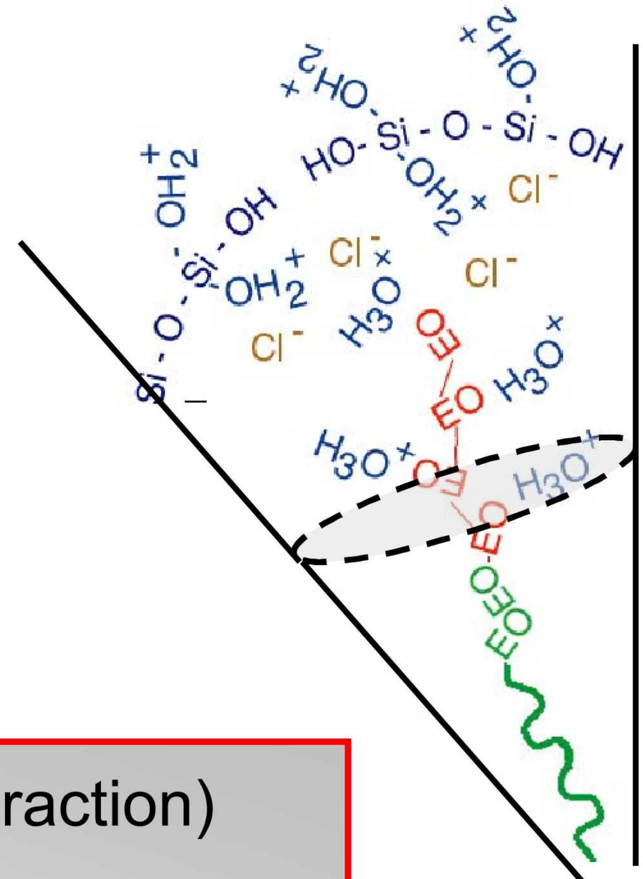


Nanoparticle Micelles with Different Shapes



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



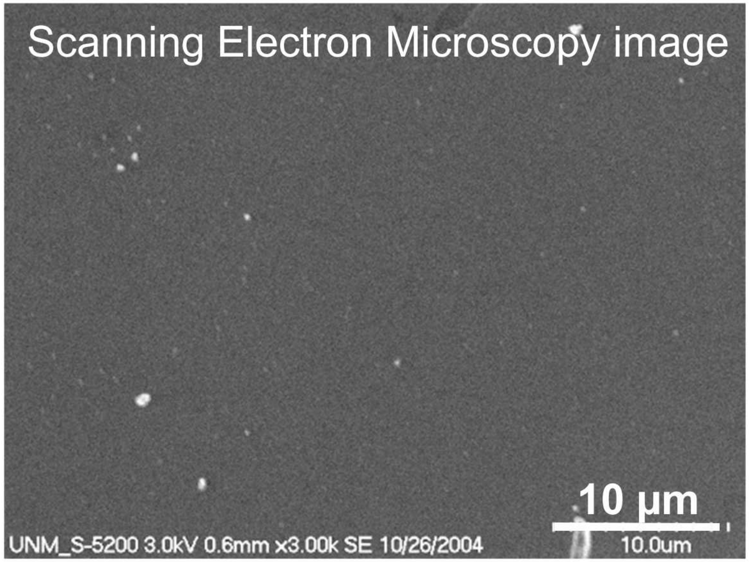


Precursor (e.g., Silica - Surfactant Interaction)

$R\ EO_{m-y}[(EO).H_3O^+]y....yX^-...wI^{\delta+}$

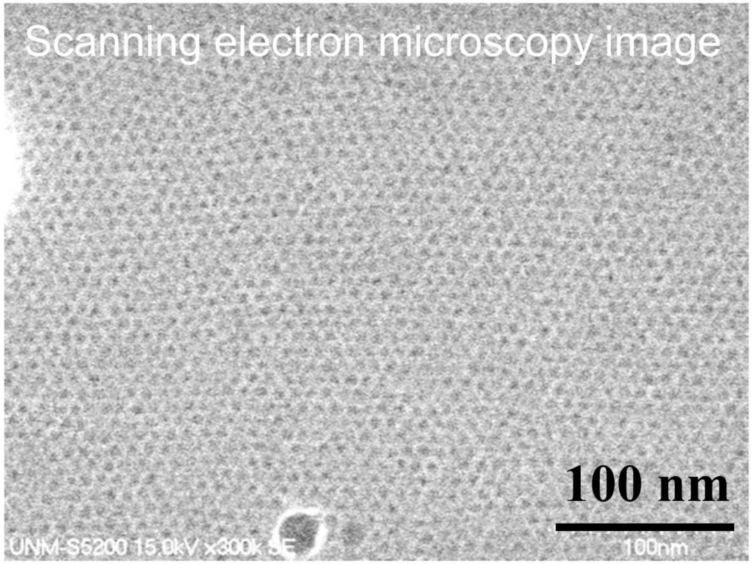
where (I = hydrophilic precursors (e.g.,silicate; δ = framework charge, surfactant head groups = charge groups, EO = ethylene oxide, R = alkyl chain)

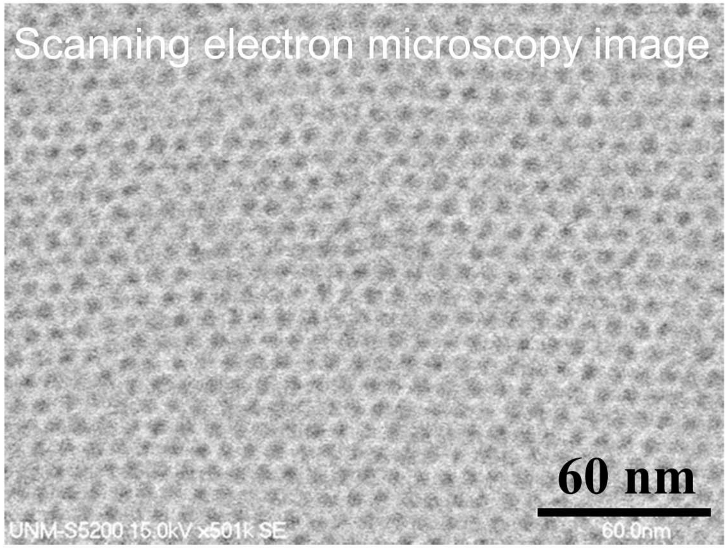
Highly Order Nanoparticle/Silica Films



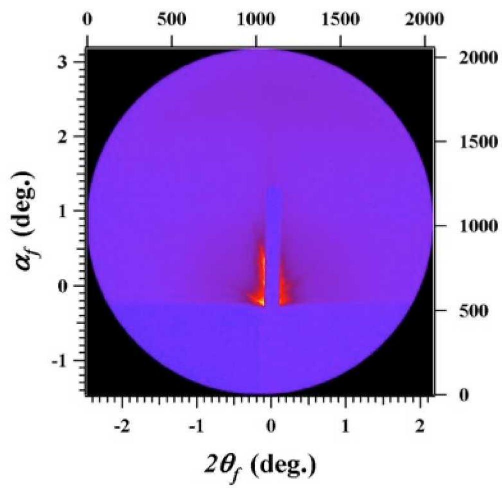
Advantages:
- Mild conditions.
- More stable in inorganic framework. (>200˚C)
- Uniform and continuous without cracking.
- Compatible with standard fabrication process.
- Robust material: metal, semiconducting, magnetic, etc

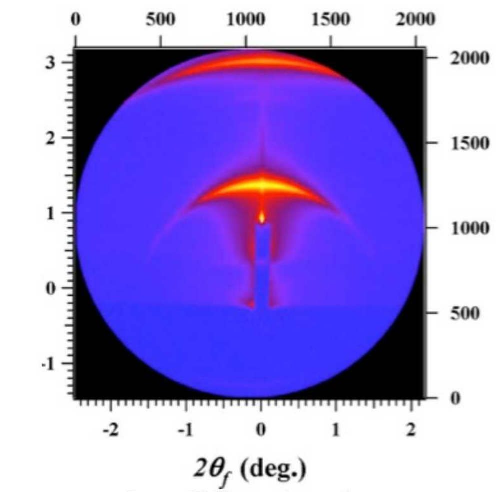
Optical picture

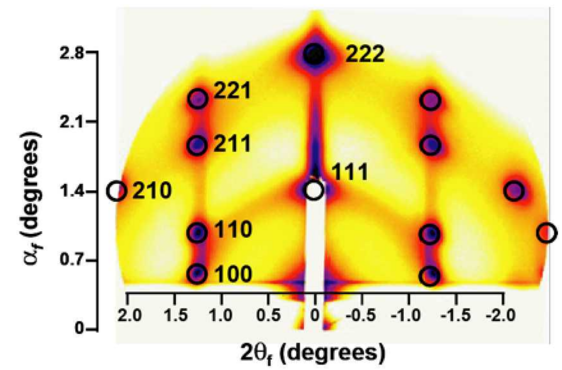




In-situ Grazing Incidence Small-Angle X-ray Scattering Ensure Long Range Order

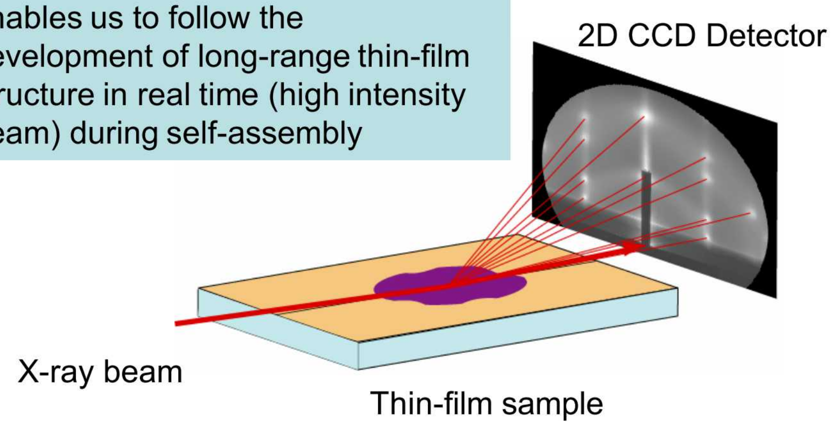




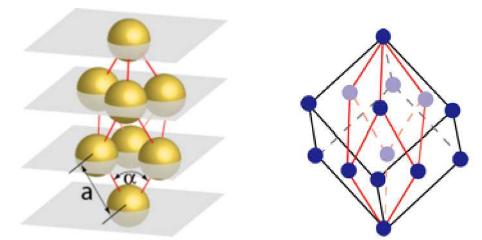


Drying time: t = 18 minutes t = 28 minutes t = 50 minutes

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 $R\bar{3}m$ showing 111 planes



Relationship between rhombohedral and *fcc* structures(α= 60°)

Fan *et al.* ***Langmuir,*** 24 (19) 10575-10578, 2008.

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Nanoparticle Coatings with Tunable Optical Property

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

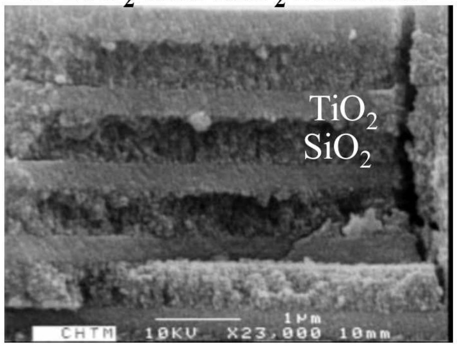
	Material	Measured Index n	Measured Absorption k
Low Index	Porous Silica (Acid Catalyzed)	1.18-1.25	<0.15 (out to 10 μm)
	Porous Silica (Base Catalyzed)	1.19-1.25	<.01 (out to 10 μm)
	Dense Silica	1.4	To Be Measured
Medium Index	TiO_2 (Acid Catalyzed)	1.4-2.4	<0.15 (out to 10 μm)
	TiO_2 (Base Catalyzed)	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

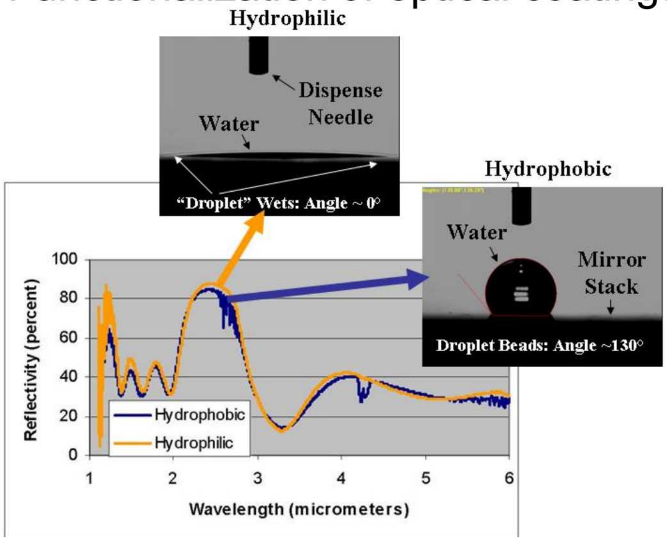
Nanoparticle Coatings for Near Infrared Reflectors

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.

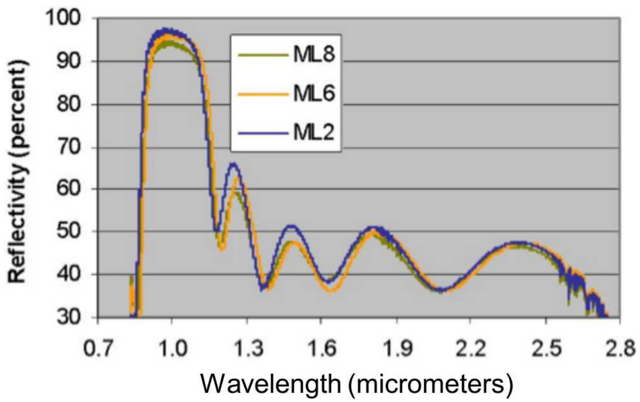
SEM image of quarter wave stacking of TiO_2 and SiO_2 reflector

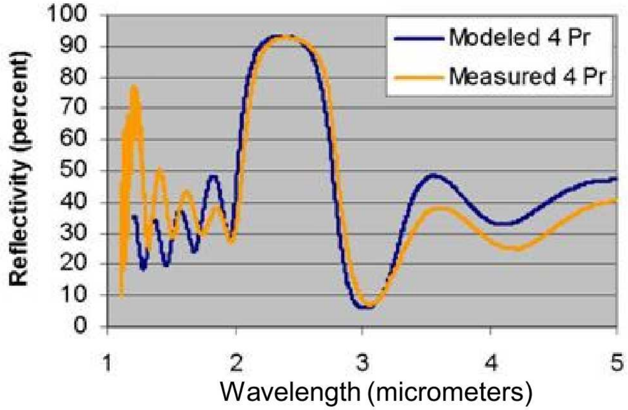


Functionalization of optical coatings



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





Model design show 99.9% and address key manufacturing issue.

iScience 11, 272–293, January 25, 2019
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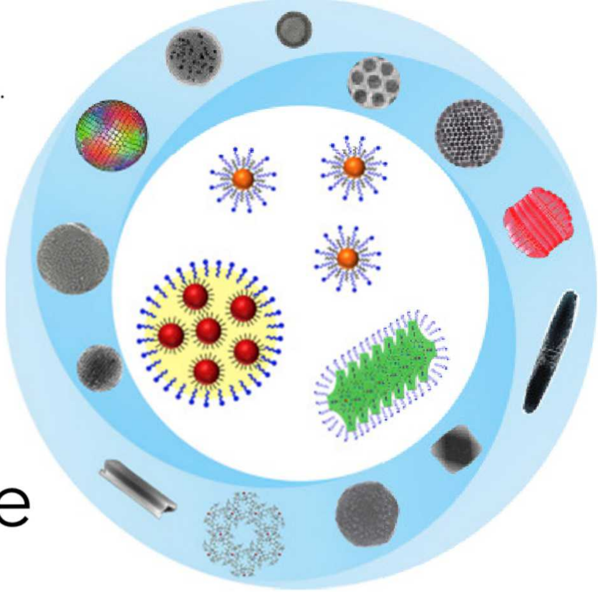
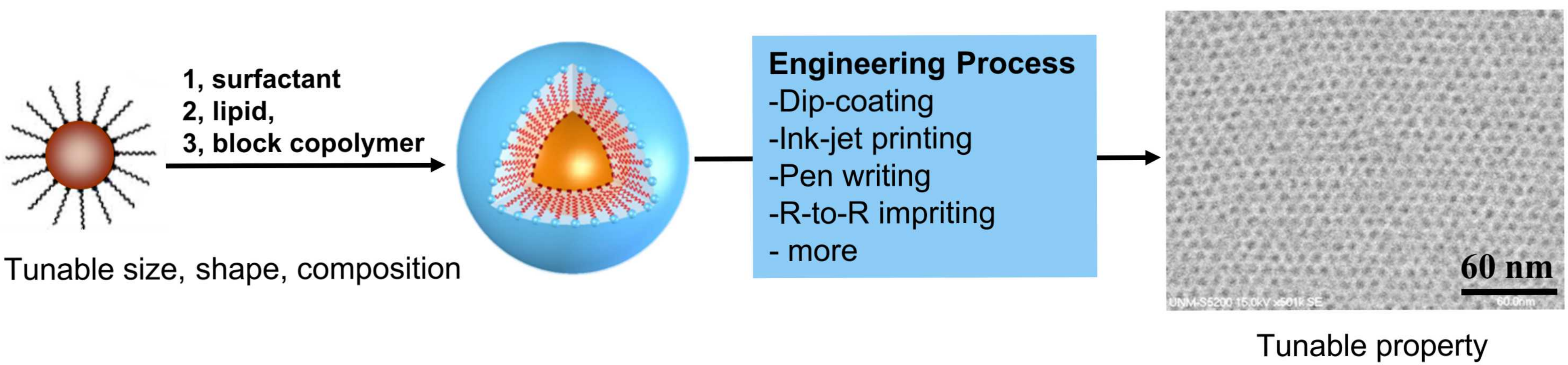
iScience



Review

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

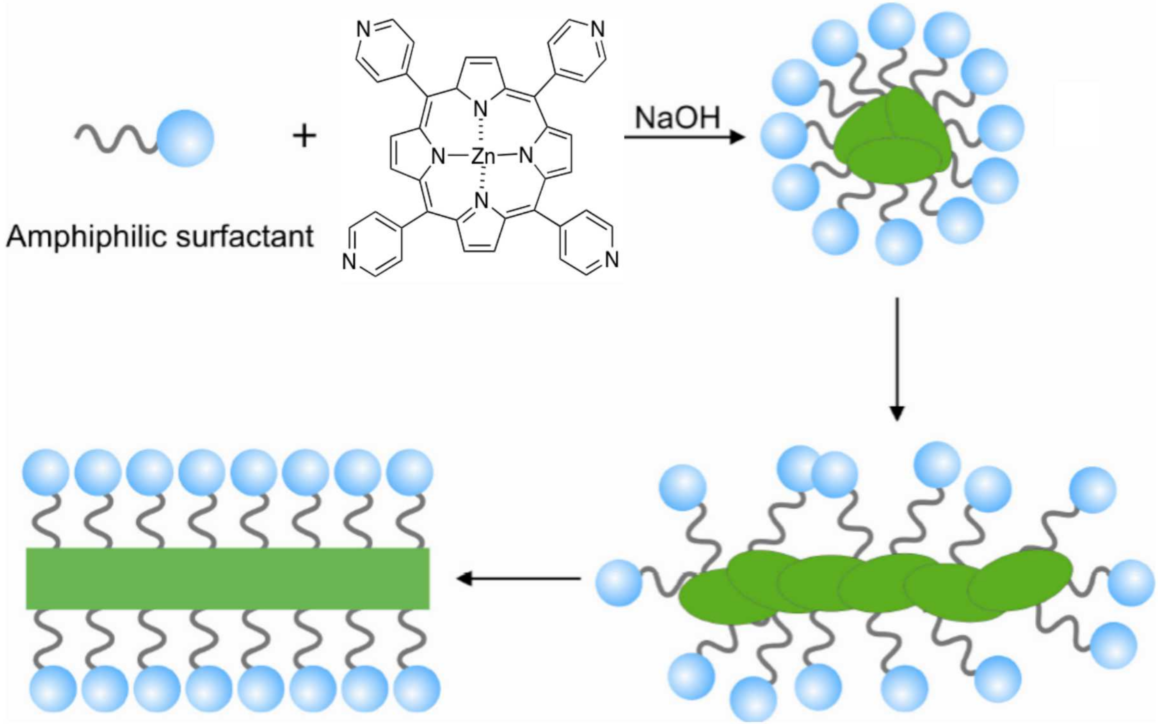
Wenbo Wei,[1] Feng Bai,[1,*] and Hongyou Fan[2,3,4,*]



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.

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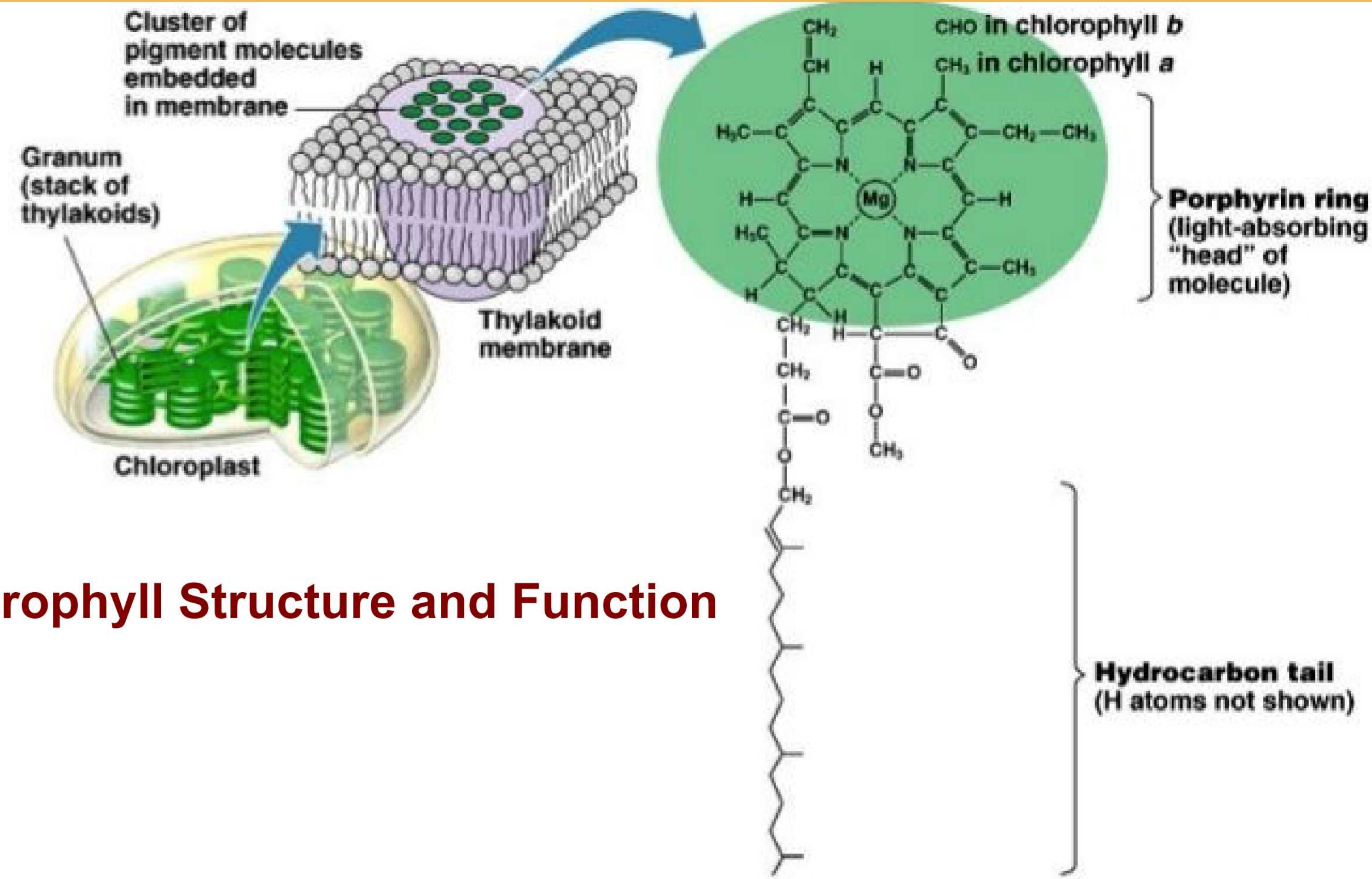
Why Porphyrins?

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.



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Chlorophyll Structure and Function

https://www.pinterest.com/katidavis86/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:

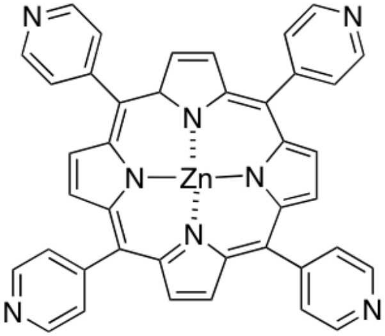
- Well-defined size and surface chemistry,
- Optical and electrical activity due to the conjugated aromatic π system,
- Covering wide range of visible spectrum.

Applications in energy conversion/storage and sensors:

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

Driving forces for self-assembly:

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



ZnTPyP

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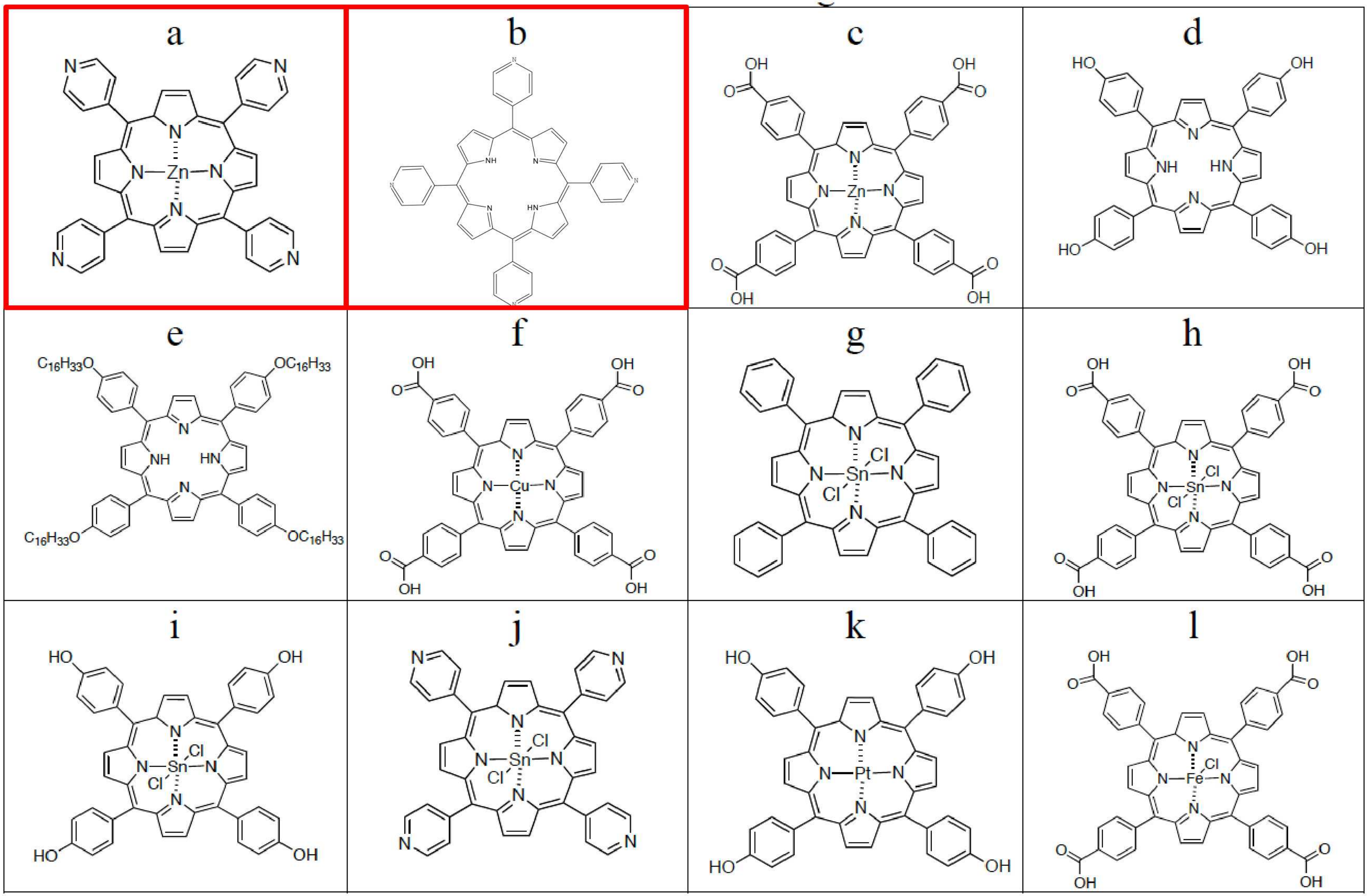
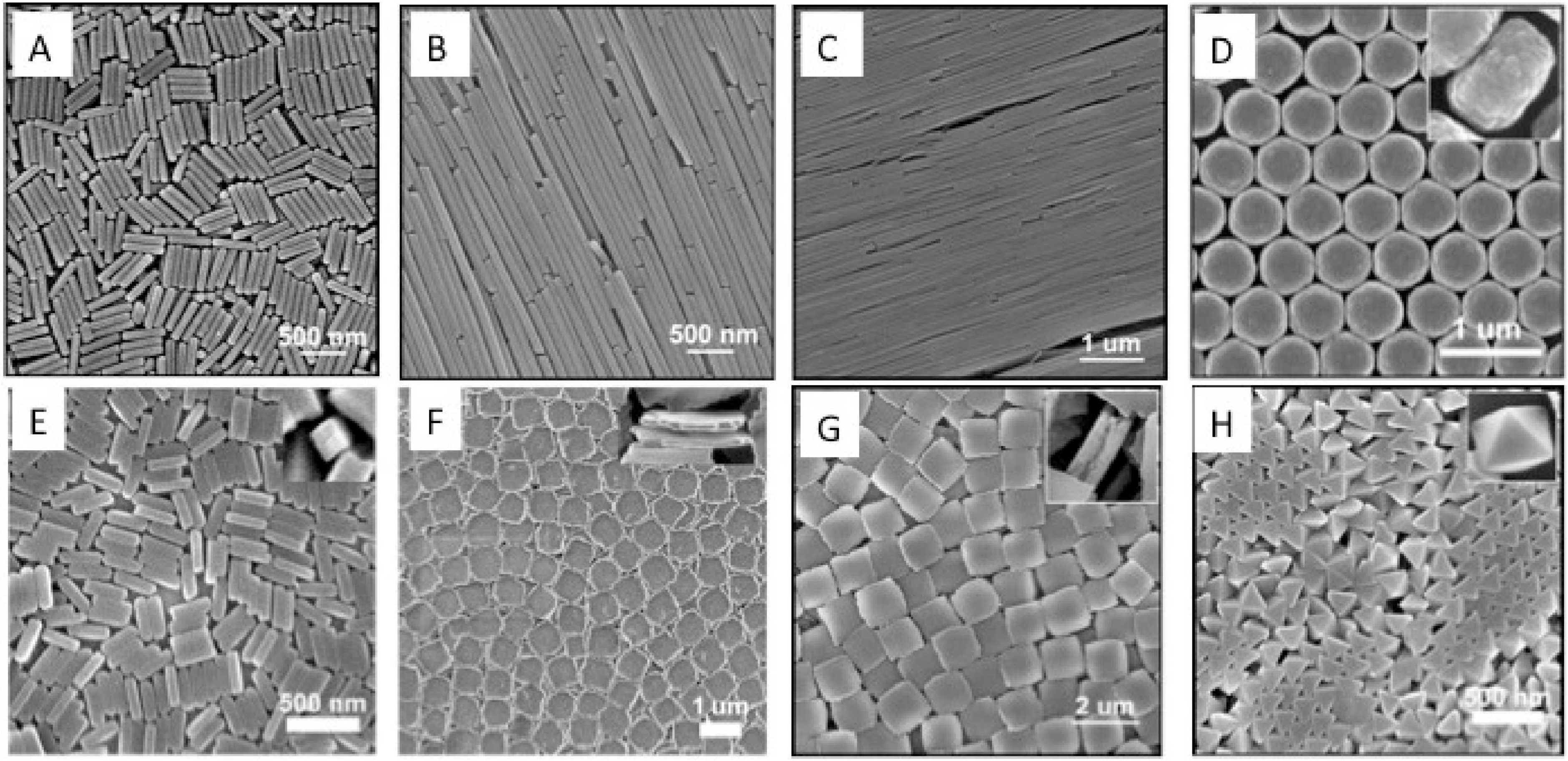
Porphyrin Used in Our Research



Hierarchically Structured Porphyrin Nanocrystals



K. Bian et al. *Nature Communicitons*, **2018**.
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F. Bai, et al. *Nano Lett.* **2011**, 11, 5196–5200.
F. Bai, et al. *Chem. Commun.*, **2010**, 46, 4941–4943.

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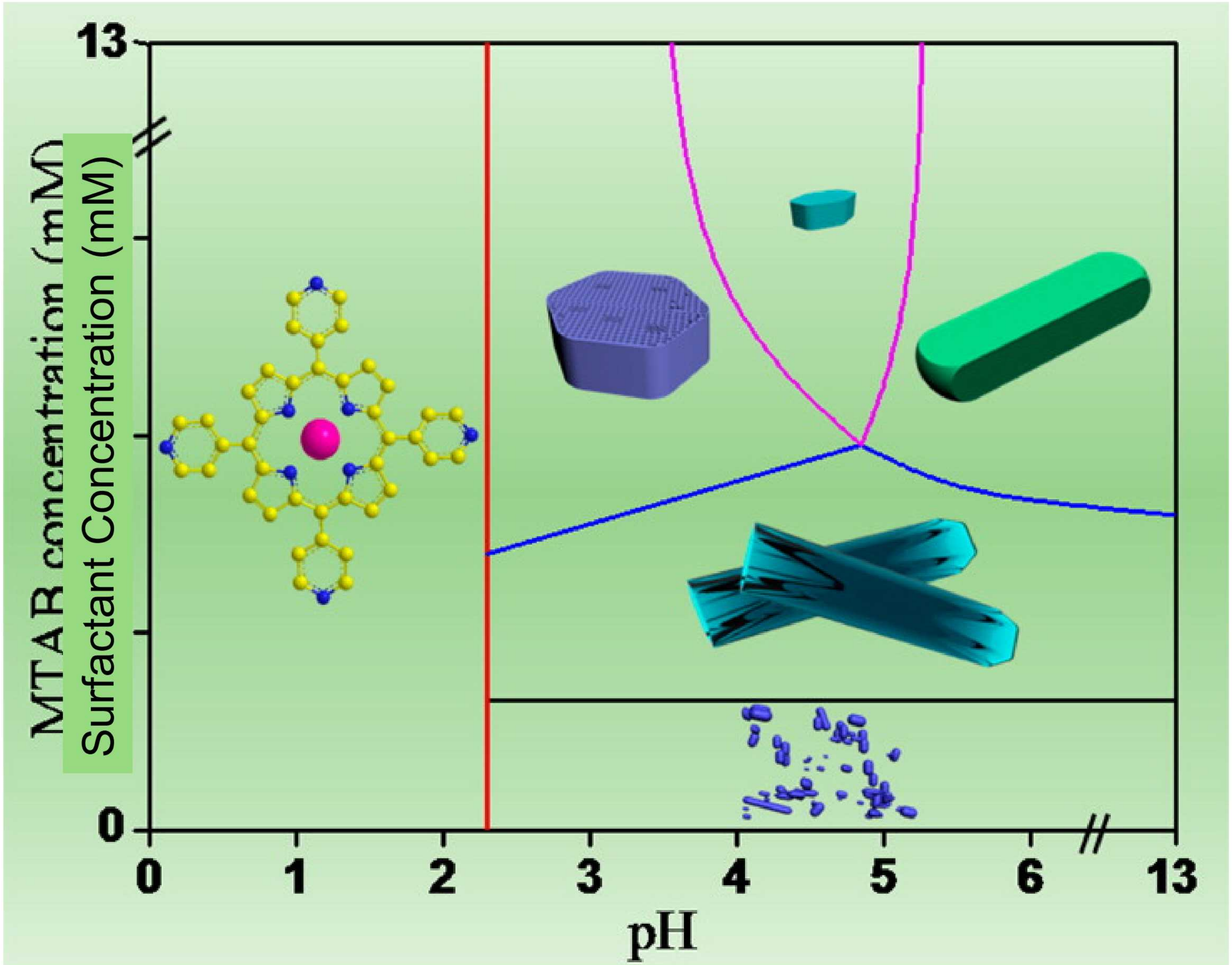
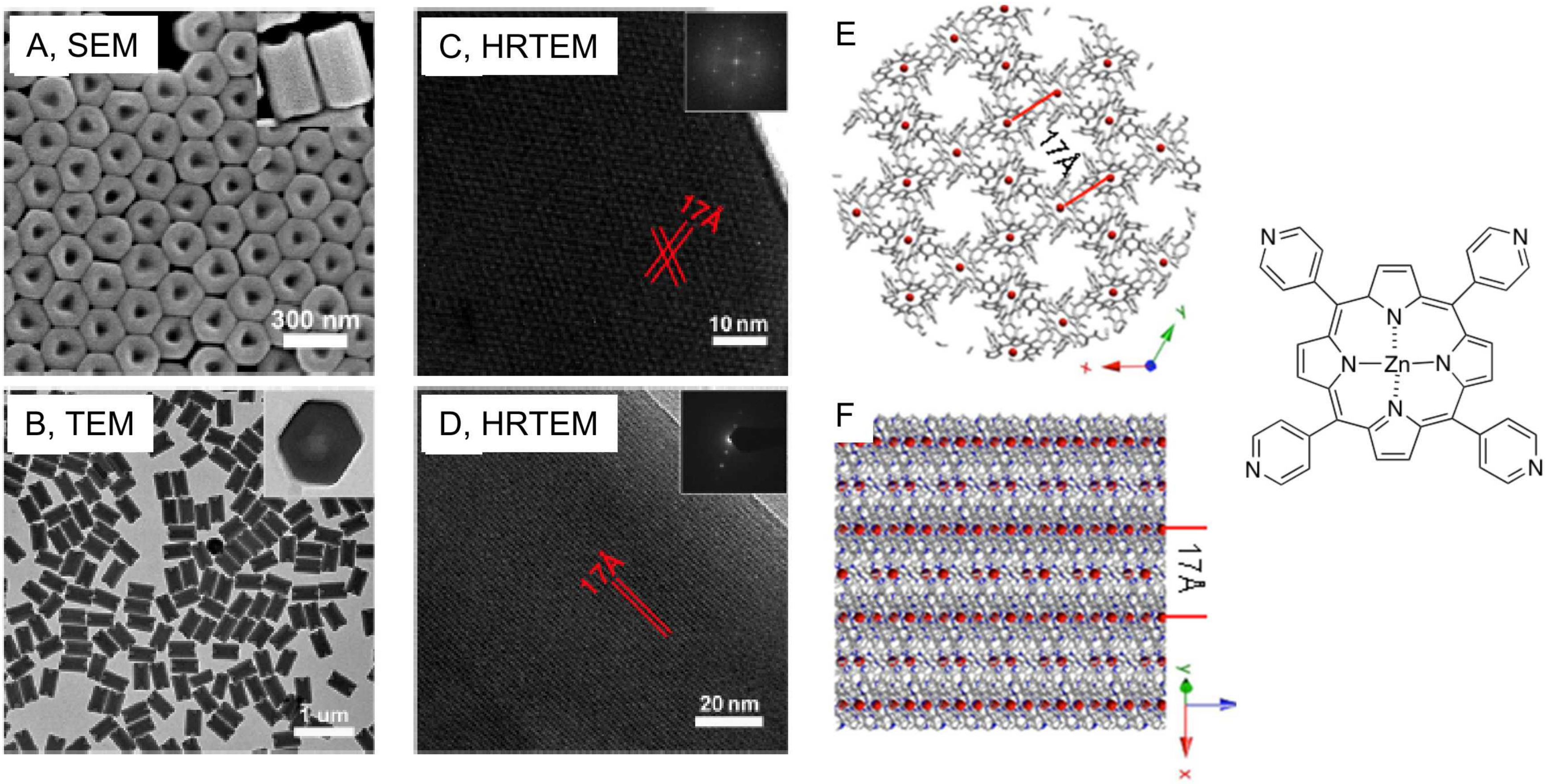
Phase Diagram of Self-Assembled Porphyrins



Nano Lett. **2014,** 14, 7175-7179.

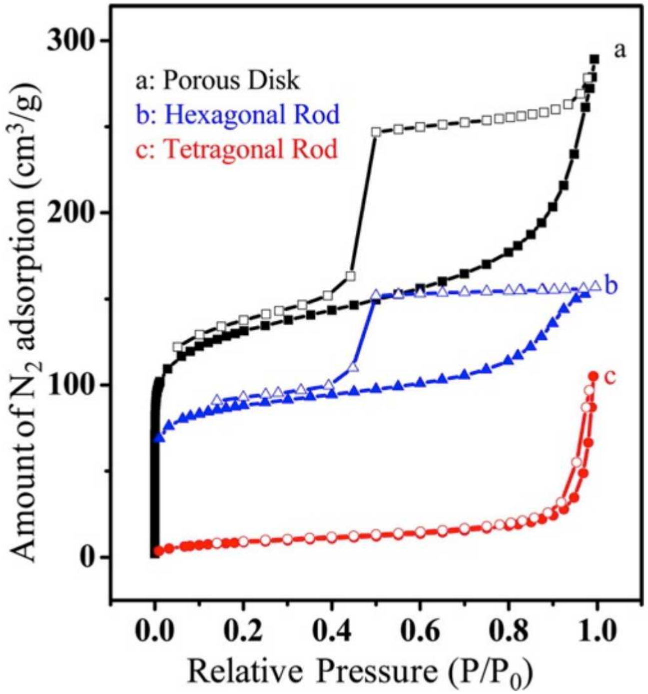
Hierarchically Structured Porphyrin Nanorods

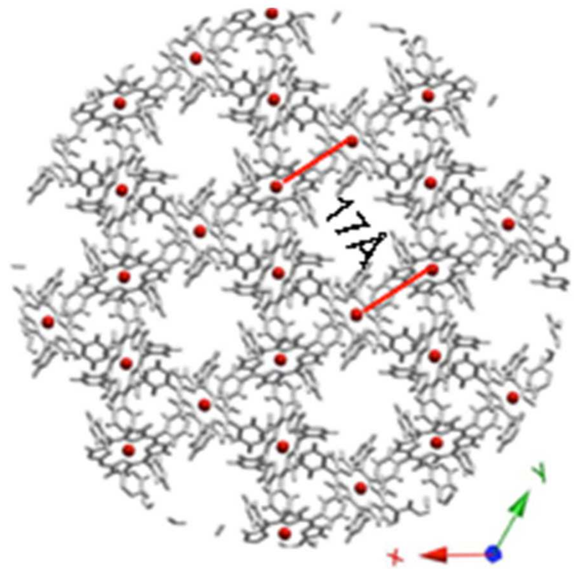


E, simulated crystal structure, viewed along the crystallographic z axis, Zn (red).
F. simulated crystal structure, viewed along the nanowire.
Crystal structure: Hexagonal R-3 (148) a=b= 33.110, c= 9.273; α=β=γ=120

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. *Nano Lett.* **2011**, 11, 3759–3762; *Nano Lett.* **2011**, 11, 5196–5200.

Nitrogen Sorption Isotherms of Porphyrin Nanocrystals



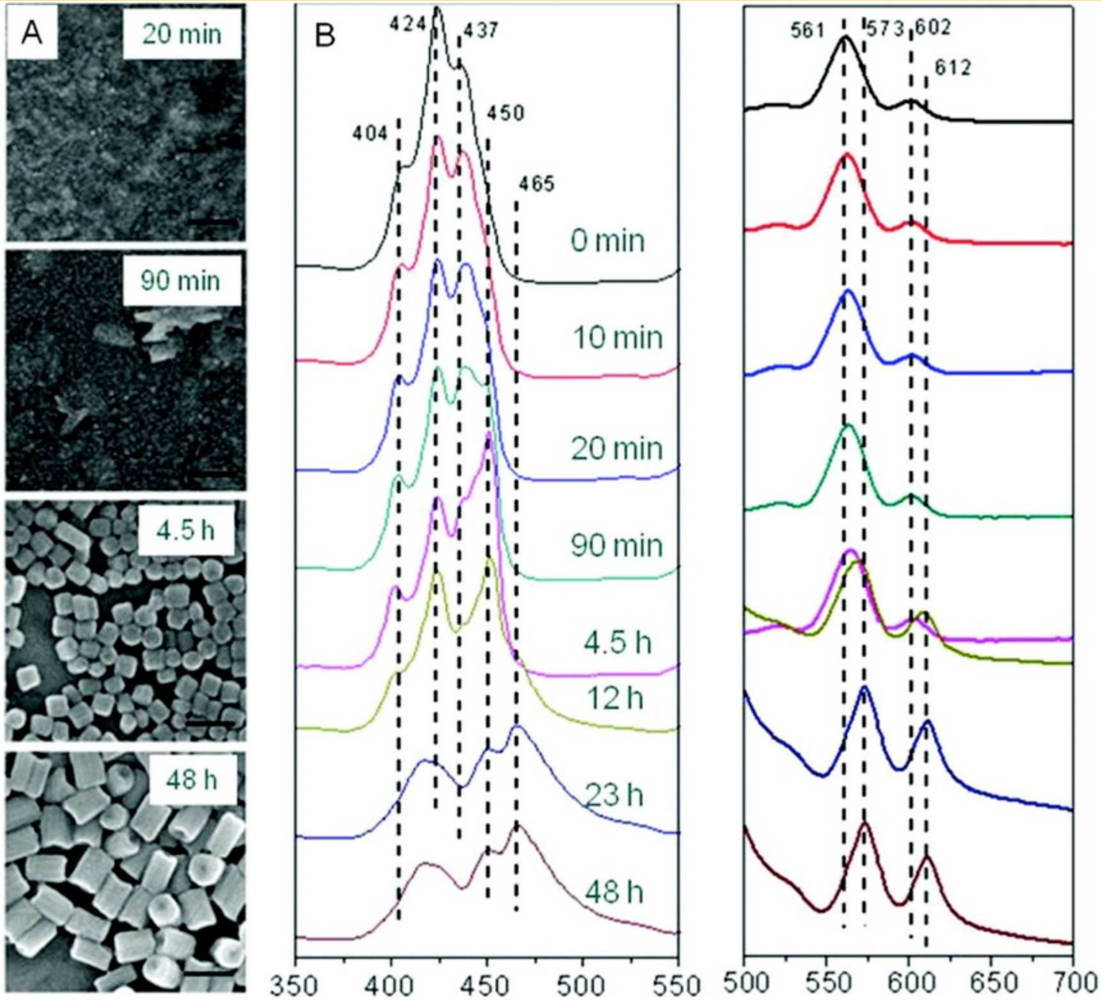


	Porosity (%)	Surface area (m^2/g)	Pore size (nm)
Tetragonal rod	34.3	371	0.81
Hexagonal rod	20.1	327	0.79
Long wire	16.1	294	0.78

Nano Lett. **2014,** 14, 7175-7179.

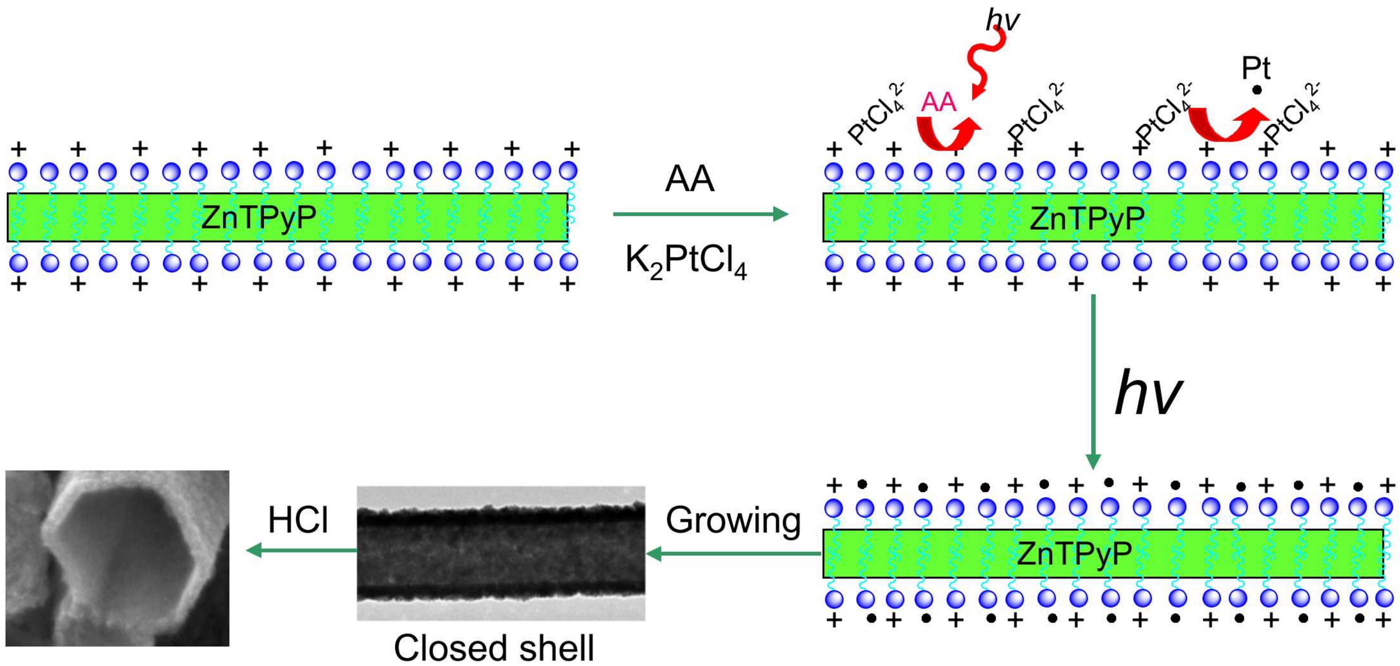
Structural Evolution during Self-Assembly

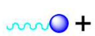
SEM images of hexagonal nanorods and UV-spectra of the reaction solution at different reaction times.

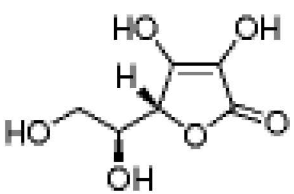


J. Wang, et al. *Nano Lett.*, **2017**, *17* (11), 6916–6921. J. Wang, et al. *Nano Lett.* **2016,** 16, 6523-6528. F. Bai; et al. *Nano Lett.* **2011**, 11, 3759–3762; *Nano Lett.* **2011**, 11, 5196–5200.

Photocatalytic Synthesis of Hollow Pt Nanostructures



 CTAB



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

$$ZnTPyP \xrightarrow{hv} ZnTPyP^{*}$$ (excited triplet π-π* state)

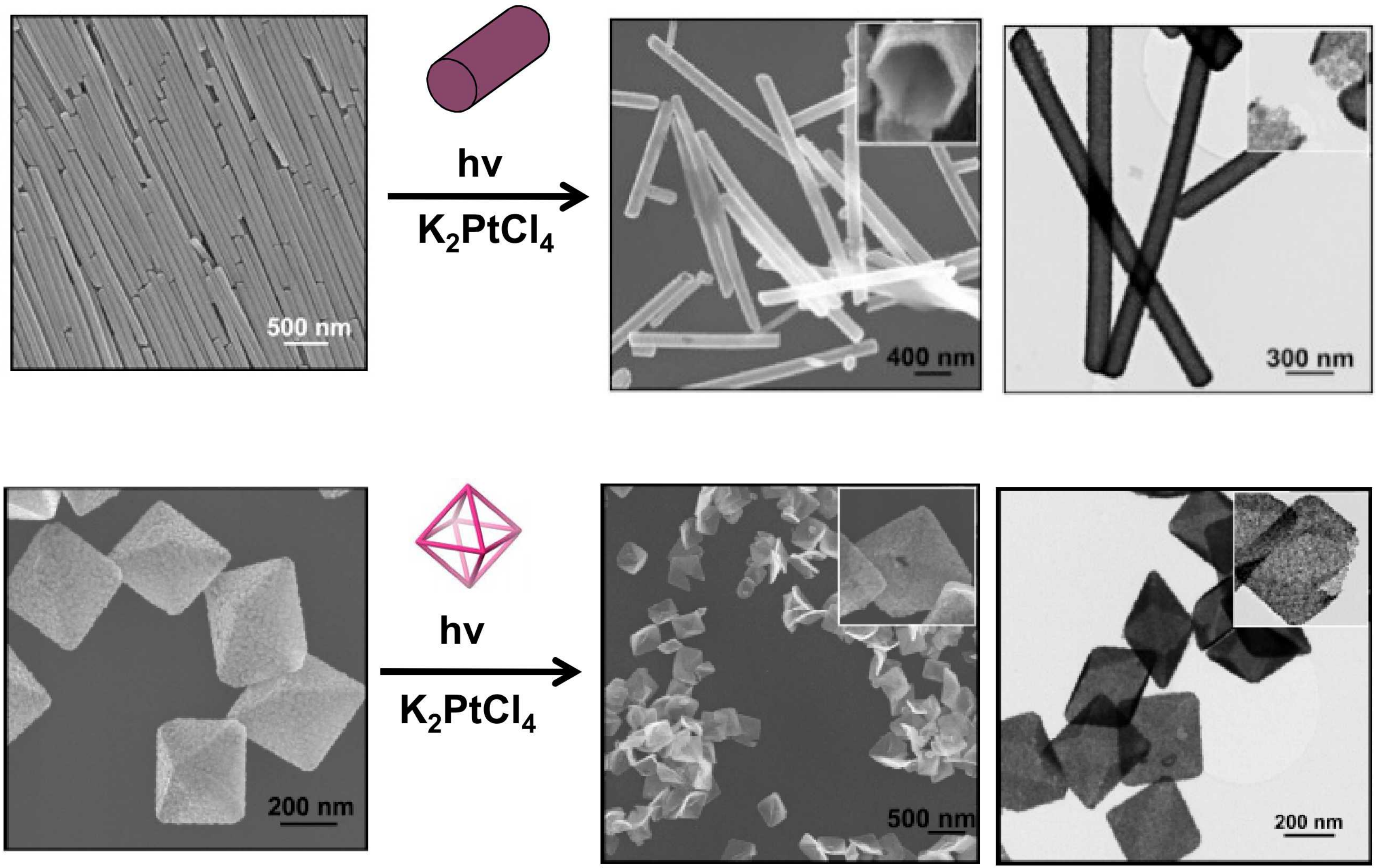
$$ZnTPyP^{*} + AA \longrightarrow ZnTPyP^{-\cdot} + ED_{0x}$$

$$4ZnTPyP^{-\cdot} + PtCl_4^{2-} \longrightarrow 4ZnTPyP + Pt^0$$

(radical anion)

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. *Nano Lett.* **2011**, 11, 3759–3762; *Nano Lett.* **2011**, 11, 5196–5200.

Photocatalytic Synthesis of Hollow Pt Nanostructures through Porphyrin Nanocrystals



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

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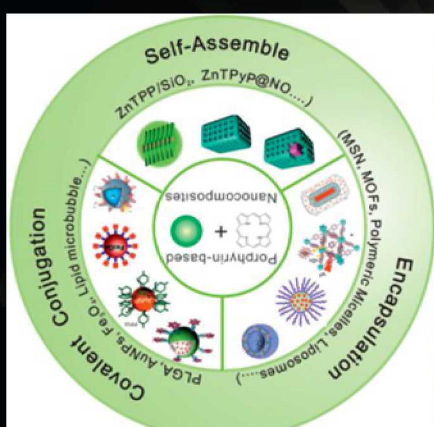
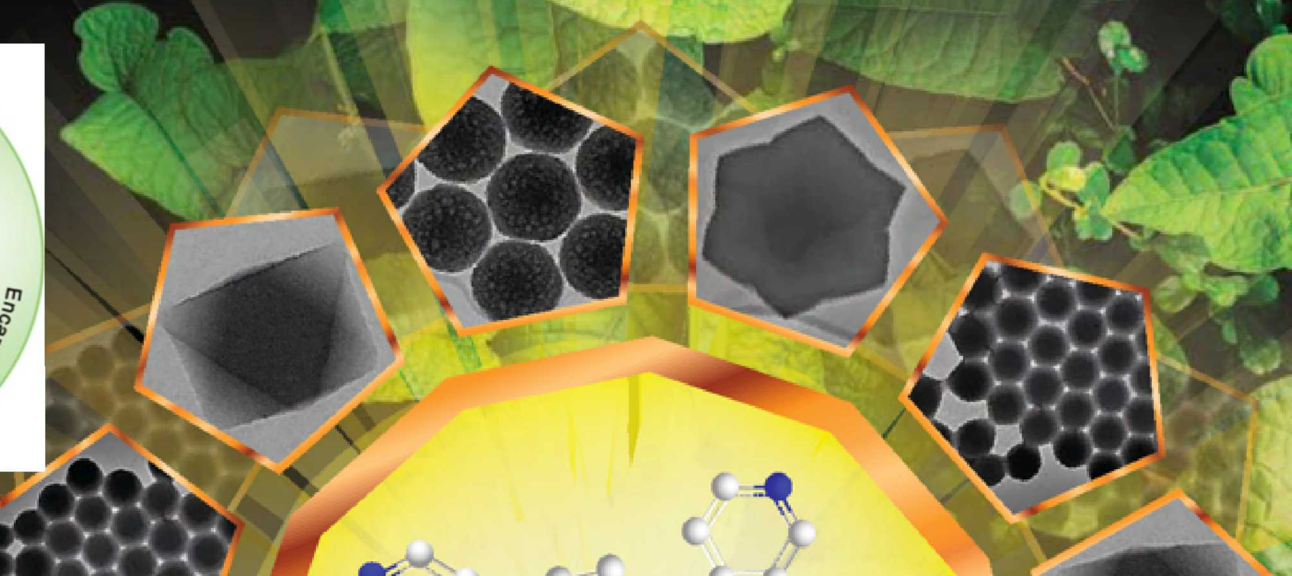
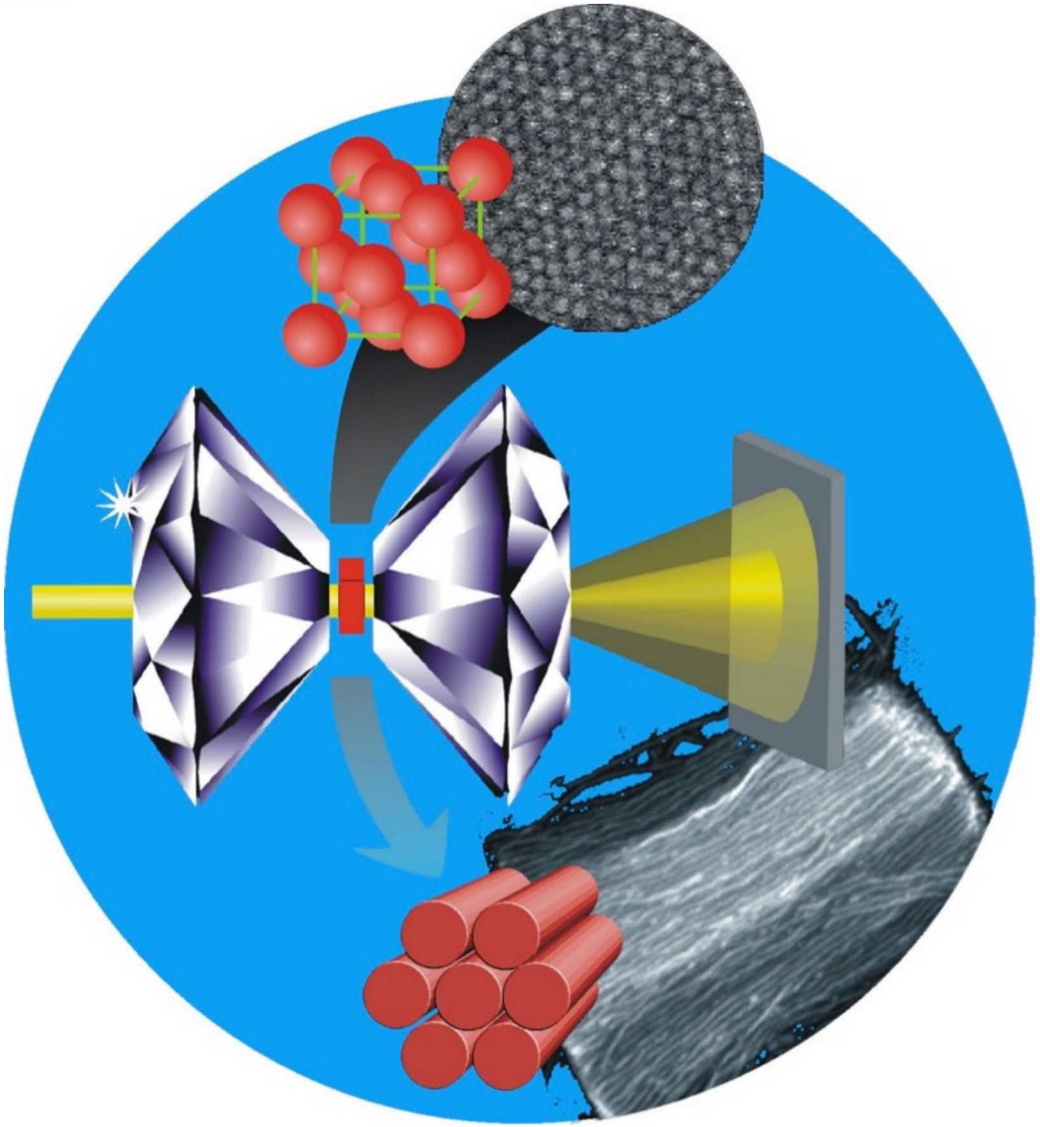
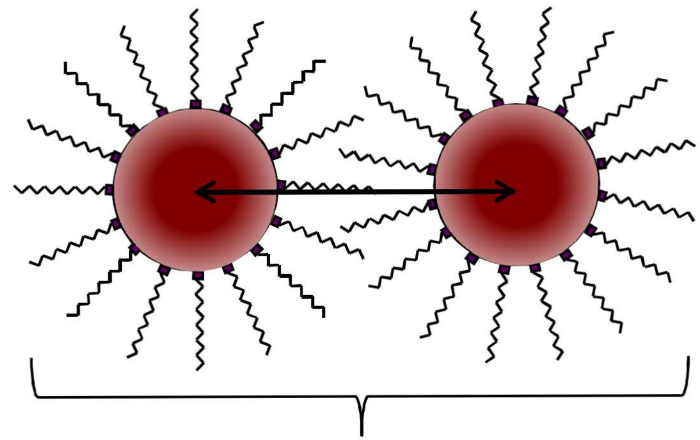
Self-assembled porphyrin and macrocycle derivatives





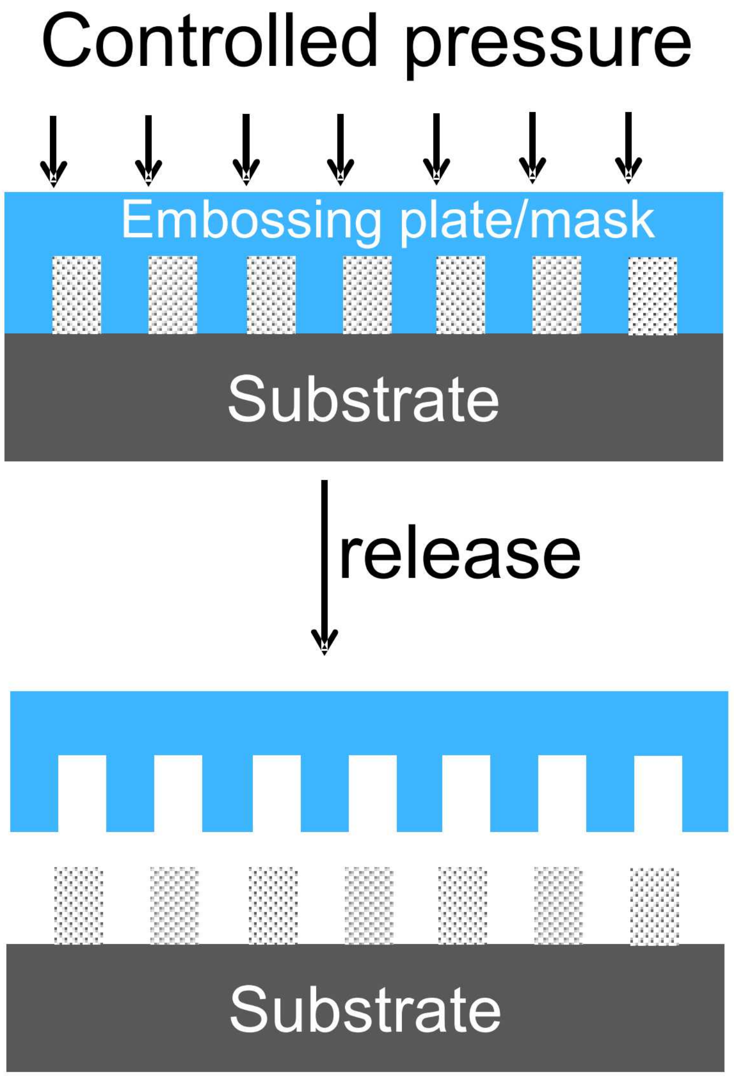
3. Pressure Induced Nanoparticle Assembly





Nanoparticle interactions and coupling

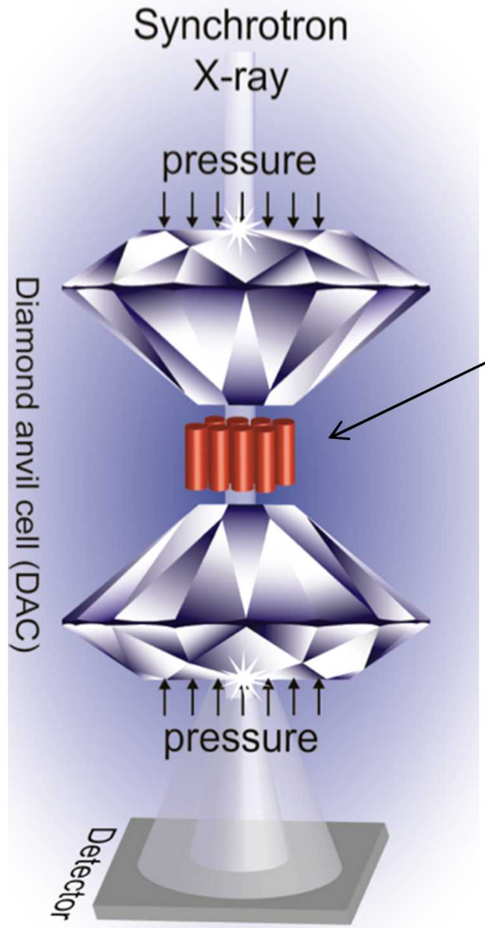
Our Research - Nanoparticle Assembly under Pressure:
Mimic Manufacturing Processes - Embossing or Imprinting



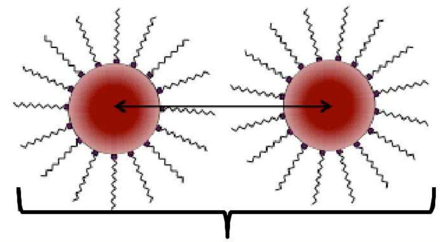
Features:
- Rapid
- Cost effective
- High throughput
- High fidelity

Pressure-Induced Assembly and Fabrication

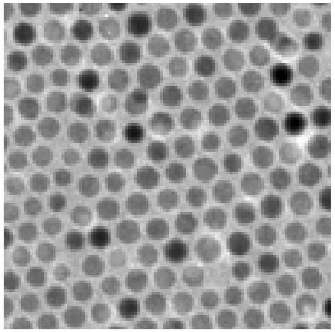
An external pressure overcomes balanced interparticle interactions, enables engineering of nanoparticle assembly, allowing fine-tuning of lattice structure and interparticle separation distance, and to fabricate new nanoparticle architectures.



Diamond Anvil Cell (DAC)



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

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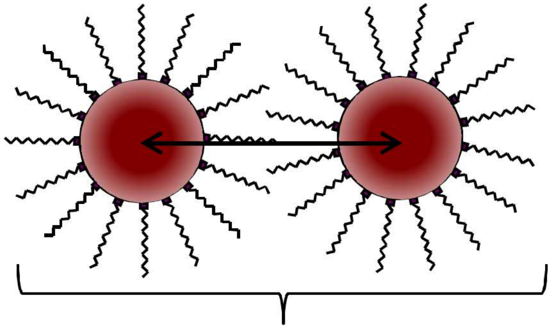
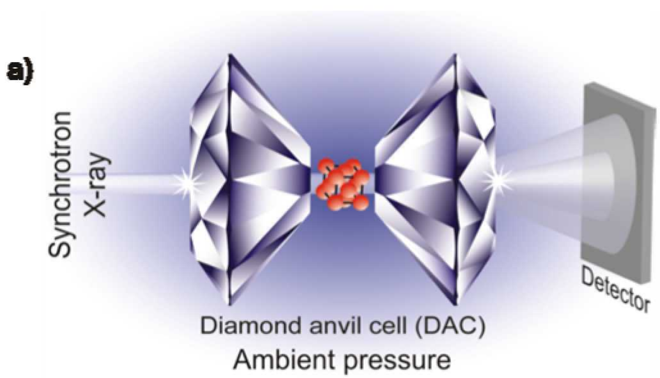
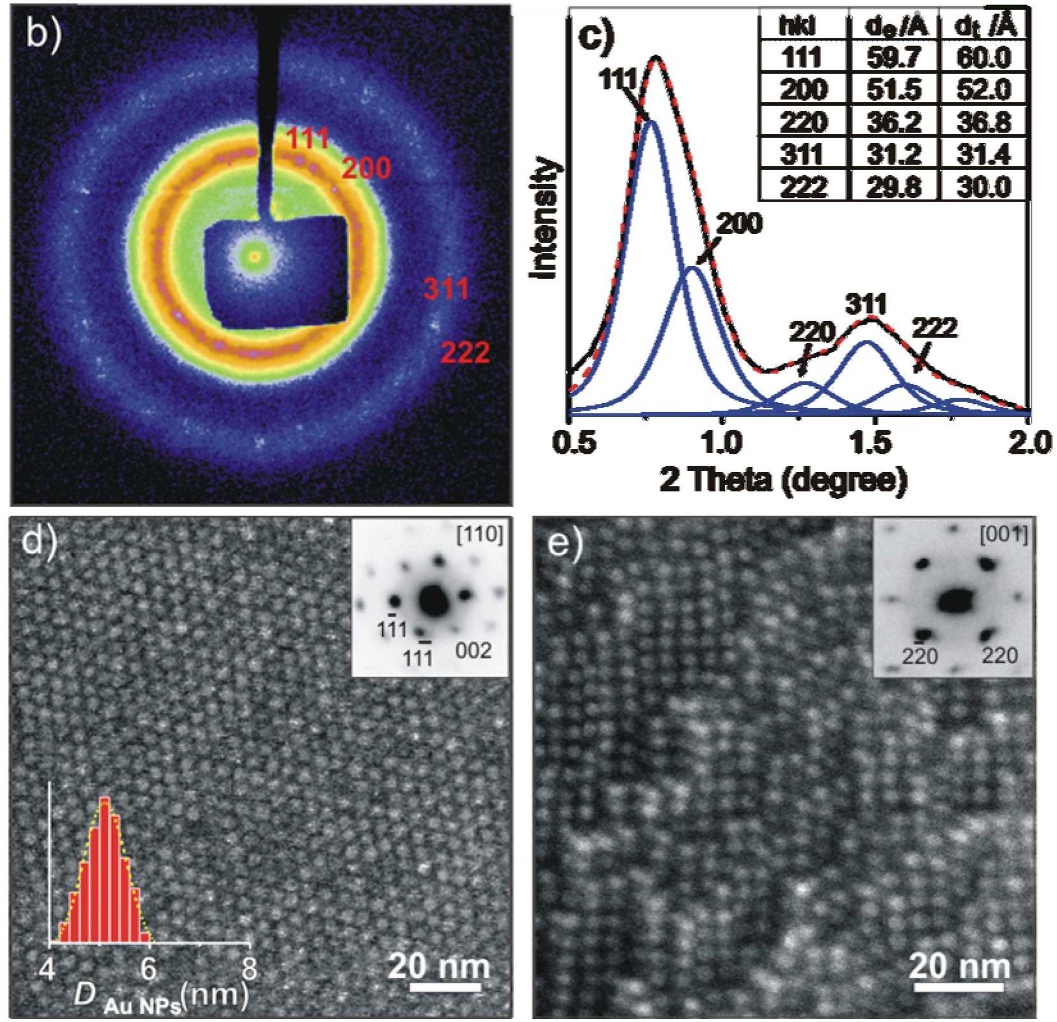
Before Compression – Starting Materials: Ordered Spherical Gold Nanoparticle Arrays



Balanced particle interactions

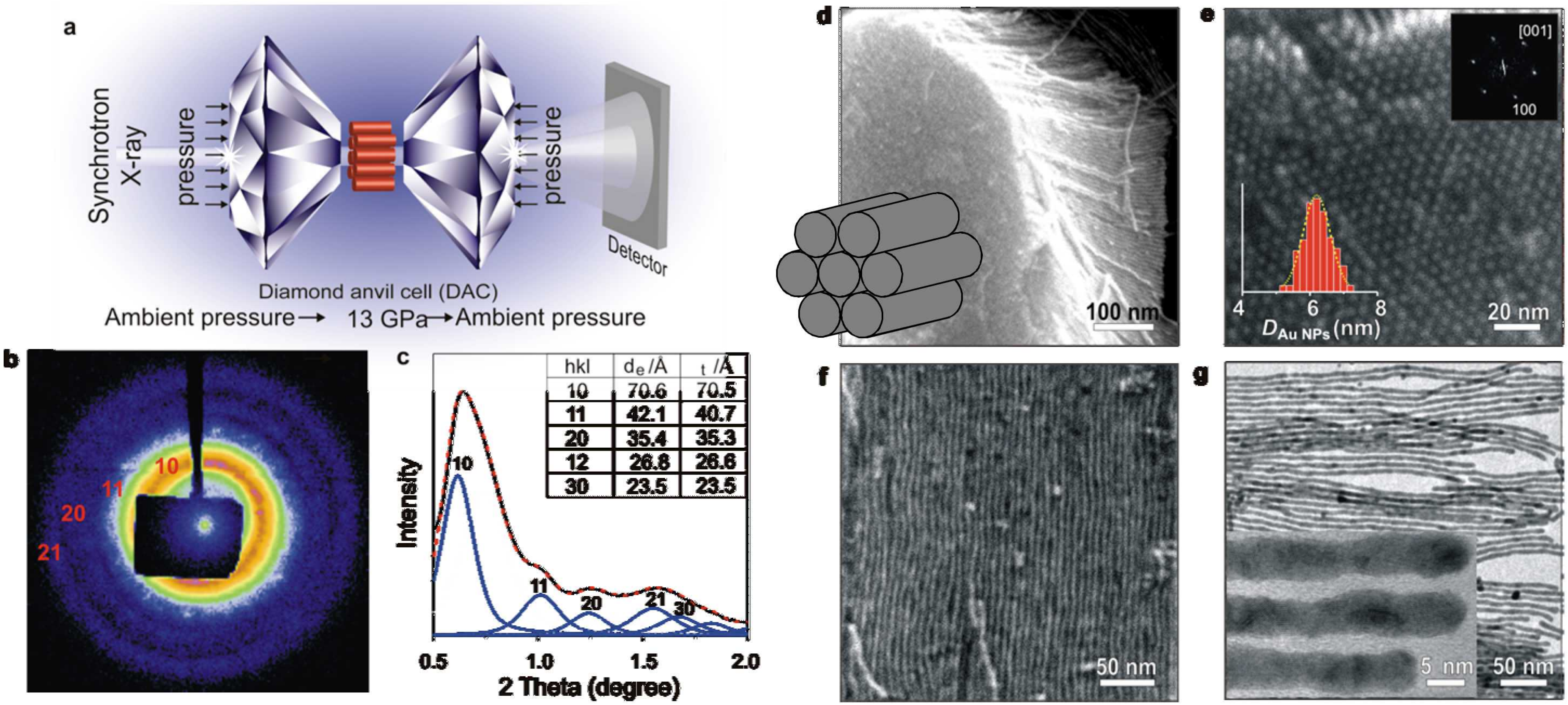


5 nm gold nanoparticles and *fcc* lattice (a = 10.4 nm)



Li, B.; Fan H., *et al*., *Nat.Commun.* 5:4179 doi: 10.1038/ncomms5179 (2014); Wang, *et al*. *J. Am. Chem. Soc.* 133, 14484–14487 (2011); Wu H., Fan H., *et al. Angew. Chem. Int. Ed.,* 49, 8431-8434, 2010.

After Compression – Formation of 1D Nanowires



Li, B. et al. *Nat. Commun*. 8, 14778 doi: 10.1038/ncomms14778 (2017).
Wu H., Fan H., *et al*. *Angew. Chem. Int. Ed.,* 49, 8431-8434, 2010.

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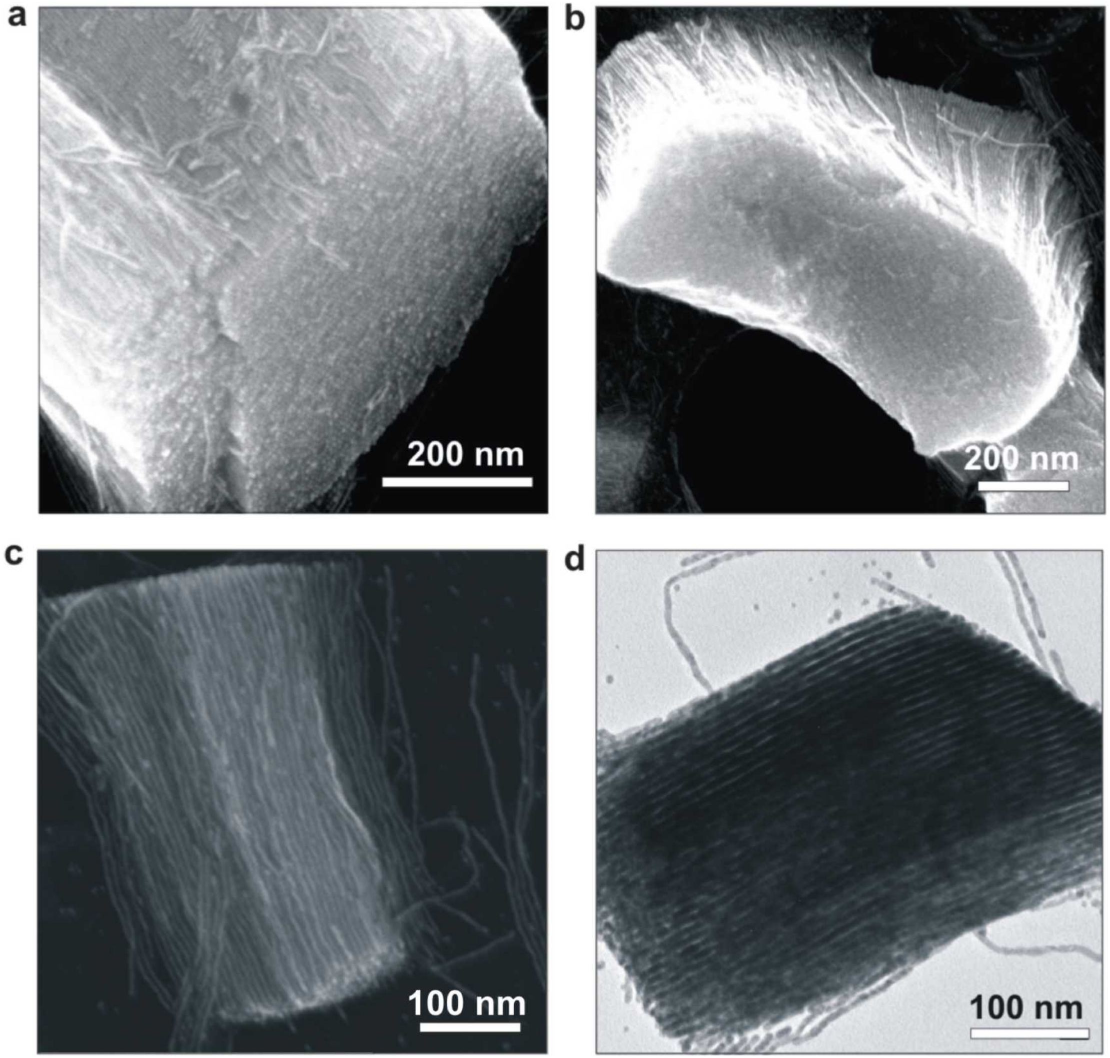
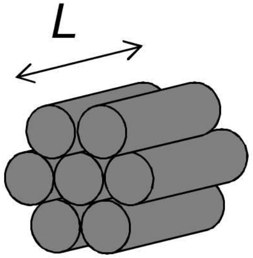
Bundles of 1D Nanowire Arrays

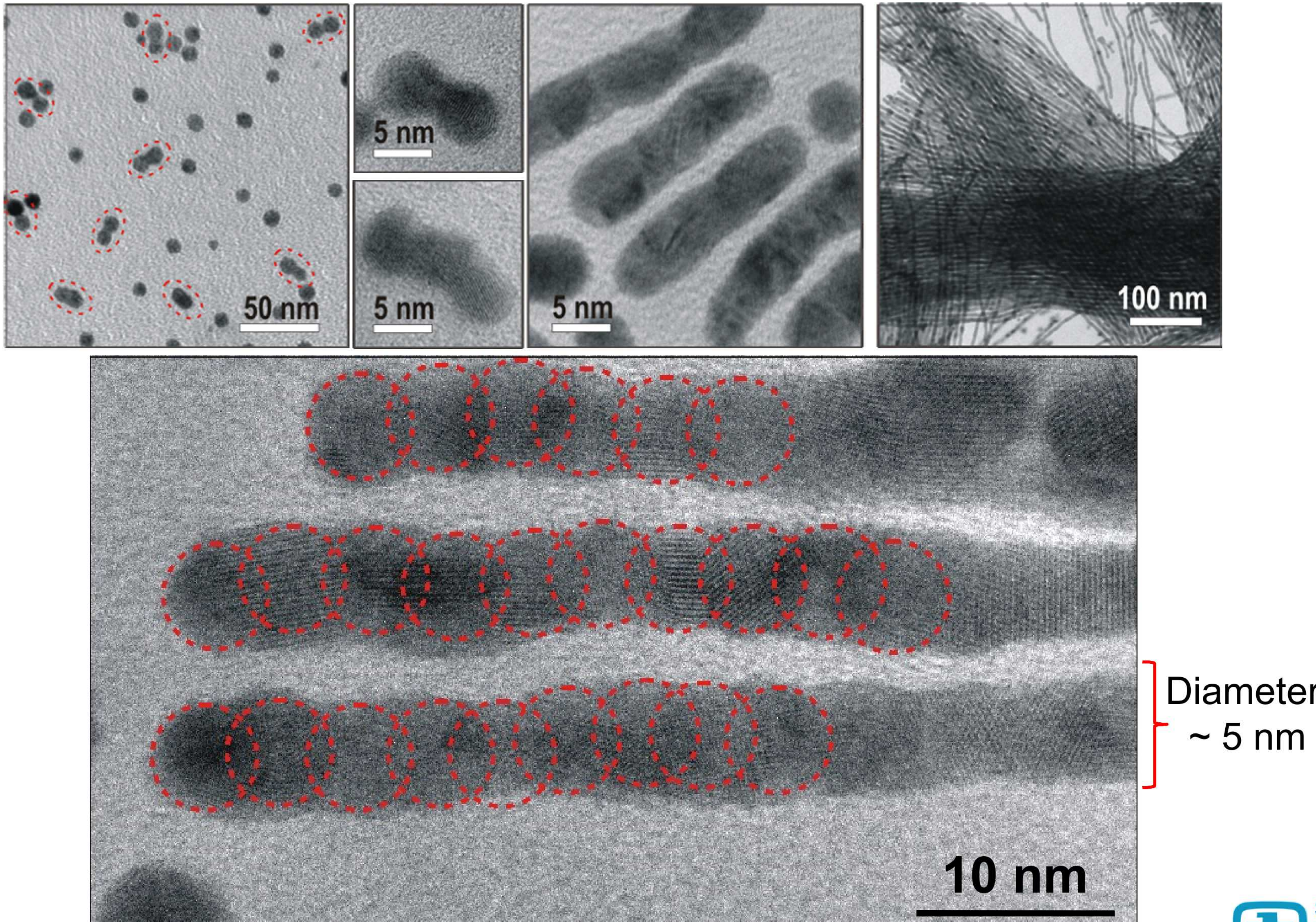


Uniform length



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

Pressure Tuned 1D Nanostructures



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

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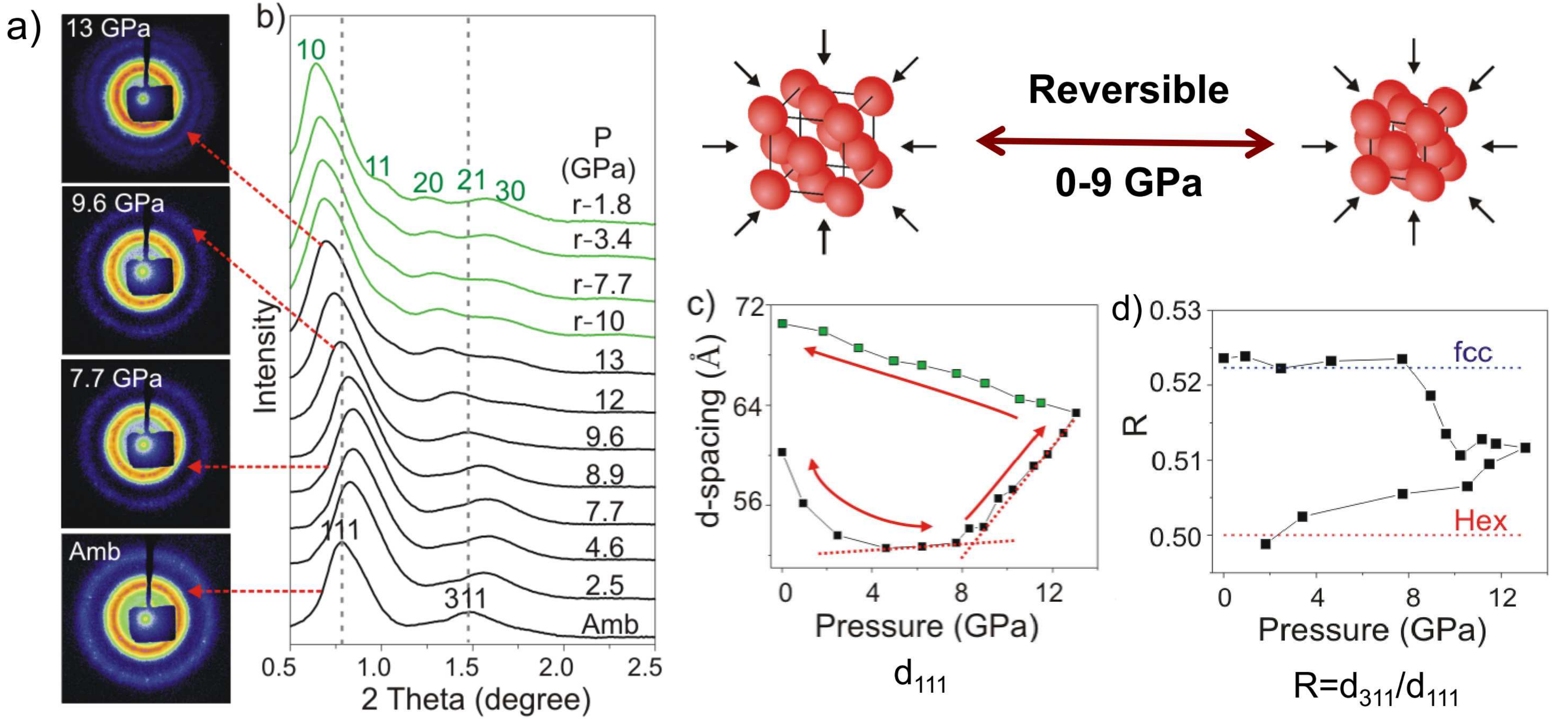
In-situ Synchrotron X-ray Studies of Nanoparticle Assembly under Pressure

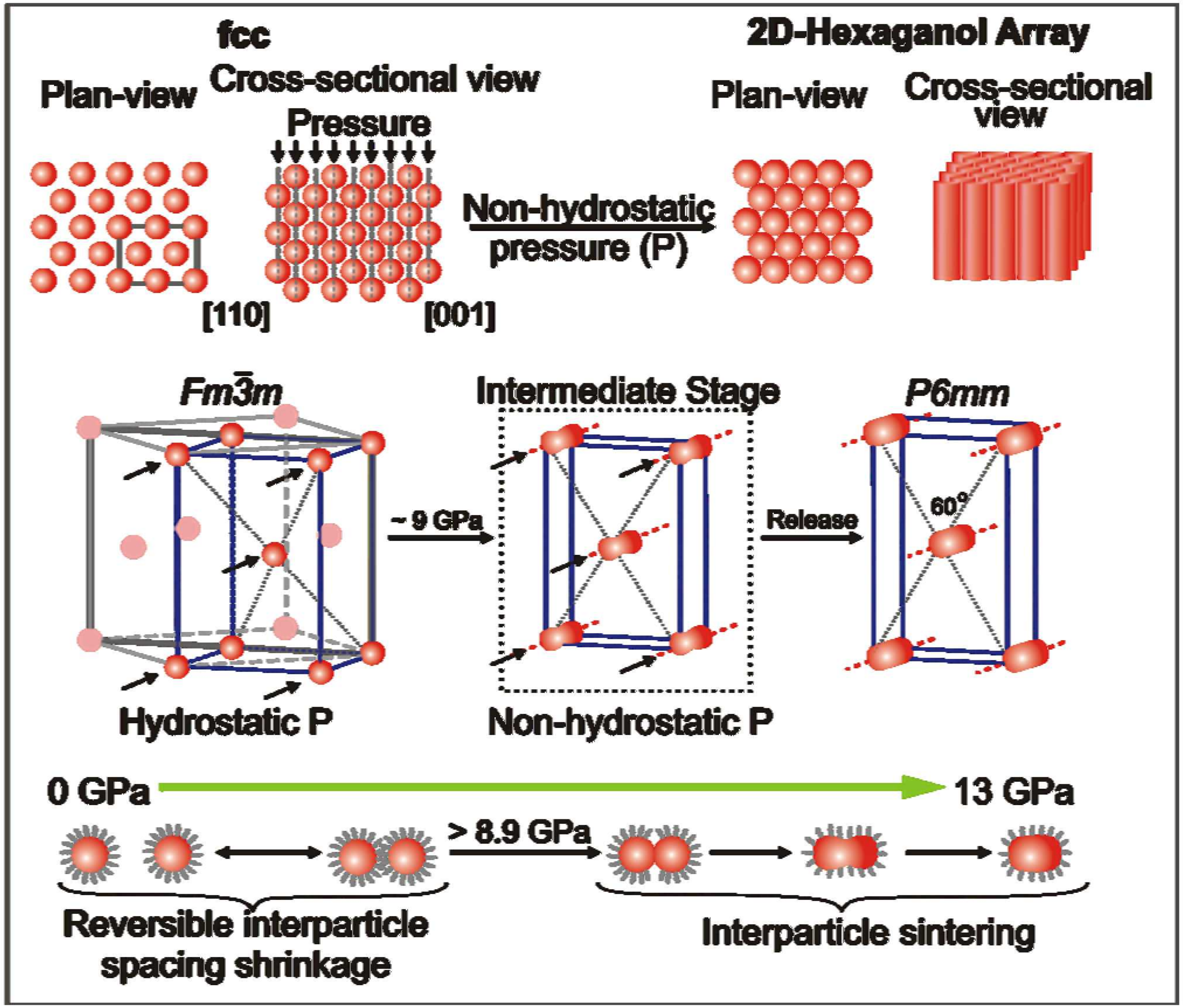
An external pressure overcomes specific interparticle interactions, enables engineering of nanoparticle assembly, allowing fine-tuning of lattice structure and interparticle separation distance, and to fabricate new nanoparticle architectures.



d_{111}

$R=d_{311}/d_{111}$

Pressure-Induced Nanoparticle Assembly Processes



Wu & Fan *et al.*, *J. Am. Chem. Soc.*, 132, 12826-12828, 2010 & *Angew. Chem. Int. Ed.,* 49, 8431-8434, 2010.

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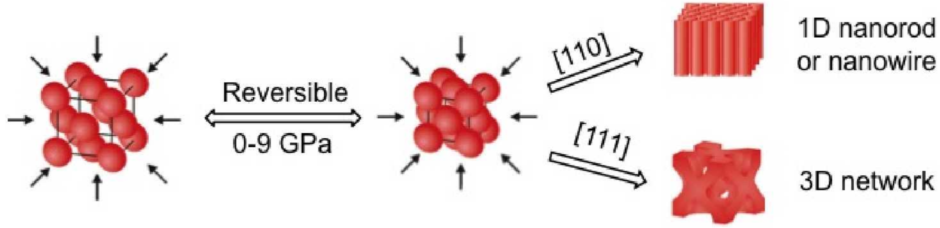
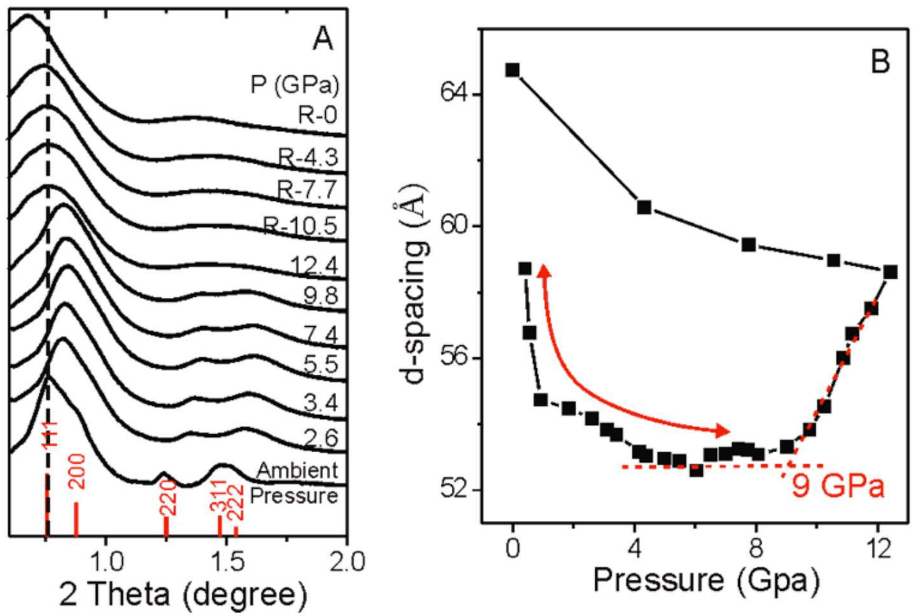
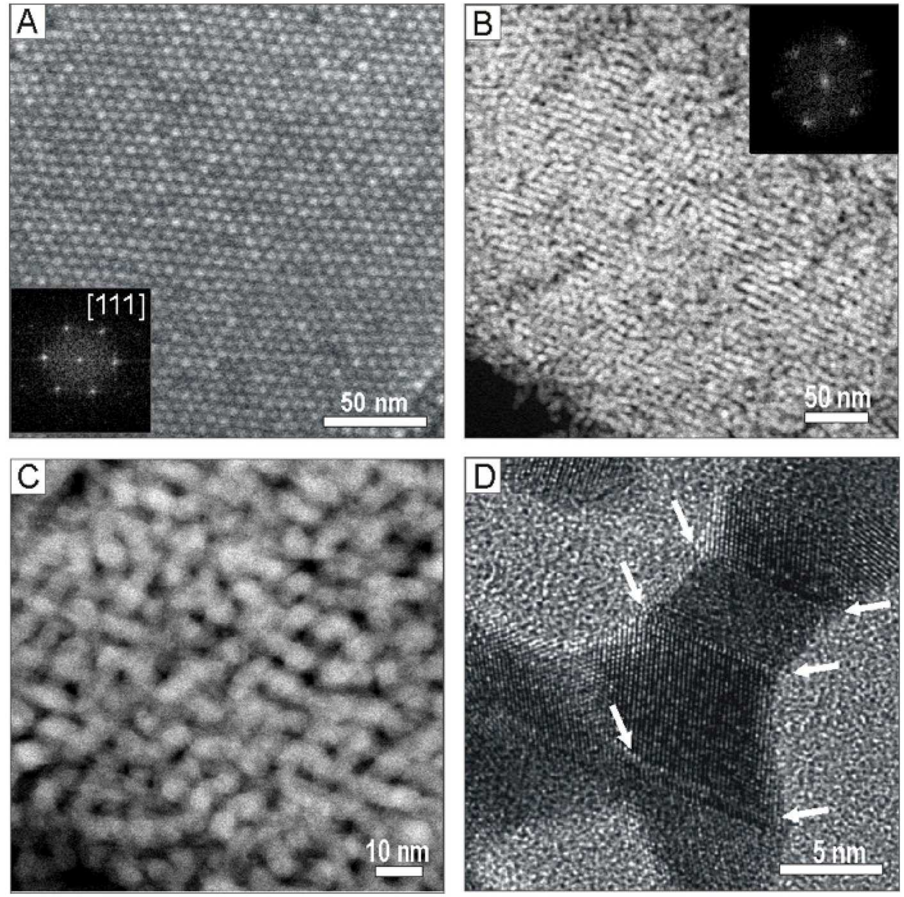
Pressure-Induced Formation of 3D Nanostructures

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







Wu H., Fan, H. *et al*., *J. Am. Chem. Soc.*, 132, 12826-12828, **2010** & *136* (21), pp 7634–7636**, 2014**.

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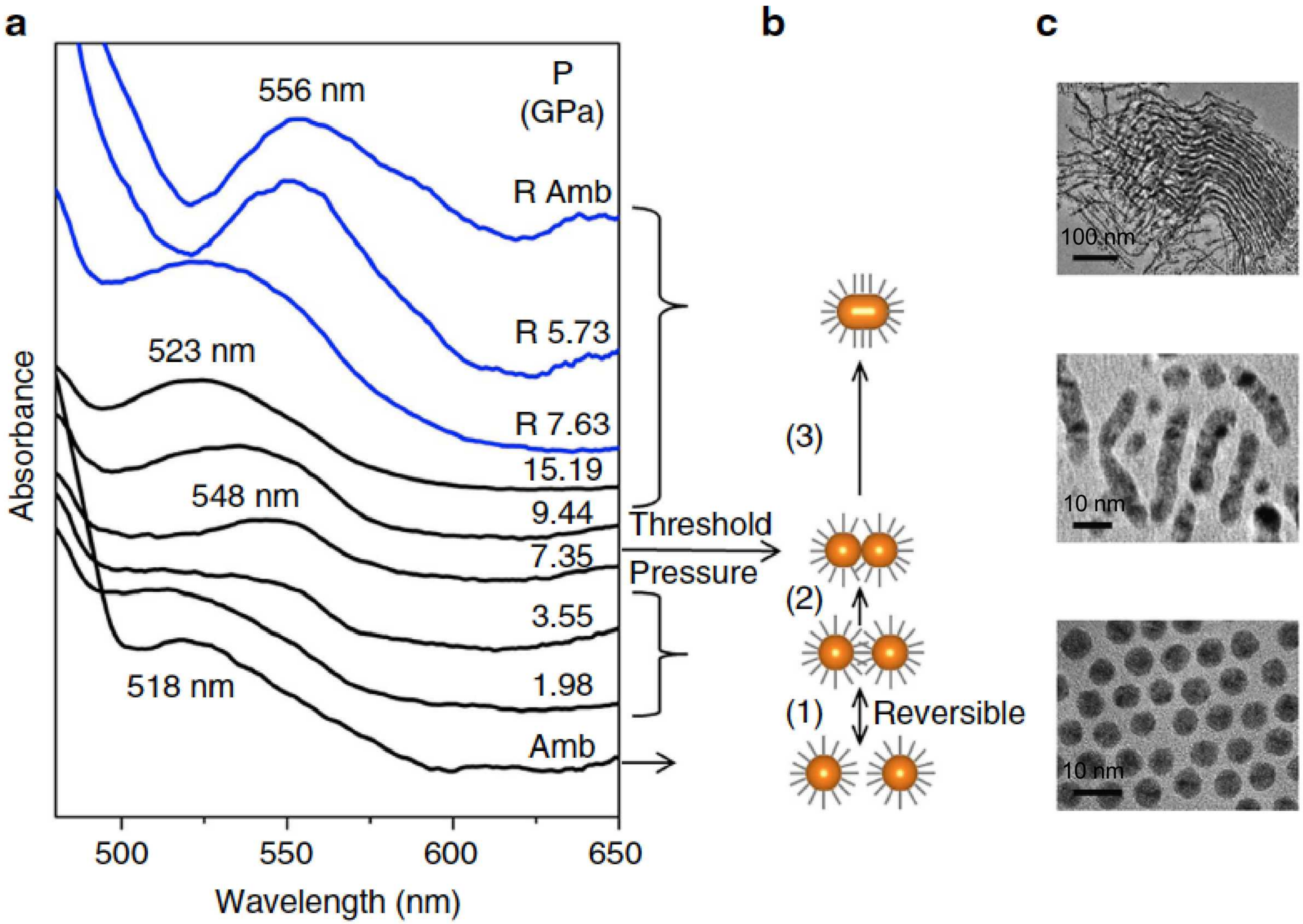
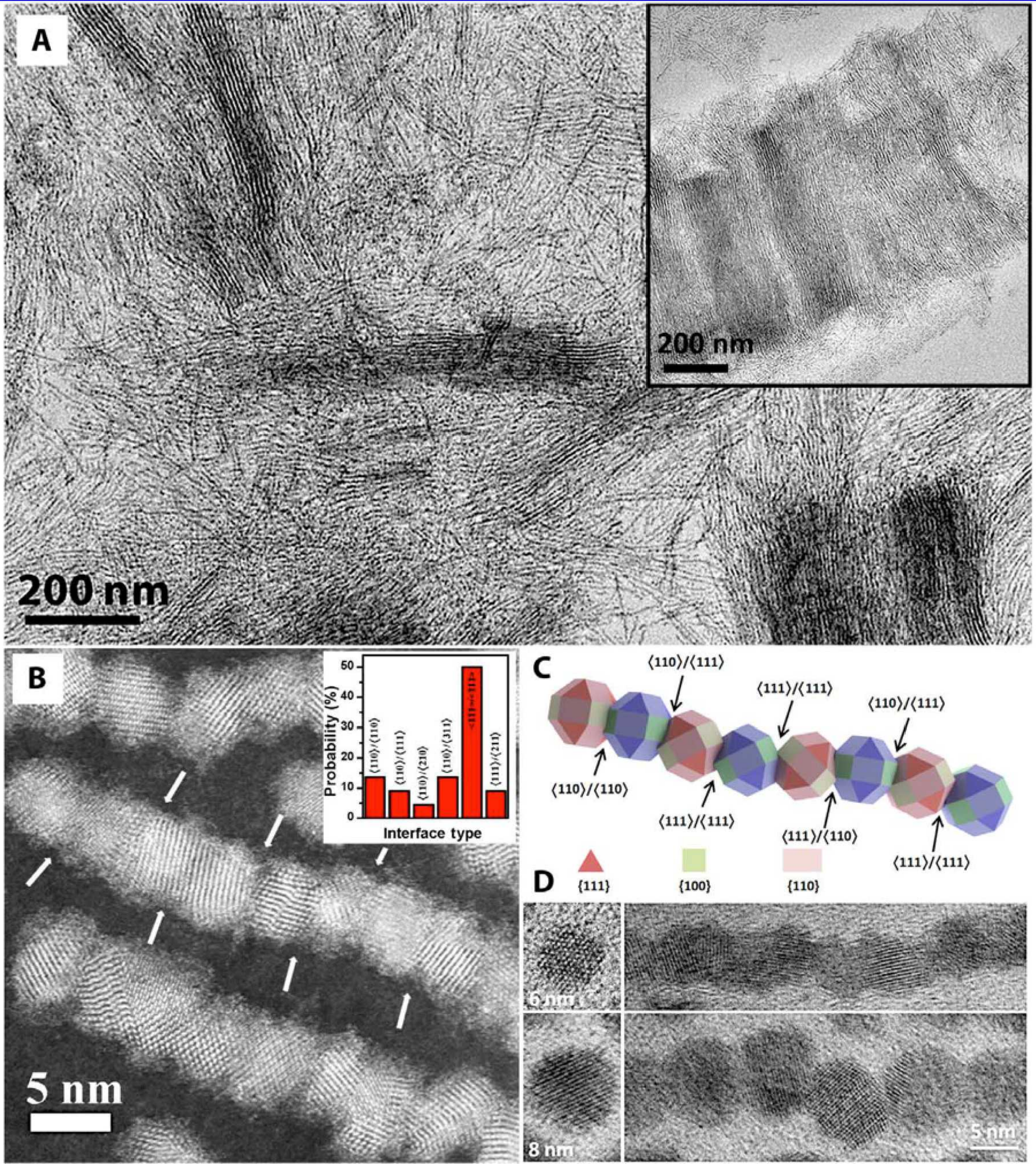
Pressure-Tuned Nanoparticle Interactions and Coupling

Structure - optical property correlation of Ag nanoparticle arrays



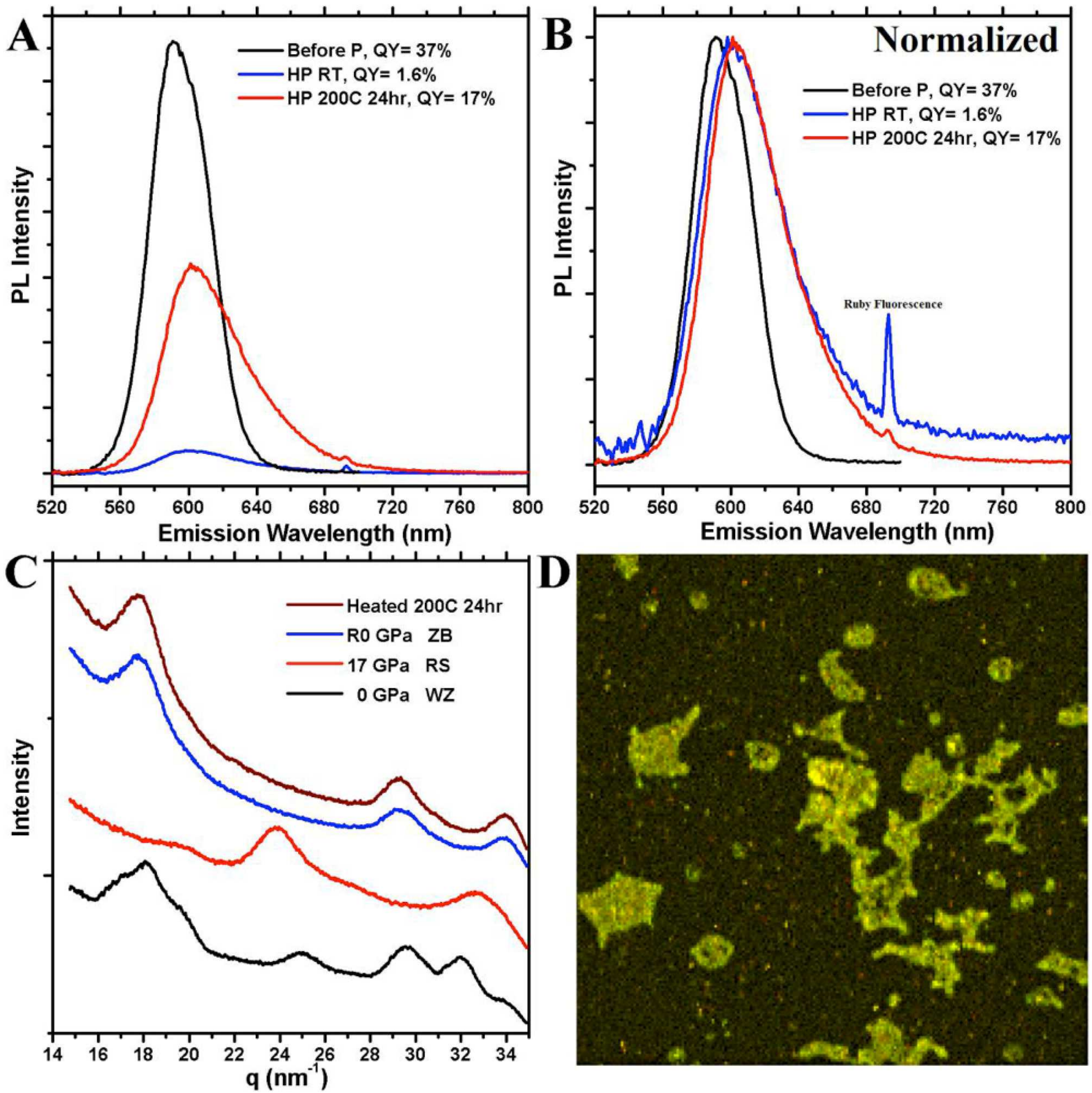
Li, B.; Fan H., *et al*., *Nat.Commun.* 5:4179 doi: 10.1038/ncomms5179 (2014).

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).

nature COMMUNICATIONS

ARTICLE

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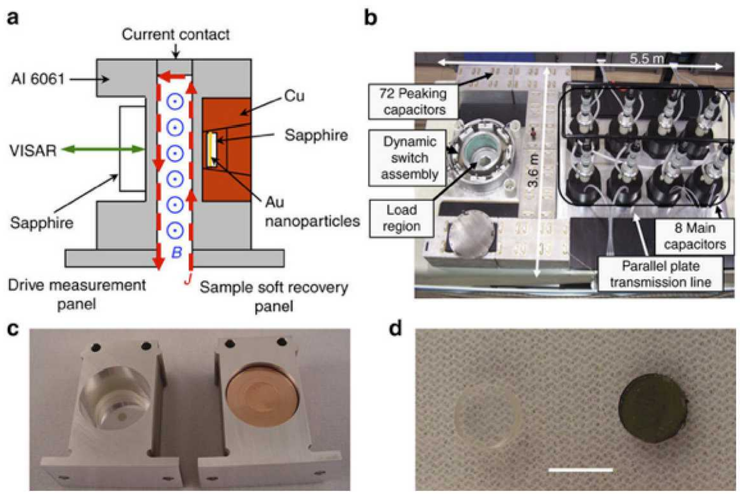
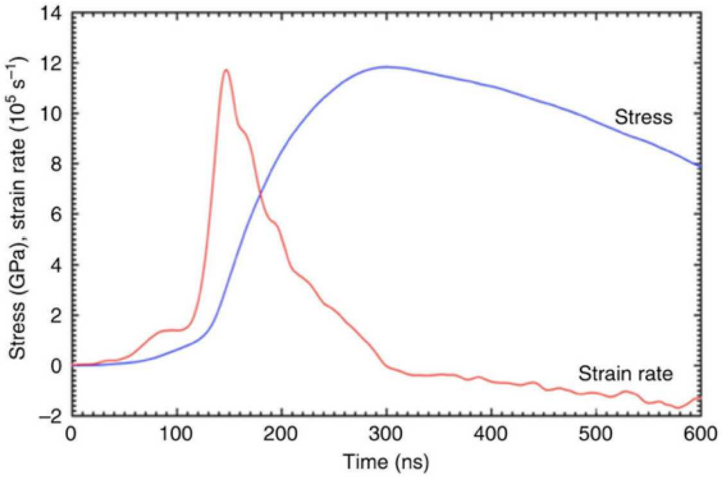
OPEN

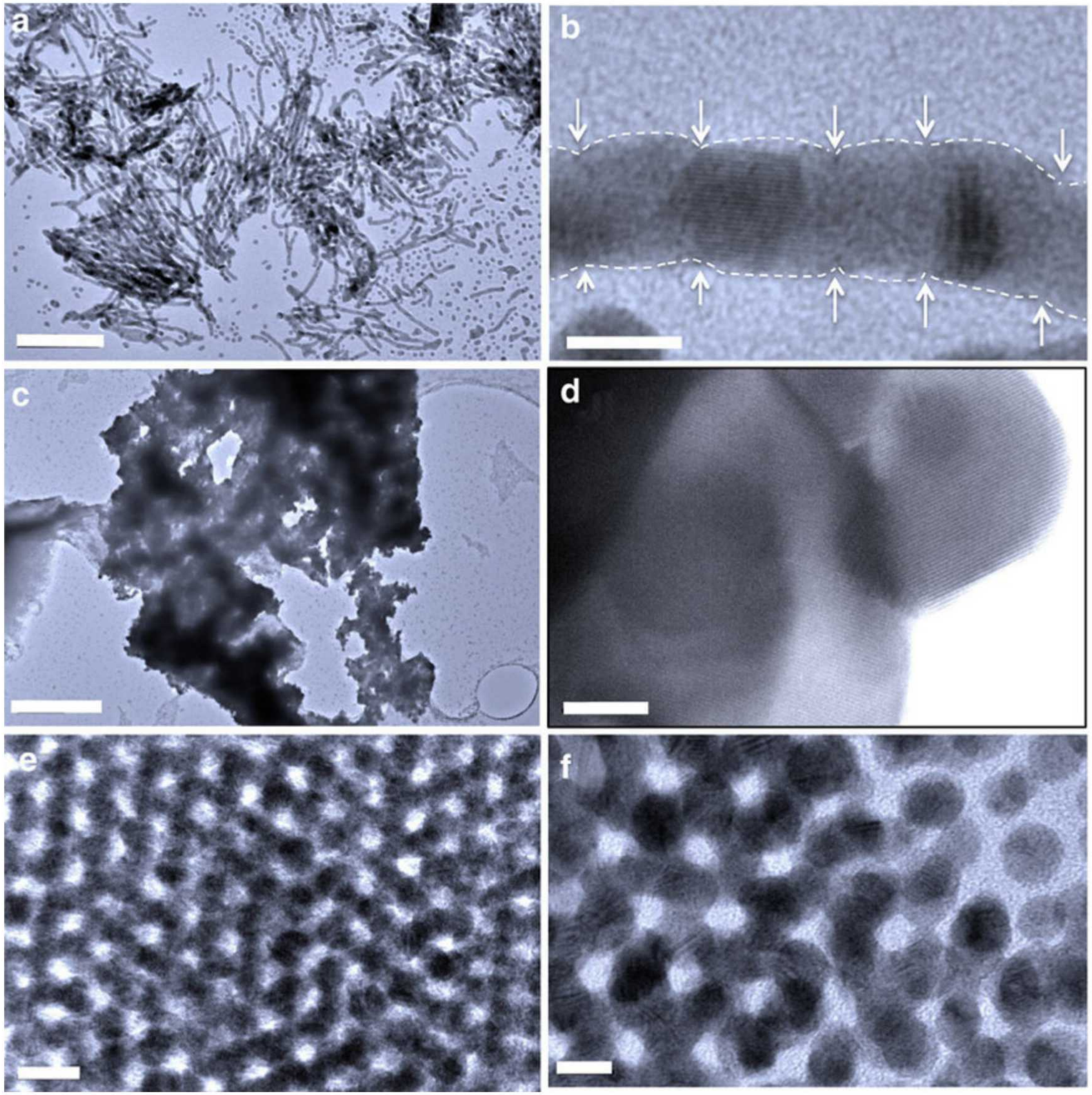
Superfast assembly and synthesis of gold nanostructures using nanosecond low-temperature compression via magnetic pulsed power

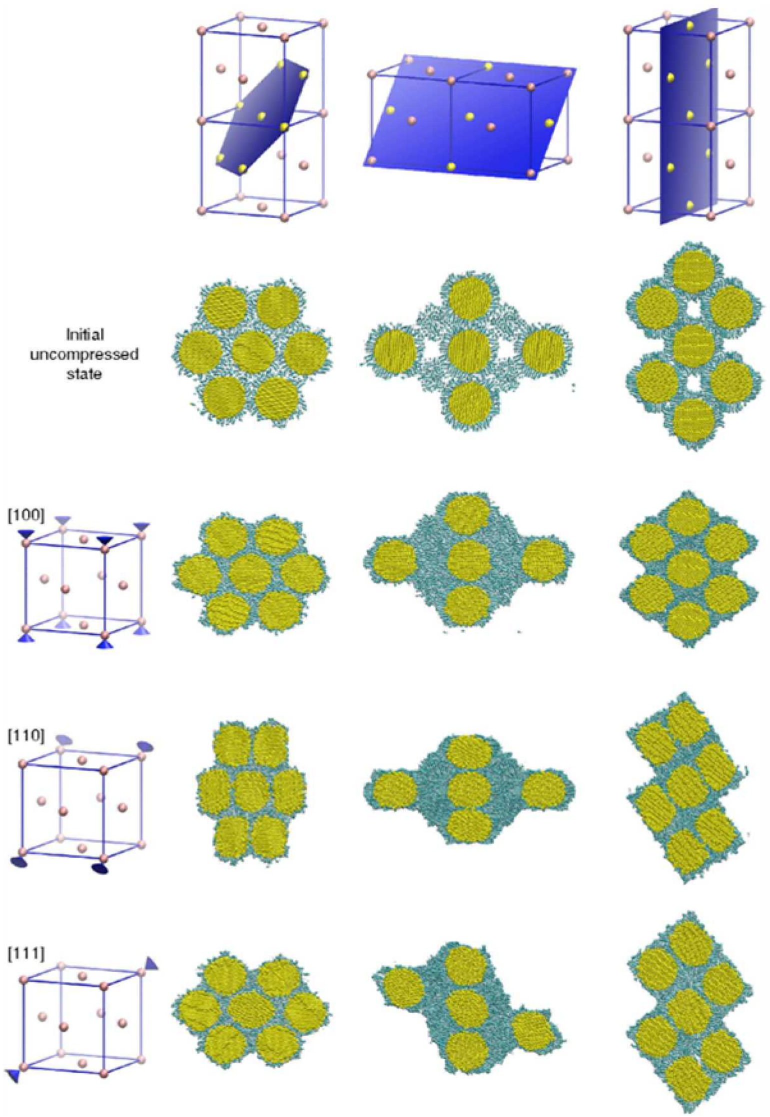
Binsong Li[1,*], Kaifu Bian[1,*], J. Matthew D. Lane[1], K. Michael Salerno[1], Gary S. Grest[1], Tommy Ao[1], Randy Hickman[1], Jack Wise[1], Zhongwu Wang[2] & Hongyou Fan[1,3,*]





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





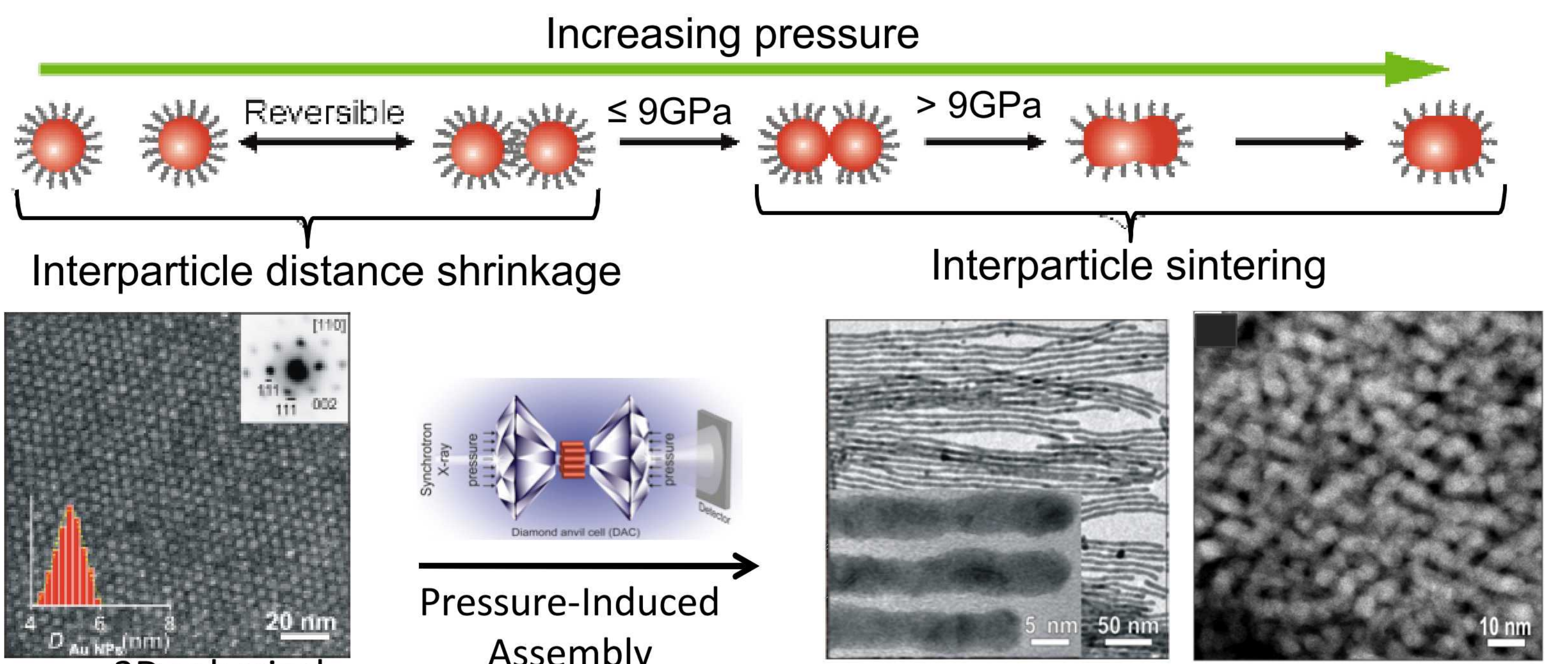
Li, B. et al. *Nat. Commun*. 8, 14778 doi: 10.1038/ncomms14778 (2017).

Summary: Pressure-Induced Nanoparticle Engineering (*Chemical Review* in press)

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 mechanically stable 1-3D nanostructures, which is not possible for current top-down and bottom up methods.



3D spherical nanoparticle array (Before compression)

1-3D nanostructures (After compression)

CHEMICAL REVIEWS

Review

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Pressure Induced Nanoparticle Phase Behavior, Property, and Applications

Feng Bai,[*,†] Kaifu Bian,[‡] Xin Huang,[§] Zhongwu Wang,[*,§] and Hongyou Fan[*,‡,∥,⊥]

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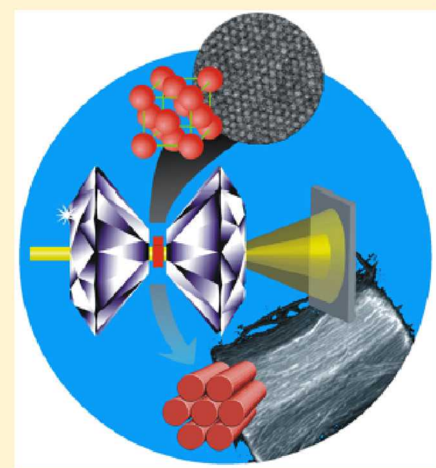
ABSTRACT: Nanoparticle (NP) high pressure behavior has been extensively studied over the years. In this review, we summarize recent progress on the studies of pressure induced NP phase behavior, property, and applications. This review starts with a brief overview of high pressure characterization techniques, coupled with synchrotron X-ray scattering, Raman, fluorescence, and absorption. Then, we surveyed the pressure induced phase transition of NP atomic crystal structure including size dependent phase transition, amorphization, and threshold pressures using several typical NP material systems as examples. Next, we discuss the pressure induced phase transition of NP mesoscale structures including topics on pressure induced interparticle separation distance, NP coupling, and NP coalescence. Pressure induced new properties and applications in different NP systems are highlighted. Finally, outlooks with future directions are discussed.



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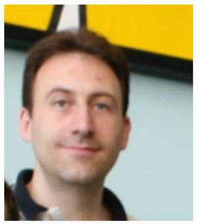

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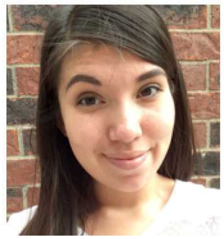
Hattie Schunk



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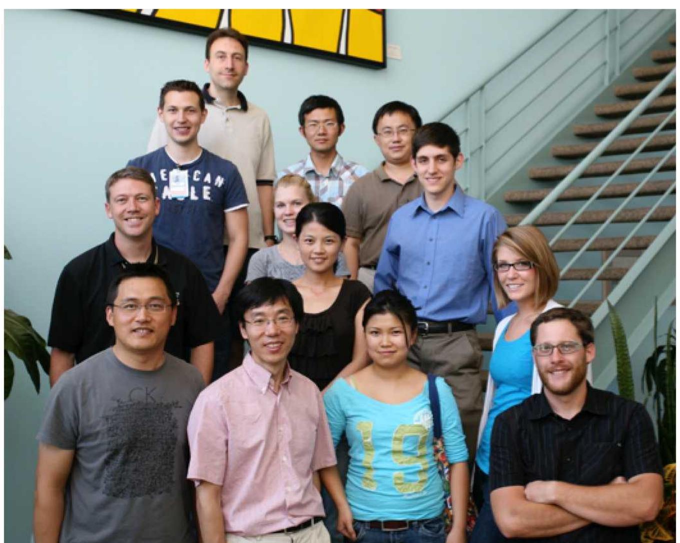

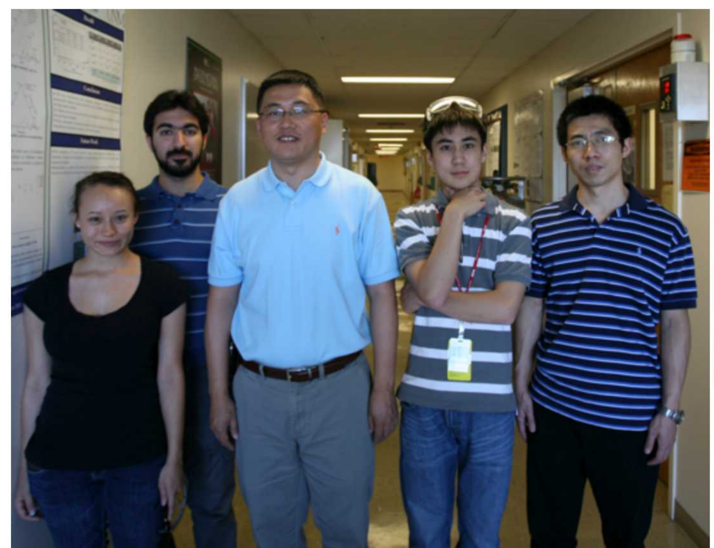

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