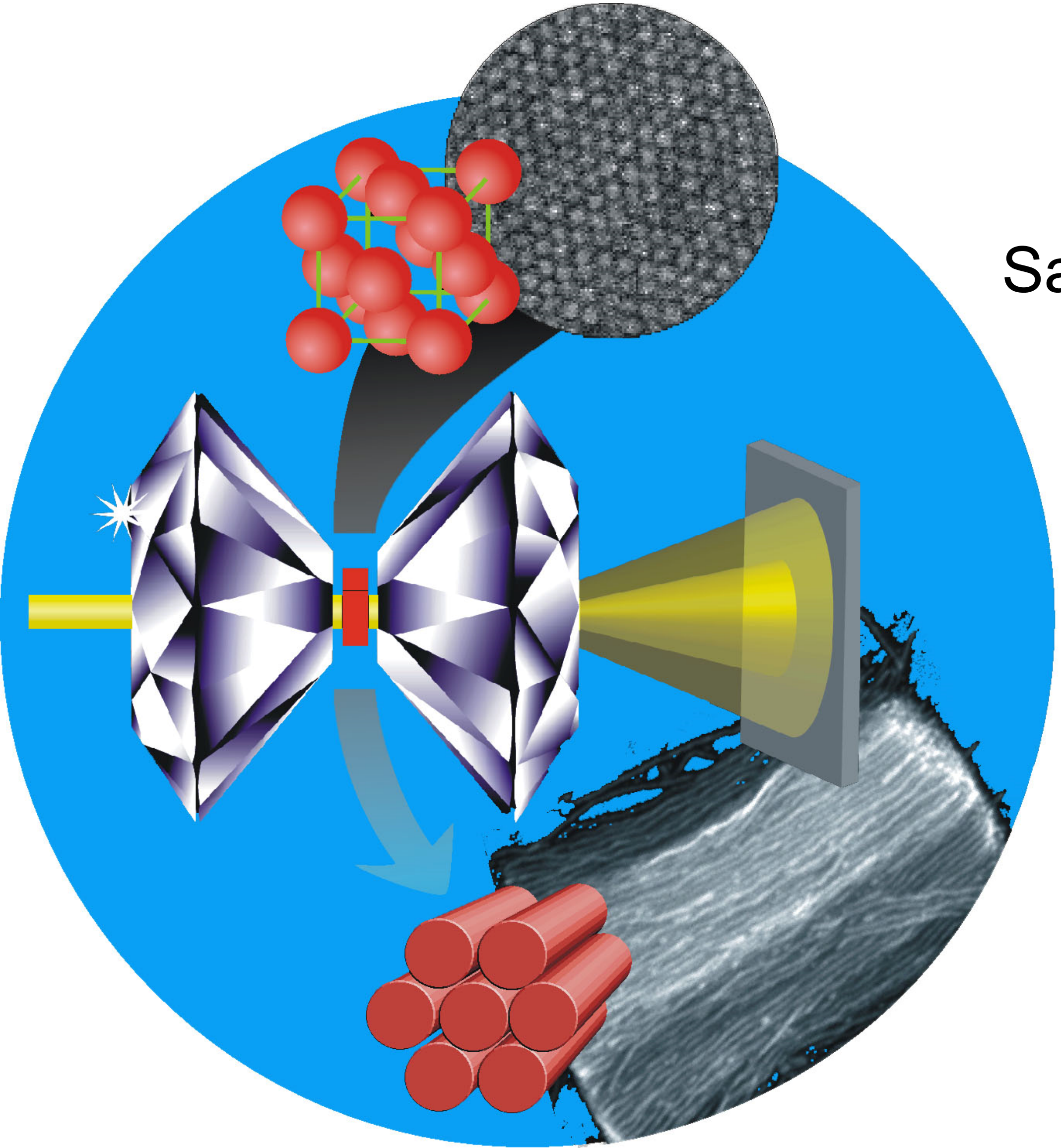
Peering into the Self- and Directed-Assembly of Nanoparticles

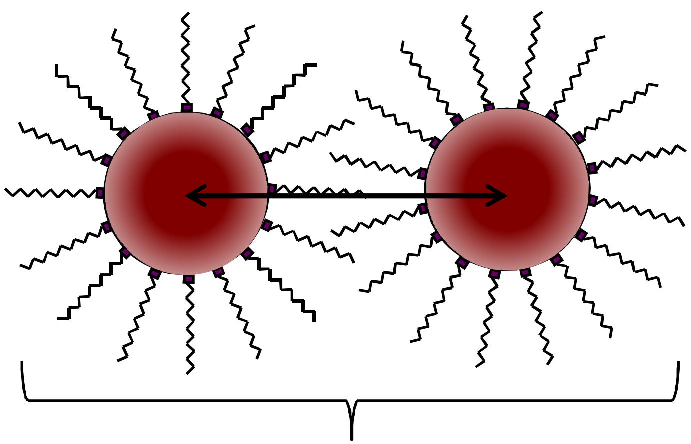
SAND2017-12628C



Hongyou Fan

Sandia National Laboratories

University of New Mexico



Nanoparticle interactions and coupling

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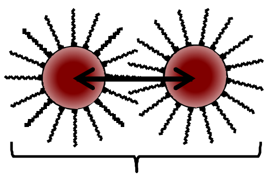
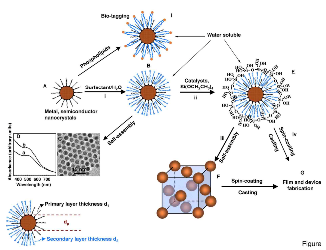
Outline

1. Introduction - Nanoparticle Self-Assembly



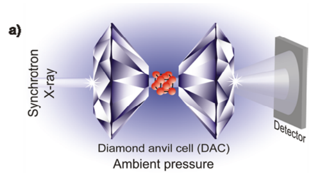
- Collective properties of nanoparticle arrays
- Nanoparticle interactions
- State of art work

2. Self-assembly of nanoparticle arrays



- Surfactant assisted formation of nanoparticle micelles
- 3D nanoparticle ordered arrays
- Synchrotron characterizations

3. Pressure-Induced Assembly and Formation of 1-3D Nanostructures



- High pressure induced assembly
- 1-3D metallic nanostructures (Au and Ag)
- Semiconductor nanowires (CdSe, etc.)
- Pressure-tuned nanoparticle coupling and collective property

4. Summary

Applications of Nanoparticles and Arrays

- **Size/shape-dependent and collective optical, electrical, and magnetic properties.**
  e.g., surface plasmon resonance (SPR), tuning refractive index for optical coatings, tuning dielectric constant, QD/solar cells, electron transport/conductance, magnetic memory, etc.
- **Chemical and biological sensing, imaging, & therapeutics.**
  e.g., Surface enhanced Raman scattering (SERS) based chem-/bio-sensor systems, MRI contrast agents, cell killing, etc.
- **Catalyst arrays for orientated growth of nanomaterials and arrays.**
  e.g., carbon nanotube arrays/films, nanowire arrays, etc.

(CdSe) quantum dot size increases

Sanderson, K., *Nature* vol.459, 760-761, 2009.

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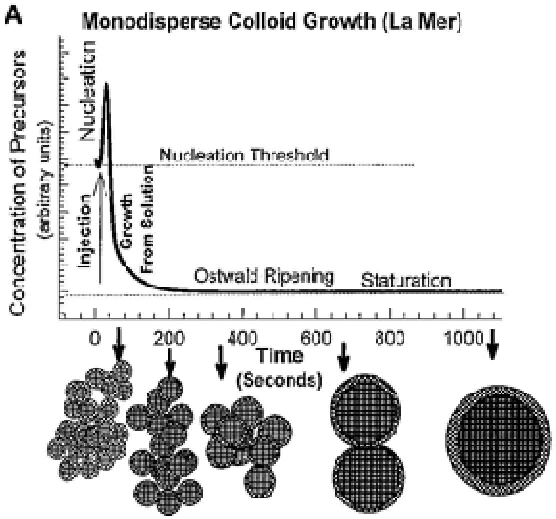
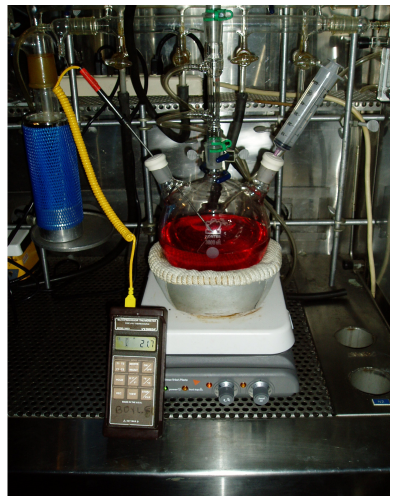
Synthesis of Nanoparticles at Ambient Pressure

(1) "Hot Soap" solution method





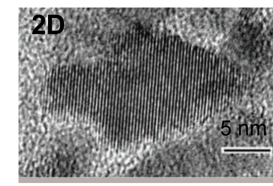
Murray, C.B. *et al.*, *Annu. Rev. Mater. Sci. 30,* 545-610, **2000**.

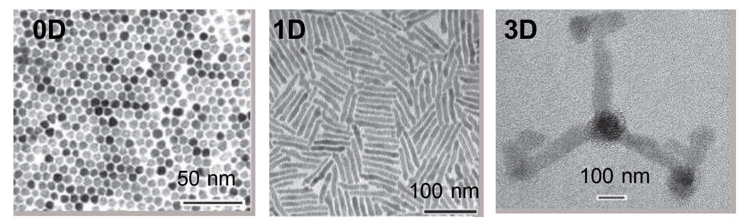
Semiconductor and magnetic nanoparticles:

e.g., CdSe, FePt, etc.

Organic ligands:

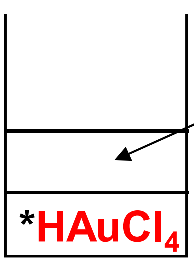
Trioctylphosphine
Trioctylphosphine oxide
$CH_3(CH_2)_nNH_2$
$CH_3(CH_2)_nCOOH$



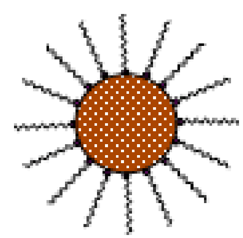


Yin, Y., *et al.*, *Nature*, v.437, 664-670, 2005.

(2) Phase transition synthesis of metal nanocrystals



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



Gold & silver nanoparticles

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

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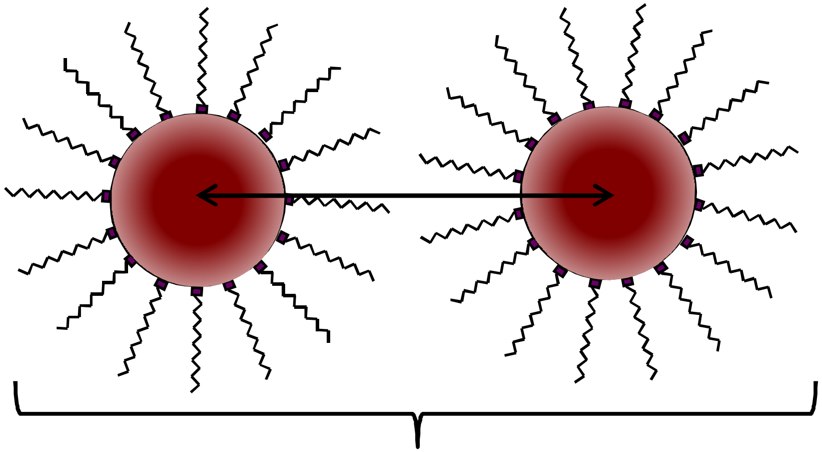
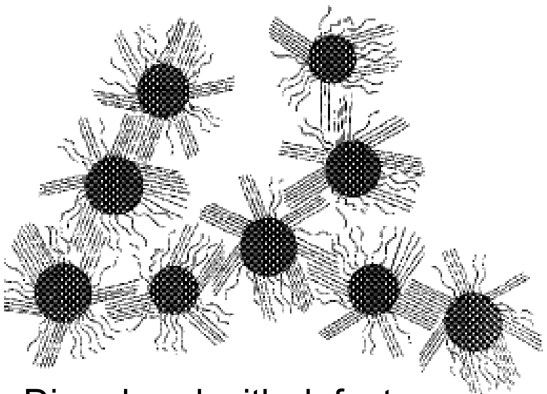
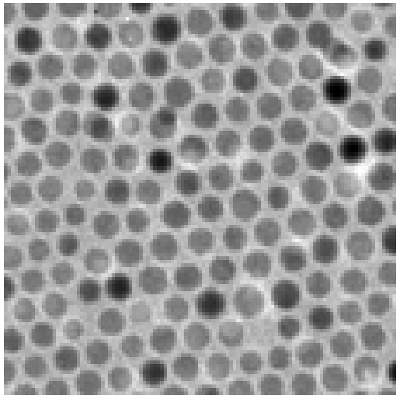
Nanoparticle Assembly at Ambient Pressure: Balanced Nanoparticle Interactions



Balanced Nanoparticle interactions:
- •Attraction
- •Van der Waals
- •Charge interactions
- •Dipole-dipole
- •…



Disordered with defects: vacancy, grain boundary, etc.

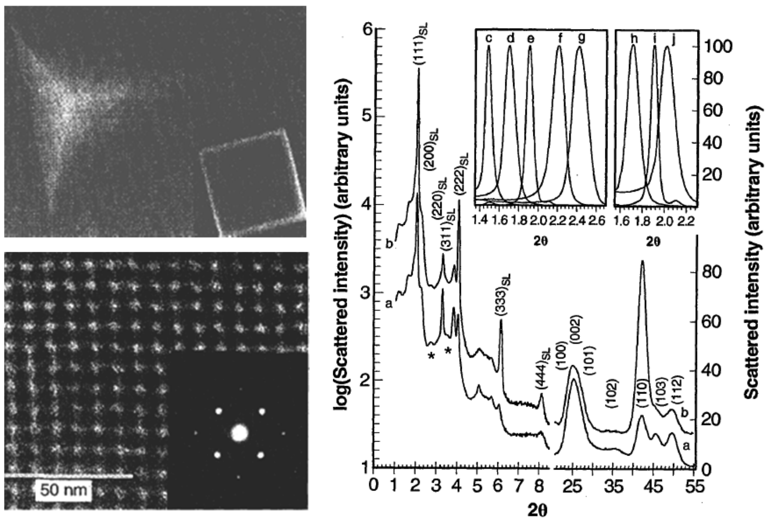


Ordered array

Lennox, R.B. *et al*. *Chem. Eur. J.* vol. 2, 359-363, 1996,

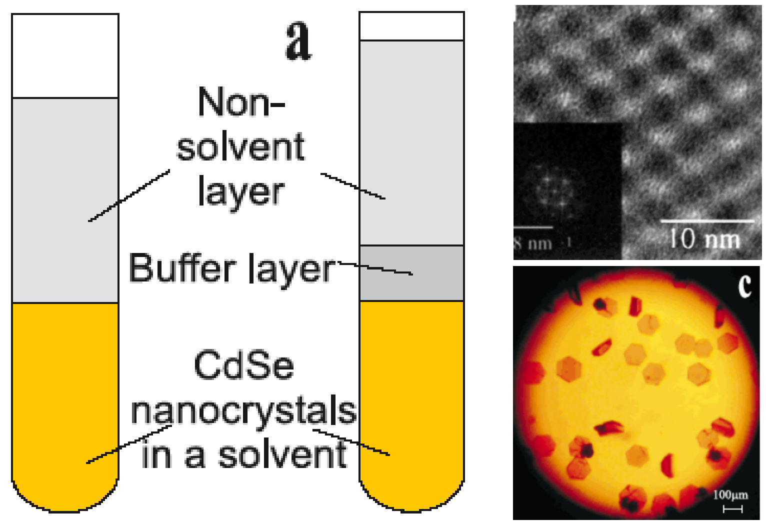
Nanoparticle Self-Assembly at Ambient Pressure: 1. Balanced Nanoparticle Interactions

1. Solvent anealing



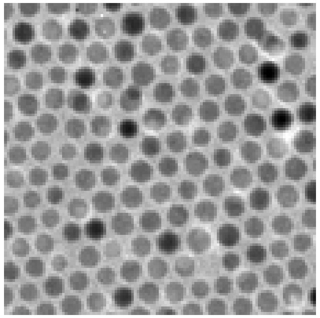
Murray, et al., *Science*, 1995.

2. Heterogeneous nucleation



Talapin, et al., *Adv. Mater*. 2001.

3. Solvent Evaporation



Ordered thin film

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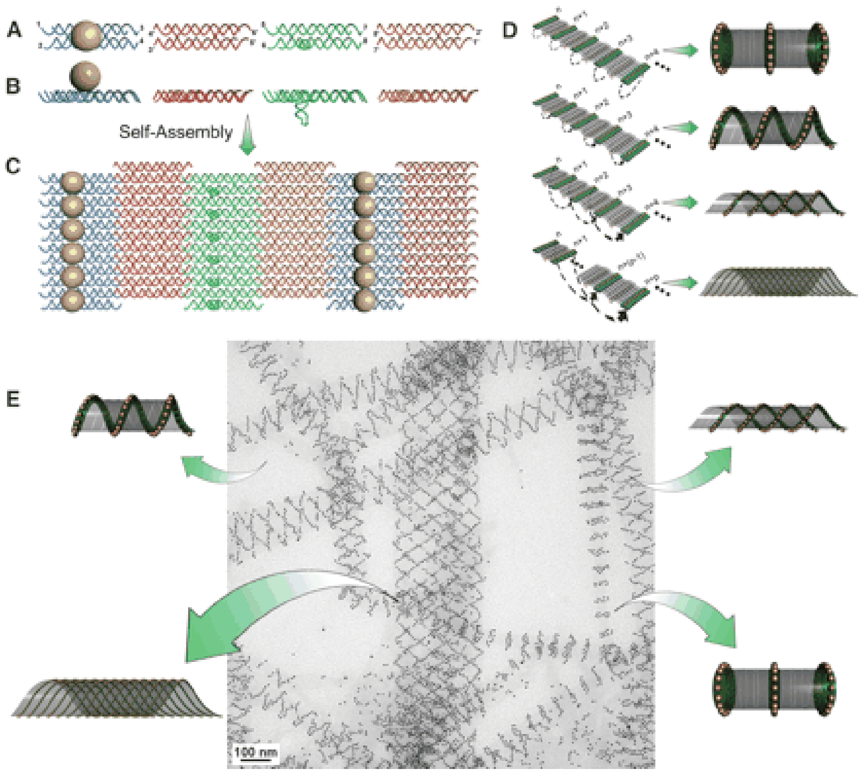
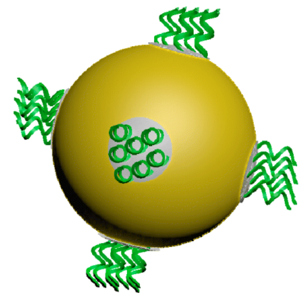
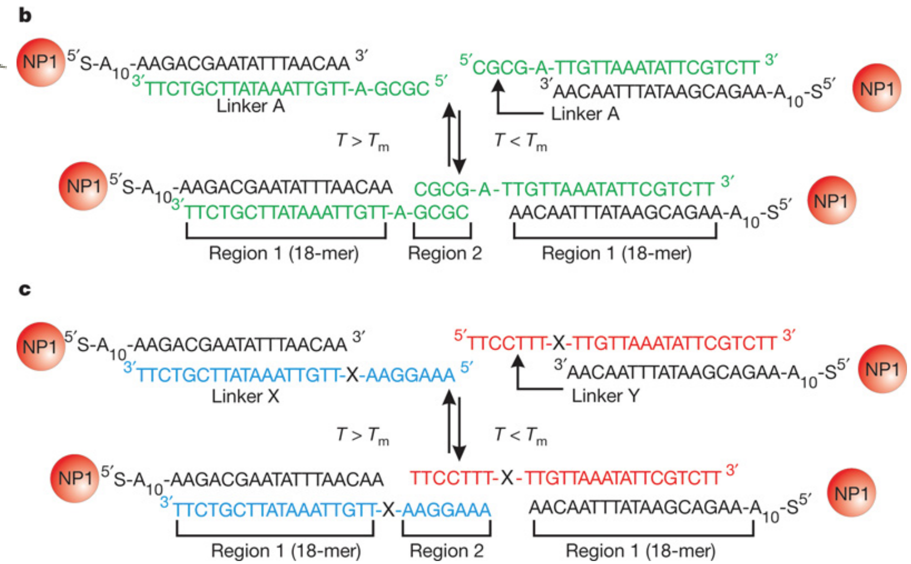
Nanoparticle Self-Assembly at Ambient Pressure: 2. DNA-Programmable Nanoparticles

Ligand-receptor interactions







Y. Li, et al. JACS, 2015, 137, pp4320-4323; Jaswinder Sharma, *et al*., *Science* 323, 112-116, 2009; Sung Yong Park, *et al*., *Nature* 451, 530-556, 2008; Dmytro Nykypanchk, *et al*., *Nature* 451, 549, 2008.

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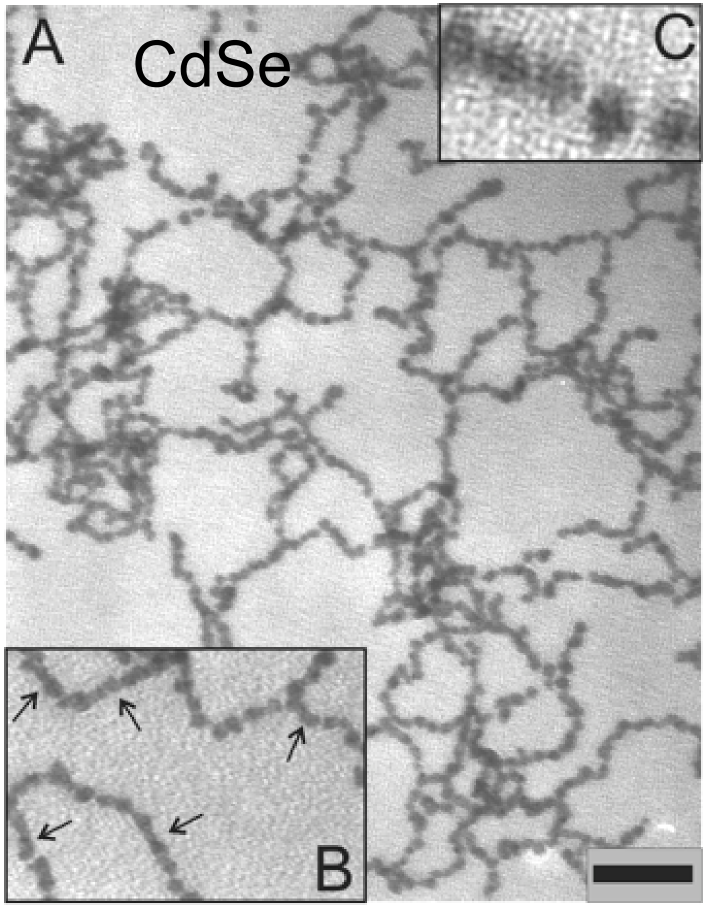
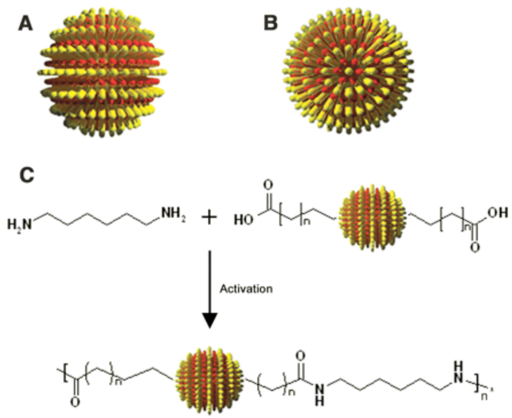
Nanoparticle Self-Assembly at Ambient Pressure:
3. Dipole-Dipole Interactions and Chemical Reactions

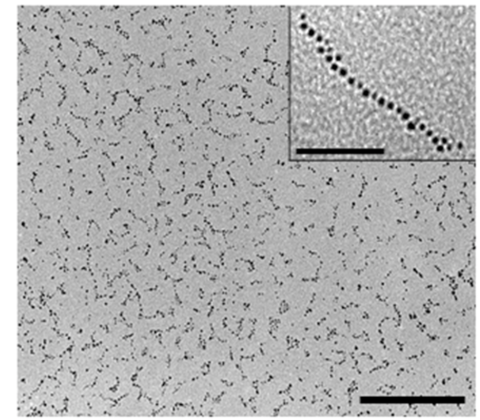
Dipole-Dipole Interaction



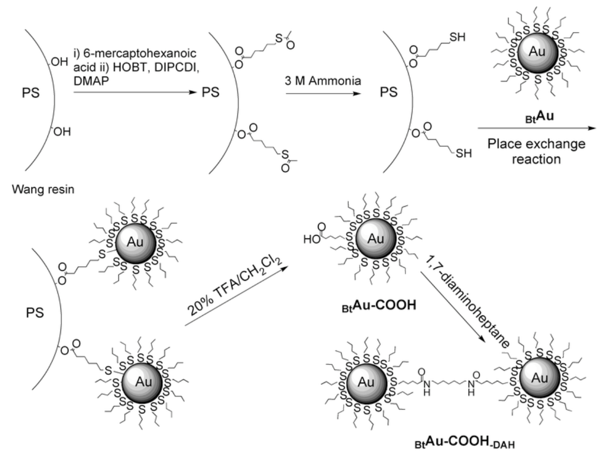
Z. Y. Tang, *et al., Science* 297, 237, 2002.

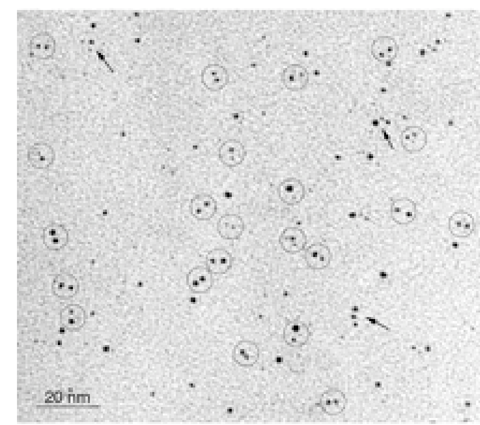
Chemical Reactions





G. A. DeVries, *et al., Science* 315, 358, 2007.





J. G. Worden, *et al., Chem. Comm.*, 518, 2004.

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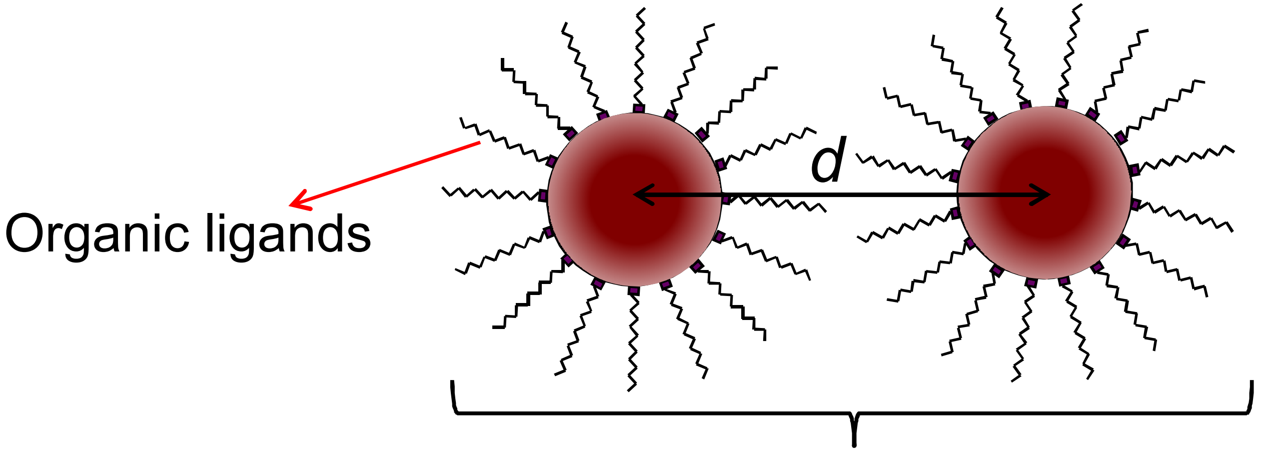
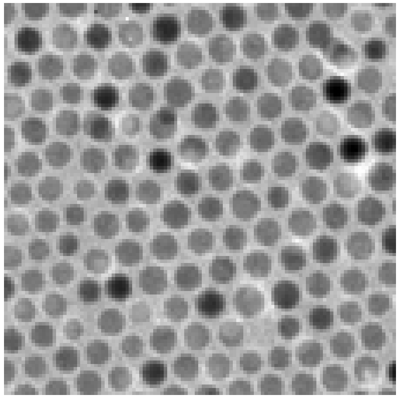
Nanoparticle Interactions and Coupling

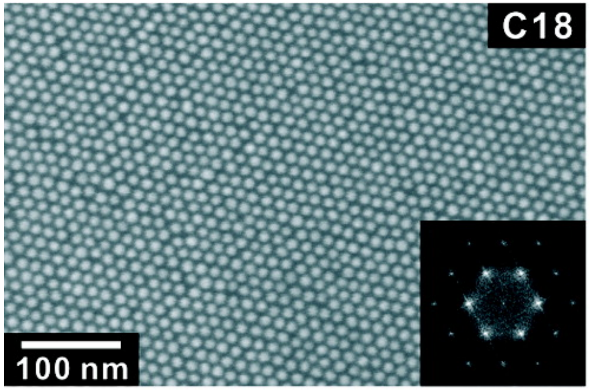
Nanoparticle coupling depends on interparticle separation distance

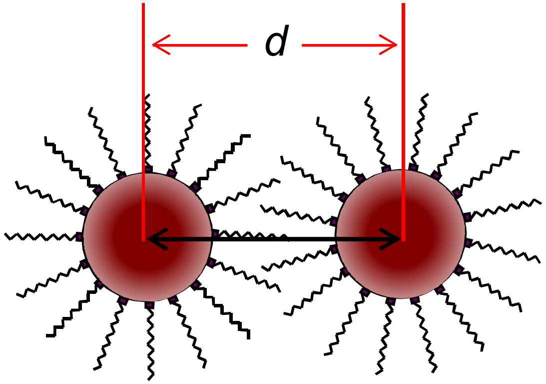


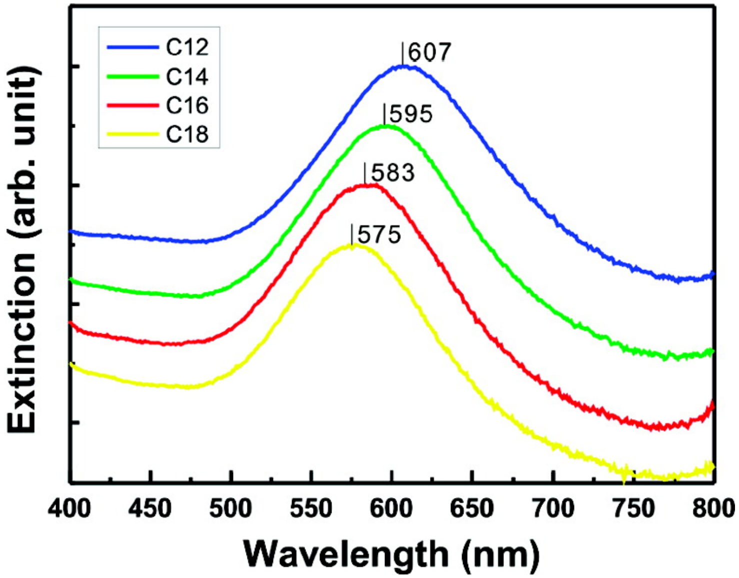


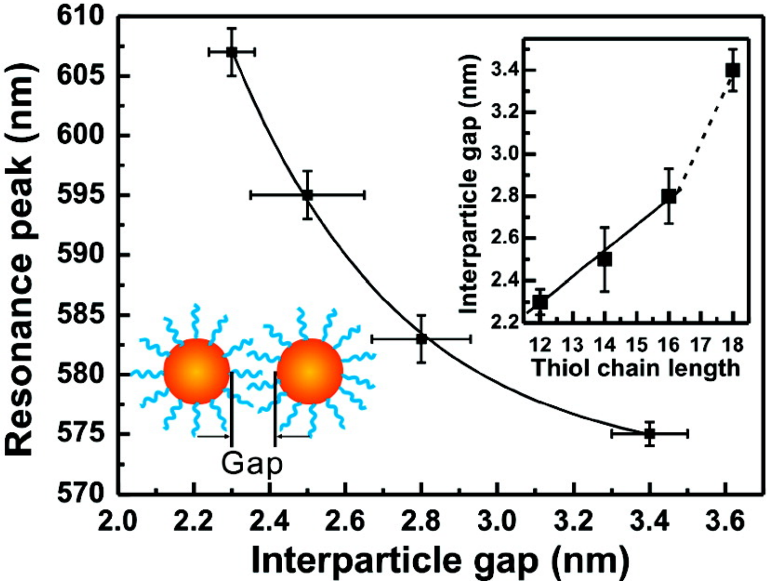
Balanced nanoparticle interactions:
- Attraction
- Van der Waals
- Charge interactions
- Dipole-dipole
- …

Tuning Plasmonic Response from Alkanethiolate-Stabilized Gold Nanoparticle Superlattices





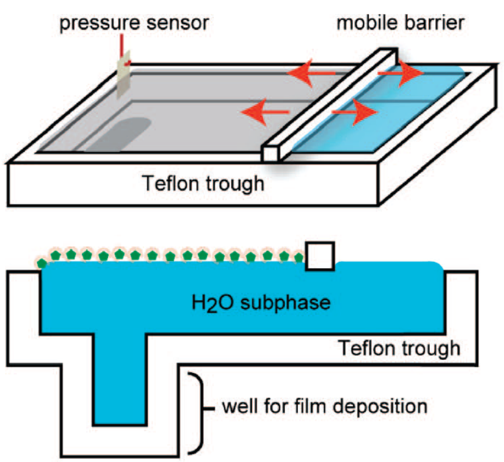


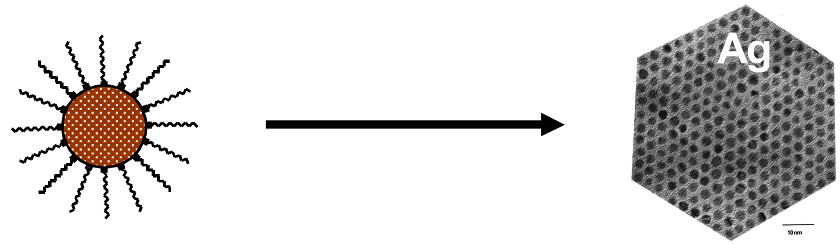


Chi-Fan Chen, *et al.*, *J. Am. Chem. Soc.,* 130, 824-826, 2008.

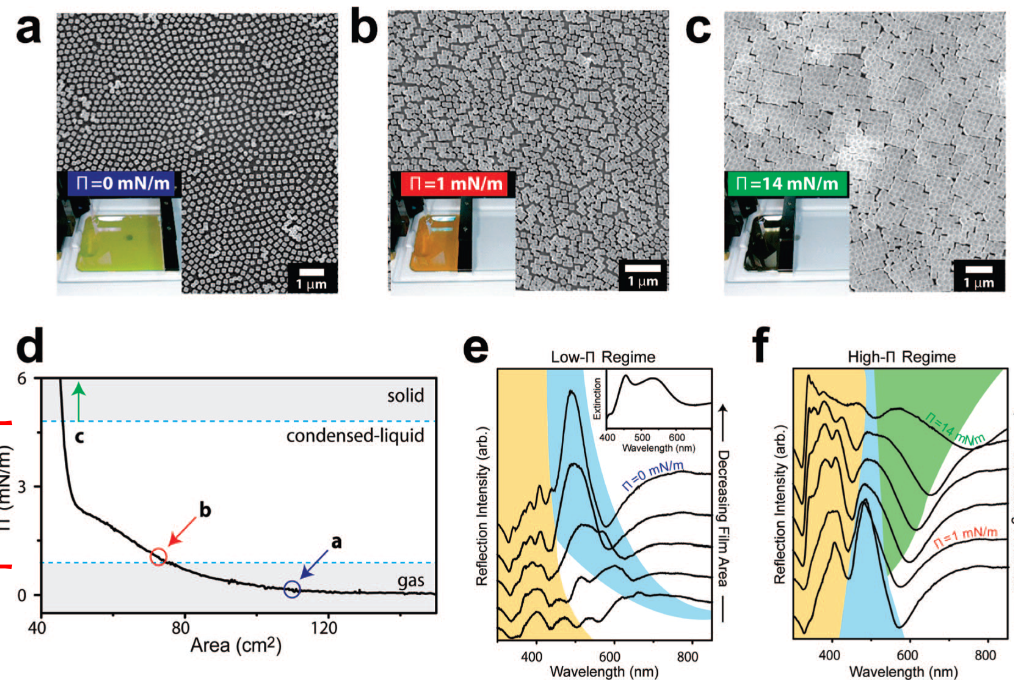
Langmuir-Blodget to Tune Nanoparticle Separaion

LB process





C. P. Collier, *et al*, *Science*, 227, 1978-1981, 1997.



- uniaxial pressure
- 2-dimensional
- limited pressure range

Tao, A. R. *et al.*, *Acc. Chem. Res.*, vol. 41, No. 12, 1662-1673, 2008.

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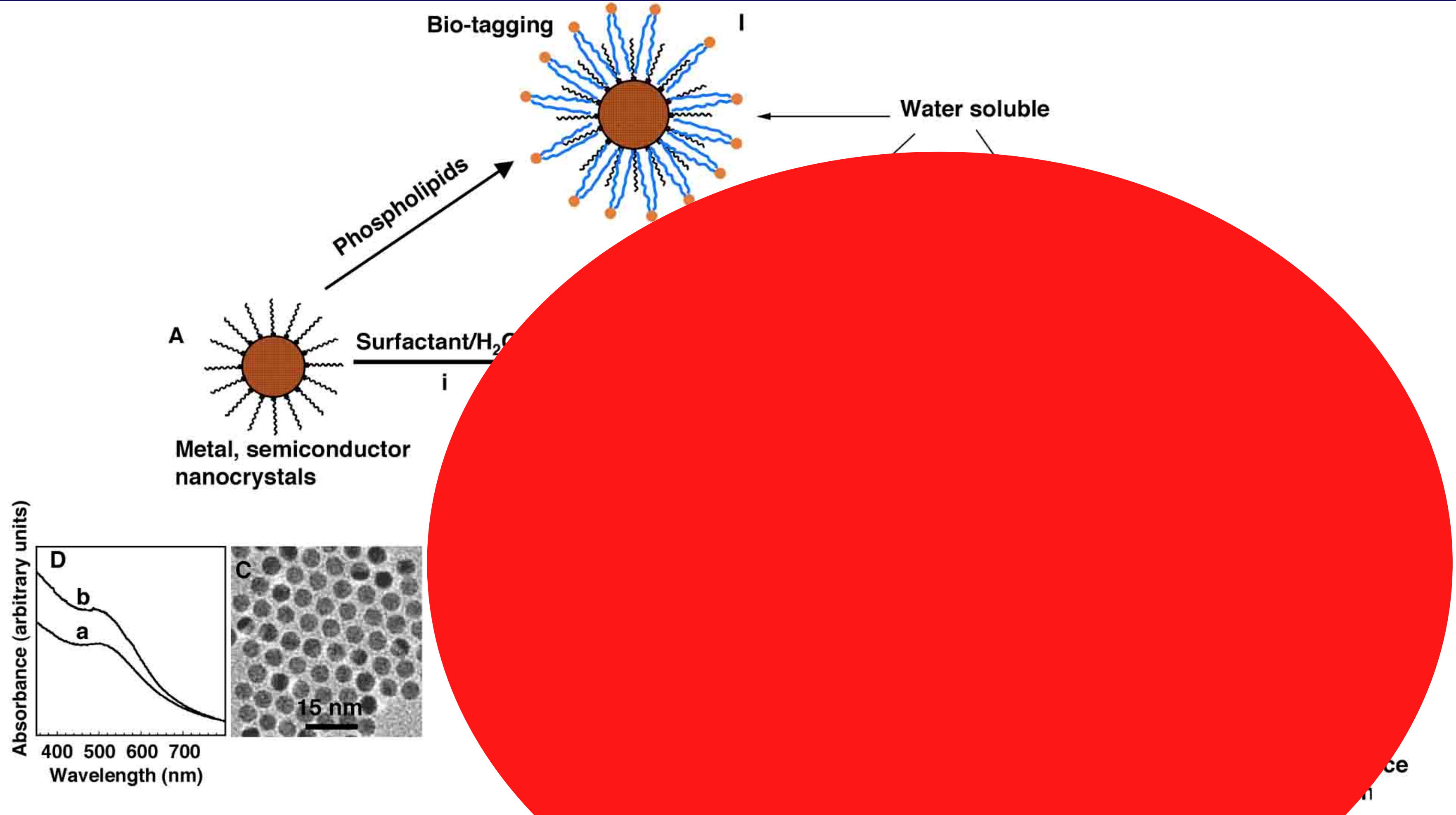
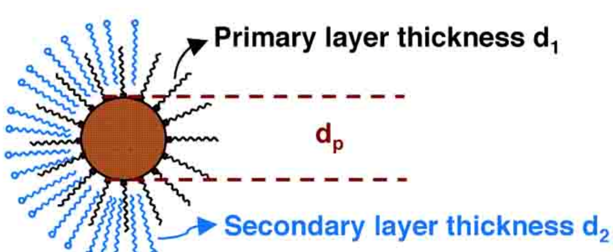
Water-Soluble Nanocrystal-Micelles and Their Self-Assembly into Robust, Ordered, Three-Dimensional Arrays





Fan H. *et. al., Science* 304, 567-571, 2004.

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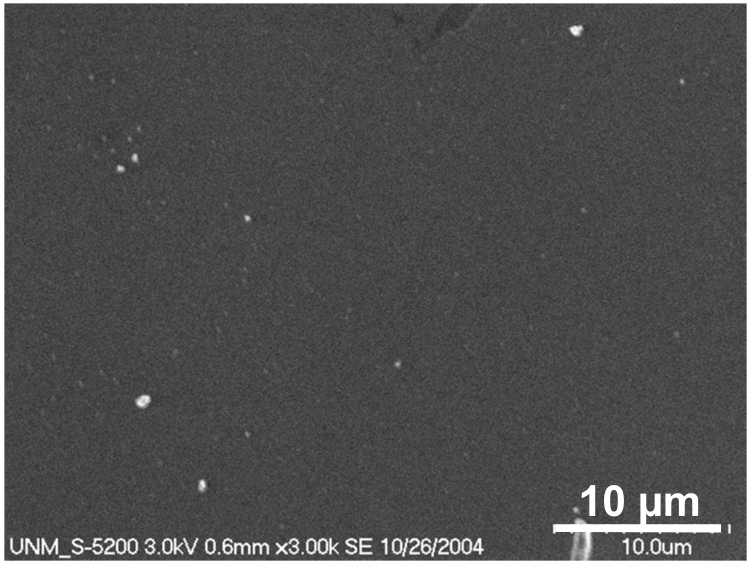
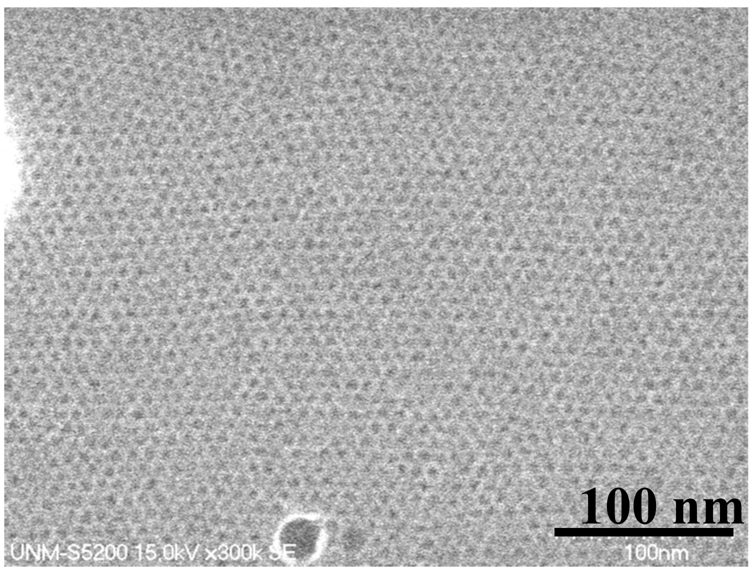
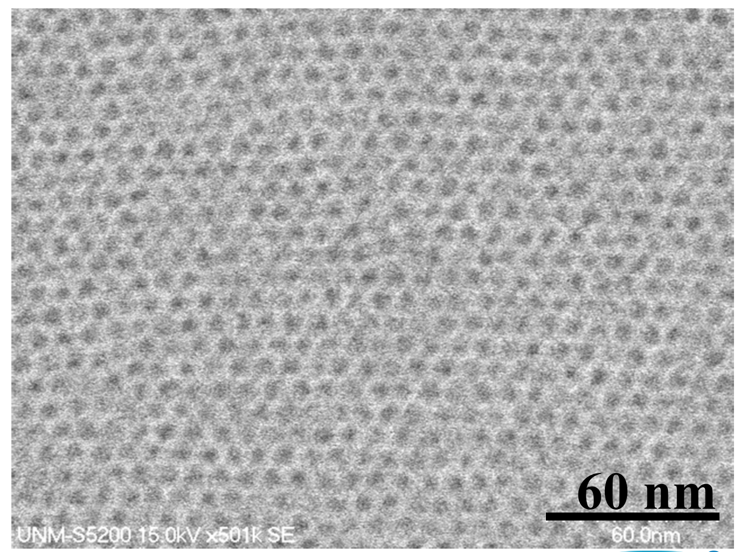
Scanning Electron Microscopy Images of Ordered Gold NC/Silica Films







Fan *et al. Adv. Funct. Maters., vol. 16*, 891-895, 2006.

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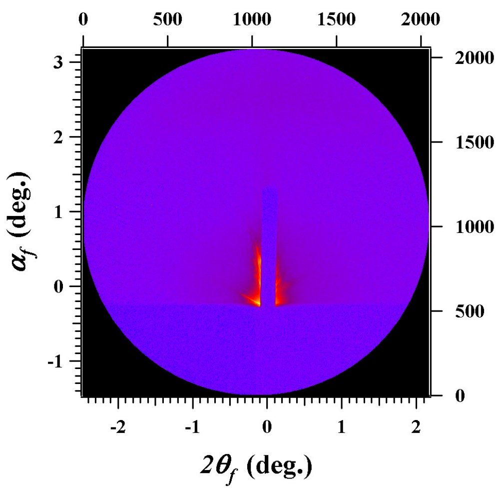
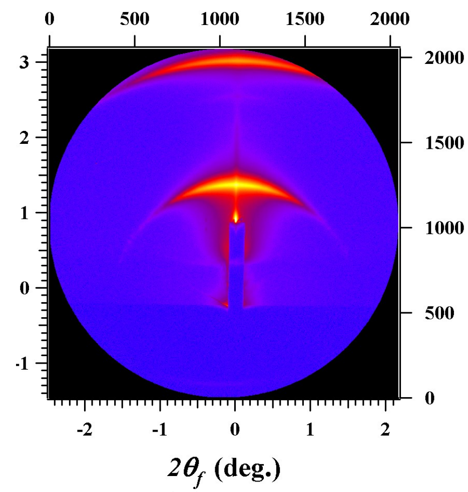
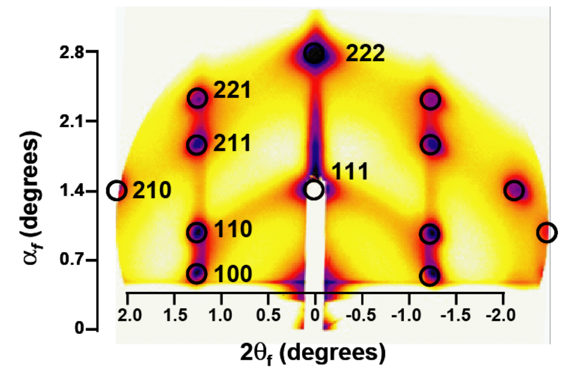
In-situ Grazing Incidence Small-Angle X-ray Scattering Characterizations of Ordered 3D Nanoparticle Films.

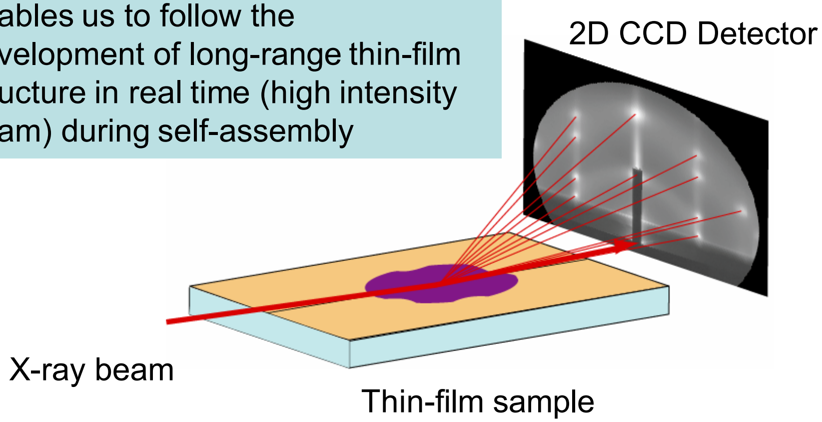




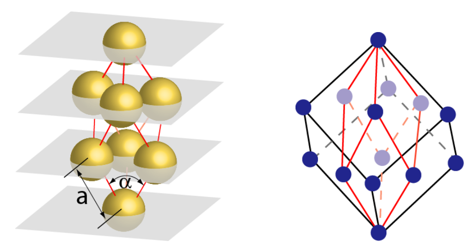


Drying time: t = 18 minutes t = 28 minutes t = 50 minutes

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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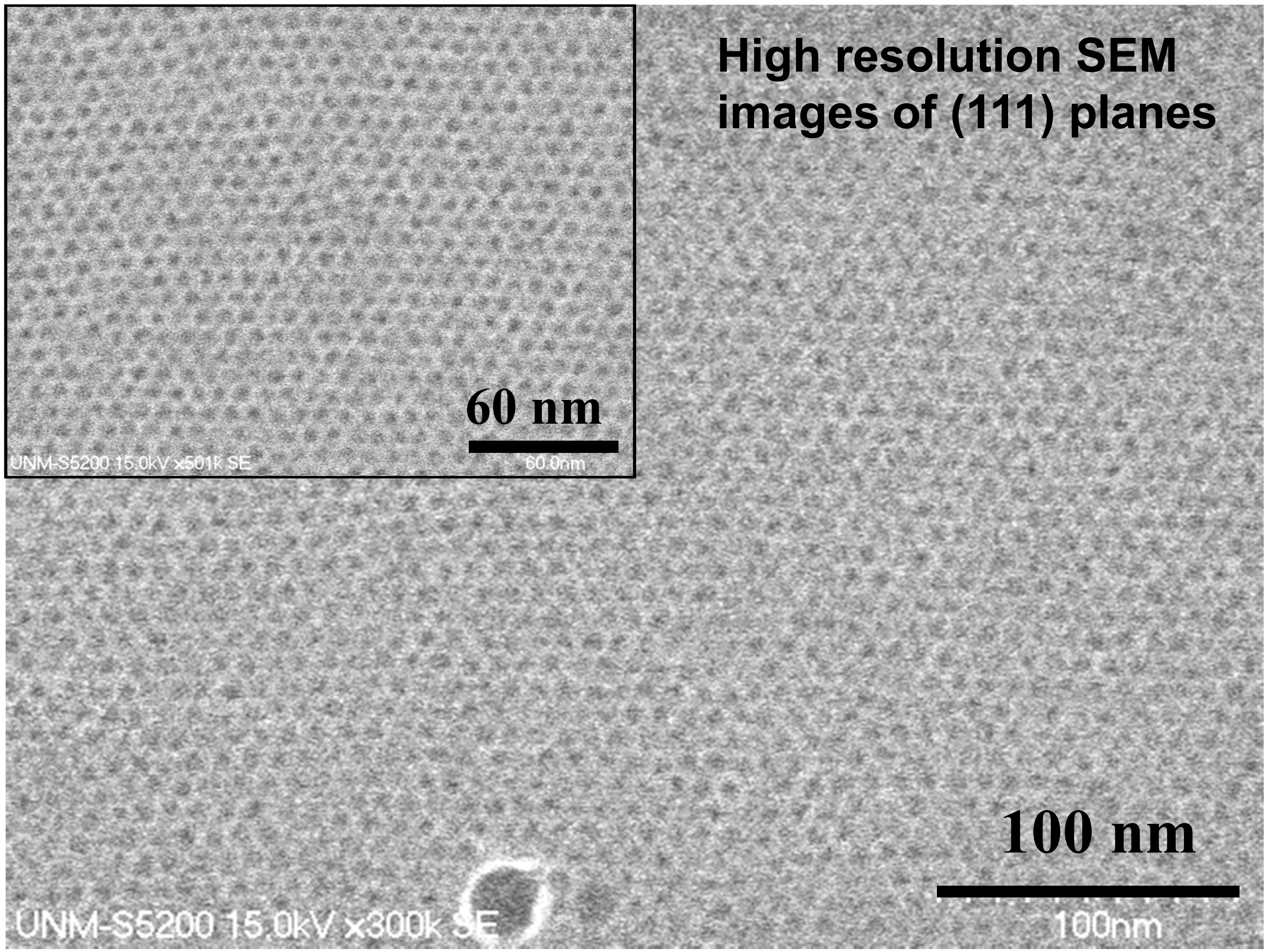
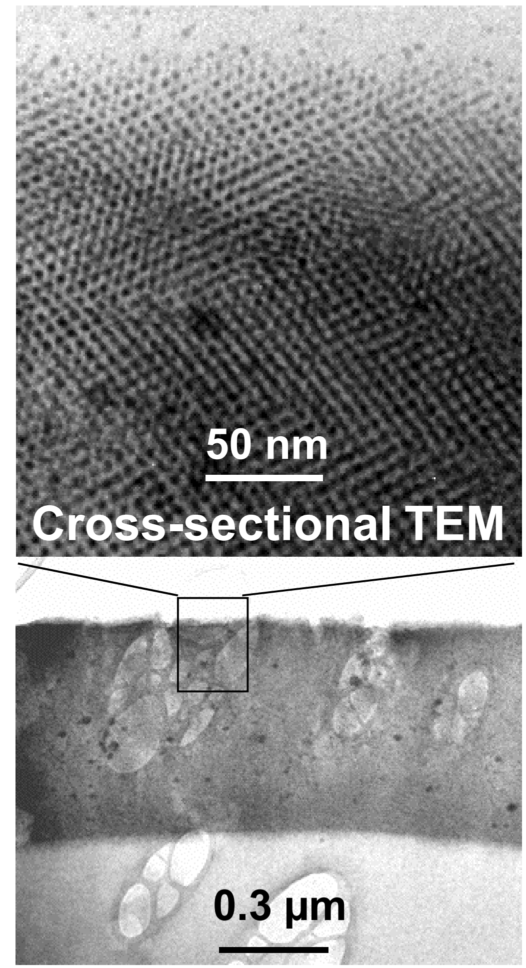
Orientated Self-Assembly of Ordered Gold Nanocrystal/Silica Films

Through control of evaporation and silica condensation, highly-orientated 3D nanocrystal/silica thin films are synthesized with {111} planes parallel to substrates.





Fan *et al. Langmuir,* 24 (19) 10575-10578, 2008*; Adv. Funct. Maters., vol. 16*, 891-895, 2006.

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Nanoparticle Films with Tunable Optical Property

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

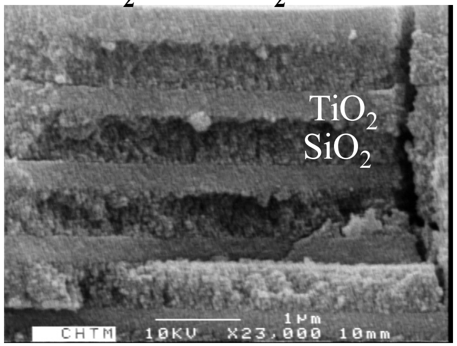
	Material	Measured Index n	Measured Absorption k
Low Index	Porous Silica (Acid Catalyzed)	1.18-1.25	<0.15 (out to 10 μm)
	Porous Silica (Base Catalyzed)	1.19-1.25	<.01 (out to 10 μm)
	Dense Silica	1.4	To Be Measured
Medium Index	TiO_2 (Acid Catalyzed)	1.4-2.4	<0.15 (out to 10 μm)
	TiO_2 (Base Catalyzed)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

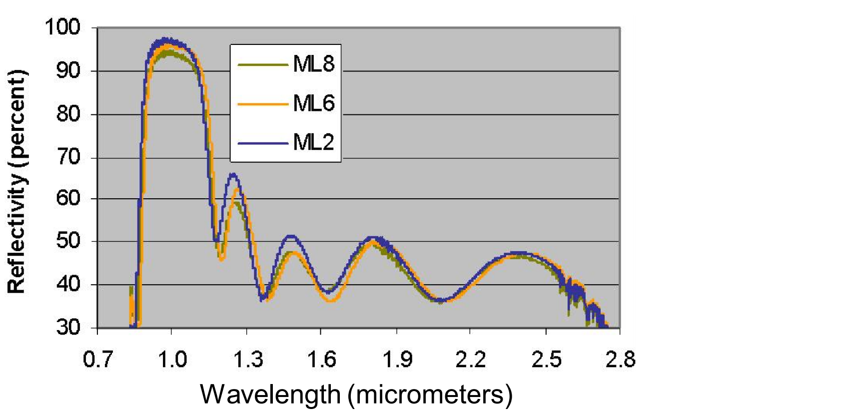
Application of Nanoparticle Coatings for Near Infrared Reflectors (2007 R&D 100 Award)

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.

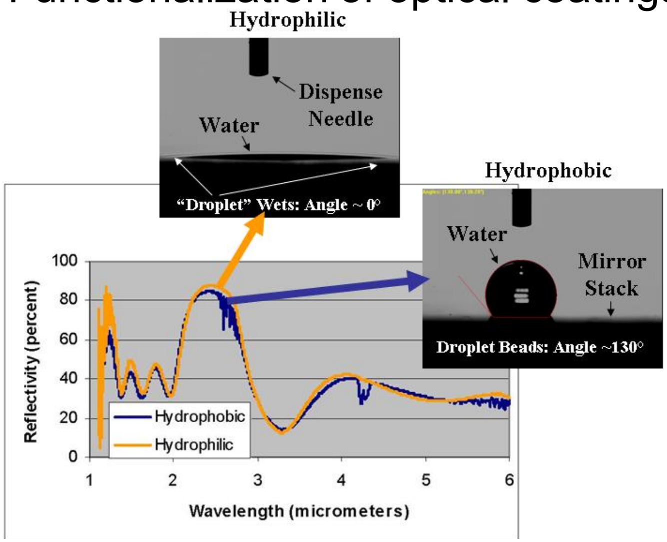
SEM image of quarter wave stacking of TiO_2 and SiO_2 reflector

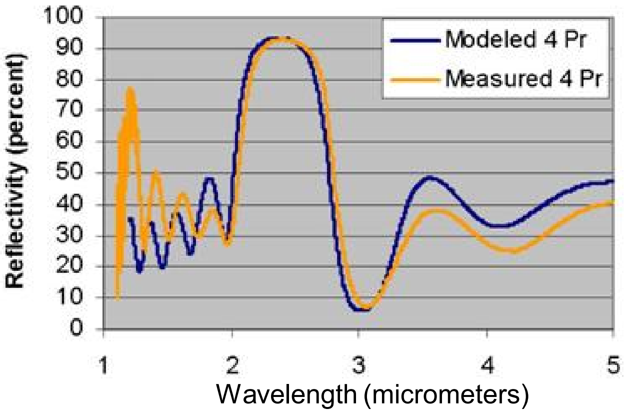


Reflectivity studies show high and reproducible reflectivity over controlled wavelength windows (1-2µm, 2-3µm, 8-12µm, etc)



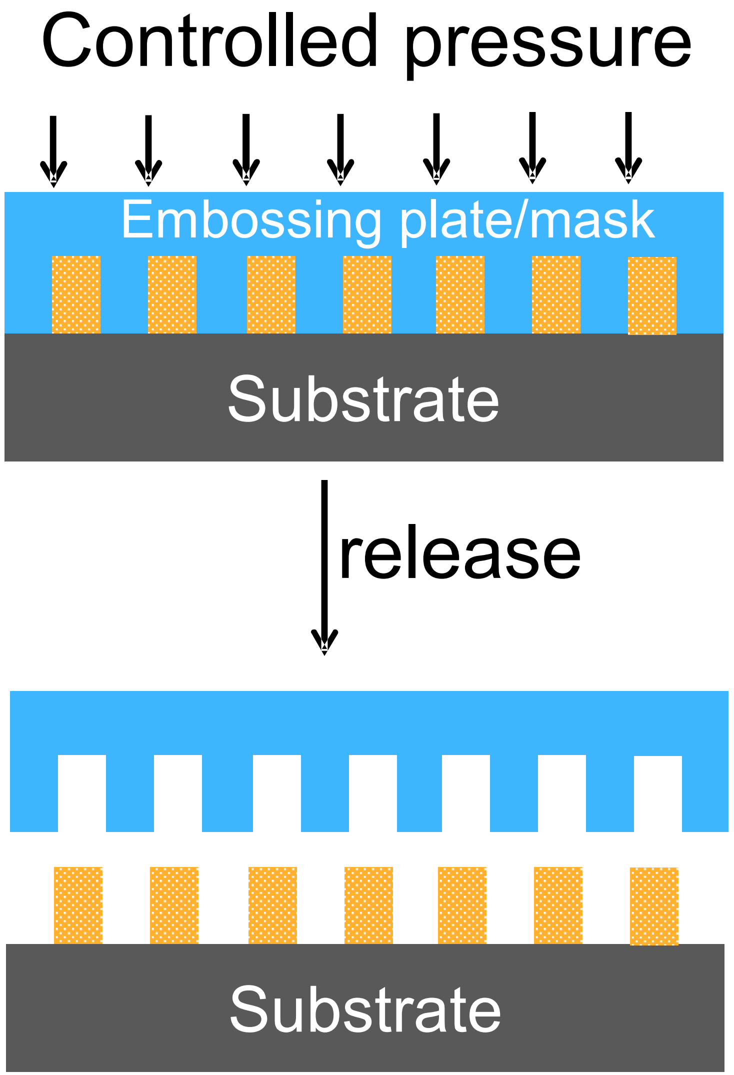
Functionalization of optical coatings





Model design show 99.9% and address key manufacturing issue.

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



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

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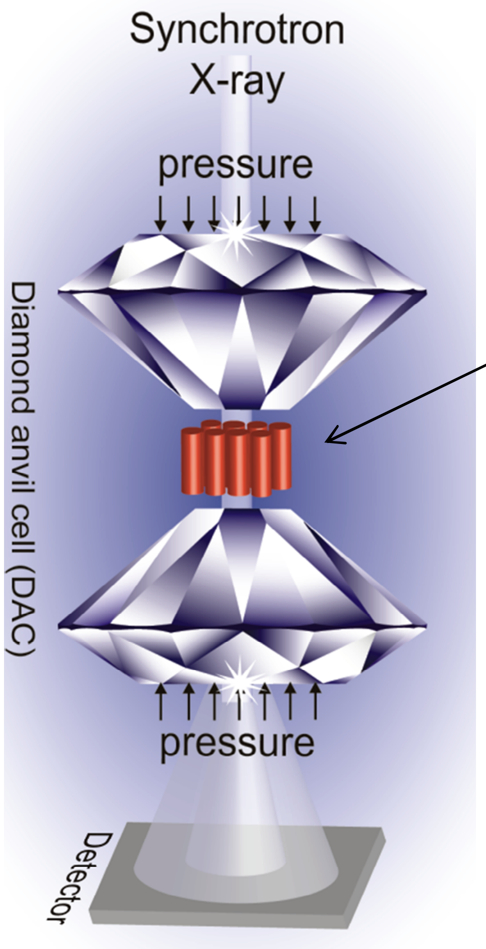
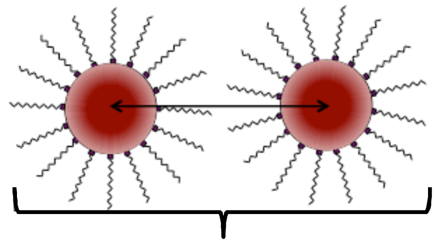
Pressure-Induced Assembly and Fabrication

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:
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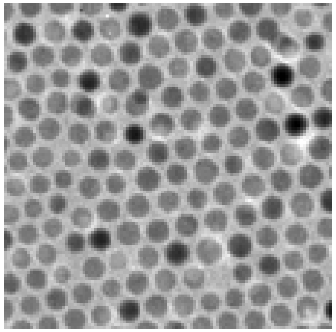
•Dipole-dipole
•…



- 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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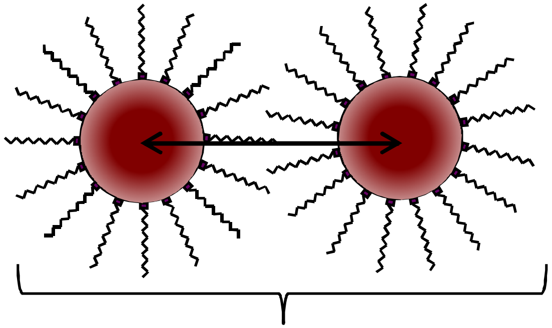
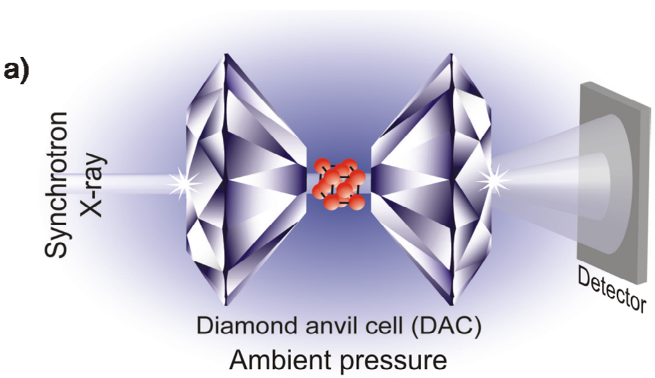
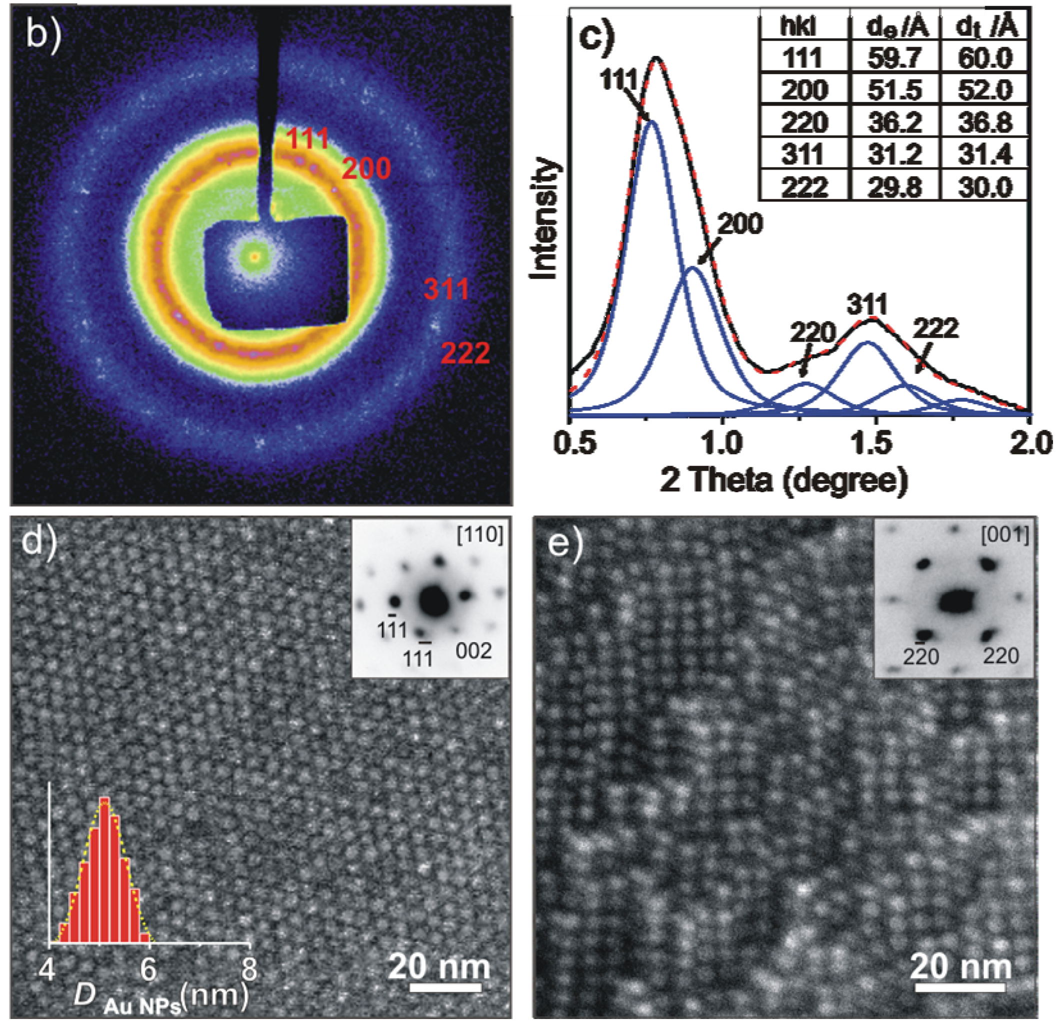
Before Compression – Starting Materials: Ordered Spherical Gold Nanoparticle Arrays



Balanced particle interactions



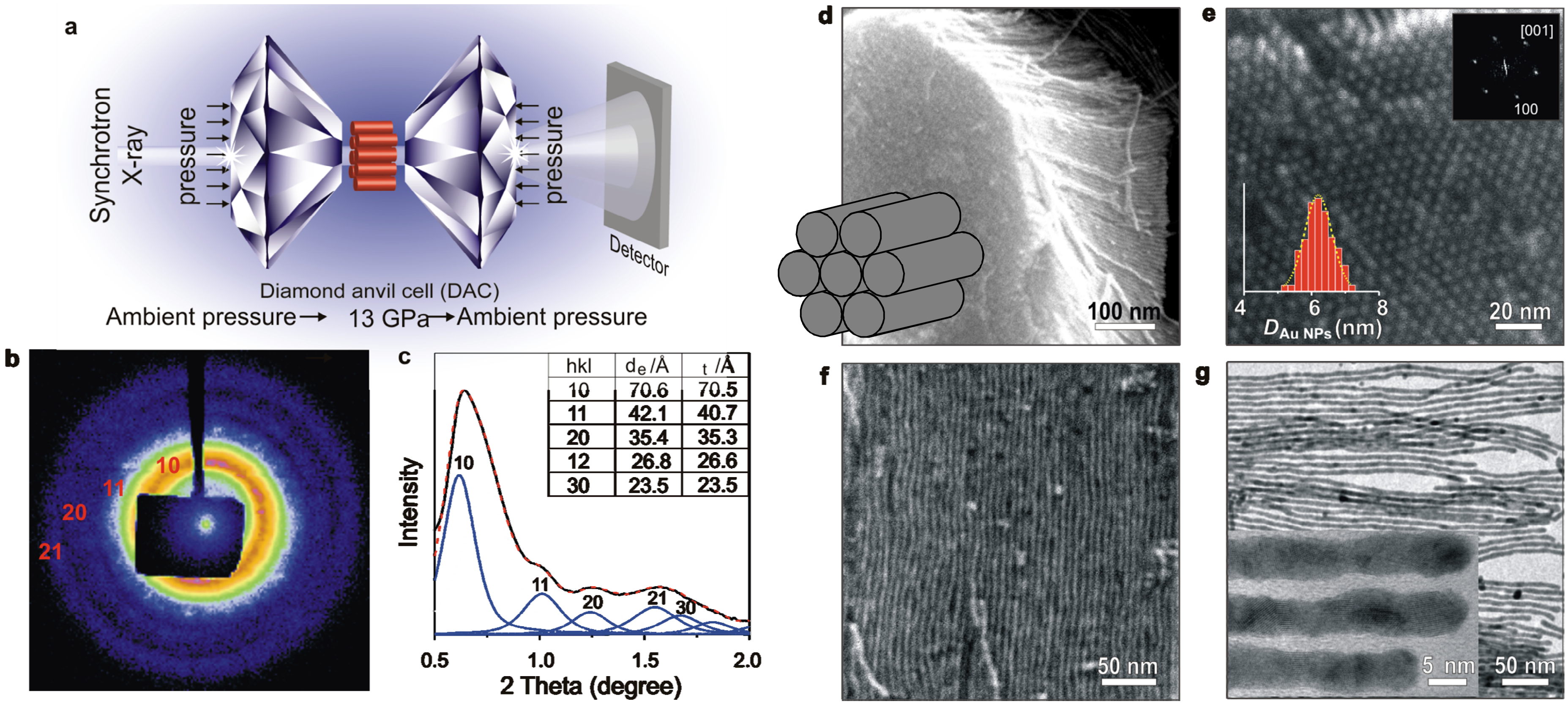
5 nm gold nanoparticles and *fcc* lattice (a = 10.4 nm)



hkl	d_e/Å	d_t /Å
111	59.7	60.0
200	51.5	52.0
220	36.2	36.8
311	31.2	31.4
222	29.8	30.0

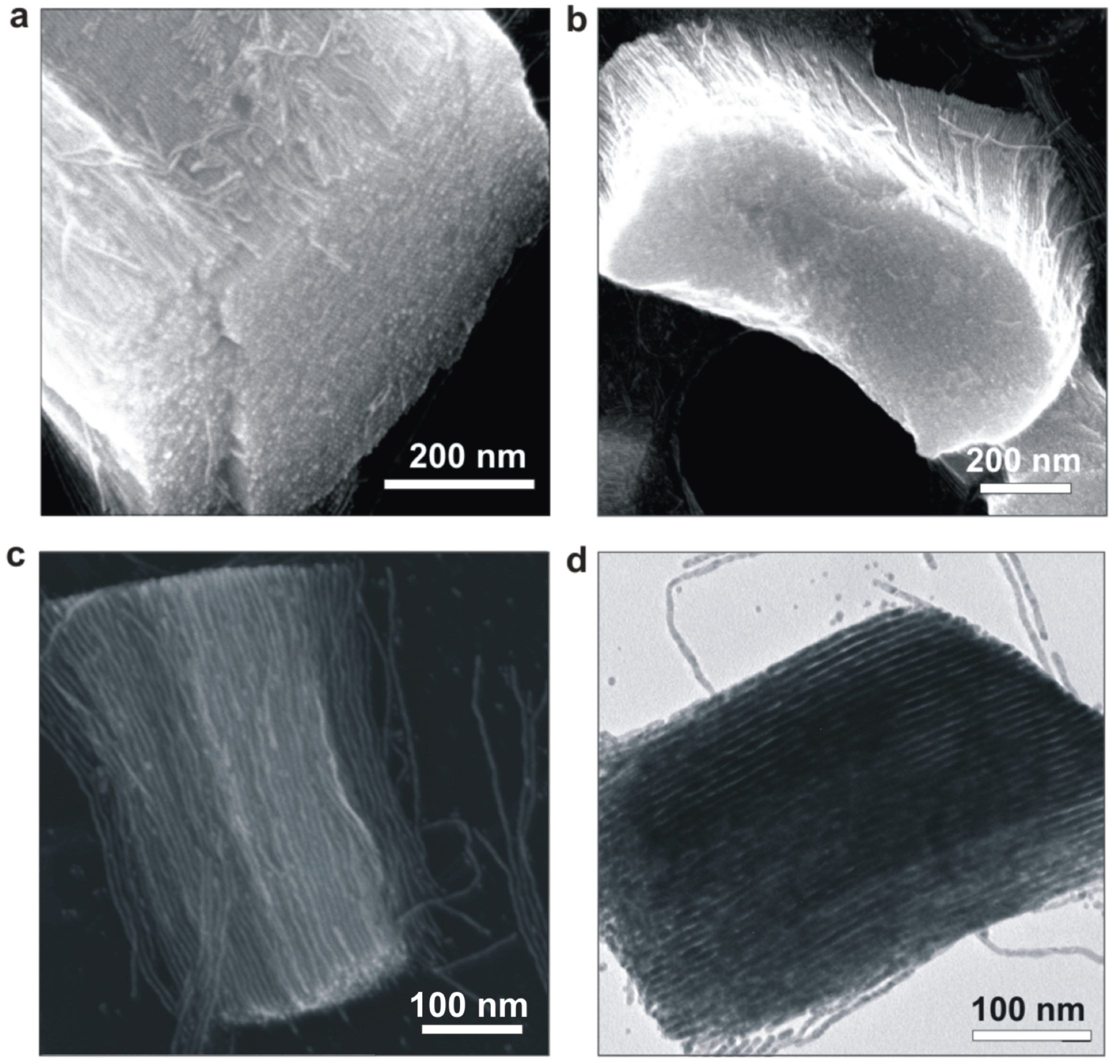
Wu H., Fan H., *et al*. *Angew. Chem. Int. Ed.,* 49, 8431-8434, 2010.

After Compression – Formation of 1D Nanowires

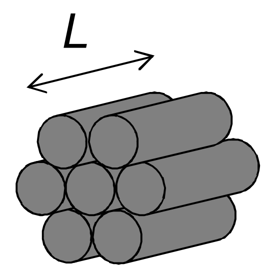


Wu H., Fan H., *et al. Angew. Chem. Int. Ed.,* 49, 8431-8434, 2010.

Bundles of 1D Nanowire Arrays

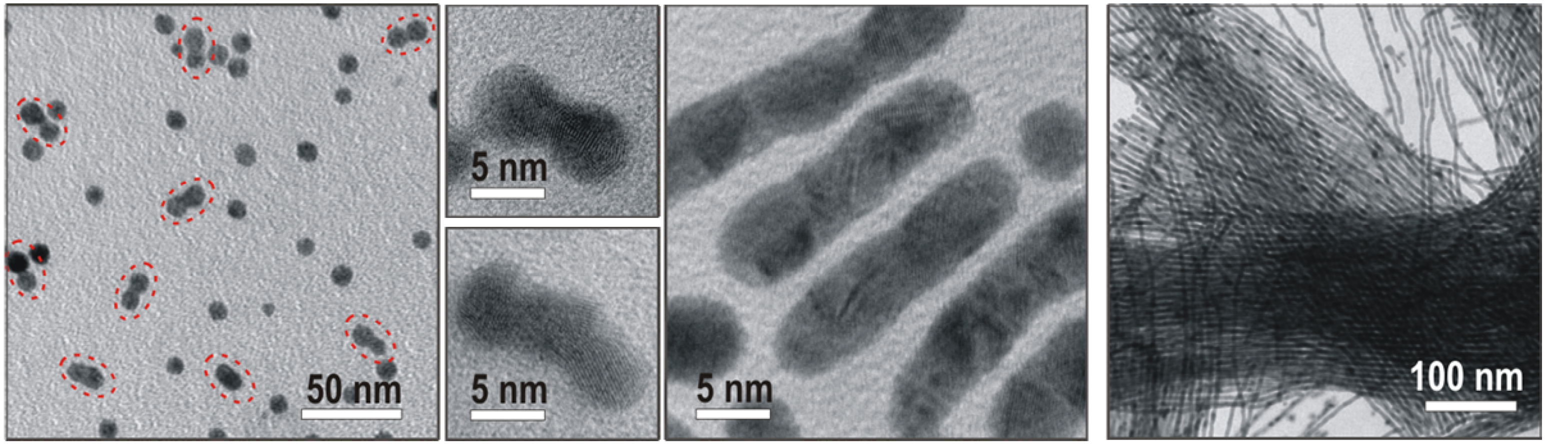


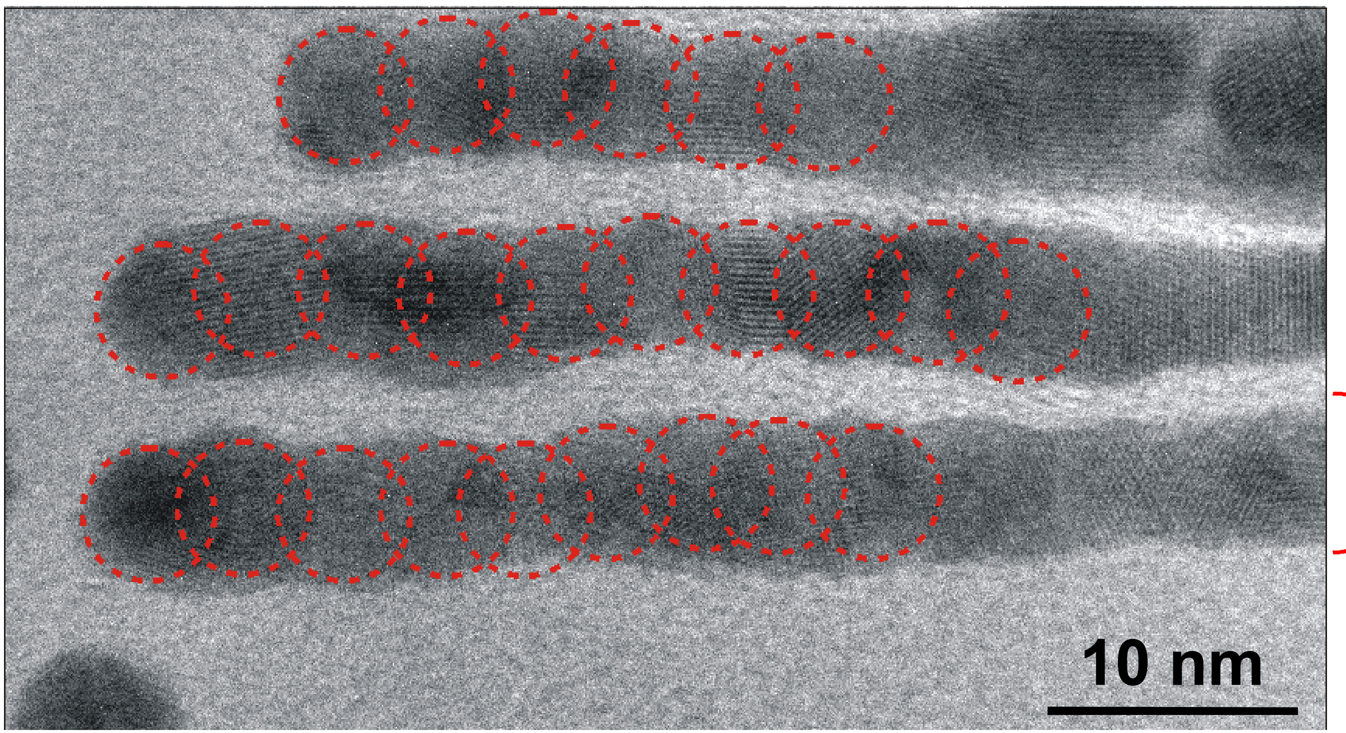
Uniform length



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

Pressure Tuned 1D Nanostructures





Diameter
~ 5 nm

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

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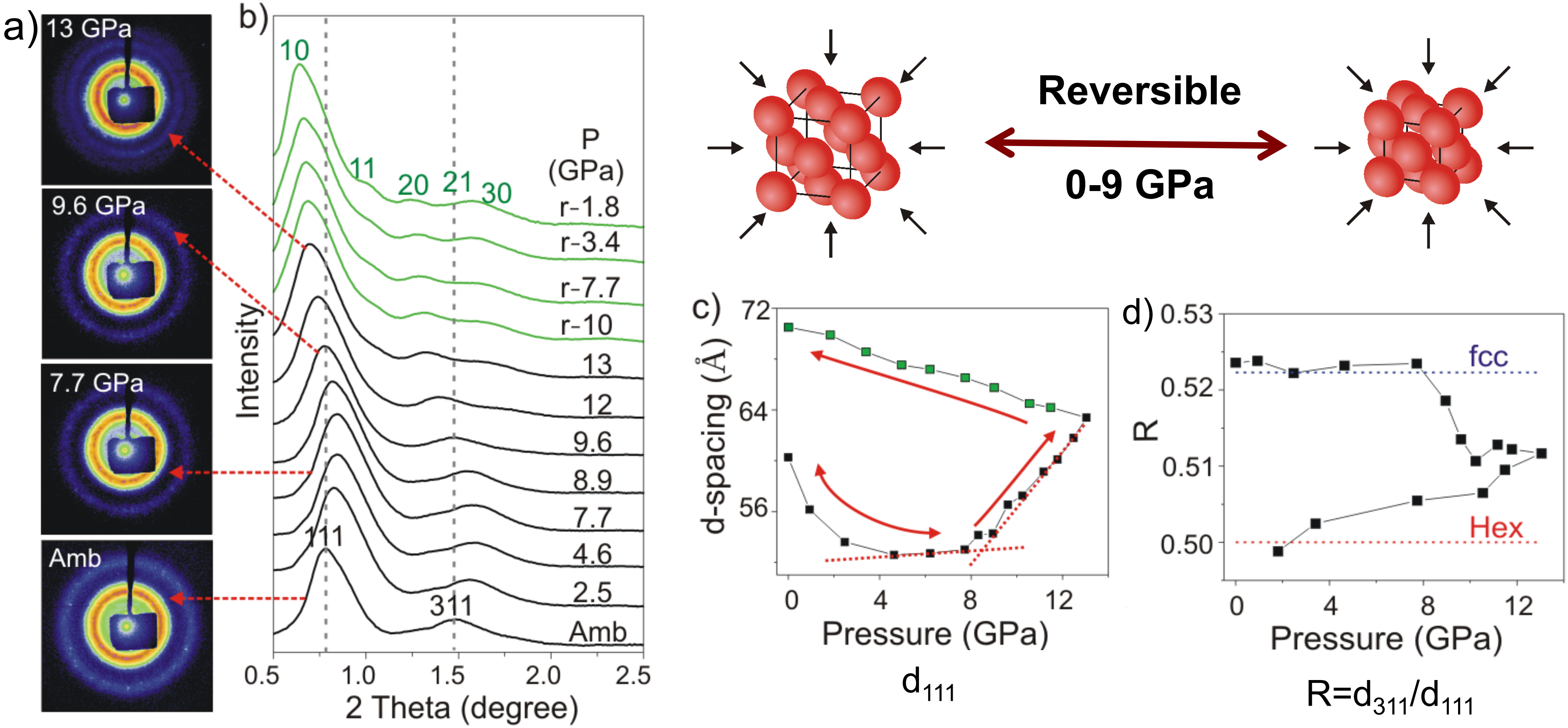
In-situ Synchrotron X-ray Studies of Nanoparticle Assembly under Pressure

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}

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

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

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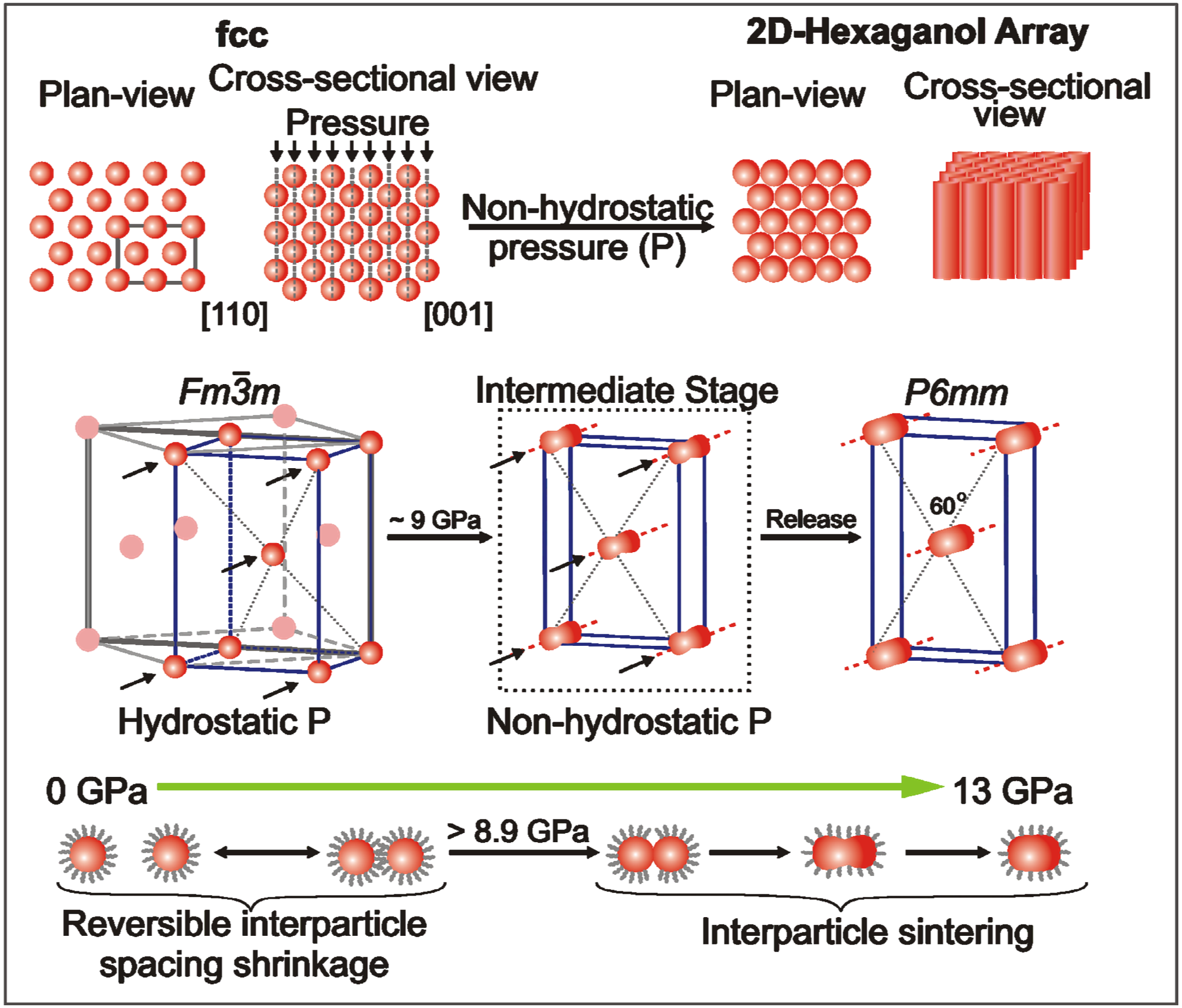
Pressure-Induced Nanoparticle Assembly Processes



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

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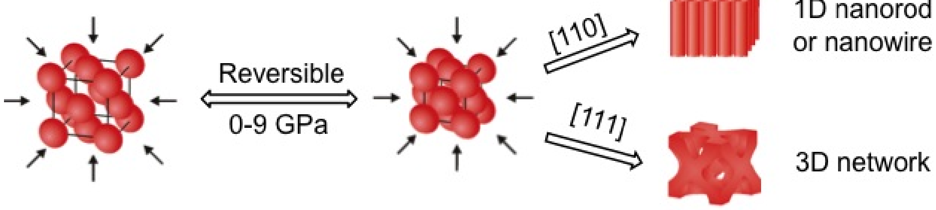
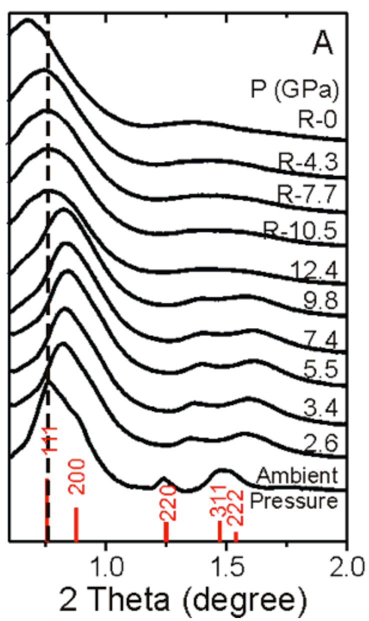
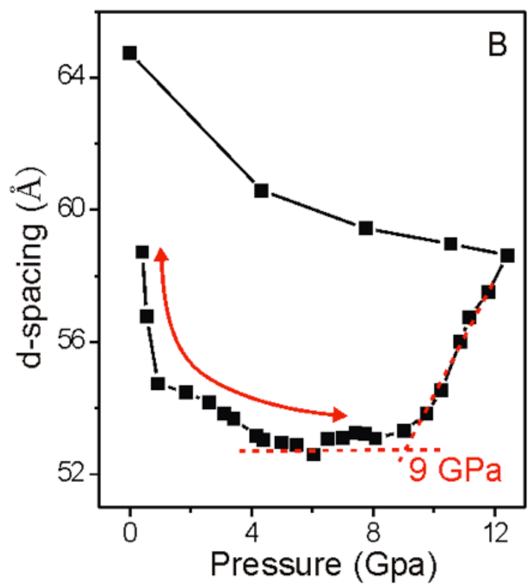
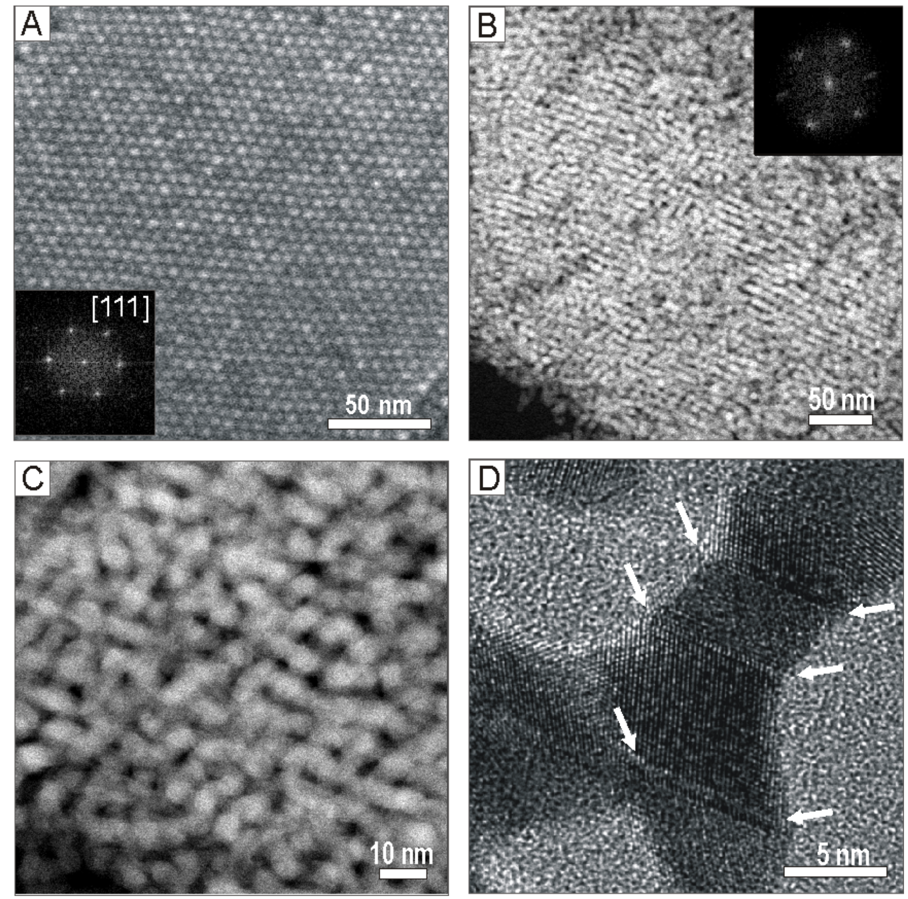
Pressure-Induced Formation of 3D Nanostructures

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









Wu H., Fan, H. *et al.*, *J. Am. Chem. Soc.*, 132, 12826, 2010 & *J. Am. Chem. Soc. 136*, pp 7634, 2014.

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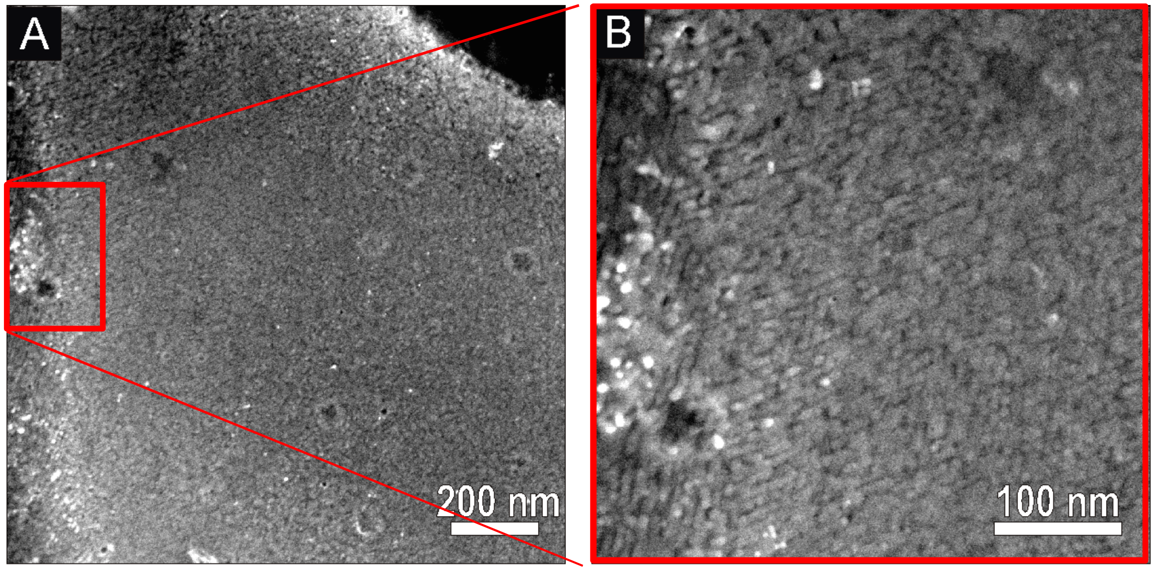
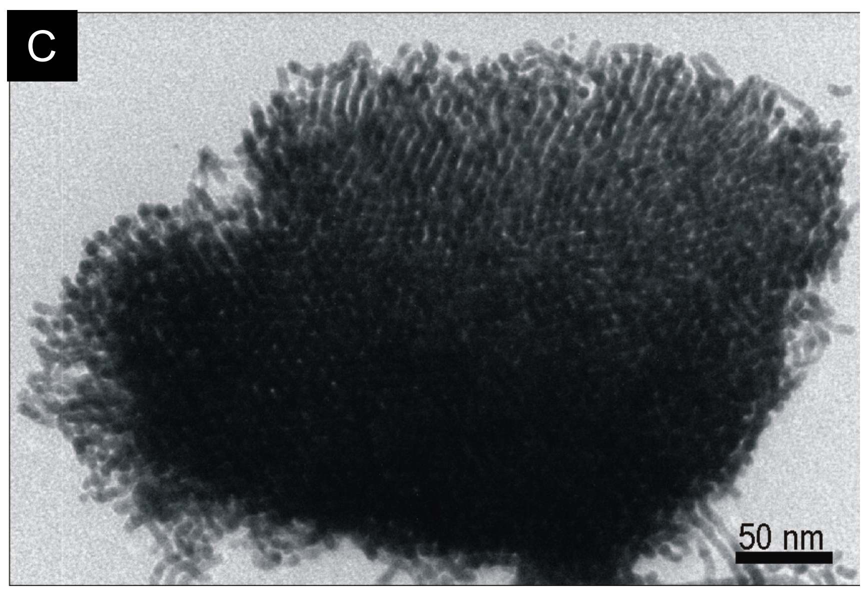
Electron Microscopy of 3D Networks

SEM images

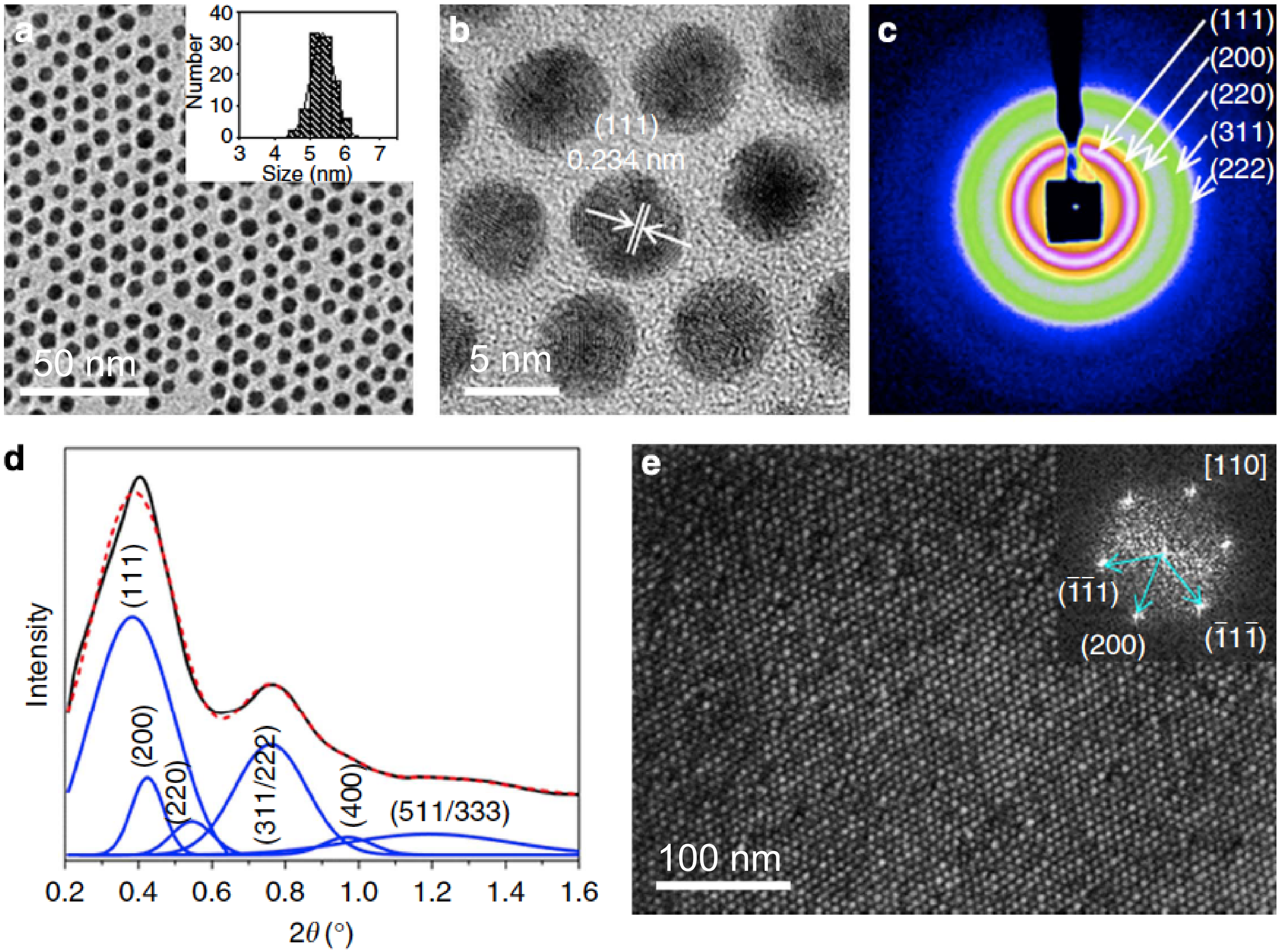


TEM image



Wu, H. et al. *J. Am. Chem. Soc.* 2014, 136, 7634−7636.

Before Compression – Starting Materials: Ag Nanoparticles



Wang, et al. *J. Am. Chem. Soc.* 2011, 133, 14484–14487.

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

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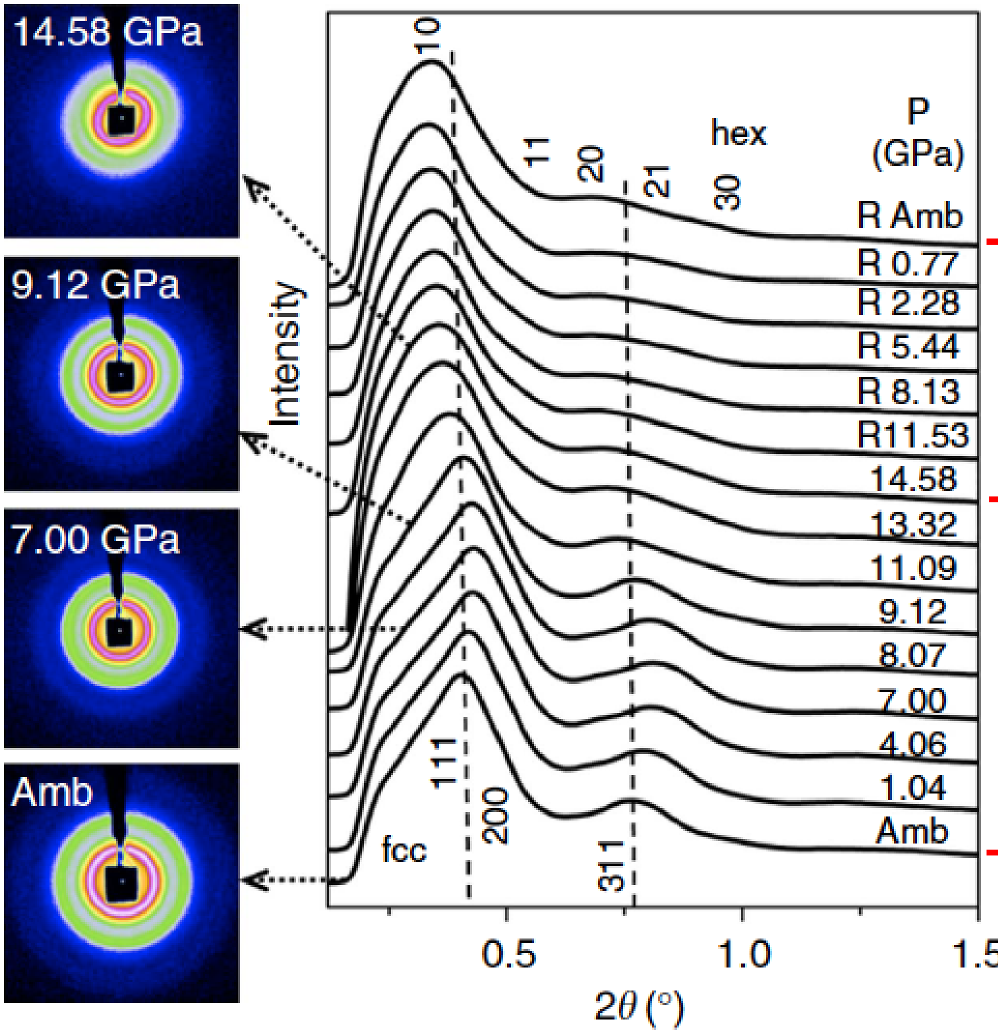
Structural Evolution of Ag Nanoparticle Arrays during Compression and Release



R-Ambient
Hexagonal
a **= 94.63 Å**

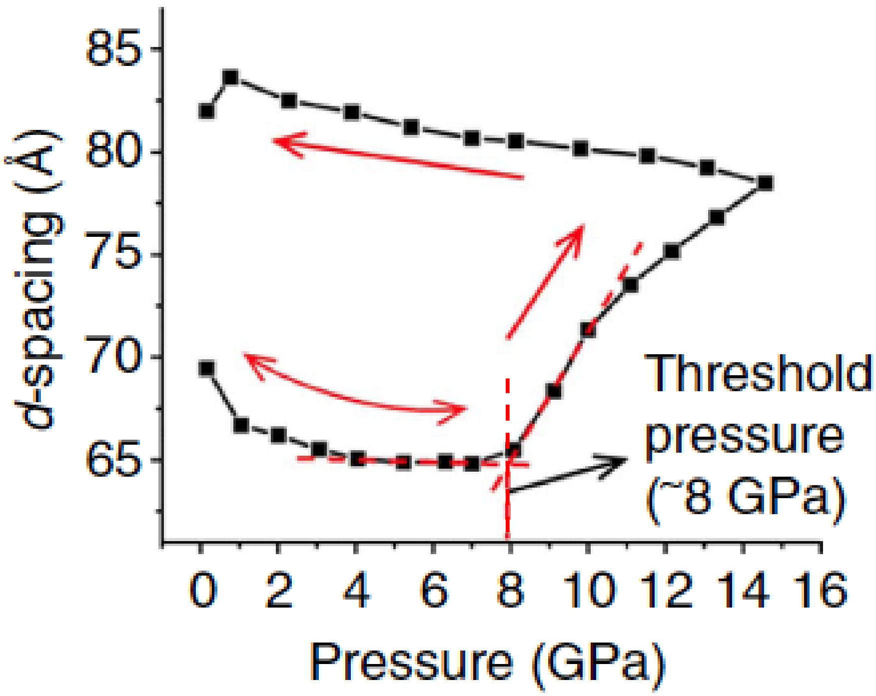
14.58 GPa
Hexagonal
a= 90.44 Å

Ambient
Cubic, *fcc*
a= 119.83 Å

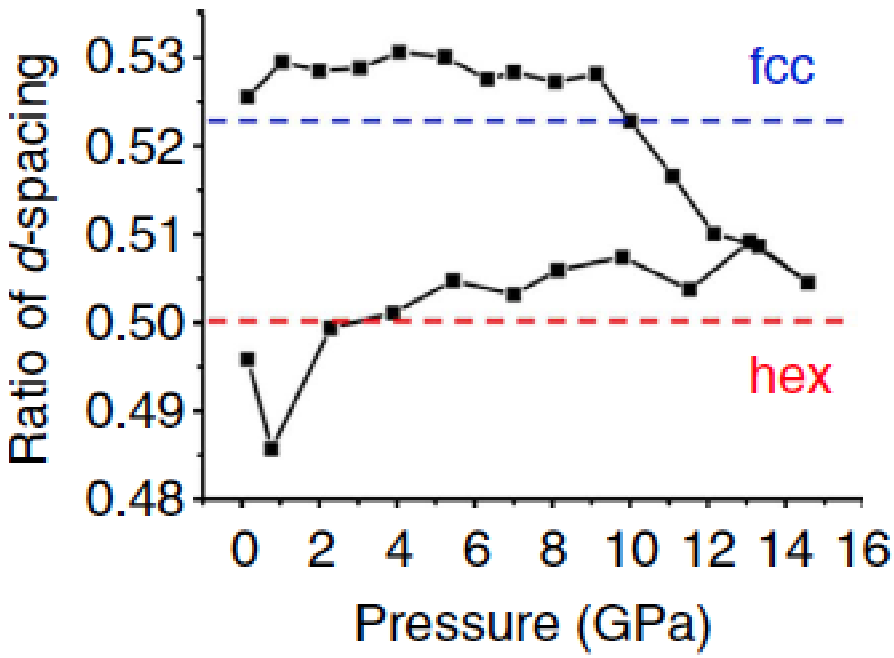
Wang, et al. *J. Am. Chem. Soc.* 2011, 133, 14484–14487.

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

Structural Evolution of Ag Nanoparticle Assemblies during Compression and Release



d_{111}

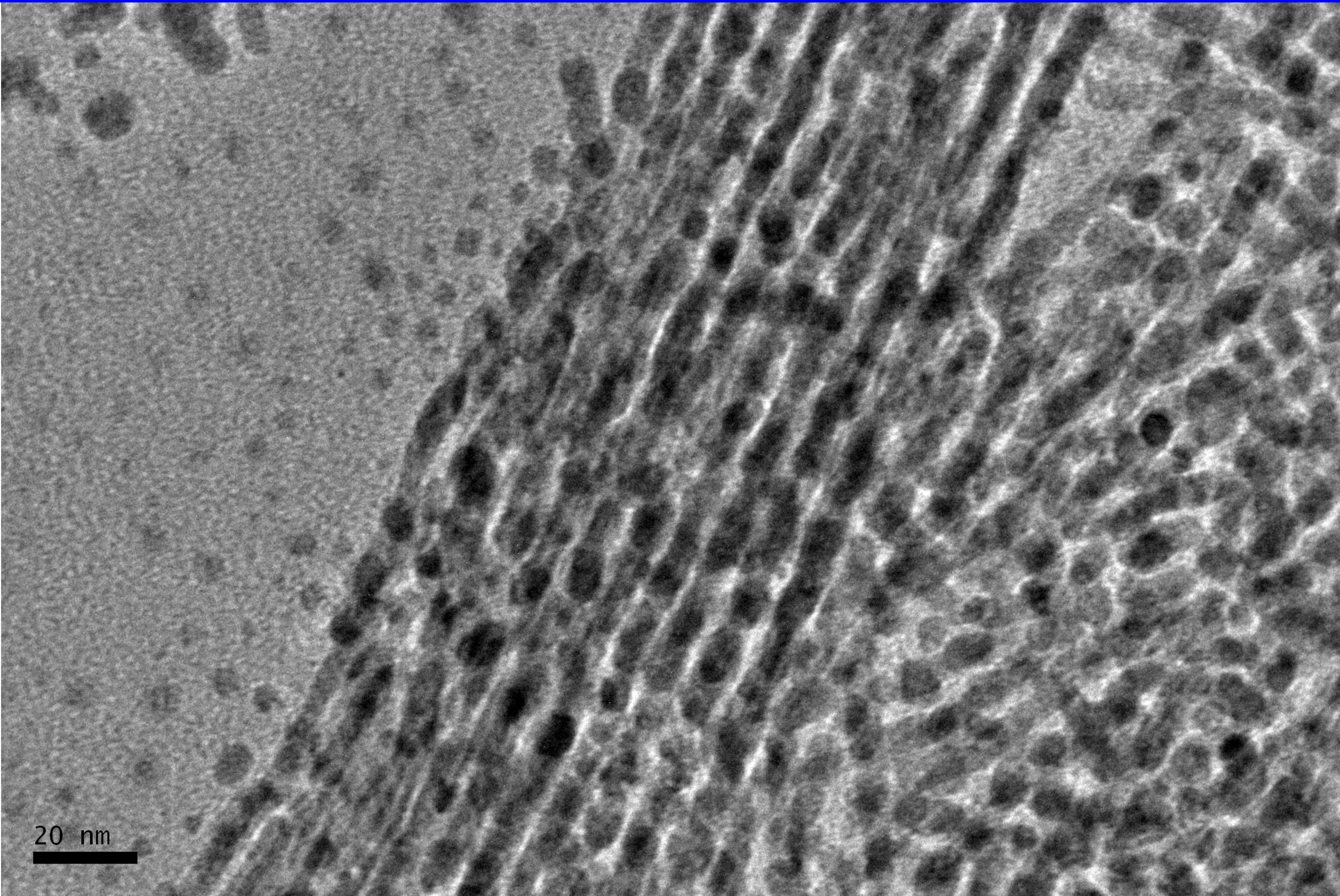


d_{311}/d_{111}

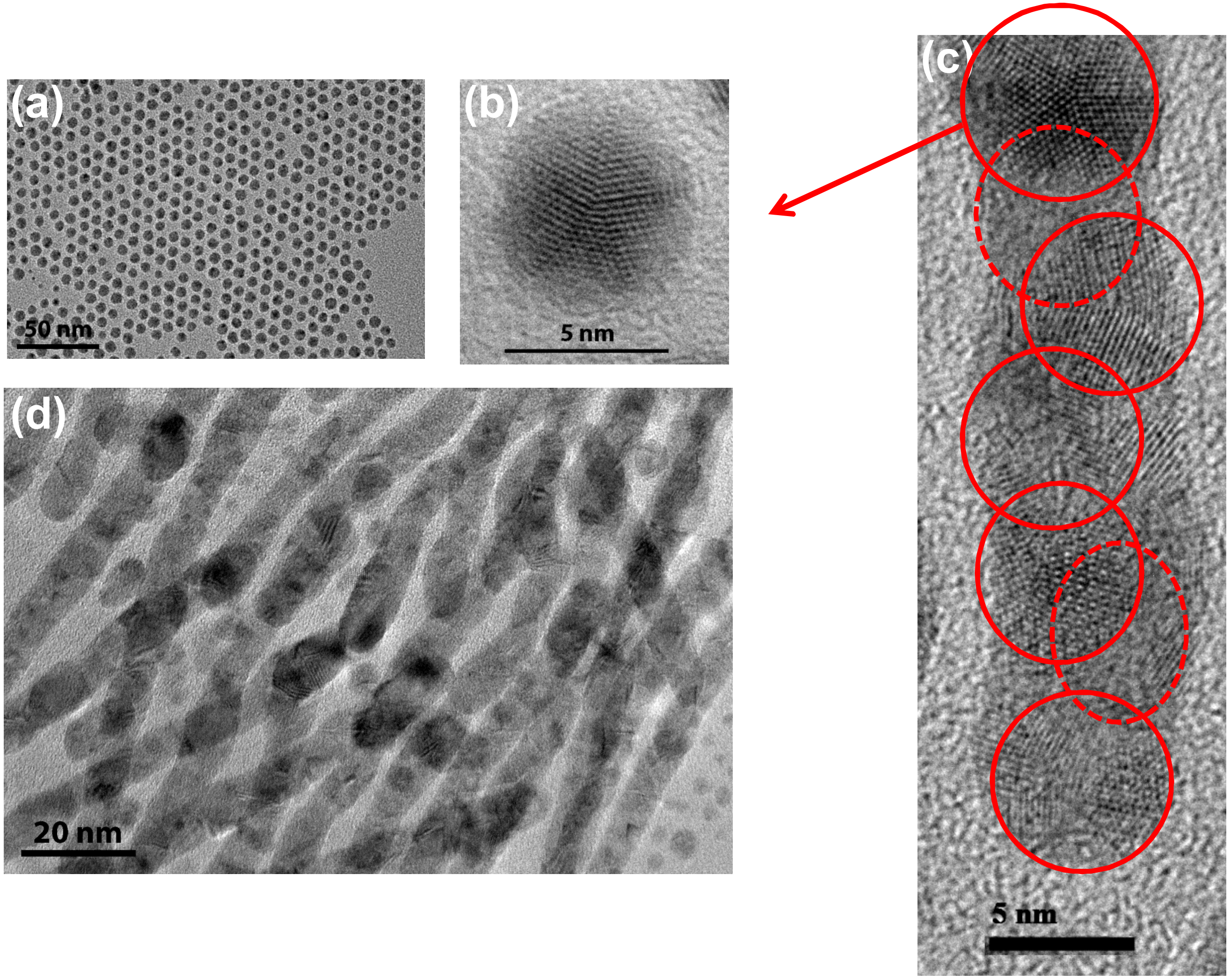
Li, W. et al., *Nano Lett.* 2014, 14, 4951−4958.

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

1D Ag Nanowires



Oriented Consolidation and Formation of Ag Nanowires

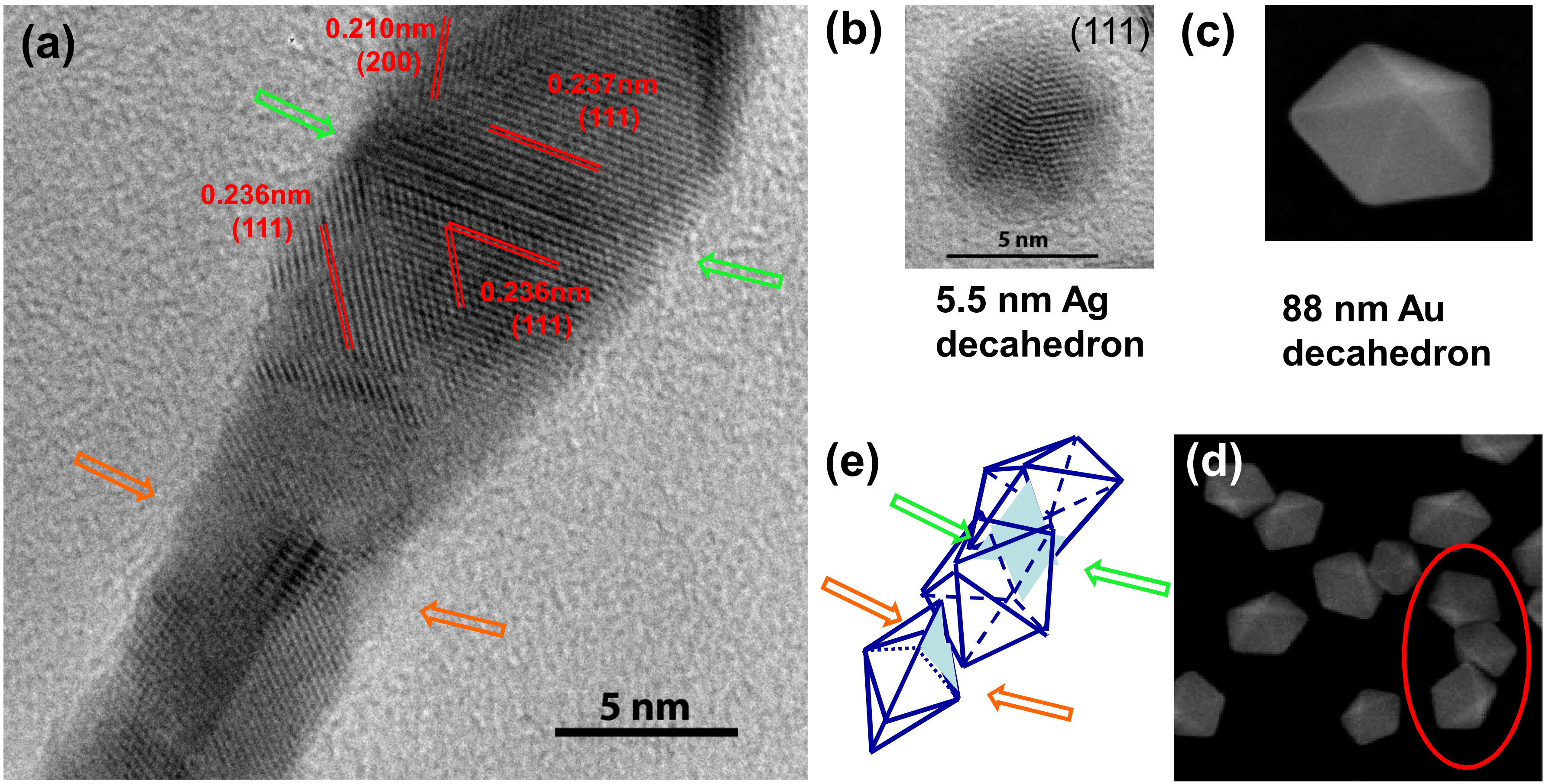


Wang, et al. *J. Am. Chem. Soc*. 2011, 133, 14484–14487.

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

Oriented Consolidation and Formation of Ag Nanowires

Ag nanoparticles connect together through (111) planes to (111) planes since (111) is the major plane on surface of decahedron-shaped Ag nanoparticles.

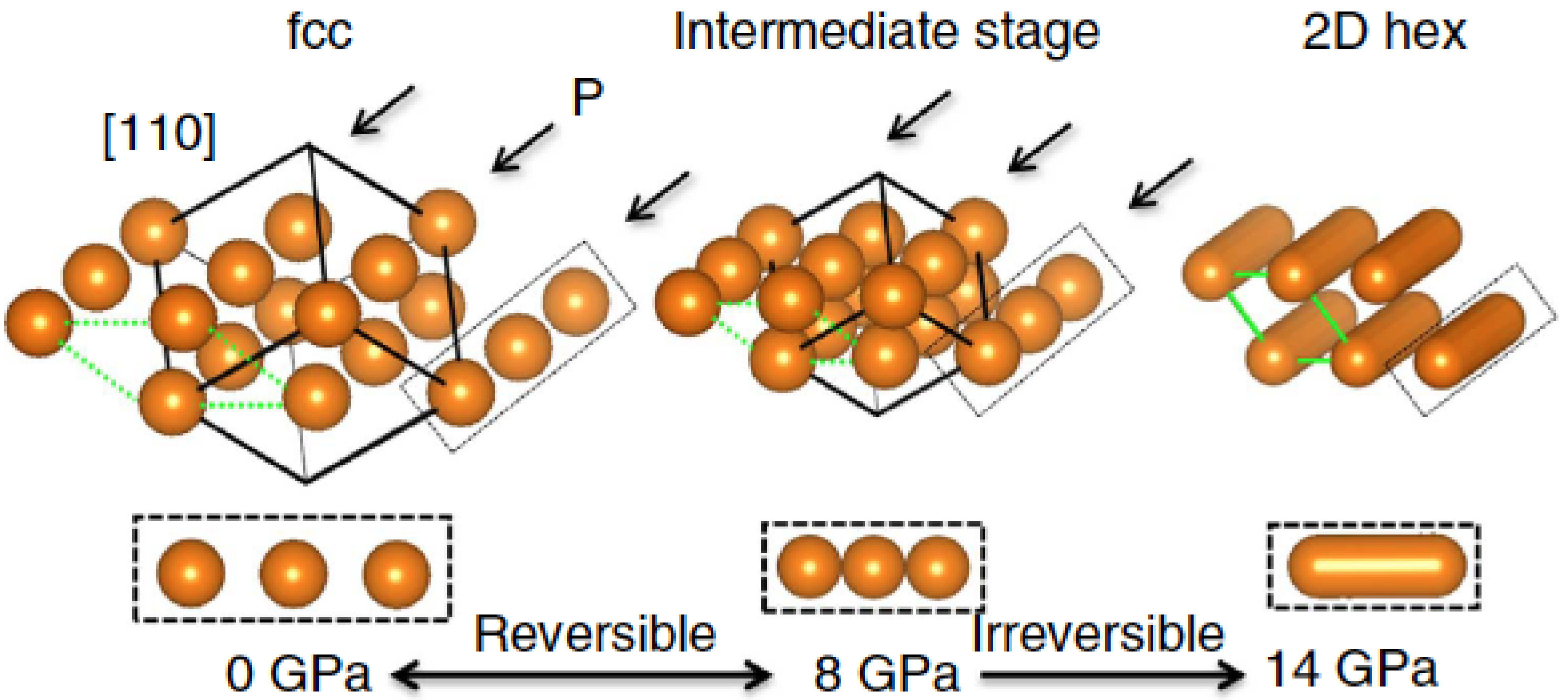


Song, H. *et al.*, *J. Phys. Chem. C,* 112, 2469-2475, 2008.

Wang, et al. *J. Am. Chem. Soc.* 2011, 133, 14484–14487.

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

Stress-Induced Assembly and Consolidation of Nanoparticle Superlattices



Li, W. et al., *Nano Lett.* 2014, 14, 4951−4958

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

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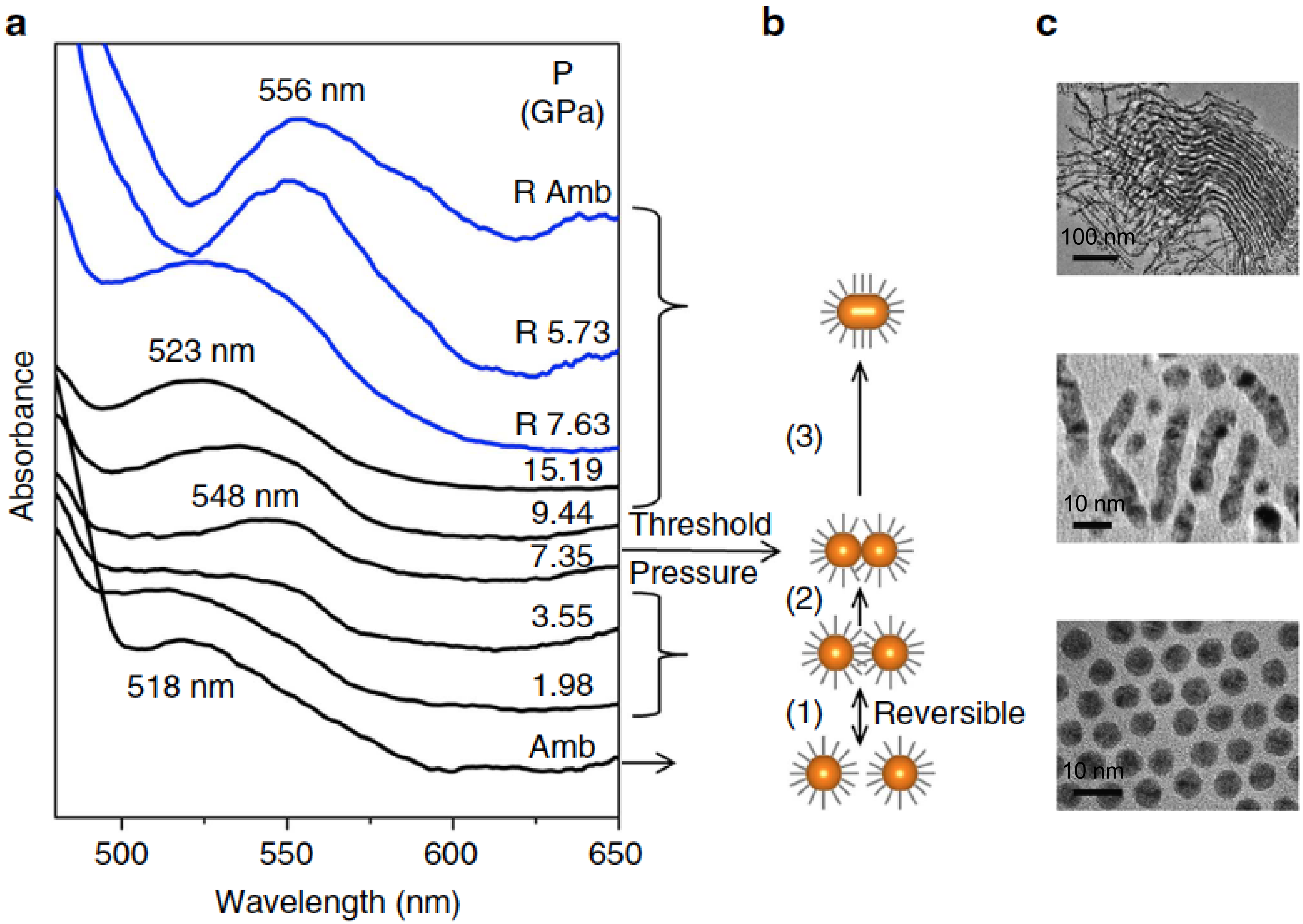
Pressure-Tuned Nanoparticle Interactions and Coupling

Structure - optical property correlation of Ag nanoparticle arrays

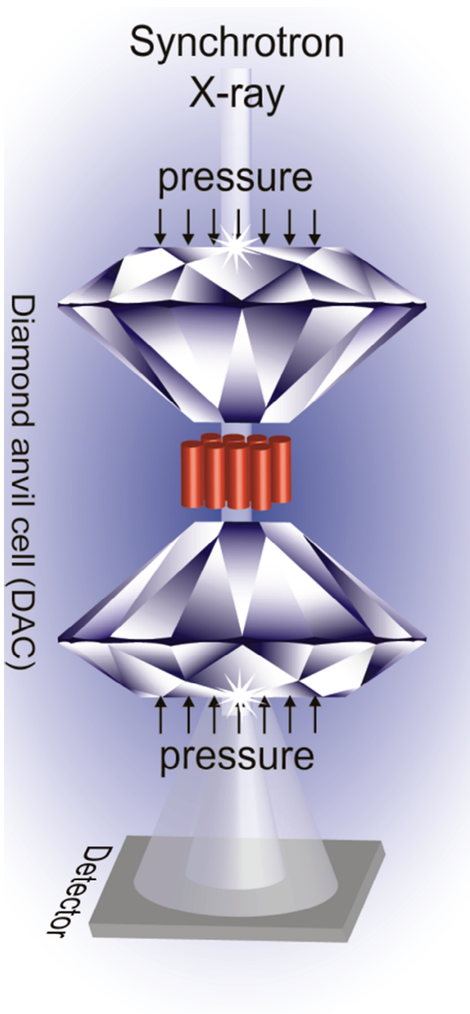


Adv. Mater. 2016, 28, 1989–1993.

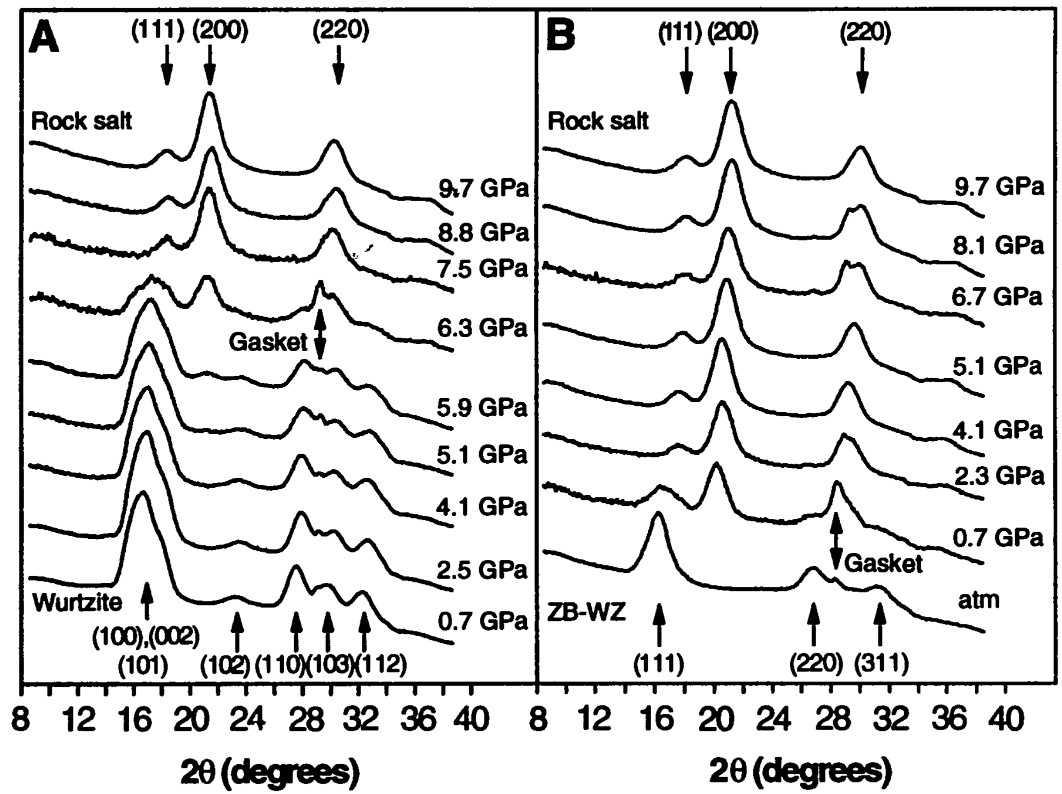
Li, B.; Fan H., *et al.*, *Nat.Commun.* 5:4179 doi: 10.1038/ncomms5179 (2014).

Semiconductor Nanoparticles (CdSe) under Pressure

Previous studies were focused on structural transformation in atomic lattice of CdSe nanoparticles and associated optical property changes under pressure.



Wurtzite → Rock salt → Zinc Blende



Tolbert S.H., Alivisatos A.P., *Science,* 265: 373-376, 1994
& *J. Chem. Phys.* 102: 4642-56, 1995.

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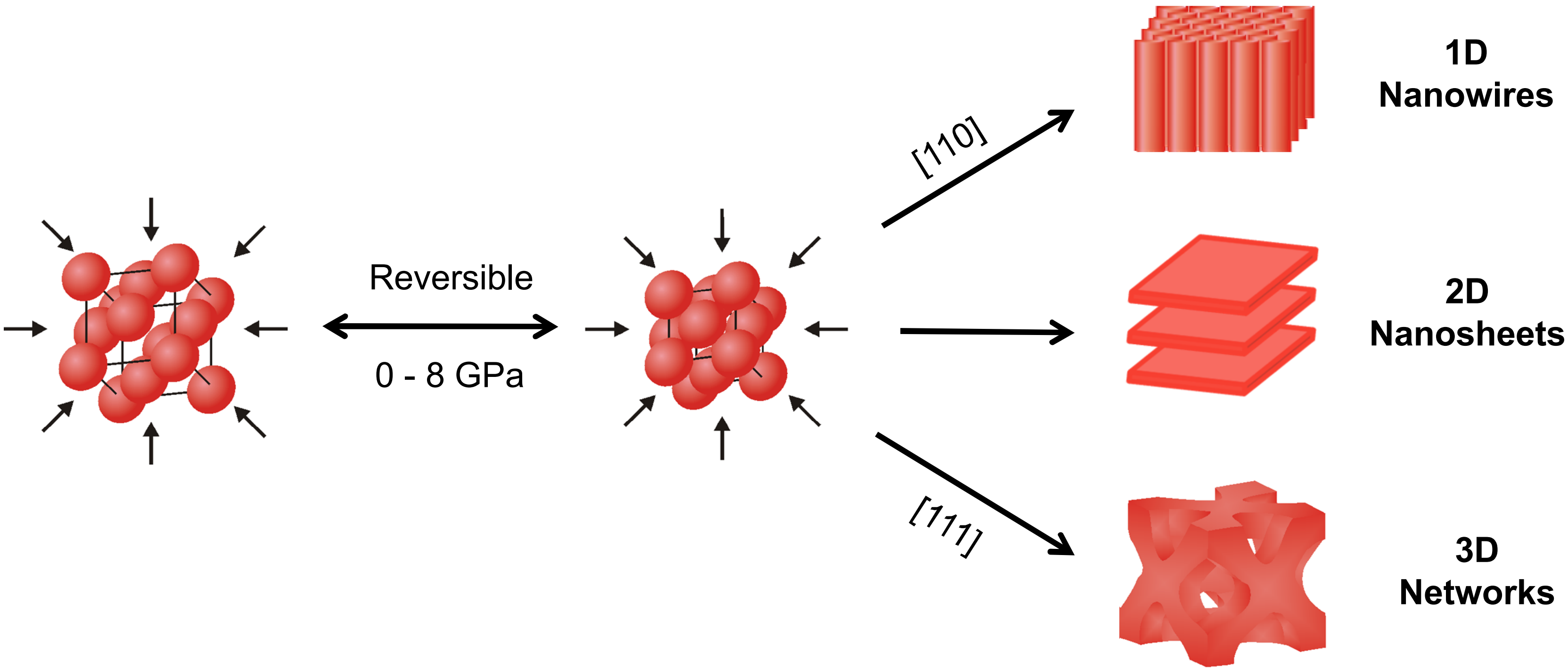
Semiconductor Nanoparticles (CdSe) under Pressure

Our studies were focused on structural transformation in CdSe nanoparticle mesophase and fabrication of new nanostructures under pressure.



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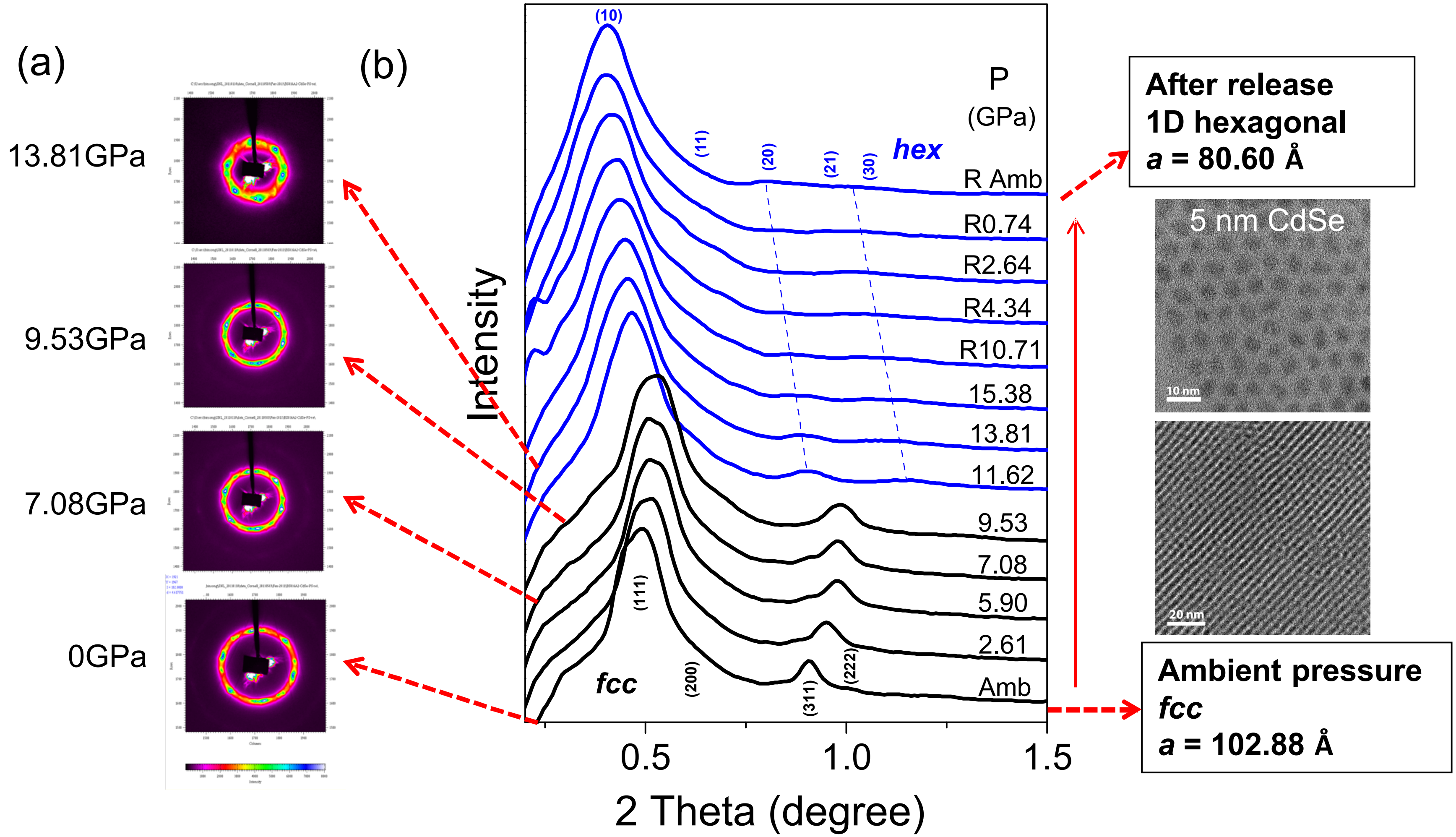
Li, B. et al. *Nat. Commun*. 8, 14778 doi: 10.1038/ncomms14778 (2017).

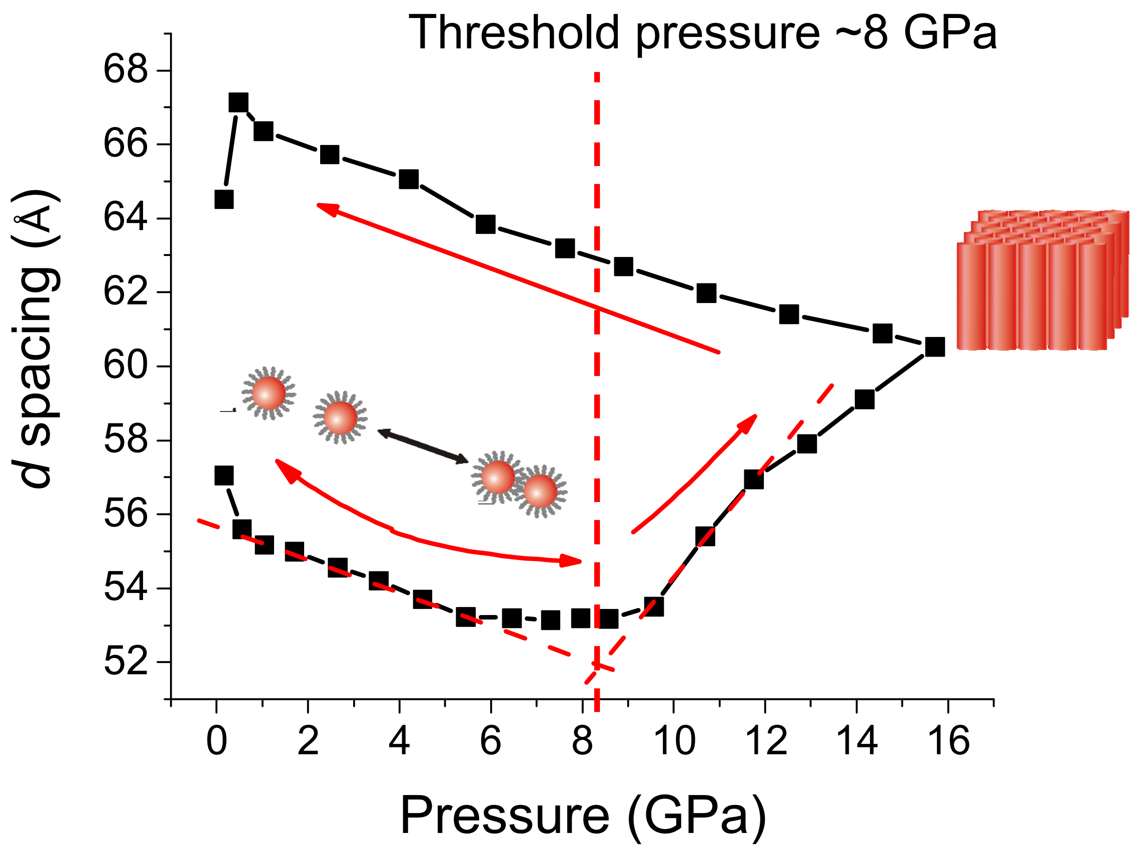
Structural Evolution of Ordered, Self-assembled CdSe Nanoparticle Arrays under Pressure

5 nm CdSe nanoparticles coated with Octadecylphosphonic acid (ODPA), Trioctylphosphonic oxide (TOPO)



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

Tunable Interparticle Spacing in CdSe Arrays during Compression and Release



Graph shows the *d*-spacing of the first Bragg reflection in each HP-SAXS spectrum.

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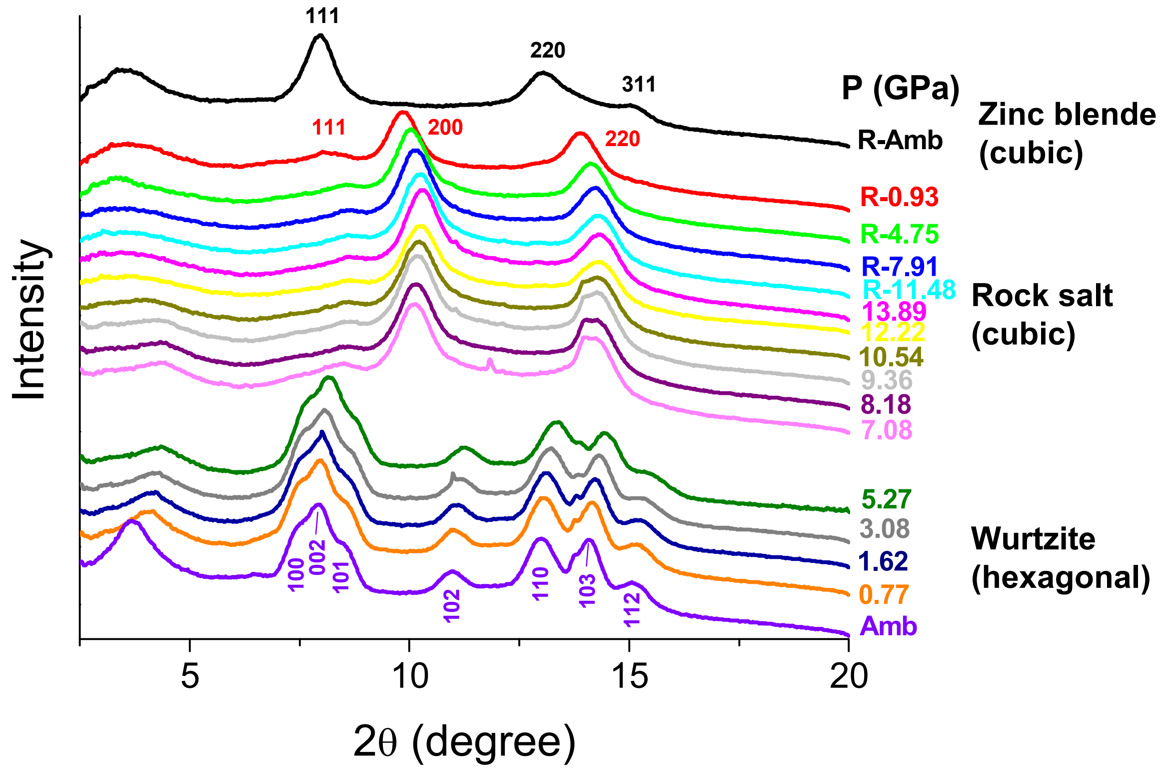
B. Li, K. Bian, et al, *Science Advances* 3, e1602916 (2017).

Atomic Lattice Phase Transition of CdSe Nanoparticles during Compression and Release



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

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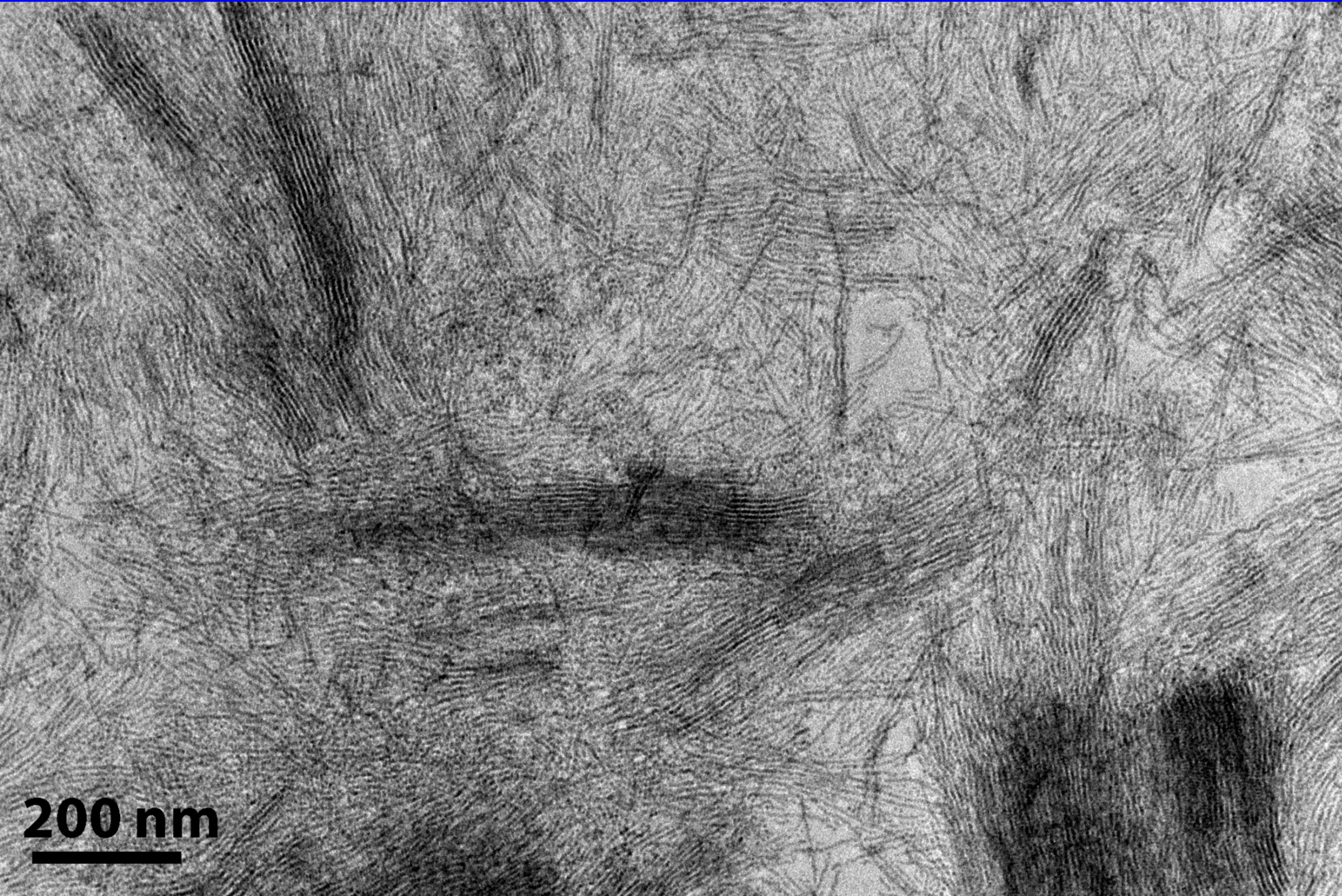
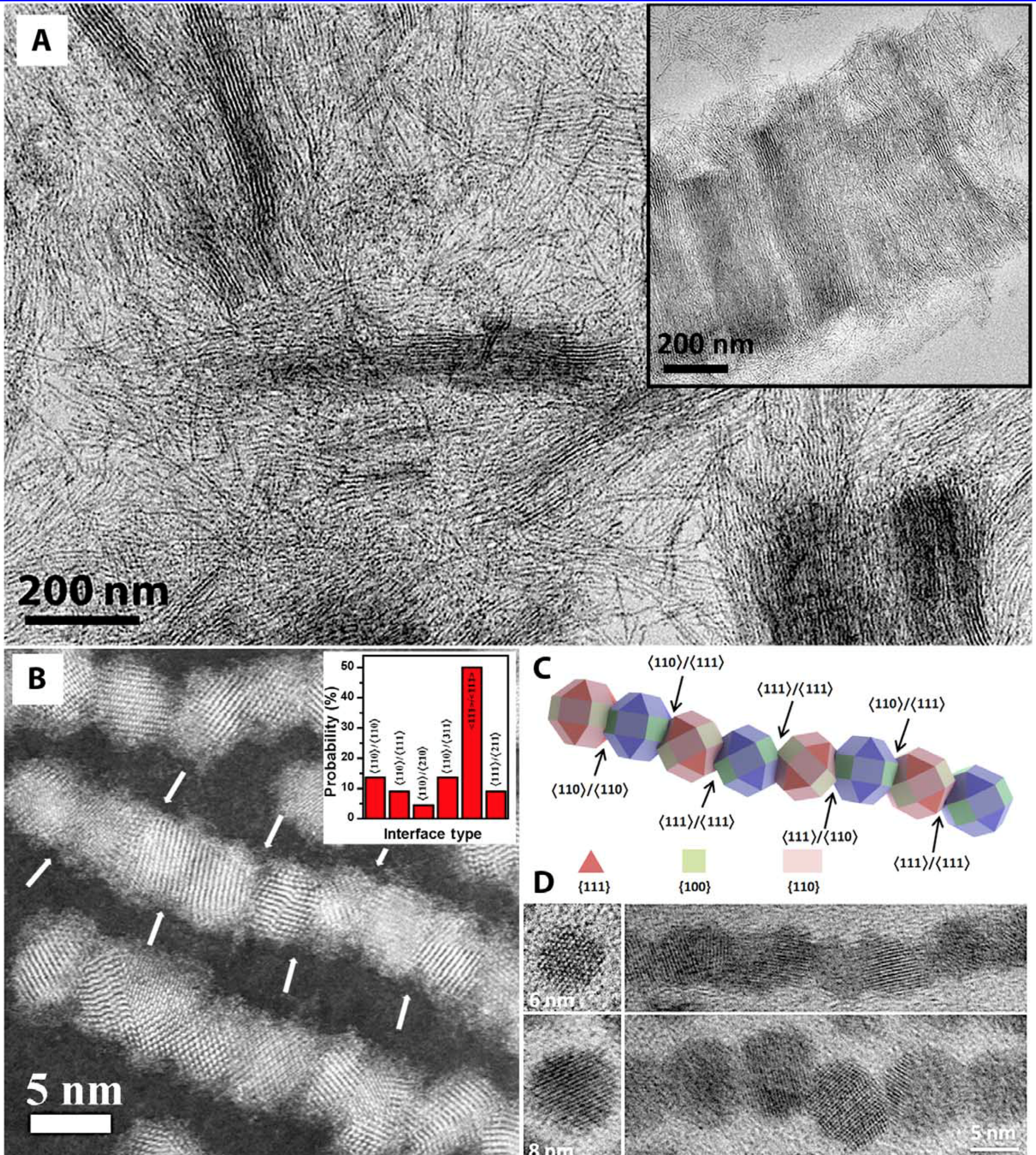
Transmission Electron Microscopy Image of CdSe Nanowires



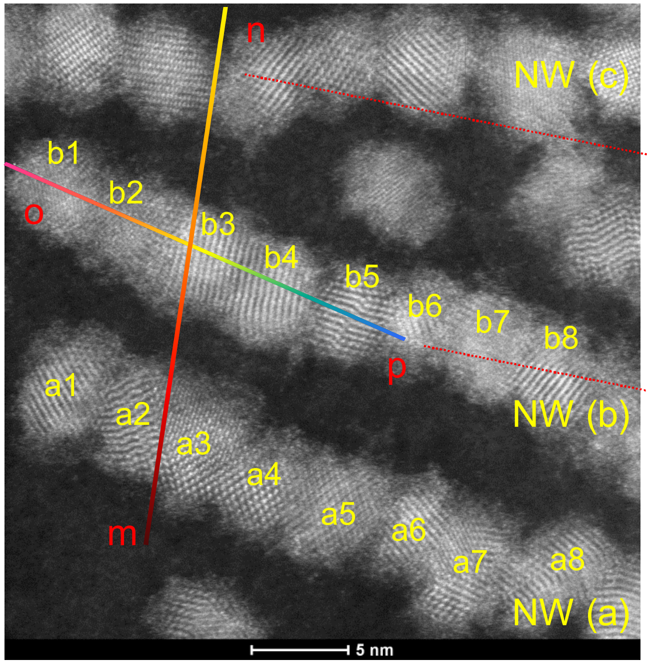
Transmission Electron Microscopy Image of CdSe Nanowires



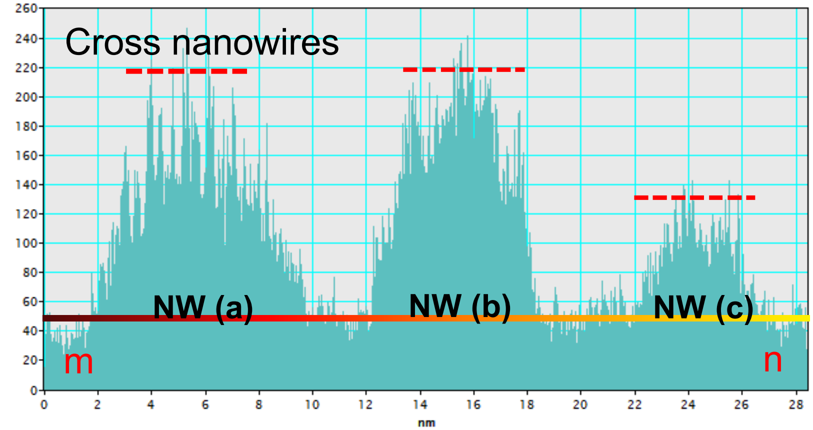
B. Li, K. Bian, et al,
Science Advances
3, e1602916 (2017).

Scanning Transmission Electron Microscopy Image of CdSe Nanowires

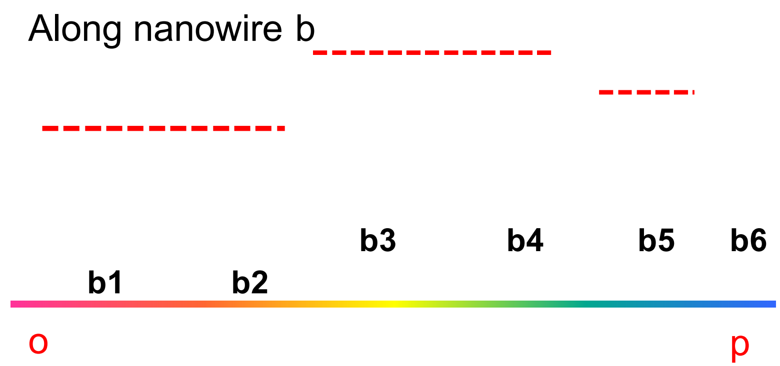
STEM image



TEM by Dr. Ping Lu



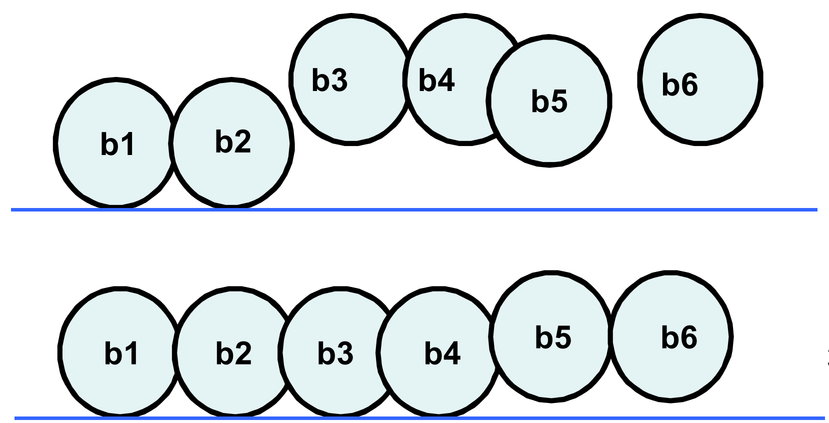
Height profile



Nanowire (b)

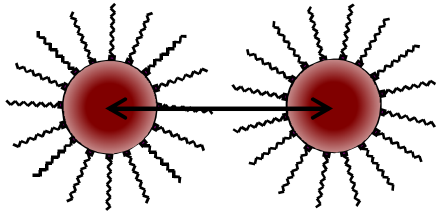
Side view

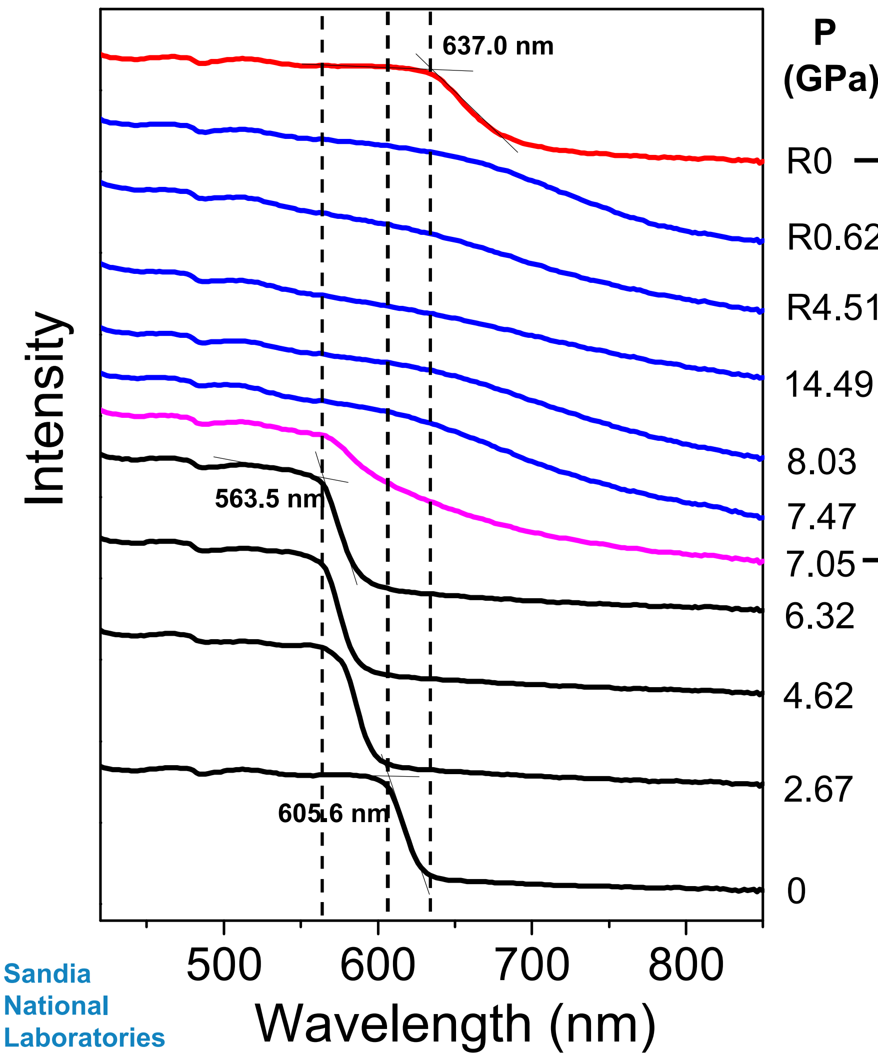
Top view

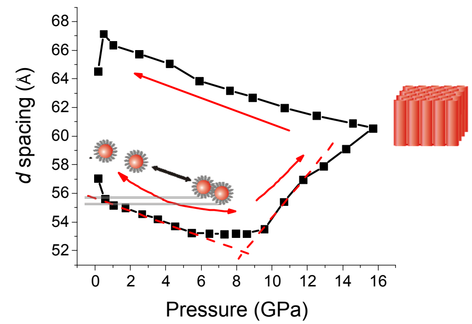


B. Li, K. Bian, et al, *Science Advances* 3, e1602916 (2017).

Stress Induced CdSe Nanoparticles Interactions







Absorption peak became sharper and stronger. Absorption peak shows 31 nm red shift (from 605.6 nm to 637.0 nm).

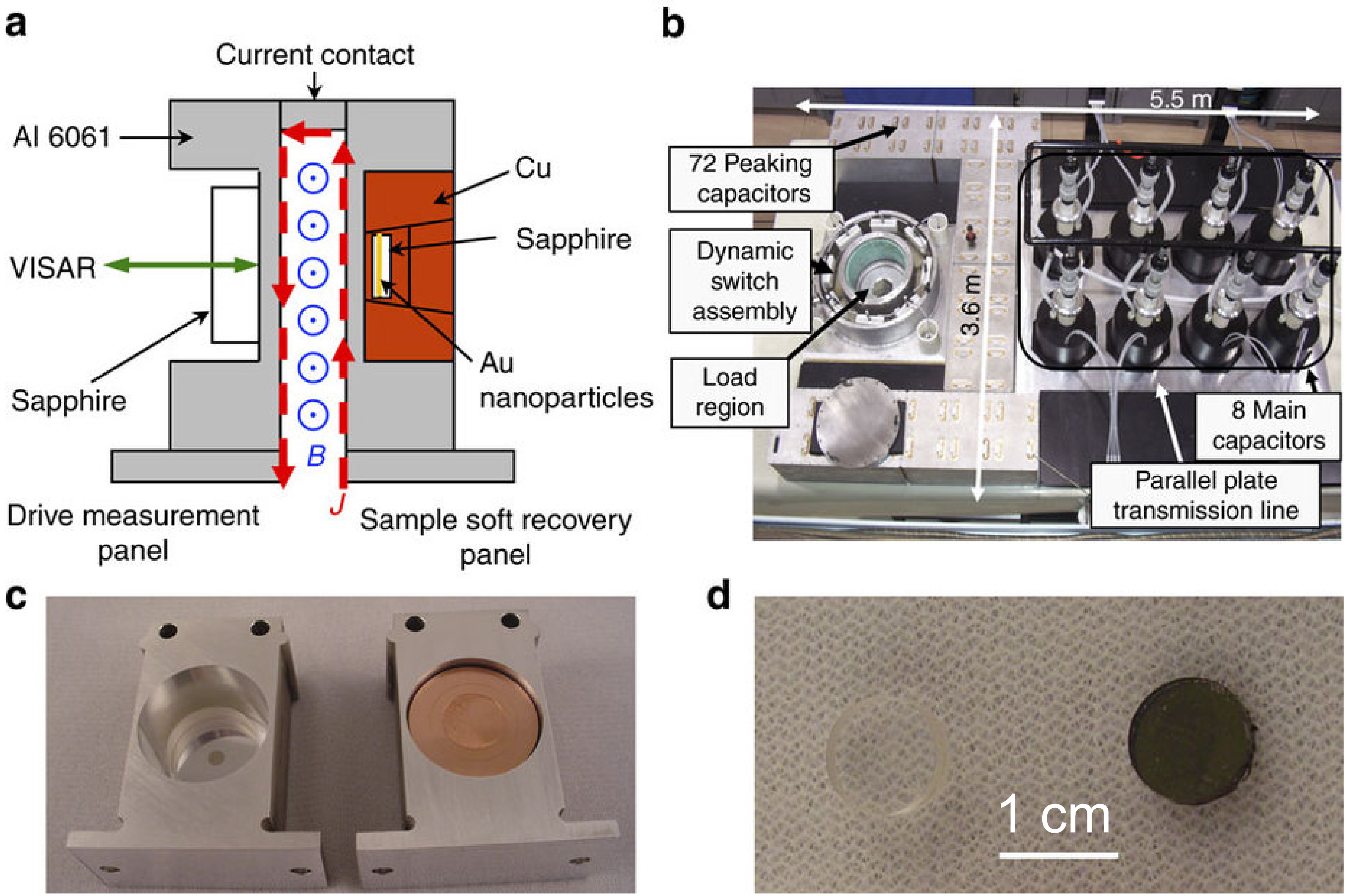
Absorption peak further extends to longer wavelength (up to about 800 nm), indicating nanowires formation.

Absorption peak starts to extend to longer wavelength at around 7 GPa, indicating the nanoparticles become consolidated.

Absorption peak blue shifts due to nanoparticle aggregation under pressure. The peak blue-shifts until pressure reaches to 4.62GPa, then remains almost no change until 6.32GPa, indicating the nanoparticles become very close or start to contact at ~ 4.62GPa.

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

Ultrafast assembly and synthesis of gold nanostructures using nanosecond compression via pulsed power



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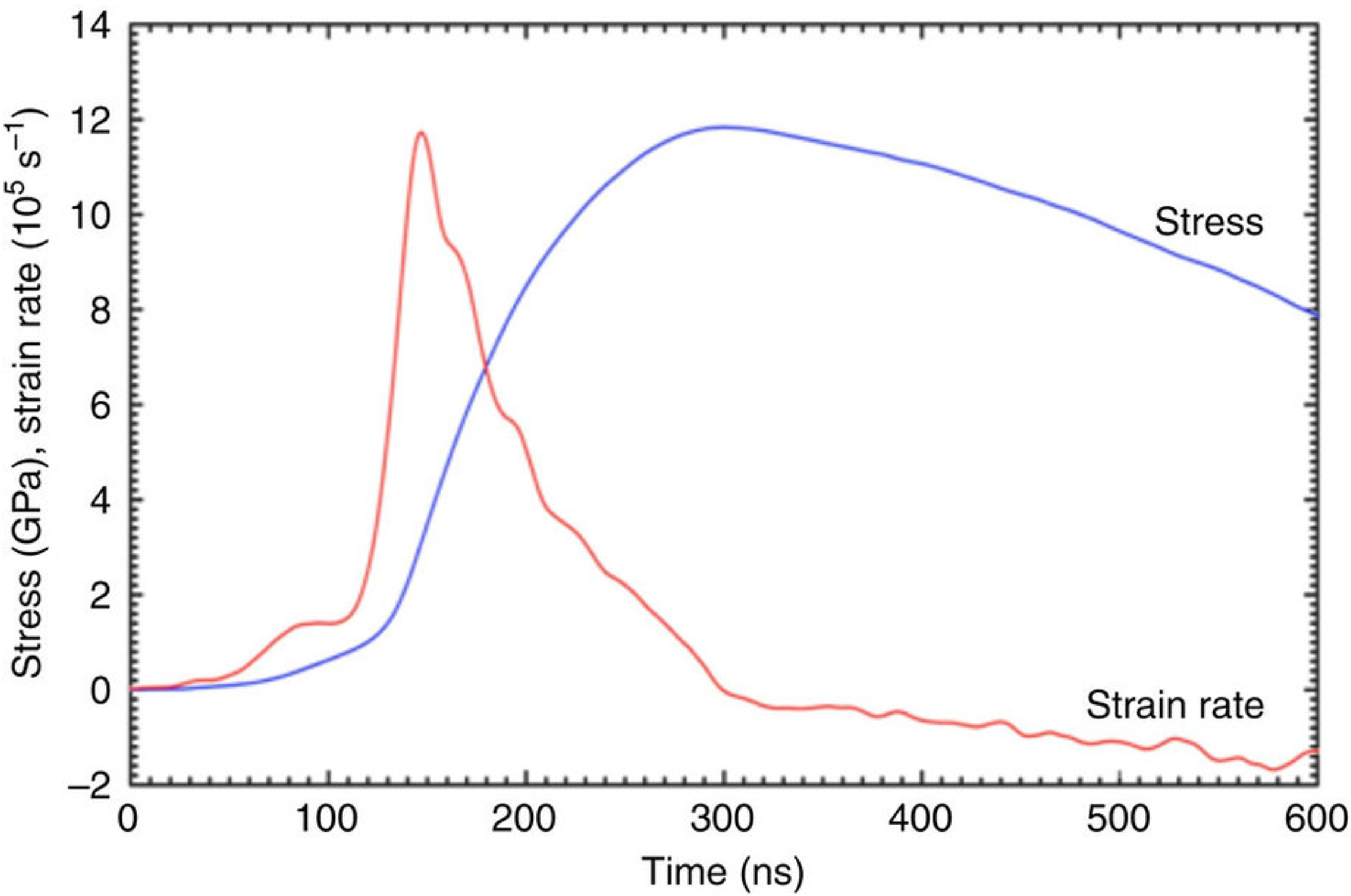
Li, B. et al. *Nat. Commun*. 8, 14778 doi: 10.1038/ncomms14778 (2017).

Ultrafast assembly and synthesis of gold nanostructures using nanosecond compression via pulsed power



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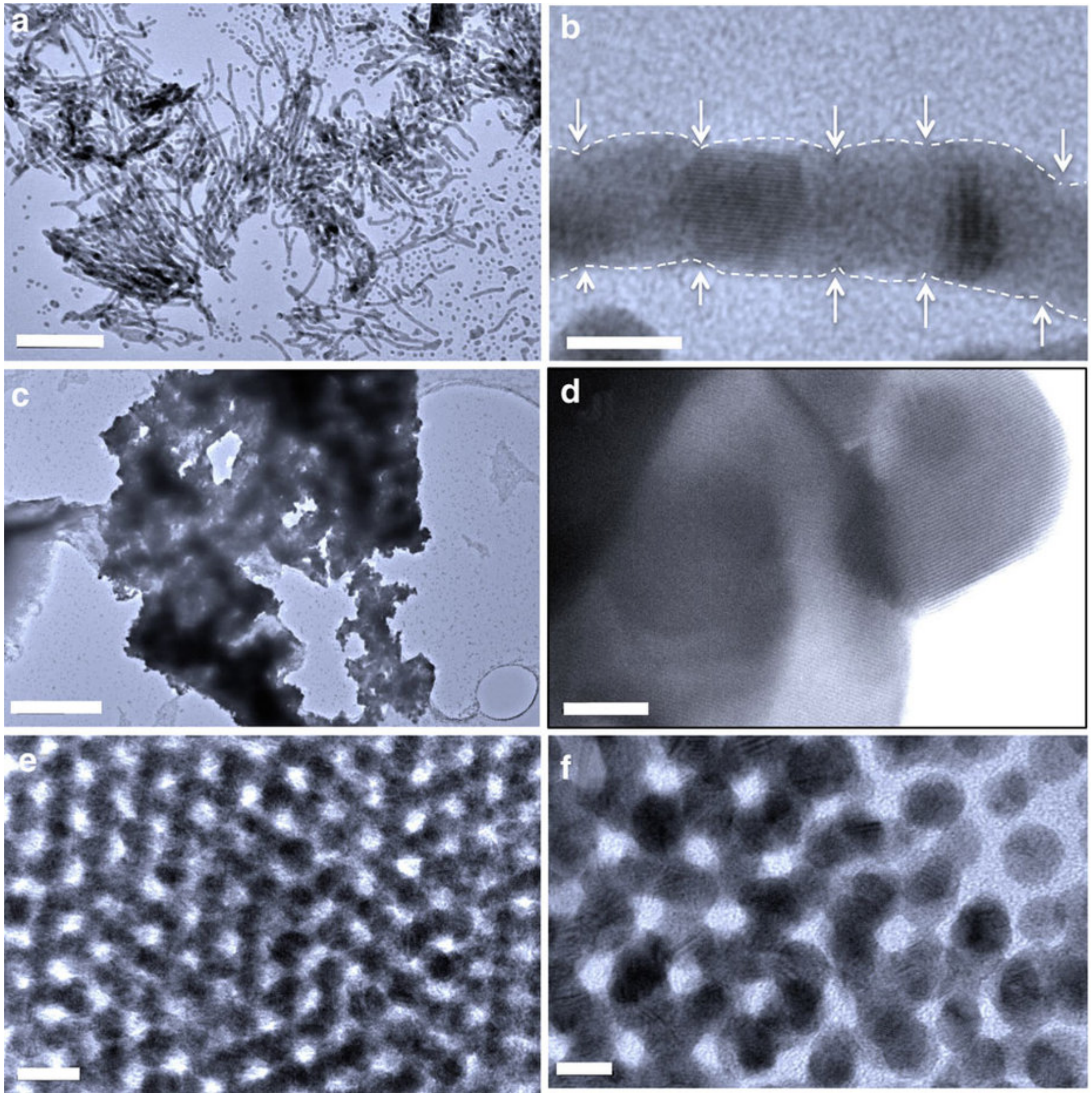
Li, B. et al. *Nat. Commun*. 8, 14778 doi: 10.1038/ncomms14778 (2017).

Ultrafast assembly and synthesis of gold nanostructures using nanosecond compression via pulsed power



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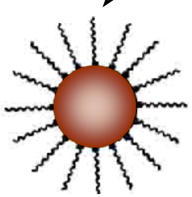
Li, B. et al. *Nat. Commun*. 8, 14778 doi: 10.1038/ncomms14778 (2017).

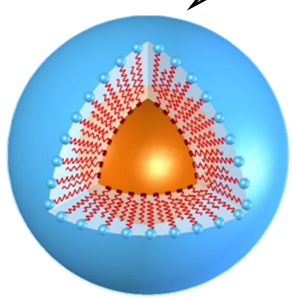
Summary: Self-Assembly to Functionalize Nanoparticles and to Fabricate Robust, Ordered Nanoparticle Films

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.



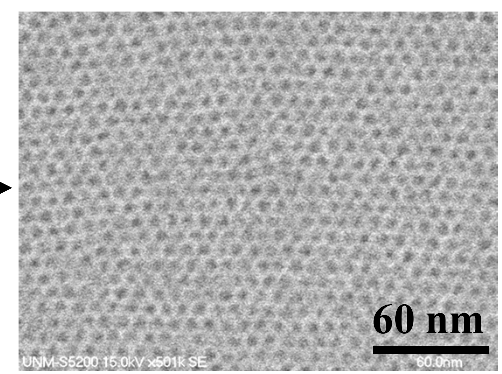
1, surfactant
2, lipid,
3, block copolymer



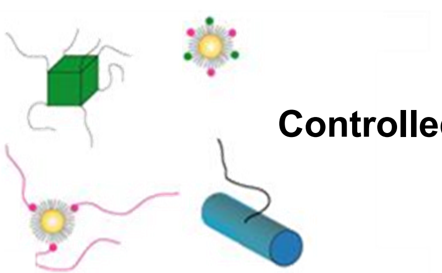
Water-Soluble & Biocompatible Building Block

Engineering Process
- -Self-assembly
- -Directed-assembly
- -Interfacial-assembly
- -Rheological control
- more

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



Robust, self-assembled nanoparticle films



Controlled size and shape

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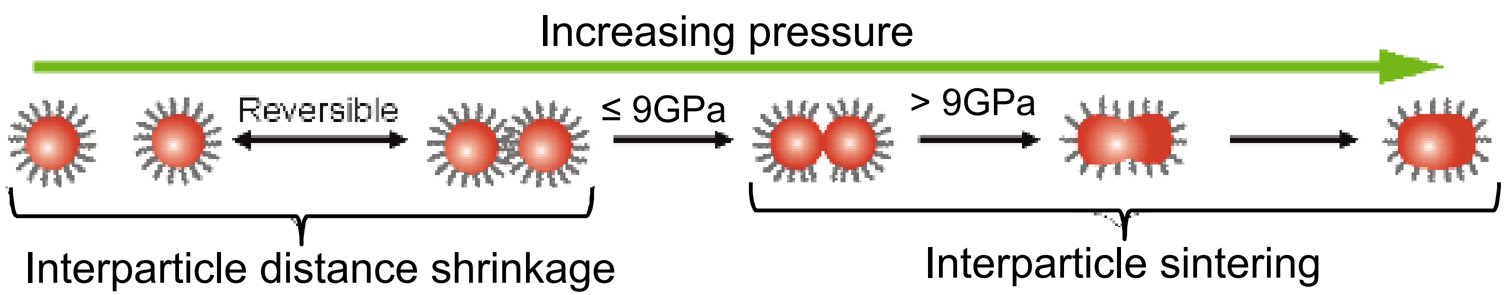
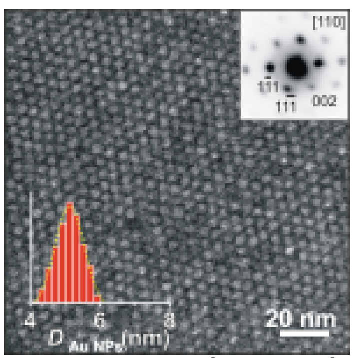
Summary: Pressure-Induced Nanoparticle Engineering

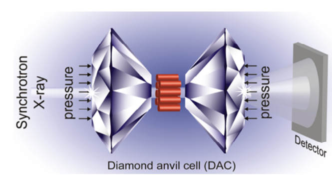
Pressure-Directed Assembly presents a paradigm shift in engineering nanoparticle arrays:

- 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.

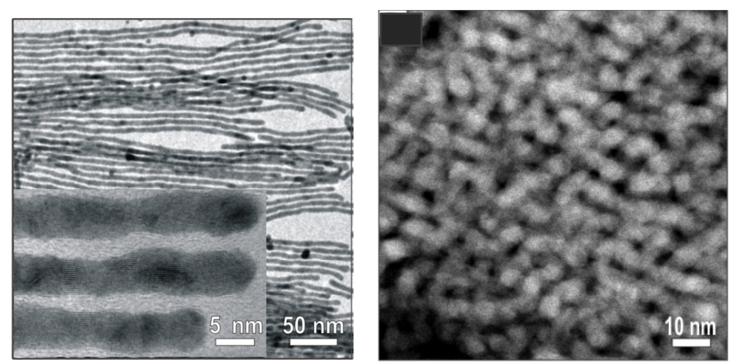




3D spherical Nanoparticle array (Before compression)



Pressure-Directed Assembly



1-3D nanostructures (After compression)

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Acknowledgements

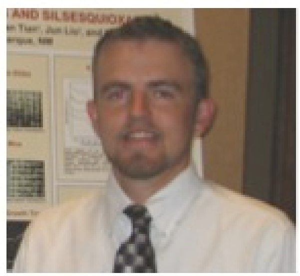
Dr. Zaicheng Sun
UNM postdoc

Dr. Feng Bai
UNM postdoc

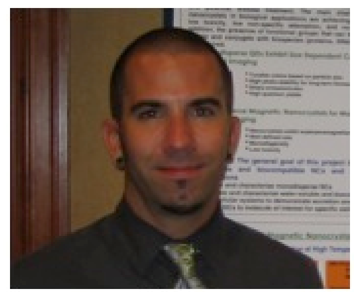
Dr. Huimeng Wu
SNL postdoc

Dr. Kaifu Bian
SNL Postdoc

Adrian Rodriguez
UNM student



Adam Wright
UNM student



Eric Leve
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