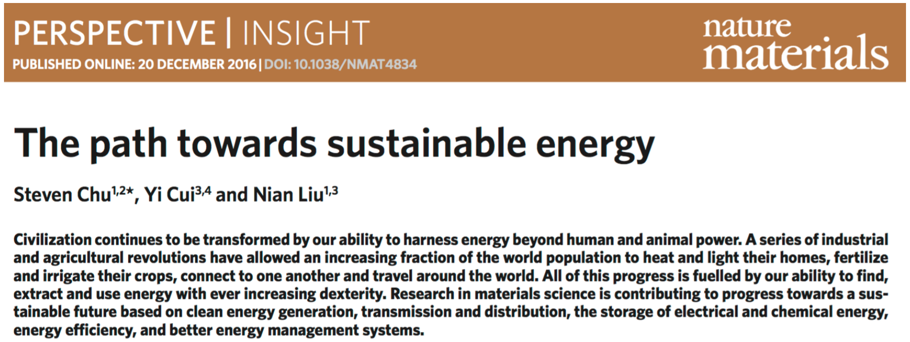
ChE 430
Colloidal synthesis of nanoparticles and their energy applications

MODULE 6: Surface Chemistry and Device Implementation

6.0. Intro and motivation
6.1 Impact of ligands on properties
6.2. Surface chemistry of nanocrystals
6.3. Deposition techniques
6.4. Nanocrystal assemblies

6.0. Introduction and motivation

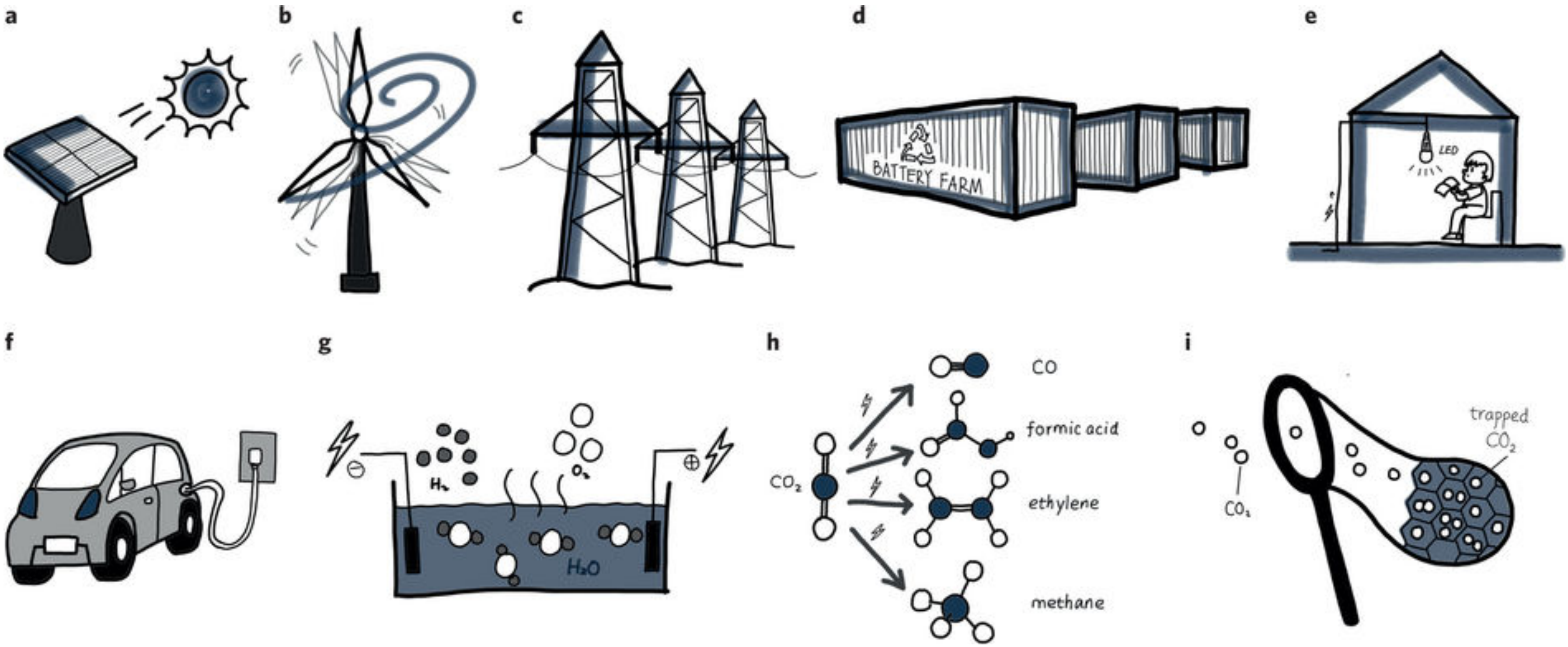


PERSPECTIVE | INSIGHT
nature materials

The path towards sustainable energy

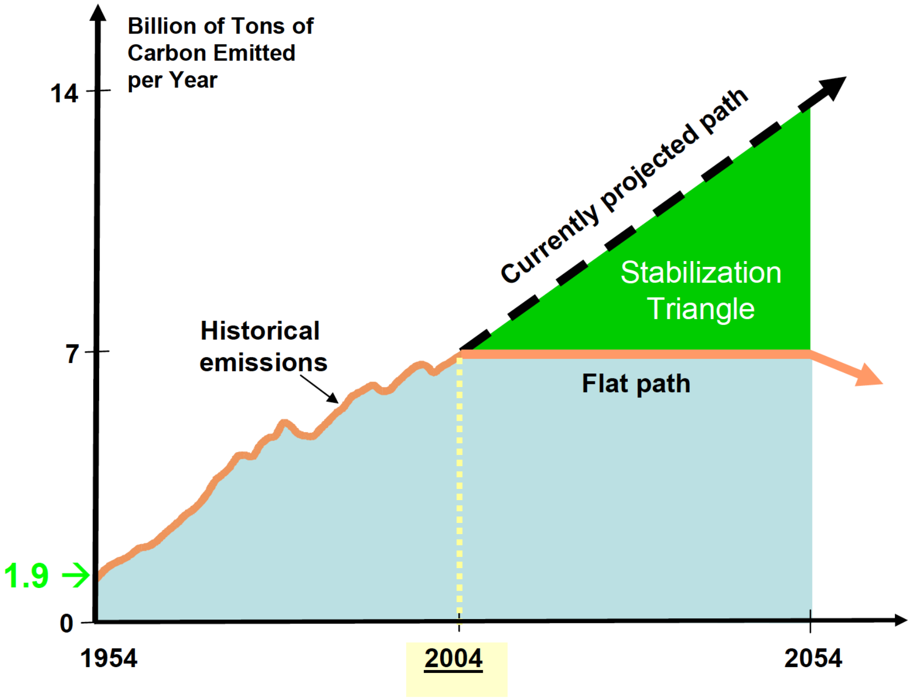
Steven Chu[1,2]*, Yi Cui[3,4] and Nian Liu[1,3]

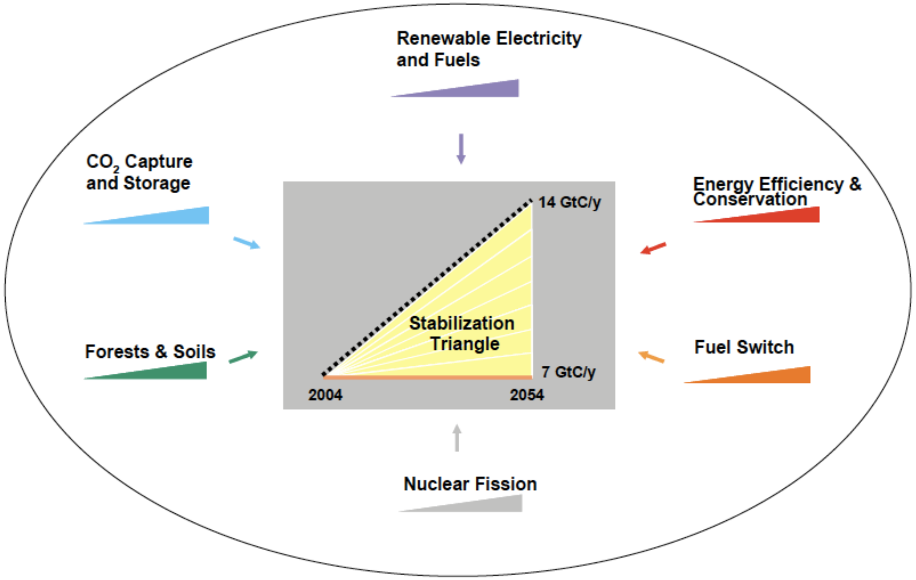
Civilization continues to be transformed by our ability to harness energy beyond human and animal power. A series of industrial and agricultural revolutions have allowed an increasing fraction of the world population to heat and light their homes, fertilize and irrigate their crops, connect to one another and travel around the world. All of this progress is fuelled by our ability to find, extract and use energy with ever increasing dexterity. Research in materials science is contributing to progress towards a sustainable future based on clean energy generation, transmission and distribution, the storage of electrical and chemical energy, energy efficiency, and better energy management systems.



6.0. Introduction and motivation

THE SEVEN WEDGES

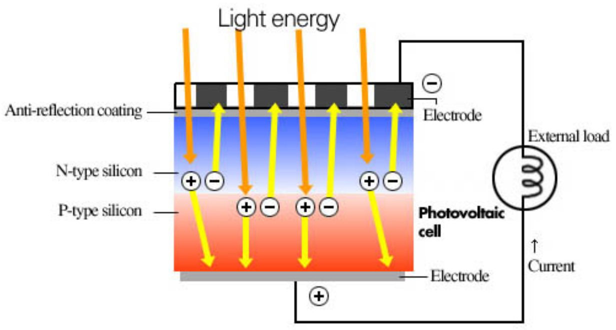


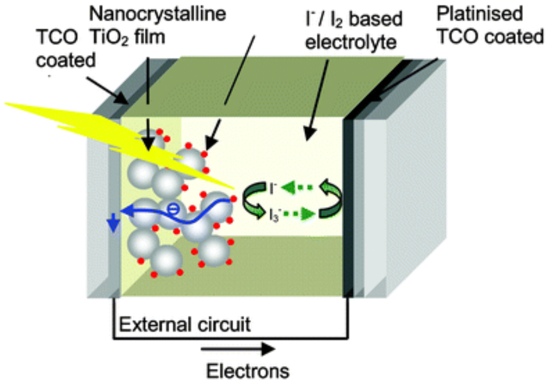


Robert Socolow, Princeton University

6.0. Introduction and motivation

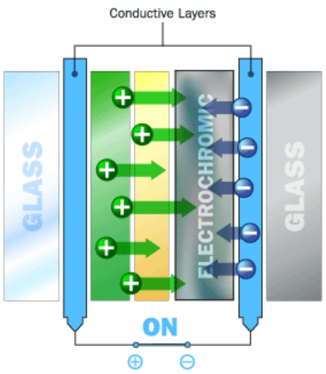
ENERGY CONVERSION





Solar Cells

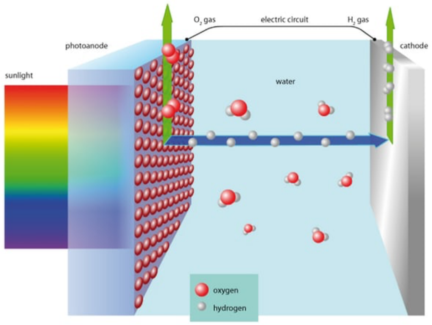
ENERGY SAVING



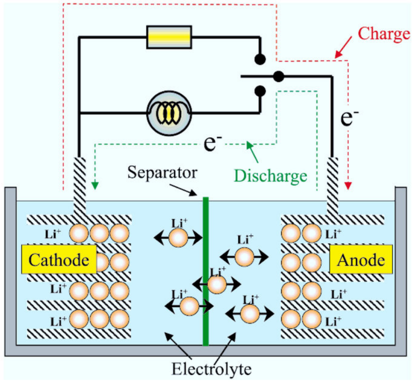
Electrochromic Windows

Briefly discussed in Module 5 but we will not go into the details

ENERGY STORAGE



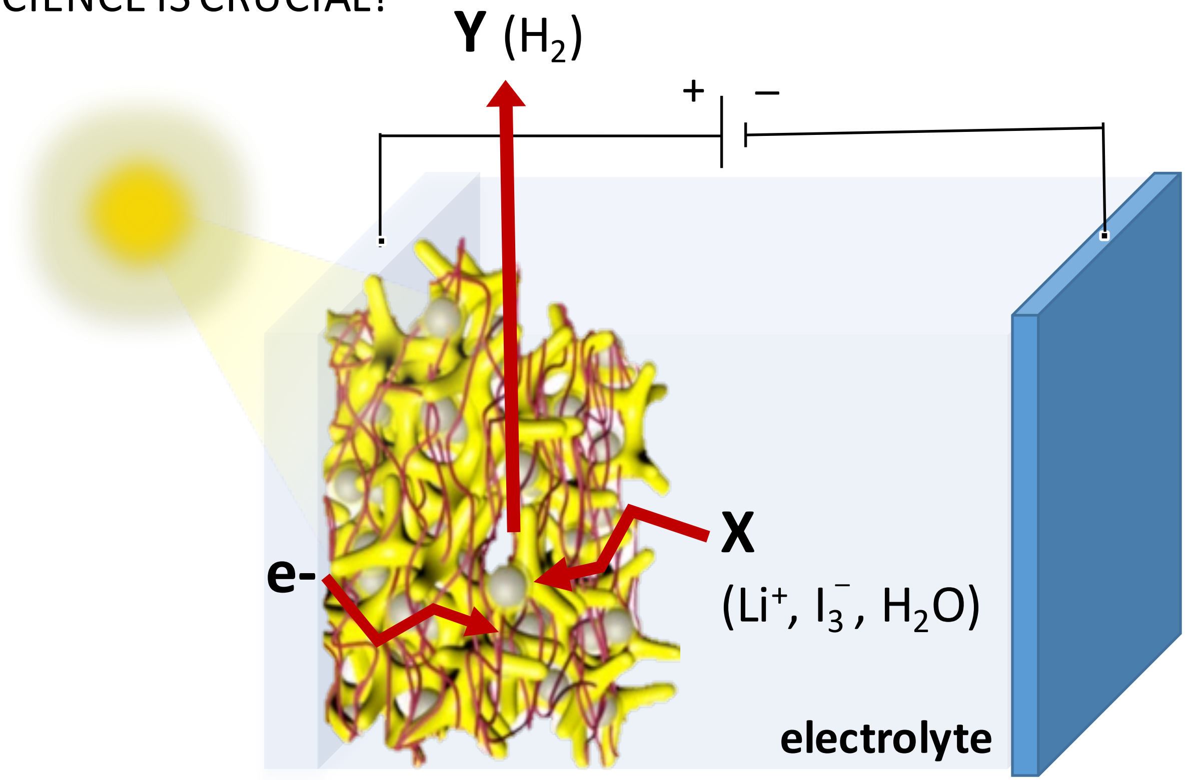
PEC cells/Electrolyzers



Batteries

6.0. Introduction and motivation

Many similarities among optoelectronic end electrochemical devices:
NANOSCIENCE IS CRUCIAL!



THE NEED:

Nanostructured *(to facilitate carrier and mass transport)* **composite** *(one single component cannot do it all!)* **materials, stable under operating conditions.**

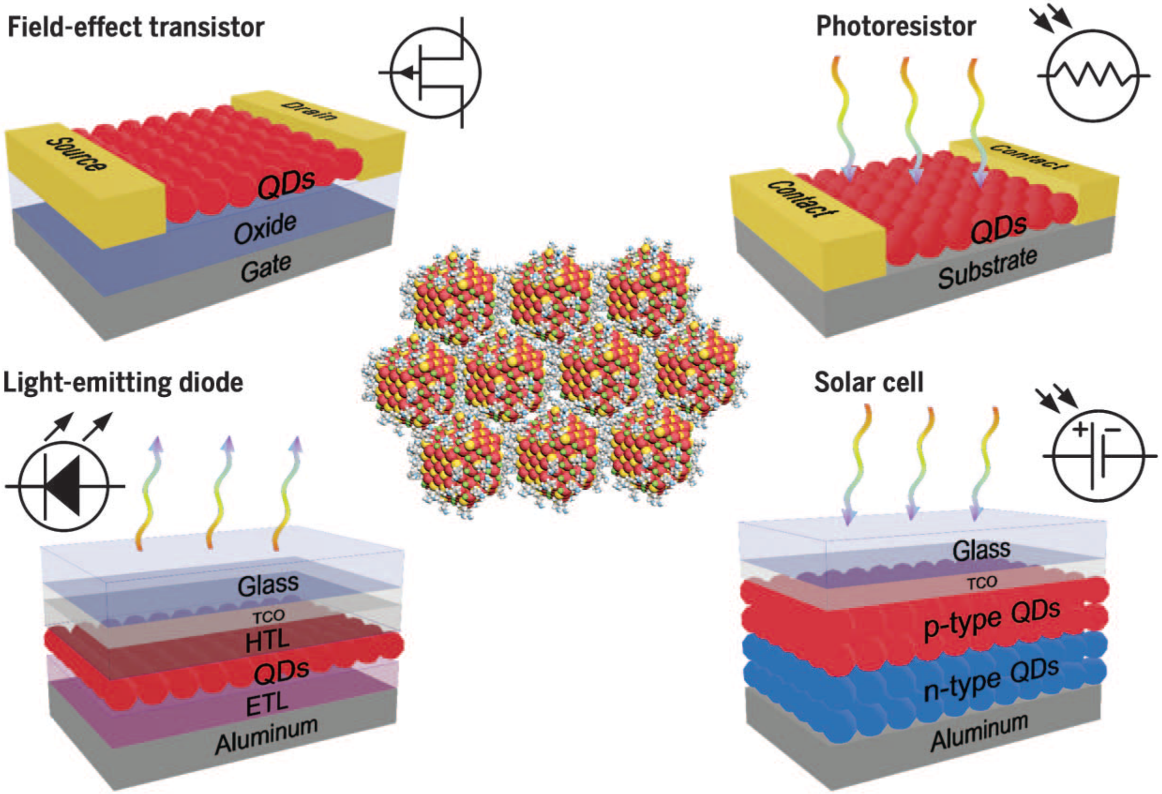
THE CHALLENGE:

To synthesize complex nanomaterials with tunable composition and morphology.

6.0. Introduction and motivation

Colloidal Nanocrystals:

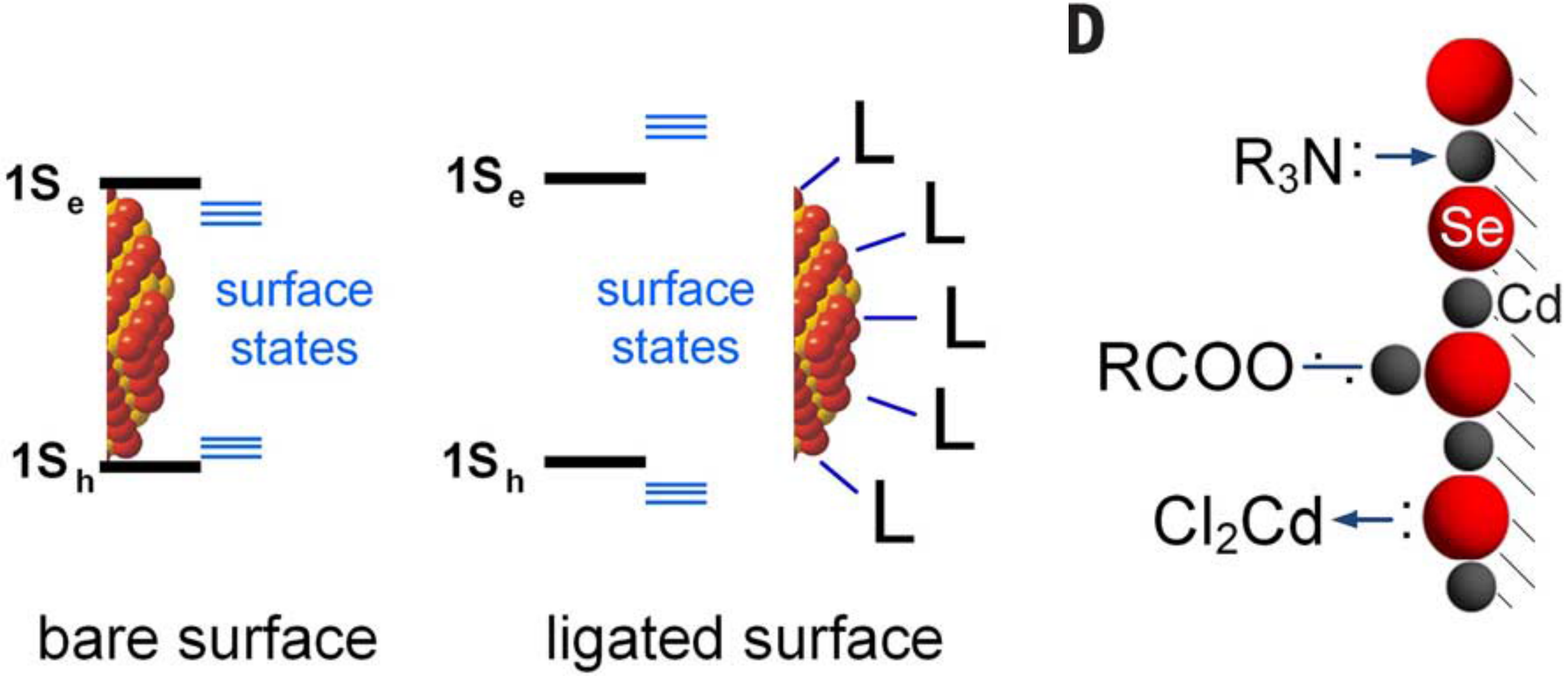
- Model Systems
- Practical Solutions
- Novel Concepts



Kagan, Liftshitz, Sargent, Talapin, *Science* (**2018**)

6.1. Impact of ligands on properties

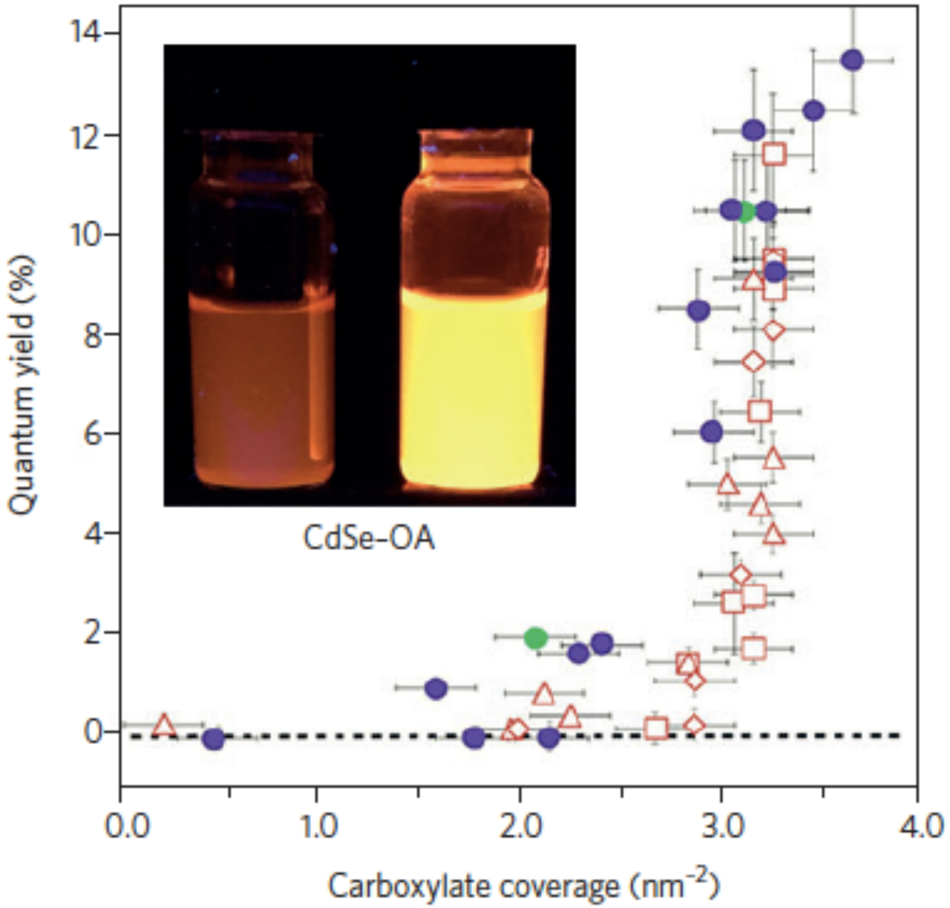
OPTICAL PROPERTIES



Kagan, Liftshitz, Sargent, Talapin, *Science* (**2017**)

6.1. Impact of ligands on properties

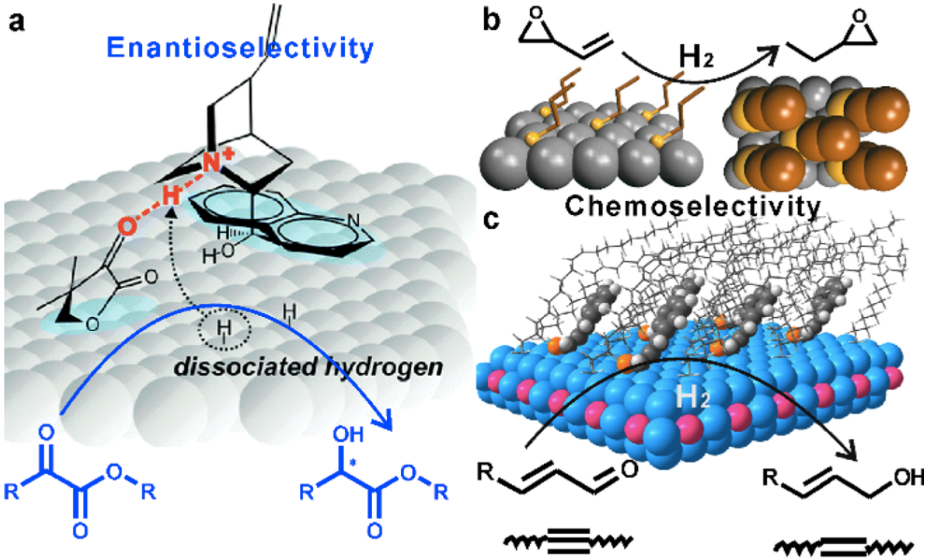
OPTICAL PROPERTIES

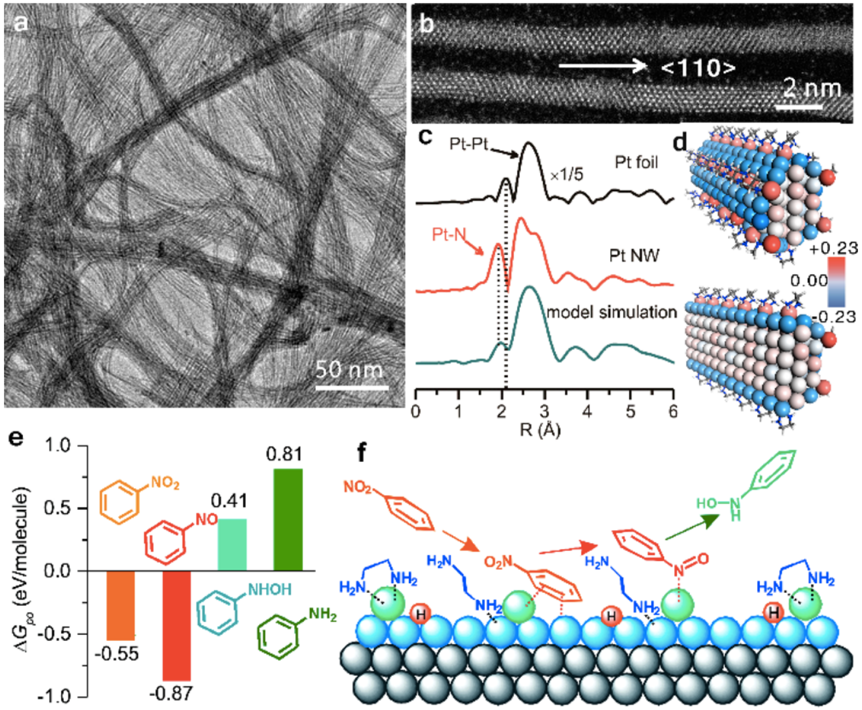


Talapin, *Nature Mater* (**2016**)

6.1. Impact of ligands on properties

CATALYTIC PROPERTIES

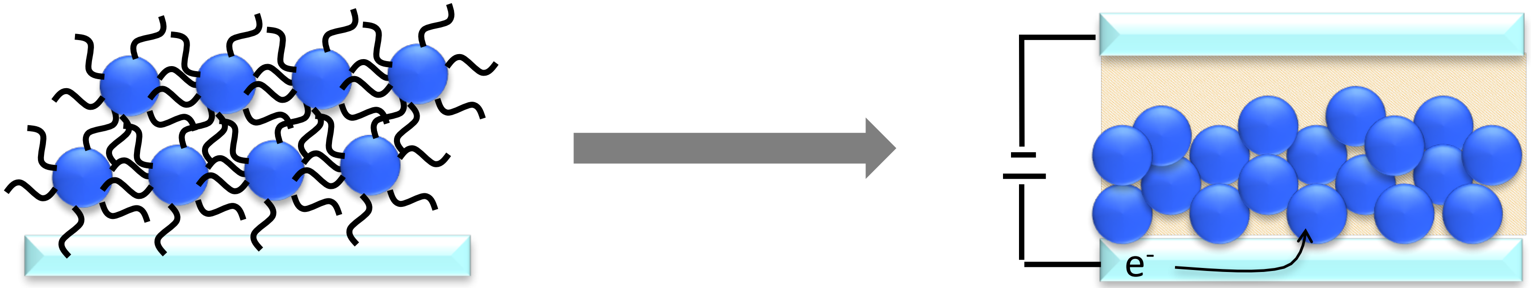




Zheng et al, *JACS* (**2017**)

6.1. Impact of ligands on properties

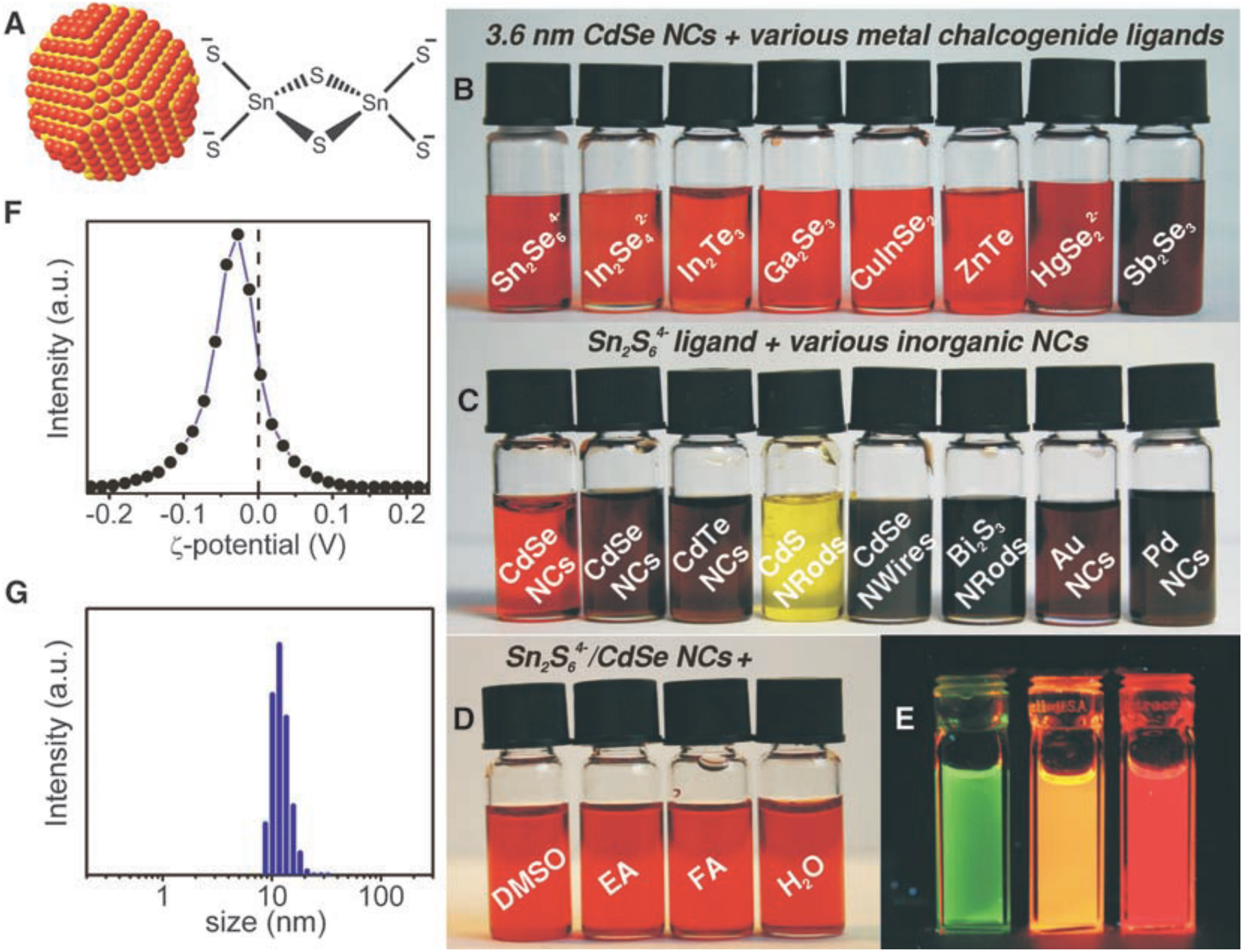
TRANSPORT PROPERTIES



Long aliphatic chains impede charge transport between quantum dots!

6.2. Surface chemistry of nanocystals

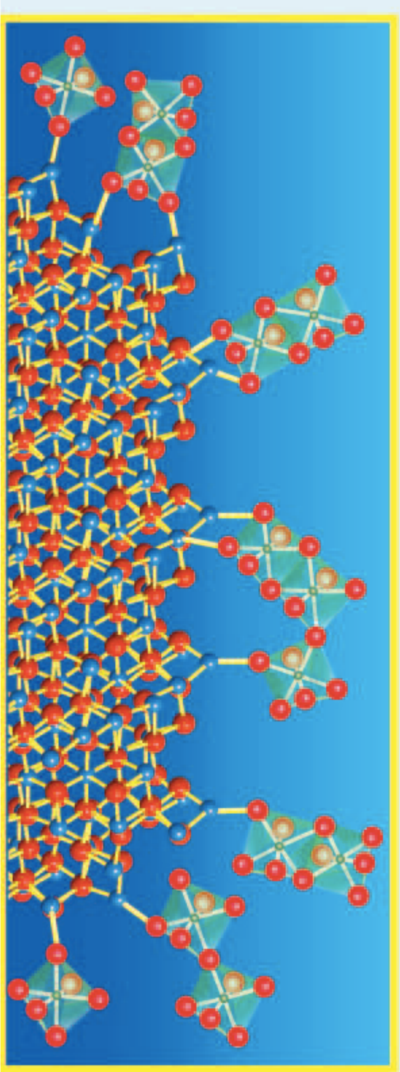
EXCHANGE OF ORGANIC LIGANDS WITH INORGANIC CLUSTERS

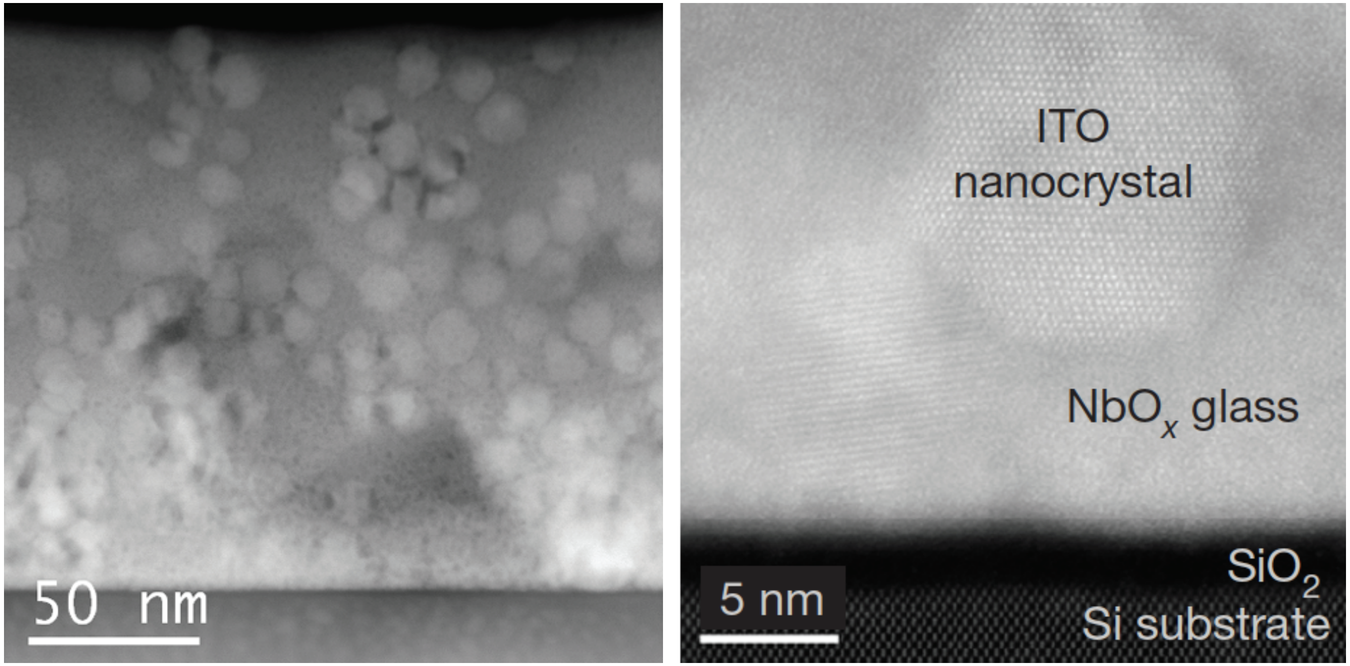


Kovalenko et al, *Science* (**2009**)

6.2. Surface chemistry of nanocystals

EXCHANGE OF ORGANIC LIGANDS WITH INORGANIC CLUSTERS



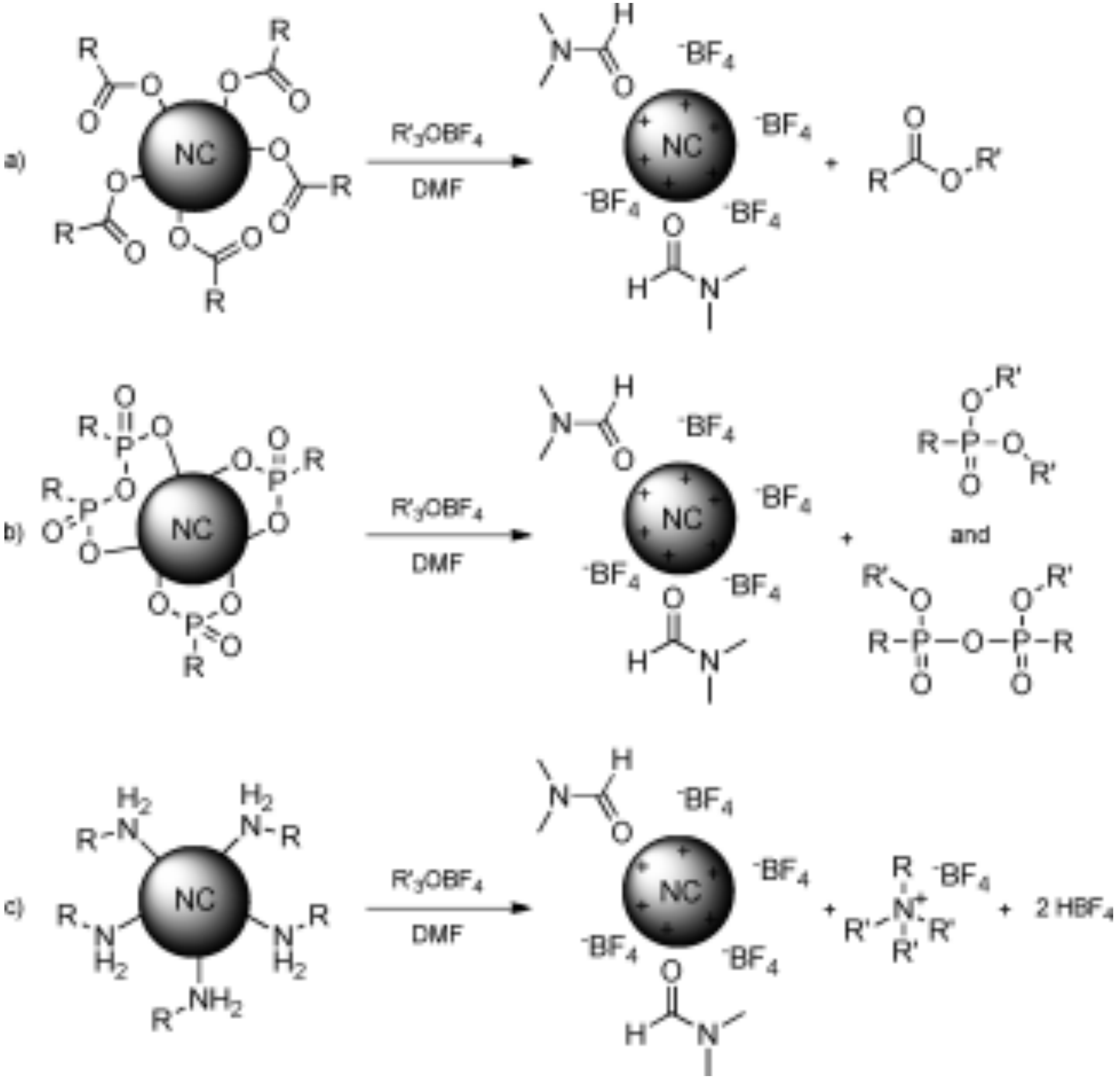


Indium-tin oxide NCs were first stabilized with niobium-based polyoxometallates, which were subsequently transformed into a niobium oxide matrix. These nanocomposites were the active material for dynamically switchable vis-NIR electrochromic windows.

Llordes et al, *Nature* (**2013**)

6.2. Surface chemistry of nanocystals

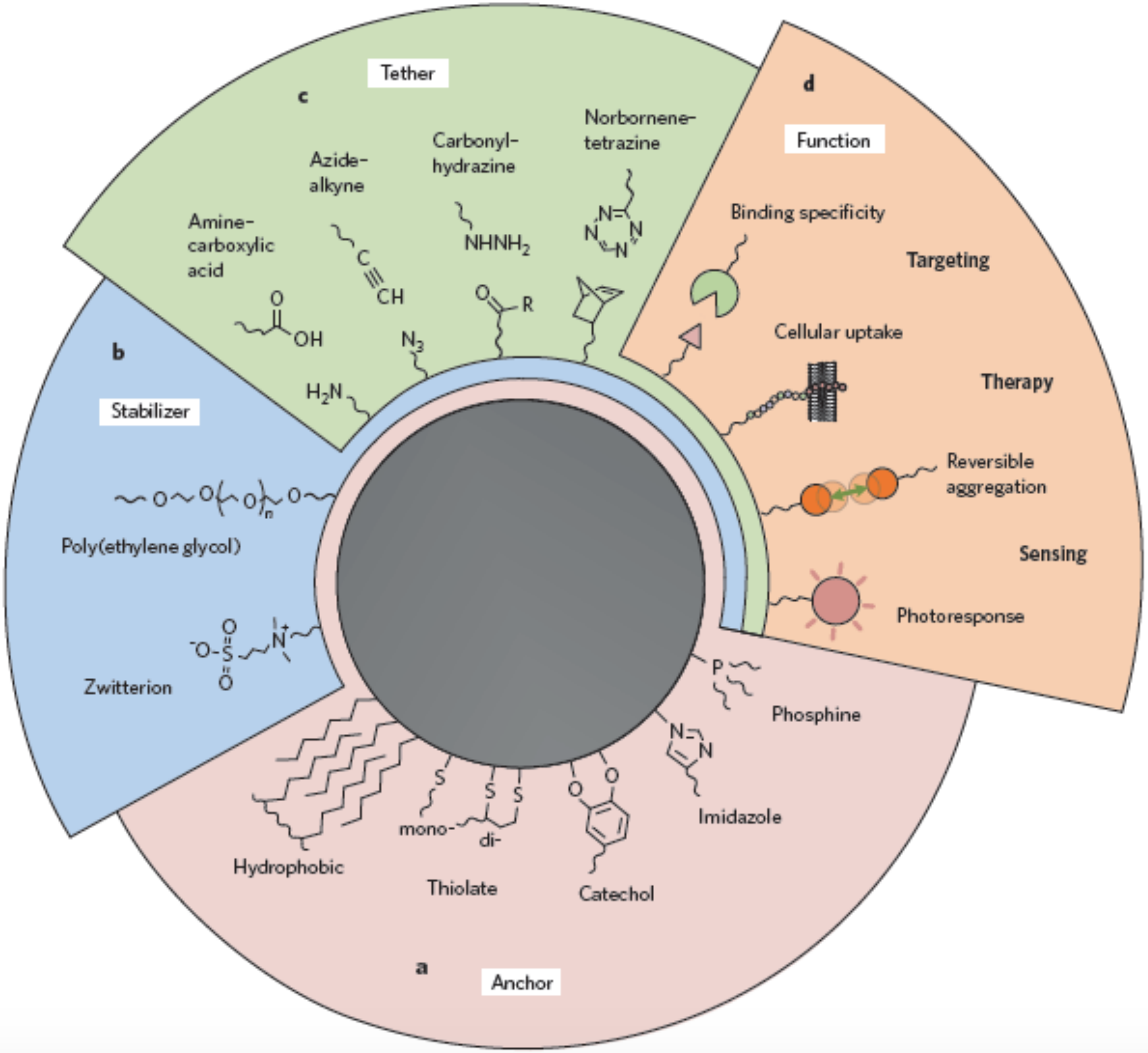
LIGAND STRIPPING



Rosen et al, *Angew.Chemie Int Ed* (**2011**)

6.2. Surface chemistry of nanocystals

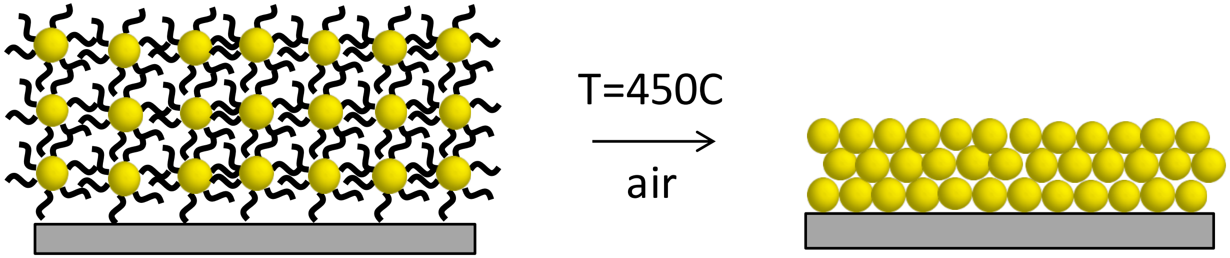
MANY MANY LIGAND EXCHANGES

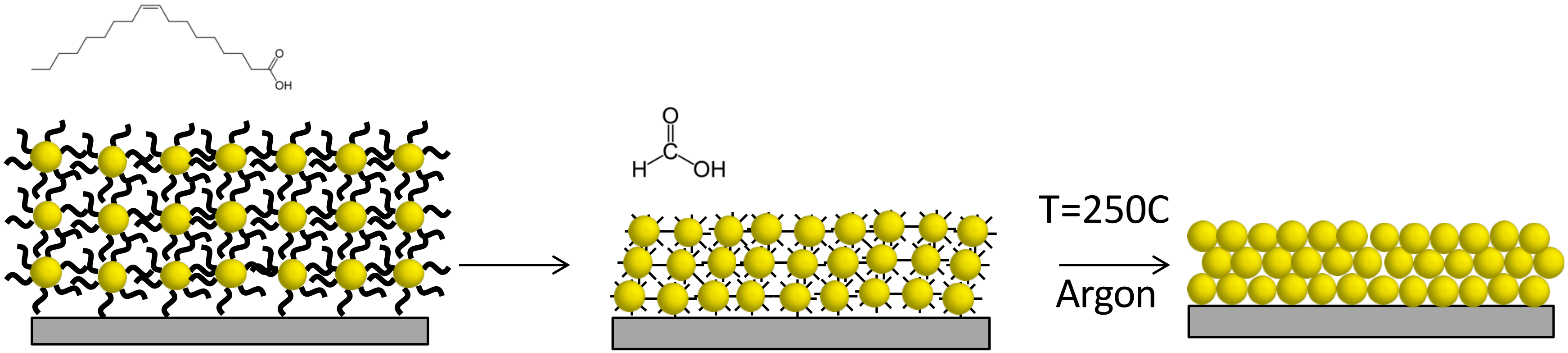


Talapin, *Nature Mater* (**2016**)

6.2. Surface chemistry of nanocystals

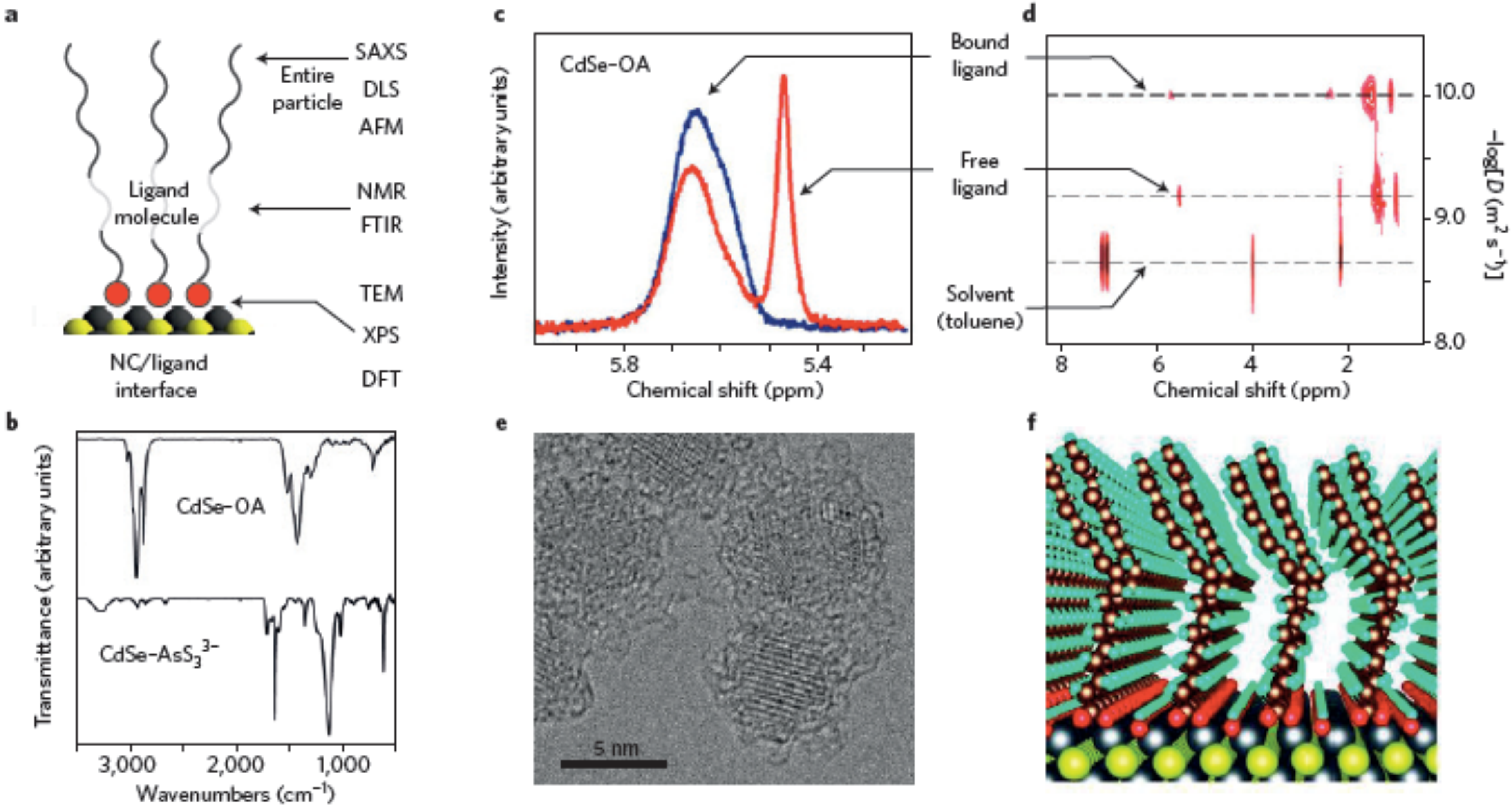
THERMAL DECOMPOSITION





6.2. Surface chemistry of nanocystals

LIGANDS CHARACTERIZATION



Talapin, *Nature Mater* (**2016**)

6.2. Surface chemistry of nanocystals

LIGANDS CHARACTERIZATION

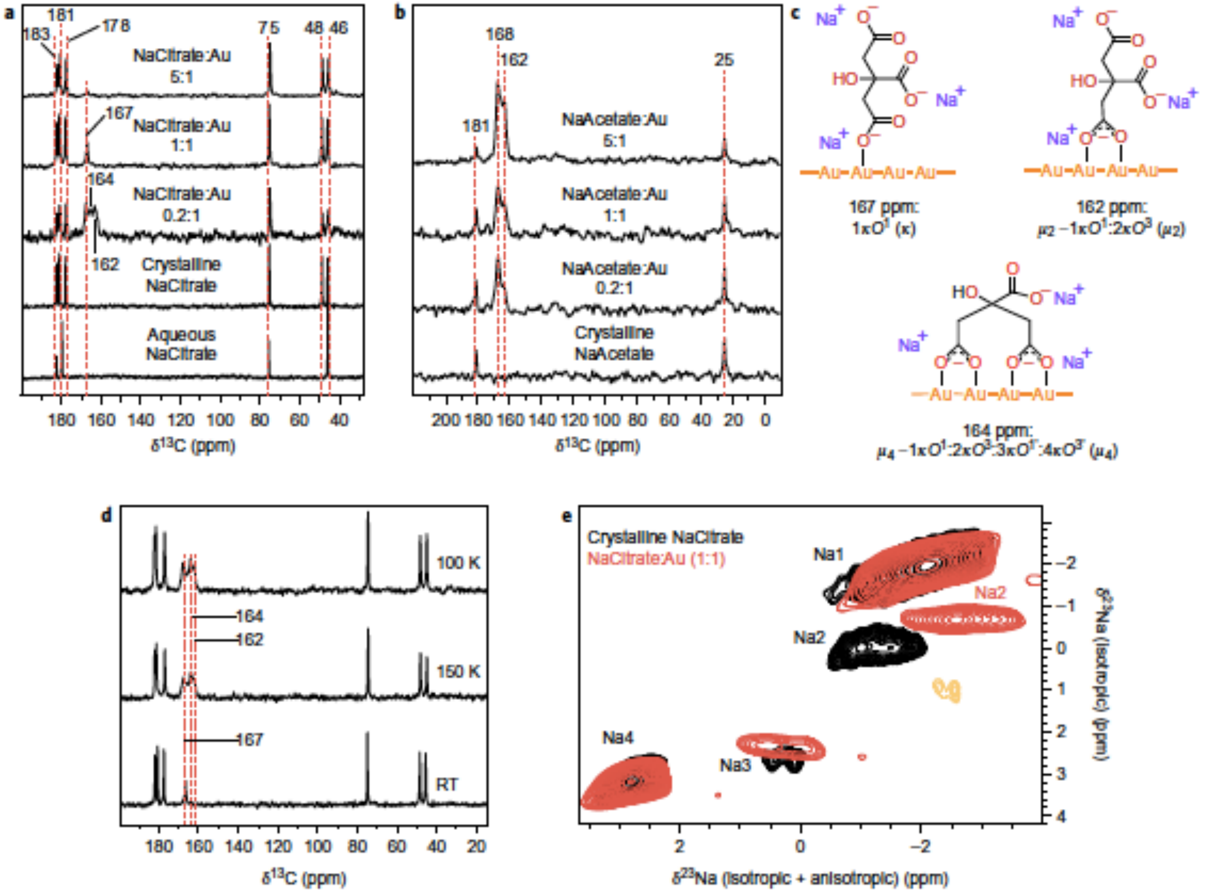
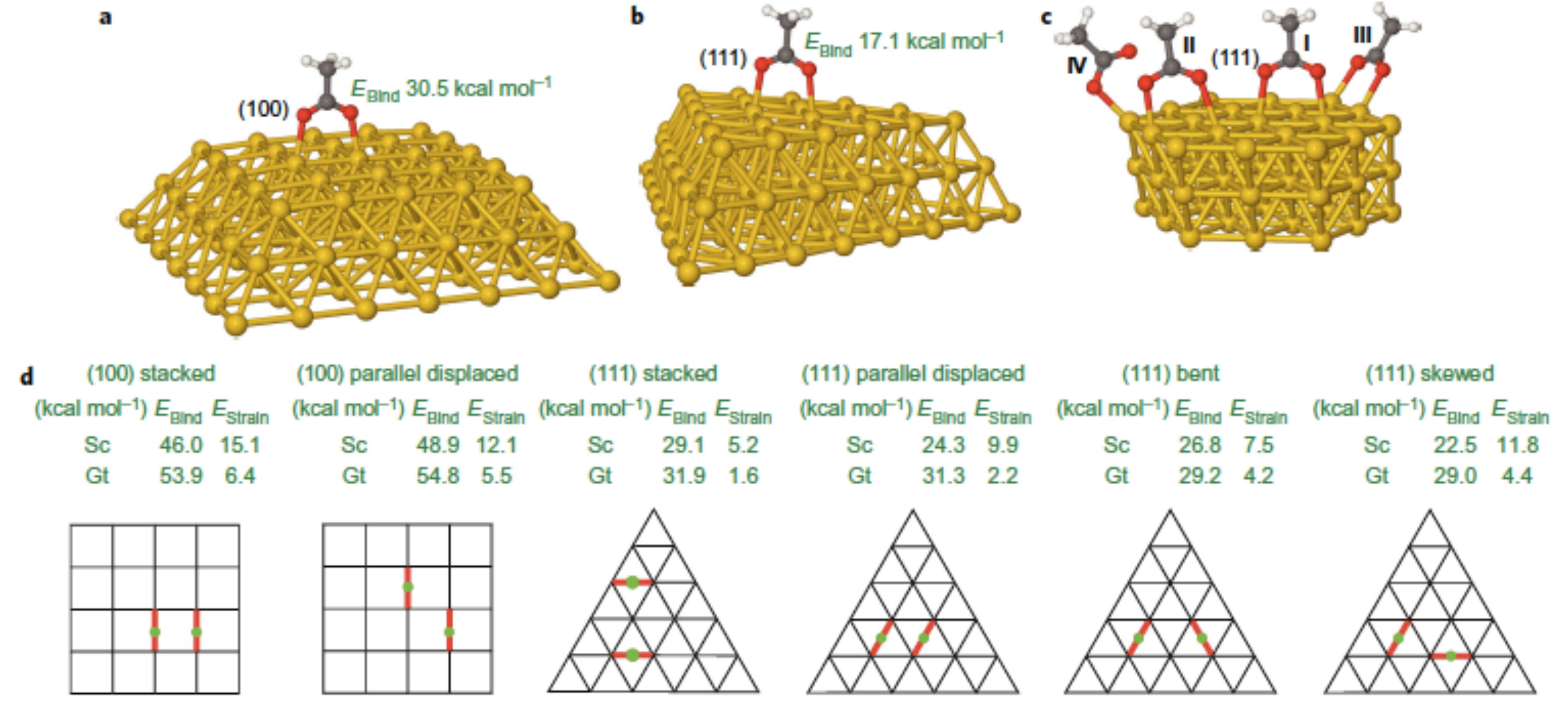


Figure 2 | ^{13}C and ^{23}Na nuclear magnetic resonance spectra and assignment of ^{13}C NMR signals to citrate binding motifs. a,b, 1D ^{13}C NMR spectra acquired at room temperature and in a magnetic field of 9.4 T for: citrate-stabilized AuNPs with variable citrate:Au ratios, crystalline 'sodium citrate' and aqueous sodium citrate (**a**); and acetate-stabilized AuNPs with variable acetate:Au ratios, and crystalline anhydrous sodium acetate (**b**). **c**, Schematic representations and assignment of the various citrate coordination modes. **d**, 1D ^{13}C CP/MAS NMR spectra at 100 K, 150 K and room temperature for a sample with a 1:1 citrate:Au ratio. The NMR signals were strongly enhanced at lower temperatures compared with room temperature: 1,024 scans were acquired for the spectrum at 100 K and 4,096 scans were acquired for the spectrum at 150 K. **e**, ^{23}Na MQMAS NMR spectra of crystalline 'sodium citrate' (black) and a sample with a 1:1 citrate:Au ratio (red) at 21.1 T. Note: except the bottom trace in **a**, which is a solution ^{13}C NMR spectrum, all spectra in **a**, **b** and **d** were acquired under 10 kHz CP/MAS conditions.

Emsley, Basset et al. *Nature Chem.* (**2017**)

6.2. Surface chemistry of nanocystals

LIGANDS CHARACTERIZATION



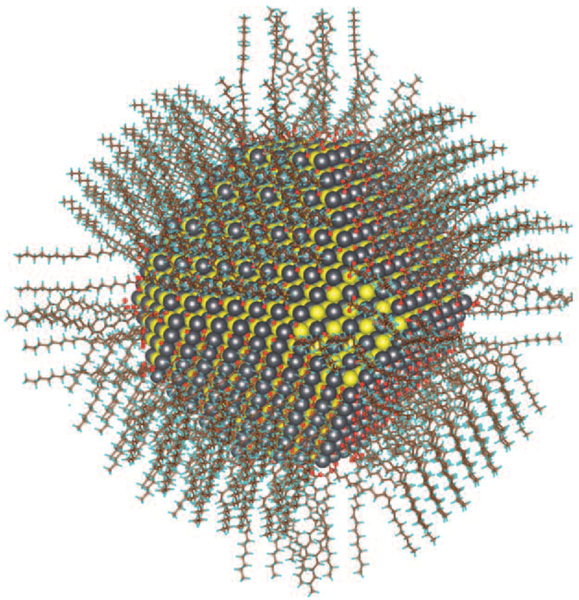
	(kcal mol^{-1})	E_{Bind}	E_{Strain}
(100) stacked	Sc	46.0	15.1
	Gt	53.9	6.4
(100) parallel displaced	Sc	48.9	12.1
	Gt	54.8	5.5
(111) stacked	Sc	29.1	5.2
	Gt	31.9	1.6
(111) parallel displaced	Sc	24.3	9.9
	Gt	31.3	2.2
(111) bent	Sc	26.8	7.5
	Gt	29.2	4.2
(111) skewed	Sc	22.5	11.8
	Gt	29.0	4.4

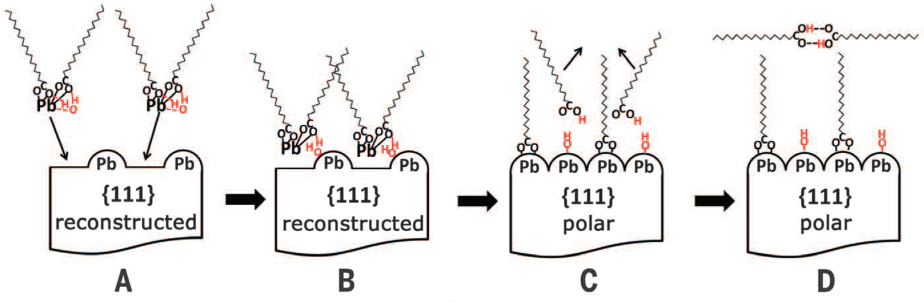
Figure 3 | DFT-optimized ligand geometries, binding energies and strain energies on Au(100) and Au(111) model surfaces. a,b, One acetate anion is found

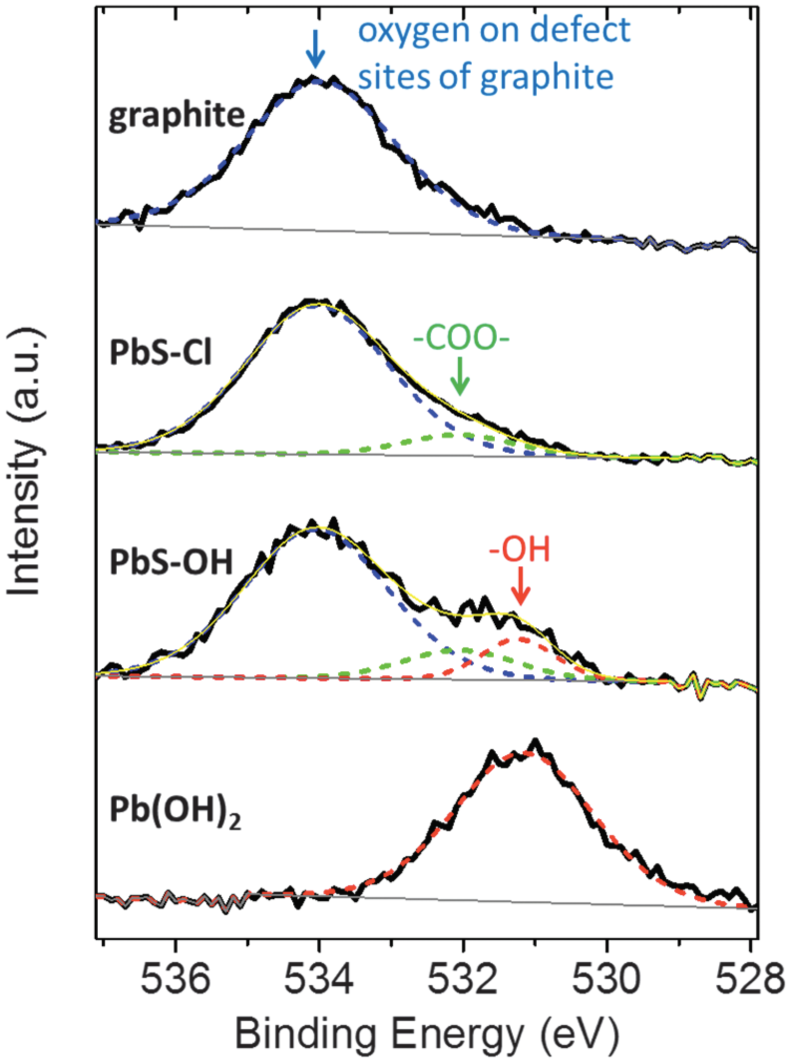
Emsley, Basset et al. *Nature Chem.* (**2017**)

6.2. Surface chemistry of nanocystals

LIGANDS CHARACTERIZATION

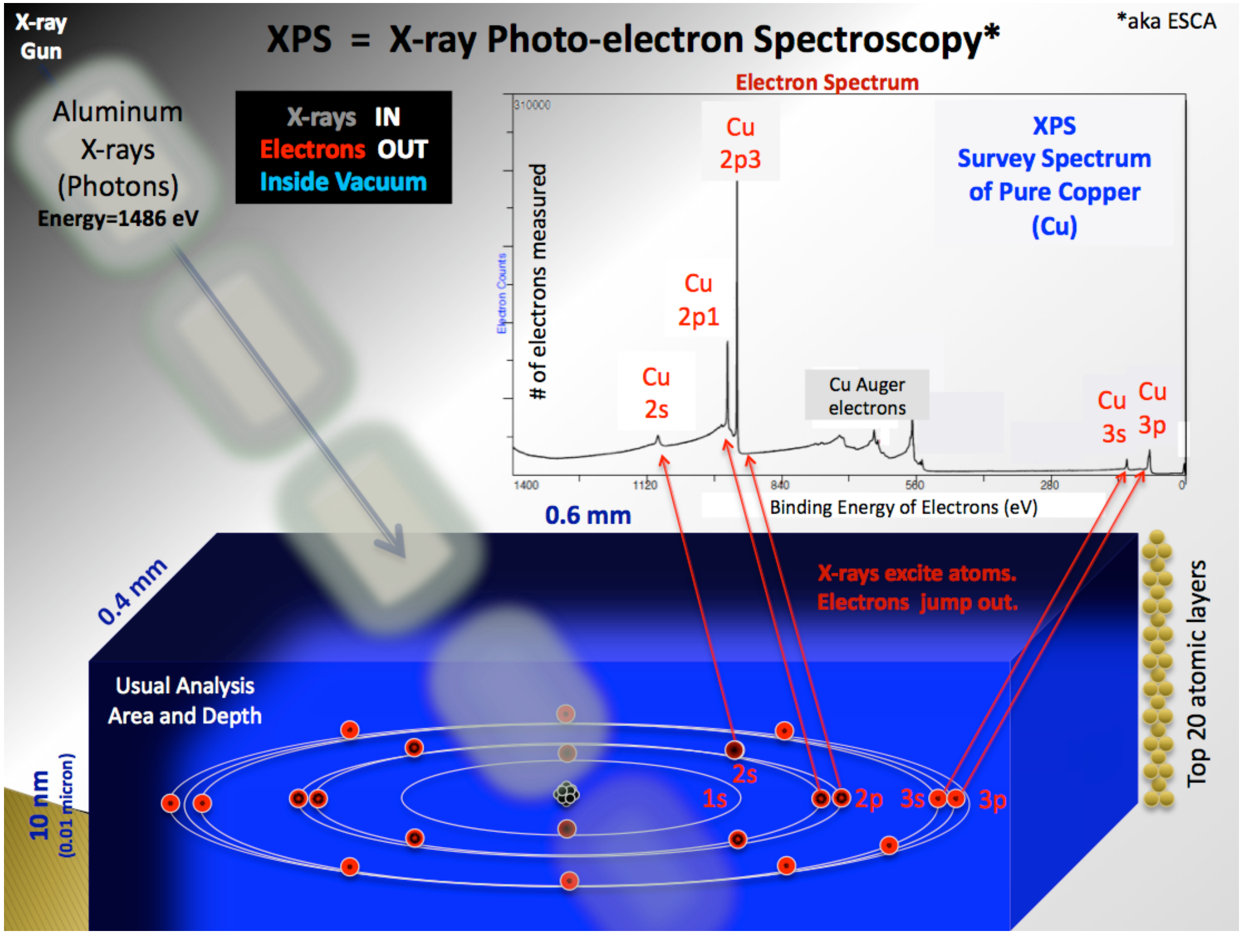






Lin-Wang Wang et al. *Science* (**2014**)

X-Ray Photoemission Spectroscopy (XPS)

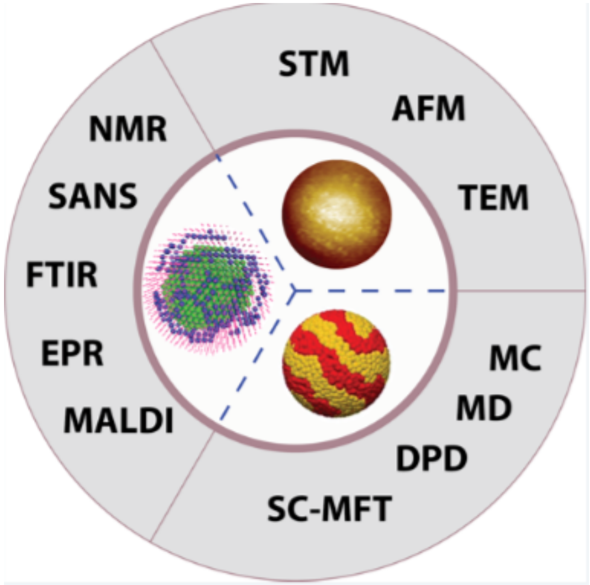


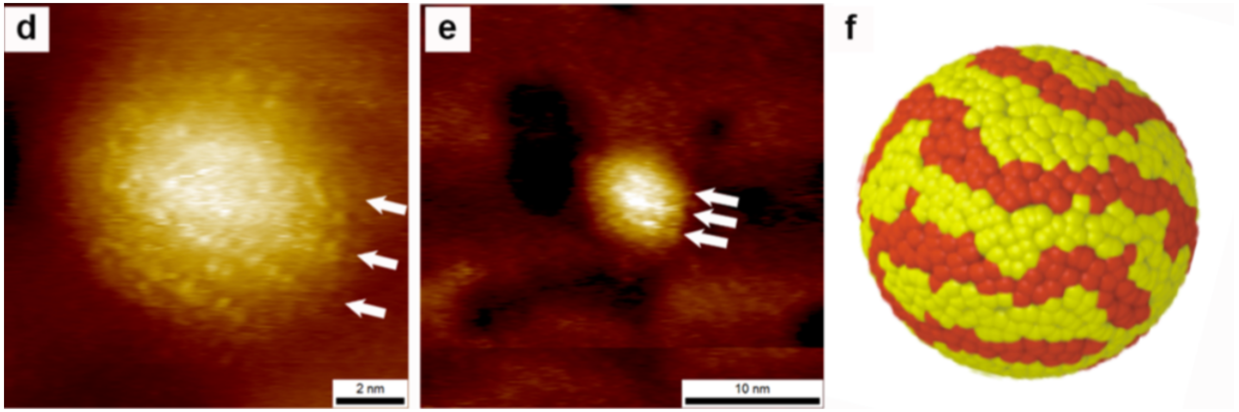
$$E_{binding} = E_{photons} - (E_{kinetic} + \phi)$$

ϕ is the work function (minimum energy to extract an electron from the material surface to the vacuum)

6.2. Surface chemistry of nanocystals

LIGANDS CHARACTERIZATION





Ong, Luo, Stellacci *Acc. Chem. Res.* (**2017**)

6.3. Deposition techniques

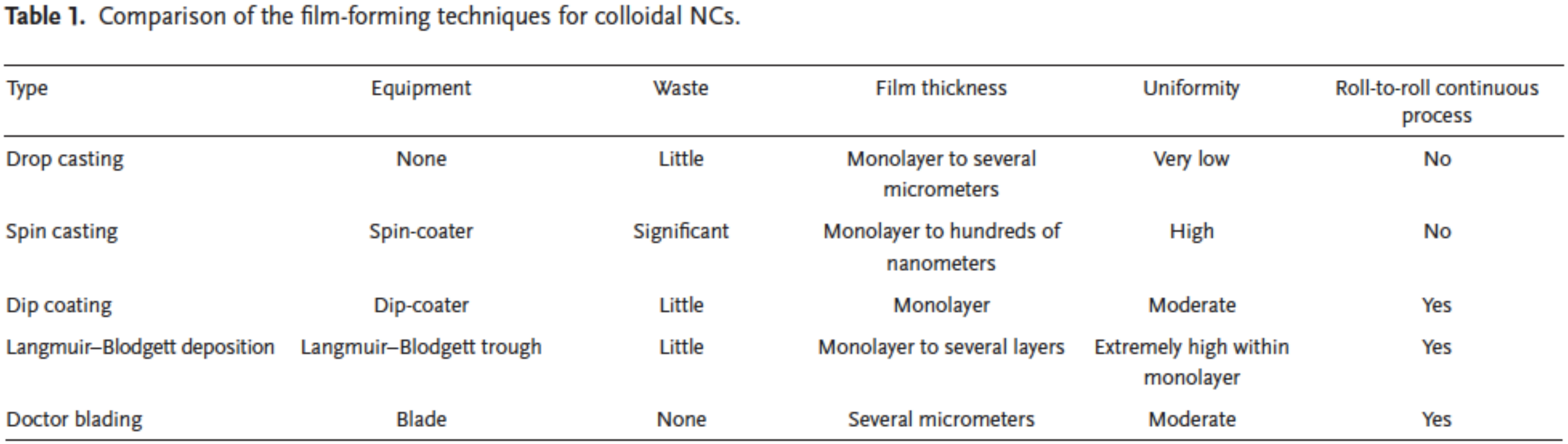


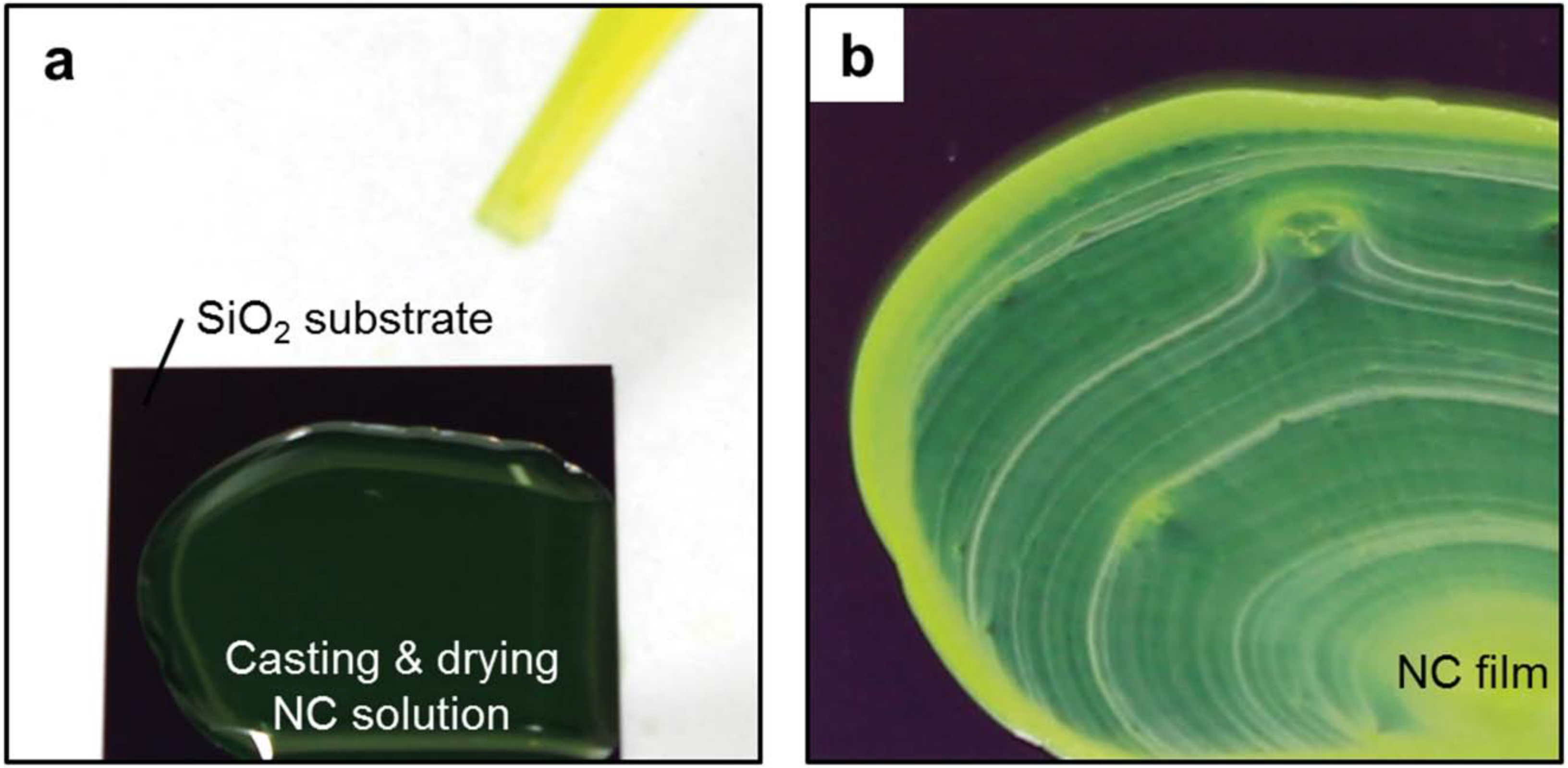
Table 1. Comparison of the film-forming techniques for colloidal NCs.

Type	Equipment	Waste	Film thickness	Uniformity	Roll-to-roll continuous process
Drop casting	None	Little	Monolayer to several micrometers	Very low	No
Spin casting	Spin-coater	Significant	Monolayer to hundreds of nanometers	High	No
Dip coating	Dip-coater	Little	Monolayer	Moderate	Yes
Langmuir–Blodgett deposition	Langmuir–Blodgett trough	Little	Monolayer to several layers	Extremely high within monolayer	Yes
Doctor blading	Blade	None	Several micrometers	Moderate	Yes

Hyeon et al. *Adv. Mater.* (**2016**)

6.3. Deposition techniques

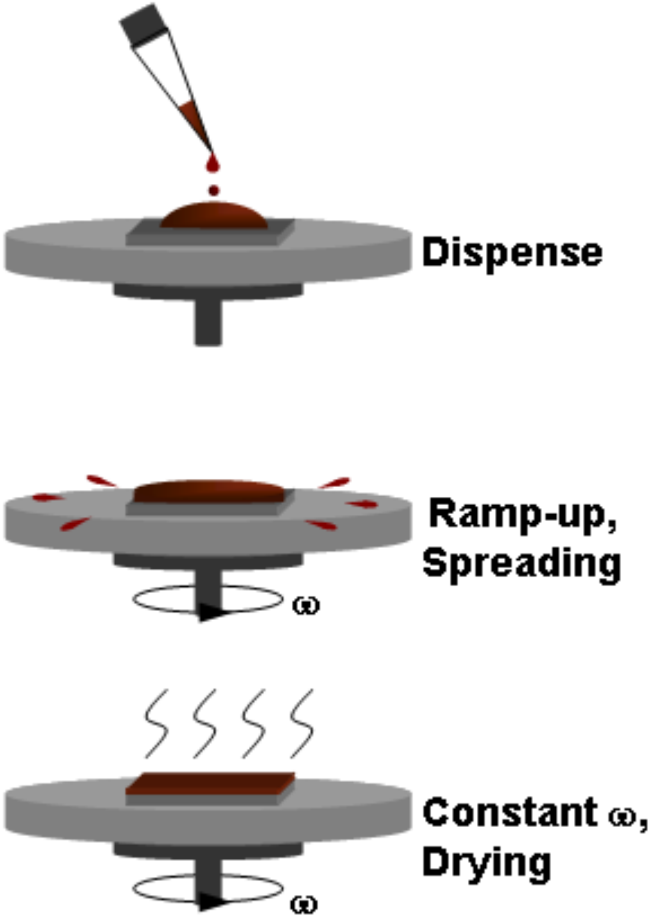
DROP CASTING

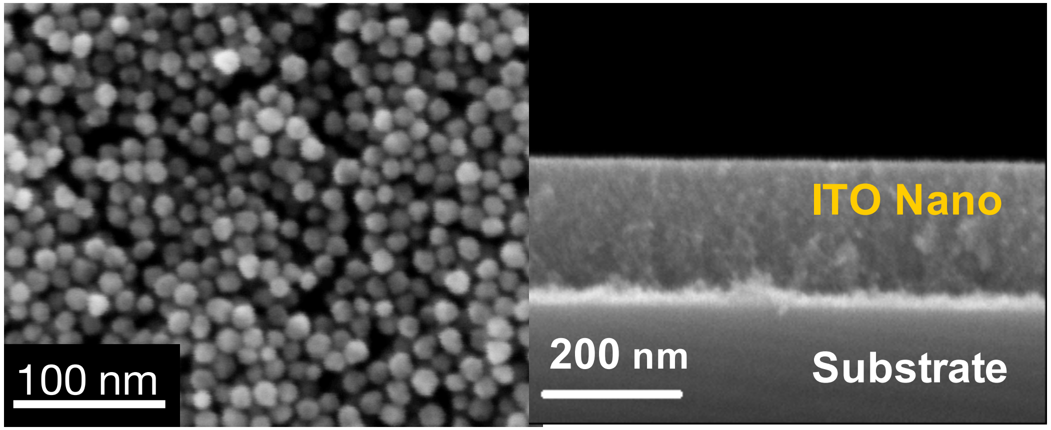


Hyeon et al. *Adv. Mater.* (**2016**)

6.3. Deposition techniques

SPIN COATING

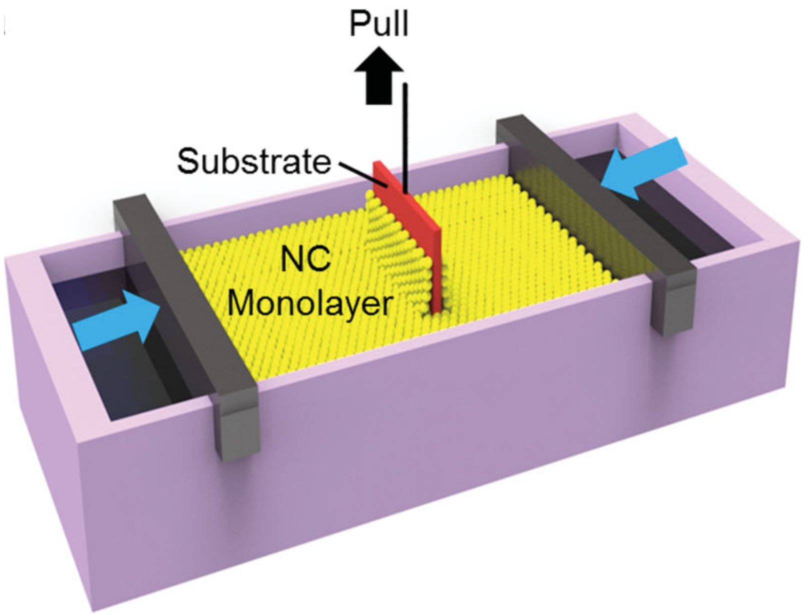


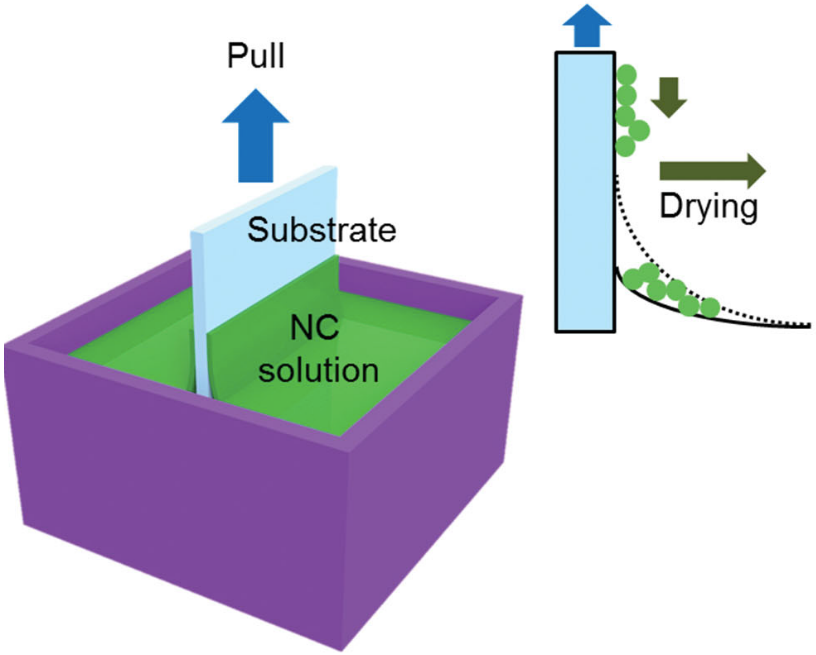


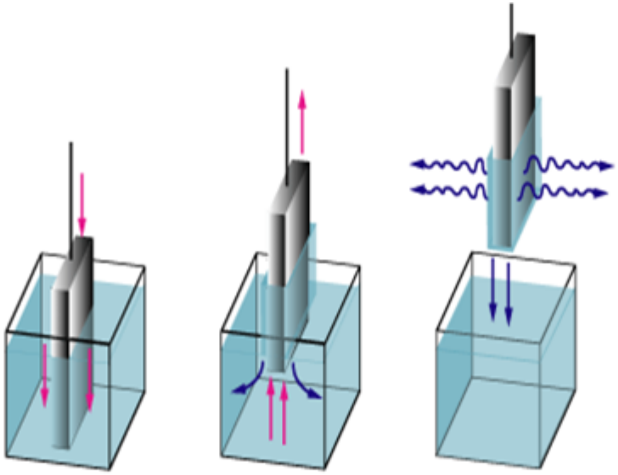
Garcia et al. *Nano Lett.* (**2011**)

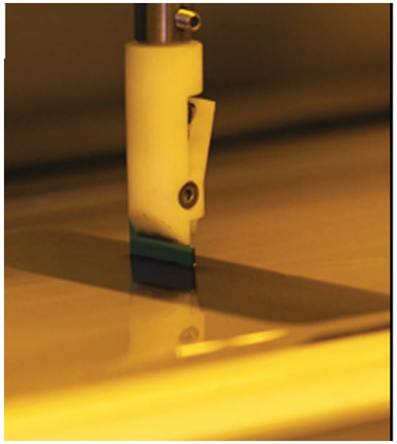
6.3. Deposition techniques

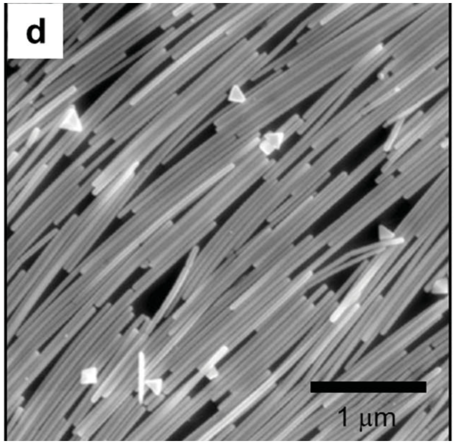
LANGMUIR BLODGET and DIP-COATING







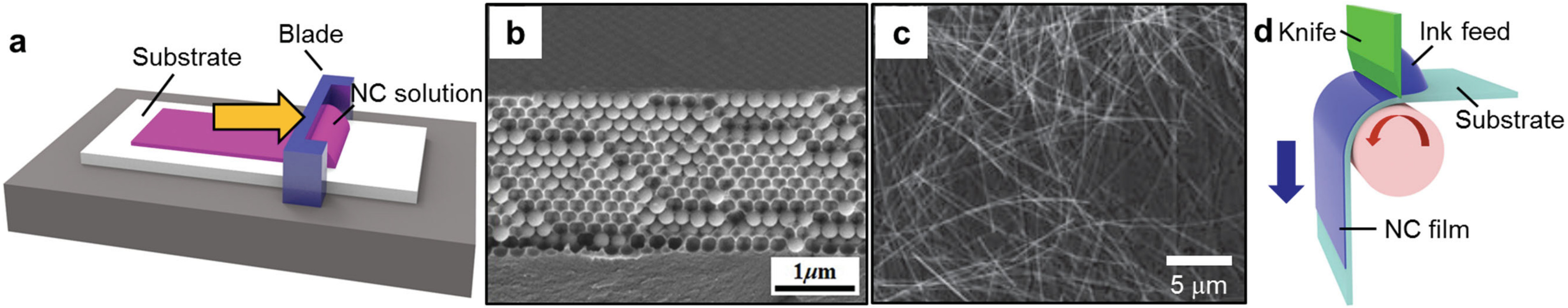


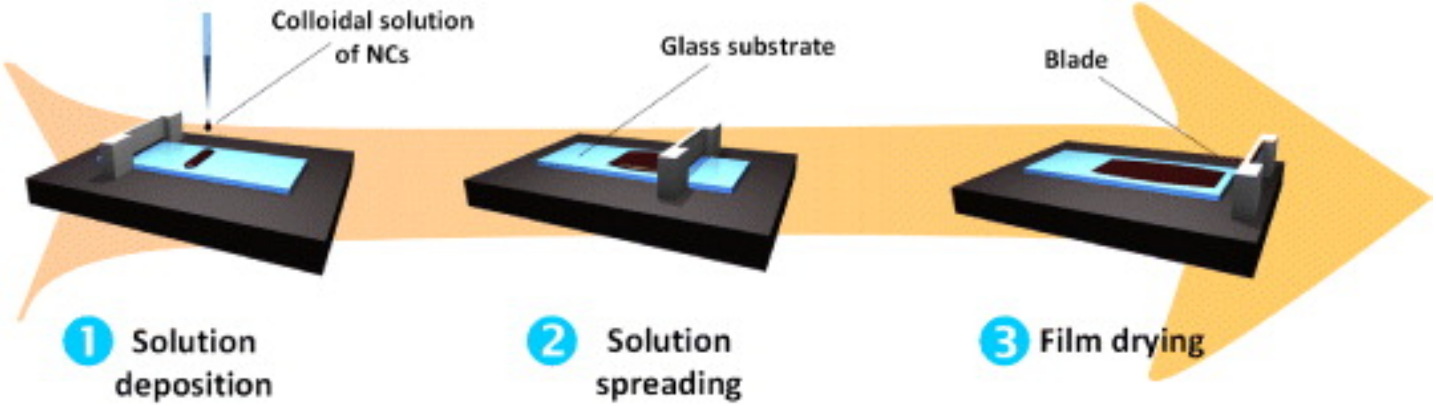


Hyeon et al. *Adv. Mater.* (**2016**)

6.3. Deposition techniques

DOCTOR BLADING and KNIFE-OVER EDGE PROCESSES

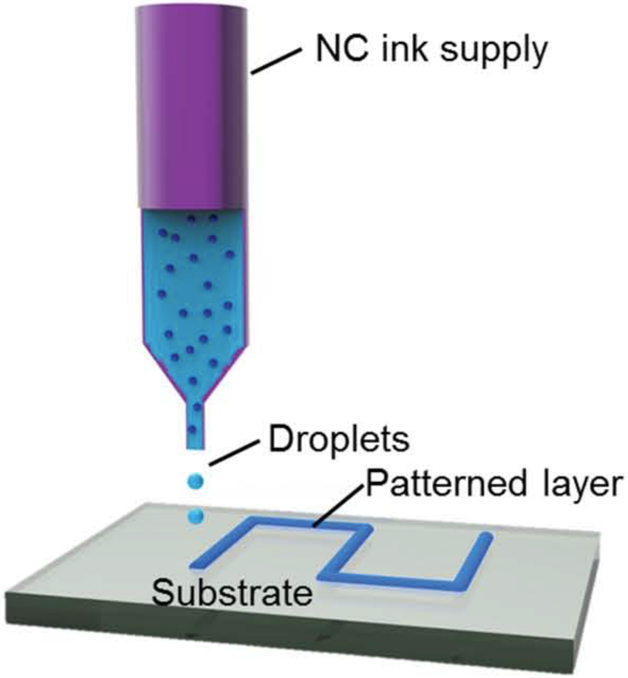


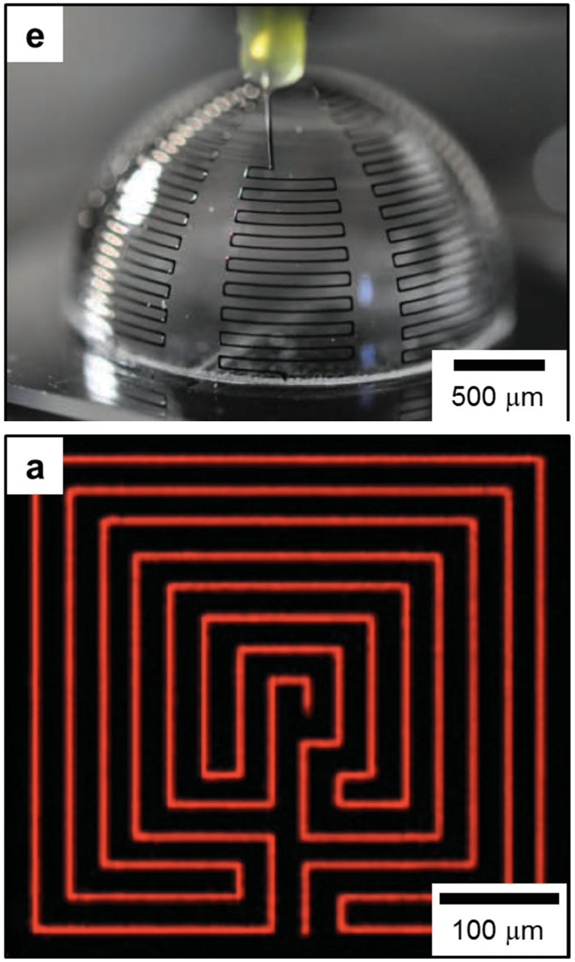


Hyeon et al. *Adv. Mater.* (**2016**)

6.3. Deposition techniques

INK-JET PRINTING



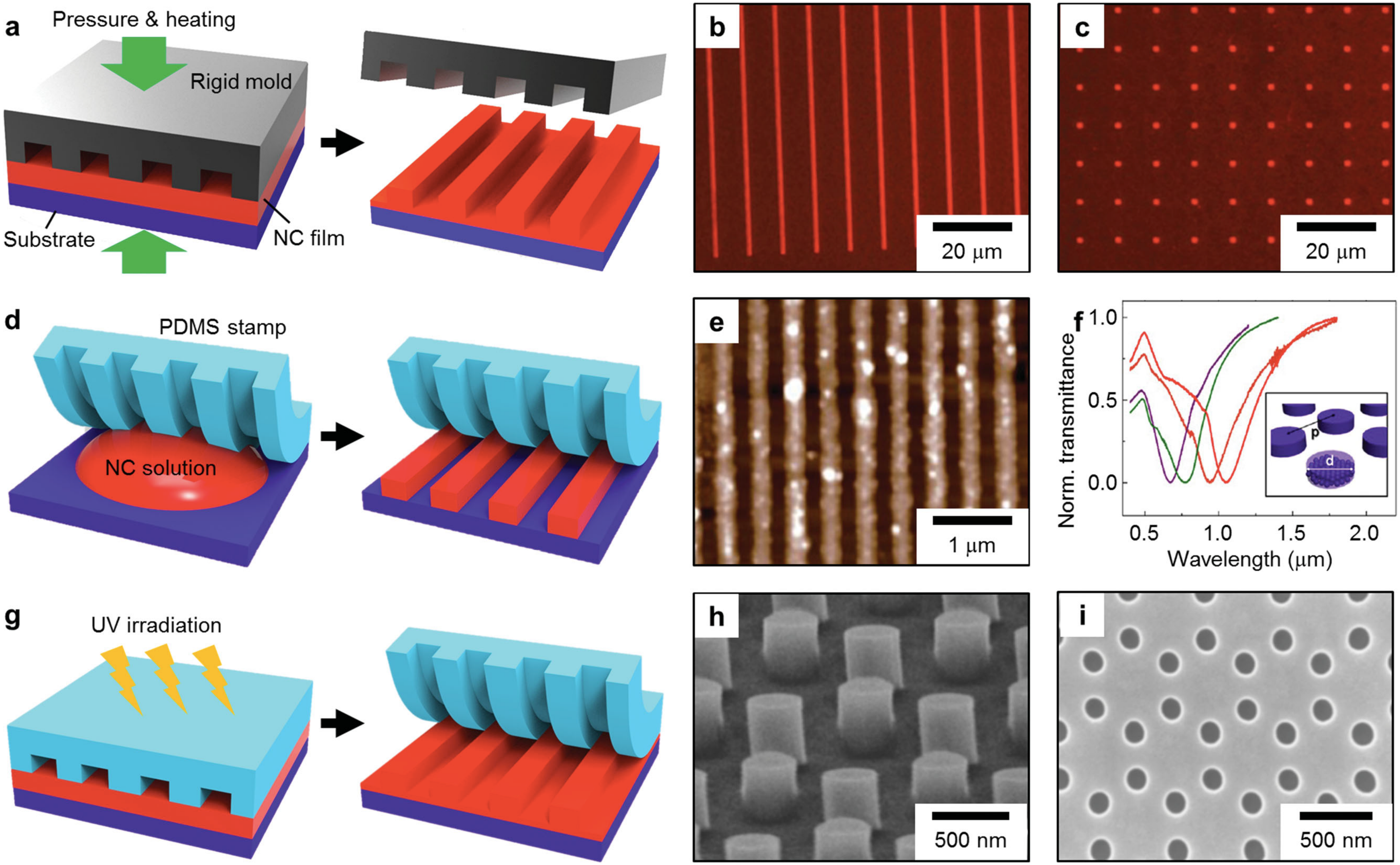


Hyeon et al. *Adv. Mater.* (**2016**)

6.3. Deposition techniques

NANO-IMPRINT LITOGRAPHY

Nanoimprint lithography (NIL) is one of the most widely used patterning techniques to reach micrometer or sub-micrometer feature sizes (down to tens of nanometer). The merits of NIL are its cost effectiveness, large-scale applicability, simple process, and extremely high resolution below the limit of the light diffraction (comparable with that of e-beam lithography).

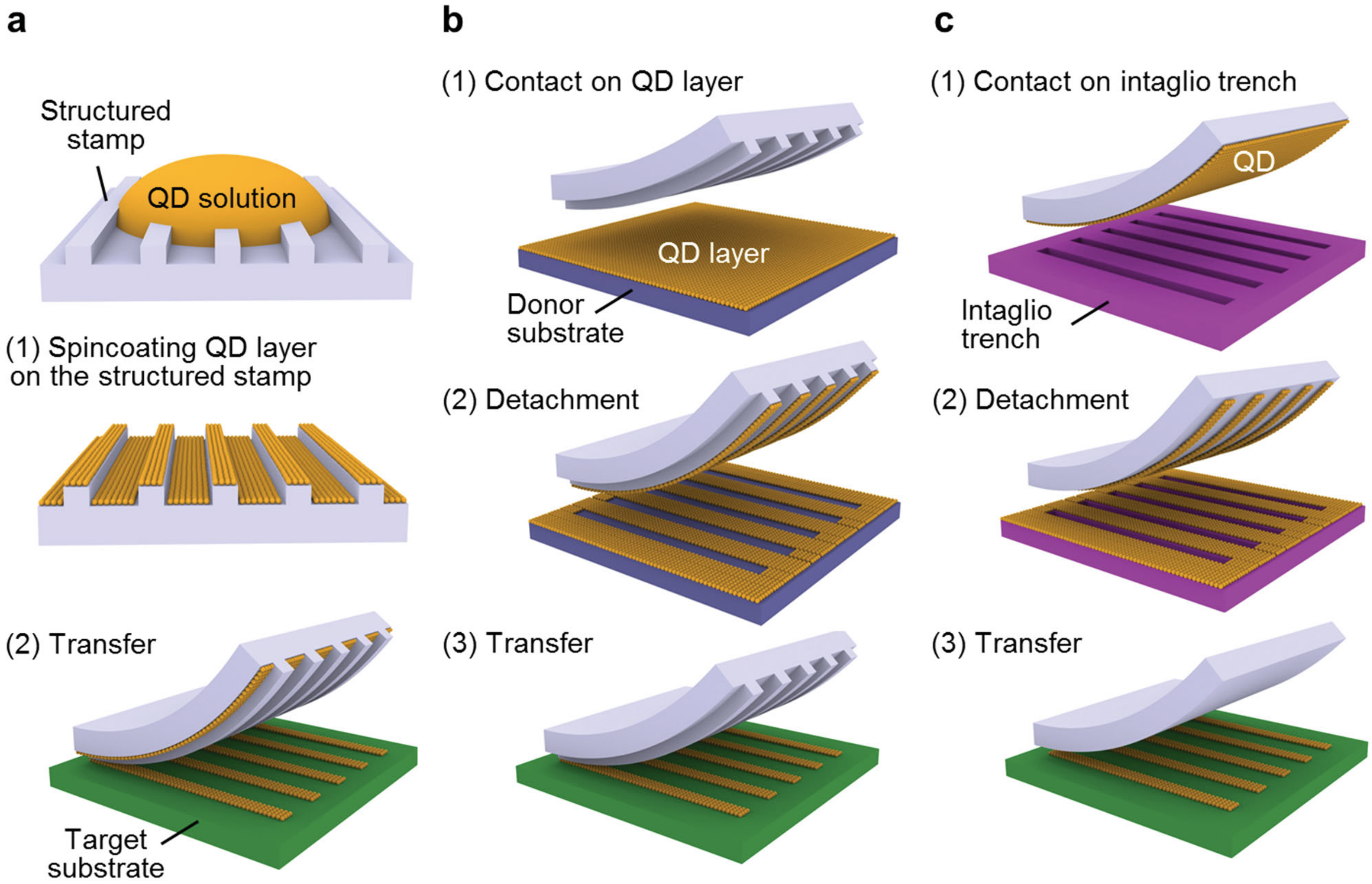


Hyeon et al. *Adv. Mater.* (**2016**)

QD-PMMA are typically patterned through NIL

6.3. Deposition techniques

MICRO-CONTACT PRINTING

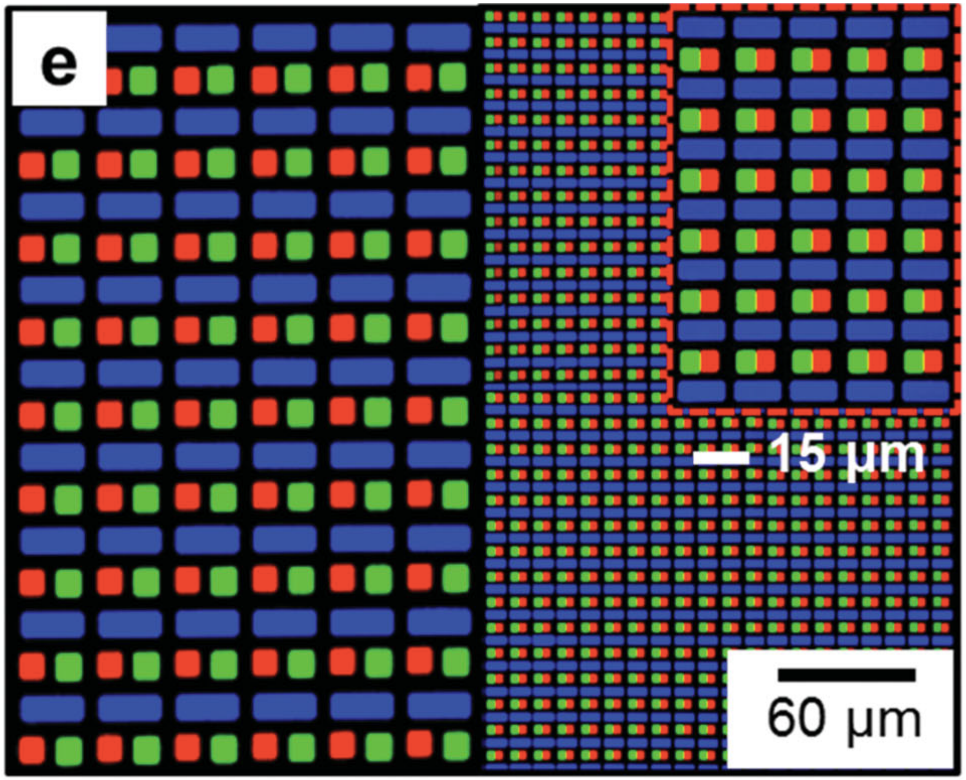


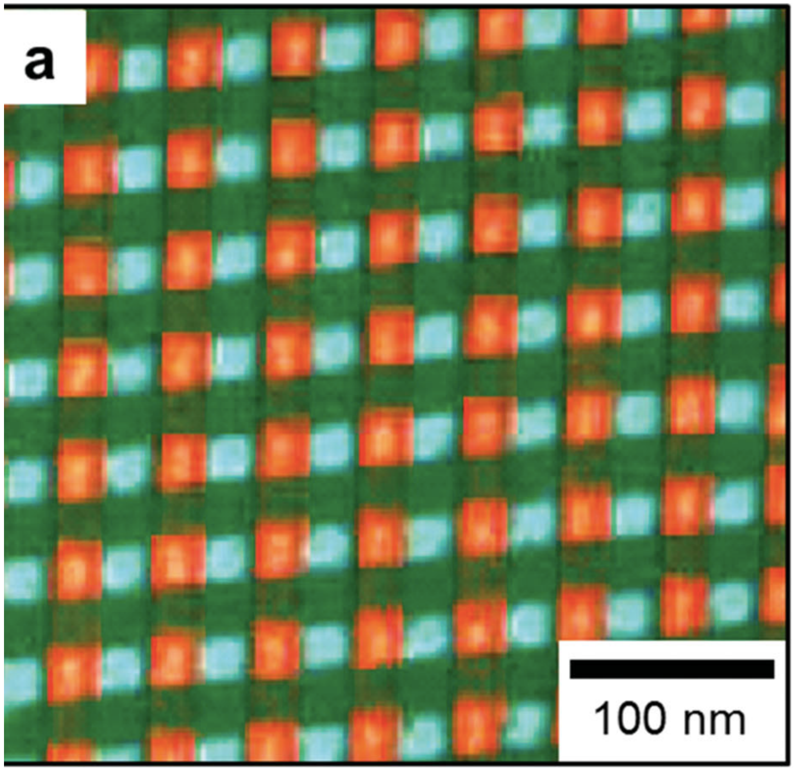
Contact printing is a powerful method for the transfer of NCs in micro-/nanoconfigurations using stamps at desired locations.[151,152] Soft, elastomeric polymers are utilized as stamps to pick up and place the NC "ink" on the target substrate.[153] This room-temperature, low-cost procedure is simple yet powerful, due to the versatile processability of various NCs on different kinds of target substrates. The contact-printing techniques are categorized into three types: additive transfer, subtractive transfer, and intaglio transfer (**Figure 12**).

Hyeon et al. *Adv. Mater.* (**2016**)

6.3. Deposition techniques

MICRO-CONTACT PRINTING

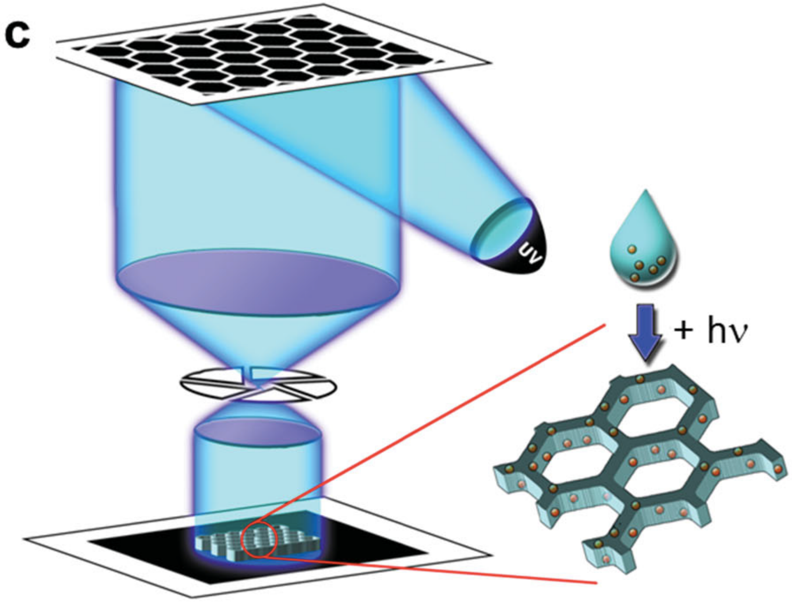




Hyeon et al. *Adv. Mater.* (**2016**)

6.3. Deposition techniques

3D PRINTING



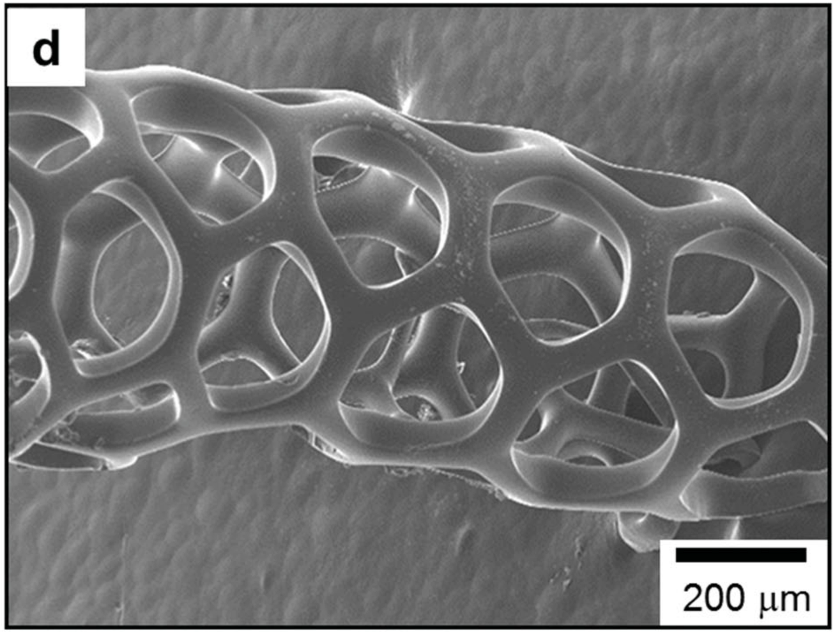
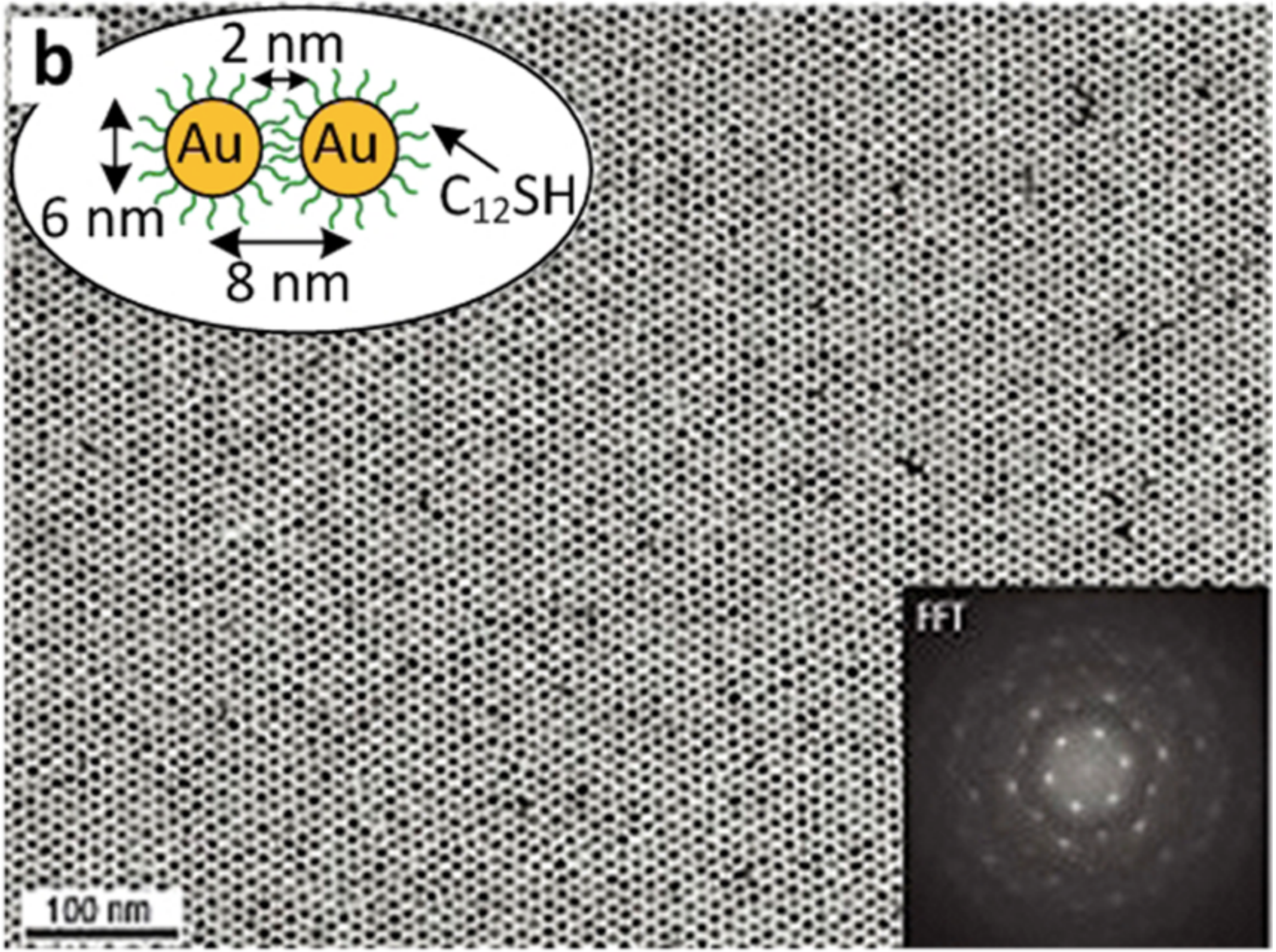


photo-polymerizable polymer + nanoparticles

Hyeon et al. *Adv. Mater.* (**2016**)

6.4. Nanocrystal ASSEMBLIES

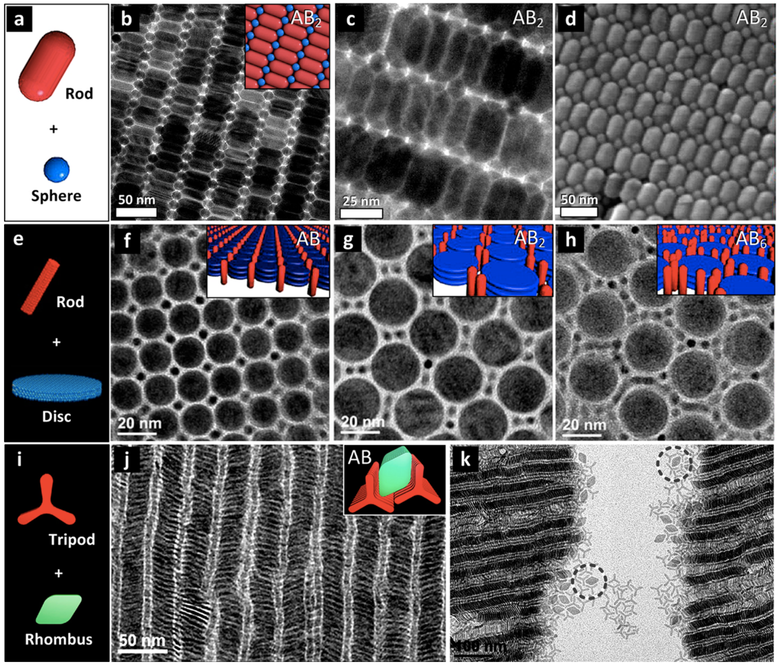
NANOCRYSTALS BEHAVE LIKE ATOMS IN A SOLID!

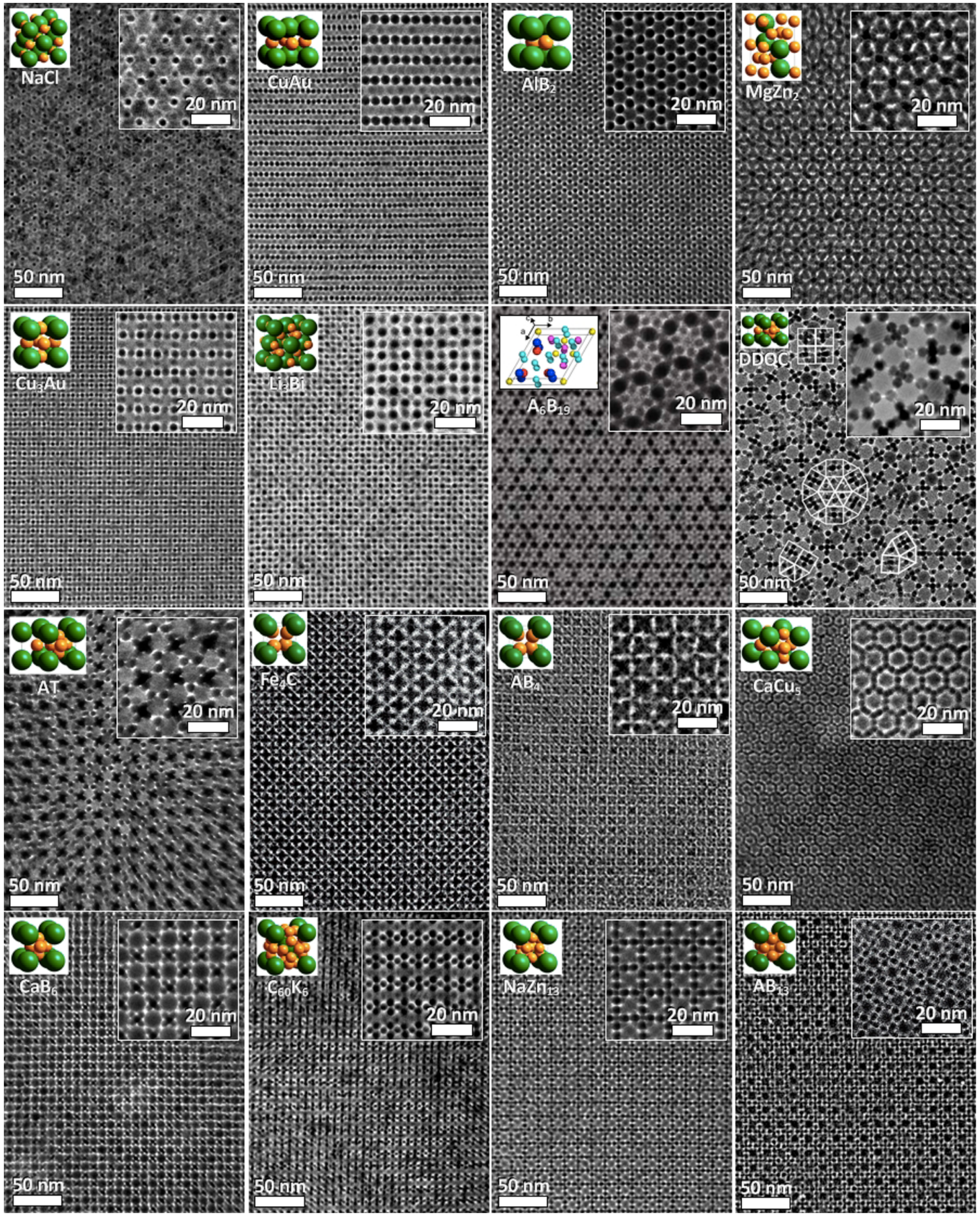


Talapin et al. *Chem. Rev.* (**2016**)

6.4. Nanocrystal ASSEMBLIES

BINARY SUPERLATTICES

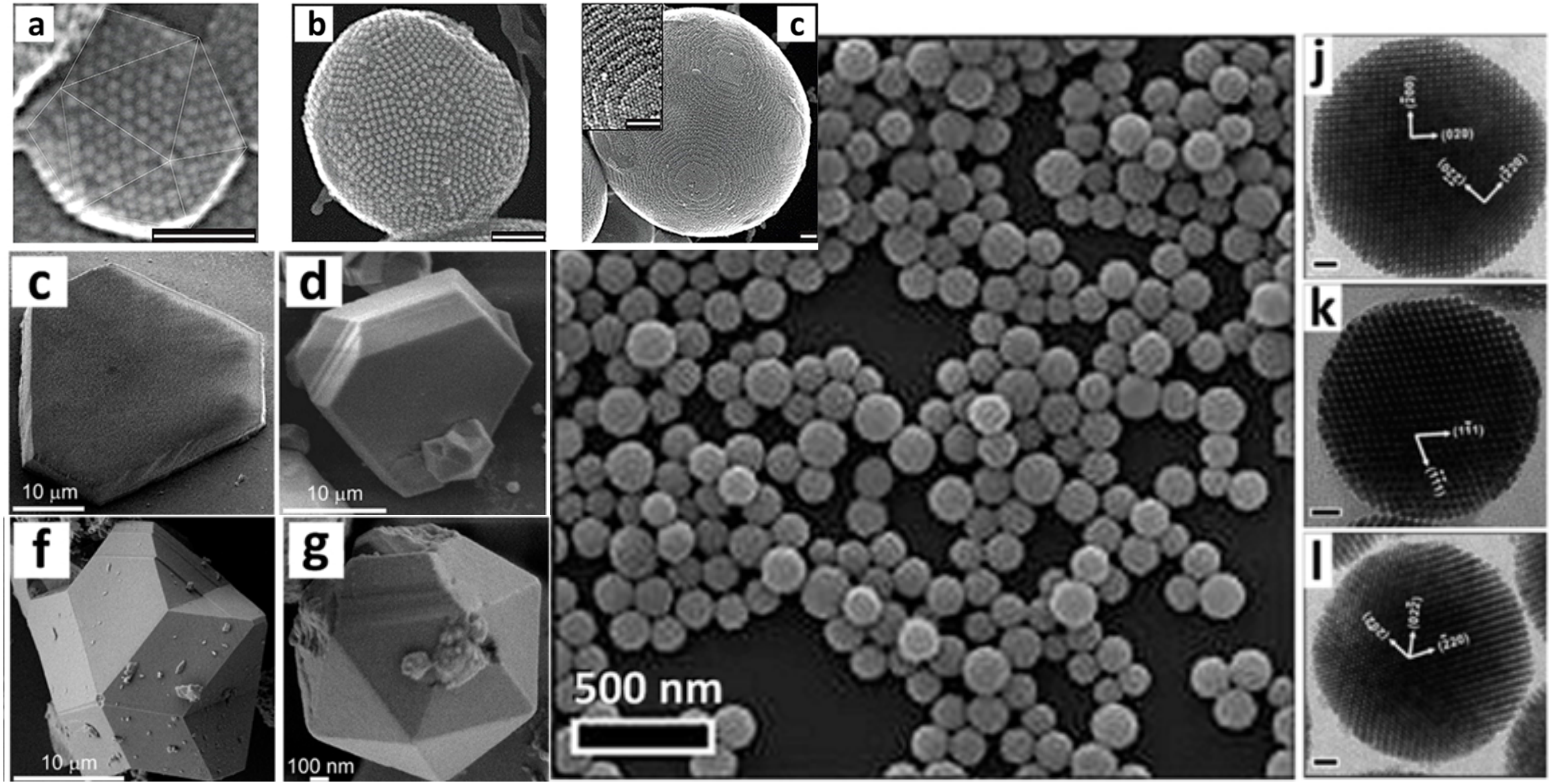




Talapin et al. *Chem. Rev.* (**2016**)

6.4. Nanocrystal ASSEMBLIES

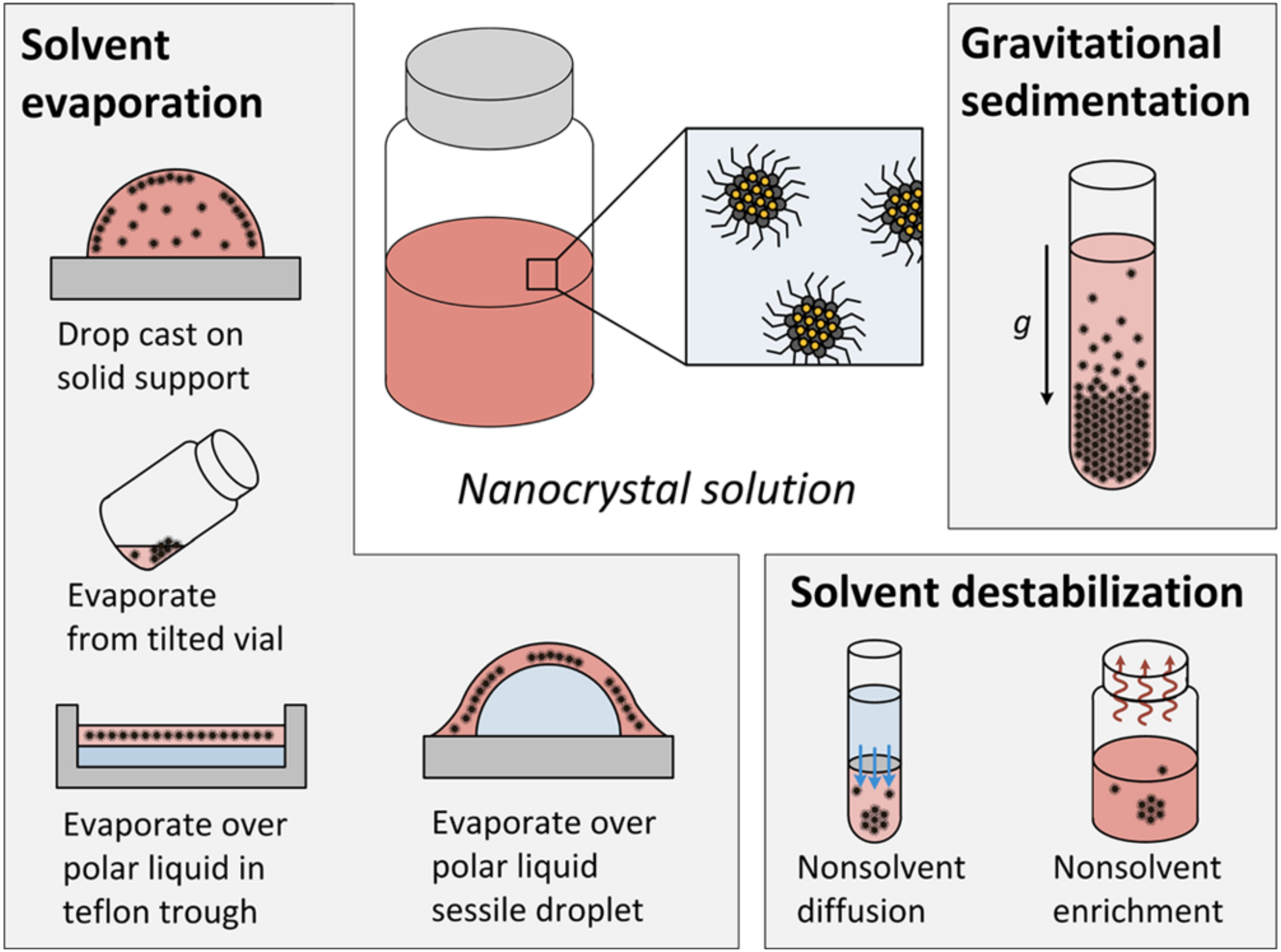
SUPER-CRYSTALS



Talapin et al. *Chem. Rev.* (**2016**)

6.4. Nanocrystal ASSEMBLIES

EXPERIMENTAL APPROACHES



Solvent evaporation

Drop cast on solid support

Evaporate from tilted vial

Evaporate over polar liquid in teflon trough

Evaporate over polar liquid sessile droplet

Nanocrystal solution

Gravitational sedimentation

Solvent destabilization

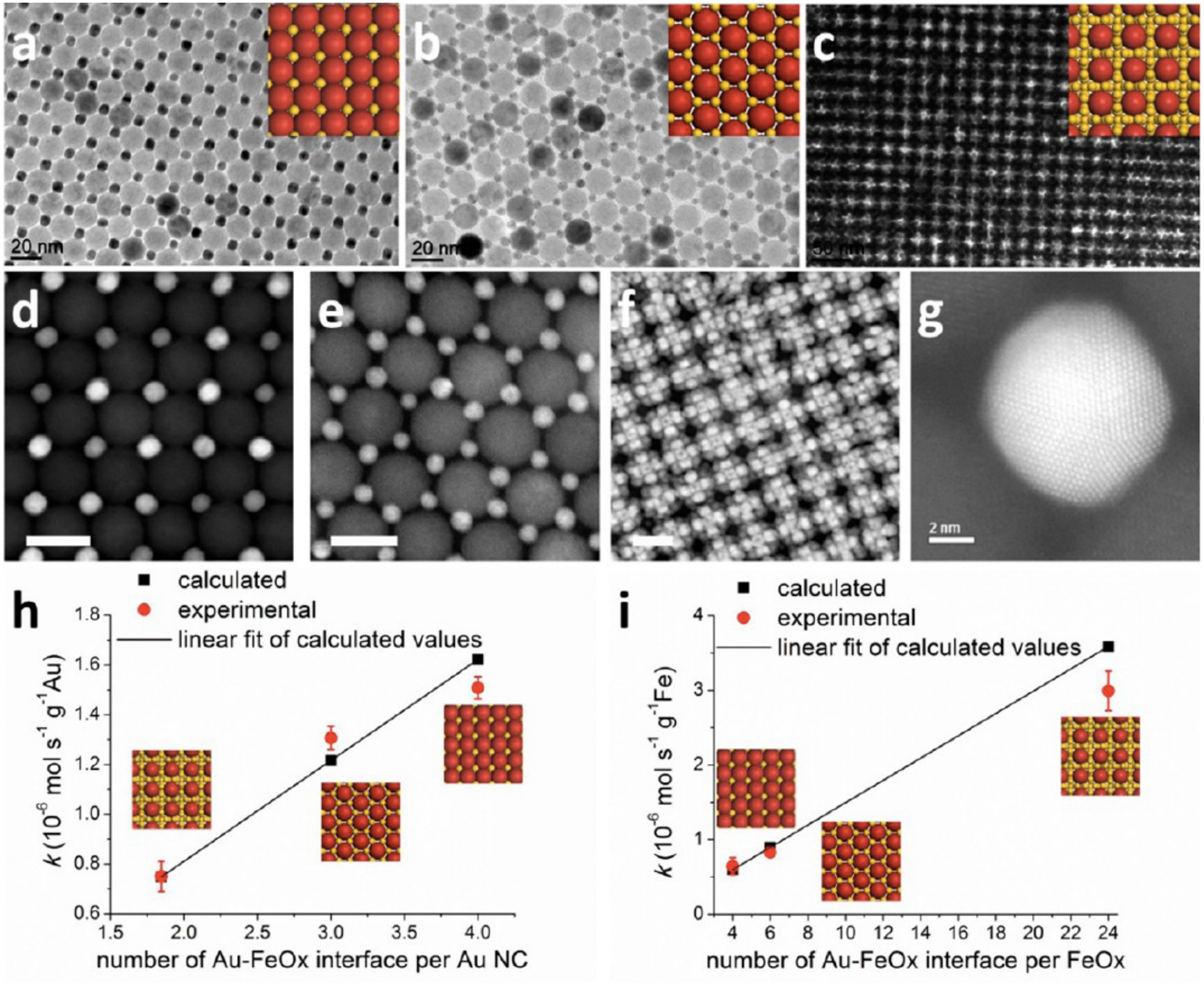
Nonsolvent diffusion

Nonsolvent enrichment

Talapin et al. *Chem. Rev.* (**2016**)

6.4. Nanocrystal ASSEMBLIES

NC SUPERLATTICES TO ENGINEER CATALYTIC CONTACTS

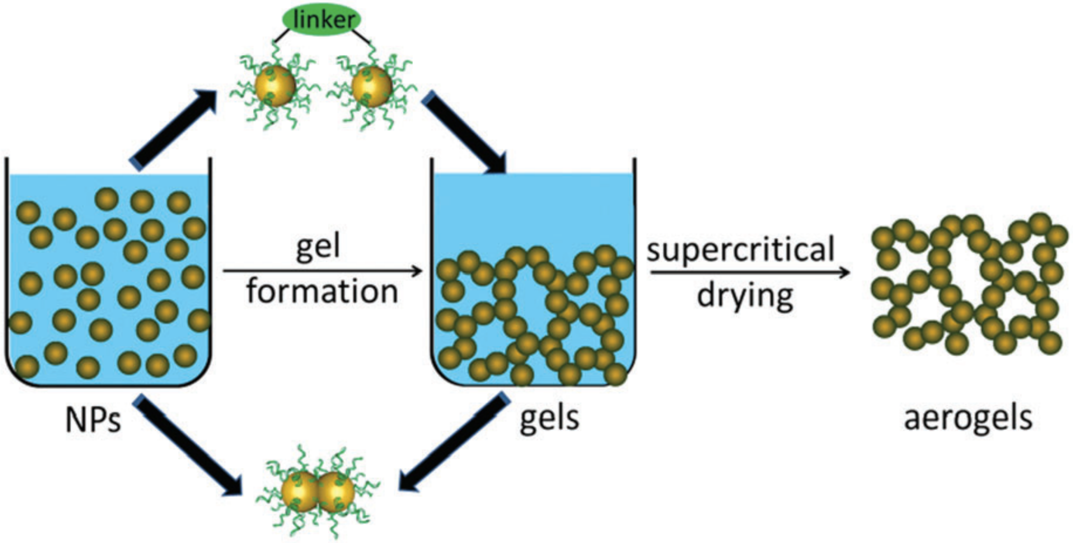


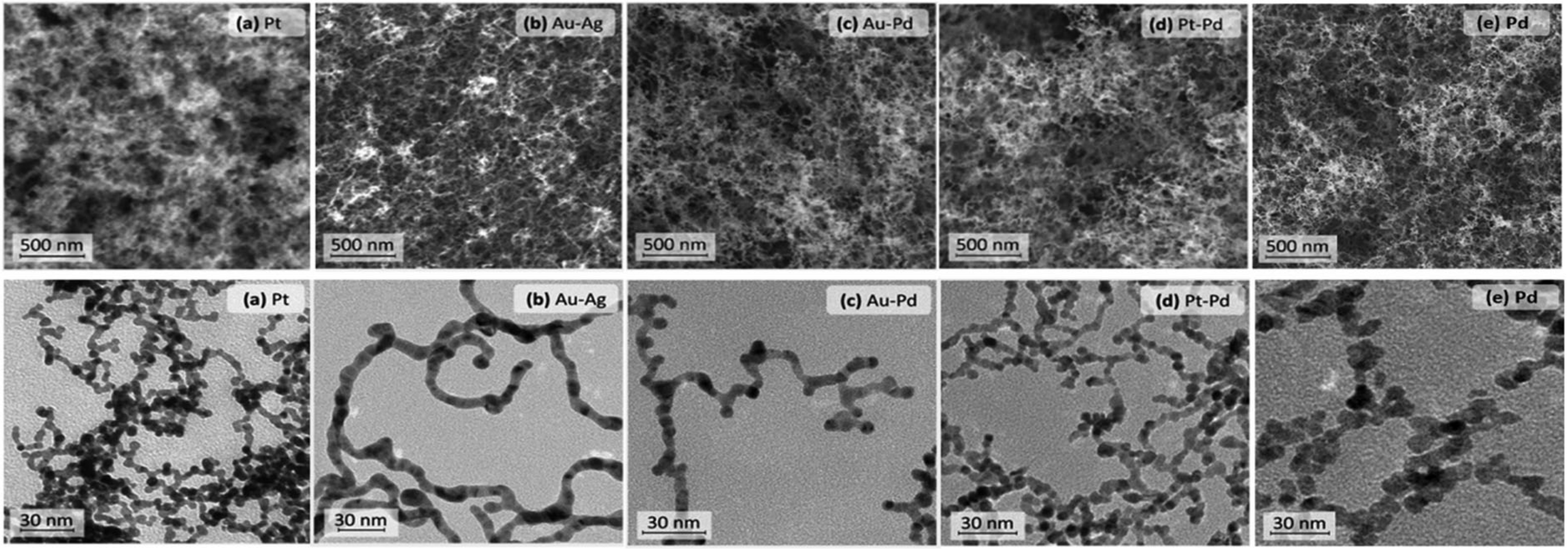
K is the reaction rate of CO oxidation expressed as rate of CO_2 production

Murray et al. *JACS* (**2013**)

6.4. Nanocrystal ASSEMBLIES

AEREOGELS



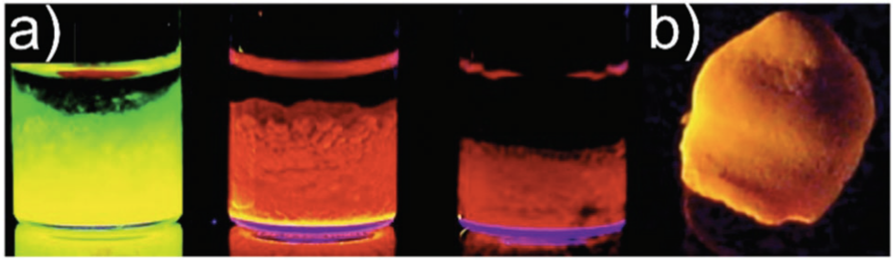


Eychmuller et al. *Chem. Comm* (**2017**)

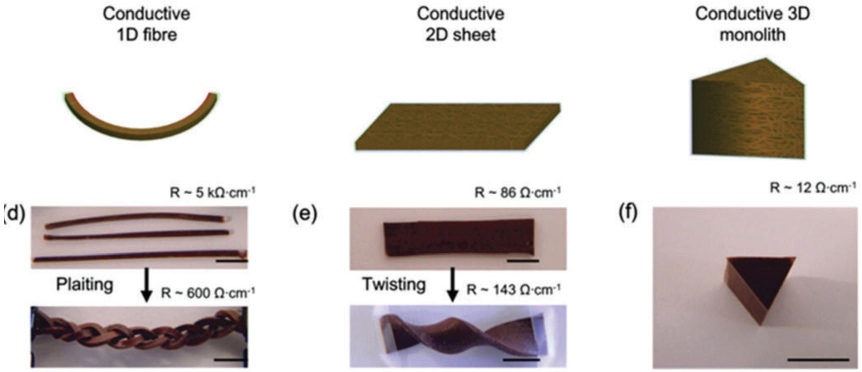
6.4. Nanocrystal ASSEMBLIES

AEREOGELS

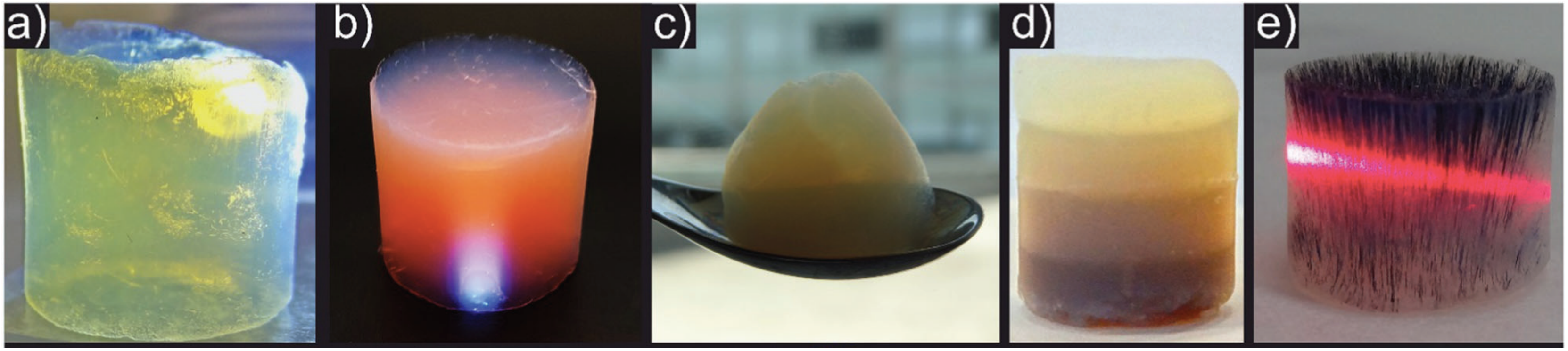
QDs-based gels



Cu NWs-PVA composite aereogels (conductive rubber)



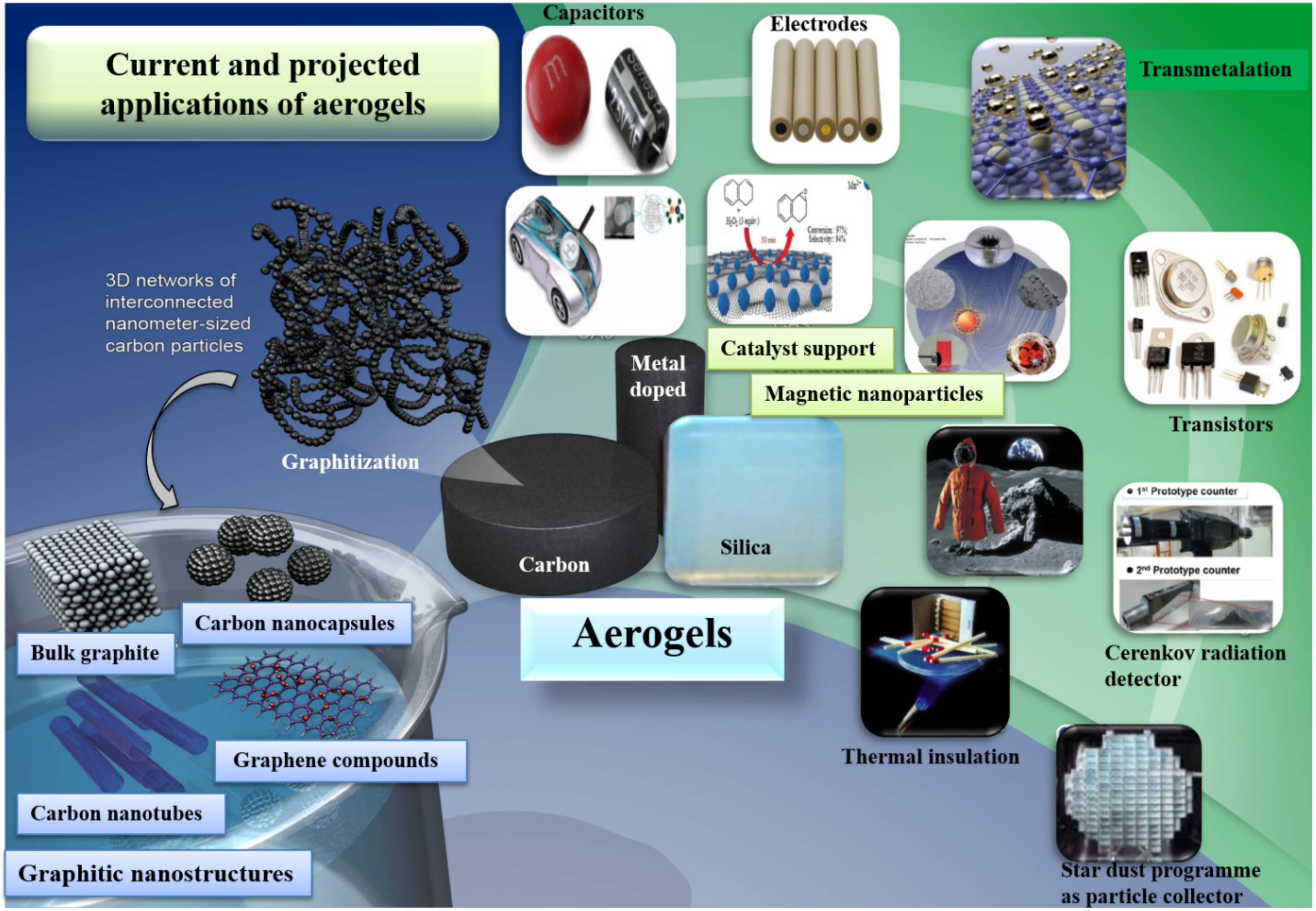
TiO_2 TiO_2 + Au TiO_2 + WO_3 TiO_2 + Fe_2O_3



Niederberger et al. *Nanoscale Horiz.* (**2017**)

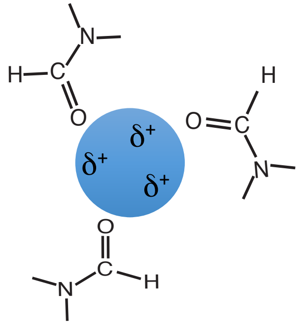
6.4. Nanocrystal ASSEMBLIES

AEREOGELS

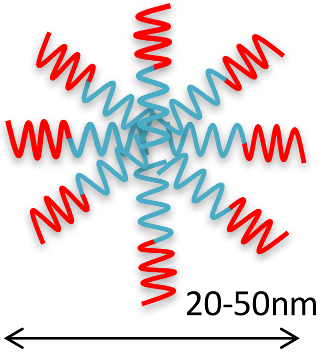


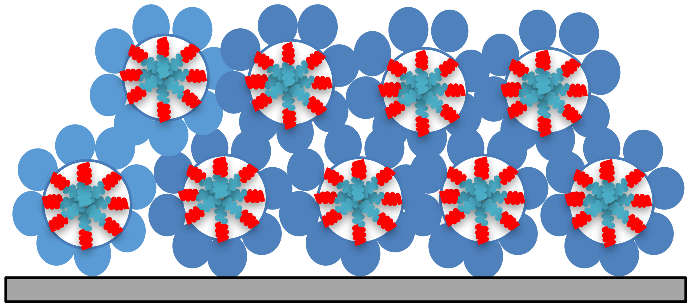
6.4. Nanocrystal ASSEMBLIES

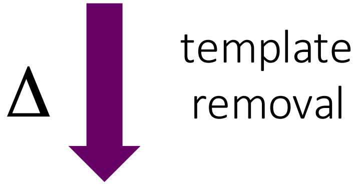
NANOCRYSTALS + POLYMERS



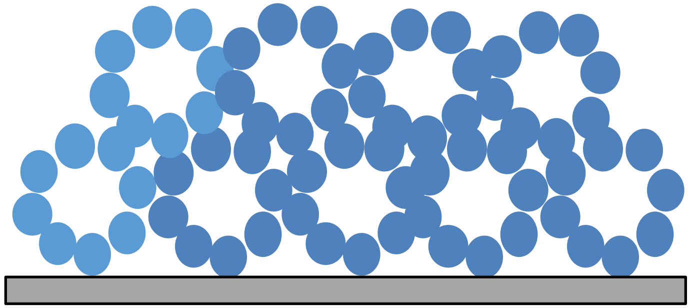
+





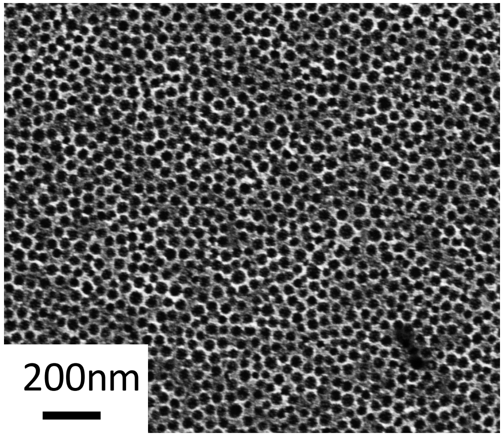


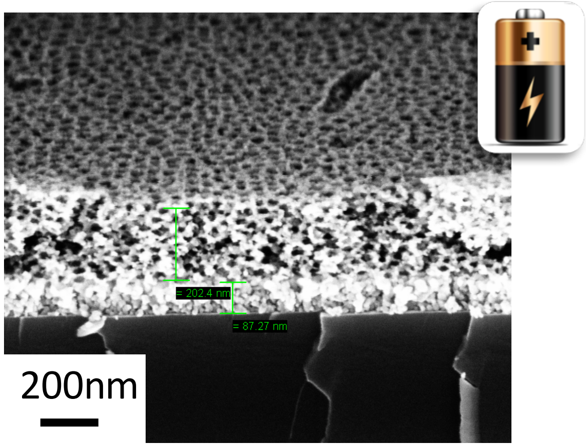
template removal



ligand-stripped NCs

micelles from **PS**-**PDMA** block copolymer

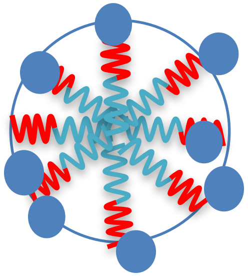


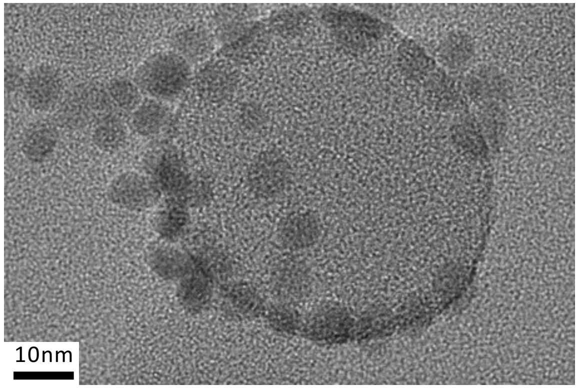


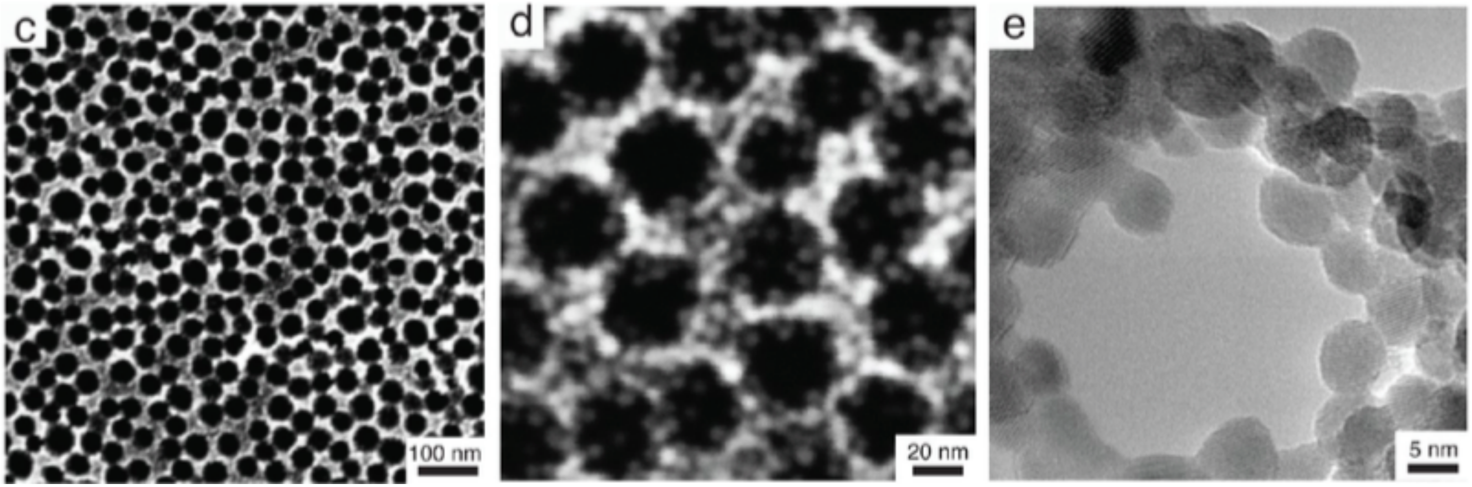
Buonsanti et al. *Nano Lett* (**2012**)

6.4. Nanocrystal ASSEMBLIES

NANOCRYSTALS + POLYMERS



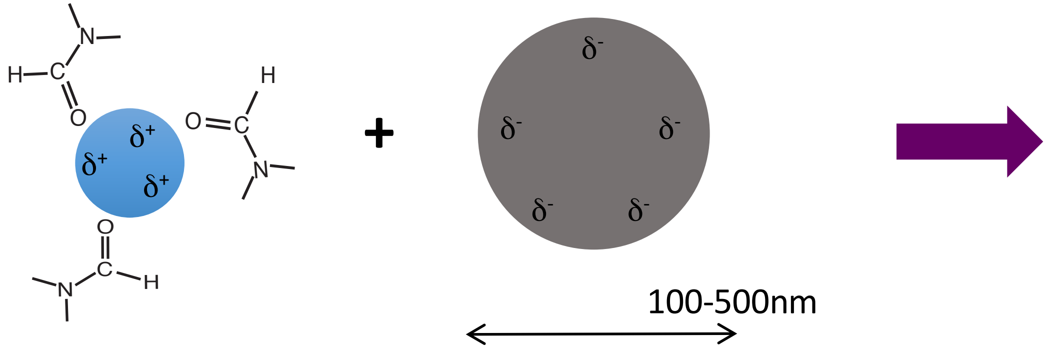




Buonsanti et al. *Nano Lett* (**2012**)

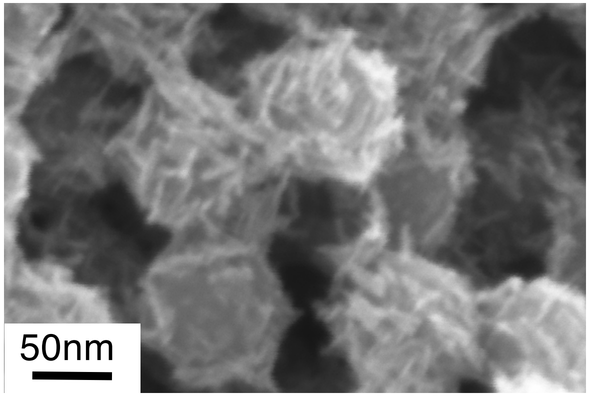
6.4. Nanocrystal ASSEMBLIES

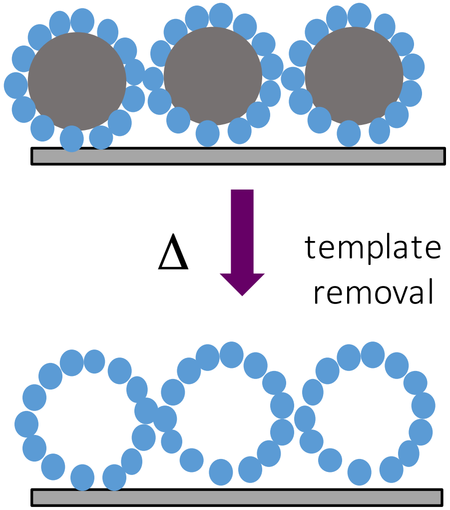
NANOCRYSTALS + POLYMERS



ligand-stripped NCs

PS beads





template removal