Ligands: Tools for the nano-goldsmith

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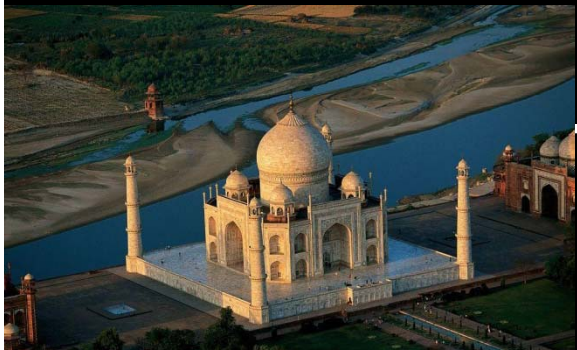
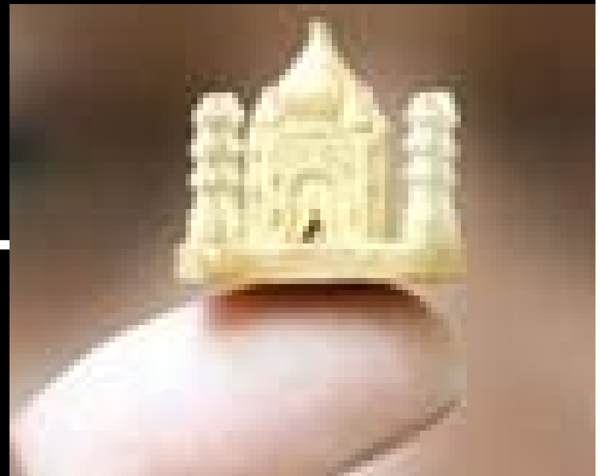
Miniaturization in art

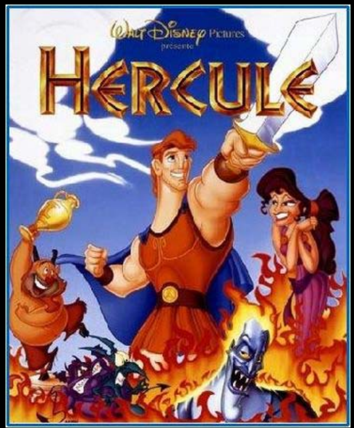
Nano comes from the greek word “na

O MAKE SO

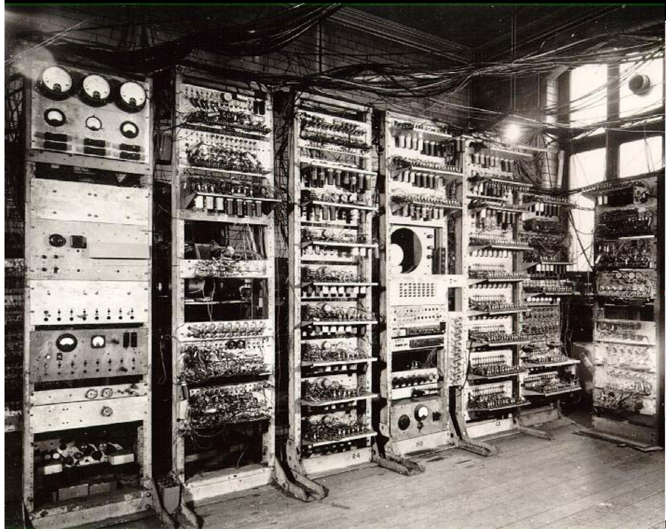




Can something "big" be done by becoming "small"?



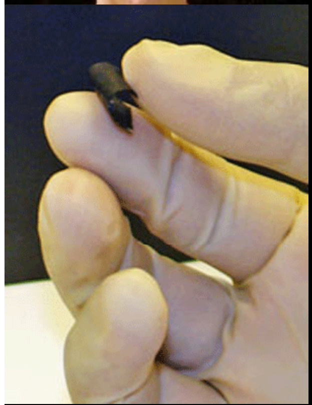
Miniaturization in science and technology

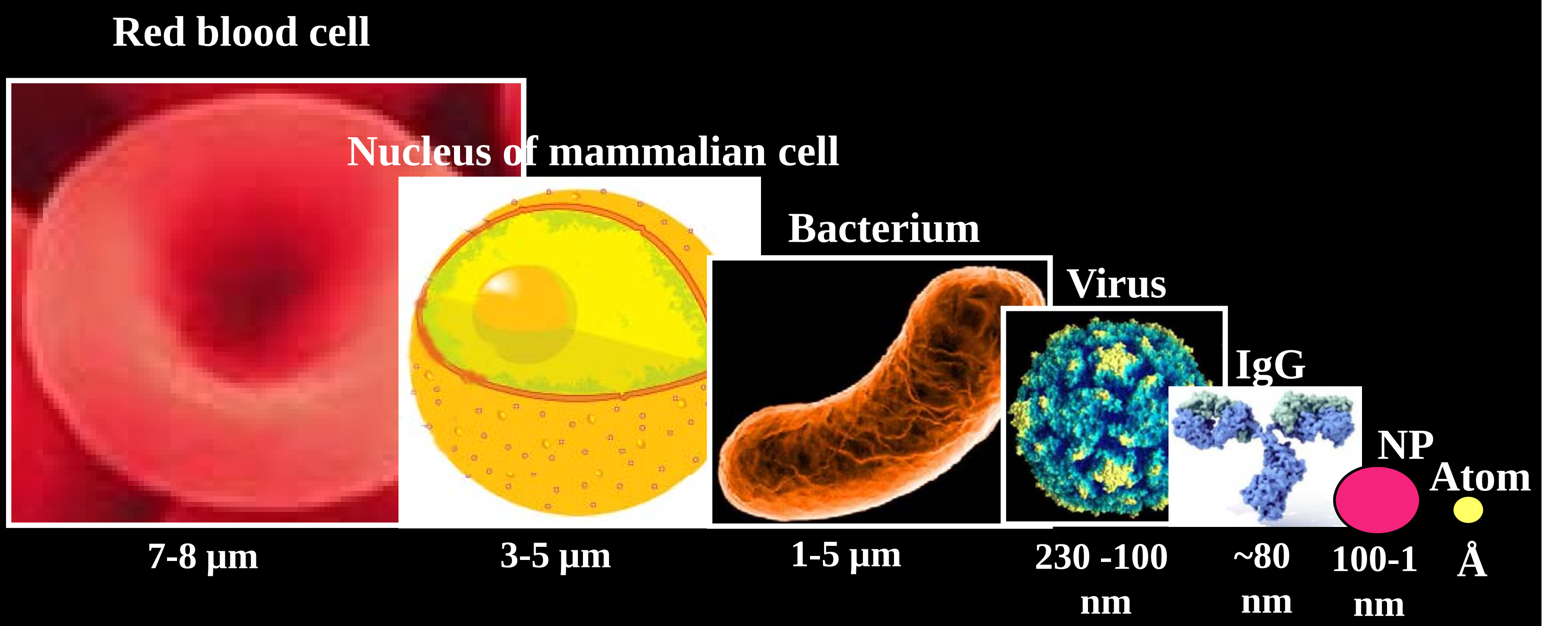


So what is nano for scientists?

Nano comes from the greek word "nanos" meaning dwarf.

In scientific terms it corresponds to 10^{-9} units



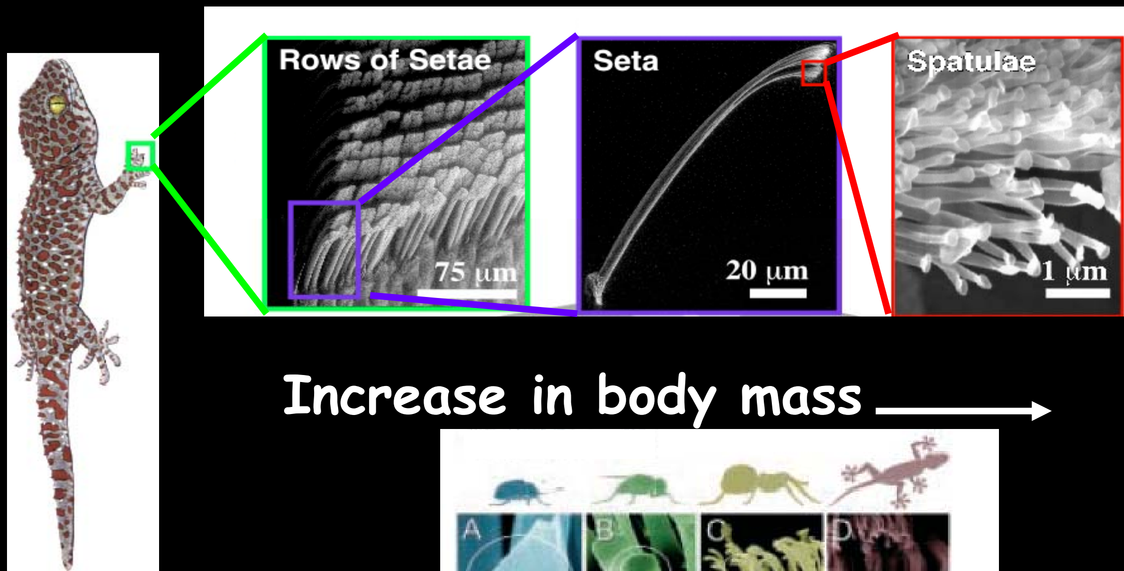


Nanometer

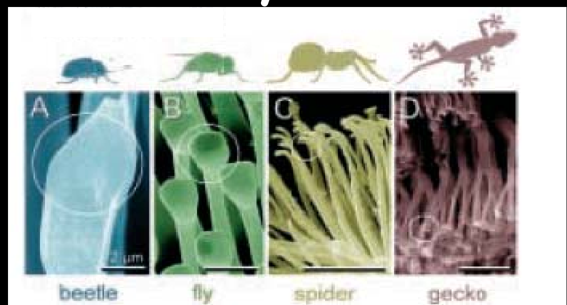
"a magical point on the length scale, for this is the point where the smallest man-made devices meet the atoms and molecules of the natural world"

-– Eugene Wang, 1999

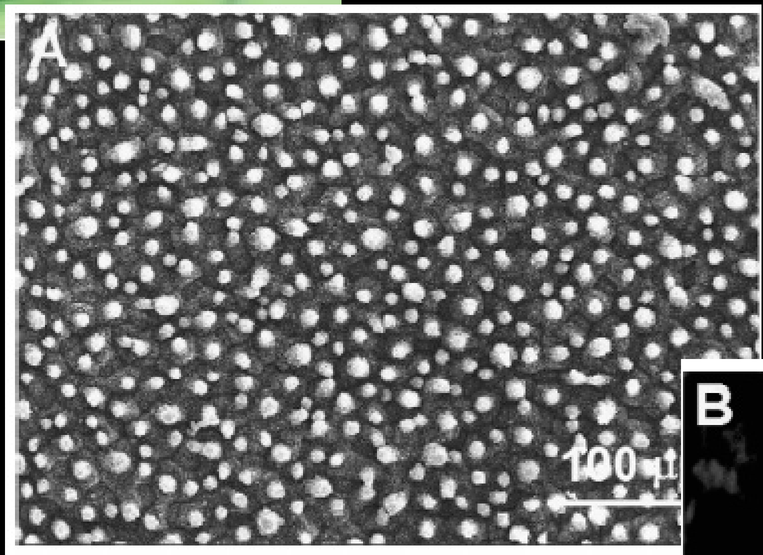
Interesting thing about Gecko feet

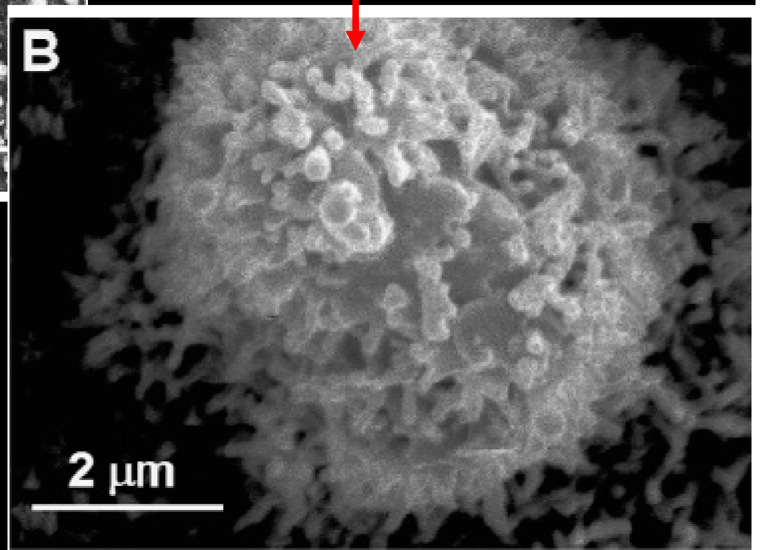


Increase in body mass →



Superhydrohpbic surfaces : lotus leaf





every epidermal
cell forms a papilla

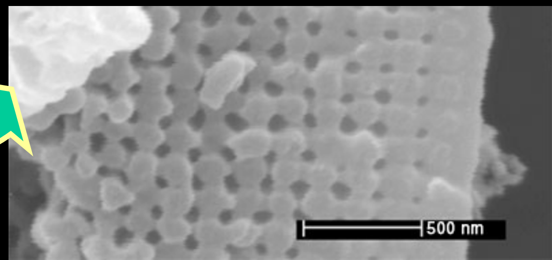
each papilla has a dense layer of
epicuticular waxes superimposed on it.

Acc. Chem. Res. 2005, 38, 644-652

Colours of peacock feathers

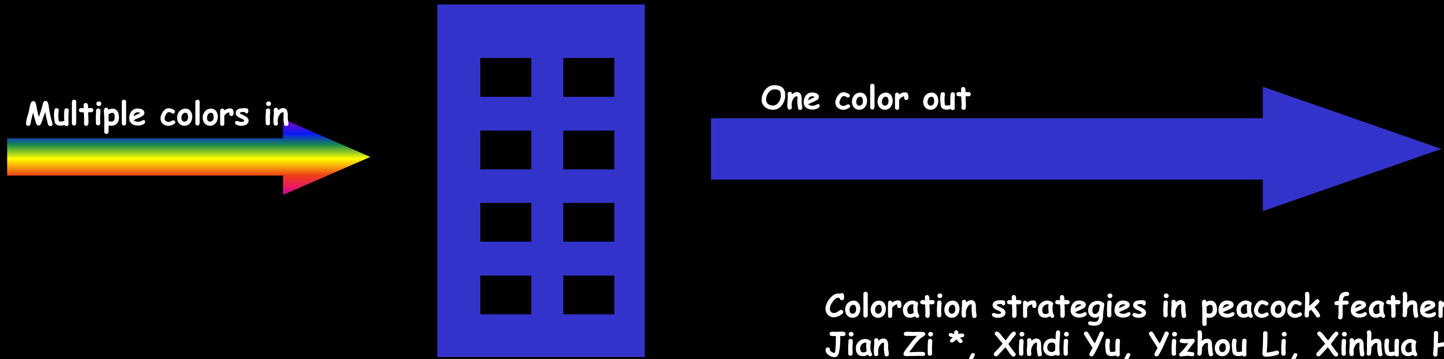
Peacock

What our eyes see



What a microscope sees

Colours of peacock feathers



Coloration strategies in peacock feathers

Jian Zi *, Xindi Yu, Yizhou Li, Xinhua Hu, Chun Xu, Xingjun Wang, Xiaohan Liu *, and Rongtang Fu
Surface Physics Laboratory (National Key Laboratory) and T-Center for Life Sciences, Fudan University, Shanghai 200433, People's Republic of China

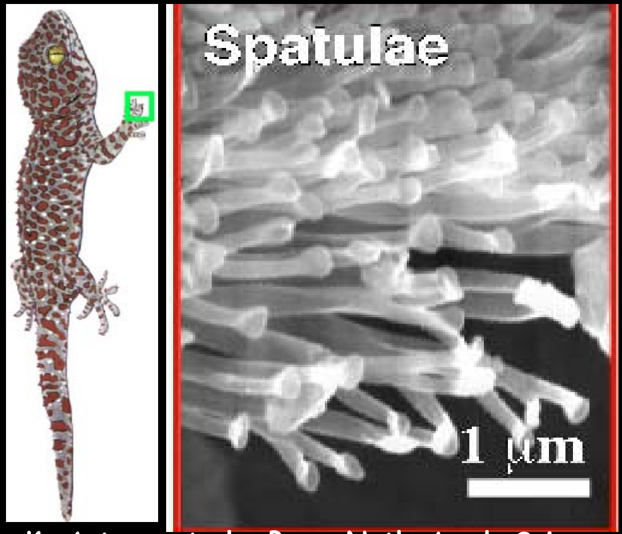
August 26, 2003

We report the mechanism of color production in peacock feathers. We find that the cortex in differently colored barbules, which contains a 2D photonic-crystal structure, is responsible for coloration. Simulations reveal that the photonic-crystal structure possesses a partial photonic bandgap along the direction normal to the cortex surface, for frequencies within which light is strongly reflected. Coloration strategies in peacock feathers are very ingenious and simple: controlling the lattice constant and the number of periods in the photonic-crystal structure. Varying the lattice constant produces diversified colors. The reduction of the number of periods brings additional colors, causing mixed coloration.

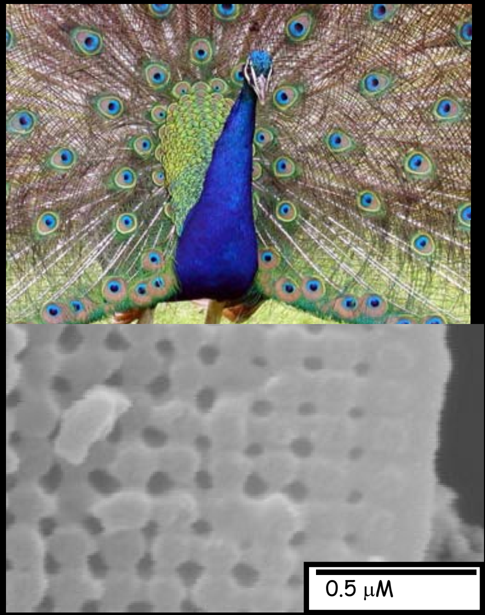
Peacock

J. Zi et al., Proc. Natl. Acad. Sci. U.S.A. 100, 12576 (2003)

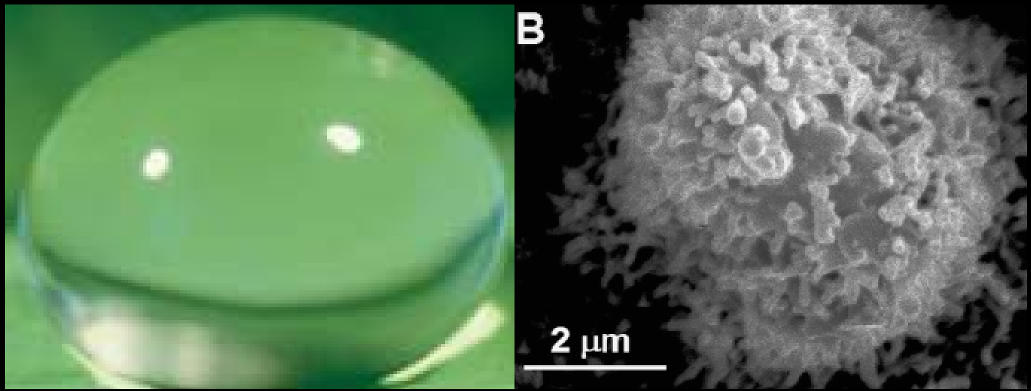
What is causing?



K. Autumn et.al., Proc. Natl. Acad. Sci. U.S.A. 99, 12252 (2002)



J. Zi et al., Proc. Natl. Acad. Sci. U.S.A. 100, 12576 (2003)



Acc. Chem. Res. 2005, 38, 644-652

A length scale smaller than micro

nano

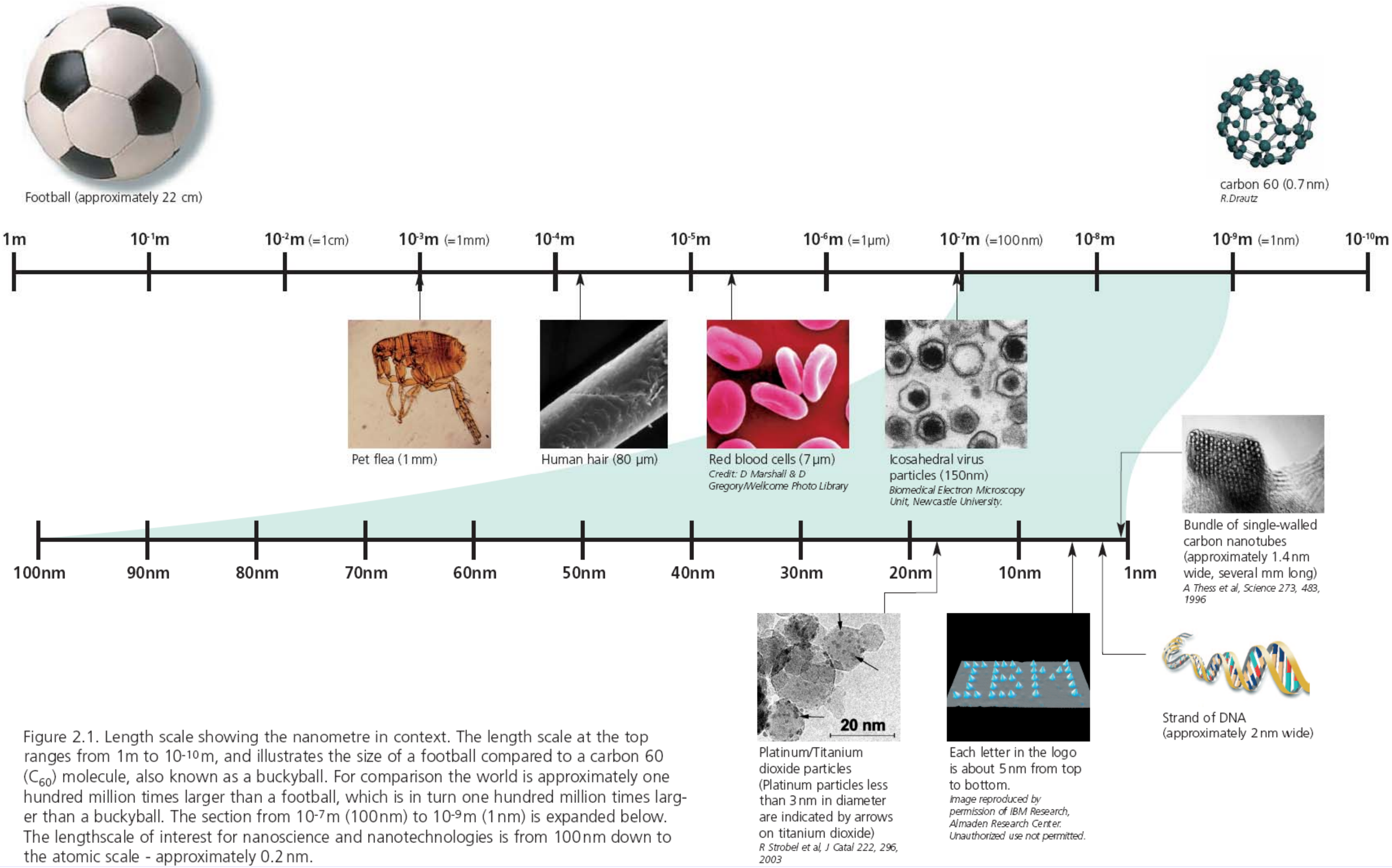
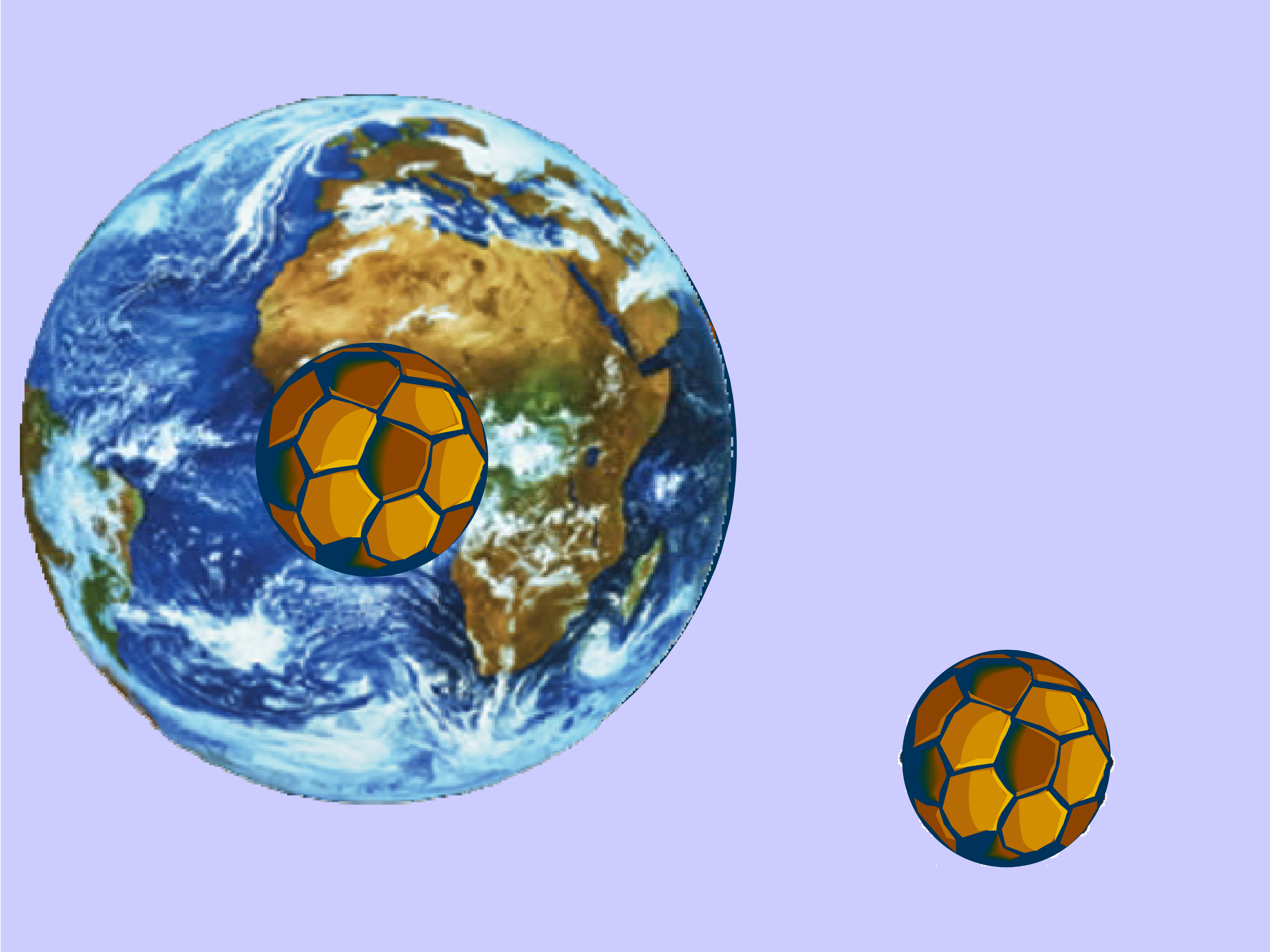


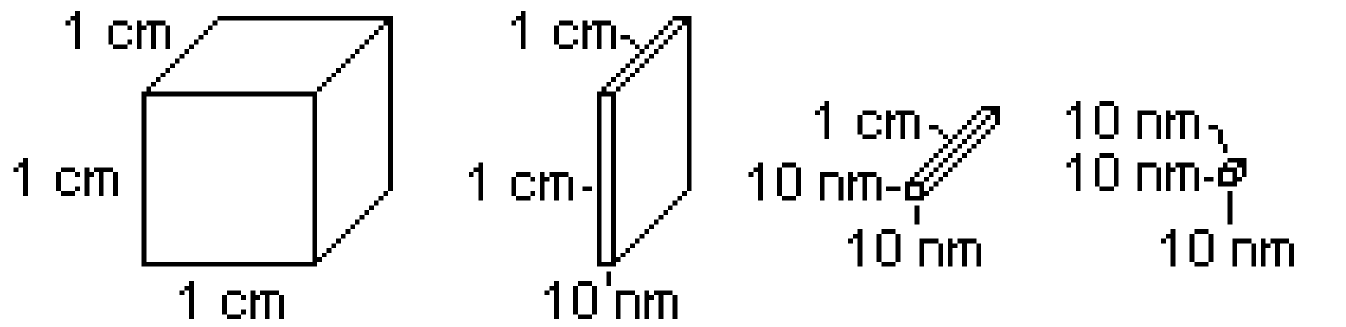
Figure 2.1. Length scale showing the nanometre in context. The length scale at the top ranges from 1m to 10^{-10}m, and illustrates the size of a football compared to a carbon 60 (C_{60}) molecule, also known as a buckyball. For comparison the world is approximately one hundred million times larger than a football, which is in turn one hundred million times larger than a buckyball. The section from 10^{-7}m (100nm) to 10^{-9}m (1nm) is expanded below. The lengthscale of interest for nanoscience and nanotechnologies is from 100nm down to the atomic scale - approximately 0.2nm.



Why nanometer?

State of Subdivision

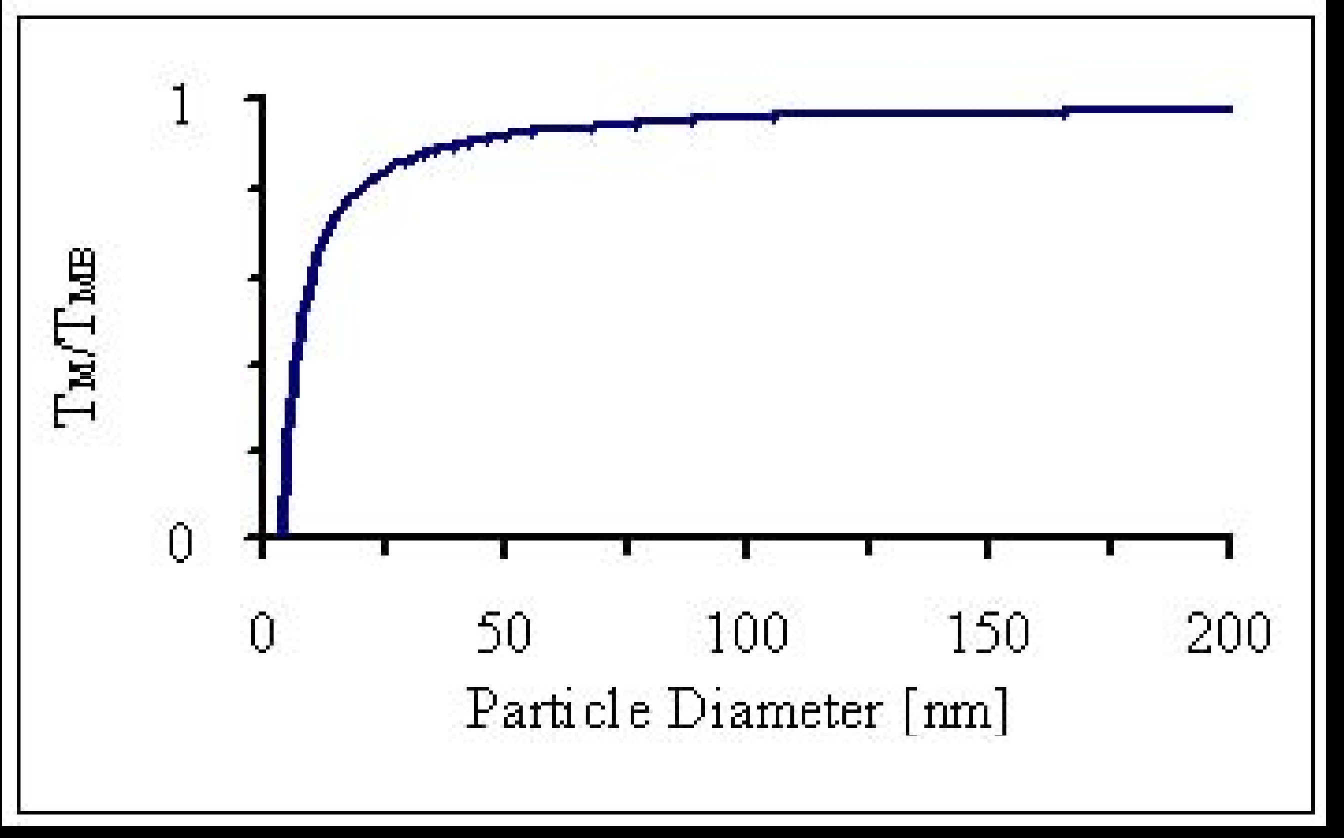
	mass	laminated	fibrillar	corpuscular



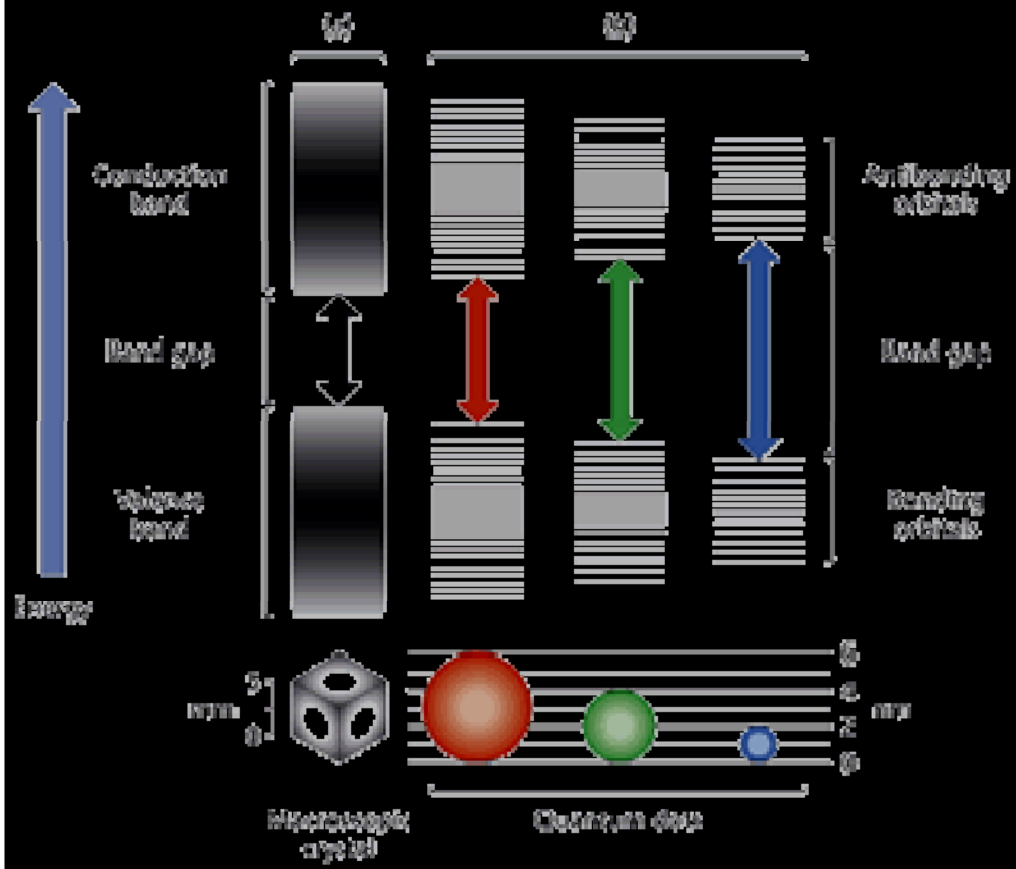
	mass	laminated	fibrillar	corpuscular
N	1	10^6	10^{12}	10^{18}
A_1, m^2	6×10^{-4}	2×10^{-4}	4×10^{-10}	6×10^{-16}
A, m^2	6×10^{-4}	200	400	600

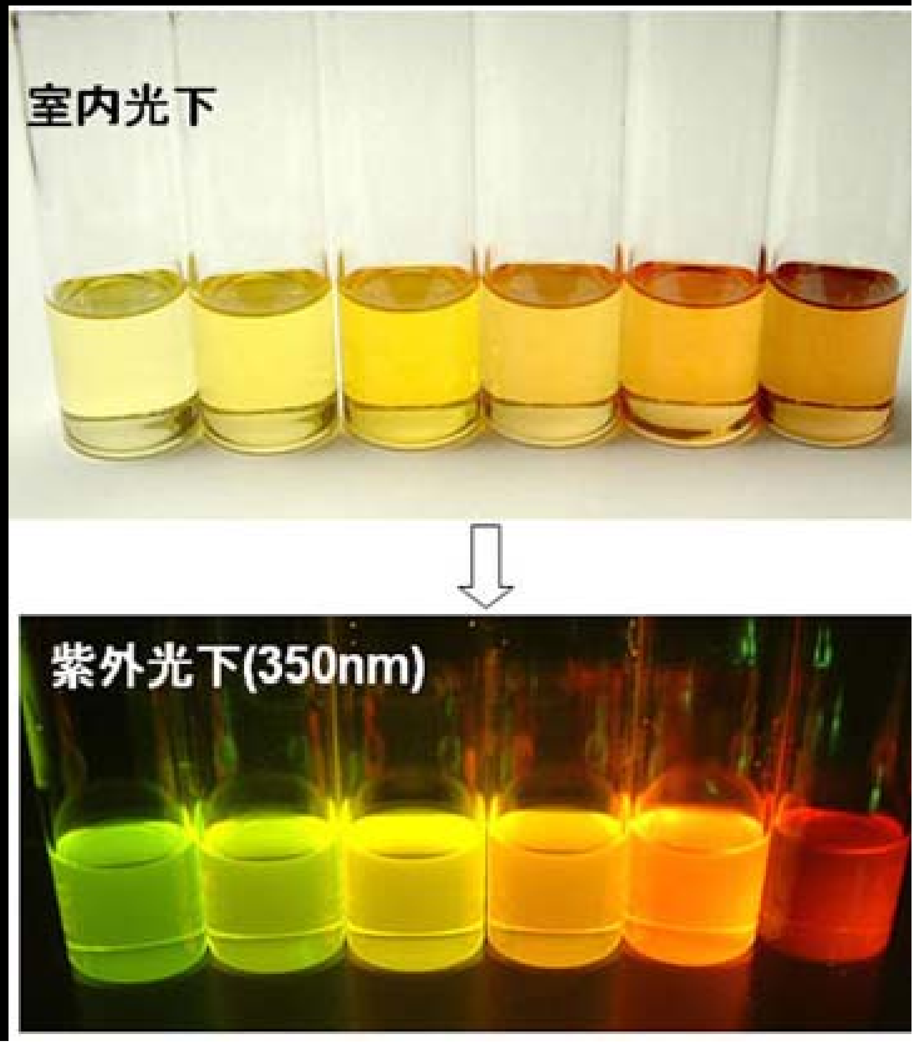
State of Subdivision and Total Area

Why nanometer?

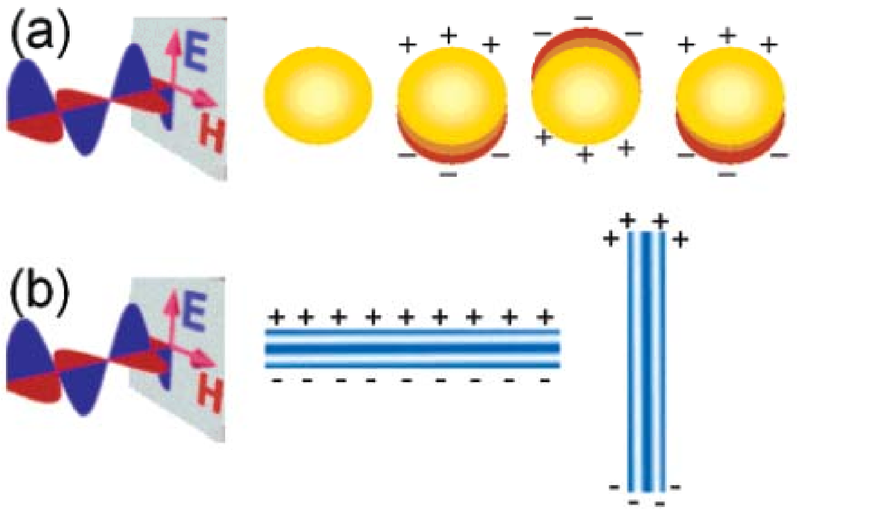


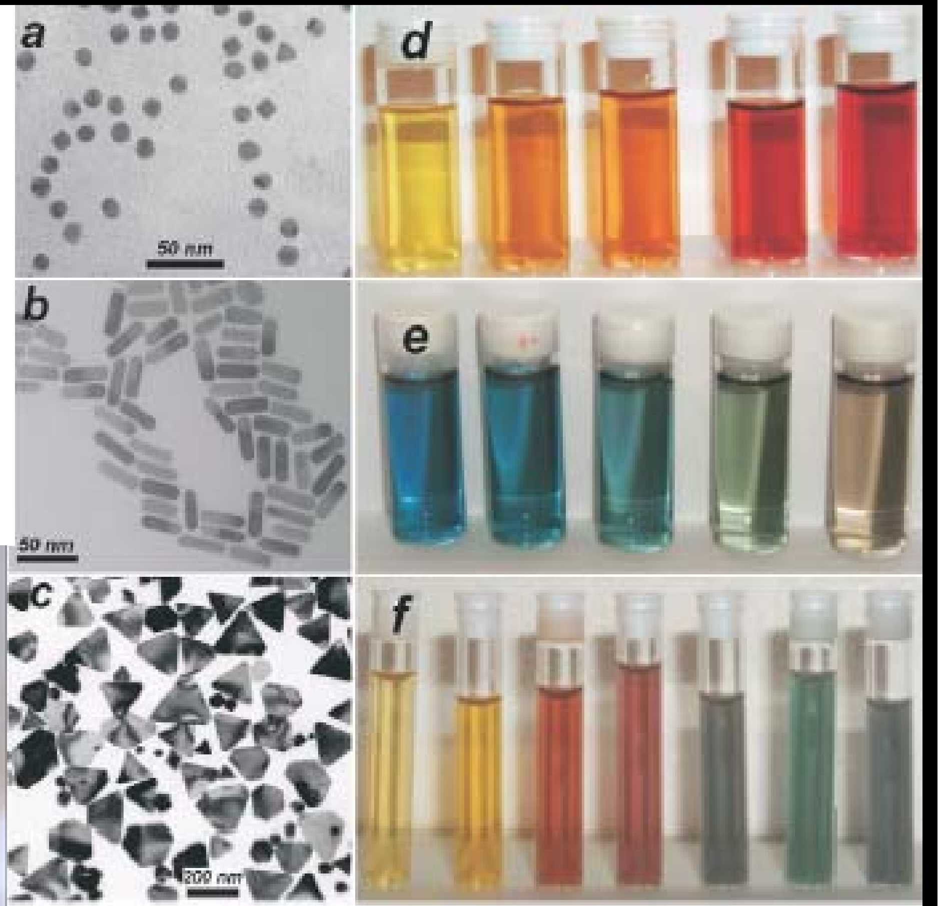
Why nanometer?

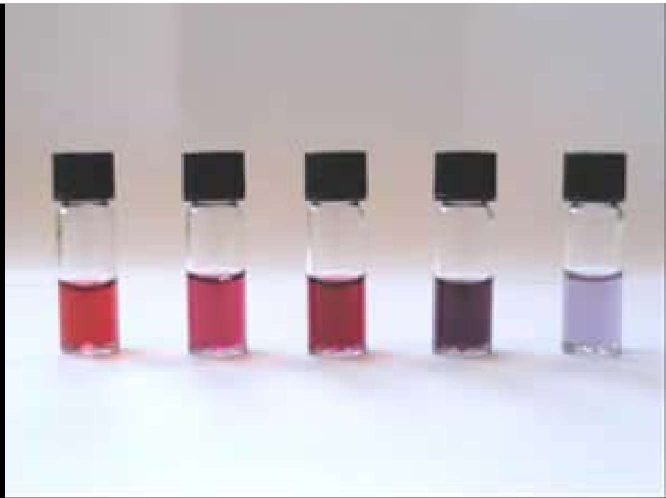


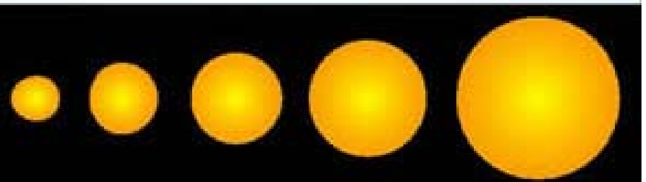


Why nanometer?









C. J. Murphy et. al. *J. Phys. Chem. B* 2005, *109*, 13857.
L. M. LizMarzan *Mater. Today* 2004, 26

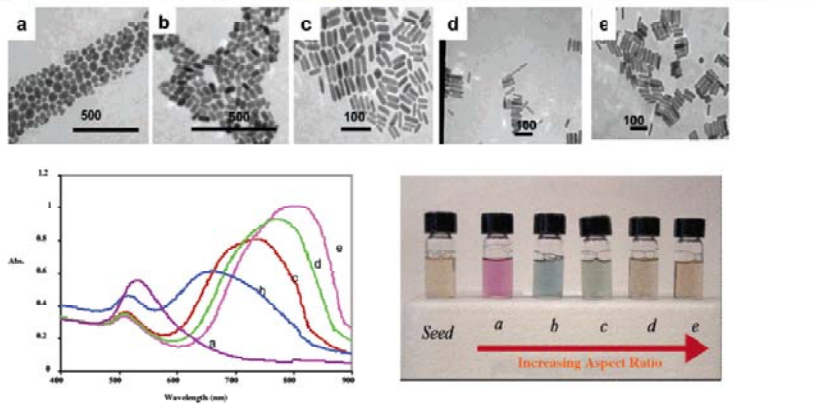


Figure 1. Transmission electron micrographs (top), optical spectra (left), and photographs of (right) aqueous solutions of gold nanorods of various aspect ratios. Seed sample: aspect ratio 1; sample a, aspect ratio 1.35 ± 0.32; sample b, aspect ratio 1.95 ± 0.34; sample c, aspect ratio 3.06 ±0.28; sample d, aspect ratio 3.50 ± 0.29; sample e, aspect ratio 4.42 ± 0.23. Scale bars: 500 nm for a and b, 100 nm for c, d, e.

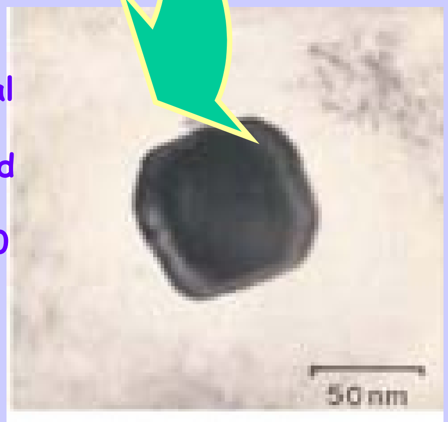
Nanoparticle colors

Lycurgus cup

Period : 4th Century AD

made by: Roman Glass makers

SEM image of a typical nanocrystal embedded in the glass Contains gold silver (7:1) alloy nanoparticles (~70 nm)
courtesy of the British museum.



European panel, 1564

"colloid" term coined

Electron microscopes developed

500 - BC Lycurgus cup

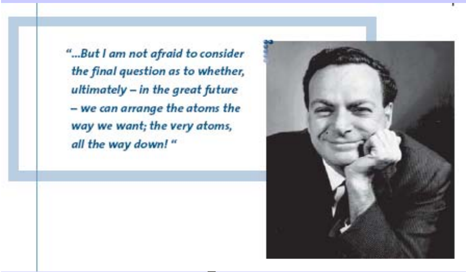
1857 Faraday

1861

1895 -1925

1930-40

Zsigmondy's work on colloids



"Nanotechnology" term coined

1959 Feynman Lecture

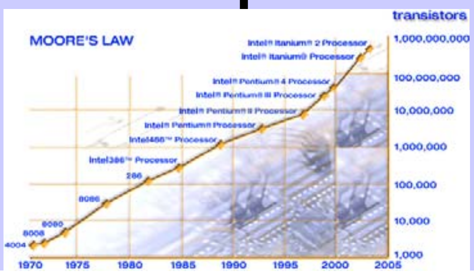
1965 Moore's law

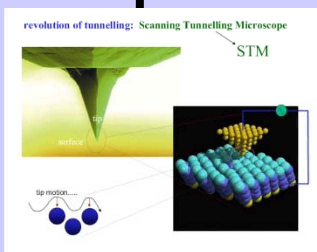
1974

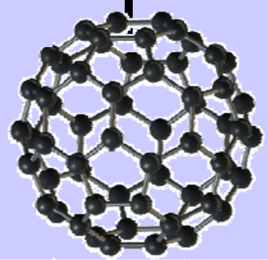
1980 STM/AFM

1980s q-dots

1985 C_{60} discovered







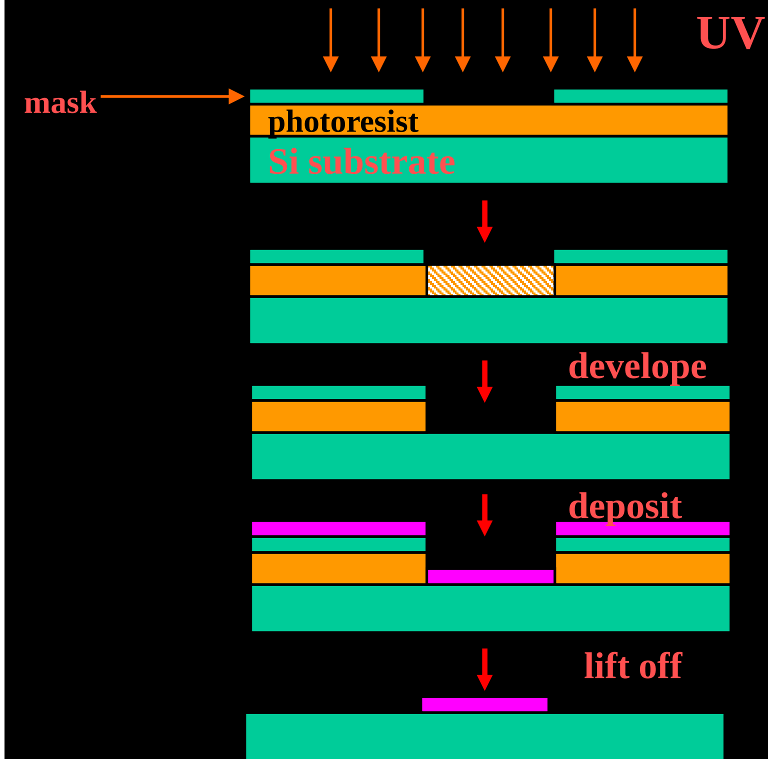
First scientific preparation

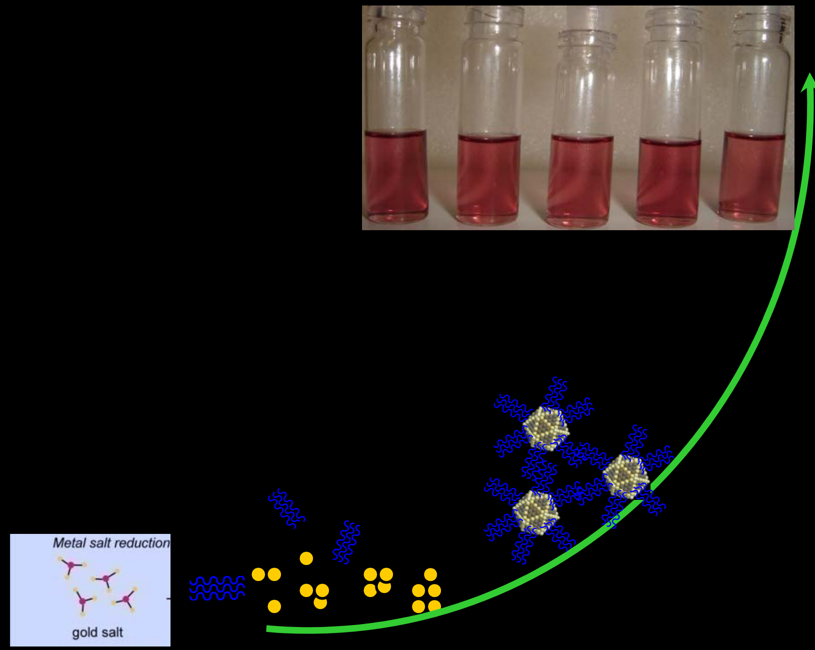
$HAuCl_4$ + P (in CS_2)

[5] In none of Faraday's papers—and there were over 460—is there a single equation. Faraday knew no algebra; he had left primary school at 13 years of age equipped only with the rudiments of "reading", "riting", and "rithmetic". Yet J. Clerk Maxwell is on record as having said that Faraday was one of the greatest of theoreticians[6] and Einstein declared him to be responsible with Clerk Maxwell for the greatest change in the intellectual framework of physics since Isaac Newton.

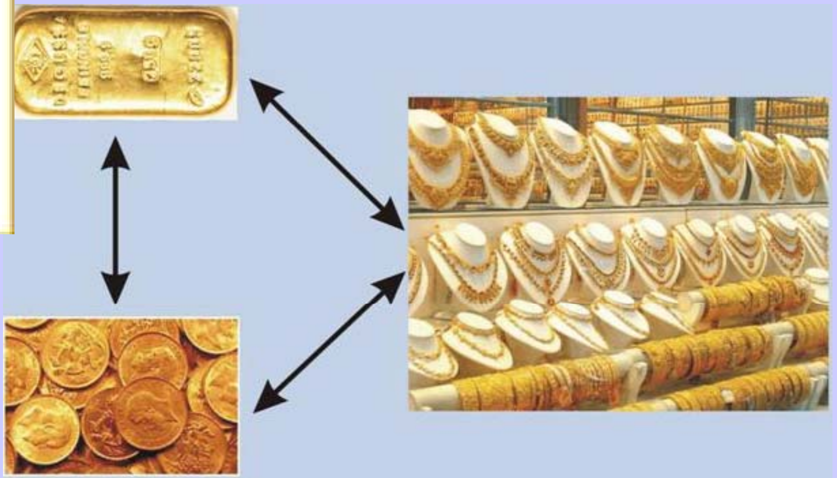
Faraday's gold sol, prepared in 1857
Still preserved in British Museum, London

Two methods of synthesis





What does a gold smith do?



Capabilities

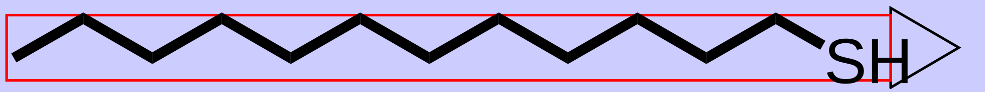
Au NPs in toluene+thiol

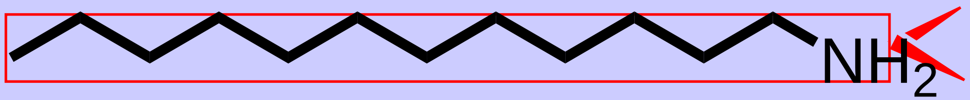
Gold ring toluene+thiol

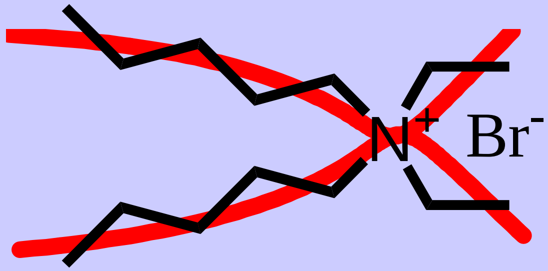
The "famous" ring experiment
Ken's lab, KSU December 2000

Faraday's gold sol, prepared in 1857
Still preserved in British Museum, London

Tools and Methods: Nanoscientist vs goldsmith

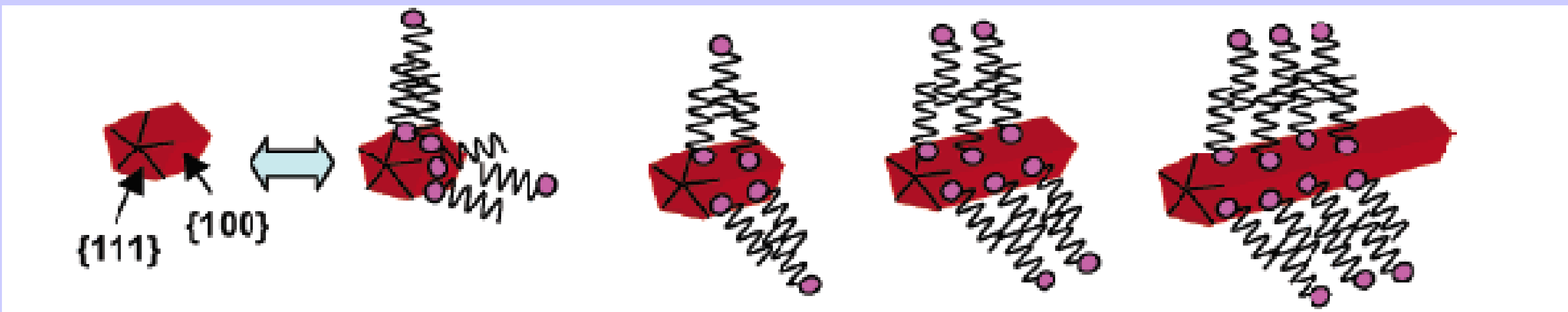




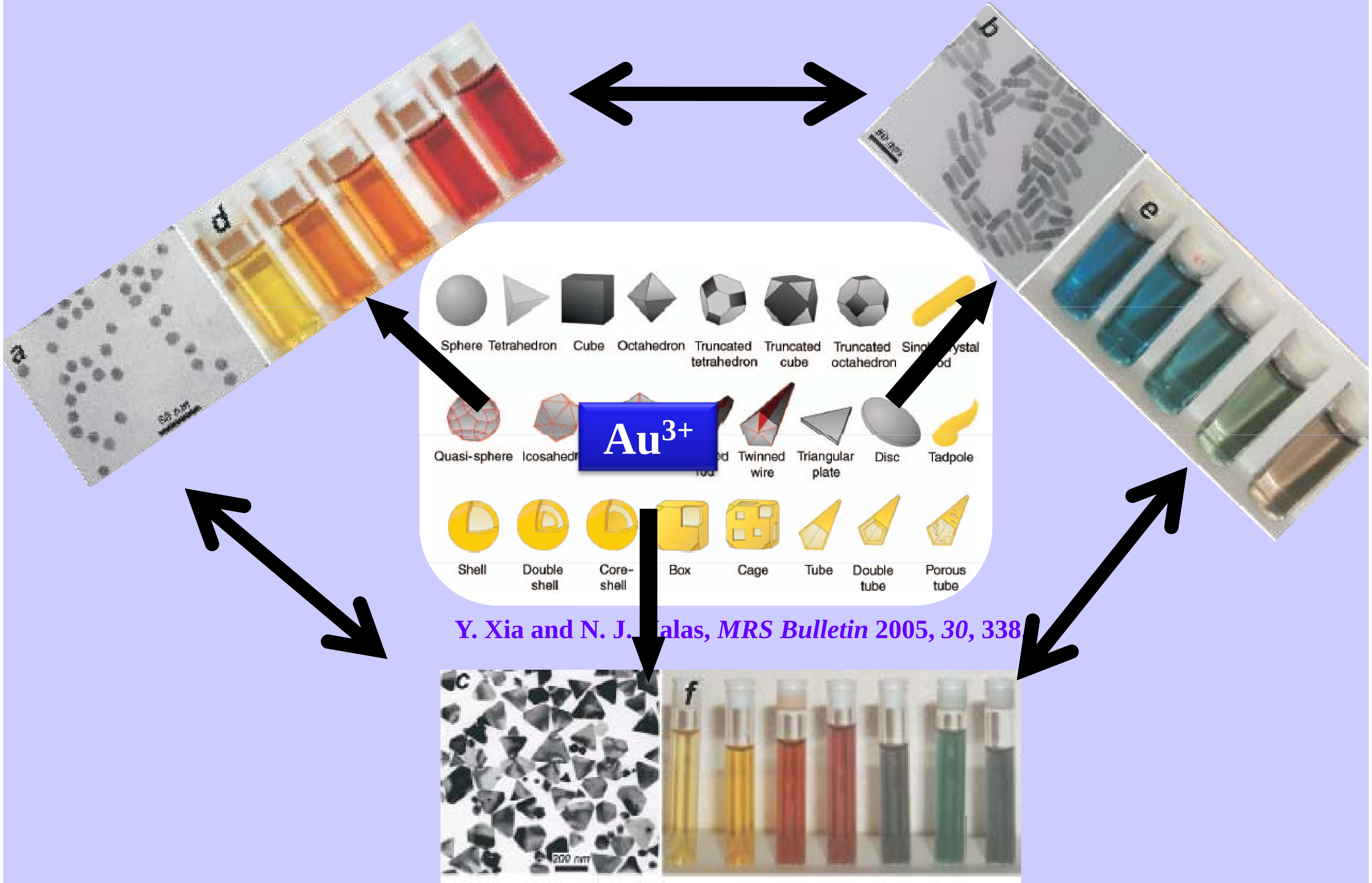


And

- Reactivity and stability of different crystallographic planes
- Ability of the above ligands to attach to gold surface (soft acid-soft base?)



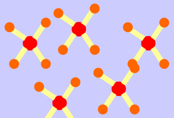
At the nanoscale



Y. Xia and N. J. Halas, *MRS Bulletin* 2005, *30*, 338.

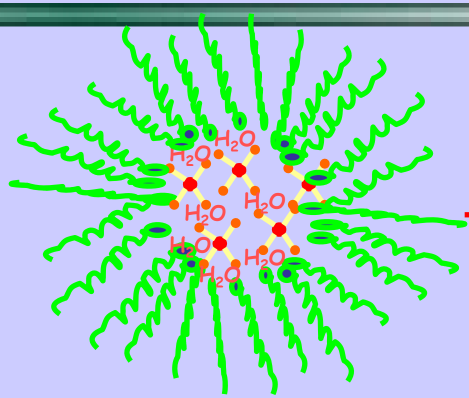
L. M. LizMarzan *Mater. Today* 2004, 26

Synthesis of Metal Nanoparticles



Metal ions
(in water)

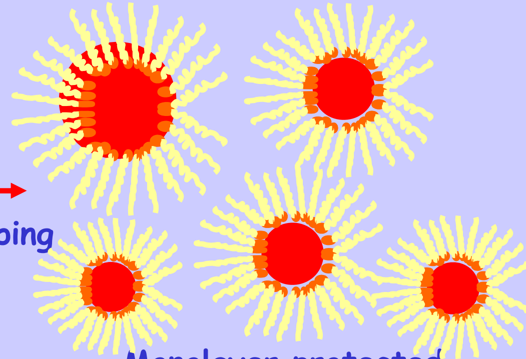
Surfactant



Reverse micelle

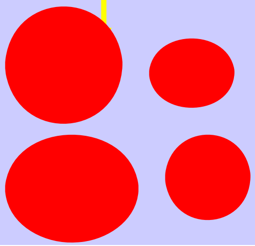
Reduction

Addition of capping agent



Monolayer protected
Metal nanoparticles

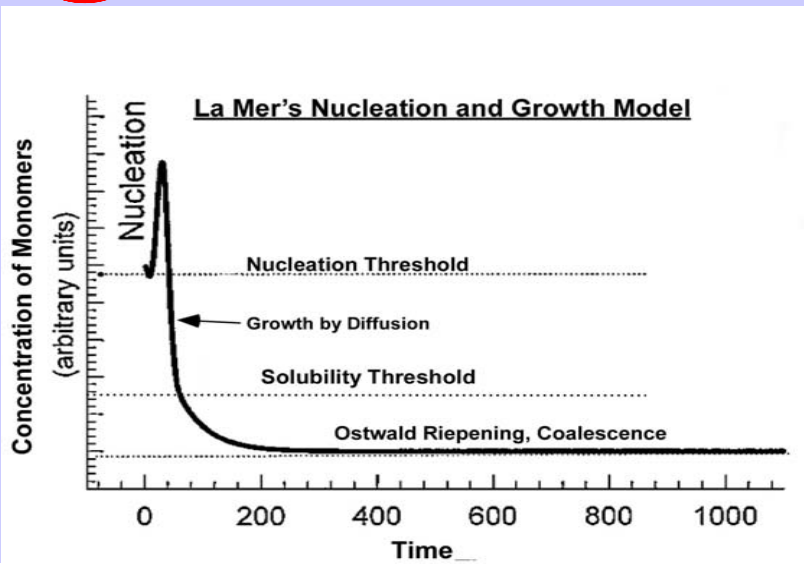
Reduction

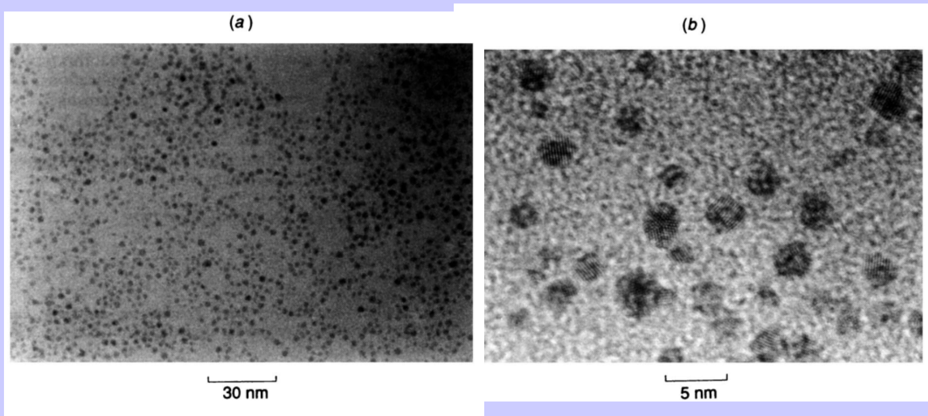


Aqueous
(citrate, biological synthesis etc.)

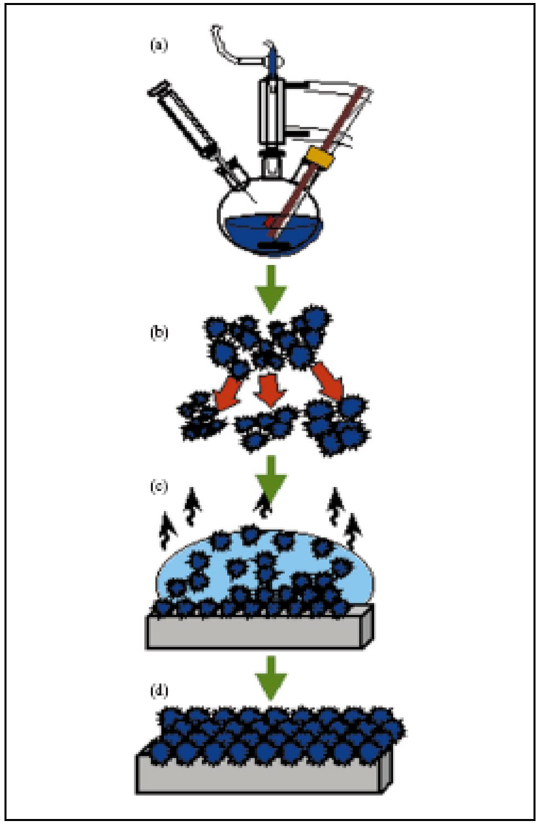
Brust et. al. 2004, Chem. Commun. 801.

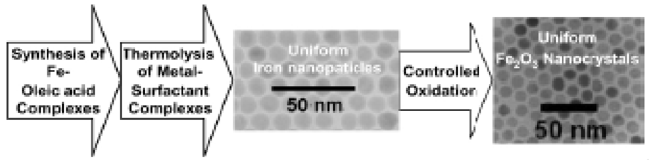
Organic
(Brust-Schriffrin method, reverse micelle process etc.)



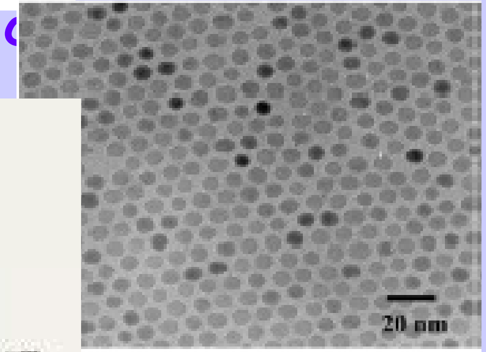


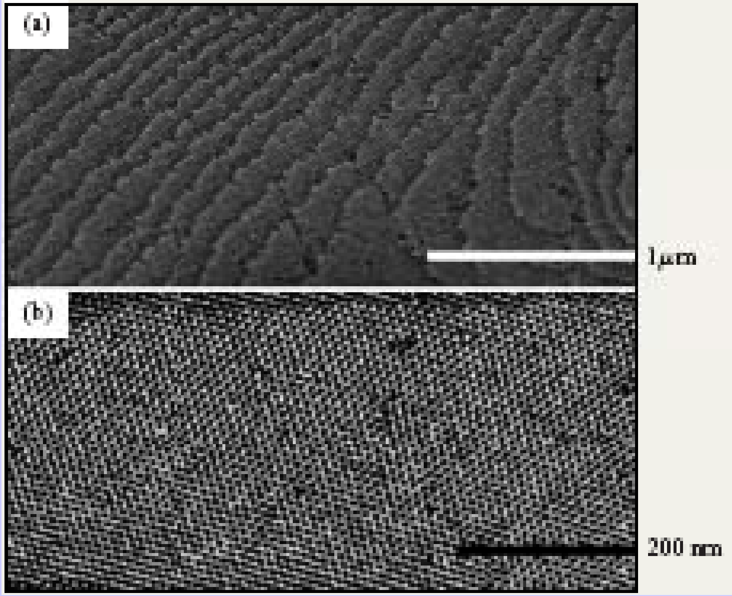
Foam based technique:background and importance



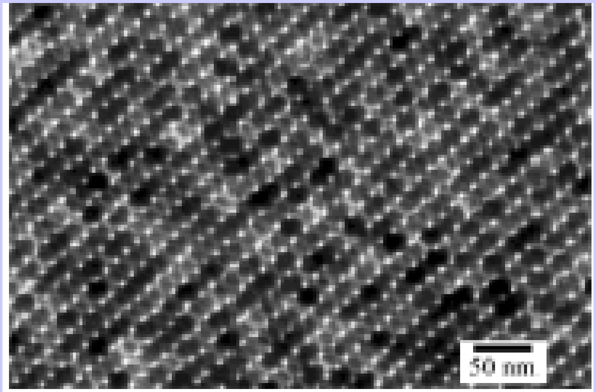


magnetic nanoparticles is c



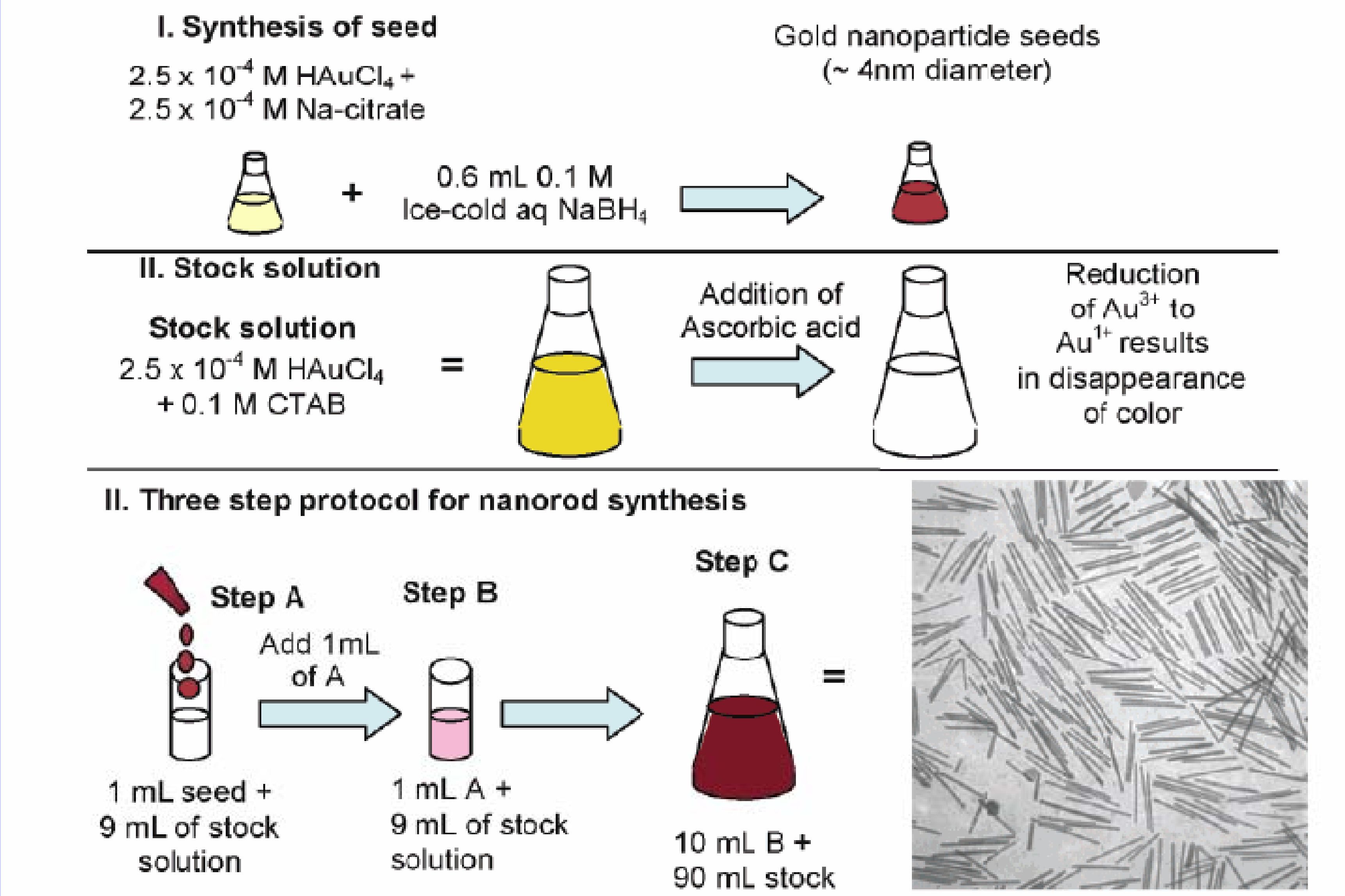


Schematic representation of the synthetic procedures to (a) synthesize NC samples by high-temperature solution-phase routes, (b) narrow the NC sample size distribution by size-selective precipitation, (c) deposit NC dispersions that self-assemble, and (d) form ordered NC assemblies (superlattices).

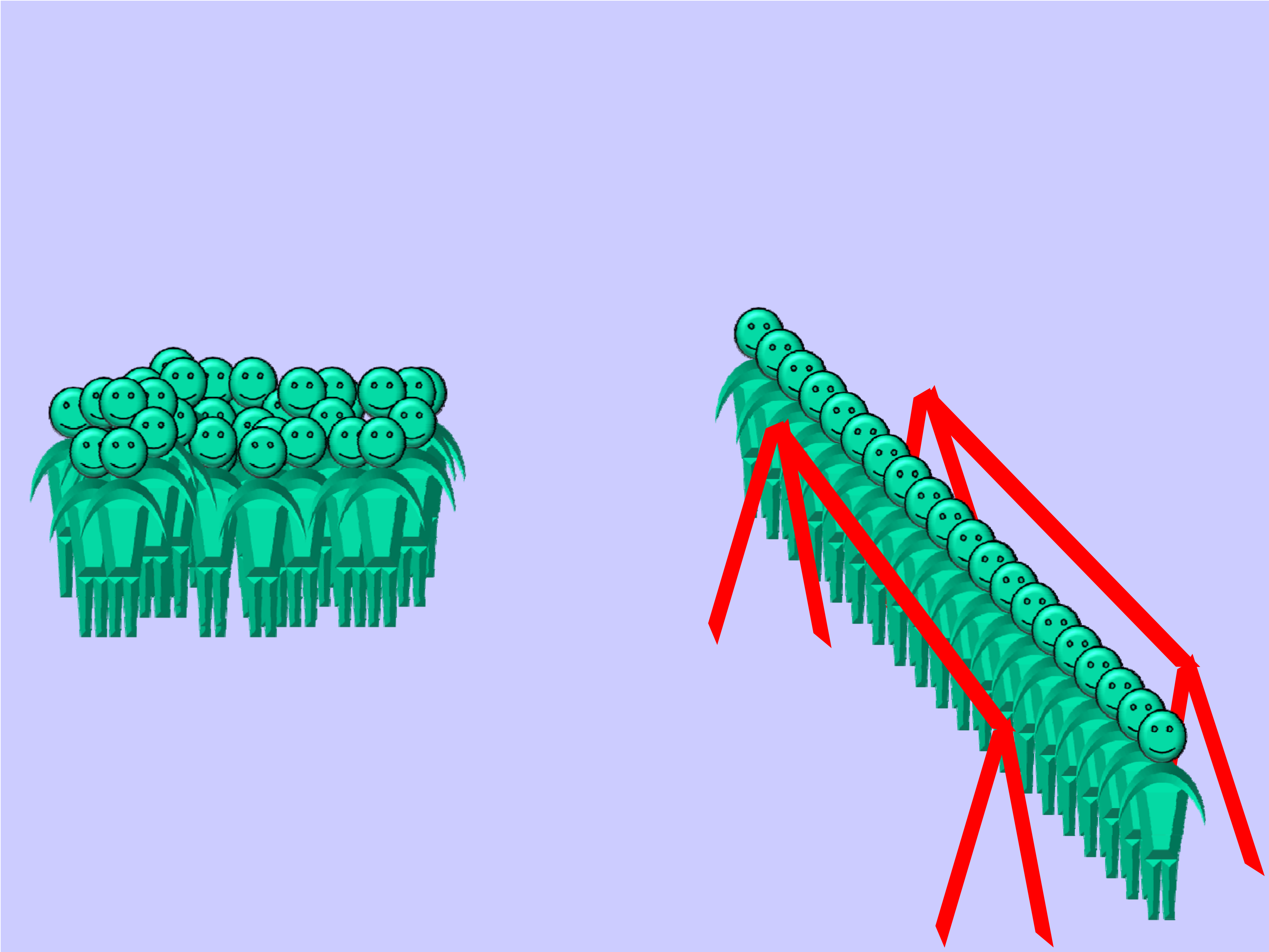


C. B. Murray Shouheng Sun W. Gaschler H. Doyle T. A. Betley C. R. Kagan, IBM J. RES. & DEV. 2001, *45*, 47.
T. Hyeon, CHEM. COMMUN., 2003, 927.

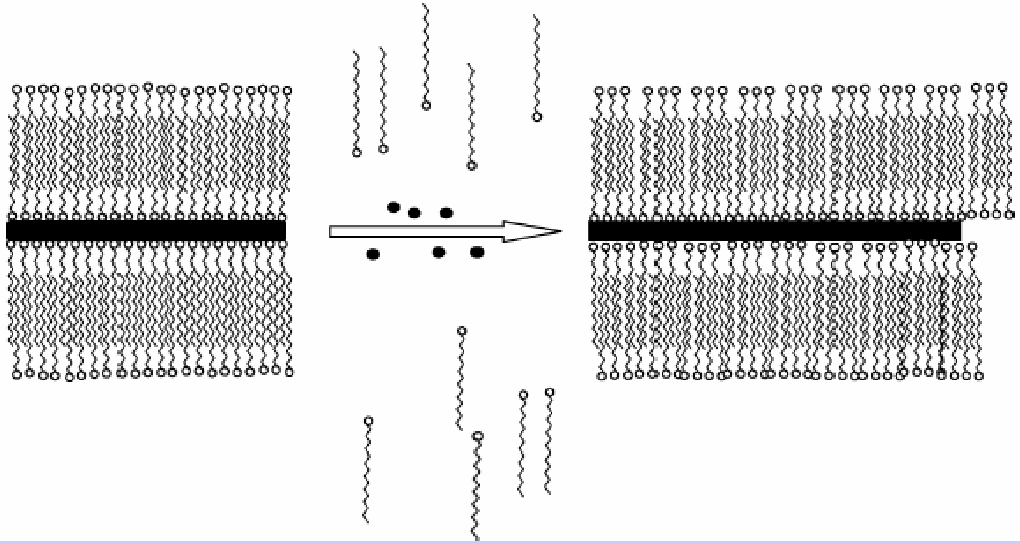
Growth of Au nanorods:Seed mediated growth method

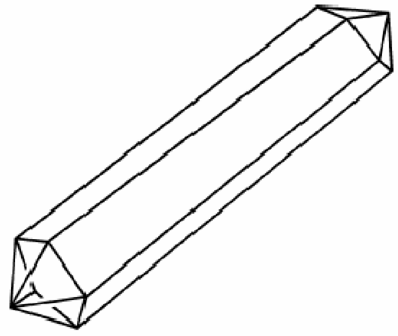


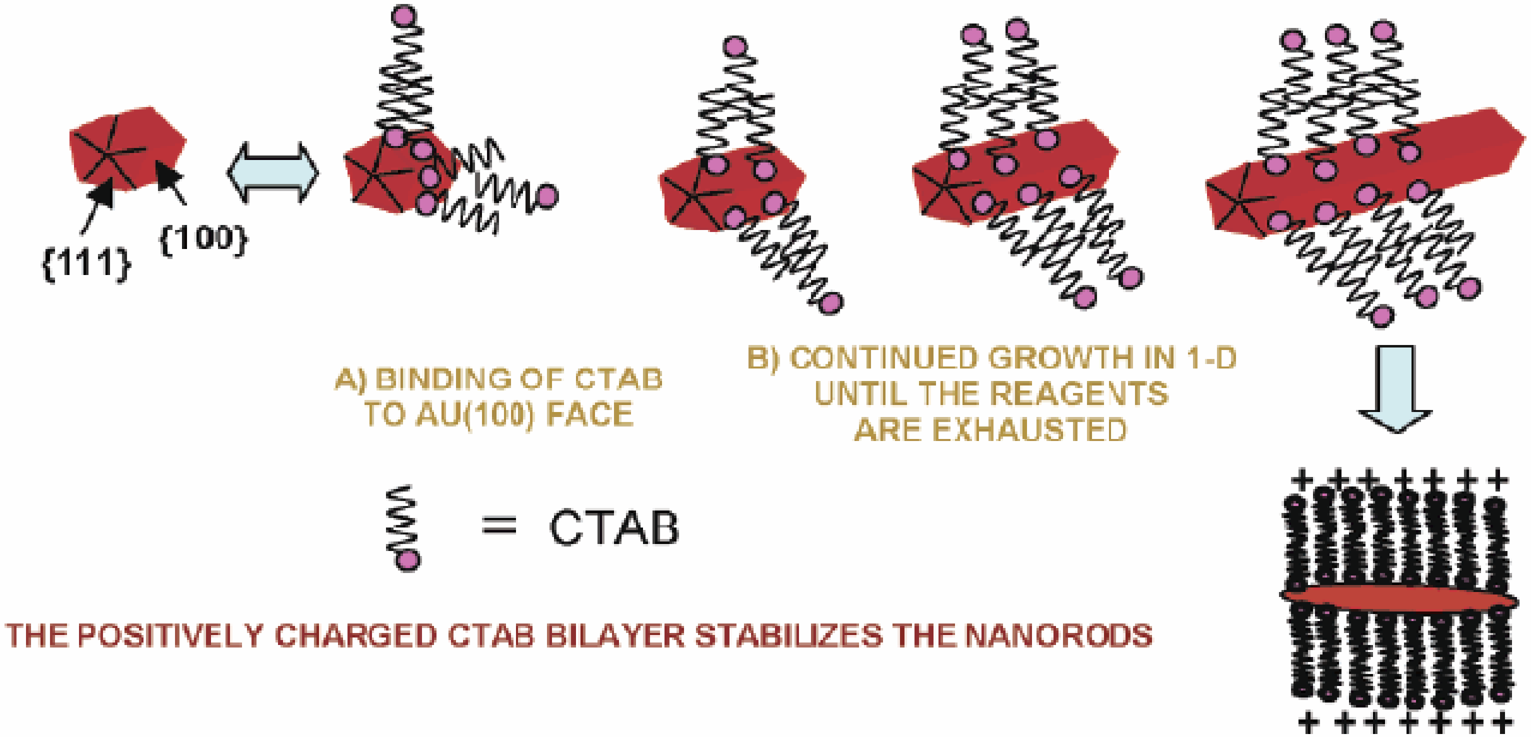
C. J. Murphy et. al. *J. Phys. Chem. B.*, 2005, 109, 13857



Growth of Au nanorods:Seed mediated growth method

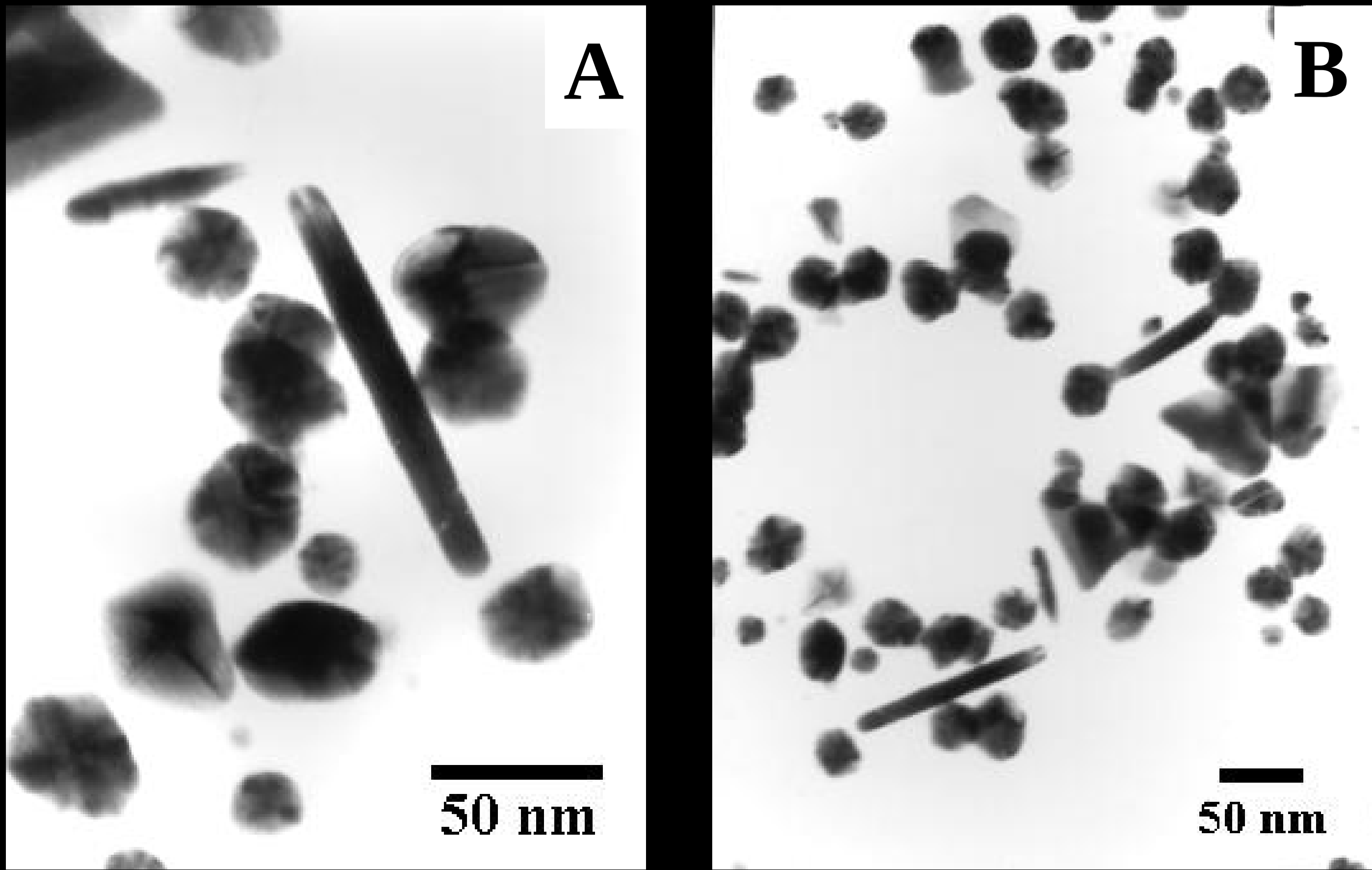






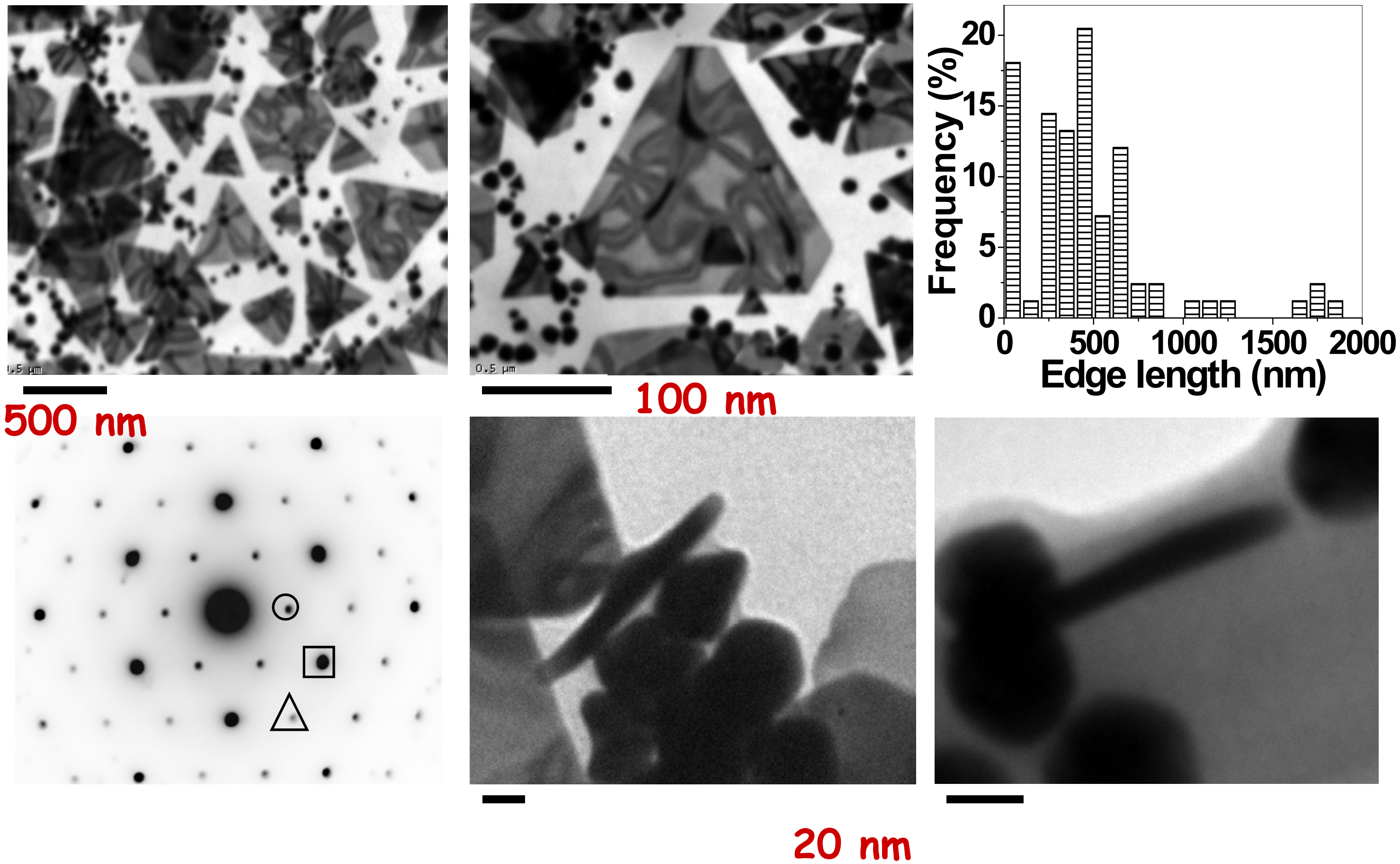
C. J. Murphy et. al. *J. Phys. Chem. B.*, 2005, 109, 13857

Gold nanoparticle synthesis using geranium leaves



J.Mater.Chem. 13 (2003) 1822.

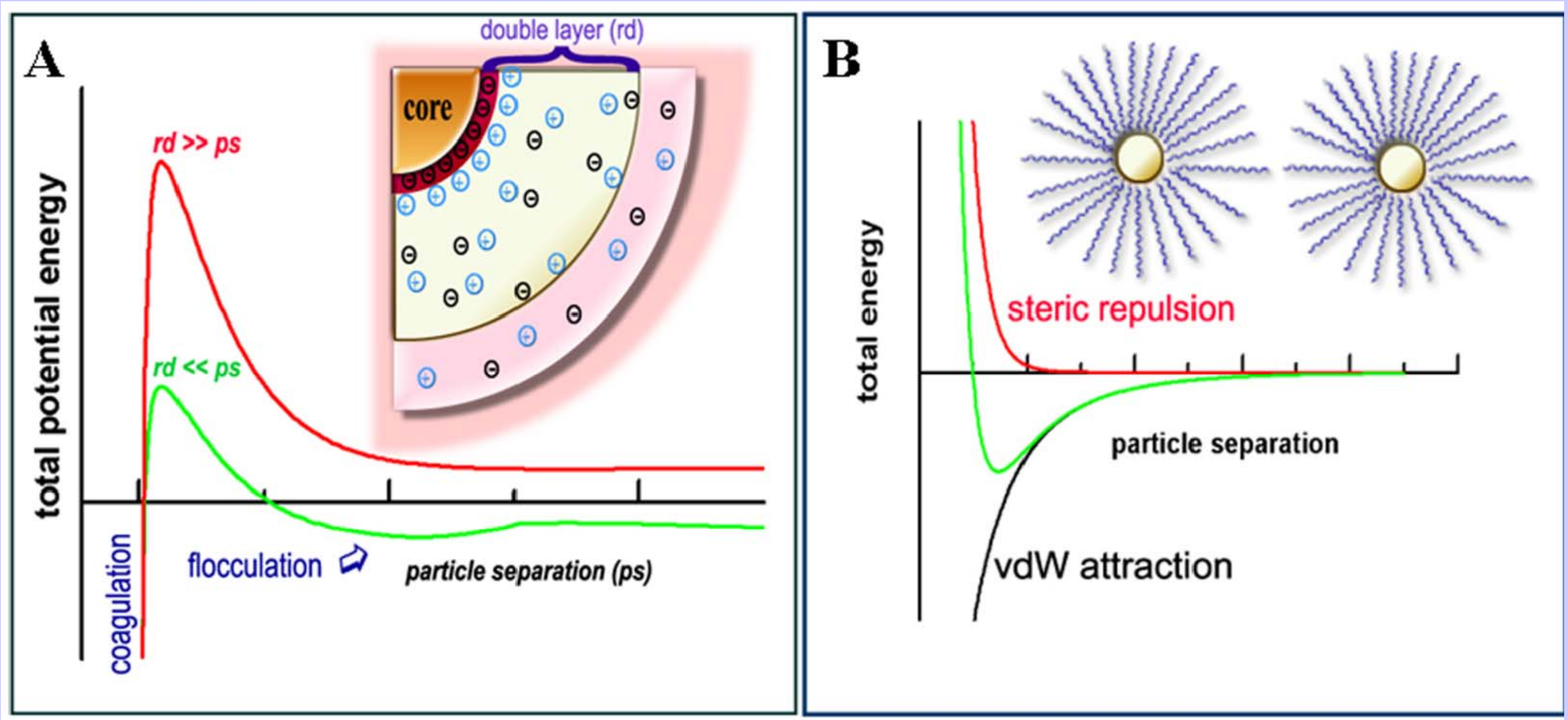
Synthesis of triangular gold nanoparticles using plant extracts



○ 1/3{422} △ {311}

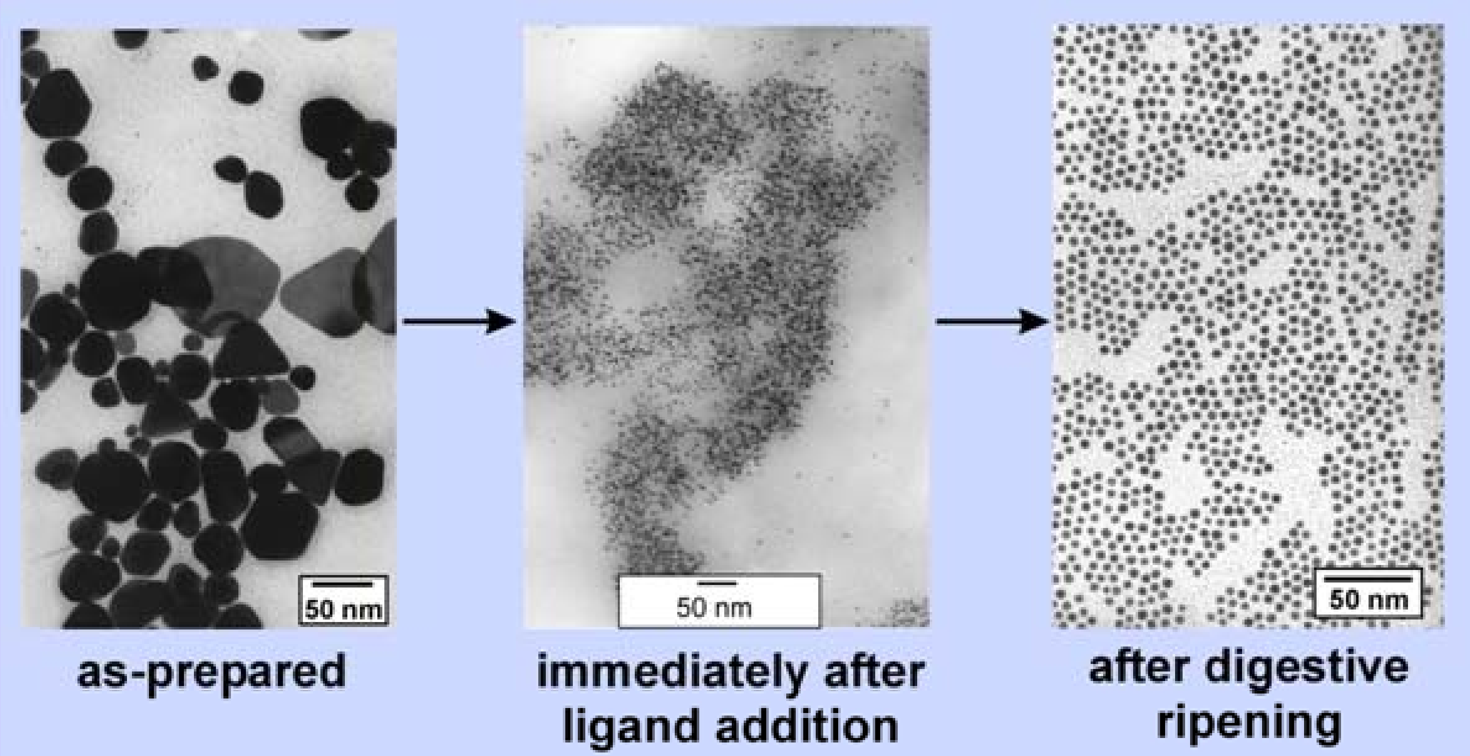
□ {220}

Factors governing the nanoparticle stability



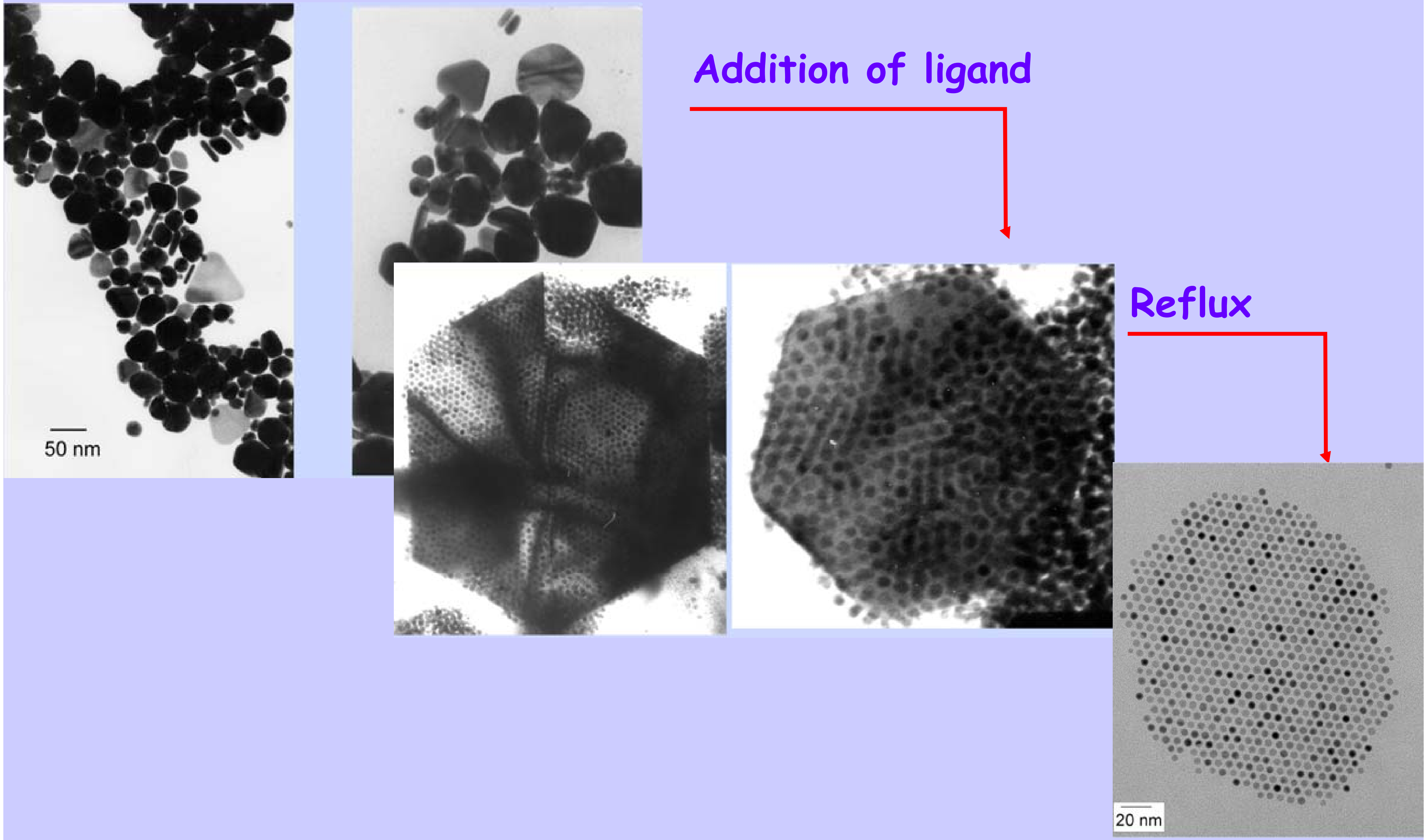
B. L. V. Prasad et al. Chem. Soc. Rev. 2008, 37, 1871

Achieving the first step:preparation of building blocks

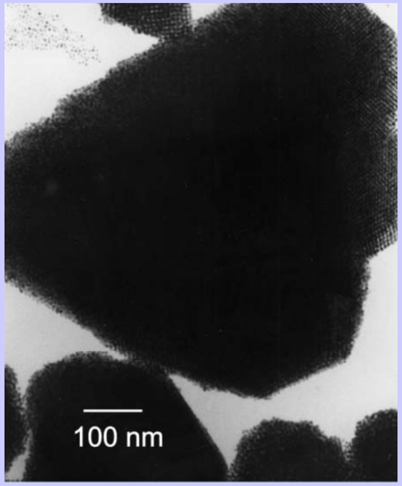


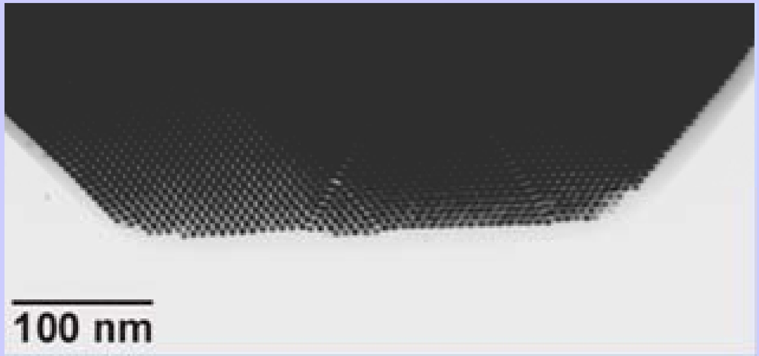
A highly polydisperse colloid can be easily converted to a very monodisperse colloid by *digestive ripening*.

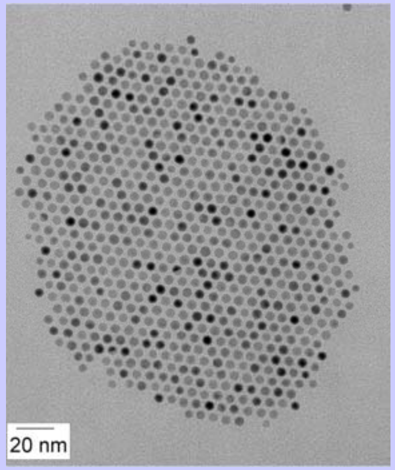
Digestive ripening:different steps



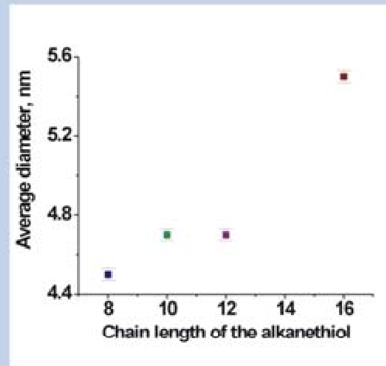
Ordered assemblies of nanoparticles in organic phase





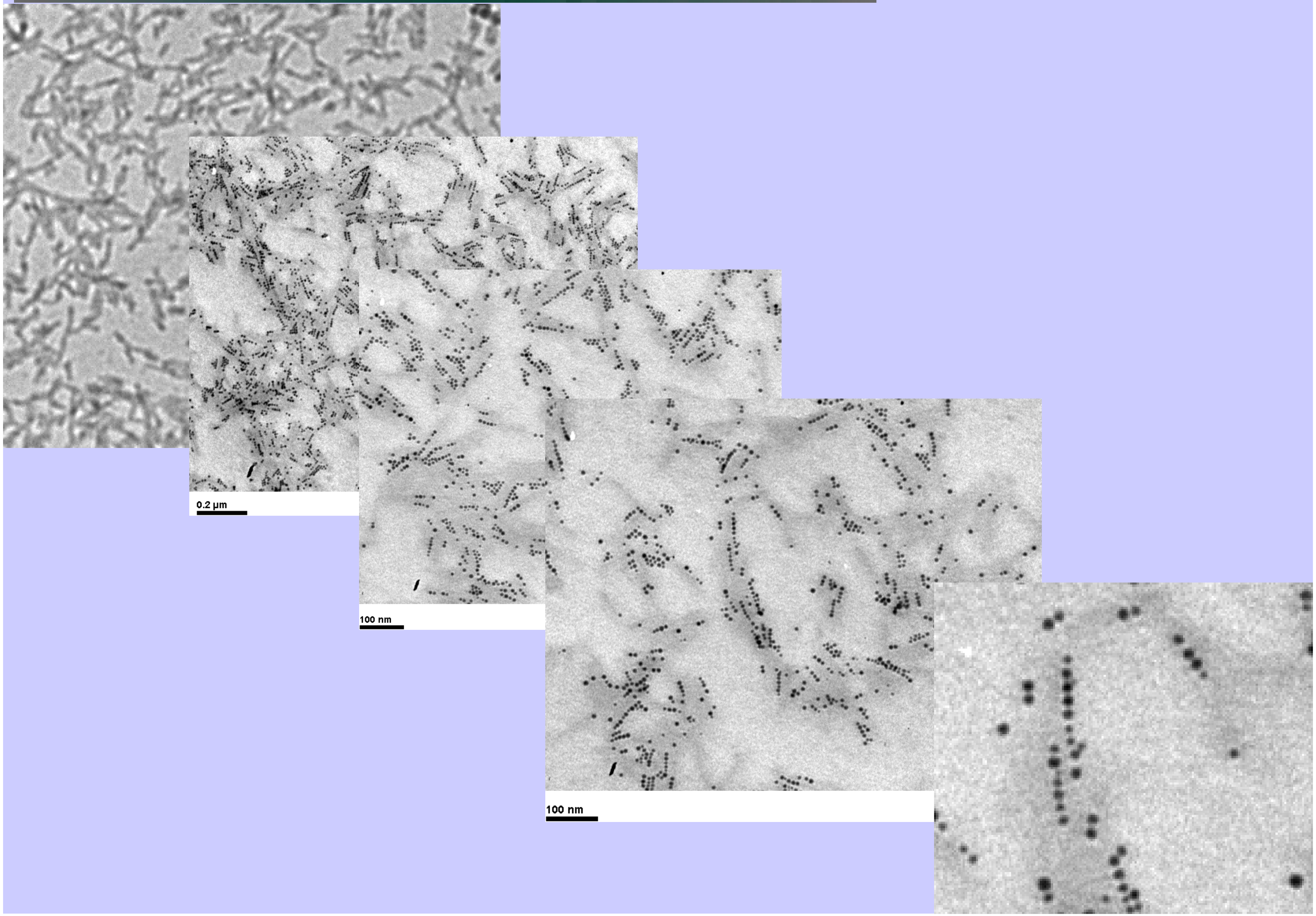


Thiol chain length	Type of superlattice	Optical spectra
Octanethiol	Only 3D superlattices	Large absorbance in NIR region >700nm
Decane- and Dodecane- thiol	Both 3D and 2D superlattices	Shoulder at 630 nm
Hexadecanethiol	Only 2D superlattices	Only gold plasmon peak at 530 nm

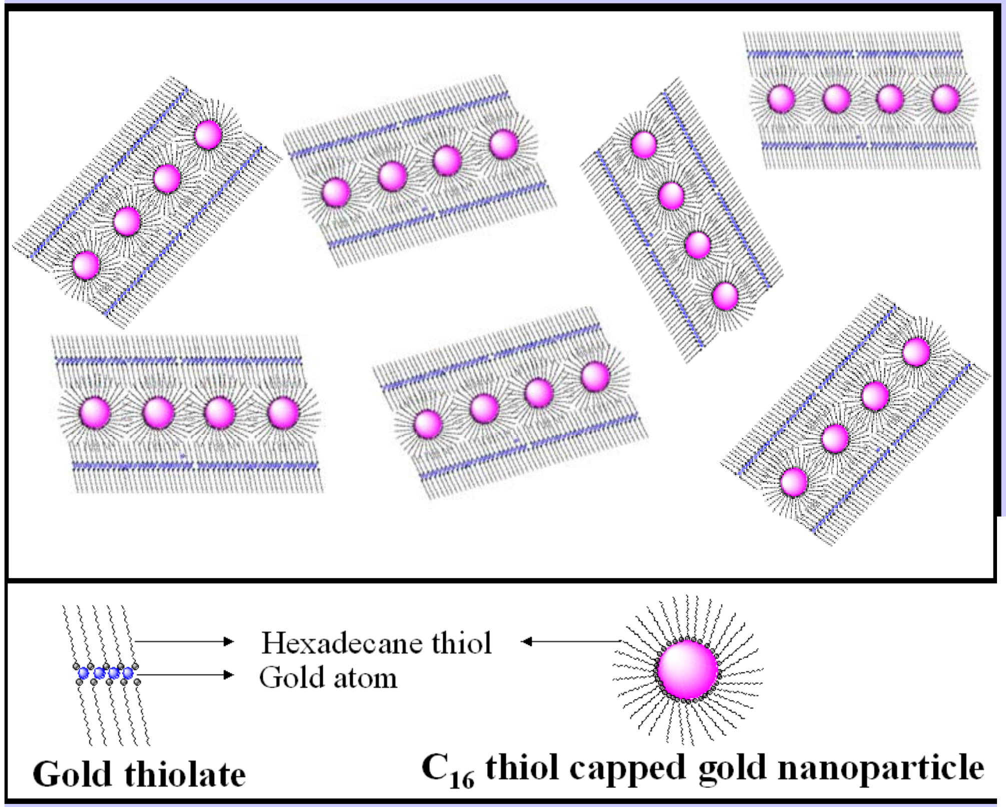


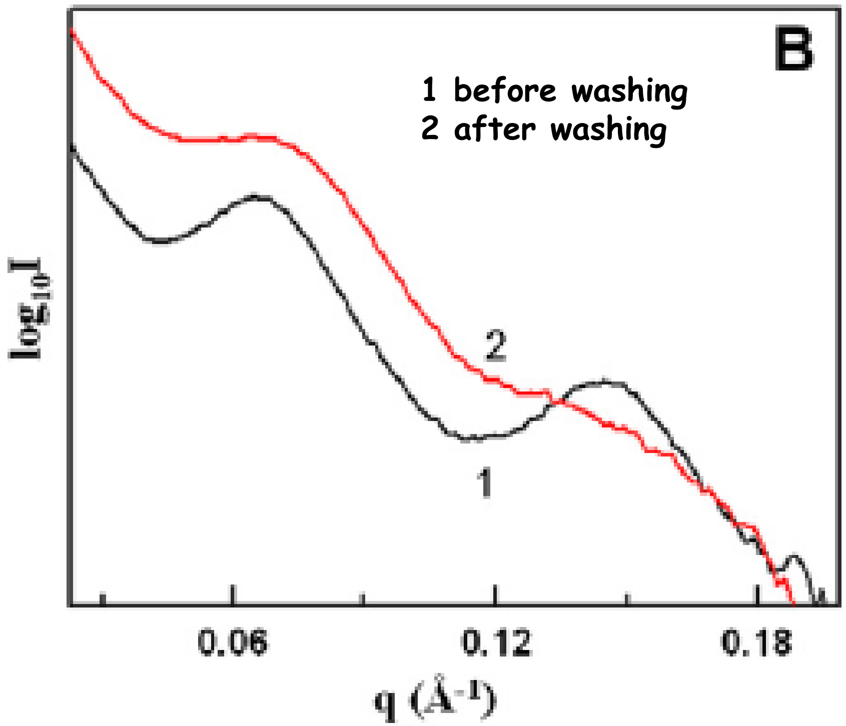
B. L. V. Prasad et. al.,, *Langmuir*, 2002, *18*,

Linear assemblies



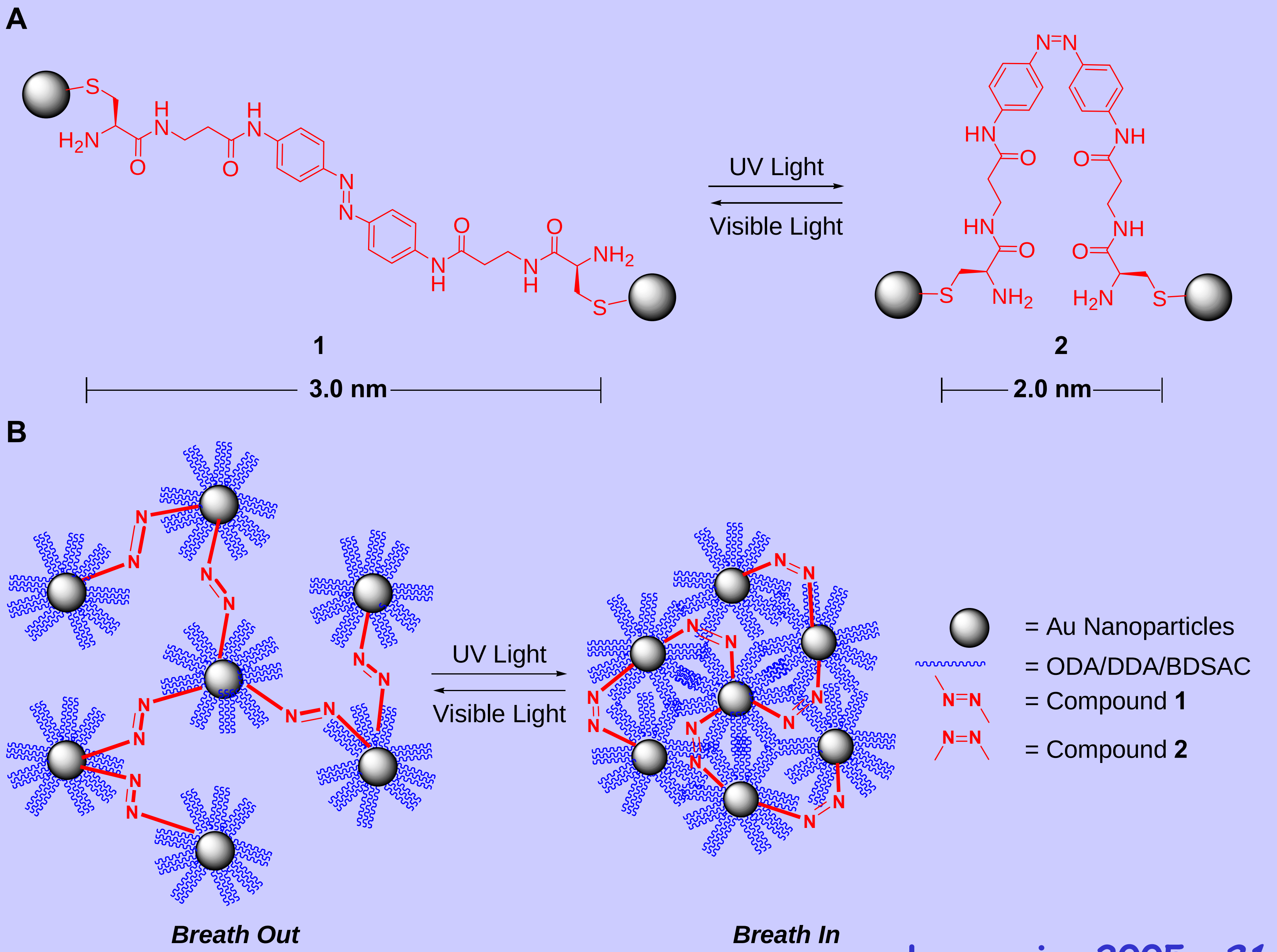
What holds these linear assemblies?





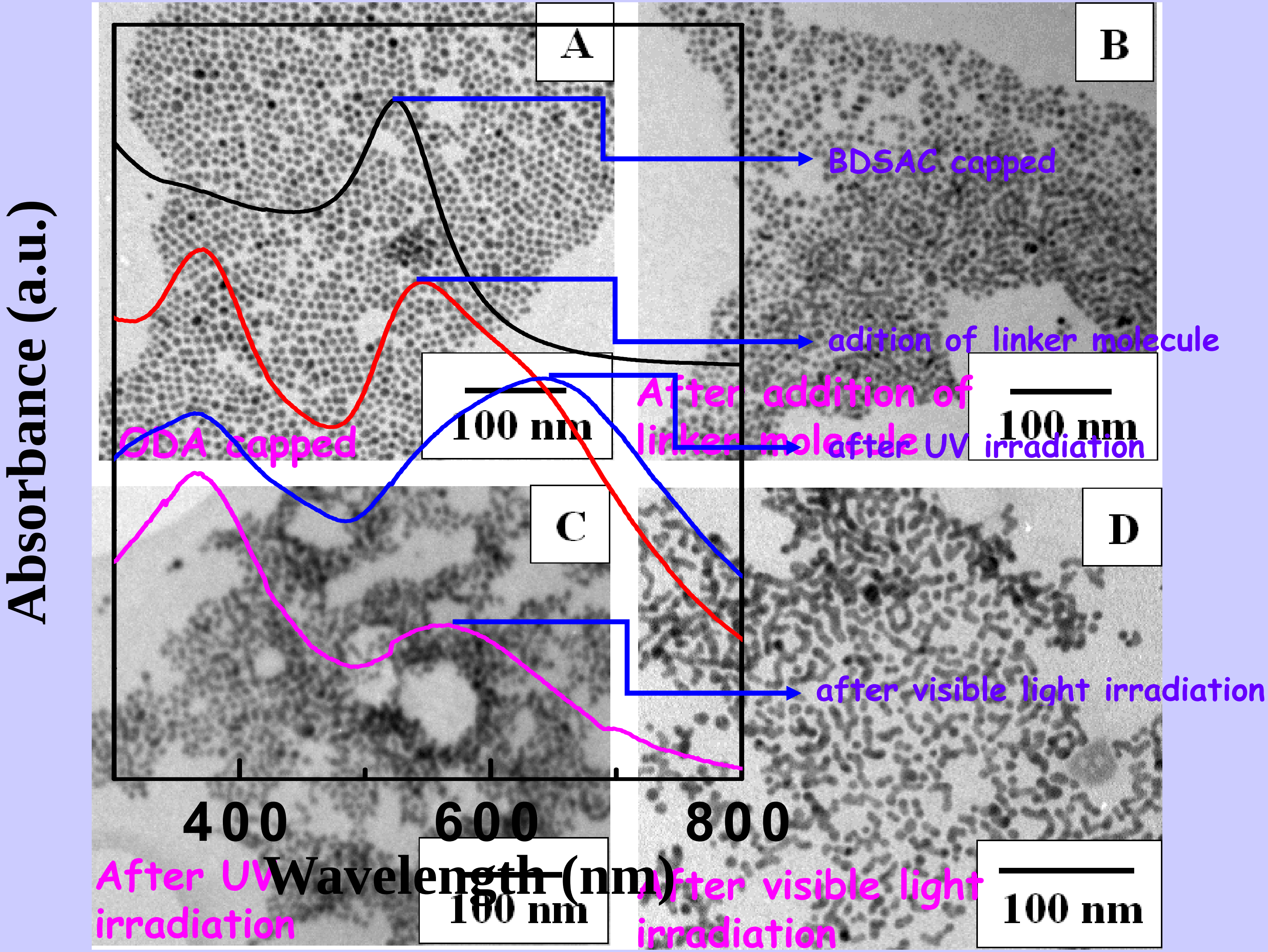
D. Sidhaye and B. L. V. Prasad, *Chem. Phys. Lett.* 2008, 454,

Photoresponsive nanoparticle networks

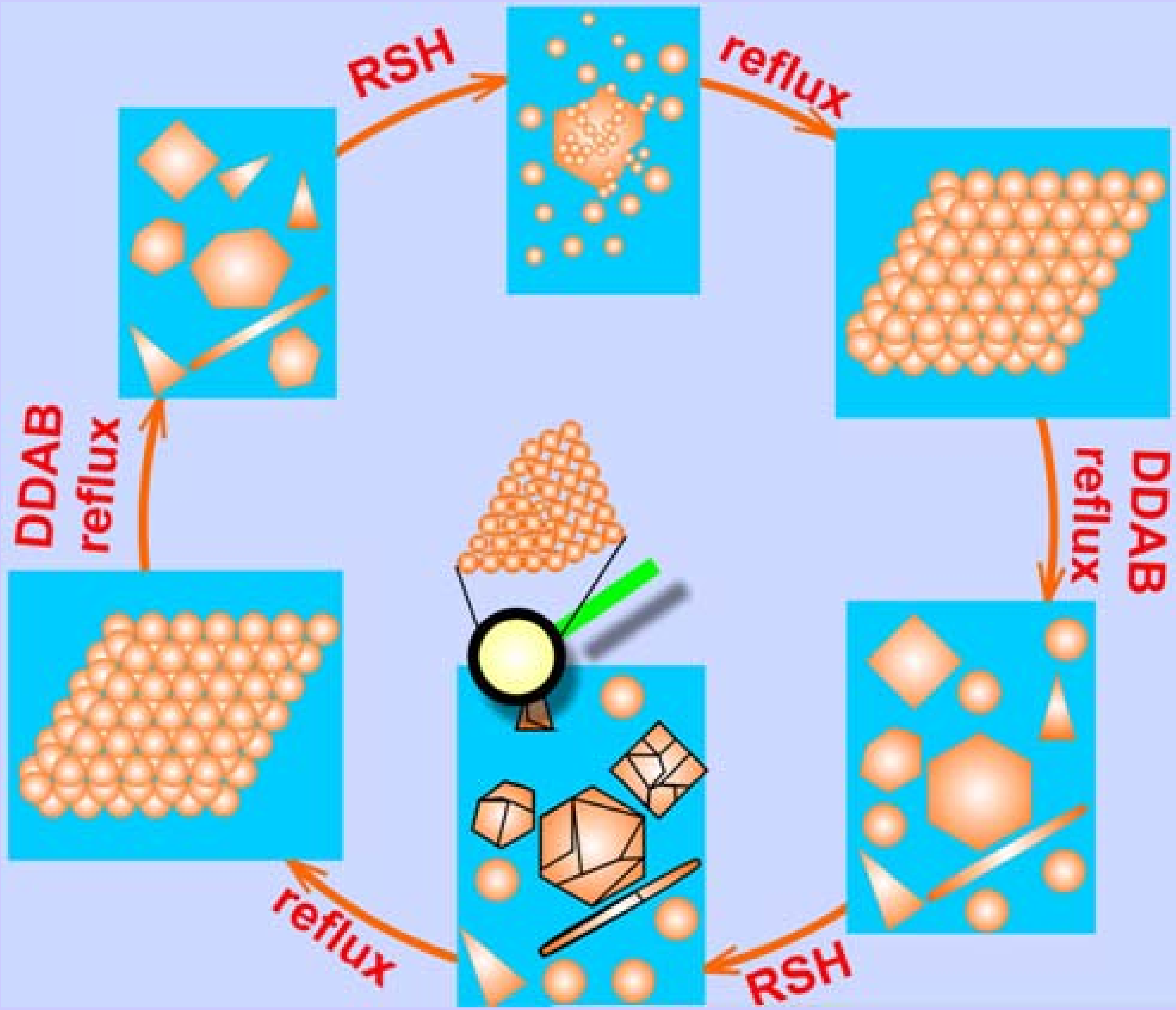


Langmuir, 2005, *21*,

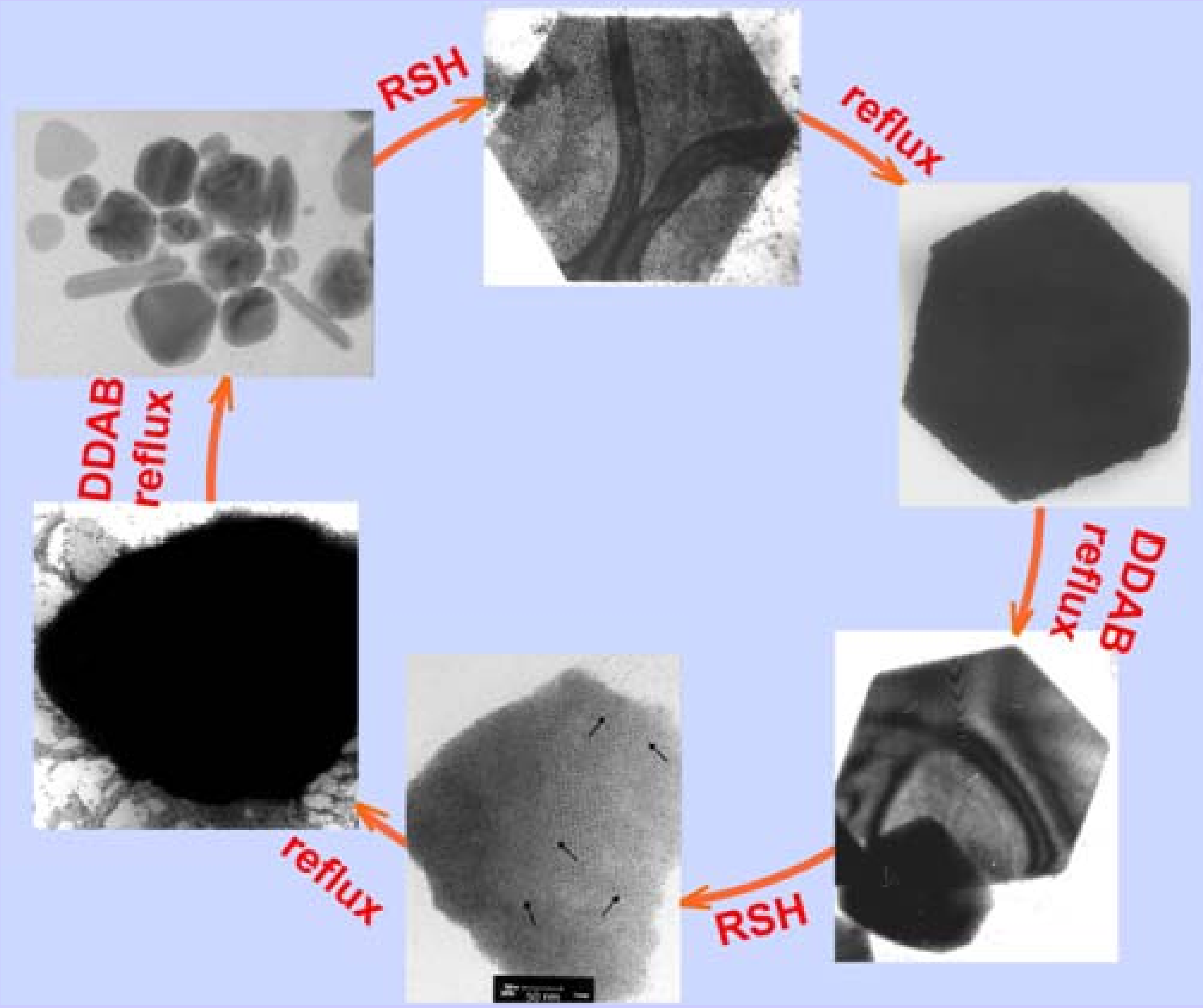
Photoresponsive nanoparticle networks



Shape Control of Nanoparticles



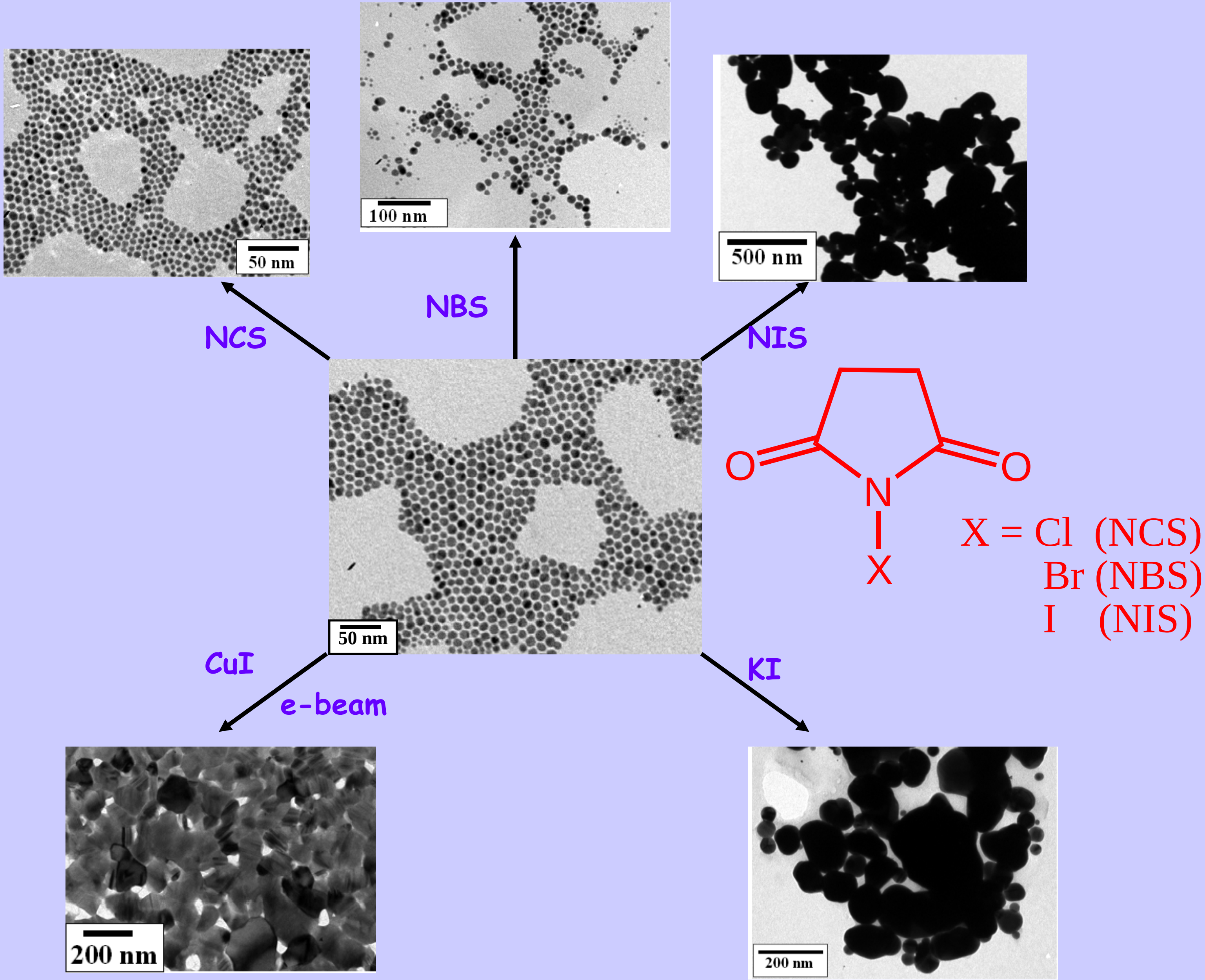
Shape Control of Nanoparticles



By just selecting a suitable ligand for digestive ripening the shape of the nanoparticles can be easily manipulated.

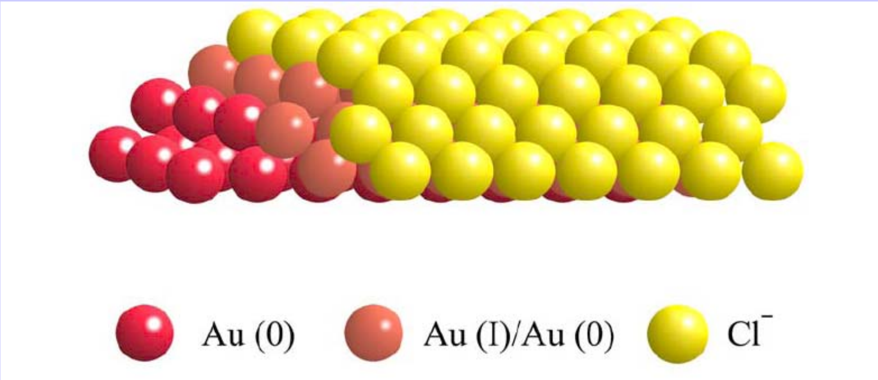
Langmuir 2005, *21*, 10280.

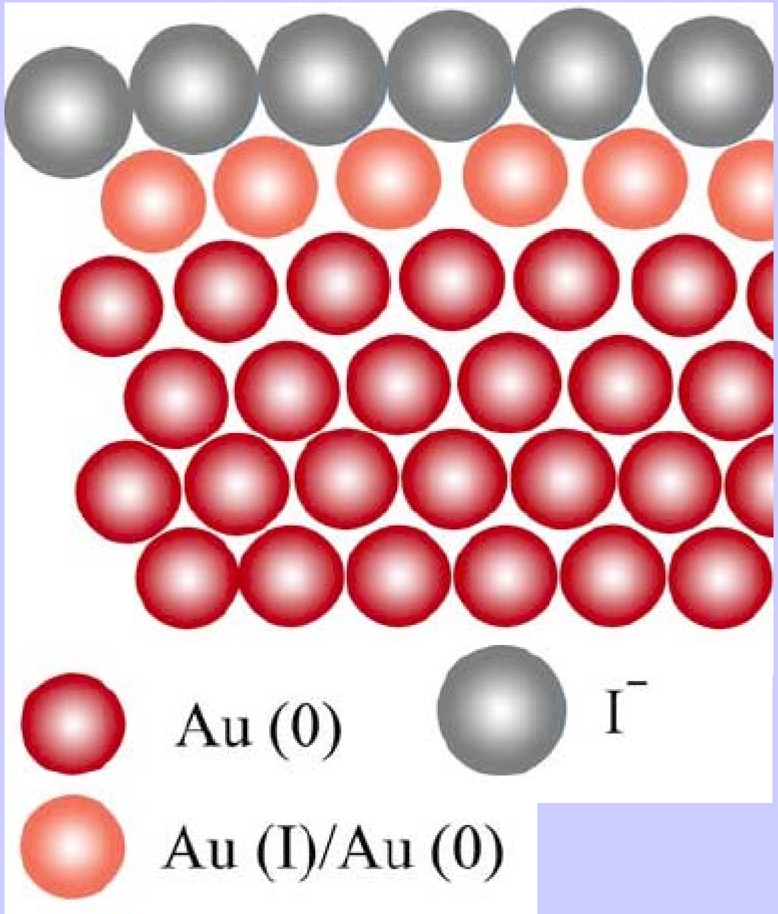
Shape control: Effect of halide ion addition



S. Singh, R. Pasricha, U. M. Bhatta, P. V. Satyam, M. Sastry and B. L. V. Prasad, J. Mater. Chem., 2007, 1614

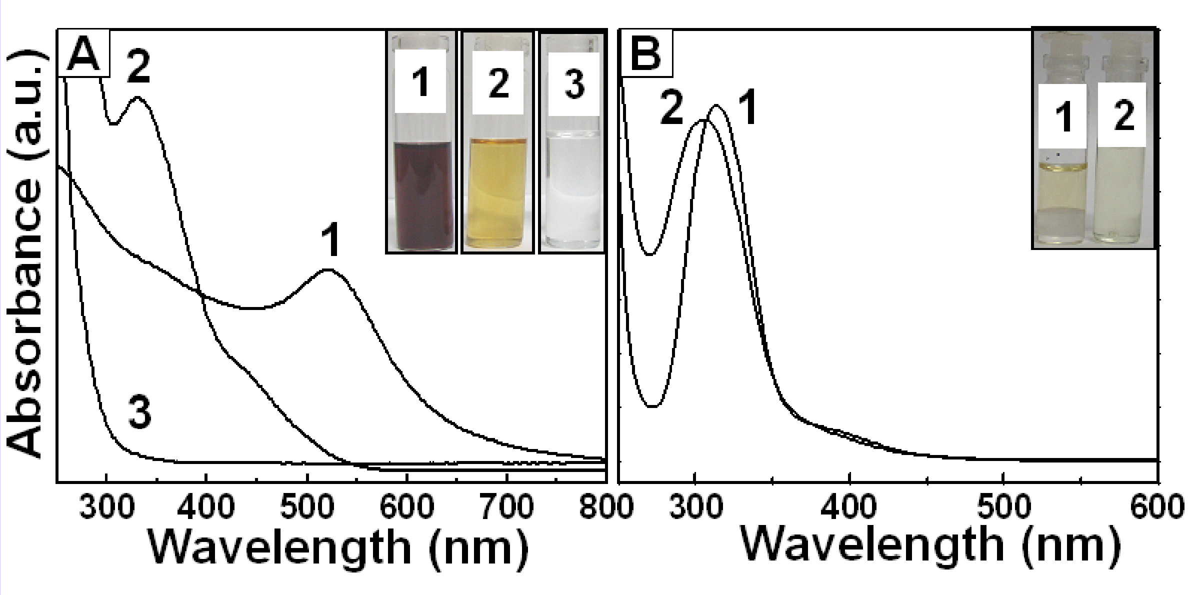
Effect of halide ion addition to to monolayer protected Au-NPs

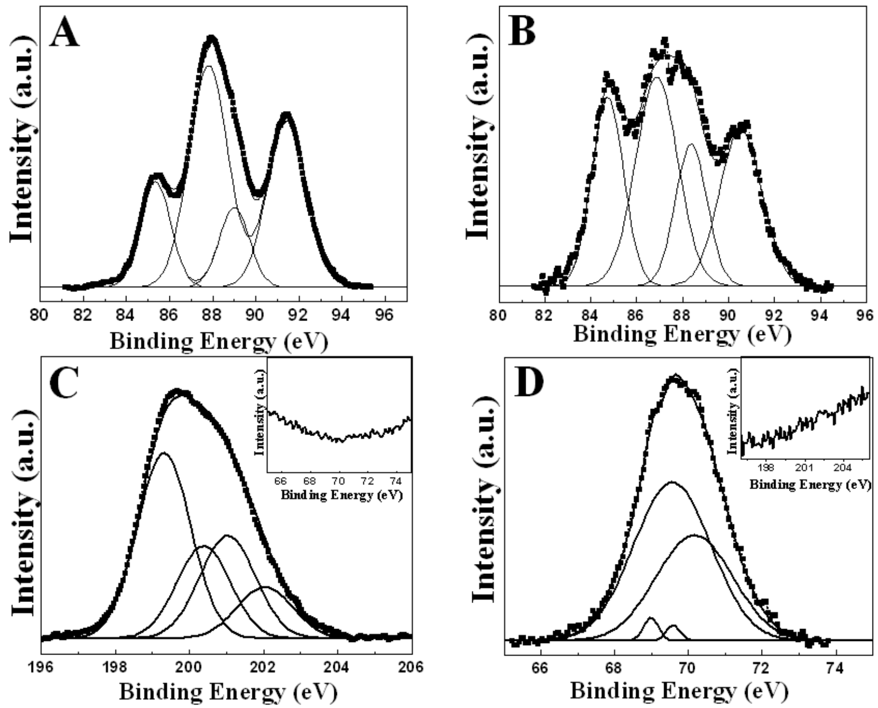




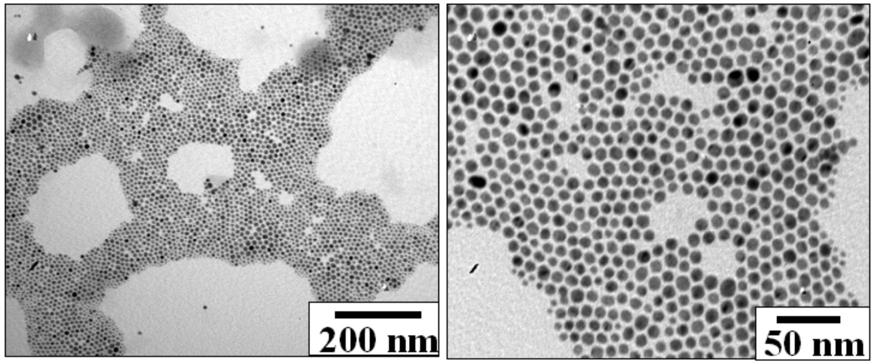
S. Shiv Shankar, Ph. D. Thesis, UoP

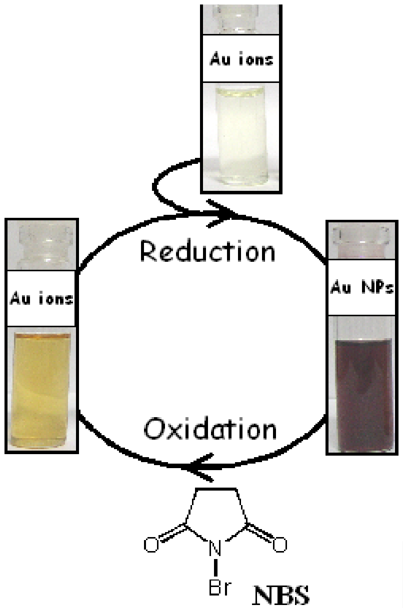
We can do better??

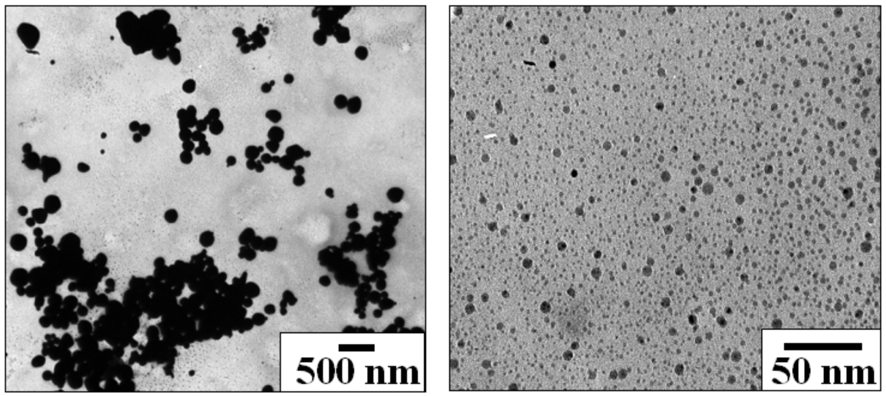




Effect of halide ion addition to to monolayer protected Au-NPs

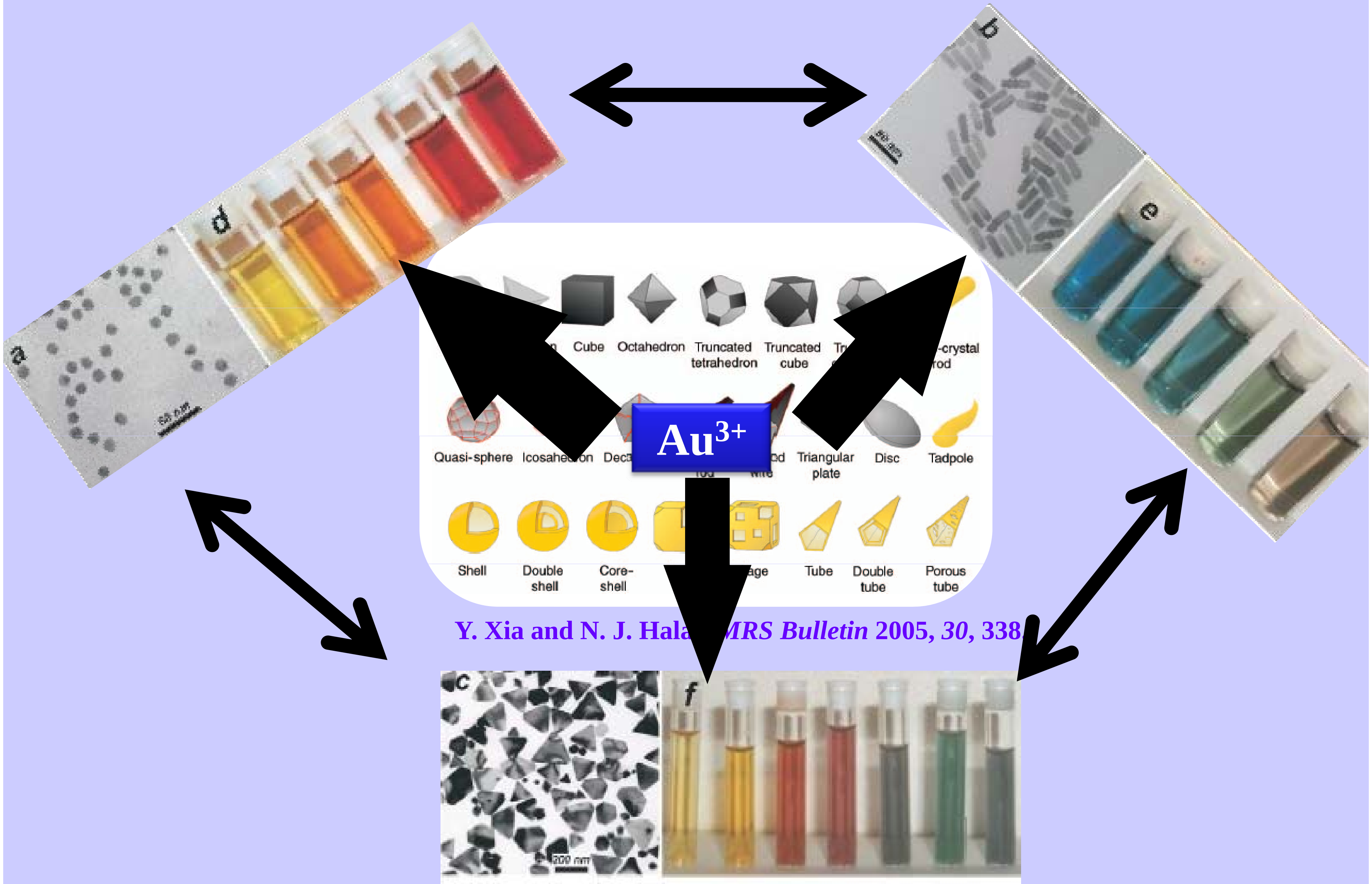






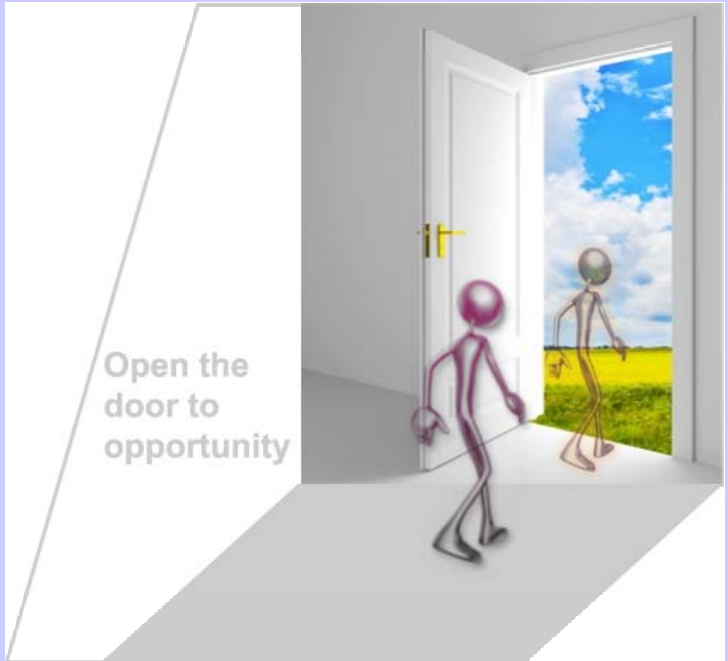
S. Singh and B. L. V. Prasad,, J. Phys. Chem. C 2007 111, 14348

What can a nanochemist do?



Y. Xia and N. J. Hala *MRS Bulletin* 2005, *30*, 338.

L. M. LizMarzan *Mater. Today* 2004, 26



Thank you all.