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SYNTHESIS ROUTES FOR LARGE VOLUMES OF NANOPARTICLES

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Metals, chalcogenides, main group elements, oxides, pnictides.

Au nanoparticles

X. The Bakerian Lecture.—*Experimental Relations of Gold (and other Metals) to Light.* By Michael Faraday, *Esq., D.C.L., F.R.S., Fullerian Prof. Chem. Royal Institution, Foreign Associate of the Acad. Sciences, Paris, Ord. Boruss. pour le Mérite, Eq., Memb. Royal and Imp. Acadd. of Sciences, Petersburgh, Florence, Copenhagen, Berlin, Göttingen, Modena, Stockholm, Munich, Bruxelles, Vienna, Bologna, Commander of the Legion of Honour, &c. &c.*

Philos. Trans. R. Soc. London **147** (1857) 145-181

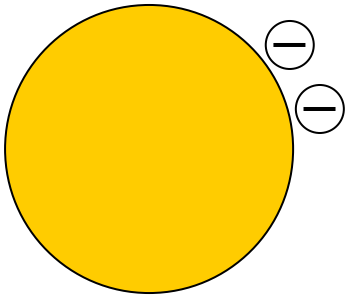
Gold leaf can be beaten to thicknesses of 1/278000 of an inch (around 90 nm). Such films are continuous and green in transmission. Further thinning with KCN gives ruby red films.

Chemical means to finely divided gold. Also deflagration of gold wires to produce ruby red particles. Chemically indistinguishable from gold.

Au nanoparticles

Aqueous reduction of metal salts (notably Au or Ag) in the presence of citrate anions at slightly elevated temperatures.

Citrate is both reducing agent as well as an electrostatic stabilizer, adsorbing on the particle surface.

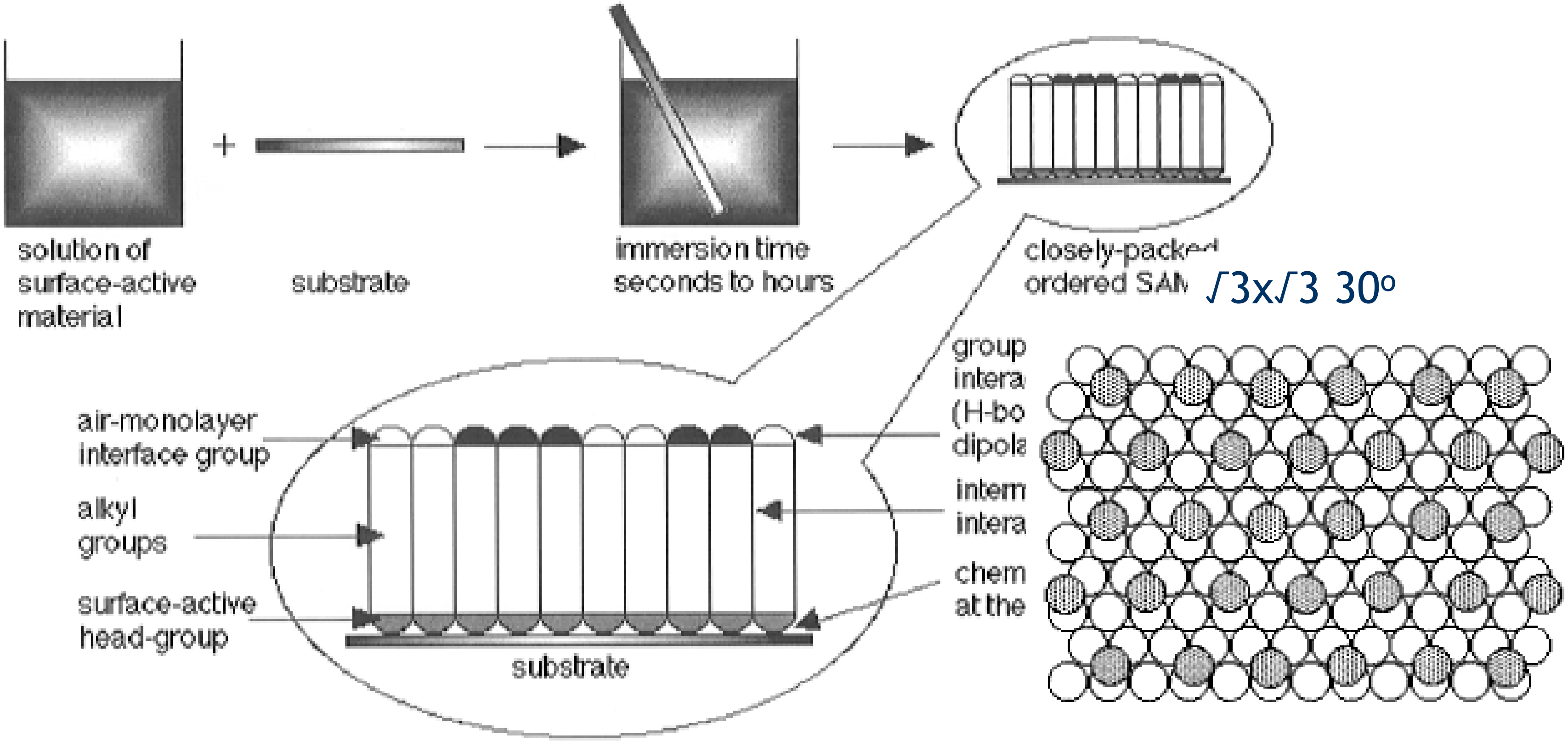


Monodispersity is of the order of $10 < \sigma < 15\%$

Flocculation of these colloids is irreversible, preventing further processing to achieve the desired $\sigma < 5\%$.

J. Turkevich, P. C. Stevenson, J. Hillier, *Disc. Faraday Soc.* **11** (1951) 55.

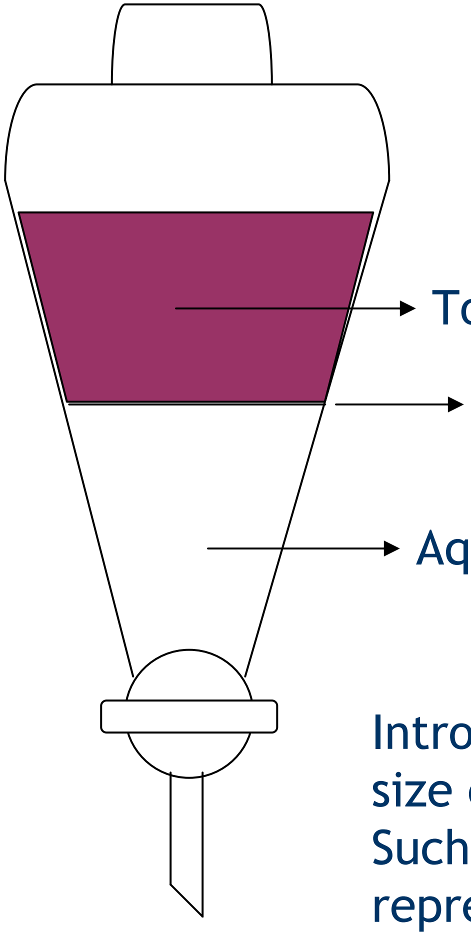
Au nanoparticles

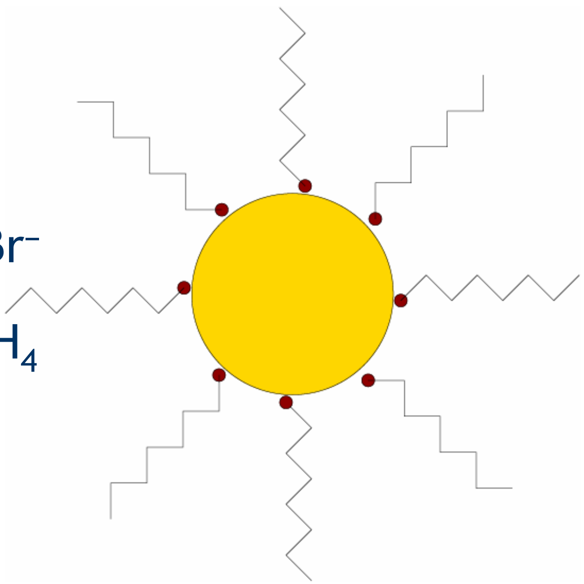


Thiols on Au(111) and also alkyl monolayers on Si and carboxylic acids on Al_2O_3.

A. Ulman, Formation and structure of self-assembled monolayers, *Chem. Rev.* **96** (1996) 1533-1554.

Au nanoparticles

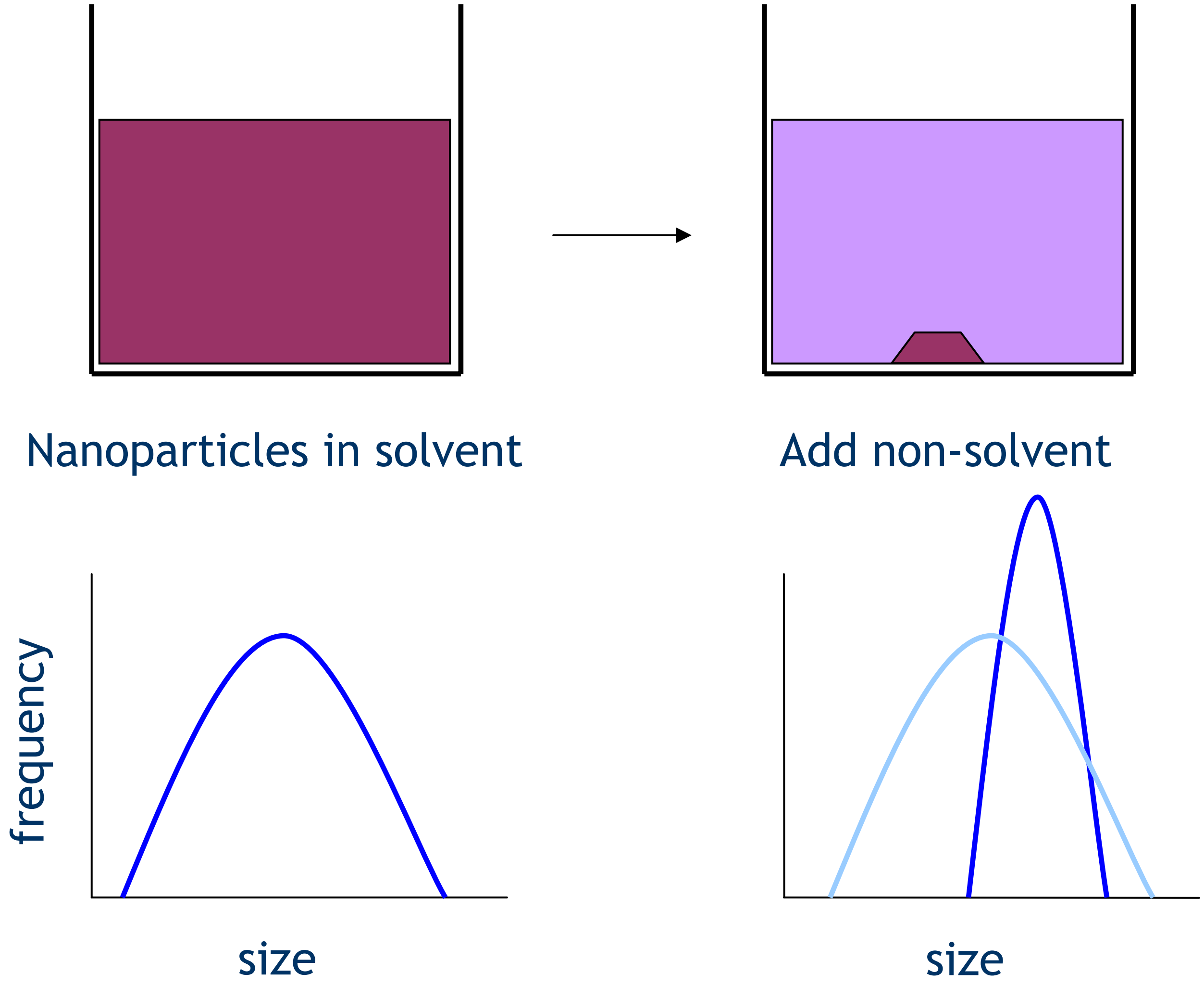




Introduction of a thiol capping agent in the toluene layer allows size control.
Such toluene-capped particles can be repeatedly dissolved and reprecipitated through suitable choice of solvent/non-solvent.

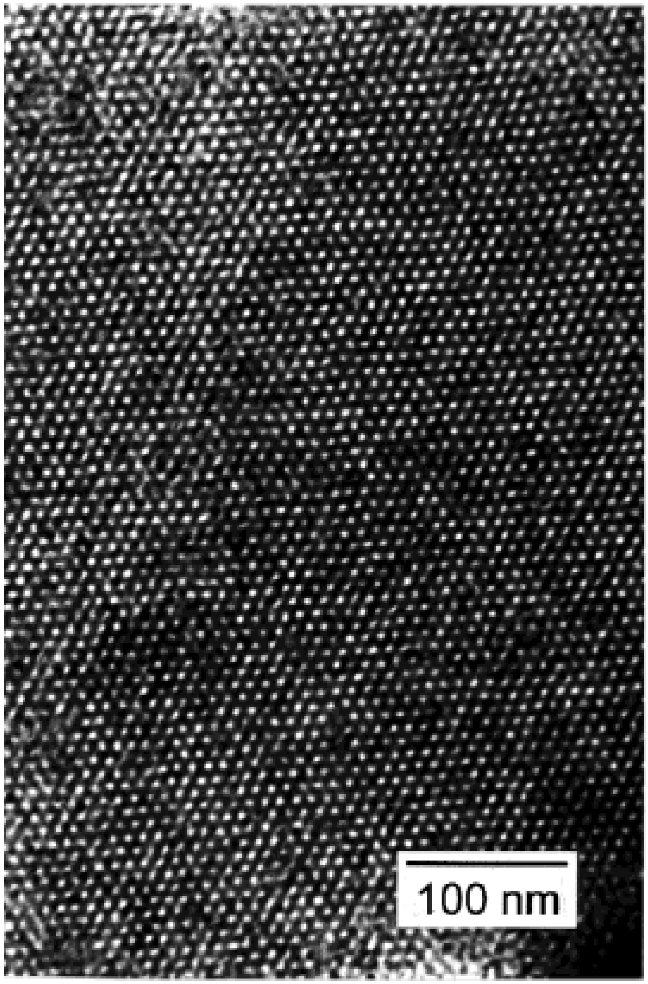
M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, and R. Whyman, Synthesis of thiol derivatized gold nanoparticles in a 2-phase liquid-liquid system. *J. Chem. Soc. Chem. Commun.* (1994) 801–802.

Au nanoparticles



A. Chemseddine and H. Weller, *Ber. Bunsen-Ges, Phys. Chem.* **97** (1993) 636–637.

Au nanoparticles



When the particle monodispersity if less than 5%, the particles spontaneously aggregate into *fcc* superlattices.

The aggregation and lattice formation is usuall considered to be entropy-driven, although dynamical effects and electrostatics can play a role.

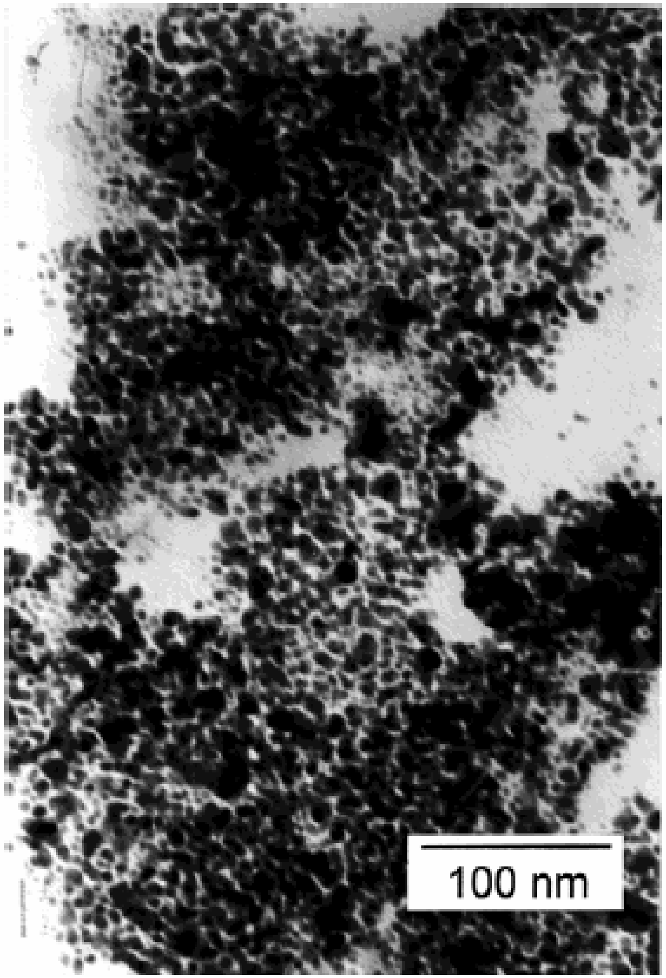
R. L. Whetten, J. T. Khoury, M. M. Alvarez, S. Murthy, I. Vezmar, Z. L. Wang, P. W. Stephens, C. L. Cleveland, W. D. Luedtke, and U. Landman, *Adv. Mater*. **8** (1996) 428-433.

Au nanoparticles

The solvated metal atom dispersion (SMAD) technique: Evaporated metal and solvent (acetone) vapor condensed at 77 K. The condensate is dispersed in toluene + capping agent.

Digestive ripening further sharpens size distribution.

Right: Au Particles as-prepared by SMAD:



S. Stoeva, K. J. Klabunde, C, M. Sorensen, and I. Dragieva, *J. Am. Chem. Soc.* **124** (2002) 2305-2311.

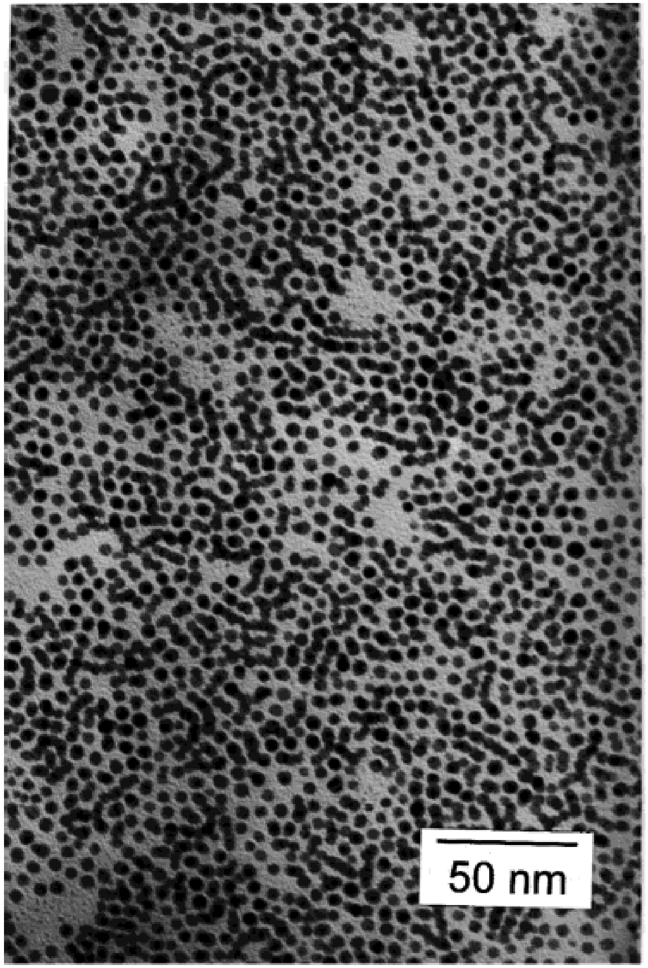
Au nanoparticles

The particles after refluxing in toluene with excess thiol. The original particles break up and reform.

Strongly suggests that nanoparticle formation is associated with non-equilibrium steady-states.

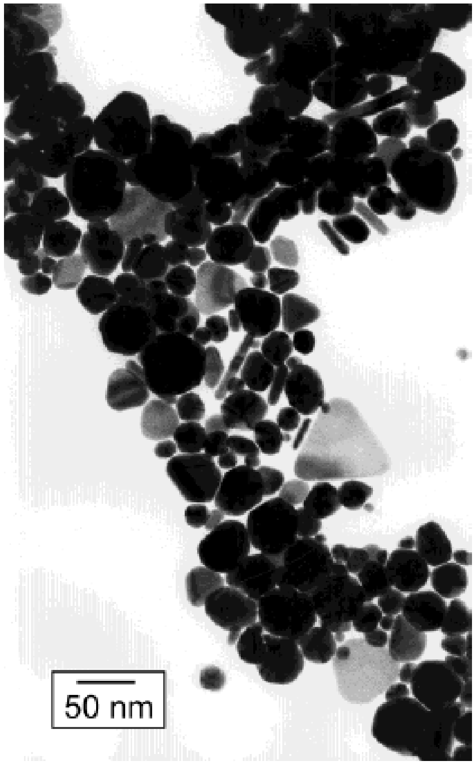
Analogy with “living” polymerization and the formation of high quality crystals.

S. Stoeva, K. J. Klabunde, C, M. Sorensen, and I. Dragieva, *J. Am. Chem. Soc.* **124** (2002) 2305-2311.

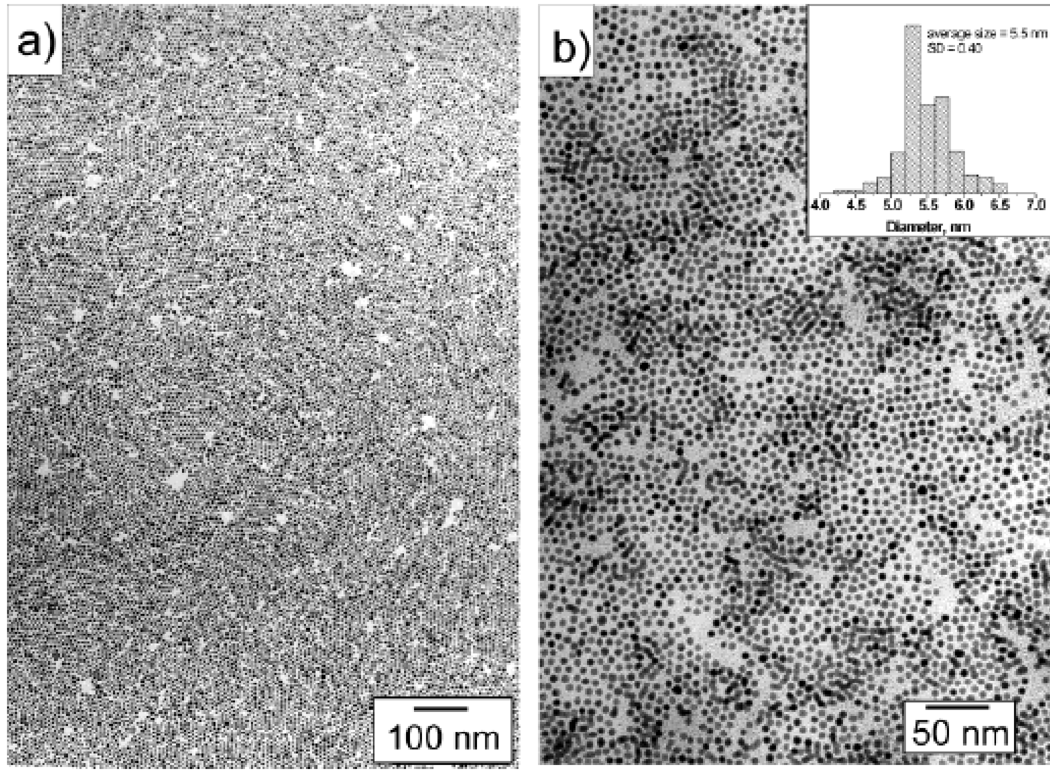


Au nanoparticles

As-prepared (reduction)

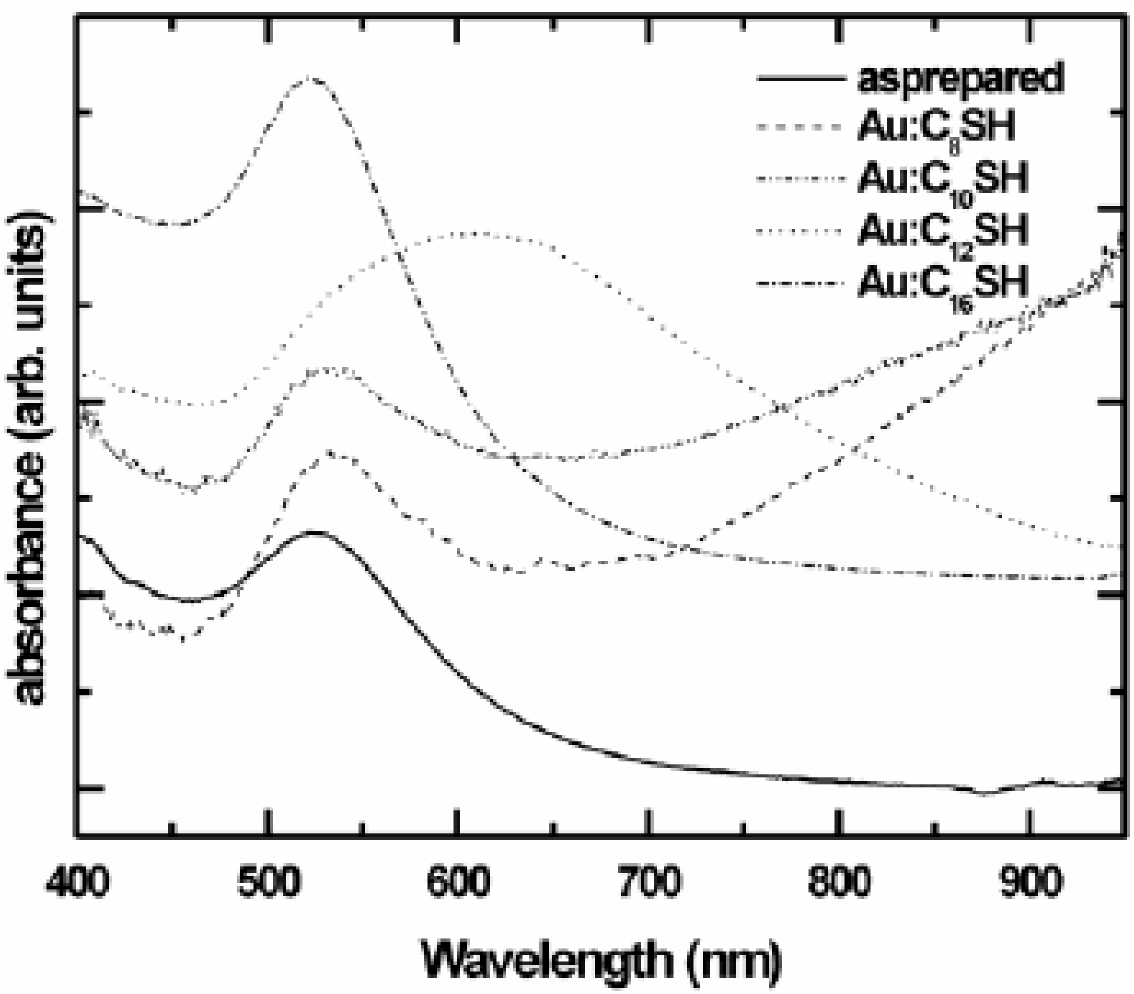


Hexadecanethiol ripened



B. L. Prasad, S. Stoeva, C. M. Sorenson, and K. J. Klabunde, *Langmuir* **18** (2002) 7515-7520.

Au nanoparticles



B. L. Prasad, S. Stoeva, C. M. Sorenson, and K. J. Klabunde, *Langmuir* **18** (2002) 7515-7520.

Au nanoparticles

Plasmons:

Wand, Brandl, Nordlander, and Halas, *Acc. Chem. Res.* **40** (2007) 53-62

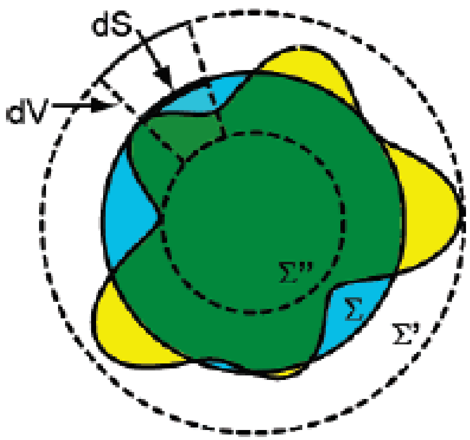
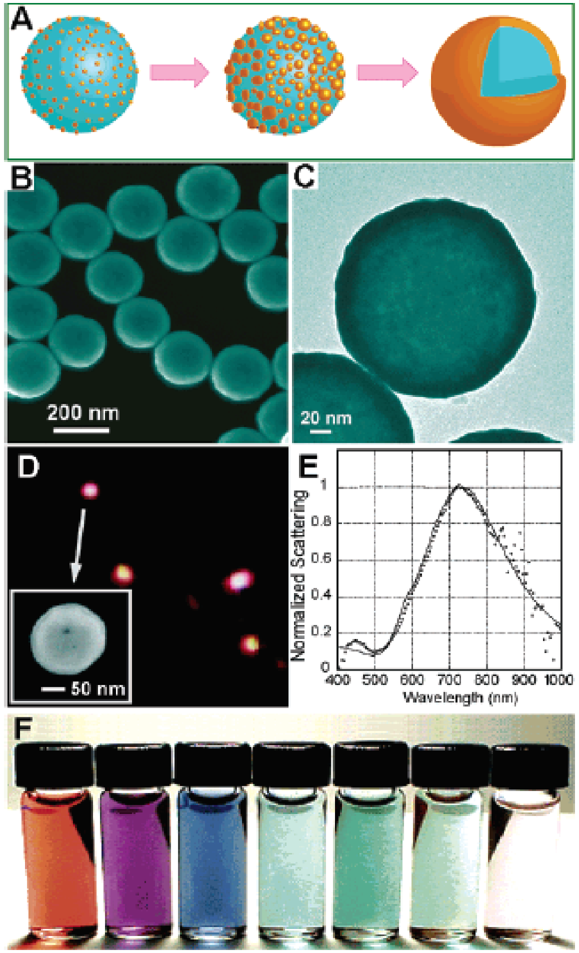


FIGURE 1. Illustration of the incompressible, irrotational fluid of conduction electrons of a finite metallic particle. The surfaces Σ' and Σ'' are the maximum and minimum boundaries of the fluid, and Σ denotes the nanoparticle boundary.



Plasmons from Au within SiO_2 shells.