Synthesis of Nanoparticles and Surface Modifications
Self-Assembly

• Static assembly
• Dynamic assembly

  – \( RT = 8.314 \text{ J/mol} \times 300 = 2.4 \text{ kJ/mol} \)

• Driving forces
  – Chemisorption
  – Surface effect
  – Hydrophobic-hydrophilic
  – Intermolecular forces
  – Capillary force
Langmuir-Blodgett Films
Langmuir-Blodgett Films
Isotherm
**Self-Assemble Monolayer (SAM)**

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**S-Au** 25-30 Kcal/mole  
**Si-O** 190 kcal/mole
Figure 7. Schematic illustration of some of the intrinsic and extrinsic defects found in SAMs formed on polycrystalline substrates. The dark line at the metal–sulfur interface is a visual guide for the reader and indicates the changing topography of the substrate itself.

(a) Insertion of a functional adsorbate at a defect site in a preformed SAM. (b) Transformation of a SAM with exposed functional groups (circles) by either chemical reaction or adsorption of another material.
Figure 21. Schematic illustrations of (a) a mixed SAM and (b) a patterned SAM. Both types are used for applications in biology and biochemistry.

Figure 22. Schematic diagram illustrating the effects that large terminal groups have on the packing density and organization of SAMs. (a) Small terminal groups such as –CH₃, –CN, etc., do not distort the secondary organization of the organic layer and have no effect on the sulfur arrangement. (b) Slightly larger groups (like the branched amide shown here) begin to distort the organization of the organic layer, but the strongly favorable energetics of metal–sulfur binding drive a highly dense arrangement of adsorbates. (c) Large terminal groups (peptides, proteins, antibodies) sterically are unable to adopt a secondary organization similar to that for alkanethiols with small terminal groups. The resulting structures probably are more disordered and less dense than those formed with the types of molecules in a and b.
Figure 23. Schematic illustration of the order–disorder transition evidenced by SAMs of alkanethioloates terminated with triethylene glycol. The EC₃ group loses conformational ordering upon solvation in water.
Temperature Programmed Desorption
Self-Assembly

- Substrates
- Interstitial adhesion layer
- Noble metal layer
- Organo-sulfur
Organosilanes

Self-assembled monolayers

- Surface
  - silicon oxide: silanisation
  - aluminum oxide: fatty acids
  - metals: thiols and sulfides

Immersion of substrate in a solution containing the adequate molecules for 12 - 24 hours yields an ordered monolayer
Metal Reduction
Synthesis of Silver Nanoparticles

1. A solution of AgNO₃ (1.0 x 10⁻³ M) in deionized water was heated until it began to boil.
2. Sodium citrate solution was added dropwise to the silver nitrate solution as soon as the boiling commenced. The color of the solution slowly turned into grayish yellow, indicating the reduction of the Ag⁺ ions.
3. Heating was continued for an additional 15 min, and then the solution was cooled to room temperature before employing for further experimentation.
Synthesis of Gold Nanoparticles

1. Add 20 mL of 1.0 mM HAuCl₄ to a 50 mL round bottom flask on a stirring hot plate.
2. Add a magnetic stir bar and bring the solution to a boil.
3. To the boiling solution, add 2 mL of a 1% solution of trisodium citrate dihydrate
4. The gold sol gradually forms as the citrate reduces the gold(III). Stop heating when a deep red color is obtained.

\[
\begin{align*}
(1) & \quad M_xO_y \xrightarrow{\text{Reducing Agent}} \text{(medium)} \xrightarrow{\Delta_T} M_n + H_2O \\
& \quad \text{(Reducing Agent = R - COH)}
\end{align*}
\]

\[
\begin{align*}
(2) & \quad M(L)_x \xrightarrow{\text{Reducing Agent}} \text{(medium)} \xrightarrow{\Delta_T} M_n + L^- \\
& \quad \text{(L=NO}_3^- , C_2H_5O^-) \\
& \quad \text{(Reducing Agent = R - COH)}
\end{align*}
\]
Construction of Core Shell Ag/Au@SiO₂ Nanoparticles

1. Under vigorous stirring, 1 ml of the silver/gold colloids solution was mixed with 250 mL of isopropanol and 25 mL of deionized water.
2. Immediately after the addition of 4 mL of 30% ammonium hydroxide, different amounts of tetraethoxysilane (TEOS) were added to the reaction mixture.
3. To obtain different silica layer thicknesses, TEOS solutions with a concentration between 50% and 100% was added to the suspension. The reaction was stirred at room temperature for 30 minutes and then was allowed to age without agitation at 4°C overnight.
4. Each suspension of silica-coated silver/gold nanoparticles was washed and centrifuged, followed by re-suspension in water. The thickness of the silica layers was determined from TEM images.
Core-Shell Nanoparticles
Figure 1. (a) Schematic illustration of a silica-core, gold-shell nanoshell, indicating inner (r_1) and outer (r_2) radii of the shell layers. (b) Depiction of a four-layer, concentric nanoshell. (c) Schematic illustration of a metallic nanorod. (d) Plot of nanoshell resonance as a function of core and shell dimensions, overlaid with reported spectral ranges of nanorod resonances (red, transverse plasmon; purple, longitudinal plasmon), and reported nanoshell and concentric nanoshell combined spectral range of plasmon response.

Figure 2. Plasmon hybridization and the sphere–cavity model for nanoshells: the interaction between a sphere (resonance frequency, \( \omega_{sp} \)) and a cavity plasmon (resonance frequency, \( \omega_c \)) is tuned by varying the thickness of the shell layer of the nanoparticle. Two hybrid plasmon resonances, the \( \omega_+ \) “bright” or “bonding” plasmon and the \( \omega_- \) “dark” or “anti-bonding,” plasmon resonances are formed. The lower-energy plasmon couples most strongly to the optical field.
Figure 5. (a) Plasmon hybridization picture applied to surface plasmon resonance sensing with nanoshells: the low-energy “bonding” plasmon, $\omega_1$, is sensitized to changes in its dielectric environment. The blue background schematically denotes the embedding medium for the nanoparticle.

(b) Experimental curves showing plasmon resonance shifts for nanoshell-coated films in various media: (i) carbon disulfide, (ii) toluene, (iii) hexane, (iv) ethanol, (v) H$_2$O, and (vi) air. The index of refraction for each embedding medium is noted on the far right of the spectra. Spectra are offset for clarity.

(c) Scanning electron micrograph of nanoshells deposited onto a poly(vinyl pyridine) functionalized glass surface, as used to acquire data in (b). Inset: individual nanoshell.
Preparation of Fe$_3$O$_4$@Ag/Au

1. To the magnetic nanoparticle suspension obtained from commercial company, add 50 ml of a solution of Au (III) salt or Ag (I) salt at concentration of 0.01–1% mmol/L, shaking for 30 minutes, allowing Au (III) or Ag (I) ion to absorb on the surface of magnetic nanoparticle sufficiently.

2. Then adding 15–40 ml of reducing agent, such as hydroxylamine hydrochloride at concentration of 40 mmol/L, reacting for 5–40 minutes.

3. Further adding 1–10 ml of a solution of Au (III) salt or Ag (I) salt at concentration of 0.01–1%, shaking for 10 minutes, coating a reduced layer of gold or silver on the surface of the magnetic nanoparticle, forming super-paramagnetic composite particles having core/shell structure, separating magnetically, washing repeatedly with distilled water.
Synthesis of TOPO/HDA capped quantum dots of CdSe

Cadmium acetate (0.107g, 0.4mmol) and oleic acid (0.27mL, 0.4mmol) in 1:2 ratio were placed in a two neck flask degassed and refilled with nitrogen, stirred at 120-130 °C under nitrogen atmosphere for 2-3 hours, obtained a clear light yellow solution. Then a mixture of capping reagent i.e. 6g of hexadecylamine (HDA) and 6g of tri-octylphosphine oxide (TOPO) prepared in separate flask was added at the same temperature and stirring was done for another 30min at temperature ~ 350 °C. The temperature was reduced and TOPSe was added at different temperatures at 250 °C through syringe immediately the color of reaction mixture became dark brown (TOPSe was prepared simultaneously in a separate vessel, appropriate quantity of Se (0.032g) powder was heated in 2mL tri-octyl phosphine (TOP) at 70-90 °C for about an hour to get a clear solution of TOPSe), stirring was continued for another 30min aliquots were taken from the reaction solution to monitor the reaction. The temperature of the reaction was reduced the stirring was done for another 1-2 hours. 50mL toluene was added before the cooling the reaction to prevent the solidification of TOPO and HDA. It was centrifuged at 3000rpm for 15min, a pallet was discarded, the supernatant solution was treated with the methanol for precipitation of CdSe nano-crystals, centrifuged at 7000rpm washed with methanol (3 x 6mL) to get product. A red residue was obtained which was re-dispersed in toluene.
Synthesis of CdSe Quantum dots

Cooperative UV and PL spectra of CdSe core
20mL (31mg, 0.16 mmol) colloidal solution of CdSe QDs from stock solution (54mg dissolved in 35mL toluene) was placed in a two-neck flask. TOPO (6g) and HAD (6g) were added and then toluene was removed through vacuum, flask refilled with nitrogen. The reaction mixture was heated at 350 °C for two hours. In another flask zinc acetate in 1:3 ratio with respect of CdSe and was dissolved in 4mL of oleic acid stirred at 120 °C for 2 hours obtained a light yellow coloured solution and temperature reduced to 60-70 °C. After cooling to room temperature, TOPSe was mixed with Zn salt solution. And the mixture was injected slowly through syringe in to reaction solution of CdSe-TOPO at 180-200 °C. The stirring was done for another an hour. The similar procedure was followed for work up of reaction as above experiment. The final product was re-dispersed in toluene.
Light emission from CdSe/ZnSe Quantum dots

UV-Visible and PL spectra of CdSe/ZnSe re-dispersed in toluene
Nanorods

I. Synthesis of seed

\[ 2.5 \times 10^{-4} \text{ M HAuCl}_4 + 2.5 \times 10^{-4} \text{ M Na-citrate} \]

\[ + 0.6 \text{ mL} 0.1 \text{ M Ice-cold aq NaBH}_4 \]

Gold nanoparticle seeds
\(~\text{4nm diameter}\)

II. Stock solution

Stock solution
\[ 2.5 \times 10^{-4} \text{ M HAuCl}_4 + 0.1 \text{ M CTAB} \]

Addition of Ascorbic acid
Reduction of Au\(^{3+}\) to Au\(^{1+}\) results in disappearance of color

II. Three step protocol for nanorod synthesis

Step A
Add 1 mL of A

1 mL seed + 9 mL of stock solution

Step B

1 mL A + 9 mL of stock solution

Step C

10 mL B + 90 mL stock

Figure 2. Seed-mediated growth approach to making gold and silver nanorods of controlled aspect ratio. The specific conditions shown here, for 20 mL volume of seed solution, lead to high-aspect ratio gold nanorods. (bottom right) Transmission electron micrograph of gold nanorods that are an average of 500 nm long.

Directional Growth

Cetrimonium bromide \((\text{C}_{16}\text{H}_{33})\text{N(CH}_3)_3\text{Br})\) (CTAB)

Ascorbic acid

Figure 5. Cartoon of the crystallography of gold nanorods. The direction of elongation is [110]. The cross-sectional view is a pentagon; each end of the rod is capped with five triangular faces that are Au(111). The sides of the rods are not as well-defined; either Au[100] or Au[110] faces, or both.
Figure 8. Proposed mechanism of surfactant-directed metal nanorod growth. The single crystalline seed particles have facets that are differentially blocked by surfactant (or an initial halide layer that then electrostatically attracts the cationic surfactant). Subsequent addition of metal ions and weak reducing agent lead to metallic growth at the exposed particle faces. In this example, the pentatetrahedral twin formation leads to Au \{111\} faces that are on the ends of the nanorods, leaving less stable faces of gold as the side faces, which are bound by the surfactant bilayer.
Figure 3. Transmission electron micrographs (top), optical spectra (left), and photographs (right) of aqueous solutions of Au nanorods of various aspect ratios. The seed sample has an aspect ratio of 1. Samples a, b, c, d, and e have aspect ratios of $1.35 \pm 0.32$, $1.95 \pm 0.34$, $3.06 \pm 0.28$, $3.50 \pm 0.29$, and $4.42 \pm 0.23$, respectively. Scale bars: 500 nm for a and b, 100 nm for c–e. Reprinted with permission from ref 16. Copyright 2005 American Chemical Society.
Nanocube and Nanorice

The graphic above depicts various magnitudes of nanorice, which is a rice-shaped nanoparticle with a non-conducting core made of iron oxide and coated by a metallic shell made of gold. Scientists plan to attach the nanorice to scanning probe microscopes to obtain very clear image quality that surpasses today's technology. For the Air Force, this technology could be used as a tool to develop new high-speed optoelectronic materials and to monitor chemical reactions. (Graphic provided by Prof. Naemi Halas)
Template Synthesis
Porous Materials

- AAO
- MCM-41
- Micro-
- Meso
- Macro-
Polymer

\[ \text{a monomer ethene} \quad \overset{n}{\to} \quad \left( \begin{array}{c} \text{C} \\ \text{C} \\ \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \end{array} \right)^n \]

\[ \text{a polymer poly(ethene)} \]
Block copolymer
Phase Segregation

A-B diblock copolymer + C (inorganic precursor)

Thermal crosslinking

Nanostructured Inorganics
Carboxyl Presenting Surfaces

EDC (1-Ethyl-3-[3-dimethylaminopropyl]carbodiimide Hydrochloride)
Amine Presenting Surface

\[ \text{NHS-AcAc} + \text{NH}_2-\text{CH}_2-\text{CH}_2-\text{O} \xrightarrow{\text{dry DMSO pyridine}} \text{O=Si} \]
Sulfhydryl Labeling
Silica Modification

Support - Si-OH + RO-Si-(CH₃)₃NH₂ → (a)

Support - Si-O-Si-(CH₃)₃NH₃ + Glutaraldehyde → (b)

Support - Si-O-Si-(CH₃)₃NH-(CH₃)₃-COH + Antibody → (c)

Support - Si-O-Si-(CH₃)₃N=C-(CH₂)₃-C≡N-Antibody
Fig. 1. (A) Emission maxima and sizes of quantum dots of different composition. Quantum dots can be synthesized from various types of semiconductor materials (II-VI: CdS, CdSe, CdTe; III-V: InP, InAs; IV-VI: PbS, PbSe...) characterized by different bulk band gap energies. The curves represent experimental data from the literature on the dependence of peak emission wavelength on quantum dot diameter. The range of emission wavelength is 400 to 1350 nm, with size varying from 2 to 9.5 nm (organic passivation/solubilization layer not included). All spectra are typically around 30 to 50 nm (full width at half maximum). Inset: Representative emission spectra for some materials. Data are from (12, 18, 27, 76–82). Data for CdHgTe/ZnS have been extrapolated to the maximum emission wavelength obtained in our group. (B) Absorption (upper curves) and emission (lower curves) spectra of four CdSe/ZnS quantum dot samples. The blue vertical line indicates the 488-nm line of an argon-ion laser, which can be used to efficiently excite all four types of quantum dots simultaneously. [Adapted from (28)] (C) Size comparison of quantum dots and comparable objects. FITC, fluorescein isothiocyanate; GFP, green fluorescent protein; quantum dot, green (4.5 nm, top) and red (6.5 nm, bottom) CdSe/ZnS quantum dot; globular, red-shaped quantum dot (size from Quantum Dot Corp.'s Web site). Three proteins—streptavidin (SAV), maltose binding protein (MBP), and immunoglobulin G (IgG)—have been used for further functionalization of quantum dots (see text) and add to the final size of the quantum dot, in conjunction with the solubilization chemistry (Fig. 2).
FIGURE 3  Maleimide functionalized QDs for conjugating thiol-containing ligands. TOPQ stabilized QDs are coated with a primary amine functionalized tri-block amphiphilic copolymer for producing water-soluble QDs, which facilitate further conjugation to ligands with free thiols through bi-functional cross-linkers.
Cells incubated with tiopronin coated QDs

Cells incubated with Tat functionlized QDs

GRKRRQRRR (Tat)
Scheme 1. Modular Design of Hydrophilic Ligands with Terminal Functional Groups Used in This Study