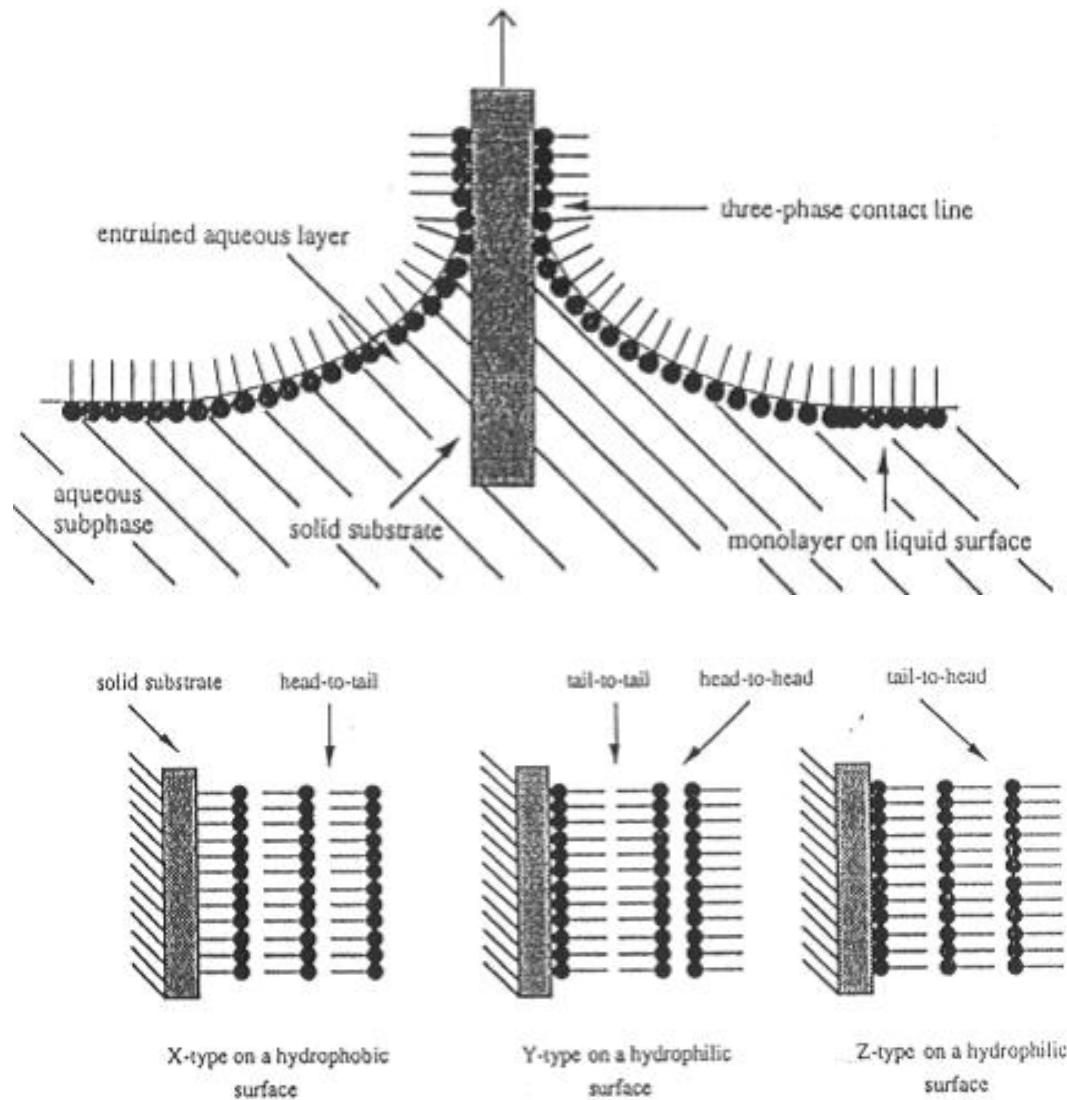
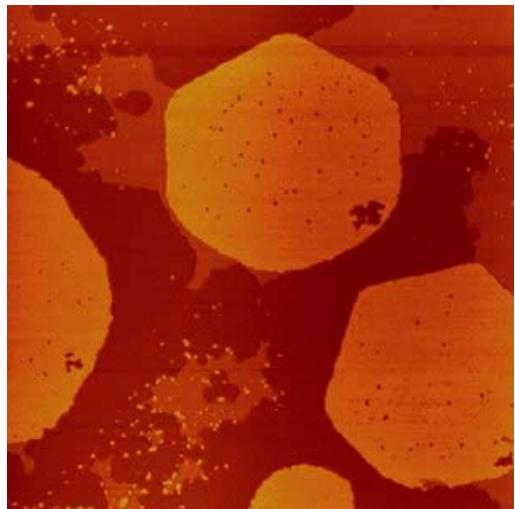


Synthesis of Nanoparticles and Surface Modifications

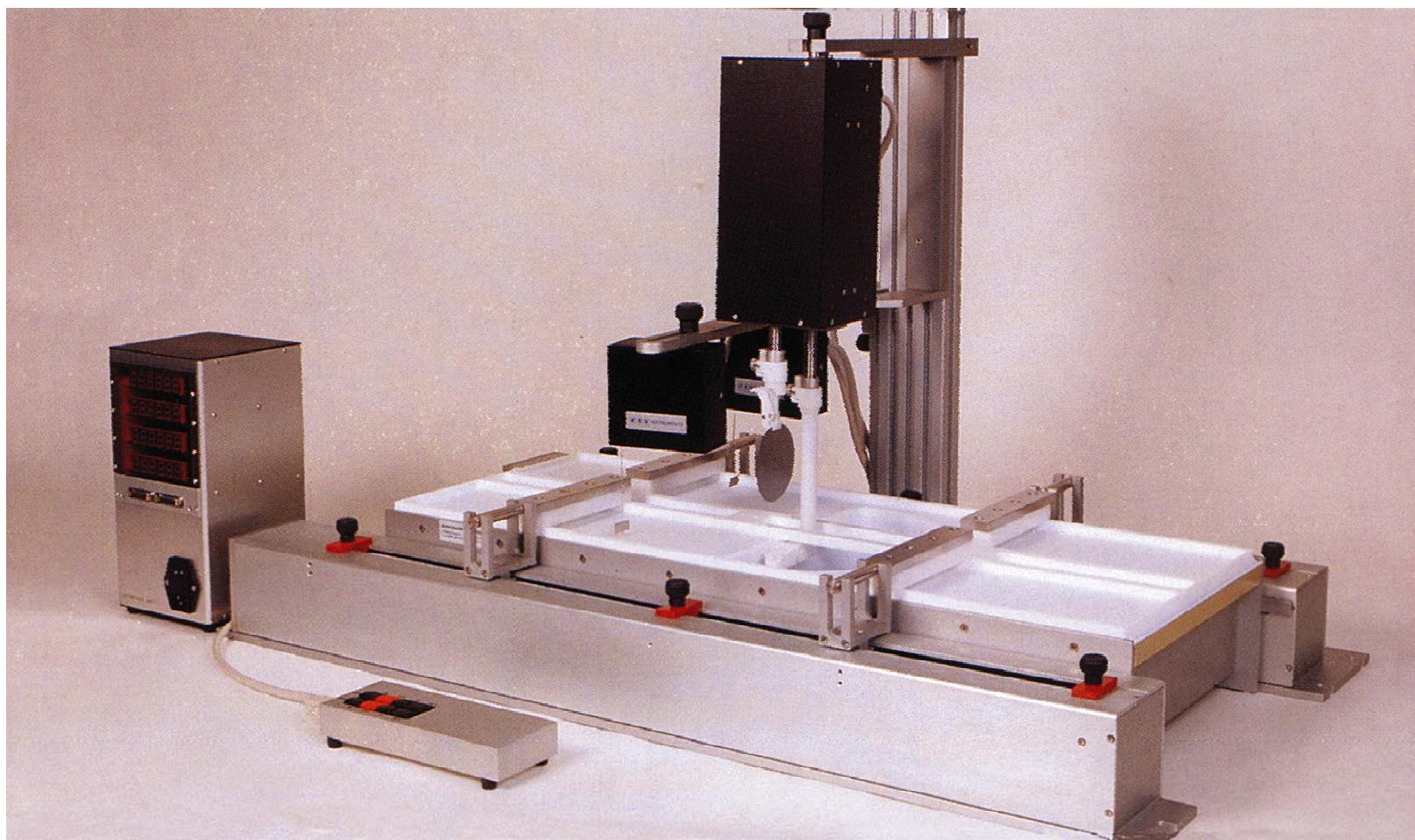
Self-Assembly

- 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

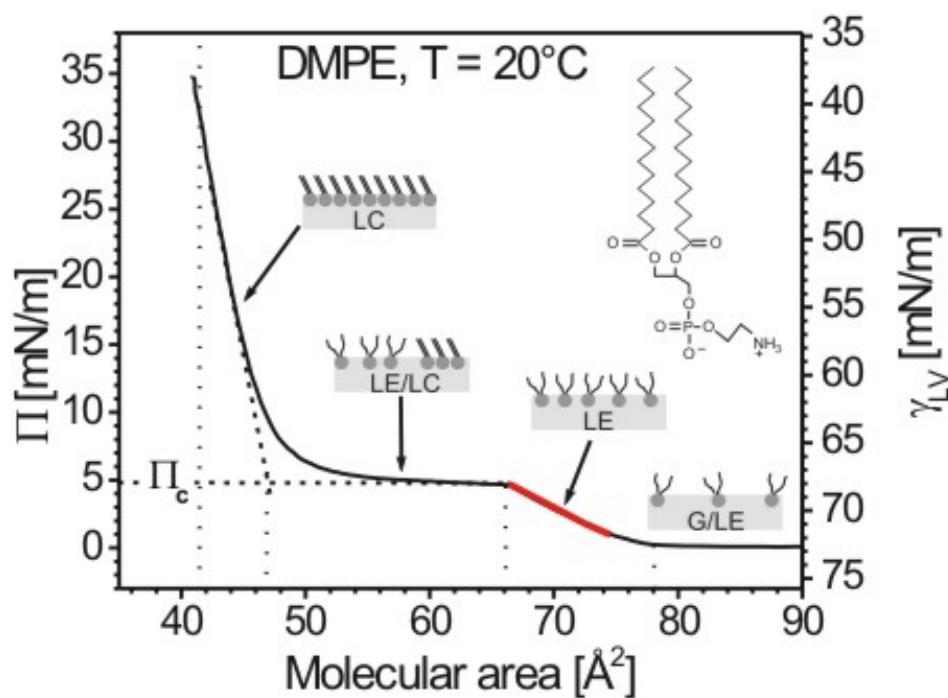
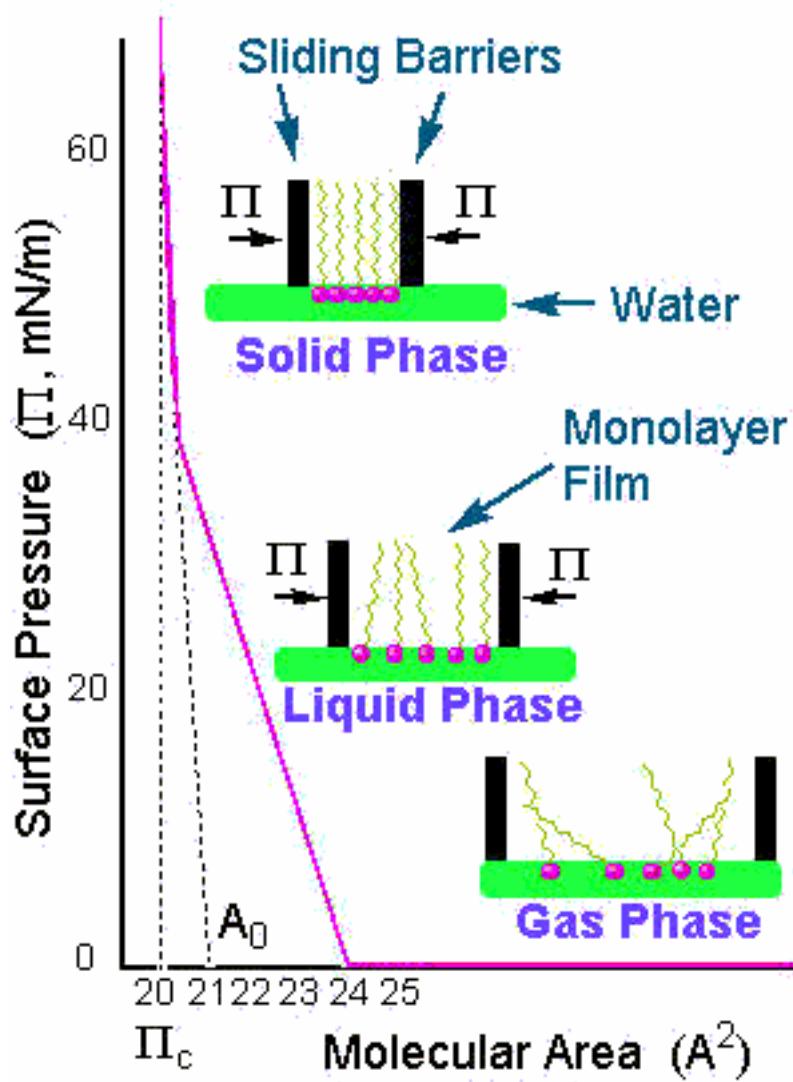
Langmuir-Blodgett Films



Langmuir-Blodgett Films

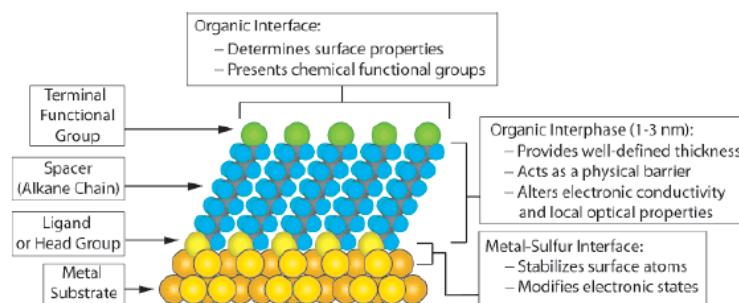


Isotherm



Self-Assemble Monolayer (SAM)

Chem. Rev. 2005, 105, 1103–1169



S-Au 25-30 Kcal/mole
Si-O 190 kcal/mole

Ligand	Substrates	Morphology of Substrate		Ligand	Substrates	Morphology of Substrate	
		Thin Films or Bulk Material	Nanoparticles or Other Nanostructures			Thin Films or Bulk Material	Nanoparticles or Other Nanostructures
ROH	Fe ₃ O ₄ Si-H Si	36 37	35	RSSR'	Ag Au CdS Pd Au	89 20 30 93	90 90-92 61
RCOO-/RCOOH	α -Al ₂ O ₃ Fe ₃ O ₄ Ni Ti/TiO ₂	38,39	40 41,42				
RCOO-OOCR	Si(111):H Si(100):H	44					
Ene-diol	Fe ₃ O ₄	45					
RNH ₂	FeS ₂ Mica Stainless Steel 316L YBa ₂ Cu ₃ O ₇ - δ	46 47 48 49			RS ₂ O ₃ ²⁻ Na ⁺ Au Cu	96 97	98
	CdSe	50					
RC≡N	Ag Au	51			RSeH	Ag Au CdS CdSe	99 100,101 60 102
R-N≡N ⁺ (BF ₄ ⁻)	GaAs(100) Pd Si(111):H	52 52 52					
RSH	Ag Ag ₉₀ Ni ₁₀ AgS Au AuAg AuCu Au _x Pd _{1-x} CdTe CdSe CdS Cu FePt GaAs Ge Hg HgTe InP Ir Ni PbS Pd PdAg Pt Ru Stainless Steel 316L YBa ₂ Cu ₃ O ₇ - δ	26 55 56 26 58 58 58 59 60 61,62 26 58 63-66 67 68 69-71 72 73 74 75 76-78 30 74,79 58 32 80 81 48 82 83 84 85	53,54 56 57 58 58 58 59 60 61,62 58 58 63-66 67 68 69-71 72 73 74 75 76-78 74,79 58 80 81 82 83 84 85		RSeSeR'	Au	101
					R ₃ P	Au FeS ₂ CdS CdSe CdTe	103 104 104 104
					R ₃ P=O	Co CdS CdSe CdTe	105,106 104 104 104
					RPO ₃ ²⁻ /RP(O)(OH) ₂	Al Al-OH Ca ₁₀ (PO ₄ ,CO ₃) ₆ (OH) ₂ GaAs GaN Indium tin oxide (ITO) Mica TiO ₂ ZrO ₂ CdSe CdTe	107 108 109 110 110 111 112 113,114 114,115 116-118 118,119
					RPO ₄ ³⁻	Al ₂ O ₃ Nb ₂ O ₅ Ta ₂ O ₅ TiO ₂	120 120 121 120,122
					RN≡C RHC-CH ₂ RC≡CH	Pt Si Si(111):H	123 37 125
					RSiX ₃ X = H, Cl, OCH ₂ CH ₃	HfO ₂	126
RSAc	Au Au	86 87				ITO PtO	127 128
RSR'	Au	88				TiO ₂ ZrO ₂	113,126,129 126,129

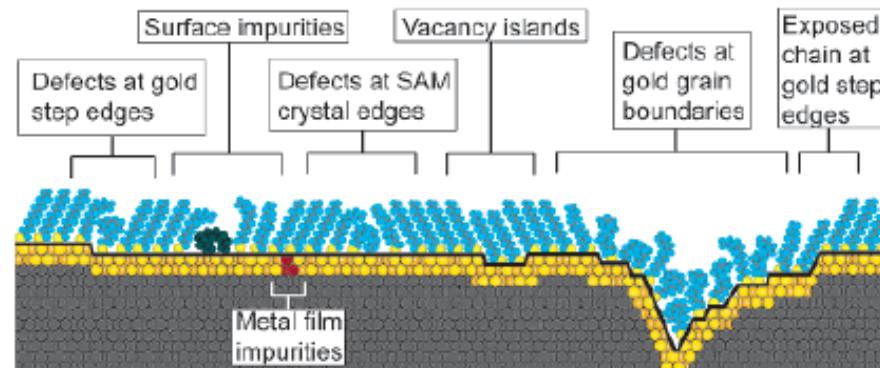
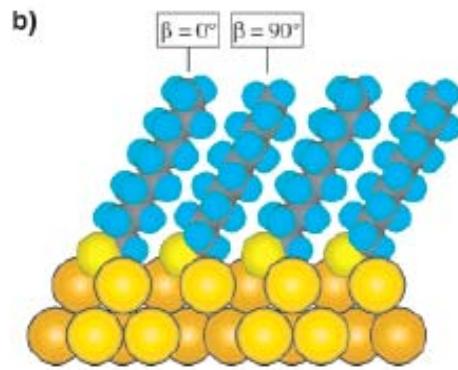
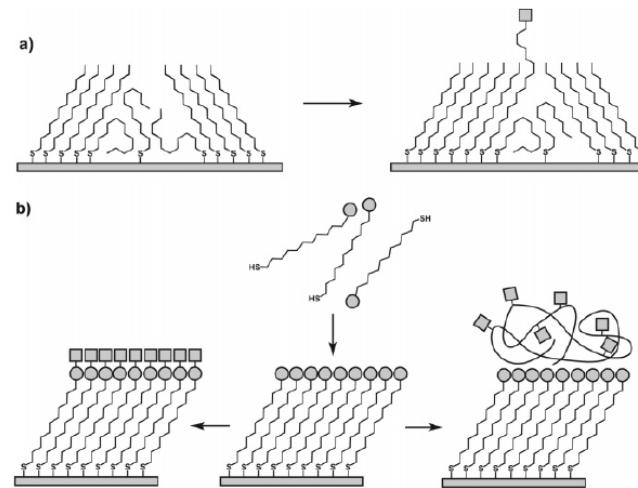
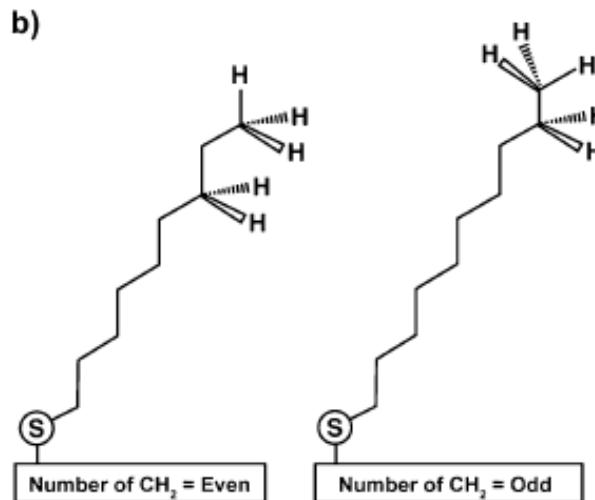


Figure 7. Schematic illustration of some of the intrinsic and extrinsic defects found in SAMs formed on polycrystalline substrates. The dark line at the metal–sulfur interface is a visual guide for the reader and indicates the changing topography of the substrate itself.



^c (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.

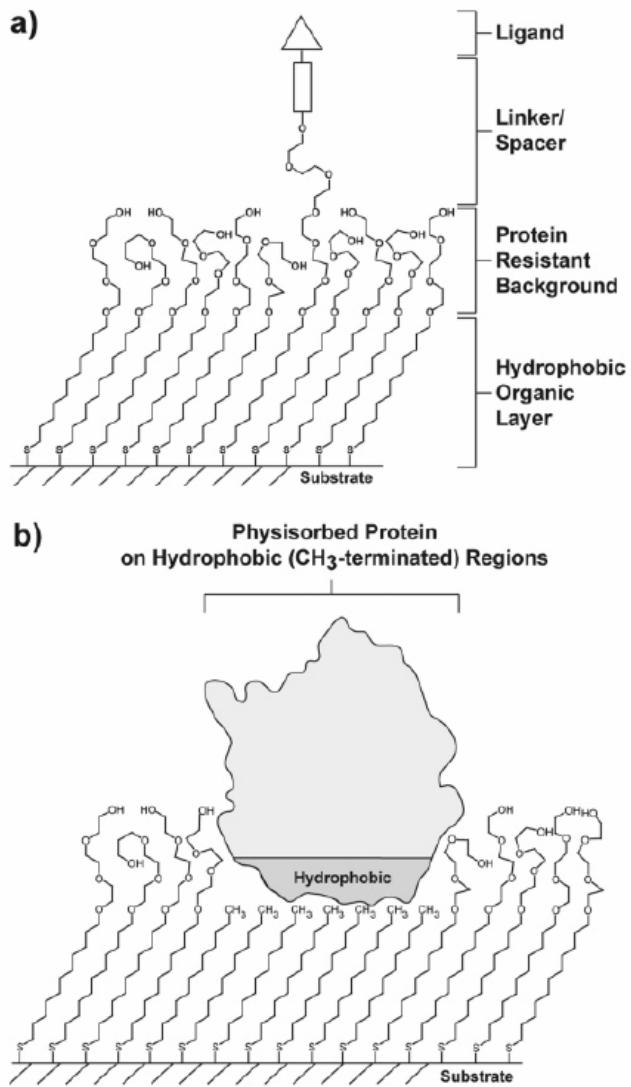


Figure 21. Schematic illustrations of (a) a mixed SAM and (b) a patterned SAM. Both types are used for applications in biology and biochemistry.

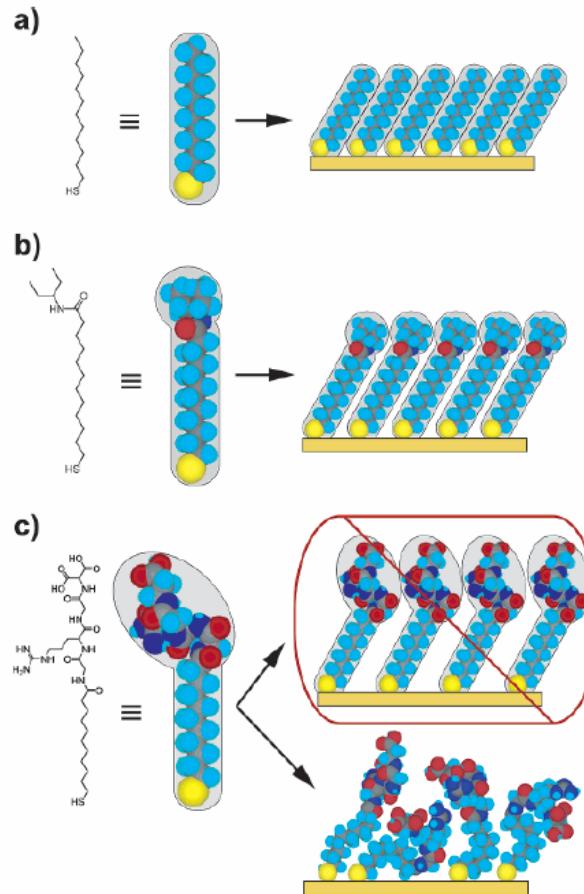


Figure 22. Schematic diagram illustrating the effects that large terminal groups have on the packing density and organization of SAMs. (a) Small terminal groups such as $-\text{CH}_3$, $-\text{CN}$, etc., do not distort the secondary organization of the organic layer and have no effect on the sulfur 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.

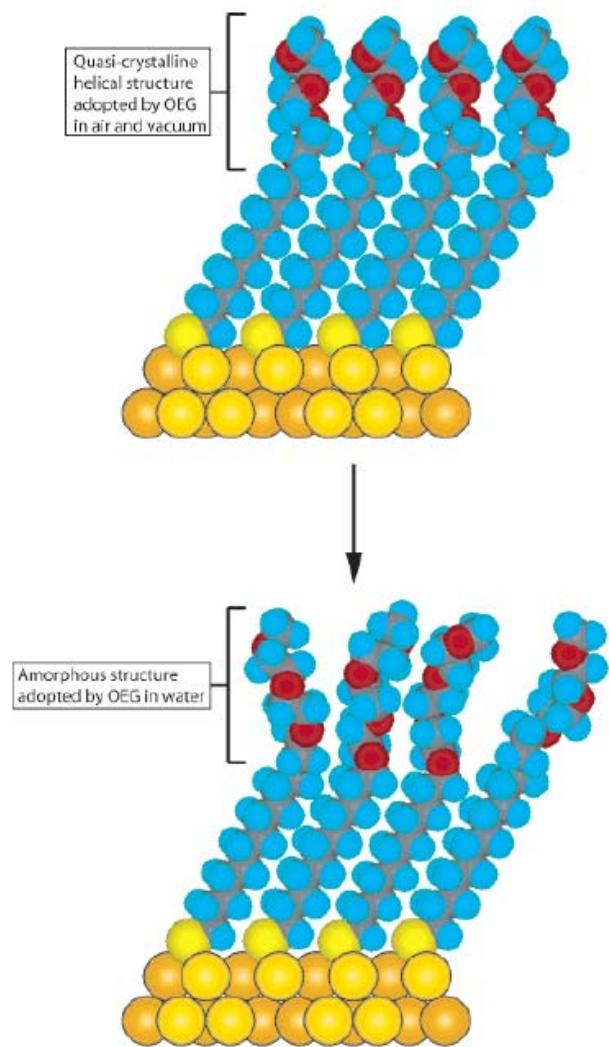
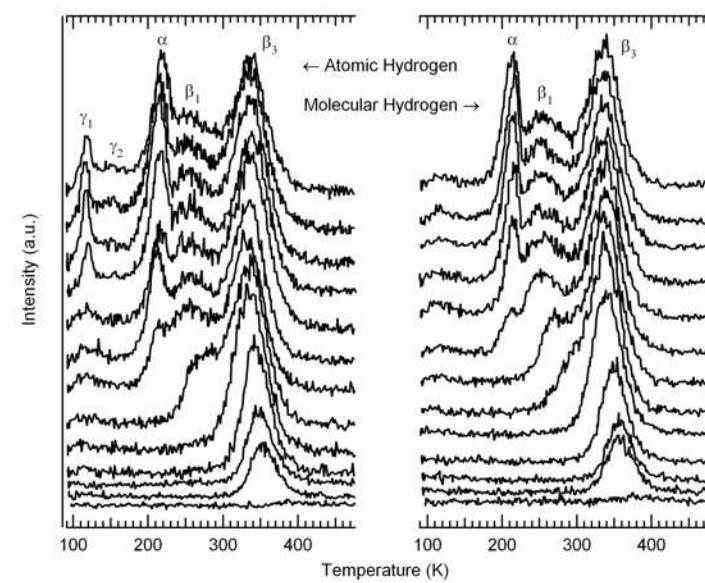


Figure 23. Schematic illustration of the order–disorder transition evidenced by SAMs of alkanethiolates terminated with triethylene glycol. The EG₃ group loses conformational ordering upon solvation in water.

Temperature Programmed Desorption

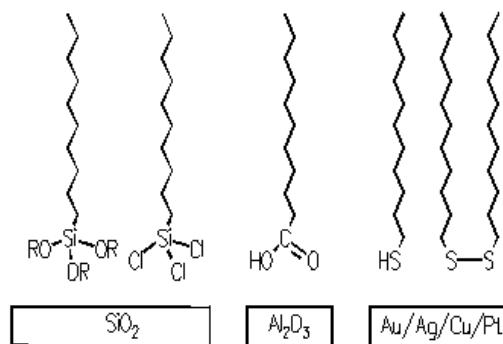


Self-Assembly

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

Organosilanes

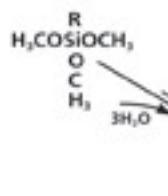
Self-assembled monolayers



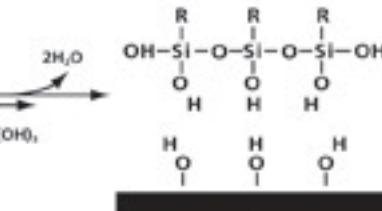
- Surface
- silicon oxide: silanisation
- aluminum oxide: fatty acids
- metals: thiols and sulfides

Immersion of substrate in a solution containing the adequate molecules for 12 - 24 hours yields an ordered monolayer

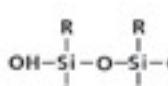
Hydrolysis (1)



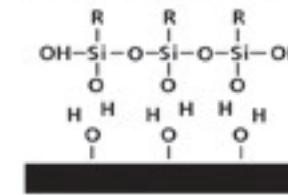
Condensation of Oligomers (2)



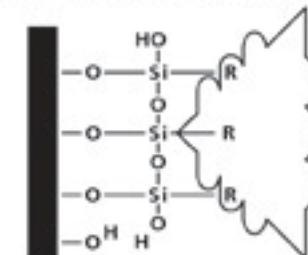
Bond Formation (4)



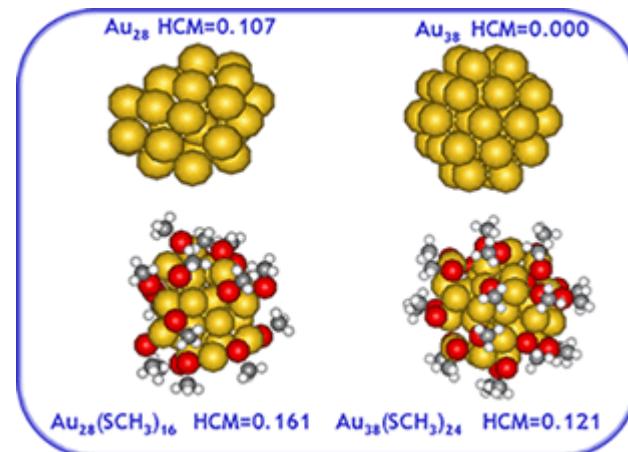
Hydrogen Bonding (3)



Reaction and bond formation of the R group (5)

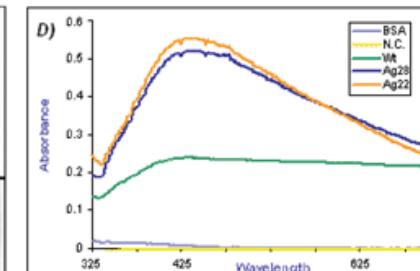
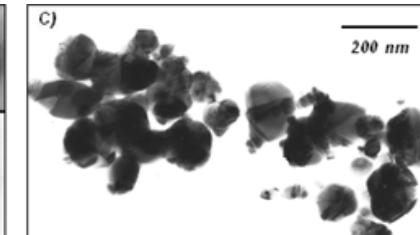
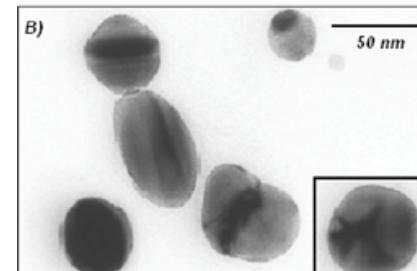
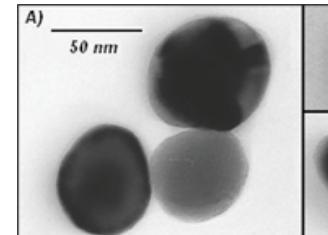
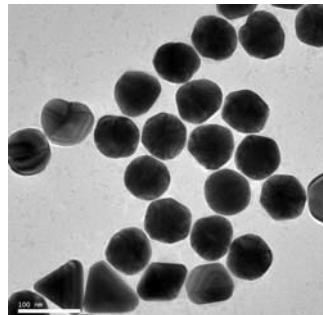
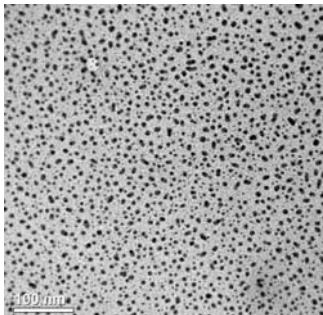
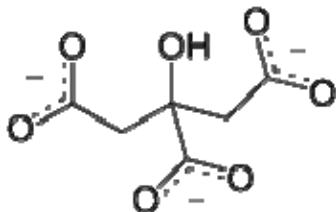


Metal Reduction



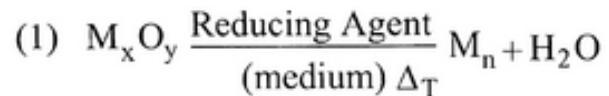
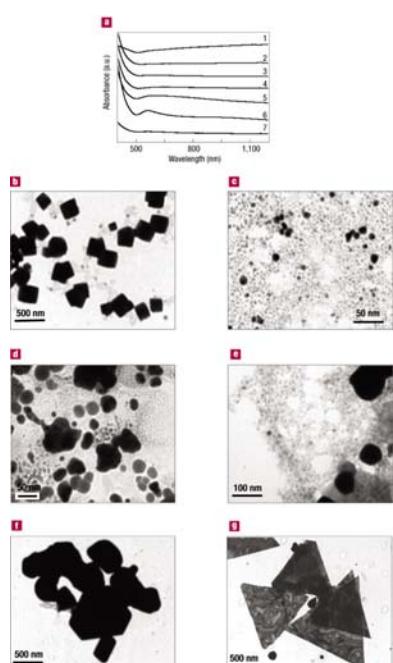
Synthesis of Silver Nanoparticles

1. A solution of AgNO_3 ($1.0 \times 10^{-3} \text{ M}$) 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.

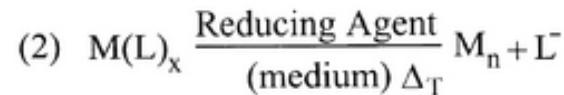


Synthesis of Gold Nanoparticles

- 1. Add 20 mL of 1.0 mM HAuCl_4 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.**



(Reducing Agent = $\text{R} - \text{COH}$)

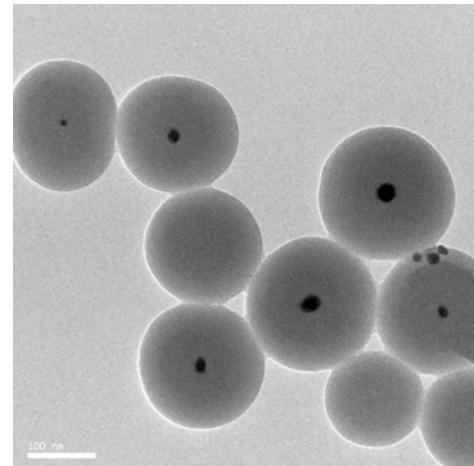
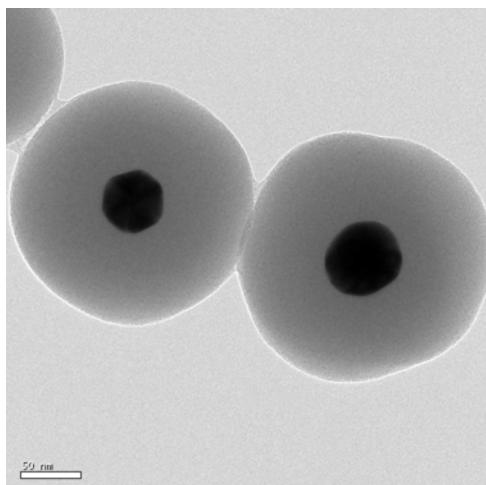


($\text{L} = \text{NO}_3^-, \text{C}_2\text{H}_5\text{O}^-$)

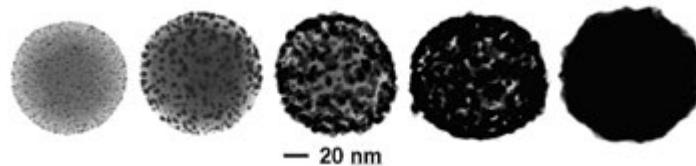
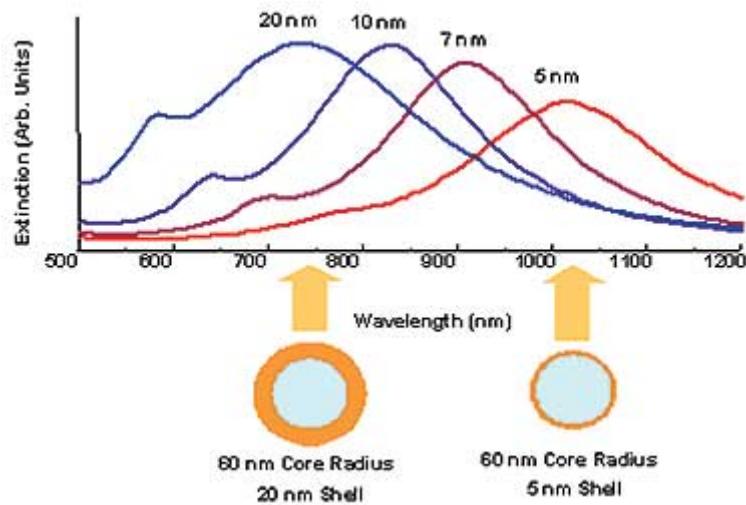
(Reducing Agent = $\text{R} - \text{COH}$)

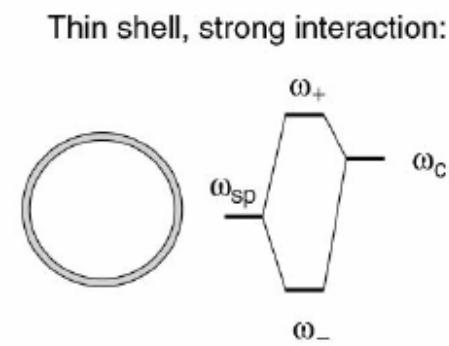
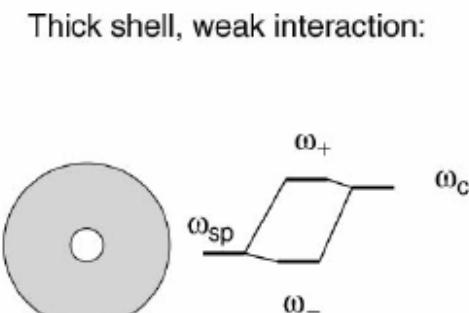
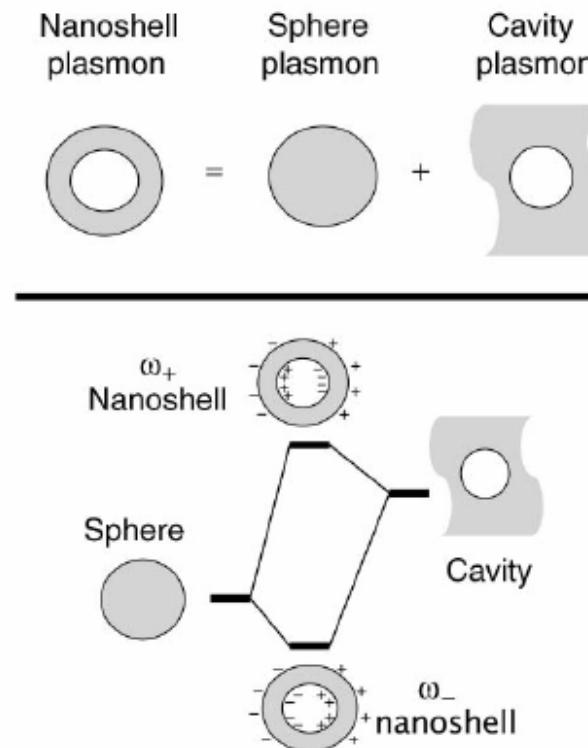
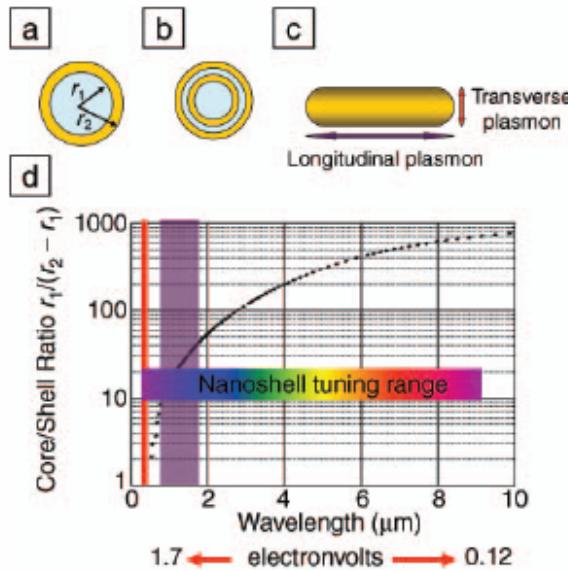
Construction of Core Shell Ag/Au@SiO₂ Nanoparticles

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





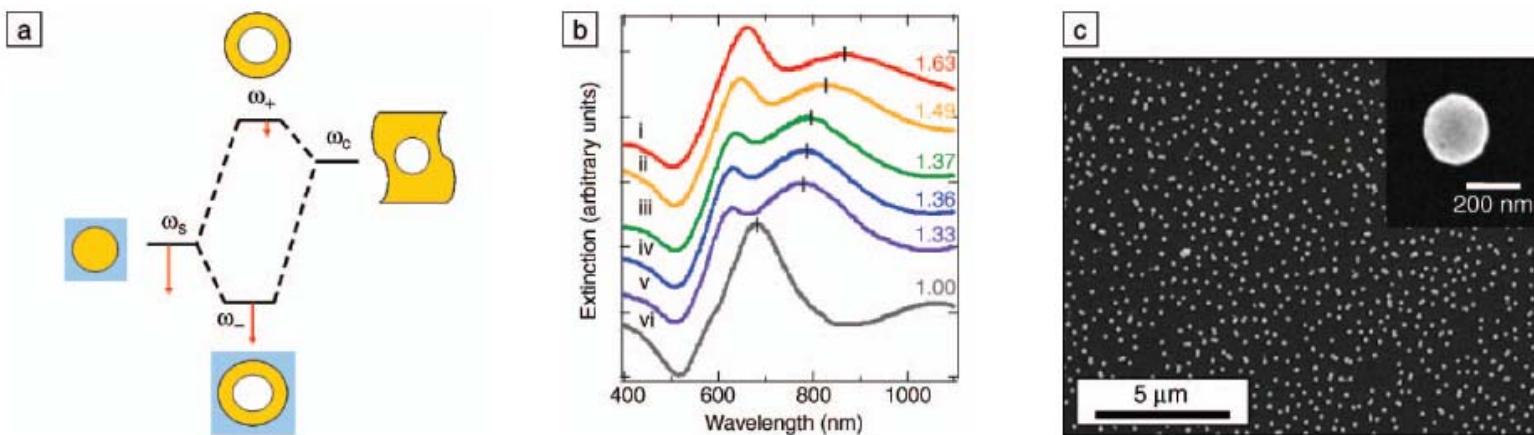


Figure 5. (a) Plasmon hybridization picture applied to surface plasmon resonance sensing with nanoshells: the low-energy “bonding” plasmon, ω_- , is sensitized to changes in its dielectric environment. The blue background schematically denotes the embedding medium for the nanoparticle. (b) Experimental curves showing plasmon resonance shifts for nanoshell-coated films in various media: (i) carbon disulfide, (ii) toluene, (iii) hexane, (iv) ethanol, (v) H_2O , 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 $\text{Fe}_3\text{O}_4@\text{Ag}/\text{Au}$

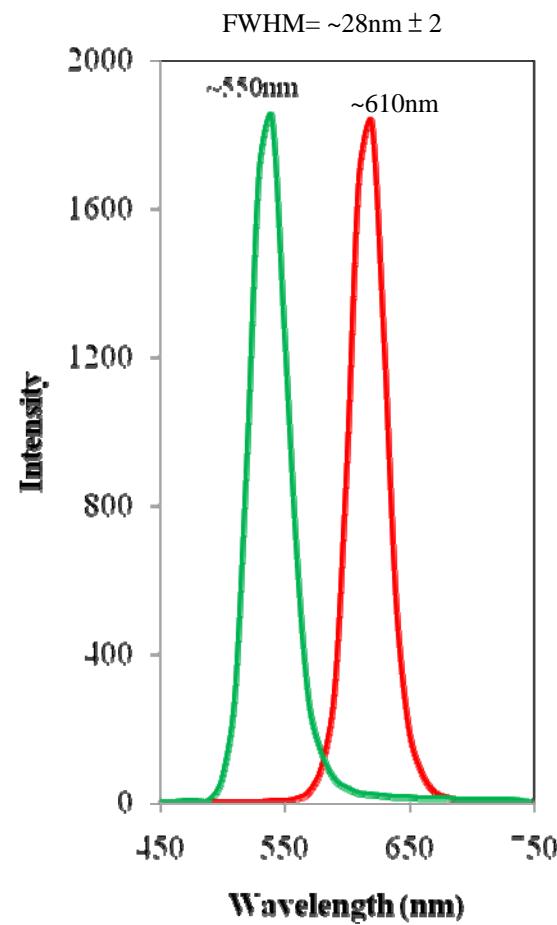
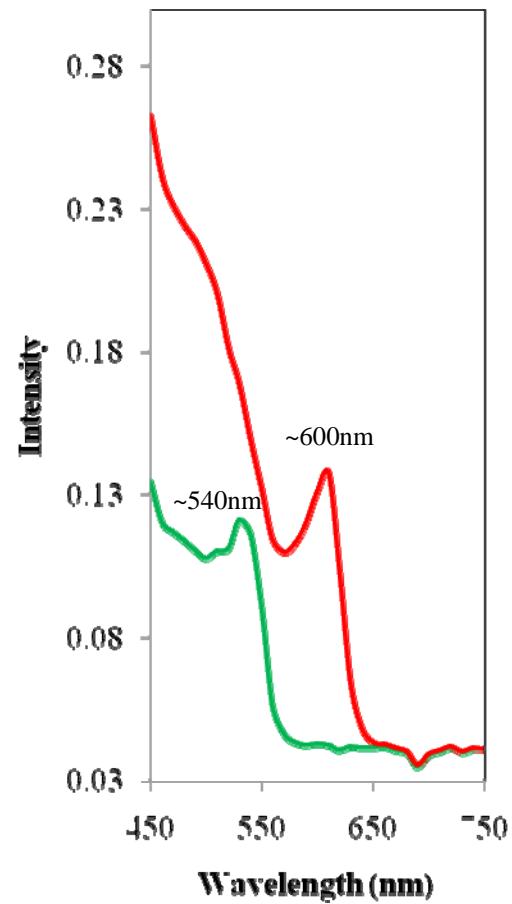
1. *To the magnetic nanoparticle suspension obtained from commercial company, add 50 ml of a solution of Au (III) salt or Ag (I) salt at concentration of 0.01–1% mmol/L, shaking for 30 minutes, allowing Au (III) or Ag (I) ion to absorb on the surface of magnetic nanoparticle sufficiently,*
2. *Then adding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

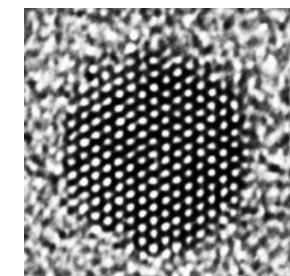
Synthesis of TOPO/HDA capped quantum dots of CdSe

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 pellet 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



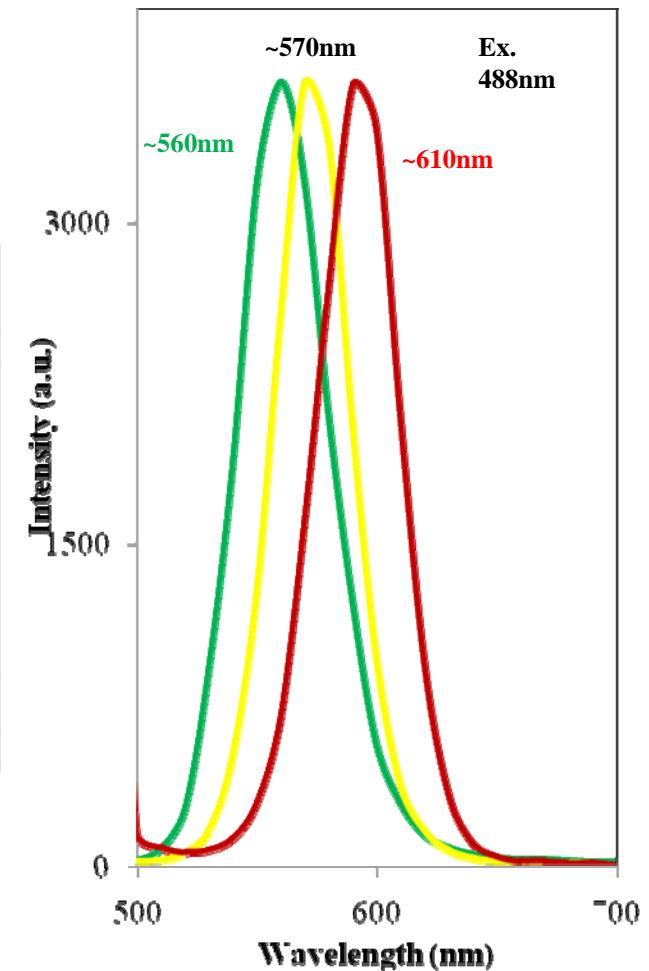
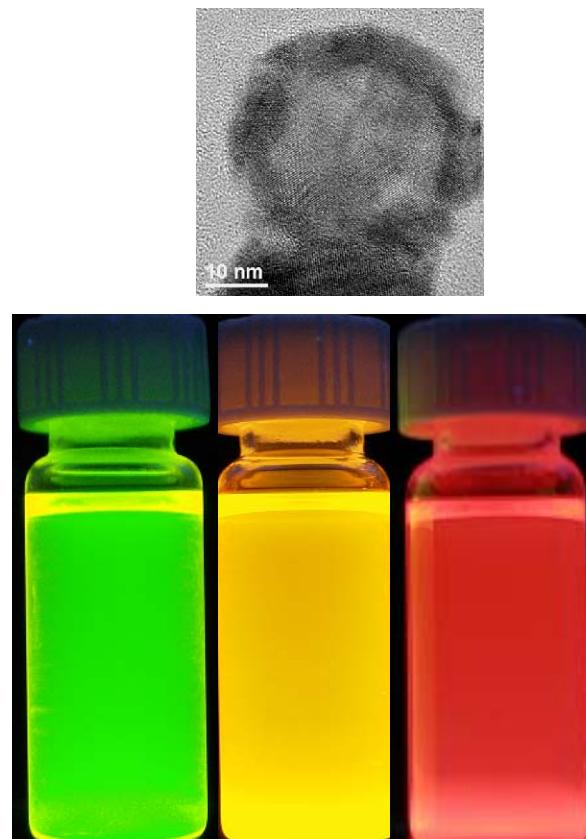
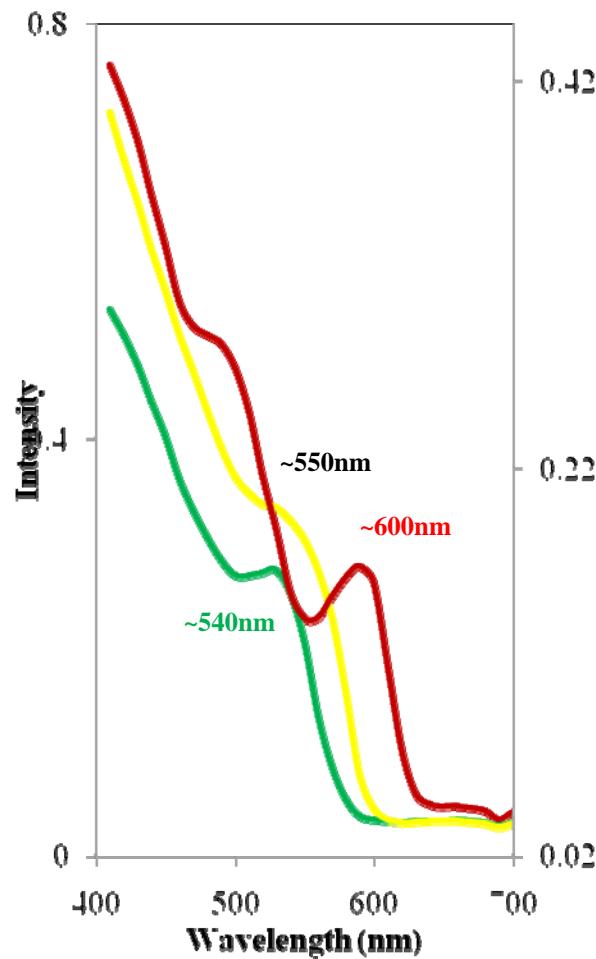
Cooperative UV and PL spectra of CdSe core



Synthesis of CdSe/ZnS Quantum Dots

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

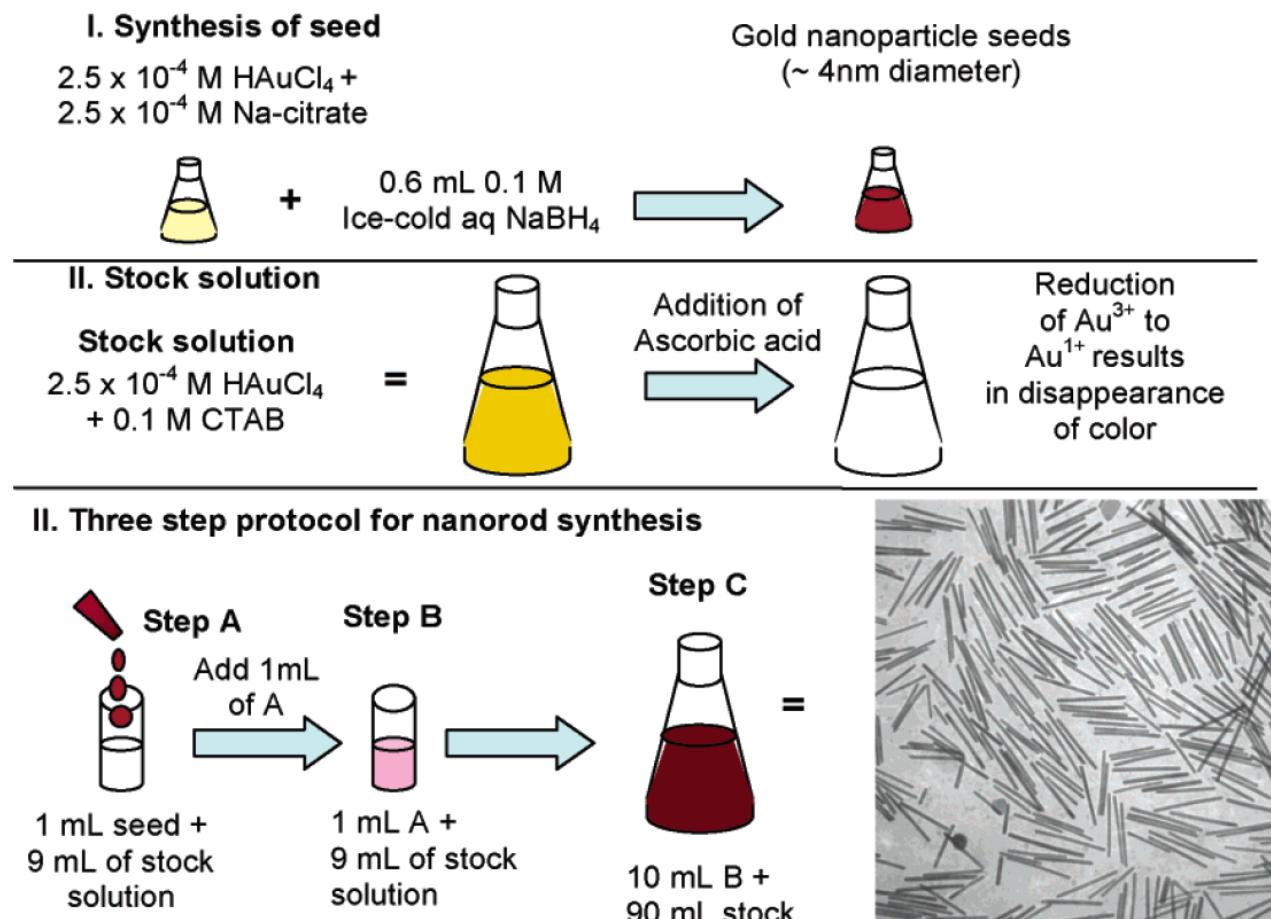
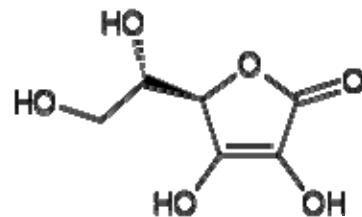
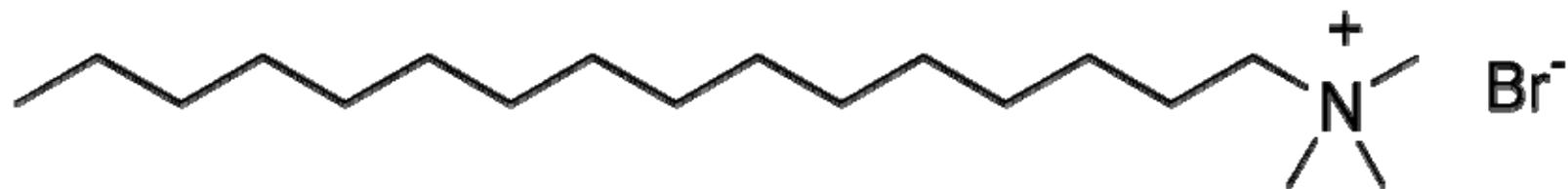


Figure 2. Seed-mediated growth approach to making gold and silver nanorods of controlled aspect ratio. The specific conditions shown here, for 20 mL volume of seed solution, lead to high-aspect ratio gold nanorods. (bottom right) Transmission electron micrograph of gold nanorods that are an average of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

Directional Growth

Cetrimonium bromide ($(C_{16}H_{33})N(CH_3)_3Br$) (CTAB)



Ascorbic acid

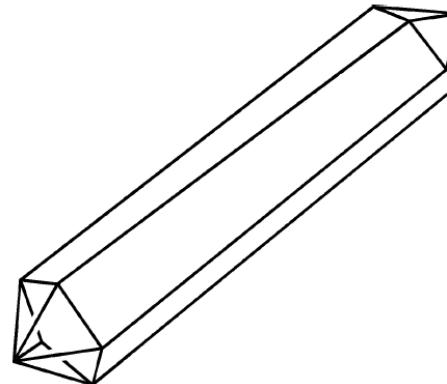


Figure 5. Cartoon of the crystallography of gold nanorods. The direction of elongation is [110]. The cross-sectional view is a pentagon: each end of the rod is capped with five triangular faces that are $Au\{111\}$. The sides of the rods are not as well-defined; either $Au\{100\}$ or $Au\{110\}$ faces, or both.

STEP 1: SYMMETRY BREAKING IN FCC METALS



STEP 2: PREFERENTIAL SURFACTANT BINDING TO SPECIFIC CRYSTAL FACES

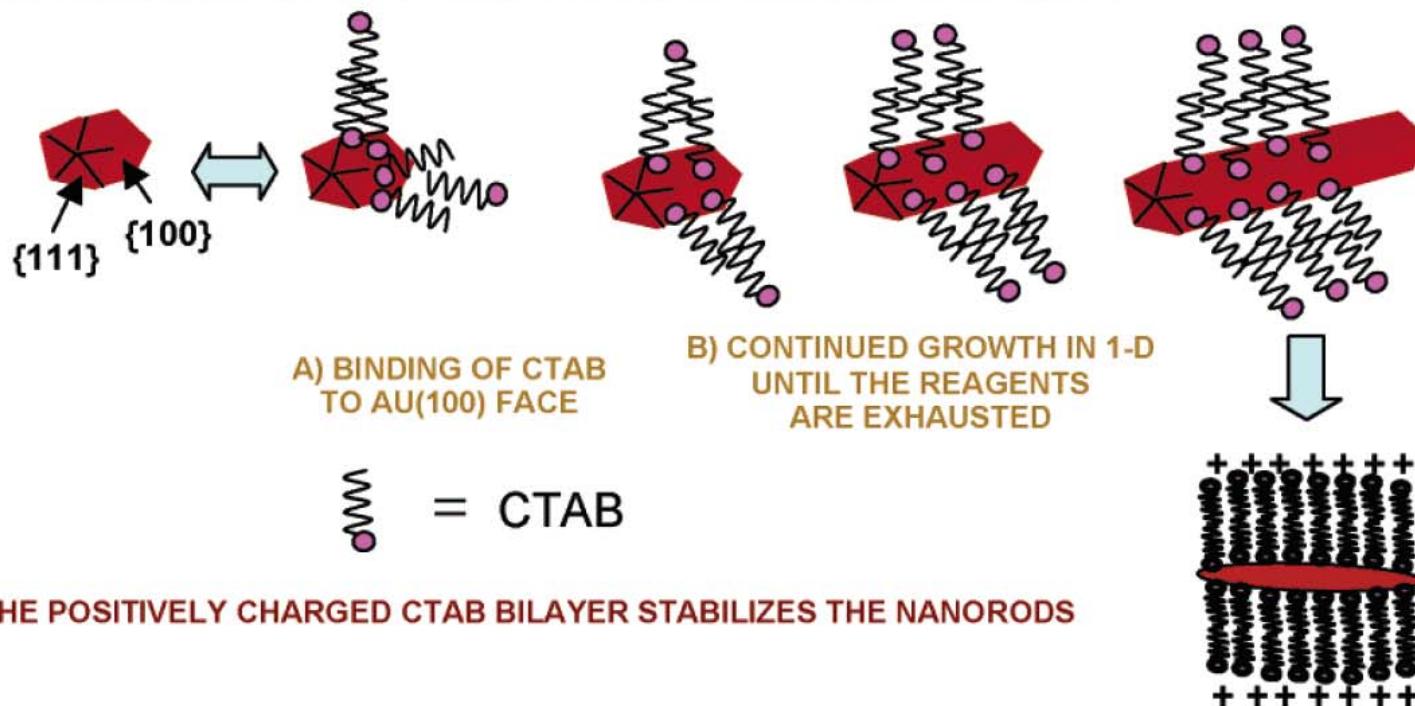


Figure 8. Proposed mechanism of surfactant-directed metal nanorod growth. The single crystalline seed particles have facets that are differentially blocked by surfactant (or an initial halide layer that then electrostatically attracts the cationic surfactant). Subsequent addition of metal ions and weak 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.

Nanorods

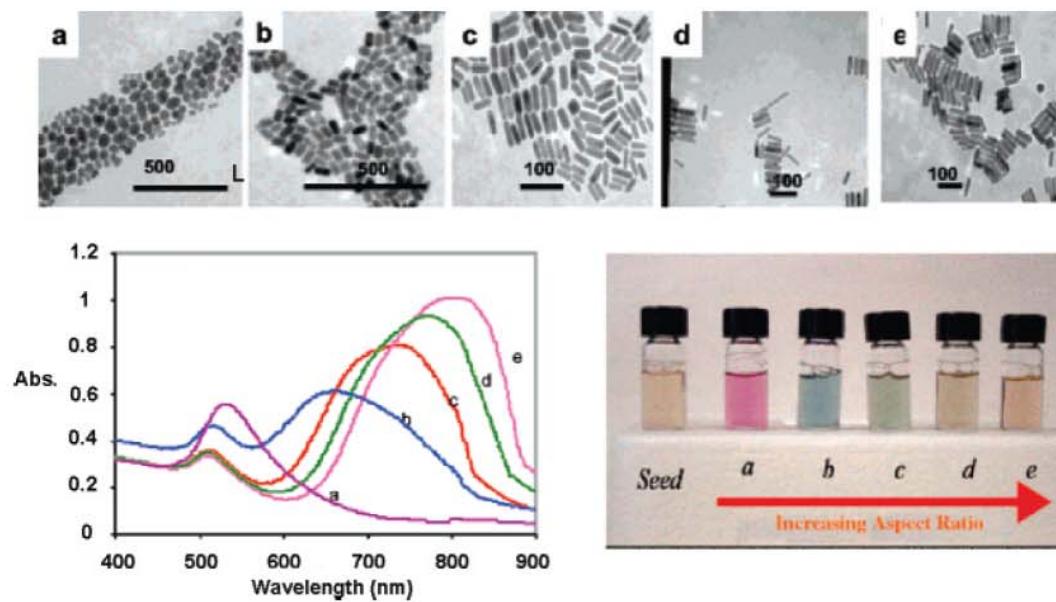
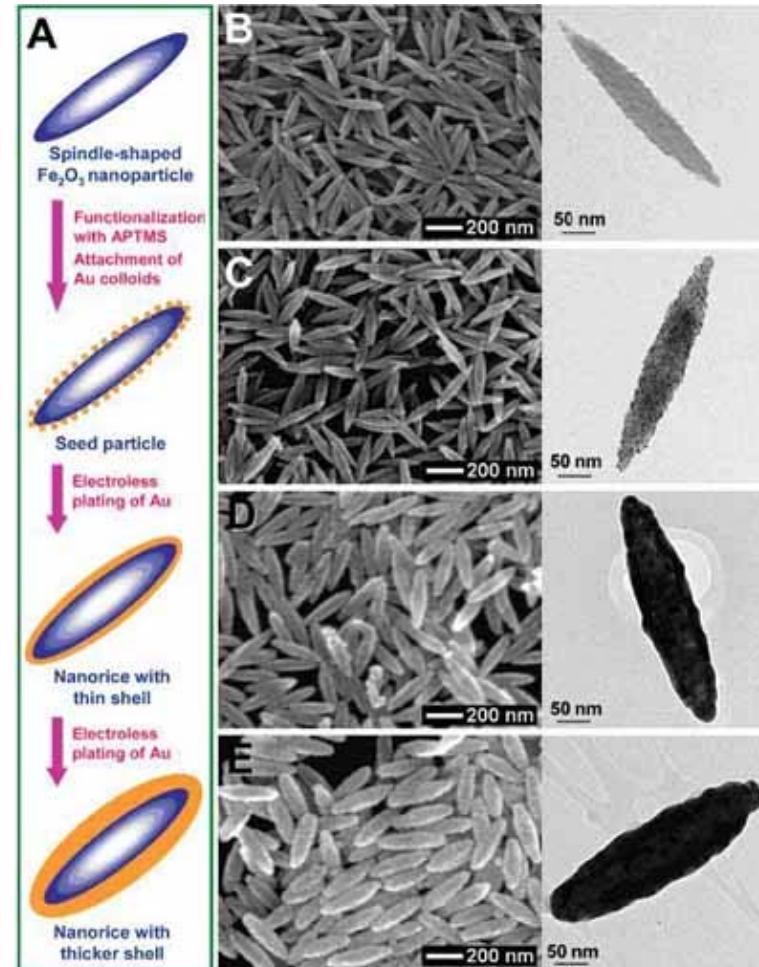
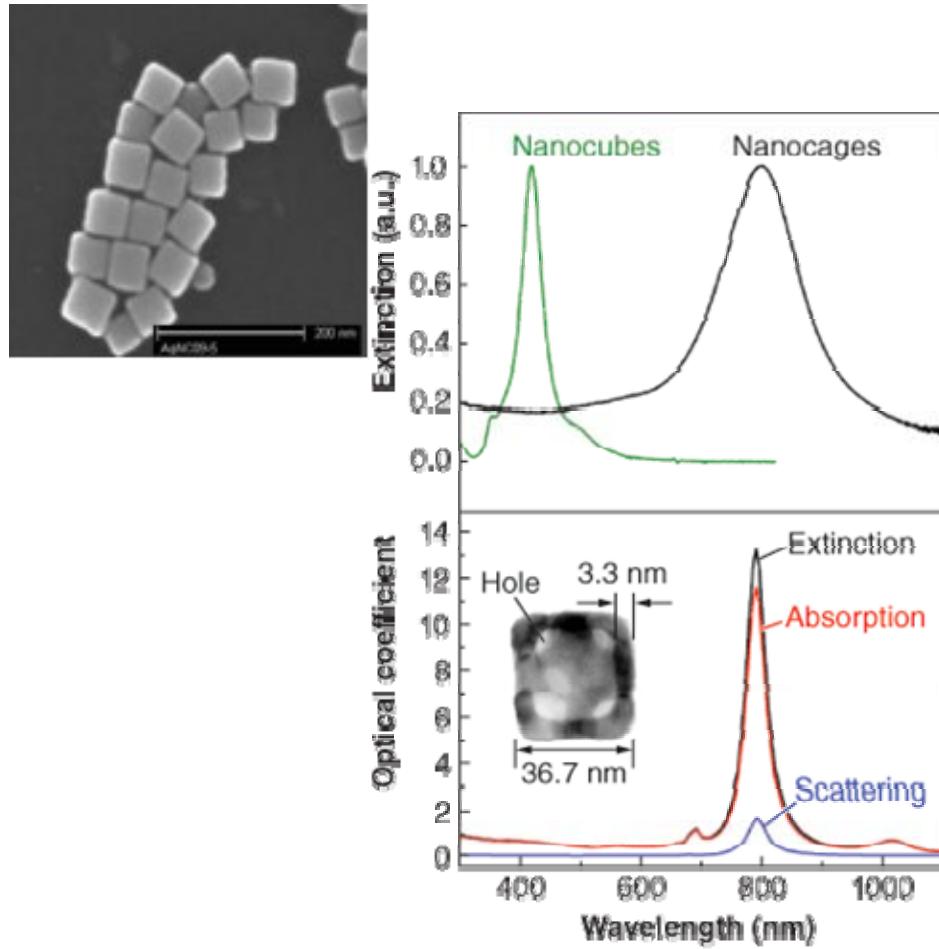


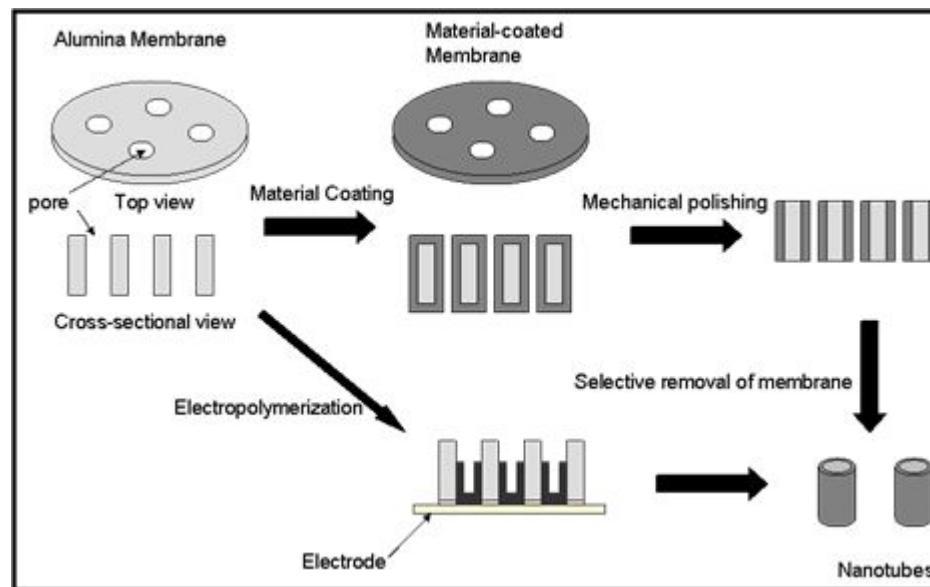
Figure 3. Transmission electron micrographs (top), optical spectra (left), and photographs (right) of aqueous solutions of Au nanorods of various aspect ratios. The seed sample has an aspect ratio of 1. Samples a, b, c, d, and e have aspect ratios of 1.35 ± 0.32 , 1.95 ± 0.34 , 3.06 ± 0.28 , 3.50 ± 0.29 , and 4.42 ± 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 covered 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. Naomi Halas)

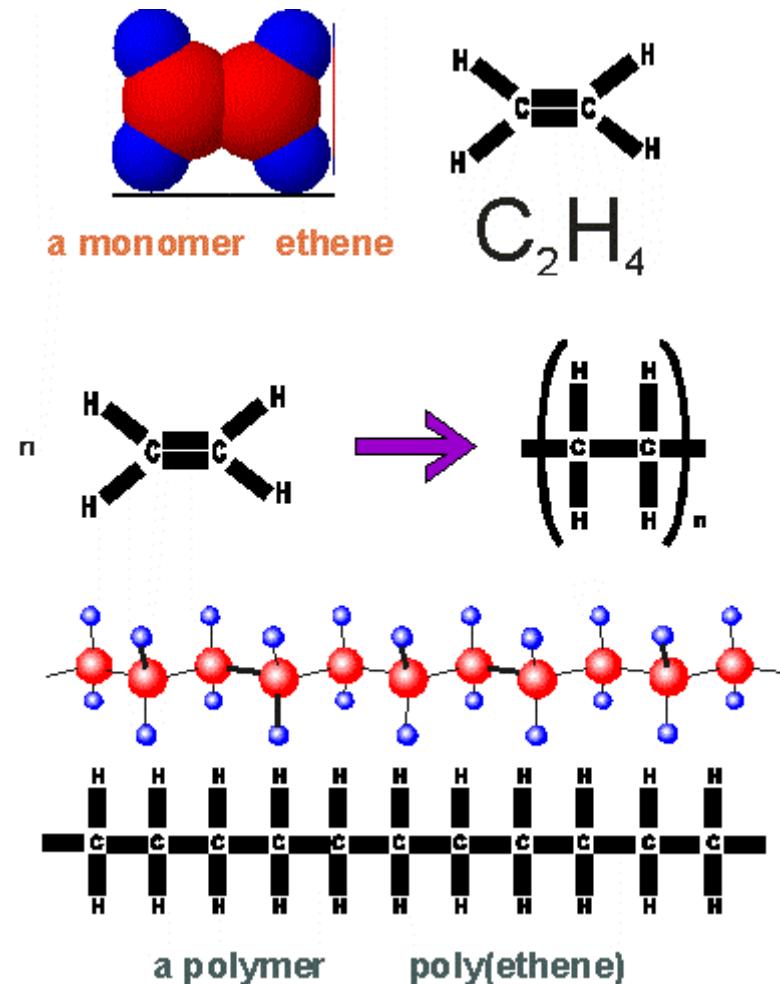
Template Synthesis



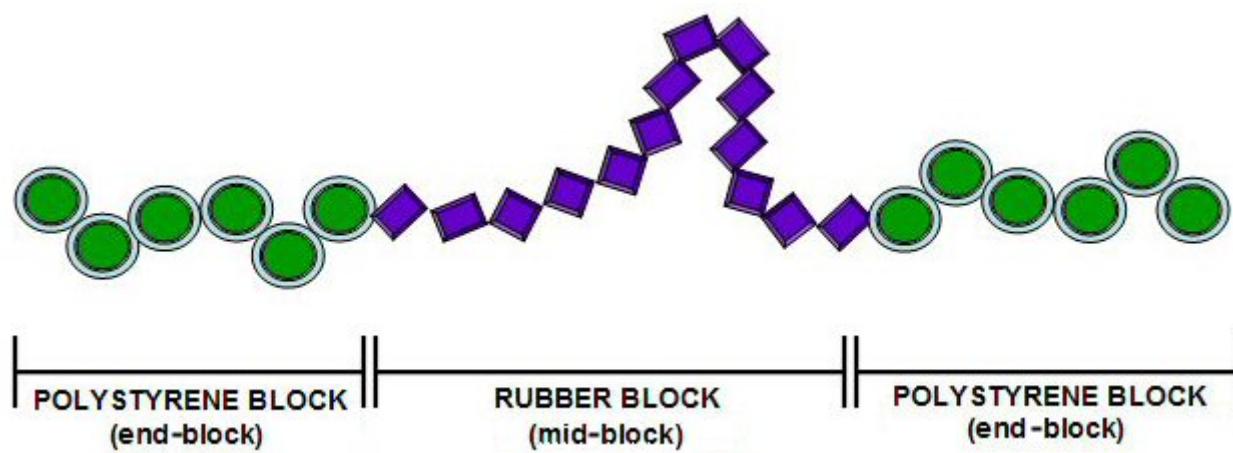
Porous Materials

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

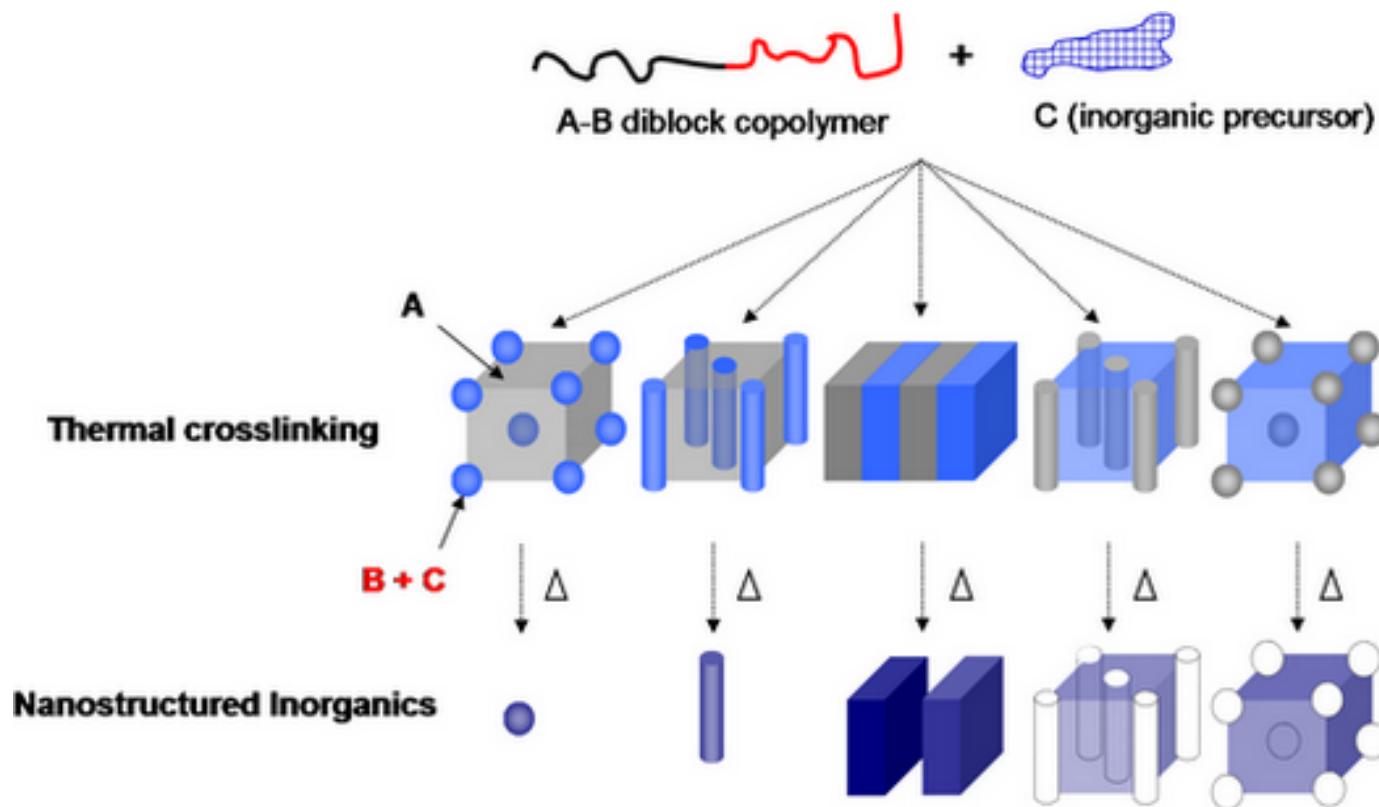
Polymer



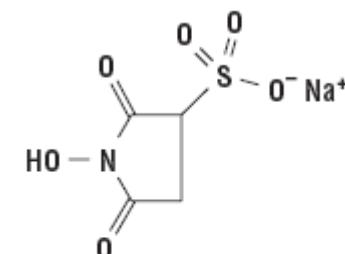
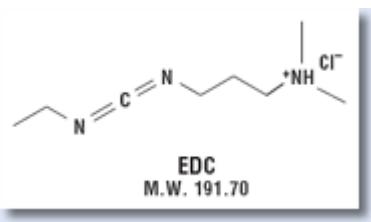
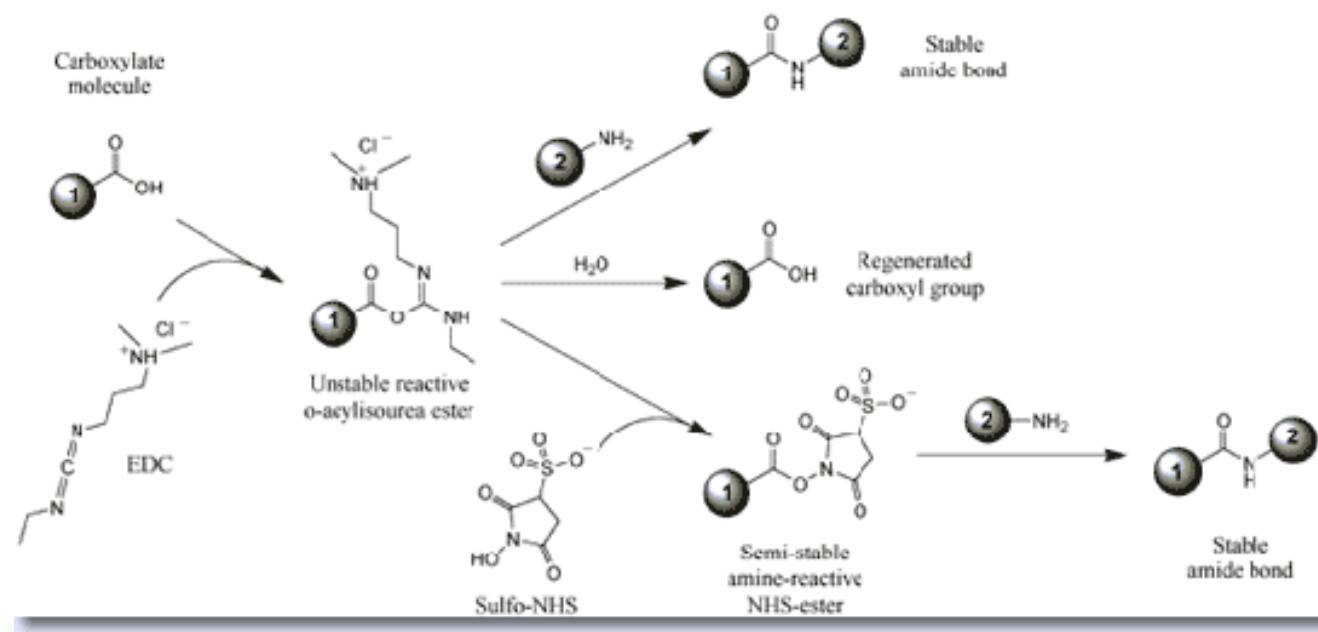
Block copolymer



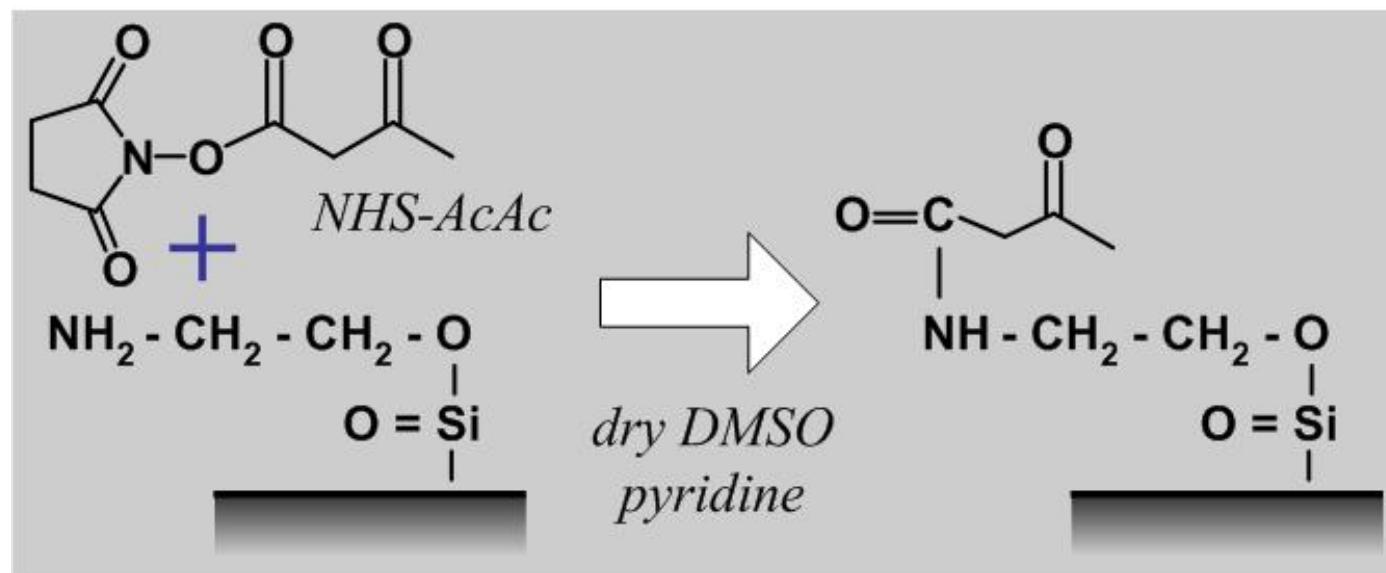
Phase Segregation



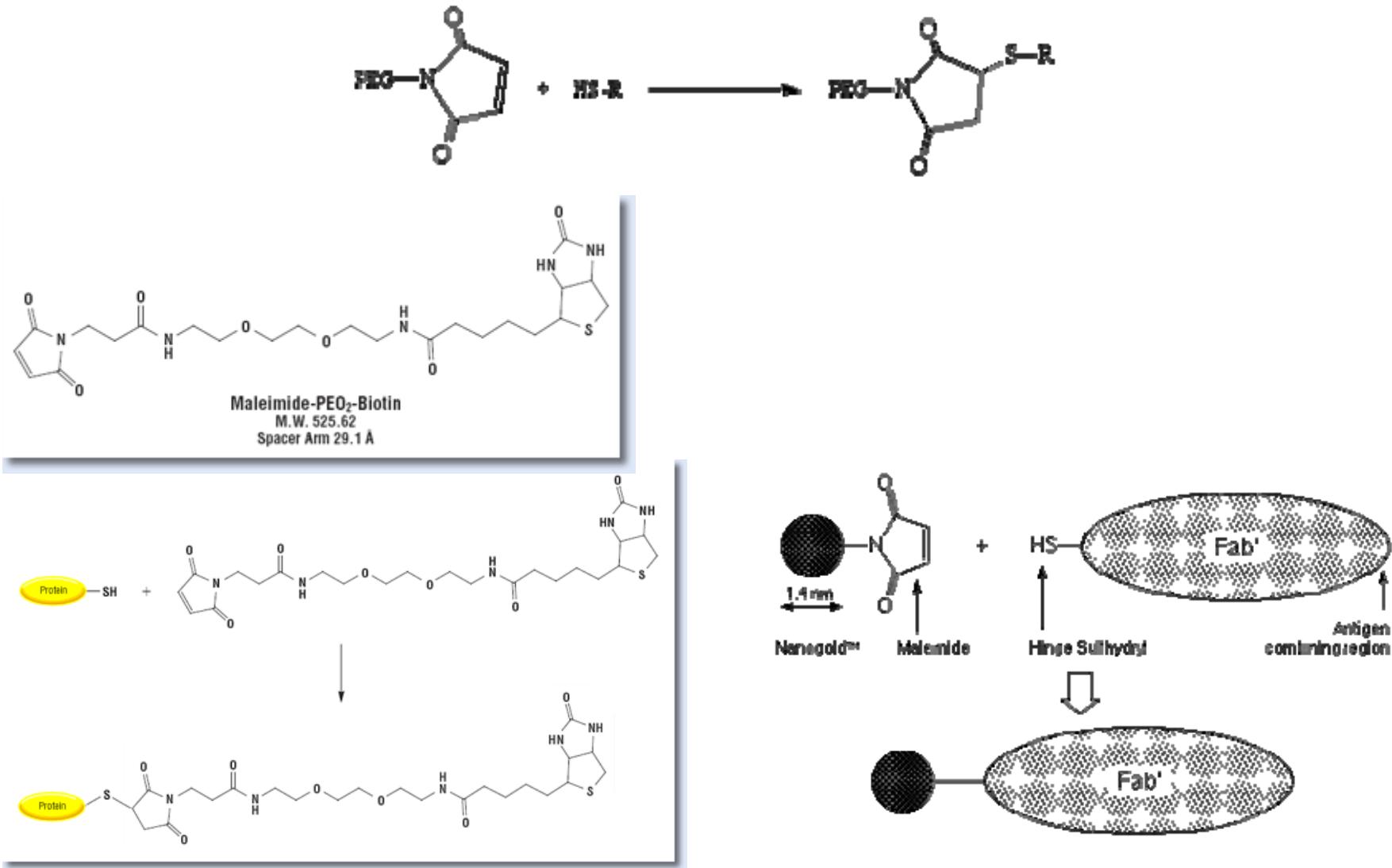
Carboxyl Presenting Surfaces



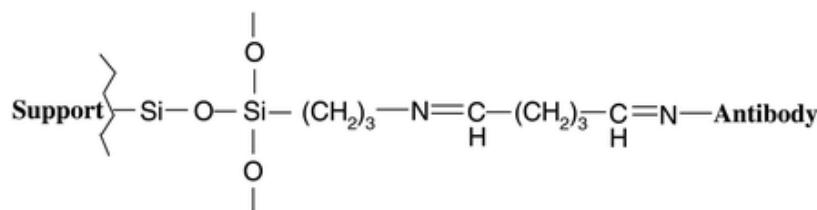
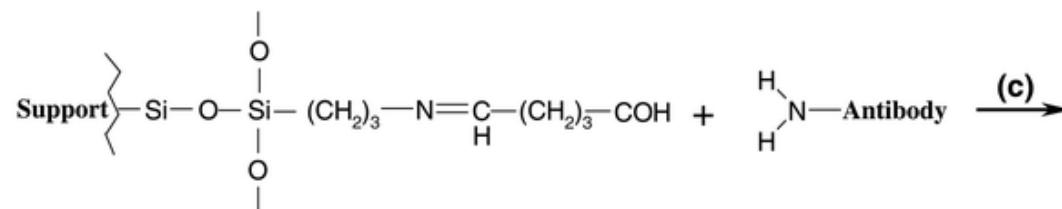
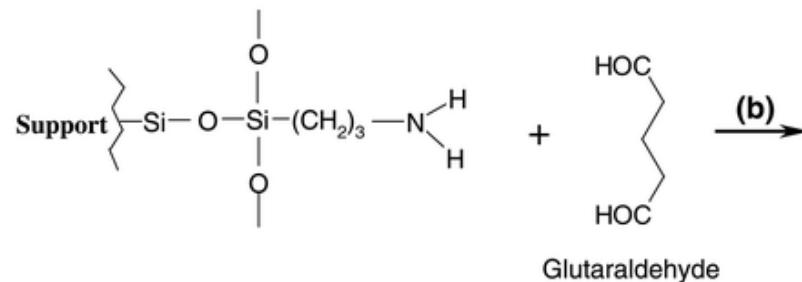
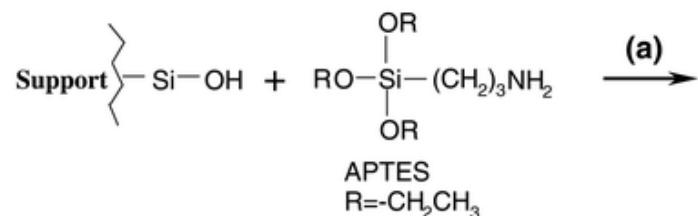
Amine Presenting Surface



Sulfhydryl Labeling



Silica Modification



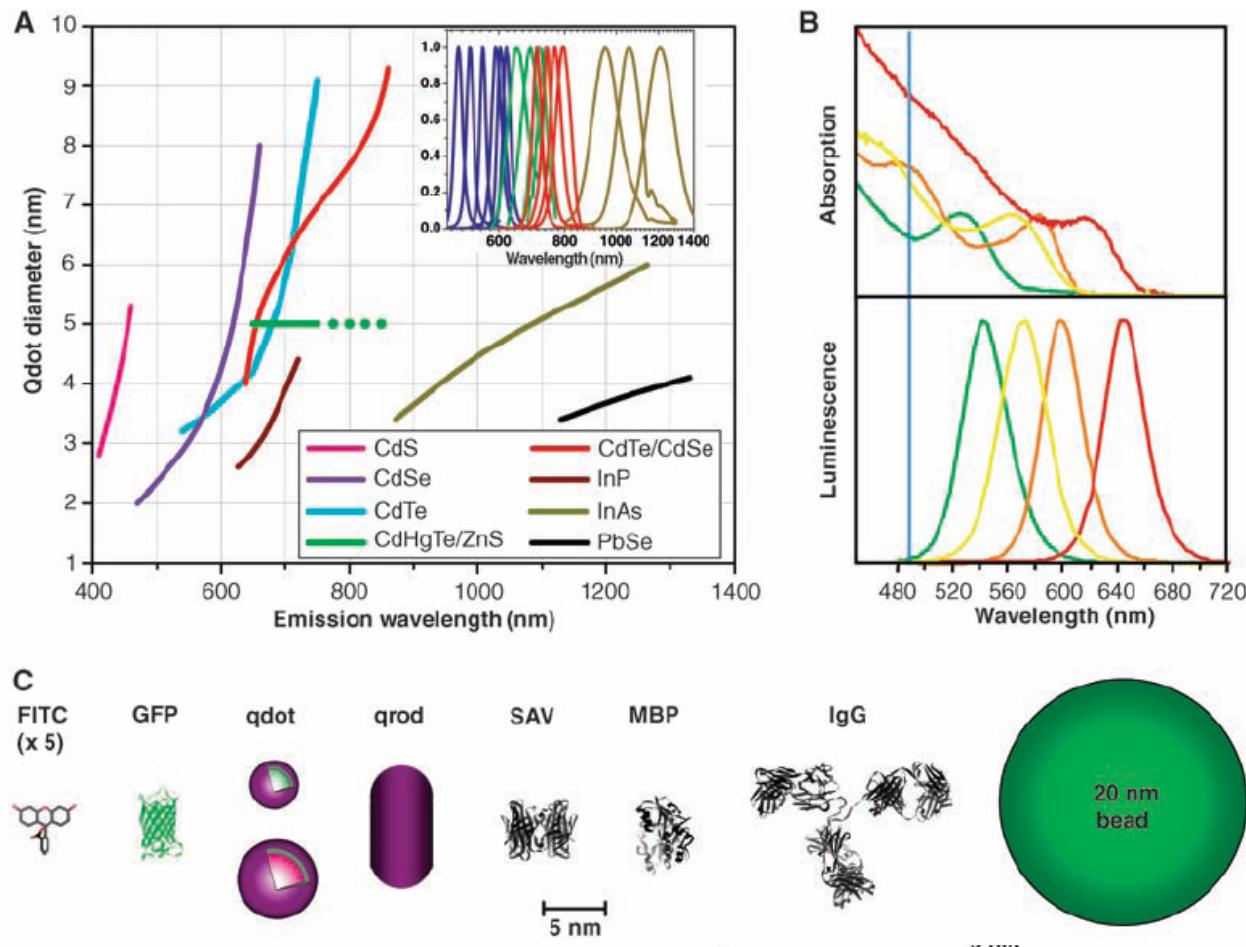
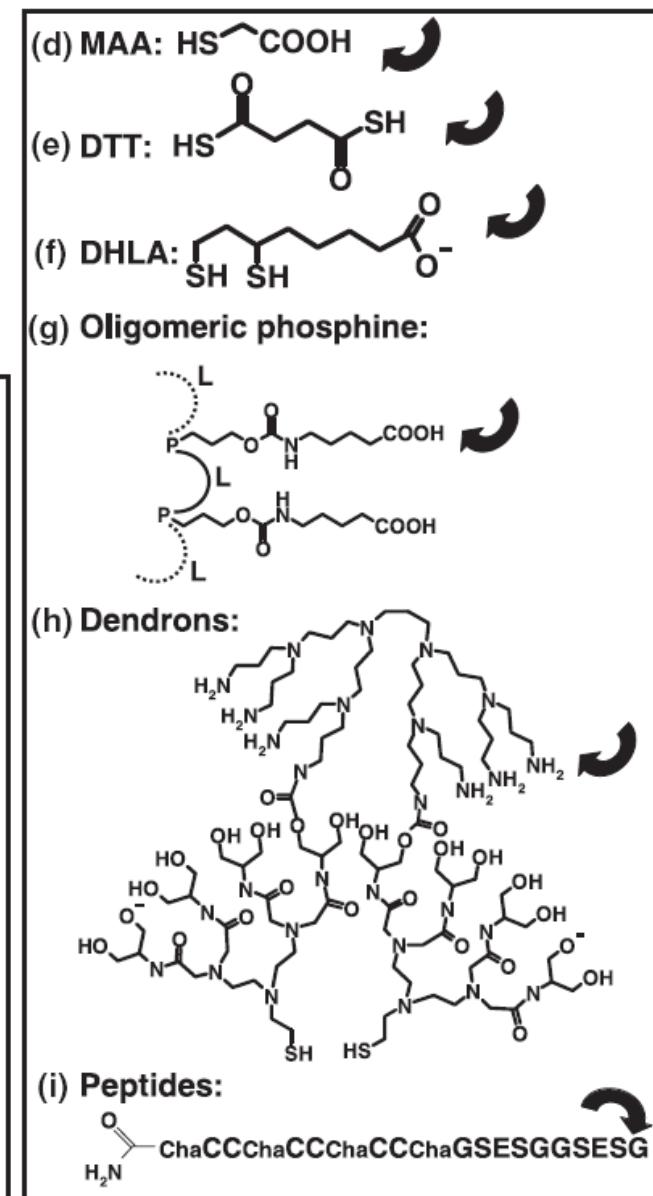
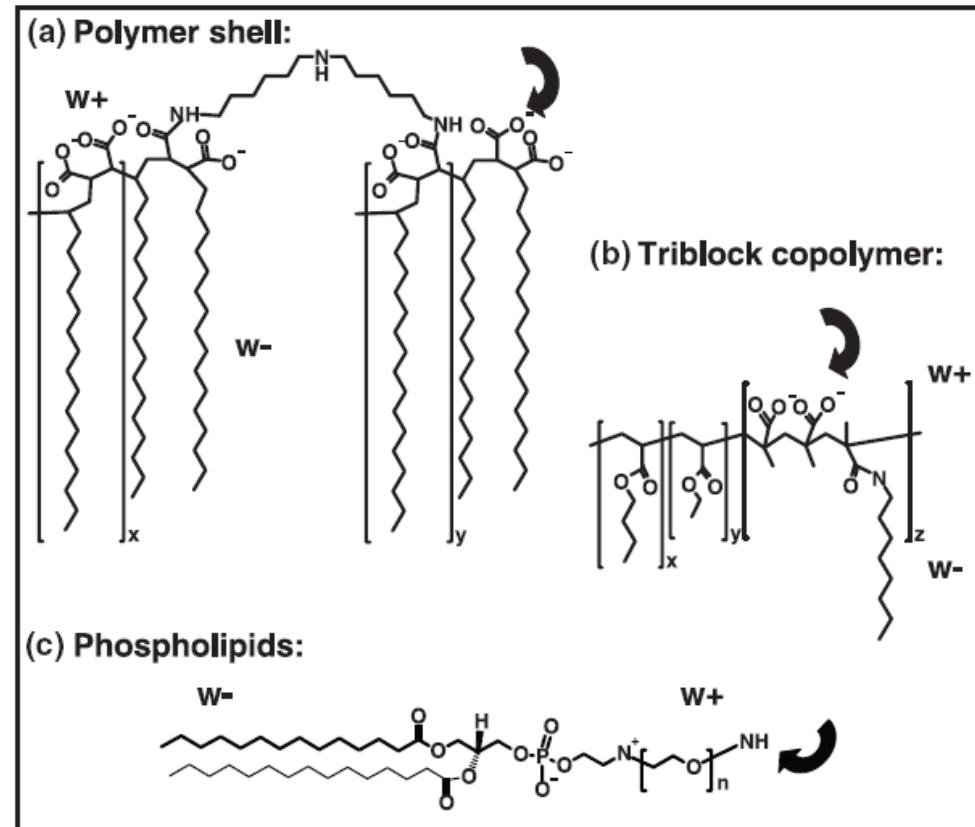
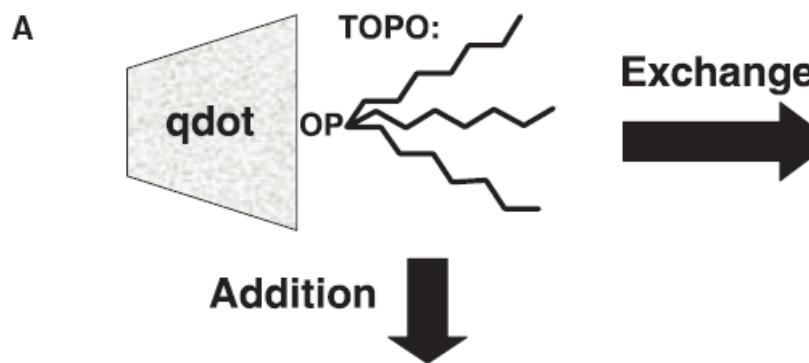
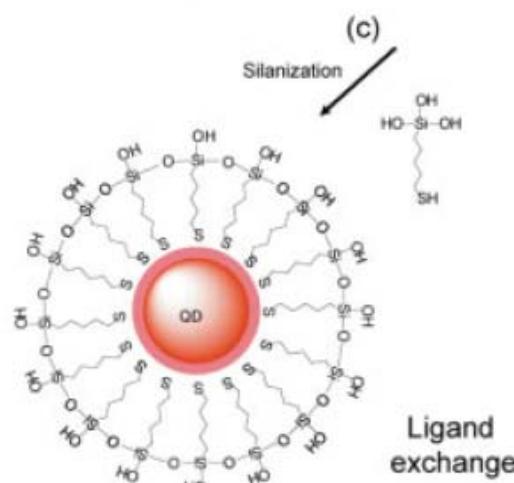
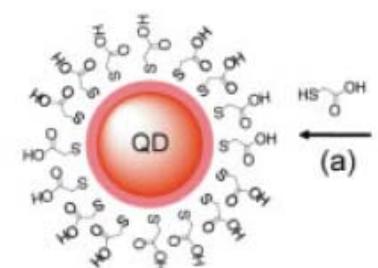
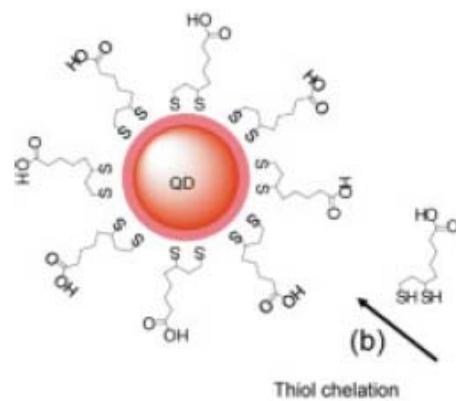
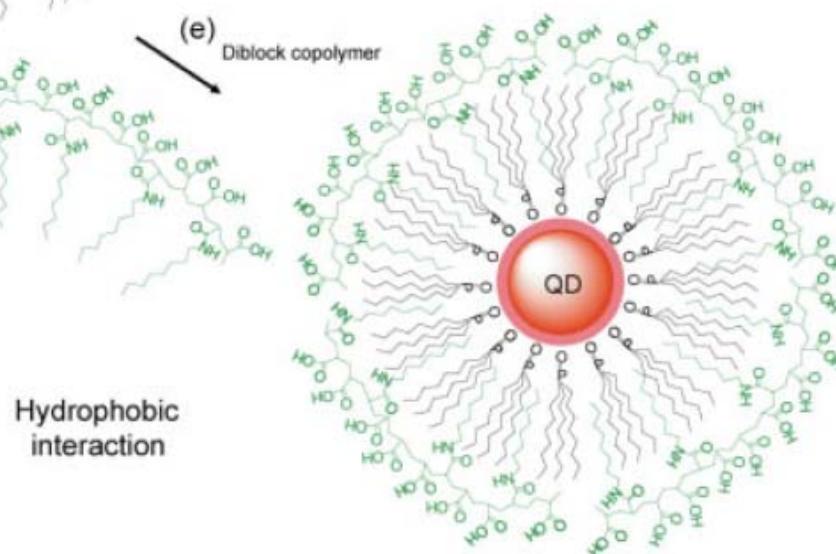
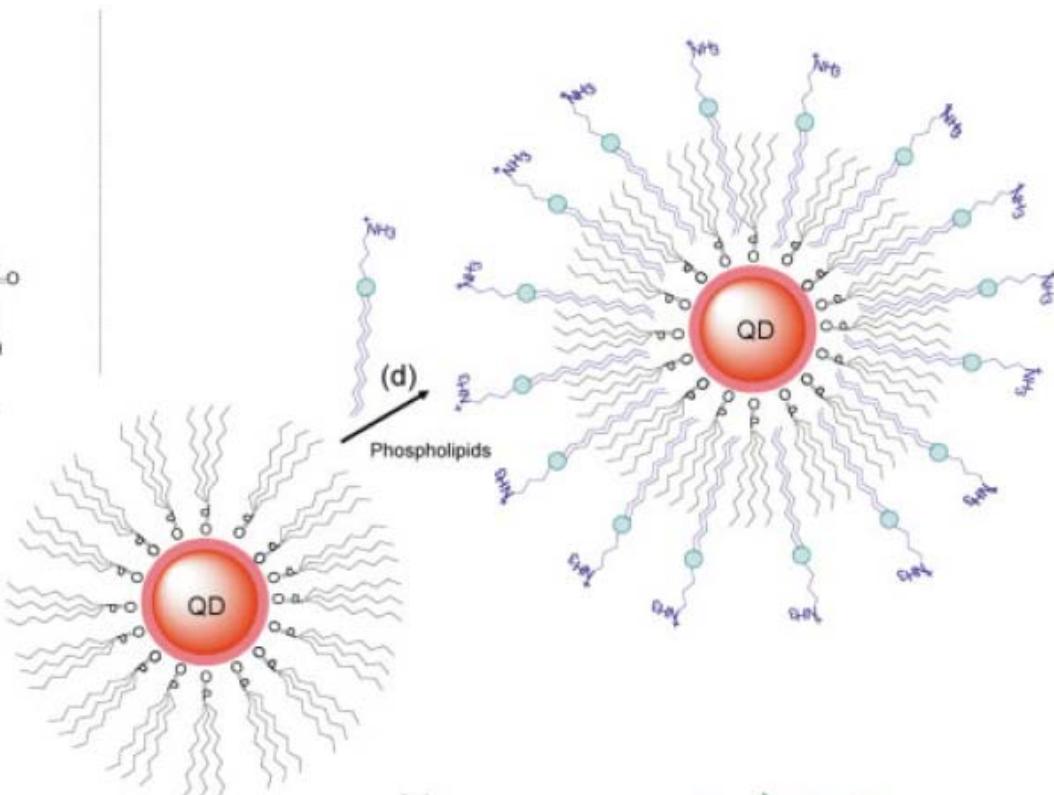


Fig. 1. (A) Emission maxima and sizes of quantum dots of different composition. Quantum dots can be synthesized from various types of semiconductor materials (II-VI: CdS, CdSe, CdTe...; III-V: InP, InAs...; IV-VI: PbSe...) characterized by different bulk band gap energies. The curves represent experimental data from the literature on the dependence of peak emission wavelength on qdot 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 qdot 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 qdots simultaneously. [Adapted from (28)] (C) Size comparison of qdots and comparable objects. FITC, fluorescein isothiocyanate; GFP, green fluorescent protein; qdot, green (4 nm, top) and red (6.5 nm, bottom) CdSe/ZnS qdot; qrod, rod-shaped qdot (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 qdots (see text) and add to the final size of the qdot, in conjunction with the solubilization chemistry (Fig. 2).





Ligand exchange



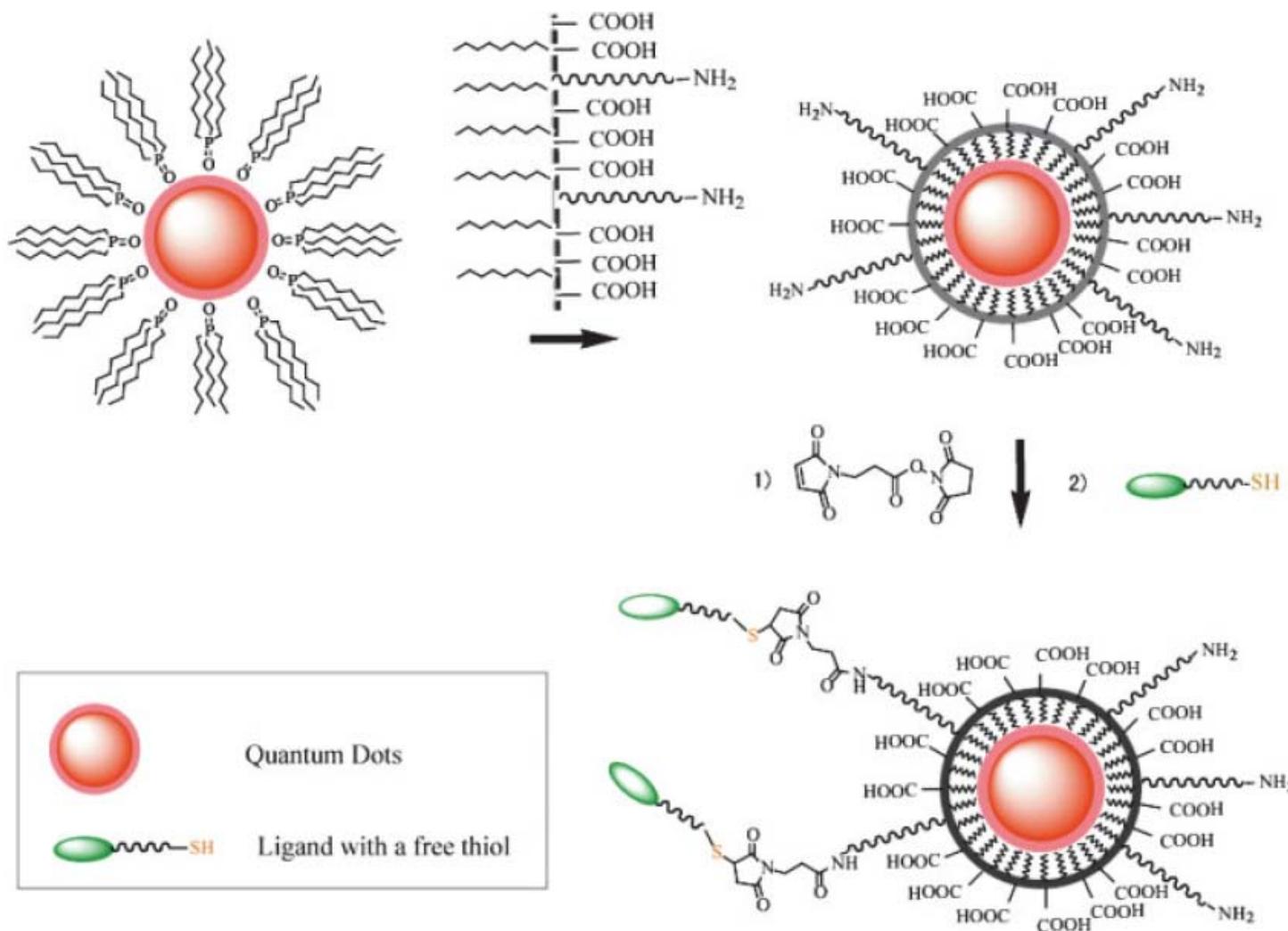
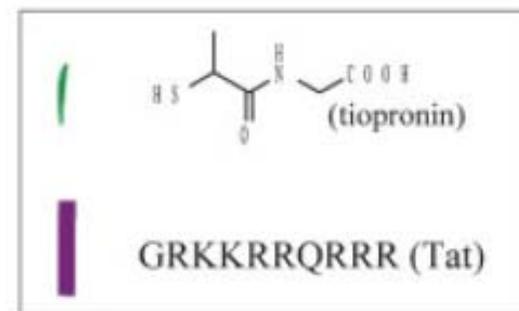
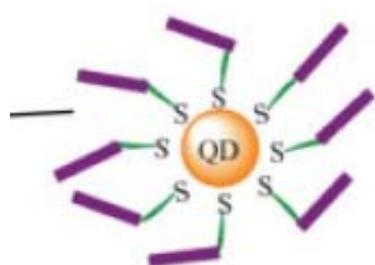


FIGURE 3 Maleimide functionalized QDs for conjugating thiol-containing ligands. TOPO stabilized QDs are coated with a primary amine functionalized tri-block amphiphilic copolymer for producing water-soluble QDs, which facilitate further conjugation to ligands with free thiols through bi-functional cross-linkers.



Cells incubated with tiopronin coated QDs



Cells incubated with Tat functionlized QDs

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

