CHAPTER II

THEORY AND LITERATURE SURVEY

Although gold is the subject of one of the most ancient themes of investigation in science, its renaissance now leads to an exponentially increasing number of publications, especially in the context of emerging nanoscience and nanotechnology with nanoparticles and self-assembled monolayers (SAMs). AuNPs are the most stable metal nanoparticles, and they present fascinating aspects such as their multi-type assemble, the behavior of the individual particles, size-related electronic, magnetic and optical properties (quantum size effect), and their applications to catalysis and biology. The use of AuNPs is promising in these fields as well as in the bottom-up approach of nanotechnology. It is considered as one of key materials and building block in the 21st century.

This chapter describes the theory and literature survey of data about this experiment. It contents with four sections. Section 2.1 is properties of gold in nanoscale. In this parts concern about the crystal structures, the surface plasmon band, the strange colors, the melting point and tunneling electrons of gold nanoparticles. Section 2.2 is properties of modifying agent, being 3-Aminopropyltriethoxysilane, 3-Mercaptopropylmethyldimethoxysilane and Poly(ethylenimine) and Self-assembled monolayers technique is shown in section 2.3. Section 2.4 is properties of polyimide and synthesis gold nanoparticles by citrate reduction is shown in section 2.5. Section 2.6 is fabrication of Gold nanoparticles thin film on modified surface. The last section is shown application of gold nanoscale on surface.

2.1 Properties of Gold in Nanoscale

2.1.1 Crystal structures

Bulk gold has face centred cubic (fcc) structure. Occasionally, rare crystals of native gold exhibits highly symmetrical cubic, octahedral or rhombododecahedral crystal forms associated with the fcc structure [26]. This generalization remains true

even when the particle is about 10 nm in size (which contain about 28,000 atoms of gold). However, for particles with smaller size, the situation is more complex. There is considerable debate regarding the structure and external form of nano-particles of between 1 and 10 nm [27]. This debate has been exacerbated by the difficulties inherent in trying to physically characterize such tiny objects. As a result, several attempts have also been made to predict the structure of gold nanoparticles by calculation. In general, the results of these calculations are not completely in complete agreement, either with each other or with the results of experimental techniques. Conflicting claims are made for icosahedral or decahedral quasi-crystal structures, amorphous structures, or octahedra, cub ͟ ͟ ͟ ͟ ͟ ͟ and truncated octahedra based on the fcc structure (Figure 2.1). The icosahedral and decaheα ͟ ͟ structures have five-fold symmetry and are r n-crystalline in the sense that they can. ͂ be packed together to make r acroscopic crystals. They are structures that exist only ͂ the nanoscale dr ain.
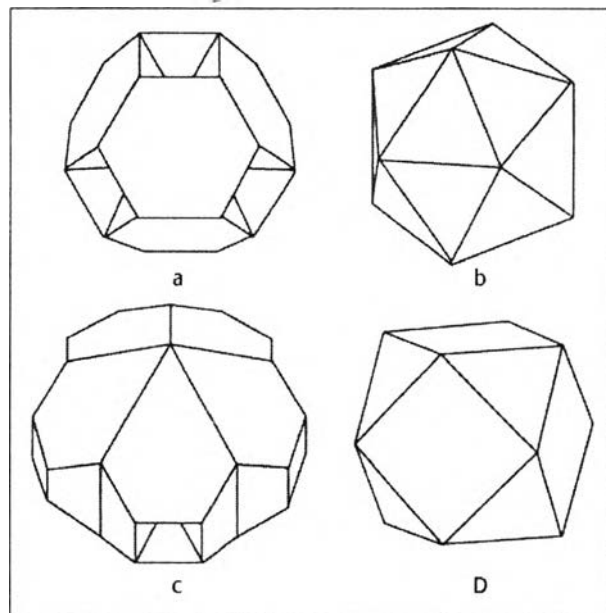
Figure 2.1 Some shapes of gold nano-particles, (a) truncated octahedron,
(b) icosahedron, (c) Marks decahedron and (d) cuboctahedron
(from Cortie and van der Lingen [28]).

The structure of gold changes at the nanoscale because the crystal structure of the elements in the bulk state is largely determined by their electronic configurations and the element will adopt the packing arrangement that minimizes its free energy.

However, for nano-particles, the surface atoms become a hugely significant factor. The internal energy of the substance must be minimized with respect to electronic configuration, surface energy and elastic strain. It appears that the icosahedron yields an efficient compromise between surface area and packing density [29], whereas certain decahedra (an example of which is the Marks decahedron) which have re-entrant facets are said to offer a compromise between surface area and strain energy.

Studies of gold nano-particles have apparently discovered all the above structures, with their presence seemingly depending very much on the particular experimental conditions. However it has been said that icosahedra and Marks decahedra tend to dominate any actual experimental particle dispersion in the sub-5 nm range [30]. This is the size range to which the catalytic activity of gold is normally attributed. To put this in context, a hemisphere of 5 nm diameter would contain about 2,600 gold atoms, whereas one of 3 nm diameters would contain only about 500 atoms. A Krugerrand coin of one troy ounce however contains about 9.509×10^{22} atoms of gold, a number so big as to be beyond human conception.

2.1.2 Surface Plasmon Band (SPB)

The deep-red color of AuNPs in water or glasses reflects the surface plasmon band, a broad absorption band in the visible region around 520 nm. The SPB is the result from the collective oscillation of the electron gas at the surface of nanoparticles (6s electrons in the conduction band of AuNPs) that is correlated with the electromagnetic field of the incoming light, i.e., the excitation of the coherent oscillation of the conduction band.

The nature of the SPB was rationalized in a master publication authored by Mie in 1908 [31]. According to Mie theory, the total cross section composed of the surface plasmon absorption and scattering is given as a summation over all electric and magnetic oscillations. The resonances denoted as surface plasmons were described quantitatively by solving Maxwell's equations for spherical particles with the appropriate boundary conditions. Mie theory attributes the plasmon band of spherical particles to the dipole oscillations of the free electrons in the conduction band occupying the energy states immediately above the Fermi energy level. The

main characteristics of the SPB of AuNPs are (i) its position around wavelength of 520 nm; (ii) its sharp decrease with decreasing core size for AuNPs with 1.4-3.2 nm core diameters due to the onset of quantum size effects that become important for particles with core sizes <3 nm in diameter and also cause a slight blue shift (the damping of the SP mode follows a 1/radius dependence due essentially to surface scattering of the conduction electrons; [32] this decrease of intensity of the SPB as particle size decreases is accompanied by broadening of the plasmon bandwidth); and (iii) steplike spectral structures indicating transitions to the discrete unoccupied levels of the conduction band with monodispersed AuNPs with core diameters between 1.1 and 1.9 nm [33].

Thus, the SPB is absent for AuNPs with core diameter less than 2 nm, as well as for bulk gold. The refractive index of the solvent has been shown to induce a shift of the SPB, as predicted by Mie theory. For AuNPs with mean diameter of 9, 22, 48, and 99 nm, the SPB maximum was observed at 517, 521, 533, and 575 nm, respectively, in aqueous media, as show in Figure 2.2 [34].
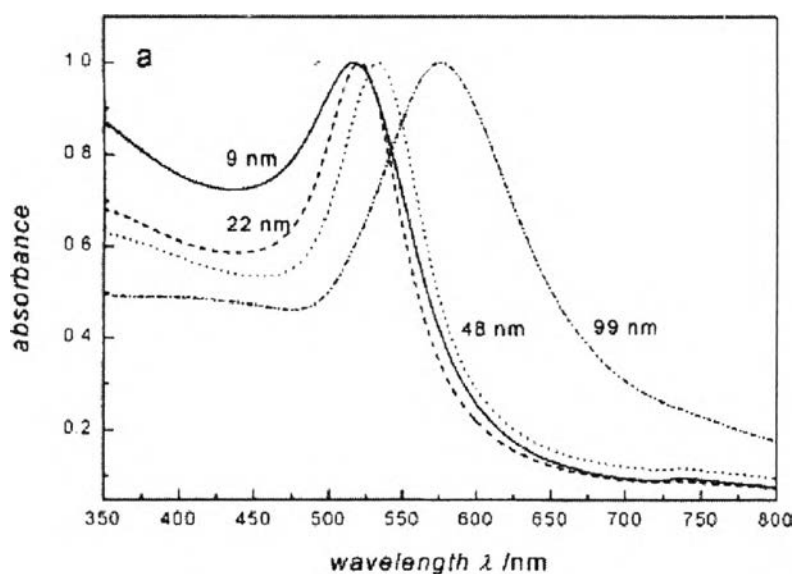
Figure 2.2 UV-vis absorption spectra of 9, 22, 48, and 99 nm gold nanoparticles in water.

The SPB maxima and bandwidth are also influenced by the particle shape, medium dielectric constant, and temperature. In Figure 2.3, the absorption spectra for the 22 nm gold nanoparticles at 18 and 72°C are shown [34]. The temperature effect is very small, resulting in just a decrease in intensity of the maximum while a

broadening of the plasmon band is not visible. Furthermore, the maximum of the plasmon absorption remains unchanged. Similar results are obtained for the other sizes.
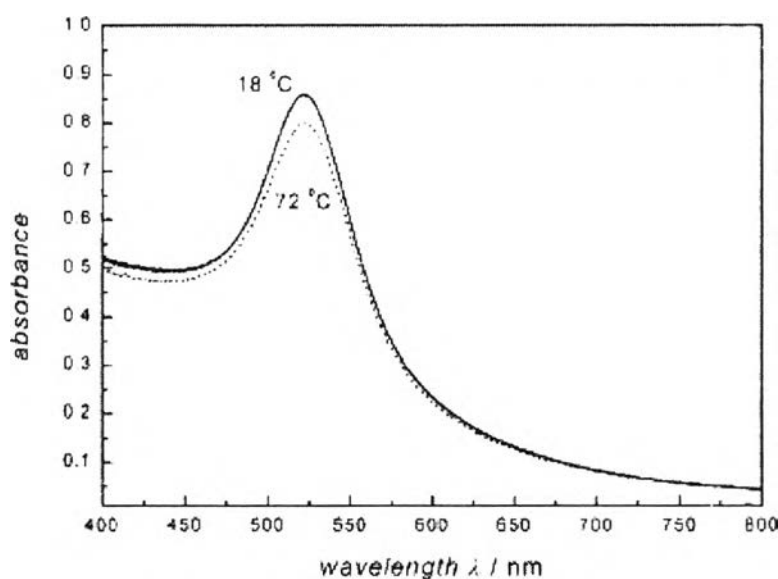

Figure 2.3 Temperature dependence of the plasmon band absorption for the 22 nm gold nanoparticles. The absorption spectra are measured at 18°C (solid line) and 72°C (dashed line).

2.1.3 Colors

Bulk gold has a familiar yellow color, caused by a reduction in reflectivity for light at the blue end of the spectrum [35]. However, the gold is divided into smaller and smaller particles, there comes a point at which the particle size becomes smaller than the wavelength of the incident radiation. New modes of interaction of the light with the gold become prominent, in particular interactions involving electronic oscillations called surface plasmons. When the particles of gold are small enough, their color is ruby red, due to their strong absorption of green light at about 520 nm, corresponding to the frequency at which a plasmon resonance occurs with the gold. This effect has been used to color glass, even in Roman times. However, if such tiny particles are allowed to coalesce in a controlled fashion, their color can be systematically varied from pink through violet to blue [36], as in Figure 2.4. This is due to a change in their absorption spectrum on aggregation, caused by increasing absorbance of the red wavelength of light.

Actually, many other metals display this type of spectrally selective resonance too, but, in general, the resonant frequency lies out of the visible range, in the near ultra-violet. Furthermore, gold is one of the very few metals noble enough to survive as a nano-particle under atmospheric conditions. This serendipitous combination of properties has encouraged its application in a diverse range of niche applications.
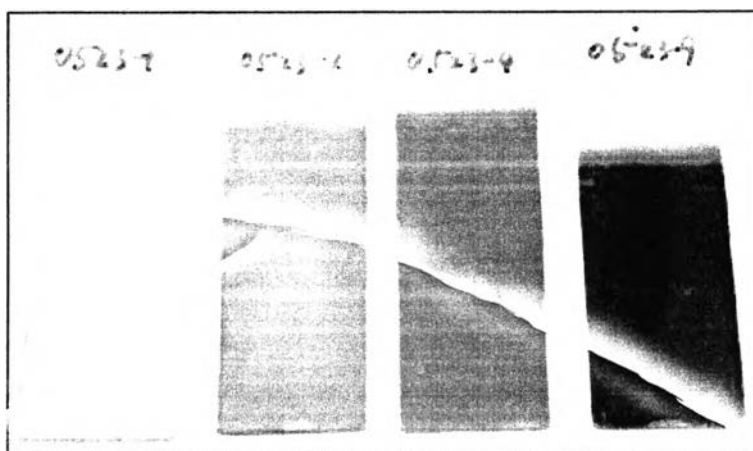
Figure 2.4 Glass slides that have been coated to varying extents with gold nanoparticles
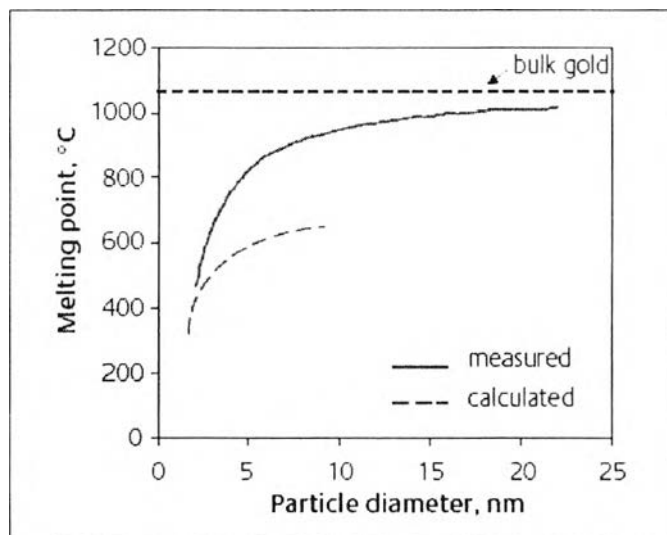
2.1.4 Melting points

Bulk gold melts at $1064\,^{\circ}C$. However, not even this property is constant as the scale of the structure is shrunk into the nanoscale. The melting point of gold nano-particles is depressed from that of the bulk material. The reason for this phenomenon is, once again, the huge increase in surface area of gold nano-particles.

The results of two studies for particles are shown in Figure 2.5, drawn from the calculations of Liu et al. [37] and measurements of Dick et al. [38]. The data differ considerably, but even taken conservatively, these calculations indicate that catalytically active gold particles in the 5 nm size range would be molten at about $830\,^{\circ}C$, particles of about 2 nm would liquefy at $350\,^{\circ}C$ and, by extrapolation, particles of about 1 nm diameter would be molten at $200\,^{\circ}C$.

This effect is not peculiar to gold of course, and direct observation of it under a microscope has been made in the case of the element indium, the bulk state of which

melts at 152°C. The melting point of 8 nm diameter nano-particles of indium has been directly observed to be only 25°C [39]. The melting point of even smaller particles of this element may lie below 0°C, a truly strange state of affairs.


Figure 2.5 Melting points of gold nanoparticles as a function of particle diameter

2.1.5 Tunneling electrons, quantized charge and white LEDs

Some of the most interesting ideas for exploiting the nanoscale domain arise from the odd electronic phenomena that occur at this scale. It is well known that electric current in most (but not all) conductors is associated with the movement of electrons, and that this can occur in metallic conductors or in semi-conductors. However, these 'classical' observations are not entirely accurate at the nanoscale. In the first manifestation of this weirdness, consider the case of a single, gold nano-particle, placed between two wires in an electric circuit but separated from them by a tiny gap, e.g. 1 nm on each side (Figure 2.6). Classically, no current would flow through this arrangement. But at the nanoscale, the physical dimensions of the objects have begun to approach those of quantum quantities such as the density distribution function of electrons. These distributions do not terminate sharply at the supposed surfaces of the objects but, rather, tail off gradually. The net result is that if two conductors are positioned close together but not actually touching, and applied a voltage between them, then there is a probability that electrons will actually 'tunnel' through the gap between them. An electric current will flow even though there is no

physical contact. So the circuit in Figure 2.6 can conduct current, a feature which has led to it being proposed as the basis of a single electron transistor or SET whose current flow is modulated by a bias on the third, gate electrode [40]. However, consider what happens when a single electron has been induced to tunnel from electrode A to the gold particle. Now there is a net negative charge on the gold particle (at least until this electron tunnels in turn to electrode B). The excess negative charge, while it lasts, will repel any subsequent electrons tunnelling events from A. Alternatively, no further current will flow until the voltage has been increased enough to overcome the repulsion of the electrons already on the nano-particle. So at the nanoscale, electric current may proceed in a kind of jerky way, in this case caused by the combination of what is known by a Coulomb blockade and of tunnelling. The overall result has been termed a Coulomb staircase [41]. Nanoscale weirdness of this kind has been used to produce a variety of interesting new electronic devices, such as the resonant tunneling diode. The exploitation of yet other nanoscale phenomena have led to the development of the latest generation of coloured LEDs, which offer conversion efficiencies that now rival those of incandescent lighting [42].
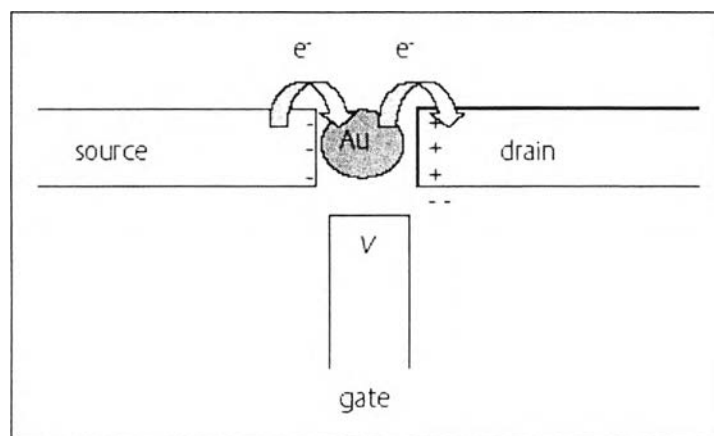
Figure 2.6 Single electron transistor based on a gold nano-particle, showing how voltage V on gate electrode controls tunneling of electrons into and off gold nano-particle inserted between source and drain electrodes.

It is worth pointing out that gold is the leading candidate for all manner of nano-sized electrical conductors. This is due to its excellent conductivity and resistance to oxidation. A nanoscale wire of almost any other metal would spontaneously oxidize in air and would crumble to a pile of oxide dust. Therefore, most schemes for molecular electronic devices invoke a gold wire or two in their
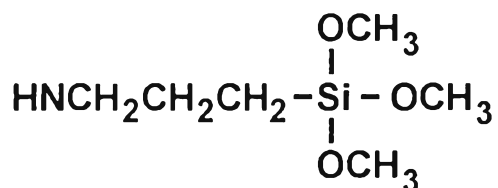
design. Recently, vapour-deposited gold has even been used as a brazing agent to weld two electrodes onto a carbon nanotube of 100 nm diameter [43].

2.2 Properties of Modifying Agents

2.2.1 Properties of 3-Aminopropyltrimethoxysilane

- **Chemical Structure**

$$HNCH_2CH_2CH_2-\overset{\displaystyle OCH_3}{\underset{\displaystyle OCH_3}{Si}}-OCH_3$$

- **Typical Physical Properties**

  - Appearance: colorless liquid
  - Molecular weight: 179.29
  - Boiling point: 213-216° C
  - Vapor pressure: < 10 mmHg
  - Vapor density: 7.7 g/l
  - Specific gravity: 1.01 g/cm3
  - Flashpoint: 98° C/ 208° F
  - Explosion limits :
    - Lower: 0.8%
    - Upper: 4.5%
  - Refractive Index : 1.423

- **Stability and reactivity**

  Chemical stability: Stable at room temperature in closed containers under normal storage and handling conditions.

  Conditions to avoid: Incompatible materials, ignition sources, moisture, exposure to moist air or water.

  Incompatibilities with other materials: Oxidizing agents, acids, alcohols, peroxides.
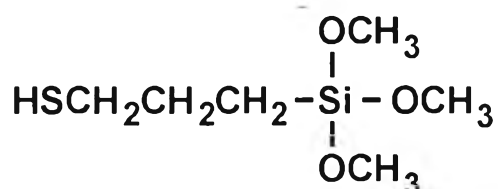
  Hazardous decomposition products: Carbon monoxide, oxides of nitrogen, carbon dioxide, silicon oxide, methanol.

2.2.2 Properties of (3-Mercaptopropyltrimethoxysilane propereties

- **Synonym:**

  3-Methyldimethoxysilypropylmercaptan, MPTMS

- **Chemical Structure**

$$HSCH_2CH_2CH_2-\overset{\overset{\displaystyle OCH_3}{|}}{\underset{\underset{\displaystyle OCH_3}{|}}{Si}}-OCH_3$$

- **Typical Physical Properties**

  - Formula: $C_6H_{16}O_2SSi$

  - Molecular weight: 196.34

  - Boiling point: 96 °C [30mmHg]

  - Flash point: 93 °C

  - Color and appearance: Clear to straw liquid with unpleasant
                                odor of sulfide.

  - Density: 1.00 [at 25°C]

  - Refractive index: 1.4502 [at 25°C]

- **Stability and reactivity**

  Chemical stability: Stable under normal temperatures and pressures.

  Conditions to avoid: Incompatible materials, exposure to moist air
                               or water.

  Incompatibilities with other materials: Strong oxidizing agents, strong
                                           acids, alcohols.

  Hazardous decomposition products: Carbon monoxide, oxides of sulfur,
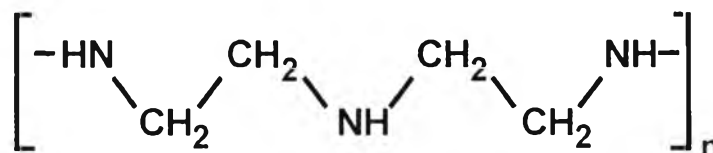   carbon dioxide, silicon oxide.

  Hazardous polymerization: Will not occur.

2.2.3 Properties of Poly(ethylenimine) propereties

- **Synonyms:**

  Polymin P, PEI

- **Chemical Structure**

$$\left[\begin{array}{c} -HN \diagdown CH_2 \diagup CH_2 \diagdown NH- \\ \diagdown CH_2 \diagup \diagdown NH \diagup \diagdown CH_2 \diagup \end{array} \right]_n$$

- **Typical Physical Properties**

  - Physical state: Viscous liquid
  - Color: clear colorless
  - Molecular weight: 25,000
  - Boiling point: 100 °C
  - Freezing/Melting point: -20 °C
  - Flash point: > 110 °C
  - Solubility in water: Soluble
  - Density: 1.07 [at 25°C]

- **Stability and reactivity**

  Chemical stability: Stable under normal temperatures and pressures.

  Conditions to avoid: Incompatible materials, do not freeze.

  Incompatibilities with other materials: Strong oxidizing agents.

  Hazardous decomposition products: Nitrogen oxides, carbon monoxide, carbon dioxide.

  Hazardous polymerization: Will not occur.

2.3 Self-Assembled Monolayers (SAMS) Technique

Self-assembled monolayers, SAMs, are formed when surfactant molecules spontaneously adsorb in a monomolecular layer on surfaces. Two of the most widely studied systems of SAMs are gold -alkylthiolate monolayers and alkylsilane monolayers.
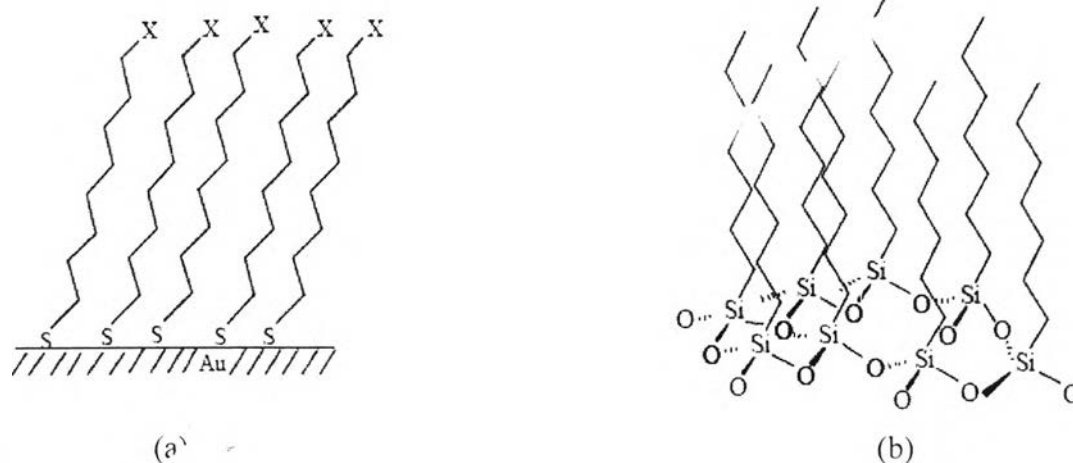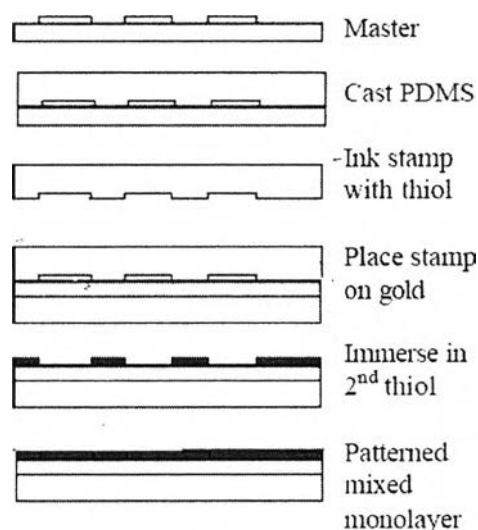

Figure 2.7. Gold thiolate monolayer (a) and alkylsilane monolayer (b).

The first gold-alkylthiolate monolayer was produced by Allara and Nuzzo at Bell laboratories in 1983 [44]. They realized the utility of combining a relatively inert gold surface with a bi-functional organic molecule in well-ordered, regularly oriented array. SAMs offer a unique combination of physical properties that allow fundamental studies of interfacial chemistry, solvent-molecule interactions and self-organization. Their well-ordered arrays and ease of functionalization make them ideal model systems in many fields [45]. SAMs are invaluable substrates in bioanalytical, organometallic, physical organic, bioorganic and electrochemistry.

2.3.1 Preparation of SAMs

Gold-thiol monolayers are stable when exposed to air and aqueous or ethanolic solutions for several months [46]. They are also quite facile to produce. A 1-5 nm film of titanium is evaporated onto a coverglass slip or silicon wafer to promote adhesion of gold to the surface. A 10-200 nm film of gold is then evaporated onto the surface. The resulting gold surface is then immersed into a 2mM solution of ethanolic

alkylthiol, (disulfide solutions may also be used). Mixed monolayers may be formed if the ethanolic solution of T-functionalized alkylthiols contains two or more different thiols. Several procedures exist for producing patterned mixed monolayers. Lithography lies at the heart of all of these techniques [47]. One popular method is microcontact printing,:CP. "Stamps" with patterned reliefs are formed from elastomers, such as poly(dimethylsiloxane), PDMS, that have been poured over a master, cured and then peeled. The masters are manufactured from photolithography, e-beam writing, micromachining or relief structures etched into metals. Each master may be used to produce up to 50 "stamps", and each stamp may be used multiple times. The "stamp" is "inked" with an ethanolic solution of T-functionalized thiol and brought into contact with the gold surface for 10-20 seconds resulting in a gold thiolate monolayer at the areas of contact.

Master

Cast PDMS

-Ink stamp with thiol

Place stamp on gold

Immerse in 2nd thiol

Patterned mixed monolayer

Figure 2.8 Microcontect Printing

2.3.2 Characterization of SAMs

Methods for studying monolayers can differ greatly from characterization techniques of solution chemistry. Ellipsometry [48] measures the change in amplitude and phase of light upon reflection. Using these values, the thickness and refractive index of a film can be calculated. This procedure can be used to determine the thickness of a monolayer before and after reactions to detect adsorption of molecules onto the SAM. Since the commercialization of surface plasmon resonance spectrometers, surface plasmon resonance spectroscopy has become a vital tool in for imaging reactions on SAMs. Surface plasmon resonance is an *in situ* technique that

measures changes in the refractive index of a monolayer attached to a metal surface [49]. This allows for collection of both kinetic and thermodynamic information about a system in real time. X-Ray photoelectron spectroscopy (XPS) [50] is a technique which quantifies the elemental composition of monolayers.

2.3.3 Applications of SAMs

SAMs have many applications in organic chemistry. Catalysis reactions are a common area where a defined presentation of a specific face of a molecule could be beneficial. Immobilizing catalysts on SAMs has been successfully performed for a number of systems [51]. Asymmetric dihydroxylation can be carried out on MPCs. Unoptimized conditions afford similar yields to monomeric solutions (~80%) and similar to polymer bound catalysts (80-90%) [52]. If the monolayer immobilizes the catalyst in a beneficial orientation, desired reaction rates can increase dramatically. Tremel and coworkers attached a ruthenium ROMP catalyst to MPCs and found that the catalyst not only catalyzed ring-opening metathesis of norborene, its turnover frequency increased from 3000 h^{-1} to 16,000 h^{-1}. When the catalyst was immobilized to a planar monolayer, the turnover frequency increased to 80,000 h^{-1} [53] . Molecular recognition is another important application for SAMs [54]. Macromolecules, including DNA [55], proteins [56], and even cells [57] can be immobilized onto monolayers. A major breakthrough came when Whitesides and Prime realized that oligio(ethylene glycol) chains prevent non-specific binding of proteins. This allows for adherence of specific bio-molecules without unspecific binding events. Utilizing techniques, such as SPR and ellipsometry, binding and recognition of bio-molecules can be measured in real time to allow for calculation of association and dissociation constants. Competitive binding experiments and many other physical properties of biological systems can be assayed using SAMs.

2.4. Properties of Polyimide

Polyimides were developed by Du Pont and first introduced on the market in 1961. They are condensation polymers derived from bifunctional carboxylic acid anhydrides and primary diamines. They contain the imides structure $-CO-NR-CO-$ as a linear or heterocyclic unit along the main chain of the polymer backbone:
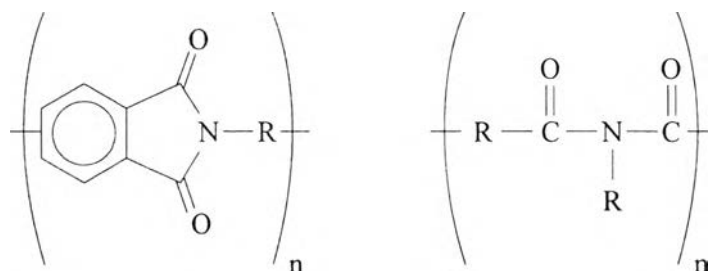
Aromatic, heterocyclic polyimides exhibit outstanding mechanical properties and excellent thermal and oxidative stability, and are of major commercial and industrial importance. These materials are widely used in place of metals and glass in high temperature applications throughout the electrical, electronics, automotive, aerospace and packaging industries. Polyimides are available in many forms, including pellets, film, extruded sheet, raw stock and in solution.

Polyimides are considered specialty plastics because of their outstanding high performance engineering properties. As such, they are priced well above commodity polymers such as polyethylene and polystyrene. Many monomers used to prepare polyimide are also specialty chemicals. Polyimides that require special processing or that are provided in a finished form such as Kapton film or machined parts of Vespel are more expensive than others.

The outstanding properties of polyimides include: [58]

1. High-temperature oxidation stability and low weight loss.
2. Temperature stability from -310 to 1000°F.
3. Flame resistance (since polyimides do not support combustion in air and will ignite only at temperature 750°F).
4. High wear resistance.
5. High radiation resistance.
6. High chemical and solvent resistance.

Thermal stability is by far the most valuable property of the polyimide polymer. It is the reason that polyimides are replacing many other materials. Polyimides have high-temperature stability and their physical and electrical properties retain even at high temperatures. The practical continuous-service temperature for polyimides range from 300 to 700°F, with stability up to 1000°F for short period of time. Softening point is generally above 1290°F.

The resistance of polyimide to organic solvents, moisture, and synthetic lubricants and greases is very high. Only slight deterioration occurs when polyimides are immersed up to 4 weeks in organic solvents such as, ketones, alcohols, aldehydes, chlorinated solvent, benzene, and naphtha. The resistance of polyimides to strong acids and bases is, however, not as good as its resistance to organic solvents.

The percentage of water absorption of polyimides after 24 hr of immersion at room temperature is only 0.7 percent. Nevertheless, hydrolytic stability is reported to be excellent.

In general, electrical properties of polyimides are very stable over a wide temperature range. The dielectric strength of polyimide can range from 3,000 volts/mil to 5,000 volts/mil, depending on the formation, thickness of the samples.

Table 2.1 Properties of high temperature polyimide films [59].

| Properties	Kapton
Tensile strength, MPa	172
Tensile modulus, GPa	3.0
Elongation, %	70
Glass-transition, T_g, °C	390
Limited oxygen index, %	37
CTE x 10^5, °C^{-1}	2
Water absorptionat 23.5 °C, %	1.3
Specific gravity	1.42
Dielectric constant, 1 kHz	3.5
Dissipation factor, 1 kHz	0.003

2.5 Synthesis Gold Nanoparticles by Citrate Reduction

Among the conventional methods of AuNPs synthesis by reduction of gold(III) derivatives, the most popular one for a long time has been citrate reduction of $HAuCl_4$ in water, which was introduced by Turkevitch in 1951 [60]. It leads to AuNPs of ca. 20 nm. In an early effort, reported in 1973 by Frens, [61] to obtain AuNPs of prechosen size (between 16 and 147 nm) via their controlled formation, a method was proposed where the ratio between the $HAuCl_4$ to trisodium citrate was varied.

Sodium citrate first acts as a reducing agent. Afterward, the negative citrate ions are adsorbed onto the gold nanoparticles and introduce the surface change that repels the particles and prevents them from aggregation.

To produce bigger particles, less sodium citrate should be added (possibly down to 0.05%, after which there simply would not be enough to reduce all the gold). Decreased amount of trisodium citrate will reduce the amount of the citrate ions available for stabilizing the particles, and cause the small particles to aggregate into bigger ones (unit the total surface area of all particles becomes small enough to be covered by the existing ions).

This method is very often used even now when a rather loose shell of ligands is required around the gold core in order to prepare a precursor to valuable AuNP-based materials. Recently, a practical preparation of sodium 3-mercaptopropionate-stabilized AuNPs was reported in which simultaneous addition of citrate salt and an amphiphile surfactant was adopted; the size could be controlled by varying the stabilizer/gold ratio (Figure 2.9). [62]
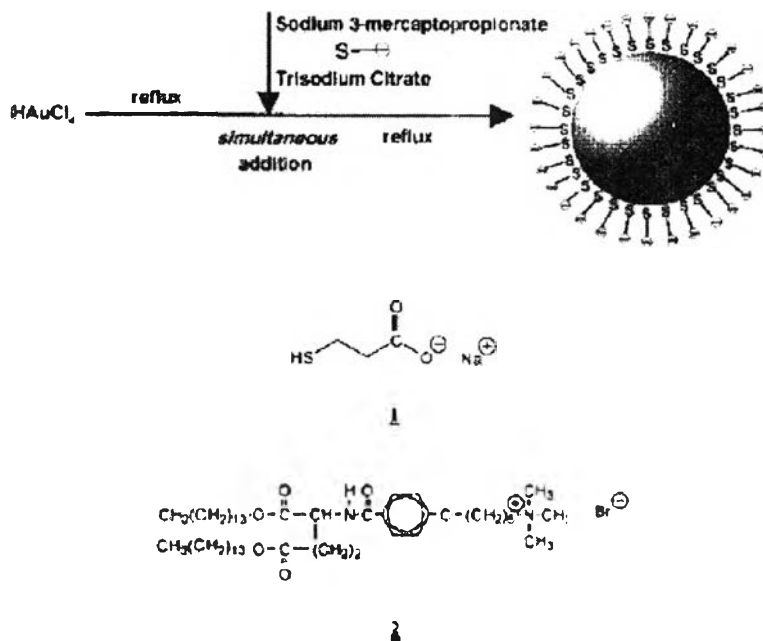
Figure 2.9. Preparation procedure of anionic mercaptoligand-stabilized AuNPs in water.

Turkevich J. [63] studied that the reduction of chlorauric acid by sodium citrate at 100 °C produced a colloidal solution (standard citrate sol) which had excellent stability and 'uniform' particie size of 20 nm in diameter. Both the average dismeter and the character of the distribution curve changed with preparative conditions – concentration, ratio of reactants, temperature (Figure 2.10). This was taken to indicate that the process of particle formation was chemical in nature and involved interplay of three steps – nucleation, growth and coagulation. 'Uniformity' of the particles in the standard citrate sol was due to a favorable juxtaposition of these three steps: nucleation took place and stopped, then growth took over and at the same time the particles attained a stability which prevented the widening of the distribution curve by coagulation. In order to understand the preparation process these three steps had to be studied individually.
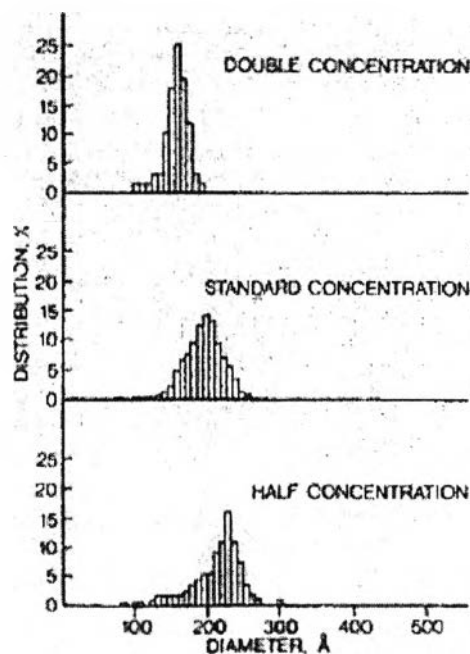
ïigure 2.10 Particle size disti.. ~n curves of gold sol prepared at different

concentrations.

2.5.1 Growth

The first step to be isolated and studied was that of growth. It ha. heen previously found that when chlorauric solution was treated at room temperature with hydroxylamine hydrochloride, no colloid was produced unless proper nuclei were present. By inoculation such a growth medium with a controlled number of appropriate nuclei, these could be made to grow to a desired size given by the following relation

$$D_f = D_n \left[\frac{Au_n + Au_g}{Au_n} \right]^{1/3} \qquad (2.1)$$

Where D_f is the final diameter, D_n is the diameter of the nucleus, Au_n is the amount of gold in the nuclei, and Au_g is the amount of gold in the growth medium. Thus to obtain 40 nm particles from 20 nm particles, one would use seven times the amount of gold in the growth medium as the 20 nm nucleating gold sol. In this way, agraded set of monodisperse colloidal gold solution was obtained in which the average particle diameters were up to 120 nm. This permitted the study of the effect

of size on the properties of colloidal gold. Examination of the particle size distribution curves of such sols showed that while they broadened on growth, the standard deviation from the mean remained approximately constant at 10 percent. This was taken to indicate that the law of growth was given by

$$\frac{dD}{dt} = const.D \qquad\qquad 2.2$$

Where D is the diameter of the gold particle. This law states that the larger is the particle the particle the faster it grows, which was checked by studying the growth rate of particles of two different diameter. The law of growth also states that the smaller is the particle size below which growth rate is negligible, which defines the size of a nucleus – originally estimated at 4 nm and later found to be 1.0 - 2.0 nm.

2.5.2 Nucleation

J. Turkevich et al. [64] then proceeded to study in mor⁻ ꭒetail the particle size distribution curve of the standard citrate sol. This 20 ꭒɯ diameter sol was grown to produce sols with two average particle diamᵉᵗ ., 40 nm and 80 nm. A search was then made for the smallest particles Ɪ each of these preparations using an electron mⅰꞔ⸜ꞗꞔ ꞁ ⸜ᵛⁱᵗʰ a resolution of 2 nm. This was found to be of diameter 9 nm for the 40 nm sol and 18 nm for the 80 nm sol, indicating that the smallest particle that could grow, the nucleus, was about 4.5 nm in diameter. Since the particle size distribution curve is the result of a nucleation process followed by a growth process, the law of which had been determined, the rate curve for nucleation could be mathematically deduced from the particle size distribution curve. The rate curve (Figure 2.11) so obtained had an unusual form – an induction period, an autocatalytic rise in the number of nuclei, a slowing down of nuclei formation and finally, a cessation of the nucleation process, although the starting reagents were still present. It was further found that the induction period increased with decrease in temperature indicating the presence of a chemical reaction with an activation energy of 15 Kcal/mole.
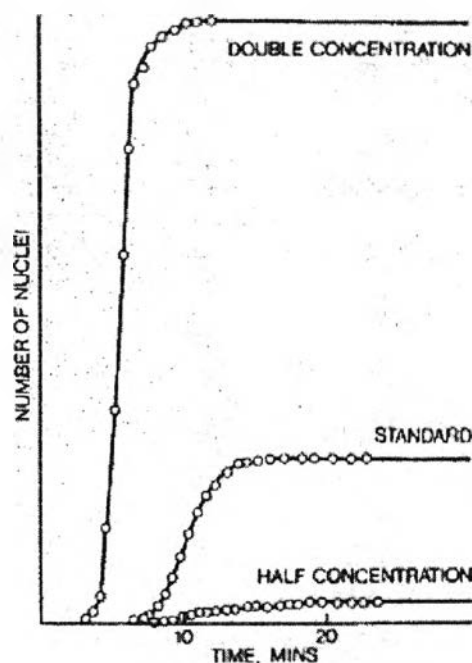
Figure 2.11 Nucleation rate curves for gold sols prepared at different concentrations.

Examination of the chemistry of the reducing agent suggested that the induction period might be due to the transformation of the citrate ion into acetone dicarboxylate ion. When the latter was used as a reducing agent, a different, more symmetrical particle size distribution curve was obtained. The nucleation curve deduced from it had no induction period but represented a unimolecular decomposition of a 'precursor' of the nucleus. This 'precursor', a complex formed from the gold ion and the acetone dicarboxylate ion, was isolated by removing the gold ion in the very early stages of preparation by means of an ion exchange resin. Electron microscopic examination revealed diffuse amorphous particles which on bombardment with an electron beam formed small, compact gold particles. Thus, gold nuclei do not form by reduction of individual gold ions to atoms which then collide to form, by fluctuations, a stable nucleus. Rather the nucleation process consists of a polymerization step. When a critical mass is attained, a reduction to metal particle takes place. The nature of polymerization step to form the 'precursor' may vary. In acid and neutral solution it is the formation of gold organic polymer, in alkaline solution a polymerization of gold hydroxide may take place [65]. The unimolecular redox decomposition of the organic gold polymer or gold facile reduction of the gold hydroxide polymer takes place when the degree of polymerization is sufficiently great

to produce a stable gold particle, a particle whose cohesive lattice energy is greater than the disruptive surface energy. The latter may be affected by adsorbed molecules. For nucleation in acid and neutral solutions, the reducing agent must have at least two reactive groups to bring about polymerization (such as citrate, hydroquinone and acetone carboxylic acid). On the other hand, for pure growth, the solution must be neutral or acidic to avoid formation of gold hydroxide and the reducing agent should have one functional group (hydroxylamine hydrochloride, hydrogen peroxide). Once a sufficient number of nuclei is formed, the growth process take over. This is a consequence of the following: the growth process is a one-step autocatalytic process catalyzed by the nucleus while the nucleus formation is a multi-step process dependent on polymerization. This viewpoint is confirmed by high resolution electron micrographs which show that standard citrate sol particles are not single crystals.

2.5.3 Coagulation

The coagulation of particles is an important step in colloid preparation. Its control during the preparation process determines the shape, structure and the size distribution of the particles. Once the preparation is complete, its absence ensures the stability of the sol. On the other hand, the nature of the coagulation process of a prepared sol determines the morphology of the coagulum.

In the standard citrate sol the particles have a negative charge due to the strong adsorption of the citrate ion to form what is known as the strong the Stren layer on the colloidal particle. The 20 nm diameter particle of the standard citrate sol was formed by pure growth form a 4.5 nm diameter nucleus. These adsorb sufficient citrate to prevent further aggregation and thus serve as nuclei for growth to form the 20 nm diameter gold particles.

2.6 Fabrication of Gold Nanoparticles Thin Film on Modified Surface

Deposition of gold nanoparticles on substrate modified by surface modifying agent, such as 3-aminopropyltrimethoxysilane (APTMS), Polyethylenimine (PEI), (3-mercaptopropyl) trimethoxysilane (MPTMS), has been reported in many papers.

M. Hu et al. [66] studied the surface structure and morphology of self – assembled 3-Mercaptopropyltrimethoxysilane layer on hydroxyl-terminated SiO_2 surface formed by MPTMS at various MPTMS concentration in benzene and introduced that the quantity of H_2O in all the solvent should be less than 30 ppm. They investigated the chemical state of sulfur in MPTMS layer on SiO_2 by using ARXPS. High resolution XPS spectra of S(2p) for SiO_2 substrate treated with MPTMS which indicates that sulfur only exists in a single chemical state in MPTMS layers. In order word, the interaction between thiols and surface silanols is negligible. For SAMs on SiO_2 formed by amine-functionalized 3-aminopropyltrimethoxysilane, however, different results have been reported. The N(1s) XPS signal shows two components assigned to free amine, and to hydrogen-bonded and protonated amine, respectively. Kallury et al. [67] reported that either surface water or surface silanols promote the amine-surface interaction and orient the amino moieties towards the SiO_2 surface.

The effect of MPTMS concentration on the structure and morphology of MPTMS layers on SiO_2 can be explained by the reaction mechanism of alkyltrimethoxysilanes with surface silanols. Alkylsiloxane hydrolysis either in solvent or on SiO_2 surface, which is followed by subsequent dehydration on SiO_2 surface, is the mechanism of SAMs formation [68]. Hydrolysis in solvent favors self-polymerization, whereas hydrolysis on SiO_2 surface, cause the formation of SAMs. Thus, trace quantities of water in solvents or on SiO_2 surfaces dominate the self-polymerization and dehydration reactions with surface silanols. Insufficient water either in solvents or on SiO_2 surfaces impedes the hydrolysis reaction, and decelerates the subsequent surface dehydration reaction self-polymerization. On the contary, excess water in solvents accelerates self-polymerization over the surface dehydration reaction, as shown in Figure 2.12.
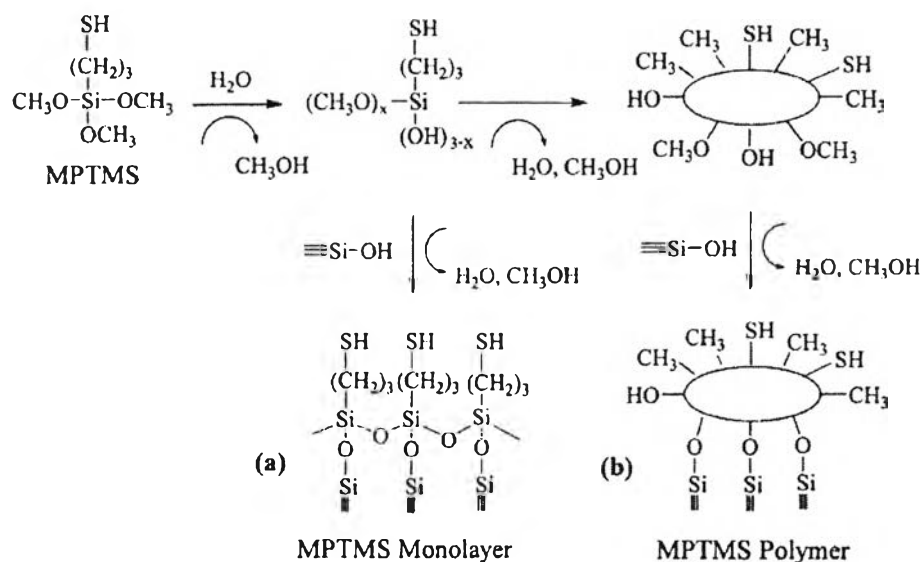
Figure 2.12 Competitive reaction in the formation of self-assembled MPTMS layers on the SiO_2 surface: (a) surface dehydration on the SiO_2 surface; (b) self-polymerization in the solvent.

At high MPTMS concentration (4×10^{-2}M) before they can diffuse to the SiO_2 surface, more MPTMS molecules are hydrolyzed by water in the solution and polymerize there, rather than forming SAMs on the SiO_2 surface. The sub-micrometer-sized polymer particles diffuse to and react with the SiO_2 surface, which leads to the formation of rough polymer layers and reduces polar terminal functional group.

The solution of 3-Mercaptopropyltrimethoxysilane (MPTMS) and benzene was used to form self-assembly monolayers (SAMs) on glass slides. Zheng-chun Liu et al. [69] confirmed that the formation of covalent bonds between MPTMS and glass surface was occurred. These strong covalent interactions of MPTMS molecules with the substrate and the short-range van der Waals forces between the molecules allowed for the formation of a highly ordered and closely packed monolayer film [70, 71].

I. Piwonski et al. [72] show preparation method of two-dimensional (2D) silica-like surface from self-assembled monolayers (SAMs) of 3-mercaptopropyltrimethoxysilane (MPTMS) on Au(111) surface. Hydrolysis and condensation of MPTMS end-groups lead to 2D SiO_2 network called glass monolayer.

It can be also described as 2D sol–gel processes. All procedures were performed in monolayer. When the state of end groups of MPTMS changes, i.e. methoxy (Si–OCH$_3$) groups undergo hydrolysis to silanols (Si–OH) groups, the surface topography changes. The similar phenomena may be observed when silanols undergo condensation and siloxy (Si–O–Si) bonds are created, as shown in Figure 2.13.

Au (1 1 1) surface
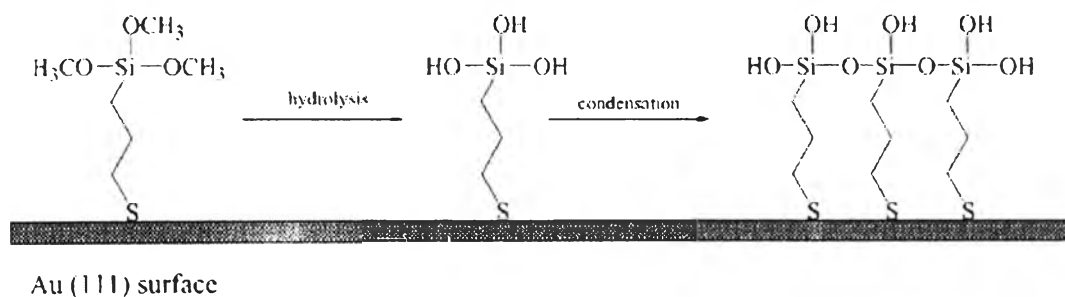
Fig. 2.13. Model of MPTMS reaction leading to 2D silica-like surface.

It is known that the behavior of MPTMS on gold surface and their organization structure are influenced by following forces: (i) interactions between thiols head groups and Au lattice; (ii) interactions between alkyl chains having dispersion character; and (iii) interactions between end groups of thiols. Final molecular organization and specific topography are the result of the balance between these three forces [73].

MPTMS agent is used for the fabrication of the copper nanoparticles thin-films on the indium-doped tin oxide substrate. MPTMS can form stable metal by forming covalent bonding between sulfur in MPTMS and copper nanoparticles [25].

Fabrication of multilayer film of gold nanoparticles is normally based on the layer-by-layer self-assembly (LBL) technique. APTMS is used as surface modifying agent and APTMS 1:3:3 solution (APTMS:CH$_3$OH:0.15 M HCl = 1:3:3 mol%) as multilayer surface modifying agent. APTMS 1:3:3 solution is used to prepare Au-SiO$_2$ core-shell monolayer. Different deposition time results in difference shell thickness [74].

Jian Wang et al. [75] show modifying silicon surface with APTMS by vapor phase deposition. Gold nanoparticles were quite uniformly scattered over such a

surface with a submonolayer coverage through specific interaction with $-NH_2$, leading to a sandwiched structure as Au nanoparticles/APTMS/Si.

It is known that silanization of APTMS in liquid-phase produces polymeric material [76]. Vapor deposition was adopted in order to reduce self-polymerization of silanes. They have noted that very different values of contact angle were reported for the APTMS-derived silicon surface ranging from 21 to 70° [77, 78], reflecting the great difference in the surface structure of differently prepared APTMS films. It is believed that high contact angle for APTMS films obtained by liquid-phase deposition may attribute to the multilayer formation, the surface reorganization, and the exposure of ethylene surface.

Ensembles of gold nanoparticles on Spherical silica have been done by using PEI as surface modifying agent. PEI was used to study electrostatic effects between the negative surface potential of the gold nanoparticles and the modified surface well as the effects of added sodium citrate on the increased shell density of gold nanoparticles [5].

2.7 Applications of Nanoscaled Gold on Surface

The unique properties of gold at the nanoscale are ensuring that gold is a candidate material for nanotechnology applications in the diverse areas of electronics, catalysis, colours and coatings and the biomedical sector. Specific examples of technologies considering or already using gold have been described, including:

- Low resistance printable gold nanoparticulate inks for flexible electronics
- Gold nanowires for interconnections in future electronic devices
- Nanoparticulate gold colloid for rapid tests and biomedical assays
- Gold-silica nanoshells for targeted destruction of cancer cells
- Improved decorative coatings using thiol stabilised gold nanoparticles
- Thermosetting gold nanoparticle containing paints exhibiting novel aesthetic effects
- Nanoparticulate gold catalysts for pollution control and chemical synthesis
- Fuel cell electrocatalysts based on carbon supported nanoparticulate gold

2.7.1 Nanoelectronic

Longer term innovations for future information technology hardware will, however, be in the form of highly integrated electronic devices, designed and fabricated on the nanometre scale. Gold is an indispensable element for nanoscale electronic components because of its resistance to oxidation and its mechanical robustness. Among other metals, only silver and platinum offer similar properties, but silver can be too reactive and platinum is significantly more expensive than gold.

The silicon chip microprocessor and the computers they operate are becoming smaller and smaller. Now they have met fundamental physical barriers that will impede further miniaturization, at least using current technology. These problems could be overcome by designing a completely new type of computer using nanotechnology.

In the area of nanoelectronics, work on using gold nanowires as potential connectors in nanodevices is underway in research centres around the world. The

University of Delaware, USA, for example, has developed new, self-assembling and repairing gold nanowires, which could find application in the development of nanoelectronics. K.D. Hermanson et al [79] have shown that a new class of microwires can be assembled by dielectrophoresis from suspensions of gold nanoparticles. These researchers at the University of Delaware have developed new, self-assembling and repairing gold microwires, which could find application in the development of nanoelectronics. These scientists used tiny particles of gold, suspended in an aqueous solution. When electrodes were inserted into the suspension, gold wires more than 5 mm in length could be formed. The wire structures grew via the application of alternating electric fields across the nanoparticle suspension. They were generally of the order of 1 micron in diameter. It has been shown that these wires can be used as microscopic sensors for certain chemicals, such as thiols and cyanides. Tne principle of makııɪ₅ ‧ ‧ral connections, by assembling rudimentary circ‧ ıs using this technique has been establisn₍ '

2.7.2 Catalyst

Of all the new uses of gold, perhaps the most interesting development is b. d on its use as a catalyst in chemical processing, pollution control and fuel cell applications, Table 2.2 [80]. The platinum group metals have long been known as important industrial catalysts. However, most researchers had overlooked gold as a possible catalyst until very recently, as its use requires careful and unconventional preparation centered on achieving a very small particle size (less than 5 nm).

Table 2.2 On-going and potential application for nanoparticulate gold catalysts

Application area	Example
Air quality control in vehicles & building etc.	Odor abatement, CO removal, gas masks
Pollution abatement	Dioxin oxidation/decomposition, NOx reduction
Hydrogen economy	Water gas shift, CO removal, Fuel anode
Chemical process	Hydrochlorination, Hydrogenation, Selective hydrogenation, Selective oxidation

One of the most exciting aspects about catalysis by gold is the 'light off' temperature that can be achieved (the temperature at which the catalyst becomes functional). Potentially, gold catalysts operate effectively at temperatures as low as -70°C. Other precious metal catalysts tend to have optimum performance in the range of 130°C-530°C. This offers the opportunity for gold to catalyze new reactions and in some cases offer alternative cost effective solutions to the platinum group metals. Gold is already being used at a new BP Chemicals plant for the production of vinyl acetate monomer (used in the production of emulsion paint and glues), which uses a gold-palladium alloy catalyst to excellent effect. Odor reduction applications are possible, as well as the potential to remove nitrogen oxides from diesel engine exhaust gases.

Recent gold catalyst used in chemical processing, combined with a redox active catalyst, is claimed for the World Gold Council for the manufacture of hydrogen from carbon monoxide [81]. The gold palladium catalyst is being used in the commercial manufacture of vinyl acetate monomer. The selective oxidation of CO in the presence of hydrogen to purify the hydrogen streams has also been widely patented, for example by Haruta and Mitsubishi [82]. In the field of selective oxidation, Dow Chemical Company have patented the selective production of propene oxide by the epoxidation of propene in the presence of hydrogen and a gold on TiO_2/SiO_2 catalyst [83] and a more recent Bayer patent [83] has indicated improved yields of product. An Arco Chemical Technology, USA patent has been filed on the direct production of hydrogen peroxide using a gold catalyst supported on titania or zirconia [83]. Another recent processing example is provided by Eastman Chemical Company on a vapour-phase carbonylation process using Au/Ir alloy catalysts for the production of carboxylic acids and esters from lower aliphatic alcohols and other organic feedstocks [83].

For gold catalyst, it has been used in pollution control and fuel cell. Perhaps the greatest commercial opportunity for gold based catalysts lies in a number of potential uses within the automotive industry. With over 50 million light vehicles produced per year, this is a huge market for the catalyst industry. Whilst the price of gold compares very favorably with platinum, it is the ability of gold as a component within a three-way catalyst to withstand the elevated temperatures required that is in

doubt. About 40% of vehicles built in Europe are now powered by diesel engines and catalytic converter systems for diesel engines tend to operate at lower temperatures than petrol engines. For gasoline engines, there is now increasing focus on the challenge of improving low cold start performance of catalytic systems. The well-known low temperature activity of gold catalysts could have a role to play in this application. A recent patent application by Toyota claiming stability of gold catalysts at 800°C, suggests that the necessary work is underway [84].

If gasoline and diesel engines are the current automotive power source of choice, then fuel cells are claimed to be the future based on their environmental friendliness. With hydrogen widely considered to be the likely long-term fuel choice for vehicles, there is probably a need for a number of new commercial catalysts in this system for hydrogen generation, hydrogen purification and of course within the fuel cell itself for catalyzing the hydrogen plus oxygen reaction, the basis of fuel cell energy generation. It is believed that there are significant opportunities for gold catalysts in this industry [85], Table 2.3.

Table 2.3 Potential areas within automotive systems for using nanoparticulated
gold catalysts

Automotive Power Source	Application for Gold Based Catalysts	Reaction (s)	Main Characteristics of Supports Gold Nanoparticulate Catalyst
Fuel Cell	Fuel processing Systems for clean H_2 production	Water gas shift reaction for H_2 production	High activity at low temperature
		Preferential oxidation of CO for H_2 clean up	High activity at low temperature
		Methanol decomposition for H_2 production	High activity
	Fuel cell catalyst	Oxidation removal of CO from H_2	Improvement in electrical conductivity
Diesel Engine	Component of TWC for diesel engine emission control	Co and HC Combustion and NOx reduction HC	Low temperature activity (and high for NOx reduction)
Petrol Engine	Low light off catalyst For petrol engine	CO and HC combustion	Low temperature activity

As well as control of automotive emissions, there are a number of potential commercial applications in other areas of pollution control. Control of mercury, which has been linked to Alzheimer's disease and autism, is expected to be the subject of legislation in 2004 by the Environmental Protection Agency in the US. They are expected to impose limits on mercury emissions from coal-fired boilers in the utility industry. Approaches to control these emissions include the oxidation of mercury via gold catalysts and an alternative metallurgical approach of using gold-coated carbon, which effectively adsorbs the mercury vapor and is recycled later. The scientific literature is now showing that decomposition of ozone is reaction that gold catalysis effectively [86]. Control of ozone which can be emitted by equipment such as photocopiers and laser printers and which can be a contributor to the formation of smog, is a significant commercial application. For example, the car manufacturer Volvo has its S80 model's radiator coated with a base metal catalyst that breaks down around 80% of ozone passing over it. Dioxin decomposition is an application where a low temperature catalyst might reduce the need for thermal incineration and its associated high energy costs. The ability of gold to oxidize CO and remove NO_x compounds offers scope for air quality improvement and control of malodors, be they in buildings, transport or other applications. The scope here for commercial applications is very large.

2.4.3 Biomedical applications

The range of current and potential future applications for gold in the biomedical sector are highlighted below, classified by the form in which the gold is employed (bulk metal, nanoparticles, or compounds), Table 2.4 As well as the current use of gold in dental alloys, the bulk properties of gold are also used in inner ear implants and coatings for patents. Gold also plays a role in targeted drug delivery through the 'pharmacy on a chip' concept, where gold-coated microcapsules of drugs are controllably released intravenously into the body. This novel technology now being commercialized came out of research at MIT, USA. The previously described potential anti-bacterial effects might find application in coatings for catheters and wound dressing materials. For gold nanotechnology, current applications in sensing and labeling (pregnancy testing kits are based on gold colloids) are being joined by emerging applications in the targeted destruction of cancer cells. Gold compounds

already find use in drugs related to the treatment of arthritis and work is now emerging suggesting gold compounds can be effective in the treatments of some types of cancer.

Table 2.4 Current and emerging uses of gold in biomedical applications

	Bulk gold / alloys	Gold Nanotechnology	Gold Compound
Dental Alloys	C		
Prothesis / implants	C		
Stents	C		
Sensors / Labelling		C	
Drug Delivery	E	P	
Arthritis Treatment			C
Cancer Treatment		P	E
Anti-bacterial	P	P	P

C-Current Application E -Emerging Application P-Possible Application

In many instances, the potential application of gold is related to the interesting optical properties of the metal at the nanoscale and its biocompatibility. One example concerns the use of gold conjugate in rapid tests. These are disposable membrane-based assays that, through visual evidence, confirm (or otherwise) the presence of an analyst in a liquid sample [87]. Applications for rapid tests include clinical applications (fertility, allergies, forensic, toxicology etc), agricultural (food safety, plant and crop disease) and environmental contamination. They aim to provide visually clear and unambiguous results in a convenient timeframe e.g. minutes. One of the most commonly recognized examples of a rapid test are home pregnancy testing kits [88].

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The majority of available tests today use the unique properties of gold particles to develop the visual signal that confirms the presence of the analyst in the test fluid. Gold is essentially inert and when prepared correctly forms almost perfectly spherical particles. Proteins will strongly bind to the surfaces of gold particles, ensuring long-term stability. As described in a recent review of the topic [89], a rapid test kit is likely to contain gold nanoparticles adsorbed with antibodies or antigens specific to the analyst being detected.

2.4.4 Advanced coatings

Colloidal gold has long been the basis of decorative effects in glass and on tableware in the form of purple and pink enamel colors. Nanoparticulated gold is now being used to produce conventional gold decoration on tableware via the use of decals; this overcomes a longstanding technical problem with the use of conventional 'liquid gold' formulations. Recently, Nippon Paint has introduced a new stabilized polymer, gold nanoparticle-containing paint. This has novel dynamic optical effects, changing color depending on the external lighting conditions [90]. It is interesting to consider other applications for these types of decorative effects. A gold paste containing 40 % of the ca. 10nm nanoparticles was used for this application, with polyester based, comb-shaped block copolymer used as the protective polymer. SEM photographs of the gold nanoparticles are shown below, Figure 2.14.

10nm
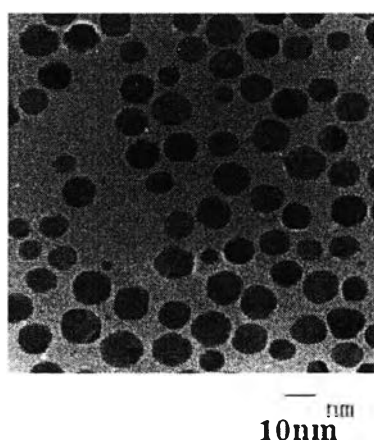
Figure 2.14 Nanoparticulate gold paste prepared by Nippon Paint

A similar type of technology could be envisaged as an anti-counterfeiting measure for security documents and bank notes. We live in a world where security officials are constantly trying to keep one step ahead of the criminal world, by introducing new technologies to prevent counterfeiting. Control of color through advanced inks is one technique that can be used and it is reasonable to assume that carefully controlled gold nanoparticles could be incorporated into inks providing novel and unique optical effects irreproducible by those without the careful preparative techniques needed to make the inks. It would be interesting if the original form of money, gold, became a component of high value bank notes to endorse their authenticity and validity.

Some interesting results from a recent World Gold Council GROW project indicate a possible new use for gold coatings might emerge. In this project it was found that a stainless steel coupon that had been exposed to E coli bacteria still had surviving viable bacteria remaining on its surface after 3 months at 4°C. This contrasted with coupons electroplated with gold where no viable bacteria are found on the gold surface after a similar period. Silver is a well established anti-bacterial agent and there is a growing body of evidence that suggests gold could well be used in this way. As well as bulk gold, nano-particulate gold and gold compounds are showing anti-bacterial properties.