Chapter III

Synthesis of Triangular and Hexagonal Gold Nanoparticles using Undialyzed and Dialyzed Lemongrass Leaf Extract

In this chapter, room temperature synthesis of highly anisotropic gold nanoparticles (triangular and hexagonal) using lemongrass (Cymbopogon flexuosus) leaf extract has been discussed. Dialysis is used as a novel method to control the size and yield of triangular and hexagonal nanoparticles. 3, 12.5 and 30 kDa cut-off dialysis bags were used for the synthesis of gold nanotriangles during dialysis of lemongrass extract against $10^{-6}$ M HAuCl$_4$ solutions. The extract dialyzed using different cut-off bags were also used for the synthesis of gold nanotriangles. The anisotropic nanoparticles display an intense absorption in the NIR region of the electromagnetic spectrum, which can be controlled by varying the amount of lemongrass extract in the reaction medium using different cut-off dialysis bags. The chapter also discusses the size of biomolecules present in lemongrass extract, which play an important role as reducing and shape directing agents for the nanotriangle synthesis.
3.1 Introduction:

Biology has always fascinated materials scientists due to their precise regulation of the morphology of crystals. Inspired by biomineralization, nanotechnologists have paid much attention towards the synthesis of materials of particular size and shape using biomolecules or organisms as reducing or templating agents. Magnetic nanoparticles present inside magnetotactic bacteria [1], siliceous structures in diatoms [2] and calcareous nanostructures in various organisms [3] etc are motivating factors for scientists to synthesize materials in nanodimensions using biological means. Metal nanoparticles are always attractive candidates because of their unique properties that are different from their bulk counterparts that endow them with numerous applications in opto-electronics [4], catalysis [5], magnetic devices [6], biosensing [7], biodetection [8], and drug/gene delivery [9]. Nowadays, colloid chemistry is challenged to control not only the size of metal nanoparticles but also the shape and morphologies. Shape control is an alternative tool to modulate the optical and catalytic properties of nanomaterials. Much effort has been devoted to the synthesis of various shapes of nanoparticles like nanocubes [10], nanorods/nanowires [11], nanodisks [12], nanotetrapods/nanoarrows/nano-tear drops [13], nanobelts/nanoribbons [14] and nanodumbbells [15] by chemical and physical methods. Recently, synthesis of metal nanoprisms has received enormous attention mainly due to their unusual optical and catalytic properties with potential application in various fields. There are several reports on the synthesis of silver nanotriangles [16] but fewer efforts have been made to synthesize gold nanoprisms [17]. The synthesis of these anisotropic nanoparticles is achieved by chemical and physical means, which are often hazardous to the environment. Thus, there are growing demands for the synthesis of nanoparticles through clean, nontoxic and environment friendly (green chemistry) procedures. Therefore, biological processes that lead to formation of nanomaterials appear to be a promising endeavor as environmentally benign nanofactories.

Beveridge and coworkers first demonstrated the deposition of gold nanoparticles within bacterial cells [18]. Reduction of Ag⁺ ions and formation of silver nanoparticles within the periplasmic space of the bacterium Pseudomonas stutzeri AG259 was shown by Klaus-Joerger and coworkers [19]. Sastry and coworkers have shown earlier that intra and extracellular synthesis of nanoparticles of various compositions and size could be
achieved by using bacteria and fungi [20]. Brown et al. have investigated the polypeptide directed synthesis of gold nanocrystals and found that polypeptides could control the morphology and orientation of nanocrystals [21]. Apart from the microorganisms used for synthesis, biomolecules like starch [22, 17d], aspartic acid [23] and phospholipids [24] have also been used as reducing and stabilizing agents for the synthesis of gold and silver nanostructures. Though microorganisms are utilized for synthesis of various compositions of nanoparticles, the use of plants or plant extracts for synthesis of nanoparticles is an under-exploited area. Plants have been used as phyto-remediation sources for removal of contaminations from soils and water for a long time [25]. Plants are also used for hyper-accumulation of heavy metals in different parts either through reduction of metals ions to lower oxidation state or complexation of biomolecules to metals in its native oxidation state [26]. Jose-Yacaman’s group has shown that live Alfalfa plants reduced Au^{3+} ions to Au^{0} oxidation state to form metal nanoparticles inside the plants [27]. They have also demonstrated the synthesis of silver nanoparticles inside Alfalfa plant shoots by supplying the Ag^{+} ions in the plant growth media [28]. In another report, oat, wheat biomass, geranium and neem plant extracts have been used as reducing agents to synthesize gold nanoparticles of various size and shape [29]. As far as commercial production of metal nanoparticles is concerned, the metal nanoparticles synthesized inside plants and micro-organisms (intracellular) suffer primarily from product harvesting and recovery that are cumbersome and expensive. Therefore, the extracellular synthesis plays a pivotal role in the synthesis of various compositions of nanoparticles in the large scale.

In this chapter, an attempt has been made to synthesize triangular gold nanoparticles using a plant extract. We discuss a single step and room temperature process for synthesis of triangular and hexagonal gold nanoparticles using lemongrass extract as the reducing and shape-directing agent. The yield of the gold nanotriangles by this method is better than other reported chemical and photo-induced methods. As compared to spherical counterparts, triangular and hexagonal gold nanoparticles show two surface plasmon resonance bands; one in the visible region at 520 nm and another in the NIR region of the electromagnetic spectrum [16, 17]. The intense absorption of the triangular nanoparticles in the NIR region could make these nanoparticles potential...
candidates for cancer hyperthermia [30] and architectural application in optical coating for blocking the NIR light from the solar spectrum [31]. The absorption by triangular nanoparticles in NIR region depends on their edge length and could be controlled by varying the concentration of lemongrass extract in the reaction medium [31]. Dialysis is a method used particularly in biology to purify a single compound from a mixture of compounds. Dialysis is the process of separating molecules in the solution by difference in their rate of diffusion through a semipermeable membrane (dialysis bag). The purification of a compound using dialysis depends upon the rate of diffusion of molecules through pores of the bag due to concentration gradients across the dialysis bag. A concentration gradient is due to the difference in concentration of solutions separated by the membrane and it determines the rate of diffusion.

Fick’s law governs the diffusion of molecules across the dialysis bag. Fick’s first law is applied in steady state diffusion i.e., when the concentration within the diffusion volume does not change with respect to time.

\[ J = -D \frac{\partial \phi}{\partial z} \]

where

- \( J \) is the diffusion flux, \( D \) is diffusion coefficient
- \( \frac{\partial \phi}{\partial z} \) is concentration gradient

The size of the pores in the bag and that of the constituents of the mixture is also an important factor for the size selective purification of a compound. Molecules (salts, water or small molecules), small enough to pass through the semipermeable membrane, tend to move into or out of the dialysis bag in the direction of decreasing concentration. Larger molecules, which have dimension significantly greater than the pore diameter, are retained inside the dialysis bag. In this chapter, dialysis is used as a tool to regulate the green chemistry approach of synthesis of nanoparticles of controlled size and shape using lemongrass extract and hence to fine-tune their optical properties. Dialysis has been used for the size selective separation of biomolecules from several sizes of biomolecules of lemongrass extract. Biomolecules of lemongrass extract, which have size below the pore size of corresponding dialysis bags, diffuse from inside the bags to external solutions.
while larger biomolecules remain inside the bags and therefore the concentrations and compositions of extract both inside and outside the dialysis bags are different. The different concentrations of extract both inside and outside the dialysis bags facilitate synthesis of varying yield and size of gold nanotriangles due to the different rate of reduction of gold ions in the solution. In this chapter, we have also strived to investigate the size of biomolecules of lemongrass extract that is responsible for nanotriangle formation using different cut-off viz; 3, 12.5 and 30 kDa dialysis bags.

### 3.2 Synthesis of gold nanotriangles and nanohexagons using lemongrass leaf extract:

#### 3.2.1 Experimental Details:

Lemongrass leaf extract was prepared by boiling 100 g of thoroughly washed and finely cut lemongrass leaves (*Cymbopogon flexuosus*) in 500 mL sterile distilled water. In a typical experiment, 10 mL of this lemongrass extract was added to 90 mL of $10^{-3}$ M aqueous HAuCl₄ solution. The reduction of AuCl₄⁻ ions was monitored by recording the UV-vis-NIR absorption spectra as a function of time of reaction of this mixture. The percentage of gold nanotriangles in solution was enhanced up to 98% by centrifuging the nanotriangle solution three times at 1000 rpm for 15 minutes followed by redispersion in water. The UV-vis-NIR spectrum of the purified gold nanotriangles was recorded from a drop-coated film on the quartz slide. Gold nanotriangles synthesized by lemongrass extract were characterized by Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM). Atomic force microscopy (AFM) analysis in the contact mode was done to find out the thickness of the gold nanotriangles.

#### 3.2.2 UV-vis-NIR spectroscopy Analysis:

UV-vis-NIR spectra were recorded as a function of time of reaction for undialyzed lemongrass extract with $10^{-3}$ M HAuCl₄ solution at room temperature. Curve 1 in Figure 3.1 shows the surface plasmon resonance band (SPR) at ca. 580 nm after 1 h of reaction. With time, the surface plasmon band at 580 nm is gradually shifted to 540 nm with increase in intensity. This change is also accompanied by appearance of a new band in the NIR region of the electromagnetic spectrum. The UV-vis-NIR spectrum of gold
nanoparticles synthesized after 2 h of reaction (curve 2 of Figure 3.1) reveals two SPR bands: one at lower wavelength at 540 nm and another at ca. 1108 nm in the NIR region of the electromagnetic spectrum [32]. The UV-vis-NIR spectra of gold nanoparticles synthesized after 3, 5 and 6 h of reactions (curves 3 to 5 respectively) show an increase in the intensity of SPR band at 540 and 1250 nm and a red shift of the band in the NIR region as compared to curve 2. The red shift in the NIR band reflects an increase in edge length of gold nanotriangles during the growth process [31-33]. Time dependent growth of the NIR band observed in the absorption spectra is a characteristic feature of either formation of aggregated nanoparticles [7a, 34] or the synthesis of anisotropic gold nanoparticles whose aspect ratio increase with time of reaction [12, 35].

Figure 3.1: A) UV-vis-NIR spectra recorded as a function of time of reaction of lemongrass extract with 10⁻⁷M HAsCl₄. Curves 1-5 correspond for spectra recorded after 1, 2, 3, 5 and 6 h of reaction respectively. B) UV-vis-NIR spectra were recorded from the purified gold nanotriangles after three times centrifugation of solution and in the form of film cast on the quartz substrate (inset of Figure B).

After complete saturation of the reaction, the NIR band does not show an increase in intensity even after a month in the reaction solution, which indicates no further growth of the gold nanotriangles. The TEM image (Figure 3.2) of gold nanoparticles synthesized using lemongrass extract shows a large percentage of gold nanotriangles and spherical nanoparticles with no aggregation of the gold nanoparticles, which have been discussed
Chapter 3

below in the text. Thus, from these results, it can be stated that the large absorption in the NIR region of electromagnetic spectra is due to the presence of anisotropic gold nanoparticles like gold nanotriangles and hexagons in the reaction solution. The absorption band observed at 540 nm is due to the combined effect of dipole plasmon band of spherical particles and transverse component of SPR band (out of plane plasmon vibration) of the gold nanotriangles and hexagons while the absorption band observed in the NIR region is due to the longitudinal component of SPR band (in-plane plasmon vibration) [32a, b, d, 36]. Figure 3.1B represents the UV-vis-NIR spectrum of purified gold nanotriangles (after three times centrifugation), which shows high intensity longitudinal SPR band along with a significant loss in the transverse SPR band at 550 nm. The loss in the intensity of the transverse component clearly indicates removal of spherical particles from solution containing gold nanotriangles by the repeated centrifugation process. Interestingly, the in-plane quadrupole plasmon mode of SPR is also observed at ca. 815 nm for the purified gold nanotriangles (Figure 3.1B), which has been reported earlier by Mirkin’s group [37]. The inset of Figure 3.1B shows the UV-vis-NIR spectrum of a purified gold nanotriangle film on a quartz substrate, prepared by drop coating and solvent evaporation of the gold nanotriangle solution onto the substrate. The UV-vis-NIR spectrum of gold nanotriangles film shows a shoulder at ca. 720 nm along with an intense longitudinal band at 1660 nm in the NIR region. The observed shoulder at 720 nm in the UV-vis-NIR spectrum for gold nanotriangle film is similar to the transverse absorption band at 550 nm of purified gold nanotriangles, measured in solution form. The observed large red shift of transverse band in spectrum may be due to change in the dielectric environment of nanotriangles during film formation on the quartz substrate [32a, 37]. The extremely large NIR absorption is a result of the in-plane plasmon vibrations or the longitudinal surface plasmon band of gold nanotriangles and hexagons.

3.2.3 Electron microscopy analysis of the gold nanotriangles:

The gold nanoparticles synthesized using lemongrass extract after 6 h of reaction were analyzed by transmission electron microscopy (TEM). The TEM image (Figure 3.2) shows a large population of triangular and hexagonal nanoparticles along with spherical nanoparticles. The edge-to-edge length and yield of nanotriangles is 0.05-2 µm and 45%
respectively. Many nanoprisms have regular edge sides with an angle of 120° (for hexagonal nanoparticles) or 60° (for triangles) between adjacent sides. The yield of gold nanotriangles formed by this method is higher than previous methods reported by other groups [16, 17]. The edges and tips of the gold nanotriangles are smooth and very sharp as observed in the TEM image (Figure 3.2A). Scanning electron microscopy (SEM) image (Figure 3.2B) also shows a large population of anisotropic nanoparticles like gold nanotriangles and nanohexagons. Some of the nanotriangles have truncated vertices, which were also observed previously for silver and gold nanotriangles synthesized using photochemical and thermal methods [16c,d, 17k].

**Figure 3.2:** A) TEM image of triangular, hexagonal and spherical gold nanoparticles synthesized using lemongrass extract before centrifugation. B) SEM image of lemongrass reduced gold nanotriangles and spherical nanoparticles. C) Selected area electron diffraction (SAED) pattern of gold nanotriangles. Triangle, circular, square and pentagonal boxes in image represent 1\(\overline{1}\{422\}, \{220\}, \{311\} \text{ and } \{422\} \text{ fcc gold lattice planes. D) TEM image of purified gold nanotriangles after three times centrifugation at 1000 rpm. E) High resolution TEM (HRTEM) image of a gold nanotriangle. F) EDAX result for a single gold nanotriangle on copper grid.

Most of the gold nanotriangles in the TEM image show dark lines and bands i.e, fringes with different contrast within particles, which arise due to stresses in particles due to buckling or warping of atomic planes with respect to the electron beam in thin gold nanotriangles [36b, 38]. The contrast present in nanotriangles due to such phenomenon is called bending contours. Liz-Marzán’s group has claimed that the origin of bending...
Chapters 71

contours might be simply due to stress in the crystalline lattice of nanotriangles, which can arise due to the presence of stacking faults in the crystal structures or due to the presence of hexagonal-like monolayer on nanoprisnm faces, which would slightly distort the (111) plane of the pure fcc cubic structure [39]. At close inspection of the nanotriangles in the TEM image, we can observe spherical nanoparticles below the nanotriangles that indicate the thin nature of triangular gold nanoparticles. Figure 3.2C shows the selected area electron diffraction (SAED) pattern of a single gold nanotriangle, which clearly indicates that it is single crystalline in nature. The hexagonal nature of diffraction spots in the SAED pattern shows that the nanotriangle is highly [111] oriented with top normal to electron beam. The hexagonal spots could be indexed on the basis of face centered cubic (fcc) structure of gold nanoparticles. The triangular, circular, square and pentagonal boxes made on SAED pattern correspond to the forbidden 1/3{422} and allowed {220} {311} and {422} Bragg reflections respectively. The forbidden reflection in the electron diffraction pattern may be originated due to the presence of twin planes [16h, 40], or due to the presence of [111] directed stacking faults lying parallel to the (111) plane of the gold nanotriangles and extending across the particles [41]. Thus, it is reasonable that the top and bottom parts of the nanotriangles are bound by atomically flat (111) planes [36d]. The TEM image (Figure 3.2D) of gold nanotriangles purified by centrifuging the solution three times at the speed of 1000 rpm shows 98% population of gold nanotriangles along with hexagonal particles, which is consistent with the UV-vis-NIR spectrum of the purified gold nanotriangles (Figure 3.1B). The high resolution TEM (HRTEM) image taken from the flat part of a gold nanotriangle shows lattice spacing of 2.36 Å that corresponds to the (111) plane from the top surface of the gold nanotriangle (Figure 3.2E). Energy dispersive analysis of X-rays (EDAX) from the nanotriangles confirms the presence of only gold in as prepared triangular nanoparticles (Figure 3.2F). The strong signal of copper in the EDAX spectrum comes from the copper TEM grid.

3.2.4 Atomic Force microscopy (AFM) measurements:

Figure 3.3 shows contact mode AFM images of triangular and hexagonal gold nanoparticles with few spherical gold nanoparticles on the surface of nanoparticles. The edges and tips of nanoparticles are observed to be smooth and sharp as can be seen in the TEM analysis (Figure 3.2A). The line profile plots shown at the bottom of Figure 3.3A...
Chapter 3

and B demonstrate that nanotriangles and nanohexagons have thickness of ca. 15 and 25 nm respectively. The average thickness of gold nanotriangle after measurement of a large number of particles is found to be 18 nm. The edge-to-edge length of the triangular and hexagonal gold nanoparticles is found to be ca. 400 nm and 800 nm respectively.

![Image of nanotriangles and nanohexagons with thickness measurements](image)

Figure 3.3: A) Atomic force microscopy (AFM) image of triangular and hexagonal gold nanoparticles. B) Higher magnification AFM image of a hexagonal nanoparticle. The line profile plots at bottom of figures A and B show that triangle and hexagon are of ca. 15 and 25 nm thickness respectively. AFM images were taken in height mode.

3.3 Size and shape controlled synthesis of gold nanoparticles:

Size and shape controlled synthesis of isotropic or anisotropic metal nanoparticles has been achieved by various methods and this control has allowed these structures to be used in a variety of applications such as biodetection [7] and catalysis [42]. Photochemical and thermal methods have been reported to control the dimension of anisotropic nanoparticles through the judicious use of plasmon excitation but these methods are hazardous to the environment [16c,d, i]. Dialysis is one of the methods to control the size and shape and therefore to fine-tune the optical property of nanoparticles through an environmentally benign approach. Different cut-off dialysis bags are used for the controlled diffusion of biomolecules of lemongrass extract to external solution. Diffusions of molecules depend on the concentration gradient across the bag.

Akhilesh Rai  
University of Pune
3.3.1 Synthesis of gold nanoparticles during dialysis of extract against HAuCl₄ solution:

3.3.1.1 Experimental details:

Before performing the experiments, different cut-off dialysis bags were boiled in Milli-Q water for 10 minutes followed by thorough washing with Milli-Q water to remove contamination from bags. 100 mL of lemongrass extract kept in different cut-off dialysis bags (3, 12.5 and 30 kDa respectively) were dialyzed against 250 mL of 10⁻³ M HAuCl₄ solutions. Scheme 3.1 depicts the dialysis of extract against HAuCl₄ solution and synthesis of gold nanoparticles both inside and outside the dialysis bag. UV-vis-NIR spectroscopy, TEM and FTIR measurements of the gold nanoparticles synthesized inside and outside the dialysis bags were carried out after 48 h dialysis of lemongrass extract in different dialysis bags.

![Scheme 3.1: Schematic shows the dialysis of lemongrass extract against HAuCl₄ solution. Insets show diffusion of biomolecules through pores of bag and synthesis of smaller and larger nanotriangles inside and outside the bag respectively.](image)

X-ray photoemission spectroscopy analysis of synthesized gold nanotriangles inside the 12.5 kDa bag, cast as a film on silicon wafer (111), was carried out to know the chemical state of nanoparticles. The charge on the gold nanoparticles synthesized inside different cut-off bags during dialysis of lemongrass extract was determined by gel electrophoresis. 40 mL of 1% ultra pure agarose (high melting agarose) was boiled in water for 10 minutes and the solution was poured in a closed rectangular chamber to form solid gel. The wells were formed by placing a Teflon comb in the gel during the solidification process. The synthesized gold nanoparticles from the different bags were
loaded in the wells and electrophoresis was done in phosphate buffer of pH 7.4 at a constant voltage of 60 volts for 1 h.

3.3.1.2 UV-vis-NIR spectroscopy analysis:

Curves 1-3 in Figure 3.4A shows UV-vis-NIR spectra of gold nanoparticles synthesized inside different dialysis bags (3, 12.5 and 30 kDa bags respectively) during dialysis of lemongrass extract against $10^{-3}$ M HAuCl$_4$ solutions. UV-vis-NIR spectra were recorded after 48 h dialysis of extract. On visible inspection, the colour of solution inside the bags turned dark ruby red from initial light brown with the time of reactions. Curves 1 and 2 correspond to gold nanoparticles synthesized inside 3 and 12.5 kDa dialysis bags respectively and show that transverse SPR band centered at 540 nm is accompanied with the longitudinal component as a weak hump at 760 nm.

![Figure 3.4: A) UV-vis-NIR spectra of the gold nanoparticles synthesized during dialysis of lemongrass extract against $10^{-3}$ M HAuCl$_4$. Curves 1-3 correspond to nanoparticles synthesized inside 3, 12.5 and 30 kDa dialysis bags respectively. B) Curves 1-3 correspond to UV-vis-NIR spectra of gold nanoparticles synthesized outside 3, 12.5 and 30 kDa dialysis bags respectively.](image)

A pronounced change is observed in the absorption spectrum of gold nanoparticles synthesized inside the 30 kDa bag. The UV-vis-NIR spectrum of gold nanoparticles synthesized inside the 30 kDa bag shows transverse SPR band at 540 nm along with the longitudinal SPR band, which appears to go beyond 1250 nm in the NIR
region (curve 3, Figure 3.4A). The intensity of transverse SPR component is higher than longitudinal SPR component in the optical absorption spectra in all cases (curves 1-3). UV-vis-NIR spectra of gold nanoparticles synthesized outside different dialysis bags are shown in Figure 3.4B. The UV-vis-NIR spectrum (curve 1, Figure 3.4B) of gold nanoparticle synthesized outside the 3 kDa bag shows a broad absorption spectrum ranging from 600 to 850 nm. While the absorption spectra of the gold nanoparticles synthesized outside 12.5 and 30 kDa bags appear to be continuously increasing from 600 nm and go beyond 900 nm (curves 2 and 3), which reveal the synthesis of anisotropic nanoparticle such as nanotriangle [17h, 31] as shown in the TEM image (Figure 3.7).

The mechanism for synthesis of gold nanotriangles could be possibly described using following models: (a) Slow rate of reduction of gold ions causes the formation of smaller spherical nanoparticles, which act as nuclei and grow to form flat nanotriangles due to aggregation and rearrangement of these smaller spherical nanoparticles [43]. (b) The initially formed spherical particles act as seed, around which nanotriangle growth occurs in the presence of the shape-directing agent. Such mechanism has also been reported by Mirkin’s group during the study of growth of silver nanoprisms by a photo-irradiation method [16c, d]. (c) Fast rate of reduction causes the formation of small-sized gold nanoparticles (nuclei) by consumption of most of gold ions in the solution and hence the small percentage of remaining gold ions further reduce on the surface of nuclei to form smaller gold nanotriangles during the growth process. Therefore, the formation of gold nanotriangles is a kinetically driven process and is facilitated by the oriented growth of smaller nuclei in the (111) plane to form the nanotriangles [44]. (d) The defect in seeds causes oriented growth of the nanoparticles, which leads to the formation of anisotropic nanoparticles [40a]. (e) The “surface wrapping mechanism” in which growth of nanoplates are fast at initial stage of reaction [45]. Once wrapping layer is formed, it promotes the growth of another layer and consequently corrugated edges are formed in nanotriangles. Chen’s group has also supported this mechanism for the synthesis of gold nanotriangles [36d].

The colour of the synthesized gold nanoparticle solution after 48 h of dialysis had a golden hue due to the partial reduction of external HAuCl₄ solution by outside diffused extract. It would be worthwhile to mention here that the synthesized gold nanoparticles
settled at the bottom of test tube in form of pellet after 10 h. The gold pellet can again be redispersed in water by ultrasonication. The difference in optical absorption properties of gold nanoparticle synthesized both inside and outside the different cut-off dialysis bags could be due to the variation in size, shape and yield of the gold nanoparticles.

3.3.1.3 TEM analysis:

3.3.1.3.a Inside of the dialysis bags:

TEM micrographs of the gold nanoparticles synthesized inside the different cut-off dialysis bags are shown in Figure 3.5. A large population of spherical nanoparticles along with small-sized gold nanotriangles (Figure 3.5A) are synthesized inside the 3 kDa dialysis bag, which is consistent with the UV-vis-NIR spectrum data (curve 1, Figure 3.4A). The histogram plot shows that the edge-to-edge length of triangular nanoparticles is 145 ± 8 nm (inset of Figure 3.5A). Figure 3.5B shows the high magnification TEM image of truncated gold nanotriangles and hexagonal nanoparticles synthesized inside the 3 kDa bag. It should be realized that biomolecules in the extract are much larger in size compared with Au^{3+} ions and thus the rate of diffusion will be higher for the ions towards inside the bag compared from biomolecules diffusion rate outwards (scheme 3.1). The concentrations of lemongrass extract inside the dialysis bags were in order of 3 kDa>12.5 kDa>30 kDa due to difference in the diffusion rate of biomolecules through pores of the dialysis bags and therefore reduction rate of diffused gold ions would also in the same order inside the dialysis bags. The higher concentration of lemongrass extract inside the 3 kDa bag causes fast reduction of diffused gold ions, which lead to the formation of a low yield of (28%) gold nanotriangles (Figure 3.6A). Figure 3.5C and D show the TEM images of a large population of gold nanotriangles and spherical nanoparticles synthesized inside the 12.5 kDa dialysis bag due to the slow rate of reduction of diffused Au^{3+} ions by remaining lemongrass extract present inside the bag. The edge-to-edge length of nanotriangles is 205 ± 20 nm (inset of Figure 3.5C), which is larger than nanotriangle formed inside the 3 kDa bag. The reduction rate of diffused Au^{3+} ions inside the 12.5 kDa dialysis bag was slow in comparison to the 3 kDa dialysis bag and hence formed a large population (54%) of the gold nanotriangles (Figure 3.6A), which is also strongly supported by TEM images (Figure 3.5C and D).
A drastic change is observed in the morphology of gold nanoparticles synthesized inside the 30 kDa dialysis bag. TEM images (Figure 3.5E and F) show a huge population of gold nanocubes along with smaller spherical gold nanoparticles, which are synthesized inside the 30 kDa bag. The rate of reduction of diffused Au^{3+} ions inside the 30 kDa bag...
was slow due to lower concentration of remaining extract present inside the bag. The composition of extract present inside the 30 kDa bag is also different from 3 and 12.5 kDa extract and thus it promotes the synthesis of gold nanocubes.

The inset of Figure 3.5F shows a high magnification TEM image of a gold nanocube, which reveals that edges of the gold cube are not very sharp and have less contrast compared with the central part. At close inspection of a high magnification TEM image of the gold nanocube, it can be seen that smaller spherical nanoparticles assemble to form gold nanocube at room temperature. The synthesis of gold nanocubes of various compositions using cumbersome methods has also been reported by many groups [10]. Thus, biomolecules of lemongrass extract, which have size bigger than 30 kDa, do not play any role in nanotriangle formation and form only gold nanocubes. Sastry and coworkers have demonstrated that one of column chromatography fraction of lemongrass extract (W1) is responsible for the synthesis of gold nanocubes [36b]. It should be noticed here that histogram plot (Figure 3.6A) does not show the population of nanotriangles for the 30 kDa bag because nanotriangles were not synthesized inside the bag and nanocubes were observed in the TEM analysis (Figure 3.5E and F).

3.3.1.3.b Outside of the dialysis bags:

The size and shape of gold nanoparticles synthesized outside the dialysis bags was analyzed by TEM measurements.
Figure 3.7: Representative TEM images of the gold nanoparticles synthesized outside of A, B) 3 kDa, C, D) 12.5 kDa and E, F) 30 kDa dialysis bags. Insets of Figure A, C and E show histogram analysis of edge-to-edge length of gold nanotriangles synthesized outside the different cut-off bags.

Triangular and hexagonal gold nanoparticles along with spherical nanoparticles are observed in the external solution of 3 kDa dialysis bag experiment (Figure 3.7A). The volume of lemongrass extract that diffuse towards outside bag through the pores of 3 kDa dialysis bag is too low in comparison to volume of external HAuCl₄ solution. Therefore the reduction rate of AuCl₄⁻ ion solution present outside the 3 kDa bag is very slow, which leads to the formation of large-sized nanotriangles. The obtained nanotriangles and
hexagons are thin and have edge-to-edge length of ca. 3.5 μm (inset of Figure 3.7A). A high magnification TEM image (Figure 3.7B) shows hexagonal gold particle of ca. 4 μm size, which is synthesized outside the 3 kDa dialysis bag. Furthermore, spherical nanoparticles below the thin hexagonal particle can also be seen in the TEM images (Figure 3.7A and B).

The TEM image of nanoparticles synthesized outside the 12.5 kDa dialysis bag shows large-sized gold nanotriangles with spherical nanoparticles (Figure 3.7C). The high magnification TEM image (Figure 3.7D) shows a broad bending contour across the entire truncated nanotriangle. A small concentration of biomolecules that have size below 12.5 kDa diffuse towards outside the bag through pores of the 12.5 kDa bag and reduce the external AuCl₄⁻ ion solution to form larger gold nanotriangles. The edge-to-edge length of triangular and truncated nanoparticles is 2.3 ± 1 μm (inset of Figure 3.7C). The high concentration of diffused lemongrass extract (size below 30 kDa) outside the 30 kDa bag promote the synthesis of smaller nanotriangles of size 250 ± 40 nm (Figure 3.7E and inset of Figure 3.7E) due to the fast reduction of AuCl₄⁻ ion solution. The TEM image (Figure 3.7F) shows plane-edged gold nanotriangles along with smaller spherical nanoparticles. The population of gold nanotriangles formed outside 12.5 kDa bag is larger (49%) in comparison to gold nanotriangles formed outside 3 kDa (22%) and 30 kDa (34%) dialysis bags due to the different rate of reduction of external AuCl₄⁻ ion solutions (Figure 3.6B) by diffused lemongrass extracts.

It may be postulated that lemongrass extract has reducing and capping biomolecules. The capping molecules also act like shape-controlling molecule to execute particular shape of the nanoparticles. The reducing molecules in the extract reduce gold ions, while shape-controlling molecules bind on the certain facets of initially formed gold nanoparticles. The growth of facets strongly bound with capping agent is hindered in particular directions whereas the facets weakly attached to the capping molecules grow faster and facilitate the formation of gold nanotriangles [17h, 46]. Therefore, the capping molecules below the 30 kDa size preferentially adsorb on the {111} facets of initially formed gold nanoparticles and suppress the growth in the <111> direction or advance the growth in the <110> direction to promote the synthesis of nanotriangle [40b, c]. It has been reported in literature that adsorption of chemical species on the surface has dramatic

effect on the surface energies. The \{111\} plane of gold nanoparticles possesses lowest
surface energy and adsorption of suitable species, such as CTAB (cetyl-
trimethylammonium bromide) \[16a, 47\], citrate \[14, 48\] and peptides \[49\] on this plane
further reduce its surface energy and stabilize nanoplates with the \{111\} plane as a basal
plane. From this result, it can be rationalized that biomolecules of lemongrass extract
below the 30 kDa size are responsible for the gold nanotriangle formation and act as
reducing and capping (shape controlling) agent.

3.3.1.4 FTIR measurement:

FTIR measurements were carried out to identify the biomolecules in lemongrass
extract bound on the surface of synthesized gold nanoparticles, which act as reducing
and/or capping agent.

![Figure 3.8](image)

*Figure 3.8:* Curves 1-3 in Panel A and B correspond to FTIR spectra of the gold nanoparticles
synthesized inside and outside 3, 12.5 and 30 kDa dialysis bags respectively.

Curves 1 and 2 of Figure 3.8A represent the FTIR spectra of gold nanoparticles
synthesized inside the 3 and 12.5 kDa dialysis bags respectively and show peaks at 1720
(C=O stretching), 1638 (stretching mode of C=C group), 1385 (O-H bending) and 1098
\(\text{cm}^{-1}\) (from straight chain primary alcohols), which possibly indicate the presence of
citral, sugar derivatives and other alcoholic compounds in lemongrass extract \[50\]. Curve
3 corresponds to gold nanoparticles synthesized inside 30 kDa dialysis bag (Figure 3.8A)
and shows that entire peak is similar to curves 1 and 2 except 1720 \(\text{cm}^{-1}\) peak, which is

*Ph.D. Thesis, 2007*  
*Akhilesh Rai*  
*University of Pune*
absent in the curve 3 indicating the absence of ketonic group on the surface of nanoparticles. The FTIR spectra of the gold nanoparticle synthesized outside the bags show peaks at 1385, 1645 cm⁻¹ (curves 1-3, Figure 3.8B) for 3, 12.5 and 30 kDa dialysis bags and a low intensity peak at 1730 cm⁻¹ for the nanoparticle synthesized outside the 30 kDa bag (curve 3, Figure 3.8B), which are similar to the FTIR spectra recorded for the nanoparticle synthesized inside the dialysis bags (Figure 3.8A). From the FTIR analysis, we could state that the sugar derivatives and citral molecules would be the main components of biomolecules, which act as reducing and capping agent for the nanotriangle formation.

3.3.1.5 XPS analysis:

A chemical analysis of the gold nanotriangles synthesized inside the 12.5 kDa dialysis bag was investigated by X-ray photoemission spectroscopy (XPS) measurement.

![XPS spectra](image)

**Figure 3.9:** XPS spectra of A) C 1s, B) Au 4f and C) Cl 2p core level recorded from the gold nanotriangles synthesized inside 12.5 kDa dialysis bag.

Figure 3.9A, B and C show C 1s, Au 4f and Cl 2p core level spectra respectively for lemongrass reduced gold nanotriangles. C 1s core level spectrum could be decomposed into three chemically distinct components at binding energies of 281.85, 285 and 287.9 eV (Figure 3.9A). The low binding energy peak at 281.85 eV is attributed to aromatic carbon of biomolecules bound on the surface of gold nanotriangles. Apart from the binding energy peak for adventitious carbon at 285 eV, a high binding energy peak at 287.9 eV is attributed to electron emission from the carbon of carbonyl groups (aldehydes
and ketonic carbons) due to induction effect [51]. Induction effects are well known for high binding energy shift of carbon attached to the electron withdrawing groups such as ketonic and carbonyl functional groups [52]. The Au 4f_{7/2} core level could be split into two chemically distinct components at 83.5 and 85.8 eV binding energies that correspond to Au(0) and Au(I) oxidation state respectively (Figure 3.9B). The presence of a small amount of Au(I) on the surface of gold nanoparticles is responsible for the high binding energy peak and is caused to stabilize nanoparticles electrostatically against aggregation in solution [53]. It is concluded from these results that the carbonyl compounds present in lemongrass extract interact with Au(I) ions present on the surface of nascent gold nanoparticles and promote the formation of triangular gold nanoparticles. Cl 2p core level could be decomposed into two components centered at 197.8 eV and 199.3 eV for Cl 2p_{3/2} and Cl 2p_{1/2} respectively (Figure 3.9C). The poor signal of Cl 2p core level observed in a spectrum suggests that a small amount of chloride ions complexed with Au(I) are present on the surface of gold nanotriangles.

### 3.3.1.6 Identification of charge on the synthesized gold nanoparticles:

The gel electrophoresis is a unique technique to know the charge on the surface of gold nanoparticles.

![Figure 3.10: Agarose gel electrophoresis image of the gold nanoparticles synthesized inside different dialysis bags. Gold nanoparticles synthesized inside 3, 12.5 and 30 kDa dialysis bags were loaded on A, B and C wells respectively.](image)

Gold nanoparticles synthesized inside the dialysis bags during dialysis of extract against HAuCl₄ solutions were loaded in the well of 1% agarose gel and were run at a 60 V across the gel for 1 h. The gold nanoparticles moved toward the positive electrode.
indicating that they have negative charge due to the presence of biomolecules on the surface of gold nanoparticles (Figure 3.10). The gold nanoparticles synthesized inside the 3 kDa bag are smaller and therefore all nanoparticles enter in the well A and form a continuous smear in the gel. In the case of well B and C, most of the nanoparticles are wedged in the well and some of the smaller nanoparticles enter and form a band in the gel towards the positive electrode.

3.3.2 Synthesis of the gold nanoparticles using dialyzed extract:

3.3.2.1 Experimental Details:

Lemongrass extracts kept in different cut-off dialysis bags (3, 12.5 and 30 kDa) were dialyzed against 250 mL Milli-Q water in three jars for 48 h. Scheme 3.2 shows the dialysis of lemongrass extract against water. After dialysis, the extracts obtained from both inside and outside the dialysis bags were collected. 250 mL of outside dialyzed extract from the bags were rotovapped (Buchi Rotavapor R-205) at 50 °C to obtain 25 mL of concentrated extract solutions.

1 mL of dialyzed lemongrass extract obtained from inside the dialysis bags was added separately to 10 mL of $10^{-3}$ M HAuCl$_4$ solutions as a reducing agent. 1 mL of the concentrated dialyzed extract of outside dialysis bags was also added to 10 mL of $10^{-3}$ M HAuCl$_4$ solutions (kept in three test tubes) to synthesize the gold nanoparticles. UV-vis-NIR spectra of all the solutions were recorded after allowing the reaction medium to stand for 48 h when the reduction of Au$^{3+}$ ions in all these reaction solutions had reached
saturation. TEM and FTIR measurements were also carried out to investigate the formation of gold nanotriangles.

Notation used in the following sections:

Dialyzed extract obtained from inside 3 kDa cut-off dialysis bags: 3 in-D extract.
Dialyzed extract obtained from outside 3 kDa cut-off dialysis bags: 3 out-D extract.
Similar notations have also been used for the dialyzed extract obtained from 12.5 and 30 kDa cut-off dialysis bags.

3.3.2.2 UV-vis-NIR spectroscopy and TEM analysis of nanoparticles synthesized using dialyzed extract from the inside bags:

It is also important to investigate the morphology and yield of gold nanoparticles synthesized using dialyzed extract obtained from the different dialysis bags.

![Graph](image)

Figure 3.11: Curves 1-3 correspond for UV-vis-NIR spectra of the gold nanoparticles synthesized using 3, 12.5 and 30 in-D extract respectively.

The gold nanoparticles synthesized using dialyzed extracts obtained from the different dialysis bags were monitored by UV-vis-NIR spectroscopy (Figure 3.11). UV-vis-NIR spectra of the synthesized gold nanoparticles were recorded after 48 h of reactions when the reduction of AuCl₄⁻ ion solution had reached saturation. Curve 1 in Figure 3.11 shows the UV-vis-NIR spectrum of gold nanoparticles synthesized by reduction of AuCl₄⁻ ion solution using 3 in-D extract. Curve 1 demonstrates a broad
asymmetric absorption spectrum with surface plasmon (SP) band centered at 584 nm.
However, the absorption spectra of gold nanoparticles synthesized using 12.5 in-D and 30
in-D extracts (curves 2 and 3 respectively, Figure 3.11) show two bands; one is transverse
surface plasmon band centered at ca. 584 nm and another is longitudinal surface plasmon
band, which appears to be red shifted beyond 1200 nm.

Figure 3.12: Representative TEM images of the gold nanoparticles synthesized using in-D
eextract obtained from 3 kDa (A, B) 12.5 kDa (C, D) and 30 kDa (E, F) dialysis bags. Insets of
Figure B and C show histogram analysis of edge-to-edge length of triangles synthesized using 3
and 12.5 in-D extract respectively. Inset of Figure F show a high magnification TEM image of
gold nanocubes.

Akhilesh Rai
University of Pune
A large red shift in longitudinal band indicates the synthesis of triangular nanoparticles with increased edge-to-edge length, which is also confirmed by the TEM analysis. TEM images of gold nanoparticles synthesized using 3 in-D extract show that a large population of spherical and aggregated nanoparticles along with gold nanotriangles of size $1.25 \pm 0.4 \mu m$ are formed (Figure 3.12A, B and inset of Figure 3.12B). TEM images (Figure 3.12C and D) also show that gold nanotriangles along with spherical nanoparticles are synthesized using 12.5 in-D extract. The edge length of gold nanotriangles is $2.4 \pm 0.4 \mu m$ (inset of Figure 3.11C) and spherical particles below the thin triangles can easily be distinguished in the TEM image. The population of gold nanotriangles synthesized using 12.5 in-D extract is larger (45%) in comparison to gold nanotriangles formed using 3 in-D extract (30%) as shown in the histogram plot (Figure 3.13A). The gold nanoparticles synthesized using 3 and 12.5 in-D extract also show mostly truncated triangles with a large number of hexagonal particles.

![Figure 3.13](image)

Figure 3.13: Histogram plot A and B show the population of gold nanotriangles synthesis using dialyzed extract obtained from inside and outside different cut-off dialysis bags respectively.

The concentrations of in-D extract obtained from the different dialysis bags were in order of 3 kDa>12.5 kDa>30 kDa bags and hence the reduction rate of AuCl$_4^-$ ion solution was fast for the 3 in-D extract in comparison to the other dialyzed extract. Therefore, the population and edge-to-edge length of gold nanotriangles synthesized using 3 in-D extract was less as compared to the 12.5 in-D extract (Figure 3.12 B and C). On the other hand, the gold nanoparticles synthesized using 30 in-D extract have unusual...
morphology and mostly gold nanocubes are observed in the TEM images (Figure 3.12E and F). It is observed that the gold nanocubes are made of assembly of smaller spherical gold nanoparticles, which has been described earlier. The inset of Figure 3.12F shows the high magnification TEM image of the gold nanocubes with no sharp edges and corners. These gold nanocubes are similar to the cubes that were obtained by the reduction of gold ions inside 30 kDa dialysis bag during dialysis of extract against HAuCl₄ solution (Figure 3.5E and F). It should be noticed here that the histogram plot does not show the population of gold nanotriangles in the case of nanoparticles synthesized using 30 in-D extract (Figure 3.13A).

3.3.2.3 UV-vis-NIR spectroscopy and TEM analysis of nanoparticles synthesized using dialyzed extract from outside bags:

Figure 3.14 shows UV-vis-NIR spectra of gold nanoparticles synthesized using concentrated out-D extract obtained from the different cut-off dialysis bags.

![Graph showing UV-vis-NIR spectra](image)

**Figure 3.14:** Curves 1-3 correspond for UV-vis-NIR spectra of the gold nanoparticles synthesized using 3, 12.5 and 30 out-D extract respectively.

The UV-vis-NIR spectrum of gold nanoparticles synthesized using concentrated 3 out-D extract shows a broad surface plasmon absorption band with a small hump at ca. 557 nm (curve 1, Figure 3.14). The absorption spectrum of the gold nanoparticles synthesized using concentrated 12.5 out-D extract (curve 2, Figure 3.14) shows the transverse surface plasmon band at 576 nm along with the longitudinal surface plasmon
band at ca. 1280 nm. The interesting change is observed in the optical property of gold nanoparticles synthesized using concentrated 30 out-D extract (curve 3, Figure 3.14).

Figure 3.15: Representative TEM images of the gold nanoparticles synthesized using out-D extract obtained from 3 kDa (A, B), 12.5 kDa (C, D) and 30 kDa (E, F) cut-off bags. Insets of Figure A and C show higher magnification TEM image while the insets of D and F show the histogram analysis of edge-to-edge length of gold nanotriangles synthesized using 12.5 and 30 out-D extract respectively.


Akhilesh Rai

University of Pune
The UV-vis-NIR spectrum (curve 3, Figure 3.14) shows a very broad absorption band with SPR peak centered at 610 nm, which appears to be red shifted by 40 nm relative to the transverse SPR band of gold nanoparticles synthesized using 3 and 12.5 out-D extracts (curves 1 and 2 respectively, Figure 3.14). The red shift is due to aggregation of nanoparticles in the solution that can be seen in the TEM images (Figure 3.15E and F). The TEM images (Figure 3.15A and B) show that flat anisotropic nanoparticles, deformed nanotriangles and aggregated spherical nanoparticles are synthesized using concentrated 3 out-D extract. The concentrations of out-D extract obtained from the different cut-off dialysis bags were in the reversed order (3 kDa<12.5 kDa<30 kDa) to the concentrations of in-D extracts. It is highly likely that low concentration of 3 out-D extract is insufficient to reduce all gold ions present in the solution and thus a small population of deformed and plate like nanostructures are formed. The inset of Figure 3.15A shows the rudimentary stage of gold nanotriangle, wherein smaller spherical nanoparticles are assembled in the form of nanotriangles. It is believed that these nanotriangles are formed due to assembly and sintering of smaller spherical nanoparticles [36b]. The fluidity of spherical nanoparticles required to assemble and form triangular or hexagonal nanoparticles could be provided by ketonic functional groups of biomolecules present in lemongrass extract [36b]. Klabunde’s group has also reported the assembly of monodisperse spherical nanoparticle into triangular and hexagonal superlattices in the solution [54]. Few reports are also available on oriented assembly of spherical nanoparticles into triangular nanoparticles [16a, 40c, 55].

TEM images (Figure 3.15C, D and inset of Figure 3.15D) show that spherical nanoparticles along with gold nanotriangles of size 600 ± 5 nm are synthesized using concentrated 12.5 out-D extract. The inset of Figure 3.15C shows the high magnification TEM image of gold nanotriangles with corrugated edges. The gold nanotriangles of small-sized (250 ± 30 nm) along with spherical nanoparticles are synthesized using concentrated 30 out-D extract (Figure 3.15E and F and inset of Figure 3.15F). The high concentration of 30 out-D extract in comparison to the other dialyzed extract caused rapid reduction of the gold ions to synthesize small-sized gold nanoparticles, when compared to the 3 and 12 out-D extract experiments (Figure 3.15 A-D). This result is similar to the TEM image of gold nanotriangles formed outside the 30 kDa dialysis bag during dialysis.
of lemongrass extract against 10^{-3} M \text{HAuCl}_4\text{ solution (Figure 3.7E and F). Therefore, the initially formed gold nanoparticles (nuclei) during synthesis and biomolecules of extract below 30 kDa play a major role in the formation of gold nanotriangles. The histogram plot shows that the population of gold nanotriangles synthesized using concentrated 12.5 out-D extract is 45\% while those synthesized using concentrated 3 and 30 out-D extract are 30\% and 42\% respectively (Figure 3.13B) due to the different rate of reduction of AuCl\textsubscript{4}^{-} ion solution.

3.3.2.4 FTIR analysis:

Figure 3.16 shows the FTIR spectra of gold nanoparticles synthesized using dialyzed lemongrass extract obtained from different dialysis bags.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3_16.png}
\caption{Curves 1-3 in Panel A and B correspond for FTIR spectra of the gold nanoparticles synthesized using 3, 12.5 and 30 in-D and out-D extract respectively.}
\end{figure}

FTIR spectra of gold nanoparticles synthesized using in-D extract obtained from the different dialysis bags show peaks at 1638, 1380 cm\textsuperscript{-1} (curves 1-3, Figure 3.16A) and peaks at 1119 and 1090 cm\textsuperscript{-1} appeared only for the gold nanoparticles synthesized using 3 in-D extract (curve 1, Figure 3.16A). The gold nanoparticles synthesized using out-D extract from the different dialysis bags show the FTIR peaks (curves 1-3, Figure 3.16B) at the same positions as was seen for the nanoparticles formed by the in-D extract. Furthermore, the FTIR spectrum (curve 1, Figure 3.16A) of gold nanoparticles synthesized using 3 in-D extract is similar to the FTIR spectrum of gold nanoparticles.
synthesized using 30 out-D extract (curve 3, Figure 3.16B), which indicates that the compositions of dialyzed extracts are almost same in both cases. The peaks from different spectra are assigned to the functional groups from citral, citronellal and other alcoholic compounds present in lemongrass extract which might act as reducing and shape directing agent for the gold nanotriangle formation.

3.4 Conclusion:

In conclusion, a green chemical approach for the synthesis of triangular and hexagonal gold nanoparticles using natural reducing and shape directing agents has been described. The yield and thickness of the gold nanotriangles are 45% and 18 nm respectively, which are better than other chemical and physical methods reported for the synthesis of triangular gold nanoparticles. Dialysis is used for the size selective separation of biomolecules of lemongrass extract through different cut-off (3, 12.5 and 30 kDa) bags. Biomolecules that have size below the pore size of dialysis bags diffuse from bags and reduce gold ions present outside the dialysis bags to form nanoparticles. Biomolecules of lemongrass extract, which have size below 30 kDa, act as reducing and capping agent to promote the synthesis of gold nanotriangles. Biomolecules selectively bind to the (111) lattice plane of initially formed smaller gold nanoparticles (nuclei) and inhibit the growth in the <111> direction and therefore advance the growth in the <110> direction to form gold nanotriangles [40b, c]. The variation in size and yield of gold nanoparticles and consequently change in the optical properties are observed for gold nanoparticles synthesized inside and outside different cut-off dialysis bags. Biomolecules of the extract larger than 30 kDa size are found to form a large percentage of the gold nanocubes at room temperature.
3.5 References:


Akhilesh Rai

University of Pune
Chapter 3


Chapter 3


