4.1. Abstract

Adopting a photochemical method, gold nanorods of different aspect ratios were synthesized. Gold nanorods possess two plasmon absorption bands; a short wavelength band at around 520 nm corresponding to the transverse mode of plasmon oscillation and a long wavelength band corresponding to the longitudinal mode of plasmon oscillation. Interactions of bifunctional molecules such as cysteine and (3-mercaptopropyl)trimethoxysilane with Au nanorods were investigated using absorption studies and transmission electron microscopy. Addition of varying amounts of these bifunctional molecules led to a decrease in the intensity of the long wavelength band, accompanied by the formation of a new absorption band in the NIR region. The spectral interconversions observed through a clear isosbestic point indicate the existence of two different forms of nanorods in suspension. The thiol groups of these bifunctional molecules preferentially bind to the \{111\} plane at the edges than \{110\} face in the lateral regions of rods, exposing the counterpart for further interactions. In the case of cysteine the appended zwitteronic groups at the ends of Au nanorods assist the dimerization through two point electrostatic interaction. In the presence of excess cysteine, a
gradual shift in the absorption band to the NIR region was observed and TEM images indicate that these dimerized nanorods assemble preferentially in an end to end fashion, through stepwise self-assembly, to yield wire type higher order nanostructures. Similar spectral features were observed in the case of (3-mercaptopropyl)trimethoxysilane and these aspects are discussed in detail.

4.2. Introduction

The shape and size of low-dimensional structures play a decisive role in controlling their optical, electrical and magnetic properties. The fabrication of such nanostructures with well-defined shape and size has received considerable interest due to their potential application as optical filters, plasmonic waveguides, biological and chemosensors. Among the various nanostructures, gold nanorods received much attention due to the ease in tuning their optical properties by varying their aspect ratios.

4.2.1. Optical properties of metal nanorods

In metallic nanoparticles, interesting optical and electronic properties are observed in ~10-100 nm scale because the mean free path of an electron in a metal is ~10-100 nm. To investigate the size dependent optical properties on this scale, metal nanorods with different aspect ratios (defined by the ratio of the length of the major axis and minor axis) have been examined by various research groups. It is reported that the Au nanorods possess two plasmon resonance bands; a short wavelength band at around 520 nm corresponding to the transverse mode of plasmon oscillation and a long wavelength band corresponding to the longitudinal
mode of plasmon oscillation (Figure 4.1).\textsuperscript{9-12} The absorption maximum of the transverse surface plasmon absorption band coincides with the plasmon absorption of the nanospheres (Figure 4.2) while the position of longitudinal surface plasmon maximum gradually shifts to longer wavelengths with increasing aspect ratio. Martin and coworkers examined the effect of aspect ratios on their absorption spectra by investigating the optical properties of nanoscopic gold particles, which

**Figure 4.1.** Transverse and longitudinal modes of vibration in Au nanorods.

**Figure 4.2.** A typical absorption spectrum of gold nanorod having an aspect ratio 3.8 (adapted from reference 8).
are prepared electrochemically by depositing Au within the pores of nanoporous alumina membranes. The aspect ratios were controlled by varying the amount of gold in the alumina membrane. They observed that for small pores, as the aspect ratio increases, the extinction intensity increases and shifts to shorter wavelengths whereas for larger pore systems, the $\lambda_{\text{max}}$ values shift to the red region.

Later, El-Sayed and co-workers have prepared gold nanorods with different aspect ratio and have carried out their detailed absorption spectral studies. They observed a linear correlation between the longitudinal surface plasmon absorption maximum and the mean aspect ratio. Further, they have supported this linear relationship theoretically using an extension of Mie theory. A plot of theoretically calculated absorption maxima against the mean aspect ratio at a fixed medium dielectric constant is shown in Figure 4.3. The intensity as well as position of the longitudinal band increases with increase in aspect ratio. They also observed a linear relationship between the absorption maximum of the nanorod and the dielectric constant of the medium for a fixed aspect ratio.

Later van der Zande et al. experimentally proved the existence of two bands by carrying out the polarization studies in presence of an applied electric field. In the absence of an electric field the gold rods are randomly oriented and the absorption spectra display two maxima: the transverse and the longitudinal modes. In the presence of an electric field, the relative magnitudes of the bands varied due to the change in the induced orientational order in the dispersed rod (Figure 4.4). When the incident light is polarized parallel to the applied electric
Figure 4.3. Plot showing the linear relation between the absorption maximum and the mean aspect ratios (adapted from reference 8).

Figure 4.4. Schematic representation of the absorbance of light by colloidal dispersions of rod-shaped gold particles (a) in the absence of electric field and when the polarized light is (b) parallel and (c) perpendicular to the electric field (adapted from reference 11).
field, transverse resonance band disappeared completely. Similarly, for perpendicularly polarized light, the transverse resonance survives at the expense of the longitudinal resonance.

The effect of temperature on the absorption of gold nanorods was studied by El-Syed and co-workers. The size and shape analysis of the TEM images of nanorods at different temperatures showed that the mean aspect ratio in solution decreases with increasing temperature, mostly as a result of reduction in their length. In contrast, heating the dried nanorods to higher temperature does not produce any significant size change. These results suggest that the observed relative instability of the nanorods in the micellar solutions is due to the instability of the micelles capping the longer gold nanorods.

4.2.2. Self-assembly of nanoparticles

Assembly of nanoscale building blocks (nanoparticles, nanorods, nanotubes etc) allow their hierarchical integration into functional assemblies and further into multifunctional through a “bottom up approach.” Such self-assembled structures may possess interesting new collective physical properties that are different from those of the bulk materials and isolated nanomaterials. Current methods for assembling gold nanoparticles as superstructures involve capillary forces, molecular and biomolecular cross-linking, and template-directed patterning. In general, these approaches produce aggregates that are either supported on substrates or phase-separated from solution in the form of colloidal crystals or precipitates.
Wang and Murray have reported the linear assembly of cationic gold nanoparticles along the DNA molecule.\textsuperscript{17} The electrostatic interaction between the phosphate backbone of the DNA and the positively charged gold nanoparticles leads to the organization of the nanoparticles on the DNA surface.

![Figure 4.5. TEM image showing the linear array of gold nanoparticles on DNA backbone (adapted from reference 17).](image)

Recently, a newer class of sensors has been reported using silver or gold nanoparticles, in which aggregation-induced electromagnetic interactions between the particles result in a color change which signals the detection. This principle has been applied to analyze various substrates such as DNA,\textsuperscript{18} lectin,\textsuperscript{19} heavy metal ions\textsuperscript{20} and proteins.\textsuperscript{21} All these methods are based on the cross-linking mechanism by the target molecule between the nanoparticles. Mirkin and coworkers\textsuperscript{18} reported a DNA analysis method by modifying two sets of gold nanoparticles with different single stranded DNA probes and by mixing with a target DNA. If the target DNA has sequences complementary to both the probes, the target cross-links the nanoparticles by hybridization of DNA, and this results in particle aggregation.
The aggregation of the nanoparticles has been exploited for sensing spectrochemically silent metal ions by functionalizing them with appropriate metal ion receptors. For example, the detection of lead ions by functionalizing the nanoparticles with mercaptopropionic acid has been reported by Kim et al.\textsuperscript{20}. The affinity of the carboxylic acid group for the divalent metal ions leads to the aggregation of the metal nanoparticles (Scheme 4.1).

Studies of the DNA functionalized metal nanoparticles have revealed that the weak London-van der Waal force of interaction also results in the aggregation of metal nanoparticles.\textsuperscript{22} The aggregation of the gold nanoparticles functionalized with single stranded DNA by sodium chloride has been studied by Sato et al.\textsuperscript{22} Compared to the bare nanoparticles, the DNA functionalized nanoparticles do not show any visible change even up to the addition of 2.5 M of NaCl. This unusual stability is attributed to the repulsive interaction between the DNA strands. In presence of a complementary DNA strand, the repulsive interactions are substantially reduced by means of duplex formation, resulting in rapid aggregation (Scheme 4.2). It was observed that even the presence of a single base mismatch at the end of the DNA strands could prevent the aggregation.
Eventhough extensive studies have been carried to organize the spherical nanoparticles, most of them lead to the formation of random aggregates. Much fewer studies have been carried out for assembling metal nanorods. El-Syed and co-workers have reported that the nanorods coated with two different types of cationic surfactants self assemble to 1D, 2D and 3D structures leading to the formation of superlattices of gold nanorods. Recently, Caswell et al. have reported an end to end assembly of Au nanorods driven by biotin-streptavidin connectors. Tailoring the optoelectronic properties of nanomaterials through the stepwise integration of nanoscale building blocks is one of the major challenges in the area of nanotechnology. No attempts were made to investigate the optical properties of assembled nanorods possessing desired shapes. Also, such closely packed metal nanoparticles and nanorods can, in principle, function as guides of electromagnetic radiation (waveguides) allowing miniaturization of devices below the diffraction limit.
In the present study, gold nanorods of various aspect ratios were synthesized photochemically and their optical properties have been investigated in detail. Interaction of bifunctional molecules such as cysteine and (3-mercaptopropyl)trimethoxysilane with Au nanorods were investigated using absorption and TEM studies. The effect of ionic strengths on the optical properties of Au nanorods was also investigated.

4.3. Results and Discussion

4.3.1. Synthesis and characterization of gold nanorods

We have adopted the photochemical reduction method for the preparation of gold nanorods, adopting a slight modification of the method reported by Jana. A mixture of surfactant and cosurfactant was prepared by dissolving an aqueous solution of CTAB (80 mmol; 15 mL of 0.08 mM CTAB stock solution was used) and 4.5 mg TOAB (0.55 mM). To the above solution, 1.25 mL of 0.024 M HAuCl₄ solution (2 mmol) was added along with 325 μL of acetone and 225 μL of cyclohexane. The role of cyclohexane is to elongate the micellar structure to form a rod like template. A small quantity of acetone is necessary to facilitate the incorporation of the cosurfactant to the micellar network. To this solution, varying concentrations of AgNO₃ solution were added and then irradiated using a 300 nm UV light in a Rayonet Photochemical Reactor for 18 h. It is reported that the presence of AgNO₃ is essential for producing and controlling the aspect ratio of spheroids/rods. In the absence of AgNO₃, spheres are preferentially formed.
Nanorods of different aspect ratios were obtained by varying the concentration of AgNO₃.

The rods formed by photochemical method were further purified by the centrifugation method, recently reported by Jana. The purification process was monitored by recording the absorption spectra at various stages and the normalized absorption spectra (normalized at 515 nm) are presented in Figure 4.6A. The suspension after irradiation contains large percentage of nanospheres (trace a, Figure 4.6A) which were purified by centrifugation. After centrifuging at 7000 rpm for 10 minutes, the residue obtained was redispersed in 0.7 M CTAB solution (4 mL). The suspension was kept for 12 hours and was decanted carefully. The residue obtained after the decantation was resuspended in water for further studies. The absorption spectrum of purified nanorods is presented in trace c of Figure 4.6A. The supernatant liquid obtained (trace b) contains mainly nanospheres.

An alternative purification method was also standardized by first centrifuging the irradiated solution at 3000 rpm for 10 minutes. Afterwards the supernatant material was collected which was again centrifuged at 3000 rpm and the residue was removed. The supernatant material was further centrifuged at 10,000 rpm for 10 min. The residue was redispersed in doubly distilled water and centrifuged at 10,000 rpm (twice) to give gold nanorods as residue. Absorption spectral features of gold rods purified by both the routes possess similar spectral properties.
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Figure 4.6A. Absorption spectrum recorded at different stages of purification: (a) recorded immediately after irradiation (b) spectrum of supernatant liquid after purification (mainly nanospheres) and (c) spectrum of purified gold nanorods.

In the present study, gold nanorods of various aspect ratios were synthesized adopting the photochemical method by varying the concentration of AgNO$_3$ solution. The integrity of the rods was checked using TEM studies. A representative TEM image obtained by drop casting Au nanorods onto a carbon coated copper grid from a concentrated stock solution is presented in Figure 4.6B. The shape as well as the dimension of gold rods are uniform and the average aspect ratio is estimated as 3.1 ([AgNO$_3$] = 0.01 M, 300 µL). One can observe square like structures in between the rods and these are images of rods, which were dropped perpendicular on the grid. The heavy capping of surfactant molecules keep the nanorods well separated and spacing between the nanorods are
more or less uniform. It may be noted that the rods are oriented in a random fashion and similar results are reported earlier by El Sayed and coworkers.  

![Figure 4.6B](image)

**Figure 4.6B.** TEM image of gold nanorods (aspect ratio 3.1) drop casted from a concentrated stock solution.

The absorption spectra of gold nanorods prepared at different aspect ratios are presented in Figure 4.7. The VIS-NIR absorption spectrum of nanorods possesses two bands. Of these one centered on 516 nm represents the transverse mode of absorption. The longitudinal plasmon band of Au nanorods shifts to NIR region with increase in the aspect ratio. We have used nanorods of aspect ratio 3.1 for various studies mentioned in the subsequent sections (Figure 4.6C and trace ‘c’ in Figure 4.7) and the rods were suspended in a mixture of CH$_3$CN-H$_2$O (4:1). The spectral properties of Au nanorods remain more or less unaffected on increasing
the composition of acetonitrile and the rods were found to be stable for several hours. The integrity of the rods, on dilution, was confirmed through TEM studies.

We have observed that the concentration of surfactant loaded on the surface of rods has a slight influence on their absorption maximum; rods loaded with less surfactant is shifted to the blue region in water.

Figure 4.6C. TEM image of gold nanorod with aspect ratio 3.1

Figure 4.7. Absorption spectra of gold nanorods prepared by adding (a) 200, (b) 250, (c) 300, (d) 375 and (e) 450 μL of 0.01 M AgNO₃ solution.
4.3.2. Effect of Cysteine

Nature adopts cooperative hydrogen bonding for assembling simple molecular units to supramolecular assemblies, which perform many complex biological functions. In the present study, we have utilized different intermolecular interactions for assembling Au nanorods using various bifunctional molecules such as cysteine and (3-mercaptopropyl)trimethoxysilane (Chart 4.1). The selection of these molecules is based on the rationale that the thiol group can bind on to the surface of Au nanorods and the appended functional groups assist in the self-assembly/functionalization of nanorods.

![Diagram of Cysteine and Mercaptopropyltrimethoxysilane](chart4_1.png)

Chart 4.1. Bifunctional molecules used in the present study.

We have studied the effect of cysteine on the absorption spectrum of the gold nanorod by systematically varying the concentration in a mixture of acetonitrile/water (4:1). After the addition of cysteine, solutions were kept for two
minutes for stabilization and spectral changes were recorded. The intensity of the longitudinal surface plasmon absorption band centered at 625 nm decreased with a concomitant formation of a new band at 800 nm (Figure 4.8). The clear isosbestic point centered at 690 nm suggests the existence of two types of gold nanorods in the solution. Interestingly, the intensity of the transverse band is more or less unaffected in this concentration range.

To have a clear picture on the interaction of these bifunctional molecules with Au nanorods, we have investigated the absorption spectral changes as a

![Figure 4.8. Absorption spectral changes of gold nanorods in acetonitrile/water (4:1) on addition of different concentrations of cysteine. [cysteine]: (a) 0, (b) 0.46, (c) 0.92, (d) 1.38, (e) 1.84 (f) 2.3 and (g) 2.76 μM. Inset shows the spectral changes at higher concentrations.](image-url)
function of time. Time dependent absorption spectral changes of gold nanorods in presence of cysteine (1.38 μM) in acetonitrile/water (4:1) mixture are presented in Figure 4.9. On addition of a high concentration of cysteine, first we observed the formation of a new red shifted absorption band at 800 nm with a concomitant decrease of the 625 nm band. A clear isosbestic point was observed at 720 nm (Figure 4.9) and no further changes were observed after 10 minutes. The time dependent spectral interconversions are similar to the spectral changes observed in the concentration dependent studies. It may be noted that the suspension precipitates on keeping for longer periods.

Figure 4.9. Absorption spectra of the nanorods in the presence of 1.38 μM cysteine in acetonitrile/water (4:1) mixture at different time intervals; (a) 0, (b) 60, (c) 120, (d) 180, (e) 240, (f) 300, (g) 360, (h) 420, (i) 480, (j) 540 and (k) 600 seconds.
One of the possibilities for the appearance of the new red shifted band in presence of cysteine is due to aggregation of gold nanorods. In the case of gold nanorods there are two modes of plasmon oscillation; each of these mode can, in principle, couple with plasmon bands of the neighboring rods. Interestingly, in the present study, we observe a selective coupling of longitudinal plasmon band whereas the transverse plasmon band remains more or less unaffected. These results suggest that the presence of cysteine lead to the coupling of the longitudinal plasmon band, resulting from an end to end assembly of gold nanorods.

For further establishing the end to end assembly, we have characterized the morphology of the gold nanorods in presence of cysteine by using Transmission Electron Microscopy (TEM). The TEM images of the gold nanorods in the absence and presence of cysteine under identical conditions are presented in Figures 4.10. TEM samples were prepared by drop casting the same solution used for spectroscopic investigation on to a carbon coated copper grid. The rods before the addition of cysteine are randomly distributed (Figure 4.10A), whereas cysteine bound Au rods are preferentially self-assembled in an end to end fashion (Figure 4.10B). Isolated arrays of end to end gold nanorod assemblies are seen in the grid and the enlarged TEM images from different regions of a grid are presented in Figure 4.11.

High-resolution crystallographic studies by El-Sayed and co-workers\textsuperscript{25} have shown that gold nanorods have stable \{110\} face, with high surface energy along
the length of the rods and \{111\} face at the ends. It has been suggested that during the synthesis of gold nanorods, CTAB preferentially bind to the \{110\} face compared to the end face due to their bigger size. Alignment of rods in an end to end fashion was recently observed by Caswell et al. and coworkers in biotin.

![Figure 4.10](image1)

**Figure 4.10.** TEM images of Au nanorods in the (A) absence and (B) presence of cysteine under identical conditions (samples were prepared by drop casting the same solution used for spectroscopic investigation onto a carbon coated copper grid).

![Figure 4.11](image2)

**Figure 4.11.** Enlarged TEM images of Au nanorods in presence of cysteine under identical conditions (samples were prepared by drop casting the same solution used for spectroscopic investigation onto a carbon coated copper grid).
capped Au nanorod-streptavidin system. As indicated by them, thiol group preferentially bind to the \{111\} plane at edges than \{110\} face in the lateral regions of rods. Moreover, the latter sides of the nanorods are protected by the bilayer of CTAB which make them less susceptible for displacement. The proposed mechanism of end to end assembly of Au nanorod is presented in Scheme 4.3. In the first step the thiol group of cysteine attaches to the ends of the Au nanorods, leaving the zwitterionic groups for further interaction. It may be noted that the rods are of high monodispersity (Figure 4.6B) and hence cysteine molecules may be evenly distributed at the edges of the rod. In the second step, the appended zwitterionic groups at the ends of Au nanorods assist the dimerization through two point electrostatic interaction. The spectral changes in Figures 4.8 and 4.9 featuring a clear isosbestic points indicate the existence of two different forms of Au nanorods. The origin of the new red shifted band is due to the dimer formation and can be explained by means of a dipolar interaction mechanism. The perturbed charge distribution on dimerized Au nanorods in the presence of external electromagnetic radiation results in an additional attractive force between the polarized negative and positive charges on adjacent rods. This additional attractive interaction, in turn, decreases the frequency of longitudinal plasmon oscillation. Such interparticle plasmon interactions were observed in closely spaced Au nanoparticles deposited on ITO glass plates and quartz. In the presence of excess cysteine we observed a gradual shift in the absorption band to the NIR region, indicating the stepwise assembly of dimerized nanorods to form oligomers,
as indicated in Step 3 (Scheme 4.3). Deviation from the isosbestic point, on addition of high concentration of cysteine supports the formation of oligomers (inset in Figure 4.8). It may be noted that the longitudinal plasmon absorption of Au nanorods of high aspect ratios are observed in the NIR region.²⁴

Step 1: Cysteine functionalization of gold nanorod at edges

\[
\text{Au} + n \left( \text{HSCH}_2\text{CHNH}_3^+ \right) \rightarrow \left( \text{H}_3\text{N}^+ \right) \left( \text{CHCH}_2\text{S}^- \right)_{n/2} \left( \text{SCH}_2\text{CHNH}_3^+ \right)_{n/2}
\]

Step 2: Uniaxial dimerization of gold nanorod through two point electrostatic interaction

\[
2 \left[ \left( \text{H}_3\text{N}^+ \right) \left( \text{CHCH}_2\text{S}^- \right)_{n/2} \right] \rightarrow \left( \text{SCH}_2\text{CHNH}_3^+ \right)_{n/2}
\]

An idealized representation of gold nanorod dimer
Step 3: Oligomerization of gold nanorod through end to end self-assembly

Scheme 4.3. Proposed mechanism of end to end assembly of Au nanorods.

Thus the two point electrostatic interaction of the cysteine capped Au nanorods assist the end to end organization of Au nanorods. These results provide a novel strategy for organizing nanorods to a wire type structure, which can be further exploited for designing higher order nanomaterials through stepwise integration of nanoscale building blocks.

We have investigated the effect of different amino acids such as tyrosine, tryptophan, glycine and proline on the absorption spectrum of gold nanorods by systematically varying their concentration in a mixture of acetonitrile/water (4:1). No noticeable spectral changes were observed under these conditions. These results indicate that the thiol functionality is essential for the end to end assembly of gold nanorods and this opens newer opportunities for the development of specific sensors for cysteine. As mentioned in the earlier section, cysteine molecules may be evenly distributed at the edges of the rod due to the high monodispersity (Figure 4.6B) and hence the Au dimer formed is proportional to the concentration of added cysteine. Changes in the absorbance at 1000 nm, which
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represent exclusively the formation of Au rod assembly, were plotted against concentration of cysteine (monomer form of Au nanorod does not possess any absorption at 1000 nm). In order to reduce the spectral contribution of Au nanorod oligomers, measurements were taken two minutes after the addition of cysteine. A linear plot was obtained and these preliminary results indicate that it is possible to use Au nanorods for the selective detection and quantification of cysteine. It may be interesting to note that at very low concentrations (circled points in Figure 4.12), a deviation from linearity is observed, indicating that a threshold concentration of cysteine is required for Au dimer formation.

![Graph showing absorbance at 1000 nm vs cysteine concentration]

**Figure 4.13.** Plot showing the linear relationship between the absorbance at 1000 nm and cysteine concentration.

4.3.3. Effect of (3-mercaptopropyl)trimethoxysilane (MPS)

With a view to organizing gold nanorods through covalent bonds, we have studied its interaction with another bifunctional molecule namely (3-
mercaptopropyl)trimethoxysilane (MPS). The effect of addition of MPS was investigated by monitoring the absorption spectrum in a mixture of acetonitrile/water (4:1). Spectral changes upon successive addition of micromolar quantities of MPS are shown in Figure 4.13. After each addition, solutions were kept for two minutes for stabilization. The spectral changes observed in the present case is very similar to those observed on addition of cysteine to Au nanorods. A decrease in the intensity of the longitudinal surface plasmon absorption band ($\lambda_{\text{max}}$ 617 nm) was observed with a concomitant formation of a new band at 915 nm (Figure 4.13). The clear isosbestic point observed at 785 nm, suggests the existence of two types of gold nanorods in the suspension. The intensity of the transverse band is more or less unaffected, as in the case of cysteine, in this concentration range suggesting a preferential end to end assembly of Au nanorods. Time dependent studies were carried out using a fixed concentration of MPS (Figure 4.14) and the formation of a new red-shifted absorption band with a clear isosbestic point at 785 nm was observed. The newly formed absorption band shifts to near-infrared region with time, and a slight deviation from isosbestic point is observed. The time dependent bathochromic shift in the absorption is more pronounced at higher concentrations of MPS. Further we have characterized the MPS capped Au nanorods using TEM studies (Figure 4.15), by drop casting the same solution used for spectroscopic investigation onto a carbon coated copper grid. At lower concentrations (micromolar range) we observed both isolated rods and linked rods on the grid
whereas at higher concentrations (millimolar range) most of the rods are linked together, giving rise to a three dimensional nanostructure (Figure 4.10B). Enlarged TEM images of Au nanorods on addition of micromolar concentrations of MPS is shown in Figure 4.16. Unlike cysteine capped Au nanorod a preferential end to end geometry is not observed in the TEM image, whereas the spectral interconversions indicate the formation of end to end dimer formation. The MPC capped Au nanorods dimerize through Si-O-Si covalent bond formation (Scheme 4.4) and the spectral interconversions observed in Figures 4.13 and 4.14 support this argument. The gradual shift of the long wavelength band to near-infrared region with time/concentrations and deviation from the isosbestic point indicates that the dimerized nanorods further

![Graph showing absorption spectral changes](image)

**Figure 4.13.** Absorption spectral changes of gold nanorods in acetonitrile/water (4:1) on addition of different concentrations of MPS. [MPS]: (a) 0, (b) 0.46, (c) 0.92, (d) 1.38, (e) 1.84 (f) 2.3 and (g) 2.76 µM.
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Figure 4.14. Absorption spectrum of the nanorods in presence of 1.38 \( \mu \text{M} \) MPS in acetonitrile/water (4:1) mixture at different time intervals; (a) 0, (b) 60, (c) 120, (e) 180, (d) 240, (e) 300, (f) 360, (g) 420 and (h) 480 sec.

Figure 4.15. TEM images of Au nanorods in the presence of (A) micromolar and (B) millimolar quantities of MPS (samples were prepared by drop casting the same solution used for spectroscopic investigation onto a carbon coated copper grid).
assemble through stepwise $-\text{Si-O-Si-}$ bond formation to form oligomers. As illustrated in Scheme 4.4 (Step 3) the oligomer formation may lead to the formation of three dimensional network of nanorods. Also, such nanostructures may get entangled and the collapse on the surface of the grid.

**Step 1: Functionalization gold nanorod by MPS**

$$\text{gold nanorod} + n \left( \text{MPS} \right) \rightarrow \left( \text{MPS} \right)_{n/2}$$

**Step 1: Dimerization of gold nanorod through siloxane bond**

$$2 \left( \text{MPS} \right)_{n/2} \rightarrow \text{MPS}$$
Step 3: An idealized representation of Au nanorod linked through siloxanes (based on absorption spectrum and TEM images)

Scheme 4.3. Proposed mechanism for the assembly of Au nanorods in the presence of MPS.

4.3.4. Effect of dodecanethiol

We have investigated the effect of of an alkyl thiol, such as dodecanethiol, which does not possess functional group which assist the self assembly or functionalization of Au nanorods (Figure 4.17). No spectral interconversions were

![Absorption spectral changes of Au nanorods in acetonitrile/water (4:1) mixture on addition of dodecanethiol in a wide range of concentrations: [dodecanethiol] (a) 0, (b) 1 μM, (c) 1 mM and (d) 550 mM.](image)
observed, ruling out the possibility of self assembly of Au nanorods. At higher concentrations both the plasmon bands got dampened, possibly due to aggregation and precipitation.

4.3.5. Effect of ionic strength of the medium

Addition of various substrates can influence the ionic strength of the medium. The effect of the ionic strength on the optical properties of Au nanorods was investigated by adding different concentrations of hydrochloric acid and sodium chloride. It was observed that, the absorption spectra of Au nanorods in water remain unaffected on adding millimolar concentrations of hydrochloric acid (Figure 4.18). In a mixture of acetonitrile/water (4:1) no spectral changes were

![Figure 4.18. Absorption spectral changed of gold nanorod in water with different concentrations of HCl. [HCl]: (a) 0.6, (b) 1.2, (c) 1.8, (d) 2.4, (e) 3.0 and (f) 3.6 mM.](image)
millimolar range showed a simultaneous decrease of both the transverse and longitudinal plasmon bands along with the formation of a new band at 730 nm (Figure 4.19).

Both the plasmon absorption bands of Au nanorods are more or less unaffected on addition of salts such as NaCl and NaBr in micromolar concentration ranges. On the other hand, a simultaneous decrease of both transverse and longitudinal plasmon bands along with the formation of a new band at 730 nm was observed (Figure 4.20) on addition of millimolar concentrations of salts.

![Absorption spectral changes of gold nanorod in 80 % acetonitrile/water mixture with different concentrations of HCl.](image)

**Figure 4.19.** Absorption spectral changes of gold nanorod in 80 % acetonitrile/water mixture with different concentrations of HCl. [HCl]: (a) 0, (b) 0.6 and (c) 1.2 mM and the TEM image of the solution dropcasted on to a carbon coated copper grid.
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The formation of a band in the red region could be either due to the formation of aggregates or fusion of the nanorods. To gain a clear picture on the mode of interaction, we have recorded the TEM images of the nanorod in presence these additives and images are presented in Figures 4.19 and 4.20. The TEM images indicate that the rods are aggregated in a random fashion which results in the simultaneous decrease of both transverse and longitudinal plasmon bands.

![Figure 4.20. Absorption spectral changes of gold nanorods in 80 % acetonitrile/water mixture on adding different concentrations of NaCl. [NaCl]: (a) 0.7, (b) 1.4, (c) 2.1, (d) 2.8, (e) 3.5, (f) 4.2 and (g) 4.9 mM and the TEM image of the solution dropcasted on to a carbon coated copper grid.](image)

4.4. Conclusions

We have photochemically prepared Au nanorods of different aspect ratios. Attempts were made to intergrate the Au nanorods to higher order nanomaterials by using bifunctional molecules such as cysteine and (3-mercaptopropyl)trimethoxysilane. In the presence of these bifunctional molecules,
dimers of the gold nanorods are formed initially through the two point electrostatic interactions, which further assemble preferentially in an end to end fashion to yield wire type nanostructures. The ends to end assemblies of the nanorods were characterized by TEM analysis. Similar results were obtained with MPS wherein a more entangled network of gold nanorods was observed. The origin of the new red shifted band in dimers/oligomers was explained through selective longitudinal interplasmon coupling mechanism. Approaches presented herein for connecting nanomaterials into desired shapes and thereby tuning their optoelectronic properties may have wide-range application in nanotechnology, particularly in nanoelectronics and plasmonics.
4.5. References


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