2.1. Abstract

Highly monodispersed gold nanorods were synthesized via a modified ultraviolet photoirradiation method. The formation of nanorods was investigated by varying the path length of the quartz reaction vessel and the nanorods were characterized by various analytical, spectroscopic and microscopic methods. Almost quantitative conversion of gold ions to nanorods was observed when the path length of the reaction vessel is 1 mm. The nanorods synthesized by following this procedure can be directly used for various studies without further purification. Gold nanorods possess two plasmon absorption bands and the solvent dependence of longitudinal plasmon resonance (LPR) was studied in various polar organic solvents as a function of dielectric constant of the medium. The observed linear dependence on the square of longitudinal plasmon absorption maximum ($\lambda^2_{LPR}$) and dielectric constant ($\varepsilon_m$) confirm the sensitivity of longitudinal plasmon oscillation in Au nanorods towards the surrounding dielectric media.
2.2. Introduction

One dimensional nanostructures such as nanorods and nanowires have drawn attention in recent years due to their wide range of potential application in electronic, photonic and sensing devices. Among various one dimensional nanomaterials reported, gold nanorods possess highly tunable optical properties by varying their aspect ratios. However, the synthesis of Au nanorods having well defined dimensions is a major challenge. For application purpose it is essential to synthesize Au nanorods which possess high monodispersity. Several procedures have been reported for the synthesis of Au nanorods which include electrochemical, seed mediated, photochemical, combined chemical-photoirradiation and bio-reduction methods. Murphy and coworkers have synthesised high quality of Au nanorods, however the formation of considerable amount of spherical nanoparticles is the major disadvantage. Filtration based separation of nanorods failed and partial separation have been reported using size exclusion chromatography and centrifugation.

Seed mediated synthesis of gold nanorods involves complex reactions leaving considerable amount of reagents such as ascorbic acid, NaCl, NaBH₄ and side products such as spherical and irregular shaped Au nanoparticles. One of the major difficulties associated with the synthesis is their purification and a standardized synthetic procedure is essential for the effective utilization of nanorods for various applications. Herein we report a modified photochemical
method for the synthesis of Au nanorods which does not need any post purification; the conversion of gold ions is almost quantitative in 150 min and can be directly used for various studies.

2.3. Results and Discussion

2.3.1. Synthesis of Gold Nanorod

The present method of synthesis of Au nanorods follows photochemical approach with minor modifications in the reaction conditions such as the concentration of surfactants and the shape of reaction vessel used for irradiation. The photochemical approach does not involve the use of strong chemical reducing agents and the aspect ratio of Au nanorods can be varied by changing the concentration of silver ions. The reaction vessel consists of two cylindrical tubes: typically a cylindrical glass tube having 150 mm length and 8 mm diameter was inserted to a quartz tube with 150 mm length and 10 mm diameter. The path length is varied by changing diameter of the inner tube and teflon spacers were used to arrest the movement of inner tube so that the path length is uniform.

In a typical procedure for the synthesis of Au nanorods, cetyltrimethylammonium bromide (CTAB; 440 mg) and tetraoctylammonium bromide (TOAB; 4.5 mg) were dissolved in doubly distilled water (15 mL) and sonicated until the reagents were dissolved completely. To this solution, 1.25 mL of 0.024 M HAuCl₄ solution was added along with 325 μL of acetone and 225 μL
of cyclohexane. AgNO$_3$ was found to be essential for nanorod formation and in the present case, 450 µL of 0.01 M AgNO$_3$ was added to the above solution (Note: the solution should be homogeneous). Reaction mixture was transferred to the vessel and irradiated with 300 nm in a Rayonet Photochemical Reactor. Upon irradiation the yellow color of reaction mixture changed to brown and the progress of the reaction was monitored by following the absorption spectrum. The cooling fan equipped in the photoreactor to prevents any rise in temperature for the reaction mixture. Reproducible results were obtained on repeating the experiment.

The UV-visible absorption spectra of Au nanorods synthesized by varying the silver ion concentration (path length of the reaction vessel is fixed as 1 mm) are presented in Figure 2.1. Trace 'e' in Figure 2.1 corresponds to the absorption spectrum of Au nanorods formed on addition of 0.27 mM of silver ions. The ratio of the optical density of longitudinal to transverse surface plasmon absorption ($I_L/I_T$) was found to be greater than 2 (Table 2.1) and the transmission electron microscopic (TEM) analysis indicate the absence of any spherical nanoparticles under this experimental condition.

Absorption spectral changes of the reaction mixture upon irradiation are presented in Figure 2.2. A decrease in the absorption band at 400 nm corresponding to AuCl$_4^-$ was observed in the initial period of 60 min (traces 'a-c' in Figure 2.2) and the yellow colored solution turns colorless. It is interesting to note that during this period, the plasmon bands corresponding to nanorods were
not observed. Formation of transverse and longitudinal bands in the spectrum (traces ‘d-h’ in Figure 2.2) indicate that the growth of nanorod occur in the time range of 60-150 min. One of the interesting observations is the lack of any noticeable increase in the intensity of the transverse and longitudinal plasmon absorption bands, when the reaction mixture was irradiated for longer periods (>150 min). These results indicate that the growth process is complete in 150 min and the hyposchromic shift in the longitudinal plasmon band (trace ‘i’) was observed on further irradiation, due to the transformation of the rods to thermodynamically stable spherical nanoparticles.\textsuperscript{19-21}
Figure 2.2. Absorption spectra displaying the evolution of Au nanorods with time, on UV irradiation in presence of AgNO₃ (0.27mM): a) 0 b) 30 c) 60 d) 90 e) 105 f) 120 g) 135 h) 150 min and i) after 18 h.

The morphologies of Au nanorods were investigated using transmission electron microscopy (TEM). The TEM images of the nanorods obtained after irradiating for 150 min (path length of the reaction vessel is fixed as 1 mm and solution contains 0.27 mM concentration of silver ions) is presented in Figure 2.3 and the corresponding absorption spectrum in Figure 2.4. Nanorods were found to be monodispersed and accumulated in various locations of the grid. The average length (Figure 2.4B) and aspect ratio (inset of Figure 2.4A) of Au nanorods were estimated by analyzing 200 nanorods and the results indicate excellent monodispersity. The average aspect ratio of the rods is estimated as 3.1 (average length and width are 36.0 and 11.9 nm respectively). The aspect ratio can be
varied by increasing the concentration of silver ions, however limited to an aspect ratio of 3.6 even on increasing the silver ions concentration. The modified photochemical method presented here is ideal for the quick synthesis of monodispersed short Au nanorods and the main advantage is that the nanorods obtained can be directly used for various studies. The complete conversion of gold ions to Au nanorods in thin cells may be due to the efficient penetration of light and their monodispersity is due to uniform absorption of light.

Figure 2.3. Transmission electron microscopic images of Au nanorods prepared in quartz reaction vessel of path length 1 mm (TEM samples were prepared by drop casting 75 μL of solution from the reaction vessel).
Figure 2.4. (A) Absorption spectrum and (B) size distribution of Au nanorods prepared in reaction vessel of path length 1 mm. Inset of A shows the aspect ratio distribution of Au nanorods.

2.3.2. Influence of Cell Thickness

Experiments were performed by systematically varying the path length of the reaction vessel to 2, 5 and 10 mm by inserting inner tubes having appropriate dimensions. Corresponding absorption spectra and TEM images (150 min of irradiation using 300 nm) are shown in Figures 2.5-2.7 and the spectral properties are summarized in Table 2.1. When the path length of the reaction vessel is 2 mm, two distinct plasmon bands were observed at 514 and 697 nm (trace ‘a’) and longitudinal surface plasmon band shifts to blue region with increase in path length (traces ‘b’ and ‘c’). Hypsochromic shift in the longitudinal plasmon band is a clear indication of the decrease in aspect ratio of nanorod (with increase in path length of the reaction vessel), which was further confirmed through TEM analysis. The spectral shifts of the plasmon bands of Au nanorods with increasing aspect
ratio were reported by various groups.\textsuperscript{10,22,23} Interestingly the nanorods formed in the reaction vessel having a path length of 10 mm cell (Figure 2.6A) were short along with considerable amount of nanospheres. TEM images confirm that the average aspect ratio of nanorods and the monodispersity increases with decrease in the path length of the reaction vessel. For each sample, the dimensions of 200 nanorods were measured and the size distributions were plotted (Figure 2.7).

Table 2.1. Absorption maxima and intensity ratio of Au nanorods as a function of path length and silver ion concentration.

<table>
<thead>
<tr>
<th>Path length (mm)</th>
<th>$\lambda_{TPR}$</th>
<th>$\lambda_{LPR}$</th>
<th>$I_i/I_f$</th>
<th>$\lambda_{TPR}$</th>
<th>$\lambda_{LPR}$</th>
<th>$I_i/I_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>514</td>
<td>725</td>
<td>2.29</td>
<td>514</td>
<td>700</td>
<td>1.82</td>
</tr>
<tr>
<td>2</td>
<td>514</td>
<td>697</td>
<td>1.54</td>
<td>516</td>
<td>630</td>
<td>1.40</td>
</tr>
<tr>
<td>5</td>
<td>516</td>
<td>517</td>
<td>1.23</td>
<td>517</td>
<td>620</td>
<td>1.31</td>
</tr>
<tr>
<td>10</td>
<td>518</td>
<td>520</td>
<td>1.14</td>
<td>520</td>
<td>611</td>
<td>1.17</td>
</tr>
</tbody>
</table>

When the path length is more than 2 mm, large distribution in size was observed since the light absorption is not uniform. Gold nanorods possess excellent stability. Au nanorods suspended in water were stable for a period of one month (5 °C) and no change for the plasmon absorption was observed (Figure 2.8).
Figure 2.5. Absorption spectra of Au nanorods prepared in reaction vessels of varying path lengths; a) 2, b) 5 and c) 10 mm.

Figure 2.6. Absorption spectra of Au nanorods prepared in reaction vessels of path length a) 2, b) 5 & c) 10 mm at different silver ion concentration; [AgNO₃]: A) 0.20 and B) 0.13 mM.
Figure 2.7. TEM images and size distribution of Au nanorods prepared in reaction vessels of varying path lengths; A) 10, B) 5 and C) 2 mm. (TEM samples were prepared by drop casting 75 µL of solution from the reaction vessel).
2.3.3. Extinction Coefficients of Plasmon Absorption

Extinction coefficients ($\varepsilon$) of the transverse and longitudinal plasmon absorption bands of Au nanorods were estimated using Beer-Lambert’s law in conjunction with transmission electron microscopy (TEM) and inductively coupled plasma (ICP) analysis. The ICP was employed to estimate the concentration of Au atoms present in nanorod solution having a known optical density. The average size distribution of nanorods was determined using TEM analysis. The aspect ratios of the samples were estimated as 2.3, 3.0, 3.2 and 3.6.

Au nanorods possess a capsule shape having two hemispherical caps at the two ends of a cylinder (Scheme 2.1). The volume of the capsule was calculated
According to the equation derived from mathematical integration calculus (Section 2.5). Expression 2.1 shows the volume relation;

$$2 \pi \frac{h_1^2}{3} (3r_1-h_1) + \pi r^2L$$

(2.1)

where ‘L’ is the length of the cylindrical part of the nanorod, ‘r₁’ is the radius of the hemispherical cap, ‘h₁’ is the cap width and ‘r’ is the half width of the nanorod as shown in the Scheme 2.1. All these values can be derived from the average length and width of the Au nanorods obtained from TEM studies. The value of ‘r₁’ is given by the equation, \( r_1 = (r^2+h_1^2)/2h_1 \).

The number of Au atoms per rod was estimated by multiplying the packing density of gold (58.01 atoms/nm³) with the volume of the nanorod. The Au nanorod concentration in a solution of known optical density was estimated by dividing the concentration of Au atoms with the number of Au atoms per rod. The

![Scheme 2.1. Capsule shape of Au nanorod with two hemispherical caps at the ends of a cylinder.](image-url)
extinction coefficients of plasmon absorption bands were obtained by dividing the optical density by the Au nanorod concentration and various parameters are listed in Table 2.2.

**Table 2.2. Parameters for molar extinction coefficient calculation**

<table>
<thead>
<tr>
<th>Av. aspect ratio</th>
<th>2.3</th>
<th>3.0</th>
<th>3.2</th>
<th>3.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Av. length of Au nanorods, nm</td>
<td>47.28</td>
<td>54.20</td>
<td>53.6</td>
<td>58.0</td>
</tr>
<tr>
<td>Av. width of Au nanorods, nm</td>
<td>20.43</td>
<td>18.48</td>
<td>17.3</td>
<td>16.2</td>
</tr>
<tr>
<td>Volume of a single nanorods, $10^4$ nm$^3$</td>
<td>1.40</td>
<td>1.31</td>
<td>1.11</td>
<td>1.09</td>
</tr>
<tr>
<td>No. of Au atoms per nanorod</td>
<td>$8.11 \times 10^5$</td>
<td>$7.62 \times 10^5$</td>
<td>$6.42 \times 10^5$</td>
<td>$6.31 \times 10^5$</td>
</tr>
<tr>
<td>Longitudinal Extinction Coefficient, $10^{10}$ M$^{-1}$cm$^{-1}$</td>
<td>$\varepsilon_{650\text{nm}} = 0.58$</td>
<td>$\varepsilon_{700\text{nm}} = 0.53$</td>
<td>$\varepsilon_{750\text{nm}} = 0.55$</td>
<td>$\varepsilon_{780\text{nm}} = 0.50$</td>
</tr>
</tbody>
</table>

2.3.4. Solvent Dependent Plasmon Resonance of Au nanorods

The dependence of plasmon resonance of Au nanorods on the dielectric properties of the surrounding medium have been explored by various groups.$^{24,25}$ Since the nanorod synthesis were carried out in water and it is difficult to transfer
nanorods from water to various organic solvents, only a few attempts have been made in this direction.²⁶,²⁷ Chris Wang and coworkers have employed ionic liquids as a medium to transfer Au nanorods from aqueous solution.²⁷ We have investigated the dependence of the longitudinal plasmon absorption band of Au nanorods (aspect ratio 3.0) on the refractive index of the medium (Table 2.3). The Au nanorods were centrifuged twice to remove excess CTAB (to avoid precipitation in organic solvents) and redispersed in minimum amount of water. Microlitre quantities of stock solution were injected to organic solvents (miscible with water) keeping the water content in the final solution as 1 %. Absorption spectral studies indicate that Au nanorods were stable at room temperature. The longitudinal plasmon absorption of nanorods underwent bathochromic shift with increase in the refractive indices (Figure 2.9A) and followed the correlation

![Figure 2.9](image)

**Figure 2.9.** (A) Absorption spectra of Au nanorods (aspect ratio 3.0) in different polar solvents: a) water, b) acetonitrile, c) acetone, d) 2-propanol, e) tetrahydrofuran, f) DMF and g) DMSO. (B) Plot of square of longitudinal plasmon resonance wavelengths of Au nanorods ($\lambda_{LPR}^2$) against the square of refractive indices of various solvents ($n^2$).
Table 2.3. Longitudinal plasmon shift of Au nanorods (aspect ratio-3.0) in various polar solvents.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Refractive index, ((n))</th>
<th>Longitudinal plasmon band (\lambda_{\text{max}}, \text{nm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>1.333</td>
<td>697</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>1.344</td>
<td>700</td>
</tr>
<tr>
<td>acetone</td>
<td>1.359</td>
<td>701</td>
</tr>
<tr>
<td>2-proponol</td>
<td>1.380</td>
<td>706</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>1.408</td>
<td>717</td>
</tr>
<tr>
<td>DMF</td>
<td>1.431</td>
<td>721</td>
</tr>
<tr>
<td>DMSO</td>
<td>1.478</td>
<td>731</td>
</tr>
</tbody>
</table>

reported by Yang et al.\(^{28}\) According to the correlation, square of the longitudinal plasmon wavelength \((\lambda^2_{\text{LPR}})\) has a linear dependence on dielectric constant \((\varepsilon_m)\) of the surrounding medium, as shown in equation (2.2),

\[
\lambda^2_{\text{LPR}} = \lambda^2_p [\varepsilon^\infty + \frac{1 - L}{L} \varepsilon_m + (1 - L)(\varepsilon_2 - \varepsilon_m) g]
\]  \(2.2\)

where, \(\lambda^2_{\text{LPR}}\) and \(\varepsilon_m\) are the variables, other terms like \(\lambda_p\) is the wavelength of bulk gold plasma frequency, \(\varepsilon^\infty\) is the high frequency dielectric constant, \(L\) is a geometric factor and \(g\) is the nanorod volume fraction. Note that the dielectric constant is equivalent to square of the refractive index of the medium in which the nanorods are embedded \((\varepsilon_m = n^2, \text{‘}n\text{’ is the refractive index})\).\(^{28}\) The plot of the longitudinal plasmon maxima and refractive index follows a straight line (Figure
2.9B), confirming the dependency of longitudinal oscillation of plasmon electrons in Au nanorods to the surrounding dielectric medium.

2.4. Conclusions

Monodispersed gold nanorods with almost quantitative yields were obtained by a modified photochemical method, by reducing the path length of reaction vessel. The formation of nanorods was investigated by varying the path length of the photoreactor. A decrease in aspect ratio of nanorods was observed with increase in path length of the reaction vessel with a large distribution in size. The linear dependence of square of the longitudinal plasmon wavelength ($\lambda_{LPR}^2$) and dielectric constant ($\varepsilon_m$) of media confirm the sensitivity of longitudinal plasma electrons oscillation in Au nanorods towards the surrounding dielectric media.

2.5. Appendix

Mathematical Expression for Calculating Volume of Au Nanorods

The volume of single nanorod is calculated as follows,

The volume of a hemisphere is,

$$\pi \int y^2 \, dx = \pi \int (r^2-x^2) \, dx$$

where; $x^2 + y^2 = r^2$

$$= \pi [r^2 x - x^3/3]_0$$

$$= \pi [r^3 - r^3/3]$$

$$= 2/3 \pi r^3$$
where, ‘r’ is the radius of the hemisphere.

Usually the volume of a hemisphere is calculated by projecting it into an x-y plane, where integration of y to the limit 0 to r will give the value of the volume. But in the case of Au nanorods, the ends of the rods are coupled with 2 spherical-caps of height ‘h1’ and radius ‘r1’, so it is easy to get the volume by integrating y to the limits of (r1-h1) to r1.

\[
x^2 + y^2 = r^2
\]

Therefore, volume of the spherical cap at one end is,

\[
= \pi \int_{r_1-h_1}^{r_1} (r^2-x^2) \, dx
\]

\[
= \pi \int_{r_1-h_1}^{r_1} (r^2-x^2) \, dx
\]

\[
= \pi \left[ \frac{r_1^3}{3} - \frac{r^3}{3} \right]_{r_1-h_1}
\]

\[
= \pi \left\{ \frac{r_1^3}{3} - \frac{r_1^3}{3} - \frac{r_1^2 (r_1-h_1)}{3} + \frac{1}{3} (r_1-h_1)^3 \right\}
\]

\[
= \frac{\pi}{3} \left\{ 2r_1^3 - (r_1-h_1)[3r_1^2 - (r_1-h_1)^2] \right\}
\]

\[
= \frac{\pi}{3} \left\{ 2r_1^3 - (r_1-h_1)[3r_1^2 - r_1^2 - h_1^2 + 2r_1h_1] \right\}
\]

\[
= \frac{\pi}{3} \left\{ 2r_1^3 - (r_1-h_1)[3r_1^2 - h_1^2 + 2r_1h_1] \right\}
\]
Similarly, volume of the cap at other end is $\frac{\pi}{3} h_2^2 (3r_2 - h_2)$

Therefore, total volume of a single Au nanorod is

$$= \frac{\pi}{3} h_1^2 (3r_1 - h_1) + \pi r^2 L + \frac{\pi}{3} h_2^2 (3r_2 - h_2)$$

Since $r_1 = r_2$ and $h_1 = h_2$, Volume become,

$$= \frac{2\pi}{3} h_1^2 (3r_1 - h_1) + \pi r^2 L$$

2.5. References


