5.1. Introduction

Fine metal particles with nanometer scale dimensions are of current interest due to their unusual properties [169,204,205]. The applications of nanomaterials depend strongly on the particle size, the interparticle distance and the shape of the nanoparticles. The morphology of metal nanoparticles is important in the field of scientific research, because small changes in the shape of nanoparticles can have great effect on a variety of physical properties of the material [92,206–212,110]. Nanoscale particles of gold are being investigated for potential applications in the field of catalysis, chemical and biological sensors and biomedical applications [205,92,10,101,213–217]. Therefore controlled preparation of nanomaterials is very important and significant. Many physical and chemical approaches have been developed to obtain special shaped nanomaterials such as nanorods, ellipsoids, cubes, etc. The physical methods produce nanomaterials from bulk materials with the help of exact and sophisticated equipments, while the chemical approach prepares nanomaterials from the atoms and molecules through simple chemical routes. In the past decade, many research groups have dedicated themselves to the preparation of metal nanomaterials following chemical approach. Several chemical synthesis methods based on colloid chemistry have been developed for the production of metal nanoparticles with different shapes [209–211,85,87,215,219–223] using CTAB as a structure directing capping agent. Chen et al. (2006) have reviewed in detail the account of chemical approach for preparing special shaped nanomaterials. Usually, chemical approaches are classified as (i) selfstructure confinement approach, (ii) hard or soft template approach, (iii) physical chemistry approach and (iv) soft solution approach. Among these the soft solution method, which is based on the reduction in the solution by mild reducing agents in the presence of additives like polymers [224,225], surfactants [213,226–229] and dendrimers [230–233], is widely used. In the case of special shaped metal nanoparticles, these additives adsorb on the precursor metal ions first and then create anisotropic confinements by selective passivation of certain facets to induce and maintain anisotropic crystal growth. This approach enables to generate special shaped nanostructures with highly crystalline and well-
controlled composition in a high yield. The ability of ionizing radiation to bring about ionization and excitation in the medium through which they travel results in the formation of reactive species, which can be utilized to reduce metal ions into metal atoms to generate metal nanoparticles. Radiolysis of water/aqueous solution results in generation of reactive species such as hydrated electron (e\textsuperscript{−}_\text{aq}) and hydrogen atom (H\textsuperscript{−}) and hydroxyl radical (‘OH). The first two radicals can easily reduce metal ions down to zero valent state [95,234]. As mentioned in chapter 3 (section 3.1) the hydroxyl radicals produced in the course of radiolysis are oxidizing in nature. To scavenge this radical, isopropyl alcohol is added to the reaction system, which subsequently forms isopropyl radical. Hence a total reducing atmosphere is created. The difference between gamma radiation method and soft solution method is that in the former the reducing species are generated in situ, whereas in later the reducing agent is incorporated in to the system from an external source. Further in radiation method, reduction is carried out at room temperature, so that additives sensitive to heat, such as polymeric systems that are not suitable for chemical reduction under heating may also be used in the radiolytic method. A particular advantage of radiolysis method is that the reduction rate is controlled by selected dose rate, which offers a wide range of conditions from slow to quasi-instantaneous atom production unlike chemical method where the local concentration of reducing species is very high and cannot be controlled very easily. The literature survey reveals that only a few articles are available on generation of anisotropic metal nanoparticles by using high energy radiation [235]. Preparation of non spherical gold nanoparticles by means of chemical route is a multi step process and requires optimization of many experimental factors, such as Au\textsuperscript{III} precursor ion concentration, the surface directing agent namely cetyl trimethyl ammonium bromide (CTAB) concentration and most importantly the seed concentration [213,221,88,236,237]. Chemical method for the synthesis of gold nanorods was proposed by Murphy et al., in 2001[227]. It is a seed mediated growth procedure, in which metal salts (Au\textsuperscript{III}) are reduced initially with a strong reducing agent (sodium borohydride), in water, to produce ∼4nm seed particles. Then in another set, metal salts (Au\textsuperscript{III}) are reduced by a weak reducing agent (Ascorbic acid) in the presence of structure-directing additives (CTAB and Ag\textsuperscript{+}) and previously synthesized Au seeds to generate Au nanorods [213,227,88]. In present work initially attempt has been made to design a system for synthesis of gold nanorods similar to chemical method. This is a two step seeded growth method, but
instead of using ascorbic acid as a reductant, gamma radiation has been used to generate reducing radicals. Radicals generated by imparting gamma energy radiation are strong reducing species. A milder reducing environment is expected to be suitable for formation of anisotropic shaped nanoparticles. Hence low dose rate condition had been chosen to control the reaction rate for generation of Au nanorods.

The above method has been further modified to design a simple and convenient synthesis process, in which the seed solution synthesis step and external addition of seed has been eliminated. In this method a total reducing environment containing a single type of reducing species has been created by carefully choosing the nature and concentration of reactants. It is a one-pot synthesis method, in which even at high dose rate gold nanorods generation has been achieved.

In another approach, anisotropic gold nanoplates have been synthesized by combining both radiolytic and chemical methods. Au seeds are generated in-situ by radiolysis and the Au nanoparticles are allowed to grow on these seeds by ascorbic acid reduction method.

In section 5.2, synthesis of different anisotropic shaped metal nanoparticle by means of gamma-radiation based method has been discussed. Initially short aspect ratio gold nanorods were synthesized by controlling the dose rate of gamma radiation. In this method previously prepared gold seed solution and CTAB were used for nanorod synthesis, where these two play important role to induce anisotropy. Here the reducing agents used were $e^{-}_{aq}$ and $H^-$ and isopropyl radical. The effect of absorbed dose and dose rate and reactant concentration in controlling the growth of particles has also been investigated.

In section 5.3 development of a modified method for producing gold nanorods has been described. Here a single type of reducing species, namely isopropyl radical has been employed unlike earlier methods where hydrated electron, $H^-$ and isopropyl radicals were used as reducing agents. Also under the present experimental protocol, synthesis of gold nanorods has been achieved without using any gold seed solution. The effect of dose, dose rate, precursor metal ion concentration and the concentration of CTAB on the formation of nanorod have also been investigated.

Section 5.4. provides details of rectangular gold nanoplates synthesized by employing both radiation and chemical method. The rectangular gold nanoplates have been formed in a single step by irradiating the growth solution containing $4 \times 10^{-4}$ mol. dm$^{-3}$ gold precursor ion
(Au\textsuperscript{III}), 0.1 mol dm\textsuperscript{-3} cetyl trimethyl ammonium bromide (CTAB), 0.2 mol dm\textsuperscript{-3} isopropanol, 6 \times 10\textsuperscript{-5} mol dm\textsuperscript{-3} Ag\textsuperscript{+} and 7.2 \times 10\textsuperscript{-4} mol dm\textsuperscript{-3} ascorbic acid for short duration of time at a dose rate of 3.4 kGy h\textsuperscript{-1} so that appropriate amount of nanoparticle seeds are generated \textit{in situ}. These seeds provide the site for nanoparticle growth and the anisotropy of the nanoparticles is controlled by the capping agent, namely CTAB and Ag\textsuperscript{+} as mentioned in the literature [79,236,238]. Hence, unlike chemical method the seed preparation step has been avoided in the present method, so that the complexity of the process and wastage of reagents in the unused seed solution has been minimized. The evolution of nanoparticle with time and the effect of experimental parameters such as absorption dose, ascorbic acid/ Au\textsuperscript{III} ratio, precursor Au\textsuperscript{III} concentration, AgNO\textsubscript{3} concentration, the concentration of CTAB and pH on the formation of nanoparticles has also been investigated.

5.2. Synthesis of short aspect ratio anisotropic gold nanorods in CTAB by using gamma radiation

5.2.1. Synthesis of Au seed solution

The Au seeds were prepared by a method similar to that described in the literature [213]. In a typical protocol, 4ml of 1\times10\textsuperscript{-3} mol dm\textsuperscript{-3} Au\textsuperscript{III} solution, 5ml of 0.2 mol dm\textsuperscript{-3} CTAB solution and 1ml of 1\times10\textsuperscript{-2} mol dm\textsuperscript{-3} ice cold sodium borohydride were mixed in the same order as mentioned. The solution was shaken vigorously for 2 minutes and kept aside for 2 hours before use. The color of the solution changed from light yellow to light brown after the addition of sodium borohydride. The formation of Au seeds is schematically represented in Figure 5.1. The resultant Au seeds have particle size in the range 3.5– 4.0 nm as determined by TEM analysis [213].

Figure 5.1: Cartoon picture of synthesis of Au seeds from Au\textsuperscript{III} ions in presence of NaBH\textsubscript{4} and CTAB
5.2.2. Synthesis of Au\text{I} solution

The aqueous solution of $4 \times 10^{-4}$ mol dm$^{-3}$ HAuCl$_4$ containing 0.2 mol dm$^{-3}$ isopropyl alcohol and 0.1 mol dm$^{-3}$ CTAB was irradiated in the gamma chamber at a dose rate 3.4 kGy h$^{-1}$ after purging with high pure N$_2$ gas till the solution turned colorless. The colorless solution is due to formation of Au\text{I} as shown in Equations (5.1- 5.3). This solution contains Au\text{I} and was used as a precursor for gold in the synthesis of gold nanorods. The concentrations of different reagents mentioned in this section were kept constant throughout the study in section 5.2 unless it is mentioned.

\begin{align}
\text{Au}^{\text{III}} + e^-_{\text{aq}}/ (\text{CH}_3)_2\cdot\text{C-OH} & \rightarrow \text{Au}^{\text{II}} + (\text{CH}_3)_2\text{C}=\text{O} + \text{H}^+ \quad (5.1) \\
\text{Au}^{\text{II}} + \text{Au}^{\text{II}} & \rightarrow (\text{Au}^{\text{II}})_2 \quad (5.2) \\
(\text{Au}^{\text{II}})_2 & \rightarrow \text{Au}^{\text{III}} + \text{Au}^{\text{I}} \quad (5.3)
\end{align}

5.2.3. Results and discussion

5.2.3.1. Irradiation at higher dose rate

The chemical method for synthesis of gold nanorods involves the reduction of Au\text{III} by weak reducing agent such as ascorbic acid in the presence of Au seeds and Ag$^+$, the surfactant CTAB is used as a structure directing agent [239,211,88]. In the present method reducing species, which are generated \textit{in situ} by gamma radiolysis, are used for the reduction of Au\text{I} to metallic Au in aqueous medium. $6 \times 10^{-5}$ mol dm$^{-3}$ of AgNO$_3$ and $1.2 \times 10^{-6}$ mol dm$^{-3}$ of seed solution (in terms of Au\text{III}) were added to aqueous solution containing $4 \times 10^{-4}$ mol dm$^{-3}$ of Au\text{I}, 0.2 mol dm$^{-3}$ of isopropanol and 0.1 mol dm$^{-3}$ of CTAB (prepared as per mentioned in section 5.2.2.) and it was irradiated with gamma rays at a dose rate= 3.4 kGy h$^{-1}$. Under these conditions most of the energy is absorbed by water resulting in the formation of highly reactive species such as $e^-_{\text{aq}}$, H$^+$ and ‘OH. Among these radicals $e^-_{\text{aq}}$ ($E^0_{\text{H}_2\text{O/e}^-_{\text{aq}}} = -2.87$ V$_{\text{NHE}}$) and H$^+$ ($E^0_{\text{H}^+/\text{H}_2\text{O}} = -2.3$ V$_{\text{NHE}}$) are highly reducing in nature. Both these radicals bring about the reduction of Au\text{I} to Au$^0$. However, in the presence of isopropyl alcohol the ‘OH radical is scavenged and isopropyl radical is generated [Equation 5.4]. The isopropyl radical thus generated is reducing in nature ($E^0 \approx -1.5$ V$_{\text{NHE}}$) and is capable of reducing Au\text{I} to Au$^0$ as shown in Equation 5.5.

\begin{align}
(\text{CH}_3)_2\text{CH} (\text{OH}) + \cdot\text{OH} & \rightarrow (\text{CH}_3)_2 \cdot\text{C} (\text{OH}) + \text{H}_2\text{O} \quad (5.4) \\
(\text{CH}_3)_2 \cdot\text{C} (\text{OH}) + \text{Au}^{\text{I}} & \rightarrow (\text{CH}_3)_2\text{CO} + \text{Au}^0 + \text{H}^+ \quad (5.5)
\end{align}
The Au atoms generated by radiolysis undergo coalescence resulting in the formation of Au nanoparticles, which get stabilized by CTAB. The absorption spectra of irradiated solution at various times of irradiation are shown in Figure 5.2.

![Absorption Spectra](image.png)

**Figure 5.2:** Absorption spectra of irradiated solution containing $4 \times 10^{-4}$ mol dm$^{-3}$ of Au$^+$, 0.2 mol dm$^{-3}$ isopropanol, $6 \times 10^{-5}$ mol dm$^{-3}$ of AgNO$_3$, 0.1 mol dm$^{-3}$ of CTAB and $1.2 \times 10^{-6}$ mol dm$^{-3}$ seed at various absorbed doses (a) 0.8, (b) 1.7 and (c) 2.6 kGy. Dose rate =3.4 kGy h$^{-1}$

As can be seen from Figure 5.2, only a single peak at 527 nm, which is the characteristic surface plasmon resonance band of Au spheres, is observed. The intensity of this band increases with increase in dose. Under similar conditions, in the synthesis of Au nanoparticles by chemical method employing ascorbic acid as a reducing agent [211], two absorption bands, one at 522 nm and the other at higher wavelength region (650–800 nm), were observed which were attributed to the formation of gold nanorods. The position of second absorption band at higher wavelength region, also known as longitudinal surface plasmon band, varies with the length of the rod. It is red shifted with increase in the length of the rod [88]. The appearance of single absorption band at 527 nm after the radiolysis indicates the formation of nanoparticles in spherical form. Although, there was an indication of formation of second absorption band during the radiolysis as evident from the appearance of shoulder at 590 nm; however, it did not grow with increasing dose and finally only a single absorption peak at 527
nm was observed. It is known from the literature that during the synthesis of gold nanorods using chemical method the kinetics of the addition of Au\textsuperscript{I} to the growing seeds governs the shape and size of the nanoparticle [88]. The radiolytic method offers wide ranges of dose rates and therefore the rate of generation of reducing species can easily be governed. The radiolysis was carried out at lower doses and the results obtained are described below.

5.2.3.2. Irradiation at lower dose rates

To investigate the effect of dose rate on the formation of Au nanoparticles, irradiation of aqueous solution containing Au\textsuperscript{I}, isopropanol, AgNO\textsubscript{3}, CTAB and seed solution at concentrations same as mentioned in section 5.2.3.1 at various dose rates was carried out. The absorption spectra of solution irradiated at a dose rate 1.7 kGy h\textsuperscript{-1} at various intervals of irradiation are shown in Figure 5.3.

![Absorption spectra of irradiated solution](image)

**Figure 5.3:** Absorption spectra of irradiated solution containing 4x10\textsuperscript{-4} mol dm\textsuperscript{-3} of Au\textsuperscript{I}, 0.2 mol dm\textsuperscript{-3} isopropanol, 8x10\textsuperscript{-5} mol dm\textsuperscript{-3} of AgNO\textsubscript{3}, 0.1 mol dm\textsuperscript{-3} CTAB and 1.2 x 10\textsuperscript{-6} mol dm\textsuperscript{-3} seed at various absorbed doses (a) 1.7, (b) 2.6 (c) 3.0, (d) 3.5 and (e) 4.5 kGy. dose rate = 1.7 kGy h\textsuperscript{-1}

At lower absorption dose two absorption maxima at 523 and 610 nm were observed (Figure 5.3a) that disappeared with further increase in radiation dose and finally only a single peak at 528 nm was observed. The appearance of two absorption maxima at 522 and 610 nm in the beginning (Figure 5.3a) indicated the tendency for formation of anisotropic shape particle. However with increase in dose the absorption maxima at 610 nm disappears and
finally only a single peak at 527 nm is observed indicating that the net result is the formation of spheres.

![Absorption spectra of irradiated solution containing 4 x 10^{-4} mol dm^{-3} of Au^{+1}, 0.2 mol dm^{-3} isopropanol, 8 x 10^{-5} mol dm^{-3} of AgNO_{3}, 0.1 mol dm^{-3} of CTAB and 1.2 x 10^{-6} mol dm^{-3} seed at various absorbed doses (a) 1.2, (b) 1.6 (c) 2.0, (d) 2.3 and (e) 2.6 kGy. Dose rate = 0.8 kGy h^{-1}](image)

When, radiolysis of the above solution was carried out at still lower dose rate, i.e, 0.8 kGy h^{-1}, the absorption spectra of solutions irradiated to various absorbed doses showed two absorption maxima as shown in Figure 5.4.

![TEM of gold nanorods synthesized by radiolytic method. Bar length = 50 nm](image)

The two bands are attributed to the formation of Au nanorods. The first absorption maximum, which is centered at 513 nm did not shift with increasing radiation dose, whereas the second one is red shifted from 643 to 670 nm with increase in radiation dose. This shift of
absorption maxima by 27 nm with increasing radiation dose may be due to increase in aspect ratio caused by the growth of nanorods. The formation of nanorods was further confirmed from transmission electron microscopy results (Figure 5.5). The TEM image showed uniform sized nanorods without presence of any spheres. The aspect ratio of nanorods was estimated to be 2.4 by measuring the length and breadth of 100 particles using ocular lens.

5.2.3.3. Suggested mechanism

The anisotropic shape generation in case of gold nanoparticles requires three most important parameters:

i) surfactant, CTAB, which provides tubular template in aqueous solution

ii) Au seed particles, which have facets to grow anisotropic nanoparticles

iii) Adsorbate ions, like Ag\(^{+}\), which block certain facets thereby facilitating directional growth

![Absorption spectra](image_url)

**Figure 5.6:** Absorption spectra of irradiated solution in absence of Ag\(^{+}\) (a) 1.7 and (b) 6.8 kGy. All other conditions are same as mentioned in Figure 5.3

In chemical method of synthesis of gold nanorods [211,227,88] it has been postulated that the presence of Ag\(^{+}\) in the growth solution is a must for getting nanorods in high yield. It was found to be true for the radiation method of synthesis of nanorods also. Keeping all other parameters same, when irradiation was carried out in absence of Ag\(^{+}\), the absorption spectra at
various doses are shown in Figure 5.6. Appearance of only single absorption maxima at 527 nm clearly indicates that only spheres were formed thus confirming that Ag$^+$ are essential for the synthesis of nanorods by radiolytic method also. The role played by Ag$^+$ in the synthesis of Au nanorod is not yet fully understood. The proposed mechanism for gold nanorod formation suggests that the surfactant forms a soft cylindrical template, with a certain size that depends on surfactant concentration. Nikoobakht and El-Sayed proposed that the silver ions located between the head groups of the capping surfactant (CTAB) can be considered as Ag–Br pairs, decreasing the charge density on the bromide ions, and therefore, the repulsion between neighboring headgroups on the gold surface, and resulting in CTAB template elongation [227,236,240]. This possibility is supported by the stronger affinity of CTAB monomers for the side facets compare to the end facets [241].

Figure 5.7: (a) Cartoon picture of gold nanorod showing (100), (110) side faces and (111) end faces
(b) Schematic representation of zipping mechanism for the growth of gold nanorods in CTAB bi-layer template
High-resolution TEM images show that nanorods have four facets [242]. According to the proposed mechanism Ag\(^+\) ions get adsorbed on the side facets, i.e., (100) and (110) thereby blocking these facets. So that the tip of growing nanorod, which contains (111) facets are free for adsorption of Au atoms [212] and growth of nanorod (Figure 5.7 a). Johnson et al, proposed a zipping mechanism [213] for rod elongation considering CTAB monomer as rigid structure (Figure 5.7 b). The concentration of Ag\(^+\) in the solution also plays an important role in the synthesis of Au nanorods. The radiolysis was carried out at various concentrations of Ag\(^+\) keeping Au\(^I\) concentration constant (4×10\(^{-4}\) mol dm\(^{-3}\)). The best and reproducible results were obtained at Ag\(^+\) concentration of 6×10\(^{-5}\) mol dm\(^{-3}\) and the same was used throughout this study. Thus in the radiolytic method nanorod formation occurs when the concentration ratio of Au: Ag is ~7. Similar results were also obtained in the seed mediated method for the synthesis of short aspect ratio Au nanorods [212] in aqueous medium using ascorbic acid as reducing agent. Ascorbic acid, which is a mild reducing agent, is used in the chemical method of synthesis of nanorods. When ascorbic acid was added to the aqueous solution containing Au\(^{III}\), Au seeds and surfactant (CTAB), Au\(^{III}\) is reduced to Au\(^I\).

![Absorption spectra of irradiated solution](image)

Figure 5.8: Absorption spectra of irradiated solution containing 1×10\(^{-4}\) mol dm\(^{-3}\) of Au\(^{I}\), 0.2 mol dm\(^{-3}\) isopropanol, 8×10\(^{-5}\) mol dm\(^{-3}\) of AgNO\(_3\), 0.1 mol dm\(^{-3}\) of CTAB and 1.2×10\(^{-6}\) mol dm\(^{-3}\) seed at various absorbed doses (a) 0.85, (b) 1.06 and (c) 1.2 kGy. Dose rate = 0.8 kGy h\(^{-1}\)
The ascorbic acid cannot reduce Au\textsuperscript{III} down to Au\textsuperscript{0} due to its low reducing power. However in the presence of Au seed, Au\textsuperscript{I} gets adsorbed on the surface of seed and the adsorbed Au\textsuperscript{I} can be reduced by ascorbic acid to atomic Au. This results in the growth of seed; however in the presence of CTAB, which preferentially binds to the growing seed along the long axis forming a bilayer \cite{88}, the addition of Au\textsuperscript{I} takes place along the short axis that results in the growth in one direction. This anisotropic addition of Au results in the formation of nanorod.

In the present method as mentioned earlier in the text, the radicals namely e\textsubscript{aq} and isopropyl radical generated during radiolysis are highly reducing in nature and can bring the reduction of Au\textsuperscript{I} to atomic Au in the solution unlike chemical method where ascorbic acid cannot reduce Au\textsuperscript{I} to Au. Therefore, in the chemical method when seeds are not added to the growth solution, nanorods formation does not occur. But in the present radiolytic method when seeds were not added to the solution, the reduction of Au\textsuperscript{I} to Au still occurs as the solution after irradiation turned pink.

![Absorption spectra of irradiated solution containing 1 x 10\textsuperscript{-3} mol dm\textsuperscript{-3} of Au\textsuperscript{+1}, 0.2 mol dm\textsuperscript{-3} isopropanol, 8 x 10\textsuperscript{-5} mol dm\textsuperscript{-3} of AgNO\textsubscript{3}, 0.1 mol dm\textsuperscript{-3} of CTAB and 1.2 x 10\textsuperscript{-6} mol dm\textsuperscript{-3} seed at various absorbed doses (a) 1.28, (b) 2.12 and (c) 3.0, (d) 3.4 and (e) 4.25 kGy. Dose rate = 0.8 kGy h\textsuperscript{-1}](image)

The irradiated solution showed only one absorption maximum at 527 nm, which is the band for spherical Au nanoparticles. Thus, in radiation method the growth of particles takes place...
by the addition of Au atoms formed in the solution upon radiolysis on the growing seed. When aqueous solution is subjected to gamma radiolysis, there is a steady-state concentration of radicals in the solution. The steady-state concentration of radicals depends on the dose rate.

In the present case all these reducing radicals, namely \( e_{\text{aq}}^- \) and isopropyl radical, react with \( \text{Au}^1 \) in the solution. Therefore, the rate of formation of \( \text{Au}^0 \) in the solution is equal to the product of steady-state radical concentration of reducing radicals and the concentration of \( \text{Au}^1 \). At high dose rate (3.4 kGy h\(^{-1}\)) no nanorods are formed but only spheres are obtained as evident from single absorption maxima at 527 nm (Figure 5.2). It appears that when the formation rate of \( \text{Au}^0 \) in the solution is high, the rate of addition of \( \text{Au}^0 \) to growing particle is high and under these conditions addition takes place isotropically which results in the formation of spheres. When dose rate is reduced by a factor of 4, the steady-state concentration of \( \text{Au}^0 \) in the solution is also correspondingly reduced and in turn the rate of addition of Au to the growing particle is reduced by a factor of 4. The results show that under slower kinetics conditions addition of Au to the growing particles takes place in anisotropic manner leading to the formation of rod. The evidence for the role of kinetics in governing the final shape of particle is further substantiated by the experimental observation where the concentration of \( \text{Au}^1 \) used for the synthesis is reduced by a factor of 4. When aqueous solution containing \( 1 \times 10^{-4} \) mol dm\(^{-3}\) of \( \text{Au}^1 \), 0.2 mol dm\(^{-3}\) of iso-propanol, \( 6 \times 10^{-5} \) mol dm\(^{-3}\) of AgNO\(_3\), 0.1 mol dm\(^{-3}\) of CTAB and \( 1.2 \times 10^{-6} \) mol dm\(^{-3}\) of seed solution was irradiated with gamma rays at 0.8 kGy h\(^{-1}\) dose rate, the absorption spectra obtained at various irradiation times are shown in Figure 5.8. Under these conditions the formation of gold nanorods takes place as evident from the appearance of two absorption maxima at 513 and 750 nm (Figure 5.8c). The second absorption maximum, which was centered at 670 nm when the concentration of \( \text{Au}^1 \) was \( 4 \times 10^{-4} \) mol dm\(^{-3}\) (Figure 5.4), was red shifted to 750 nm at lower \( \text{Au}^1 \) concentration of \( 1 \times 10^{-4} \) mol dm\(^{-3}\). It is reported that the longitudinal plasmon band is red shifted as the length of nanorods increases. At lower precursor concentration, the length of rod increases indicating that the addition of Au takes place in a more directional manner, i.e. on the tip of the growing rod. Under this condition the steady-state concentration of \( \text{Au}^0 \) in the bulk is 4 times lower compared to the condition where \( \text{Au}^1 \) concentration is \( 4 \times 10^{-4} \) mol dm\(^{-3}\). This clearly indicates that the formation of nanorod is controlled by kinetics, i.e. lower the steady-state concentration of Au in the bulk, lower is its addition rate to the growing rod and
in turn higher is the probability of its addition in a particular direction, which results in the formation of nanorod. This hypothesis was further confirmed when synthesis of gold nanorod was carried out at high concentration of \( \text{Au}^1 \) \( (1 \times 10^{-3} \text{ mol dm}^{-3}) \) at the same dose rate of 0.8 kGy h\(^{-1}\). Under these conditions no nanorods formation was observed as absorption spectra shows only single absorption maxima at 530 nm whose intensity increases with increase in dose as shown in Figure 5.9. Thus by proper choice of \( \text{Au}^1 \) concentration and dose rate, nanorods of gold can easily be generated in the aqueous medium using gamma radiolysis technique.

5.3. Modification of synthesis method for preparation of gold nanorods at high dose rate and in absence of \( \text{Au}^1 \) seeds

5.3.1. Synthesis of \( \text{Au}^1 \) solution

The \( \text{Au}^1 \) solution was synthesized as mentioned in section 5.2.2. Aqueous solution containing \( 4 \times 10^{-4} \text{ mol dm}^{-3} \) H\( \text{AuCl}_4 \), \( 0.2 \text{ mol dm}^{-3} \) isopropyl alcohol and \( 0.1 \text{ mol dm}^{-3} \) CTAB was purged with high pure \( \text{N}_2 \) gas and it was irradiated in the gamma chamber at a dose rate 3.4 kGy h\(^{-1}\) till the solution turned colorless. This solution was used as a precursor for gold in the synthesis of gold nanorods. The concentrations of different reagents mentioned in this section were kept constant throughout the study in section 5.3 unless it is mentioned.

5.3.2. Synthesis of rod-shaped gold nanoparticles

To the \( \text{Au}^1 \) solution prepared by gamma radiolysis \( 2.75 \times 10^{-2} \text{ mol dm}^{-3} \) of acetone, \( 0.2 \text{ mol dm}^{-3} \) isopropyl alcohol and \( 6 \times 10^{-5} \text{ mol dm}^{-3} \) of \( \text{Ag}^+ \) were added, the final solution was purged with \( \text{N}_2 \) and it was subjected to gamma irradiation. The concentration of \( \text{Au}^1 \) was adjusted by diluting the solution with appropriate amount of water. The solution was irradiated in the gamma chamber and the resulting colored solution containing gold nanorods was first analysed by UV-visible spectroscopy.

5.3.3. Results and discussion

5.3.3.1. Reaction of isopropyl radical with \( \text{Au}^1 \)

When the precursor solution containing \( 4 \times 10^{-4} \text{ mol dm}^{-3} \text{ Au}^1 \), \( 2.75 \times 10^{-2} \text{ mol dm}^{-3} \) acetone, \( 0.2 \text{ mol dm}^{-3} \) isopropanol and \( 6 \times 10^{-5} \text{ mol dm}^{-3} \) of \( \text{Ag}^+ \) was subjected to gamma
irradiation at a dose rate = 3.4 kGy h⁻¹, the primary radicals of water radiolysis namely \( e_{aq}^- \), \( H^- \) and \( \cdot OH \) undergo the following two reactions:

\[
\cdot OH/H^- + (CH_3)_2 CH-OH \rightarrow (CH_3)_2 \cdot C-OH + H_2O/H_2 \tag{5.6}
\]
\[
e_{aq}^- + (CH_3)_2 C=O \rightarrow (CH_3)_2 \cdot C-OH + OH^- \tag{5.7}
\]

<table>
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<td>( 7.7 \times 10^9 )</td>
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<tr>
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<td>Acetone</td>
<td>( H^- )</td>
<td>( 2.0 \times 10^6 )</td>
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<td>Isopropanol</td>
<td>( \cdot OH )</td>
<td>( 1.6 \times 10^9 )</td>
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</tbody>
</table>

The rate constant for the reaction of radicals of water radiolysis with acetone and isopropyl alcohol is given in Table 5.1. In the present system the concentration of acetone has been kept almost seven times lower than that of isopropyl alcohol to minimize the possibility of reaction of acetone with \( OH^- \). At the same time the concentration of acetone has been kept higher than the precursor \( Au^1 \) concentration, so that the \( e_{aq}^- \) and \( H^- \), instead of reacting with \( Au^1 \), preferably react with acetone to generate isopropyl radical. Thus, in the present method all the primary radicals of water radiolysis are converted into a single type of radical namely isopropyl alcohol radical, which reduces \( Au^1 \) present in the solution into \( Au^0 \) as shown in Equation (5.2). The absorption spectrum of irradiated solution is shown in Figure 5.10. As can be seen from Figure 5.10, two absorption maxima one at 511 nm known as transverse surface plasmon absorption band and other in higher wavelength region known as longitudinal surface plasmon absorption band at 701 nm are observed, which are characteristic of gold nanorod thus confirming the formation of nanorod upon irradiation.
Figure 5.10: Absorption spectrum of gold nanorods synthesised by the reaction of Au$^+$ with isopropyl radical in the presence of CTAB. Concentration of Au$^+$ = 4 x 10$^{-4}$ mol dm$^{-3}$ and dose = 2.8 kGy, Dose rate = 3.4 kGy h$^{-1}$

5.3.3.2. Effect of precursor Au$^+$ concentration

In order to understand the role of the concentration of precursor Au$^+$ on the formation of nanorod, gamma radiolysis of solution containing 2.75 x 10$^{-2}$ mol dm$^{-3}$ acetone, 0.21 mol dm$^{-3}$ isopropanol and 6 x 10$^{-5}$ mol dm$^{-3}$ of Ag$^+$ and varying concentration of Au$^+$ was carried out. The dose delivered to sample was based on the concentration of Au$^+$ used. The theoretical calculation of dose required to reduce a certain concentration of metal ion has been mentioned in section 3.2 of chapter 3. The absorption spectra of the irradiated solution are shown in Figure 5.11. At Au$^+$ concentration of 4 x 10$^{-4}$ mol dm$^{-3}$ the absorption maxima ($\lambda_{\text{max}}$) of longitudinal band is positioned at 701 nm and with decrease in concentration of Au$^+$ the $\lambda_{\text{max}}$ is red shifted as shown in Figure 5.11.
Chapter 5

5.3.3.3. Effect of CTAB concentration

In the chemical method it has been reported that concentration of CTAB plays an important role for obtaining nanorods in high yield [243]. Therefore in the present study effect of CTAB on nanorod formation was investigated. The absorption spectra of irradiated solution containing varying concentration of CTAB are shown in Figure 5.12. At CTAB concentration of 0.1 mol dm$^{-3}$, absorption maxima is observed at 729 nm whereas decrease in the concentration of CTAB resulted in the blue shift of the absorption maxima with considerable broadening of peak as shown in Figure 5.12. The blue shift clearly indicates that shorter rods are formed with decreasing CTAB concentration and also broadening of absorption peak indicates that size distribution is non uniform. Therefore, for getting uniform sized nanorods in higher yield, the concentration of CTAB should be not less than 0.1 mol dm$^{-3}$. The results are similar to those obtained by chemical methods reported earlier [243].
Figure 5.12: Effect of CTAB concentration on nanorod formation: (a) 0.1 mol dm$^{-3}$, $\lambda_{\text{max}} = 729$ nm (b) $8 \times 10^{-2}$ mol dm$^{-3}$, $\lambda_{\text{max}} = 699$ nm and (c) $5 \times 10^{-2}$ mol dm$^{-3}$, $\lambda_{\text{max}} = 680$ nm, Dose rate = 3.4 kGy h$^{-1}$, $[\text{Au}^+] = 2.5 \times 10^{-4}$ mol dm$^{-3}$

5.3.3.4. Mechanism of rod formation

The mechanism of Au nanorod formation is similar to as explained in section 5.2.3.3. The optimized concentration of Ag$^+$ ($6 \times 10^{-5}$ mol dm$^{-3}$) was used in the present study also. In our previous work (section 5.2.3.) under similar conditions of dose rate and precursor concentration, as used in the present study, nanorod formation was not observed and only Au spheres were obtained. There are two major differences between the experimental procedure in the present and the earlier method i.e.,
i) the nature of reducing radical
ii) the presence/absence of Au seed.

It is known that isopropyl radical ($E^0 = -1.5$ V vs. NHE) is milder reducing agent as compared to $e_{\text{aq}}^-$ ($E^0 = -2.9$ V vs. NHE) and H$^+$ ($E^0 = -2.3$ V vs. NHE). The rate constants for the reaction of isopropyl radical with Au$^+$ are not reported in the literature, however with other metal ions such as Ni$^{2+}$, the rate constant ($7.2 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$) for the reaction of isopropyl radical [244] is 50 times lower in magnitude as compared to hydrated electron [245], which
reacts with Ni$^{2+}$ with rate constant equal to $3.5 \times 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$. The Au atom formed upon radiolysis is unstable in the aqueous medium and undergoes coalescence with other Au atoms resulting in the growth of particle. The kinetics of the growth of the particle will depend on the rate at which Au is produced in the system. Since in the present study isopropyl radical used to reduce Au$^{I}$ to Au is expected to react slowly as compared to other reducing radical such as hydrated electron and H·, the rate of growth of particle is slow. Thus by using the milder reducing radical i.e., isopropyl radical the nanorod formation takes place at higher dose rate and in the absence of any seed. This observation supports the role of the kinetics in governing the shape of Au nanoparticles as reported in the literature [225]. In our previous work (section 5.2.3.) the kinetics of formation of nanorods was controlled by reducing the dose rate. At lower dose (0.8 kGy h$^{-1}$) nanorod formation occurred while irradiation at higher dose rate resulted only in the formation of spheres.

![Figure 5.13: TEM image of gold nanorods prepared by the reduction of Au$^{I}$ using isopropyl radical generated by gamma radiolysis](image)

The modified method to synthesize gold nanorods is simpler and more convenient as compared to earlier developed methods. In the earlier method the longitudinal absorption band was positioned at 671 nm at dose rate 0.8 kGy h$^{-1}$ when the precursor Au$^{I}$ concentration was $4 \times 10^{-4}$ mol dm$^{-3}$. In the current method for the same Au$^{I}$ concentration, the longitudinal band has been observed at 701 nm even at a dose rate of 3.4 kGy h$^{-1}$, indicating the formation of longer rod. It is known from the literature that as the length of rod increases, the longitudinal
plasmon band is red shifted [5]. Thus the shift in the longitudinal plasmon band by 30 nm is due to the formation of longer nanorods. This is further confirmed from the TEM image, which is shown in Figure 5.13. From this figure average aspect ratio is calculated as 3 by measuring the length and width of 100 nanorods. In principle the seeds are not required in the radiation method unlike chemical method. In the later case the synthesis of nanorods cannot be achieved without the presence of seeds. In the present method, isopropyl radical generated during radiolysis is reducing in nature and bring the reduction of Au\textsuperscript{I} to atomic Au in the solution unlike chemical method where ascorbic acid cannot reduce Au\textsuperscript{I} to Au\textsuperscript{0}. The Au\textsuperscript{0} formed in the solution undergo coalescence with other atoms that results in the formation of small clusters of Au\textsubscript{n} in the solution. Thus in radiolytic method seeds are generated in-situ and their subsequent growth results in the formation of nanoparticles. The final shape of the particles depends on the rate at which the particle growth takes place. The slower growth rate results in the formation of gold nanorod. The slower kinetic condition is achieved in the present method by using isopropyl radical to bring about the reduction of Au\textsuperscript{I} to Au\textsuperscript{0}. The role of kinetics is also evident from the results obtained when the concentration of precursor Au\textsuperscript{I} is varied as shown in Figure 5.11. The result shows with decreasing Au\textsuperscript{I} concentration, there is an increase in aspect ratio of nanorods. With decreasing concentration of Au\textsuperscript{I}, the rate of formation of Au in the solution is also reduced, which results in the slower growth of nanorod. Thus, when the growth kinetics of rod is slow the material addition takes place more anisotropically that result in longer rod formation. Therefore the kinetics of the rod formation may also be controlled by changing the concentration of precursor Au\textsuperscript{I}.

5.3.3.5. Irradiation in the presence of Au seeds

The effect of addition of Au seeds to the solution prior to irradiation on nanorod formation was investigated. The results are shown in Figure 5.14, wherein the absorption spectrum of irradiated solution recorded in presence and in absence of seeds is presented. As can be seen from this figure, in both the cases nanorod formation takes place, however when seeds are present the absorption spectra is red shifted by 15 nm (\(\lambda_{\text{max}} = 700 \text{ nm}\)) as compared to the one in the absence of seed (\(\lambda_{\text{max}} = 685 \text{ nm}\)). This is because the seeds act as well-defined site for Au atoms formed from radiolytic reduction process, so that the final nanorods become longer and more uniform in size distribution. Whereas, when seeds are not added externally, seeds are generated in-situ by radiolysis of Au\textsuperscript{I}, which is a random process, so that the seeds have
wide size distribution, hence the nanorods formed are shorter as compared with, in presence of seed.

![Graph showing absorbance vs wavelength](image)

**Figure 5.14:** Effect of seed on nanorod formation: (a) in presence of seed \([1.28 \times 10^{-6} \text{ mol dm}^{-3}]\), \(\lambda_{\text{max}} = 700\text{nm}\) and (b) in absence of seed, \(\lambda_{\text{max}} = 685\text{ nm}\), Dose rate = 3.4 kGy h\(^{-1}\), \([\text{Au}^{III}] = 4 \times 10^{-4} \text{ mol dm}^{-3}\)

### 5.3.3.6. A comparison of radiolytic method with chemical method

The radiolytic method for the synthesis of nanorod is carried out in the absence of Au seed whereas in chemical method seeds have necessarily to be added to the system. As known from the literature, the seed solution that is prepared by the reduction of \(\text{Au}^{III}\) by sodium borohydride is stable only for few hours and cannot be used, thereafter, which results in the loss of precious gold metal. Due to the availability of a large number of reactive reducing species and wide range of dose rates, the radiolytic method offers several ways to control the kinetics of the growth process, which cannot be achieved in the chemical method. In radiolytic method since the reactive reducing species are generated in situ, the reaction can be stopped at any stage by simply removing the system from the radiation zone whereas in chemical method does not offer this convenience as reducing agent is added externally and cannot be removed from the system. Thus the radiolytic method reported in this section is very simple, easy and effective way of generating short aspect ratio gold nanorods in a one-
pot. The schematic of generation of Au nanorods by radiolytic and chemical methods have been represented in Figure 5.15 and Figure 5.16 respectively.

Figure 5.15: Cartoon picture depicting one-pot synthesis of gold nanorods through \textit{in situ} generation of Au seeds in gamma radiation method

Figure 5.16: Cartoon picture depicting stepwise synthesis of gold nanorods by external addition of Au seeds in chemical method

5.4. A facile method to synthesize anisotropic plate like gold nanoparticles by combining radiation and chemical methods

The chemical methods for synthesis of gold nanoplates reported in the literature are high temperature polyol methods [246,247] in which Polyols are used as media and also reducing agent. In some other methods polyols are used as media and an appropriate reducing agent is used to reduce gold at higher temperature. The methods include microwave induced [248], UV light induced [249], and electrochemical processes [250] to reduce gold ions. In most of these methods Poly(vinylpyrrolidone) (PVP) is used as a stabiliser. Other than polyols, mild reducing agent, such as ascorbic acid [211] has also been used to reduce gold to achieve gold nanoplates. It is well known that certain reducing agents or stabilisers can control the crystallization of gold, and consequently yield a special form of gold crystals [211]. In this work gold nanoplates have been synthesized by using radiolytically synthesized Au seeds in
one pot. The milder reducing agent like ascorbic acid has been used here to generate Au nanoplates. The morphology and dimension of the Au nanoparticles depend on the concentrations of the seed particles and surfactant, CTAB, in addition to the reactants (Au$_{III}$ and Ascorbic acid) [211].

**5.4.1. Synthesis of Au$^I$ in solution phase**

In order to reduce Au$_{III}$ to Au$^I$, $7.2 \times 10^{-4}$ mol dm$^{-3}$ ascorbic acid was added to yellow colored aqueous solution containing $4 \times 10^{-4}$ mol dm$^{-3}$ of Au$_{III}$, 0.1 mol dm$^{-3}$ CTAB, 0.2 mol dm$^{-3}$ propanol and $6 \times 10^{-5}$ mol dm$^{-3}$ Ag$^+$. After addition of ascorbic acid the solution turned colorless, which indicate reduction of Au$_{III}$ to Au$^I$. Although ascorbic acid was present in excess in the reaction medium, but being a mild reducing agent, it could not reduce Au$^I$ to Au$^0$ in solution. The Au$^I$ obtained by this method was used as a precursor for gold in the synthesis of rectangular gold nanoparticles.

**5.4.2. In situ generation of Au seeds**

The above solution containing Au$^I$ was subjected to gamma irradiation at a dose rate of 3.4 kGy h$^{-1}$. As soon as the reaction medium was exposed to gamma radiation, the reduction of Au$^I$ to Au$^0$ took place by transient species generated from water radiolysis (Equation 5.5 and Equation 5.8).

$$\text{e}^{-}_{\text{aq}} + \text{Au}^I \rightarrow \text{Au}^0 \quad (5.8)$$

Subsequently Au$^0$ atoms coalesce to form Au seeds in situ [101]. The seed particle size was controlled by the high concentration of capping agent CTAB, which does not allow the seed to grow beyond a particular size. By controlling the exposed radiation dose the concentration of seeds in the system can be controlled.

**5.4.3. Synthesis of rectangular plate like gold nanoparticles**

The irradiated solution was kept undisturbed for 2h for subsequent growth of gold nanoparticles. As it is known from the literature, in the presence of Au seed, Au$^I$ gets adsorbed on the surface of seed and the adsorbed Au$^I$ can be reduced by ascorbic acid to atomic Au, which subsequently grows to form nanoparticles. Although the formation of maximum amount of gold nanoparticles was over within 35 minutes after irradiation (confirmed by spectral measurement), for complete conversion the UV–visible spectra were recorded after 2 hour of irradiation.
5.4.4. Results and discussion

5.4.4.1. Spectroscopic and microscopic characterization of Au nanoplates

The anisotropic nature of the gold nanoparticles was confirmed by the presence of two distinct peaks in the visible region of UV-visible spectra of the irradiated sample (Figure 5.17) and from the transmission electron microscopy (TEM) results. The optical properties of anisotropic gold nanoparticles are mainly governed by the longitudinal dipolar mode, i.e., the peak at higher wavelength in the UV-visible spectra.

![Absorbance vs Wavelength](image)

Figure 5.17: Absorption spectra of gold nanoparticle solutions irradiated at various absorption doses: dose (Gy) = (a) 28.3, (b) 56.6, (c) 85, (d) 113.3, (e) 170 for $4 \times 10^{-4}$ mol dm$^{-3}$ Au$^{III}$, $7.2 \times 10^{-4}$ mol dm$^{-3}$ ascorbic acid, 0.1 mol dm$^{-3}$ CTAB, $6 \times 10^{-5}$ mol dm$^{-3}$ Ag$^+$, 0.2 mol dm$^{-3}$ isopropanol and dose rate of 56.6 Gy/min

The TEM picture (Figure 5.18) confirmed the formation of rectangular plate-like gold nanoparticles. The average aspect ratio of these rectangular nanoplates was estimated to be 2.5 by measuring the length and breadth of 100 nanoparticles using ocular lens.
5.4.4.2. Mechanism of formation of gold nanoplates

(i) Formation of Au$^+$

In the presence of an adsorption surface or Au seeds, ascorbic acid can reduce Au$^{III}$ to Au$^+$ and finally to Au$^0$. But in absence of any seed the reduction process stops at Au$^+$ and there is no formation of Au$^0$. Hence, the aqueous solution containing Au$^{III}$ and other reagents as mentioned earlier in the text (section 5.4.1) when mixed with ascorbic acid Au$^+$ species were formed in the solution.

(ii) Formation of seed

In chemical method, seeds have to be added externally to the growth medium, so that Au$^+$ in the solution gets adsorbed on these seeds and gets reduced by ascorbic acid to form nanoparticles. But in radiolytic method due to presence of reactive transient radiolytic species, seeds are generated in situ. The primary radiolytic products of water such as, e$_{aq}^-$, H$^-$ and ·OH in presence of isopropanol ((CH$_3$)$_2$ CH OH) brings about the reduction of Au$^+$ to Au$^0$. The irradiation was carried out for small duration of time to ensure that very low concentration of Au$^0$ are generated in the growth solution and Au$^0$ being unstable coalesce with each other to form Au seeds.

(iii) Formation of nanoplates

The seeds are generated in the solution by gamma irradiation. Immediately after the irradiation is stopped the growth process starts, which is visually observed as the color is
developed in the previously colorless solution. The growth step is similar as in the case of chemical method.

Figure 5.19: Proposed schematic of rectangular plate like gold nanoparticle formation

Figure 5.20: Absorption spectra of (a) growth solution containing AuIII before addition of ascorbic acid, (b) growth solution containing AuI before irradiation. Absorption spectra of gold nanoparticle solutions, kinetics of growth of particles: time (in minutes) = (c) 15, (d) 20, (e) 25, (f) 30, (g) 35, (h) 45, (i) 65, for 4 x 10^{-3} mol dm^{-3} AuIII, 7.2 x 10^{-4} mol dm^{-3} ascorbic acid, 0.1 mol dm^{-3} CTAB, 6 x 10^{-5} mol dm^{-3} Ag^{+}, 0.2 mol dm^{-3} isopropanol and absorption dose of 56.6 Gy

The AuI get adsorbed on the seeds and the ascorbic acid present in the solution reduces these adsorbed AuI to Au0. Though the exact mechanism of growth of nanoplates has not been clearly understood, it is proposed that the cationic surfactant CTAB forms a bilayer template as in case of nanorods formation, so that the addition of new Au0 atoms progress in the open
ends of this bilayer to form rectangular shaped gold nanoparticles as shown in the Figure 5.19. The final shape of nanoparticle depends on the nature of seed particles and the facets present in the seeds. The progress of nanoplates growth was monitored to find the time for completion of the reaction. In Figure 5.20, the spectrum at 394 nm (Figure 5.20a) disappeared after addition of ascorbic acid (Figure 5.20b) indicating the reduction of Au$^{III}$ to Au$^{I}$ by ascorbic acid. The growth of nanoparticles was monitored after gamma irradiation, which is shown in Figure 5.20. Within 15 minutes after irradiation the rectangular nanoplates are formed, after that their concentration increases with time and the particle formation saturates in 35 min.

5.4.4.3. Effect absorption dose

As mentioned earlier the seeds are generated by irradiating the growth solution. The absorbed dose was varied by varying the irradiation time. The concentration of the seeds was controlled by controlling the absorbed dose. The effect of dose on nanoplate formation is shown in Figure 5.17. for dose of 56.6 Gy, the longitudinal spectrum is narrower suggesting there is a narrow distribution of the size of gold nanoparticles.

5.4.4.4. Effect of ascorbic acid concentration (AA/Au$^{III}$)

This may be due to uniformity in the size of seeds formed at this dose. For dose less than this value, the concentration of seeds produced is very low, which affects the final concentration of nanoparticles, resulting in lower longitudinal absorbance value.

Figure 5.21: Absorption spectra of gold nanoparticle solutions for different ascorbic acid/Au$^{III}$: (a) AA/Au$^{III}$ = 1.6, (b) AA/Au$^{III}$ = 1.8 and (c) AA/Au$^{III}$ = 2, for $4 \times 10^{-4}$ mol dm$^{-3}$ Au$^{III}$, 0.1 mol dm$^{-3}$ CTAB and 0.2 mol dm$^{-3}$ isopropanol and absorption dose of 56.6 Gy
As the dose increases from 56.6 Gy the longitudinal peak gets broadened due to wide size distribution of Au nanoparticles, because the sizes of seeds are not uniform. Hence in all other experiments the seed concentration corresponding to the absorption dose of 56.6 Gy is chosen. The effect of ascorbic acid concentration on Au nanoparticle formation is shown in Figure 5.21. It is more convenient to express this factor in terms of AA/ Au\textsuperscript{III} ratio. Ascorbic acid is a two hydrogen donor reducing agent. Hence for complete conversion of Au\textsuperscript{III} to Au\textsuperscript{0}, (AA/Au\textsuperscript{III}) should be more than 1.5. Here it has been observed from Figure 5.21, at least AA/Au\textsuperscript{III} = 1.8 is required to get good uniformity in the particle size distribution, which is seen from narrower longitudinal peak in Figure 5.21b.

5.4.4.5. Effect of Au\textsuperscript{III} concentration

As the Au\textsuperscript{III} concentration increases from $1.06 \times 10^{-4}$ to $1.0 \times 10^{-3}$ mol dm\textsuperscript{-3} the longitudinal spectra in (Figure 5.22) blue-shift from 843 to 650 nm, which is an indication of shorter aspect ratio gold nanoplates formation for higher concentration of Au\textsuperscript{III} precursor ion.

![Figure 5.22: Absorption spectra of gold nanoparticle solutions, Au\textsuperscript{III} concentration variation: (a) $[\text{Au}^{\text{III}}] = 1.06 \times 10^{-4}$ mol dm\textsuperscript{-3} (b) $[\text{Au}^{\text{III}}] = 2.55 \times 10^{-4}$ mol dm\textsuperscript{-3}, (c) $[\text{Au}^{\text{III}}] = 4 \times 10^{-4}$ mol dm\textsuperscript{-3}, (d) $[\text{Au}^{\text{III}}] = 4.9 \times 10^{-4}$ mol dm\textsuperscript{-3}, (e) $[\text{Au}^{\text{III}}] = 5.96 \times 10^{-4}$ mol dm\textsuperscript{-3} and (f) $[\text{Au}^{\text{III}}] = 1 \times 10^{-3}$ mol dm\textsuperscript{-3}, for 7.2 $\times 10^{-4}$ mol dm\textsuperscript{-3} ascorbic acid, 0.1 mol dm\textsuperscript{-3} CTAB, 6 $\times 10^{-5}$ mol dm\textsuperscript{-3} Ag\textsuperscript{+}, 0.2 mol dm\textsuperscript{-3} isopropanol and absorption dose of 56.6 Gy]
This result is in agreement with the results reported by Murphy et al. [88], wherein the authors suggested that the kinetics of addition of Au\textsuperscript{I} to the growing seeds governs the shape and size of the nanoparticles. In the present work as the Au\textsuperscript{III} concentration increases the kinetics of growth of nanoparticles also increases. It has been reported earlier (section 5.2, 5.3) that slower the kinetics, better the anisotropic growth. Hence at higher Au\textsuperscript{III} concentration shorter aspect ratio nanorods have been formed. The anisotropic gold nanoparticles have been synthesized by several researchers by taking low concentration of Au\textsuperscript{III} precursor ion [213,88,236], as at high concentration only nanospheres have been observed. But in this work even at $1.0 \times 10^{-3}$ mol dm\textsuperscript{-3} of Au\textsuperscript{III} concentration anisotropic nanoparticles are formed.

5.4.4.6. Effect of AgNO\textsubscript{3} concentration

Silver nitrate plays a very important role in controlling the shape of nanoparticles and also it affects the nanoparticle yield [92]. From Figure 5.23, in absence of AgNO\textsubscript{3}, only the transverse band (Figure 5.23a) is present in the spectrum, hence only spheres are formed.

![Figure 5.23: Absorption spectra of gold nanoparticle solutions, AgNO\textsubscript{3} concentration variation: (a) No [Ag\textsuperscript{+}], (b) [Ag\textsuperscript{+}] = 1 \times 10^{-5} mol dm\textsuperscript{-3}, (c) [Ag\textsuperscript{+}] = 3 \times 10^{-5} mol dm\textsuperscript{-3}, (d) [Ag\textsuperscript{+}] = 6 \times 10^{-5} mol dm\textsuperscript{-3}, (e) [Ag\textsuperscript{+}] = 8 \times 10^{-5} mol dm\textsuperscript{-3}, (f) [Ag\textsuperscript{+}] = 1 \times 10^{-4} mol dm\textsuperscript{-3} and (g) [Ag\textsuperscript{+}] = 3 \times 10^{-4} mol dm\textsuperscript{-3}, for 4 \times 10^{-5} mol dm\textsuperscript{-3} Au\textsuperscript{III}, 7.2 \times 10^{-4} mol dm\textsuperscript{-3} ascorbic acid, 0.1 mol dm\textsuperscript{-3} CTAB, 0.2 mol dm\textsuperscript{-3} isopropanol and absorption dose of 56.6 Gy]
When a small amount of AgNO$_3$ was added to the system the longitudinal band started to develop, and with increase in AgNO$_3$ concentration upto $8 \times 10^{-5}$ mol dm$^{-3}$ this band gradually red-shifts to 839 nm indicating increase in aspect ratio of gold nanoparticles. Above this concentration, the spectrum deforms (Figure 5.23f), so this is not a favorable condition for well defined nanoplate formation. The role played by Ag$^+$ in the synthesis of anisotropic Au nanoparticle is similar as explained in section 5.2.3.3. Also in chemical method Sau et al. reported that with further increase or decrease of Ag$^+$ concentration from a particular value affects the anisotropic growth due to change in kinetics of growth [212].

5.4.4.7. Effect of CTAB concentration

The variation of CTAB concentration is shown in Figure 5.24. For 0.1 mol dm$^{-3}$ CTAB concentration the plasmon band is well defined and narrower. Below this concentration the spectrum deforms indicating wide distribution in shape of the nanoparticles at lower CTAB concentration [212]. Hence CTAB concentration below 0.1 mol dm$^{-3}$ was unsuitable for formation of rectangular plate like gold nanoparticles.

![Absorption spectra of gold nanoparticle solutions, CTAB concentration variation](image)

**Figure 5.24**: Absorption spectra of gold nanoparticle solutions, CTAB concentration variation: (a) [CTAB] = 0.1 mol dm$^{-3}$, (b) [CTAB] = $7 \times 10^{-2}$ mol dm$^{-3}$, (c) [CTAB] = $5 \times 10^{-2}$ mol dm$^{-3}$, for $4 \times 10^{-4}$ mol dm$^{-3}$ Au$^{III}$, $7.2 \times 10^{-4}$ mol dm$^{-3}$ ascorbic acid, $6 \times 10^{-5}$ mol dm$^{-3}$ Ag$^+$, 0.2 mol dm$^{-3}$ 2-propanol and absorption dose of 56.6 Gy
5.4.4.8. PH effect

The pH was adjusted by using HCl and NaOH to growth solution before irradiation and the UV-visible spectra of nanoparticle solution at different pH has been shown in Figure 5.25. The natural pH of the growth solution is 3.24. For pH > 3.24, the solution instantly turns pink, which is an indication of sphere formation. The reason may be for pH more than 3.24 the reducing property of ascorbic acid changes [251]. At pH lower than 3.24 the system shows irregular spectral behaviour and for pH=1.56 the spectrum almost disappears probably due to presence of Cl\(^-\) from HCl. It is reported in the literature that Cl\(^-\) adversely affects the formation of anisotropic nanoparticle formation [252].

![Absorption spectra of gold nanoparticle solutions. pH effect: pH = (a) 3.24 (natural pH of the solution), (b) 2.58, (c) 2.33, (c) 2.01 and (d) 1.56, for 4 x 10\(^{-4}\) mol dm\(^{-3}\) Au\(^{III}\), 7.2 x 10\(^{-4}\) mol dm\(^{-3}\) ascorbic acid, 0.1 mol dm\(^{-3}\) CTAB, 6 x 10\(^{-5}\) mol dm\(^{-3}\) Ag\(^+\), 0.2 mol dm\(^{-3}\) isopropanol and absorption dose of 56.6 Gy](image)

Figure 5.25: Absorption spectra of gold nanoparticle solutions. pH effect: pH = (a) 3.24 (natural pH of the solution), (b) 2.58, (c) 2.33, (c) 2.01 and (d) 1.56, for 4 x 10\(^{-4}\) mol dm\(^{-3}\) Au\(^{III}\), 7.2 x 10\(^{-4}\) mol dm\(^{-3}\) ascorbic acid, 0.1 mol dm\(^{-3}\) CTAB, 6 x 10\(^{-5}\) mol dm\(^{-3}\) Ag\(^+\), 0.2 mol dm\(^{-3}\) isopropanol and absorption dose of 56.6 Gy

5.5. Conclusions

In summary, the present study demonstrated that CTAB-capped anisotropic gold nanoparticles with novel and controllable sizes and shapes, such as rods (varying aspect ratio) and plates could be synthesized using radiolytic synthesis route. A simple, one-pot, seed-less
method for synthesizing anisotropic gold nanoparticles, such as nanorods and nanoplates has been developed by using gamma irradiation technique. By proper choice of dose rate and precursor concentration and/or nature of reducing radical the gold nanorods can be synthesized in aqueous media. By combining both radiolytic and chemical method to synthesize rectangular gold nanoparticles in one-pot external addition of seed have been successfully avoided.