Gold nanorods: Synthesis and modulation of optical properties

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Abstract

Gold nanorods are increasingly becoming popular due to their potential in the field of biotechnology, photonics and optoelectronics. They display optical extinction which can be tuned from visible to infra red region of the electromagnetic spectrum just by changing the aspect ratio (ratio of length to width). However, synthesis of gold nanorods of desired aspect ratio by chemical method is a challenging task. Numerous parameters involved in the synthesis makes the control of the aspect ratio rather difficult. It is also important to reduce the percentage of spherical nanoparticles formed as a byproduct. We have investigated the effect of all the parameters involved in the synthesis of nanorods on the longitudinal plasmon band and its tunability. Also, transformation of gold nanorods to peanut like shape was observed when they were subjected to different pH environments. The mechanism of this shape transformation is explained in detail.

Keywords: gold nanorods, optical properties, seed mediated growth, pH, shape transformation

Metal nanoparticles offer a wide area of application owing to their size and shape dependent optical properties [1]. Recently, there has been significant interest in gold nanorods due to their potential application in the field of biomedical imaging, photo thermal therapy and optoelectronics [2]. Gold nanorods exhibit two different absorption bands namely transverse and longitudinal plasmon band corresponding to oscillation of electrons along the width and length of nanorods when electromagnetic radiation is incident on them. The position of longitudinal plasmon band can be shifted towards infra red region by changing the aspect ratio of nanorods. Gold nanorods of different aspect ratios have been synthesized by various techniques with considerable success [3, 4]. Aspect ratio of gold nanorods is found to be extremely sensitive to nucleation conditions which are further dependent on large number of experimental parameters involved in the seed mediated synthesis.

We have synthesized gold nanorods in aqueous solution by seed mediated growth method and studied the dependence of longitudinal plasmon band on various experimental parameters like temperature, pH, amount of seed, ageing of seed, and other experimental conditions. Apart from these, we observe a strong modulation of optical properties of pristine gold nanorods on addition of KOH in different amounts [5]. Significant blue shift in the absorption spectra was observed on increasing the amount of KOH with the effect being maximum for the rod having highest aspect ratio. We attribute the blue shift in the absorption spectra to the pH dependent shape transformation of gold nanorods and the mechanism is explained in detail. A slight change in the shape of gold nanorod can lead to significant changes in their optical absorption spectrum. Therefore, there is a need to study the shape transformations of gold nanorods by various methods so as to ensure their optical and mechanical stability for applications in sensors or optoelectronic devices.

Experimental

Gold nanorods of different aspect ratios were synthesized by seed mediated growth method. The seed mediated growth method [3] consists of two steps: 1) Formation of spherical nanoparticles of size 3-4 nm and 2) growth of these particles in a growth solution which contains a surfactant, week reducing agent, silver nitrate.

Spherical gold nanoparticles (seed): Five milliliters of 0.2 M CTAB solution was mixed with 5 ml 5×10^{-4} M $HAuCl_4$. This solution was stirred, and 0.6 ml of 0.01 M ice-cold $NaBH_4$ was added to it all at once. Vigorous stirring of the solution was continued for 2 min.

Growth solution: Three samples, A, B, and C, were prepared by addition of 0.2, 0.25, and 0.3 ml of 0.004 M $AgNO_3$ solution, respectively, to a mixture of 0.2 M CTAB and 0.15 M benzyl dimethyl hexadecyl ammonium chloride. To these solutions, 5 ml of 1×10^{-3} M $HAuCl_4$ was added followed by a gentle mixing of the solution and addition of 70 µl of 7.88×10^{-2} M ascorbic acid in each case. Addition of ascorbic acid changed the color of the growth solutions from dark yellow to colorless. Finally, 12 µl of seed solution was added and the solutions were left undisturbed for 24 hours.

Characterization

Absorption measurements were carried out with a Perkin Elmer (Lambda 950) UV-Vis-NIR spectrometer. pH of the solutions were recorded with MFRS Toshniwal Inst CL 54 pH meter. Transmission Electron microscopy images were obtained using a JEOL 1200 EX instrument.

Results and discussion

Synthesis of gold nanorods by various methods is well documented [3]. These methods include electrochemical method, seed mediated growth method, synthesis in alumina membranes etc. Out of these, seed mediated growth method is most popular because maximum tunability of longitudinal plasmon band can be achieved.

As mentioned in the experimental section, seed mediated growth method comprises of two steps viz. formation of seed nanoparticles and growth of these seeds in a growth solution. Seed solution is usually aged for 5 minutes after the preparation and then added to the growth solution. The growth solution consists of more precursors of gold, CTAB and sometimes a cosurfactant BDAC, silver nitrate and a week reducing agent ascorbic acid.

When the seed nanoparticles are put into the growth solution, they start growing. CTAB has more affinity towards {110} facets of gold nanoparticles. As they grow, CTAB starts preferentially adsorbing on side facets (i.e. {110}) of particles due to which growth is restricted along that direction. This leads to development of rod like structures.

Effect of ageing of seed solution: Absorption spectrum of seed solution taken immediately after preparation showed slight hump at 530 nm indicating the formation of very small (3-4 nm). On keeping this solution for several hours, increase in the intensity of peak was observed along with the narrowing of size distribution which indicated the formation of bigger sized particles by Oswald ripening. As the particle grows, it develops certain crystal facets, which determines the final shape of the nanoparticles. Some of these crystal facets can be selectively

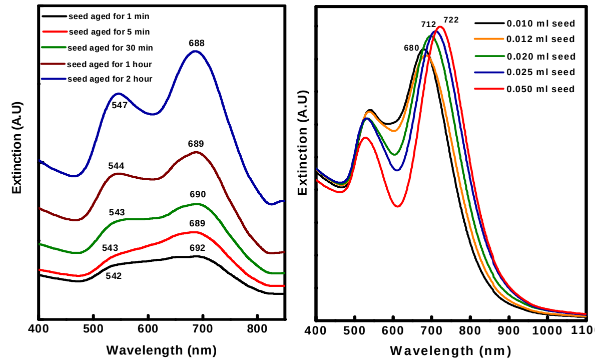

Fig. 1: Effect of (a) seed ageing and (b) amount of seed volume on longitudinal plasmon band

capped so that the particle acquires a particular shape. Hence it is very important to add seed solution after certain period of time in order to avoid the side effects which include formation of large sized particles with arbitrary shape. Fig. 1a shows absorption spectrum of different solutions of gold nanorods synthesized by varying the ageing period of seed. Seed solutions aged for 1, 5, 30, 60 and 120 minutes were added to different growth solutions. Absorption spectra of these growth solutions were recorded after 24 hours. It is clearly observed from the figure that the transverse and longitudinal plasmon band were more distinct and resolved in case of growth solution with seed aged for 2 hours. Intensity of longitudinal plasmon bad increased on increasing the ageing period of seed solution without much change in the peak position of longitudinal plasmon band. However, if the seeds were aged for longer time (not shown in the fig), only one peak was observed at 530 nm indicating the formation of spherical nanoparticles. This can be attributed to the fact that on increasing the ageing period beyond 2 hours, the particle no more has relatively unstable {110} facets, which are responsible for rod formation. Also, for very small ageing period viz. 1 or 2 minutes two peaks are not well resolved. The reason for this could be the incomplete decomposition of $NaBH_4$ within one or two minutes and this ultimately can lead to new nucleation of gold particles when added into the growth solution forming spherical particles along with rod like shapes.

Amount of seed solution: Amount of seed solution was varied from 10 to 50 µl. Fig. 1b shows the effect of increasing the amount of seed solution on the longitudinal plasmon band. In this case seed solution was aged for 5 minutes. The longitudinal plasmon band was found to shift towards higher wavelength on increasing the amount of seed solution. The effect of amount of seed solution on aspect ratio of nanorods is rather controversial. It is expected that increasing the amount of seed solution should lead to shift of the plasmon band towards lower wavelengths due to a decrease in the aspect ratio. Since more number of seed particles is available for growth to form nanorods, the gold from the precursor will reduce on different seed particles rather than already growing rod like particles leading to decrease in the length of the nanorod and hence decrease in the aspect ratio. However, this is not observed in our case. On increasing the amount of seed solution from 10 to 50 µl longitudinal plasmon band shifted from 680 to 722 nm i.e red shift is observed. This indicates an increase in the aspect ratio. The reason could be that on increasing the seed solution, although length of the particle decreases, width decreases further, ultimately causing increase in the aspect ratio and hence the longitudinal plasmon band shifts towards higher wavelength.

Amount of silver nitrate: This factor was found to be most crucial in tuning the longitudinal plasmon band. El-Sayed et al [3] have achieved wide tunability in the absorption band by using silver nitrate. Silver nitrate assists in binding of CTAB to {110} facets of gold nanorods. It is suggested that Ag precipitates on {110} facet of gold nanorods thereby restricting the growth along that direction and formation of rod like structure. The Ag ion decreases the charge density on bromide ion. This leads to decrease between the neighboring CTAB molecules and hence template elongation leading to an increase in the aspect ratio and red shift in the longitudinal plasmon band. We could tune the longitudinal plasmon band from 720 to 900 nm (fig. 2) by varying the amount of silver nitrate from 0.25 to 0.5 ml.

pH and temperature: pH and temperature of growth solution was varied in order to observe the effect on longitudinal plasmon band (Fig. 3a). Rod formation was observed only in acidic pH. At basic pH, only one peak at 530 nm was observed indicating the formation of spherical nanoparticle. On increasing the pH, reducing power of ascorbic acid increases. This causes reduction of Ag ions to metallic silver which no longer assists in formation of rods.

On increasing the temperature of growth solution, stability of CTAB bilayer reduces causing gradual decrease in the intensity of longitudinal plasmon band (Fig. 3b). This was accompanied by an increase in the intensity of transverse plasmon band. Formation of gold nanorods requires quiescent growth conditions i.e the process is kinetically controlled. Increase in the temperature leads to the enhancement of the rate of reaction and hence does not favor the formation of nanorod of desired aspect ratio.

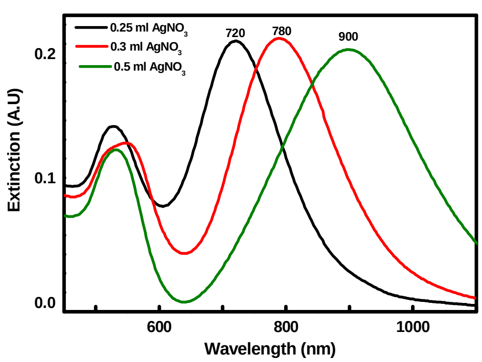

Fig. 2: Effect of amount of silver nitrate on longitudinal plasmon band

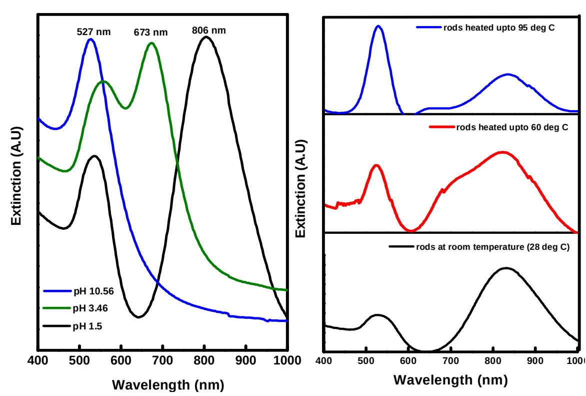

Fig 3: Effect of a) pH and b) temperature on longitudinal plasmon band

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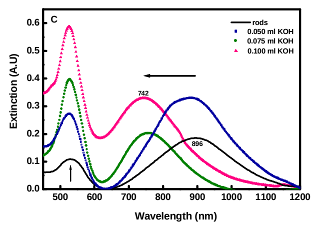
Modulation of optical properties of gold nanrods on addition of KOH:

Once the condition for formation of nanorods of desired aspect ratio was optimized, their behavior in different pH environments was studied [5]. Nanorods having longitudinal plasmon band at 896 nm was chosen (Fig. 4). The nanorods were not separated from growth solution in this case. Molarity of $HAuCl_4$ and $AgNO_3$ in the growth solution is such that it contains unreacted gold and silver ions in the solution. On adding different amounts of KOH, strong shift in longitudinal plasmon band towards lower wavelength along with an increase in the intensity of transverse plasmon band was observed. TEM images (Fig 4) of gold nanorods before and after addition of KOH is shown. A transformation in the shape of gold nanoparticles from rods to peanut like structure is observed.

The shape transformation of gold nanorods in the presence of growth solution has been explained in detail [5]. The side facets of gold nanorods are completely covered with a bilayer of CTAB. The amine group in the outer layer is protonated. Addition of KOH changes the pH of the solution. With increase in pH up to 7 there is an increased probability of ion pair formation between OH^- ions and CTA^+ ions leading to less coverage of gold nanorods by CTAB. At basic pH, reducing power of ascorbic acid increases. It has been reported [6] that during the synthesis of gold nanorods, all the gold and silver atoms in the growth solution are not reduced. Therefore, at high pH (above 7), unreacted gold and silver ions in the growth solution get reduced and deposit on the gold nanorod surface which is already less protected by CTAB. Since ends of the rods are less protected as compared to side faces (preferential binding of CTAB towards {110} facets), faster deposition of unreacted gold ions takes place on {111} facets at the ends at high pH. This could lead to a shape transition of gold nanorods into peanut or dumbbell like structure, ultimately causing decrease in the aspect ratio and blue shift in the absorption spectra. Blue shift in the absorption spectra is also accompanied by an increase in the intensities of transverse plasmon band as compared to the longitudinal plasmon band possibly indicating an increase in the width. Increase in the width of the particle leads to decrease in the aspect ratio of rods. It has been well established that absorption maximum of longitudinal plasmon band decreases linearly with the decrease in aspect ratio [7]. For very high pH values (~ 10-12), again a red shift in the spectra are observed which could be due to complete removal of CTAB, leading to aggregation of gold nanorods as irregular structures. In this case, longitudinal absorption maximum of gold nanorods can again slightly red shift.

Since response of gold nanorods to factors like changes in refractive index, pH, aggregation etc are being used for sensing various analytes, it becomes important to note that pH dependent shape transformations of gold nanorods can be a very effective tool in this regard. This study can be very helpful in monitoring the bimolecular or enzymatic reactions which exhibit pH changes, especially acidic to basic transition.



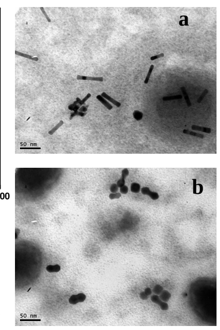


Fig. 4: Vis-NIR absorption spectra for rods with SPl band at 896 nm and TEM images of nanorods (a) before and (b) after addition of 100 µl KOH

Conclusions

Dependence of plasmon band of gold nanorods on various parameters was studied using UV-Vis spectrometer. Plasmon absorption maximum of gold nanorods was found to depend on the temperature, pH, amount of seed solution, ageing period of seed solution and amount of silver nitrate. Modulation in optical properties of gold nanorods was done on addition of different amounts of KOH. The effect was attributed to the shape transformation of gold nanrods due to change in pH.

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