

Pulsed laser excitation of phosphate stabilised silver nanoparticles

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Abstract. Laser flash photolysis studies were carried out on two types of silver nanoparticles prepared by γ -radiolysis of Ag^+ solutions in the presence of polyphosphate as the stabiliser. Type I silver nanoparticles displayed a surface plasmon band at 390 nm. Type II silver nanoparticles showed a 390 nm surface plasmon band with a shoulder at 550 nm. On photoexcitation in the surface plasmon band region, using 35 picosecond laser pulses at 355 nm and 532 nm, the type II solutions showed transient bleaching and absorption signals in the 450–900 nm region, which did not decay appreciably up to 5 nanoseconds. These transient changes were found to get annealed in the interval t where $5 \text{ ns} < t < 100 \text{ ns}$. Extended photolysis of the nanoparticle solutions with repetitive laser pulses resulted in a decrease in the values of the average particle size which were measured by employing the dynamic light scattering technique.

Keywords. Pulsed laser excitation; silver nanoparticles; surface plasmon band; sodium polyphosphate stabilizer.

1. Introduction

Nanoparticles, representing the transition region between individual atom/molecule and bulk material have been attracting considerable research input, owing to some unique physical and chemical properties which they exhibit. Colloids and nanoparticles of silver are one of the most widely studied and well characterised metal systems due to the high stability of the silver nanoparticles (SNP)¹. The silver nanoparticles give transparent aqueous solutions characterised by a strong surface plasmon band (SPB) at $\approx 390 \text{ nm}$ in the optical absorption spectrum². The presence of the SPB gives a convenient handle for the spectroscopic investigations on the metal nanoparticles. The position and shape of SPB of SNPs is strongly dependent on their size, chemical environment of the dielectric media and the nature of the species adsorbed on particle surfaces^{3–5}. SNPs also have large electric fields³. Metal NPs exhibit excellent photochemical activity due to their high surface/volume ratio and unusual electronic properties^{6–10}. Photochemical effects on SNPs have been investigated by a number of workers^{6–10}. Henglein and coworkers^{5,6} have observed the photochemical dissolution of SNPs when photoejected electrons are

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scavenged by N_2O . The excitation of SPB of silver and gold NPs has been studied recently by the femtosecond (fs) transient absorption technique^{8,9}. These results show that plasmon resonance on photoexcitation is created in ~ 150 fs and subsequent relaxation processes occur by electron–phonon interactions and phonon cooling mechanism via phonon–solvent interactions in 2 and ~ 40 picoseconds (ps) respectively. Transient absorption studies of Ahmadi and coworkers show that the SPB bleaches and a new broad and weak absorption appears at > 600 nm for gold NPs, with both absorptions decaying in the ps time-scale⁹. Kamat *et al* have prepared silver NPs by the chemical reduction method and excited with 18 ps pulses at 355 nm and observed the bleaching of the SPB with rise in the absorption in the red region which was attributed to the photoejection of electrons¹⁰. They interpret their results in terms of breaking the bigger NPs (40–60 nm) into smaller ones (5–20 nm). Wavelength dependence of size selectivity for fragmentation was also seen by them. The weak broad absorption band at > 600 nm has been attributed by these workers to hydrated electrons (e^-_{aq}). Similar fast relaxations by electron–phonon coupling have also been seen at metal films and metal–quartz interfaces¹¹. Recently some work has also been reported on the shaping of the NPs by laser irradiation by Takami *et al*¹².

The present study is carried out with the following considerations. Nanoparticles prepared in a liquid environment would be generally associated with other ionic or neutral species present in the form of a stabilizer, complexing agent, etc. Surface modifications of silver particles by different additives have been studied in the past¹³. It is conceivable that the method of preparation of the nanoparticles could influence the relaxation process following the photoexcitation of the particles in the SPB. Roberti *et al* have prepared SNP by reduction of AgNO_3 with NaBH_4 ⁸. Kamat *et al* have used the method of reduction of AgClO_4 by sodium citrate¹⁰. We generated SNP by gamma-irradiation of aqueous AgClO_4 solutions using polyphosphate as the stabilizer^{14–17}. The polyphosphate was shown to be somewhat unique as the stabilizer, in that in addition to stabilizing the metallic clusters of silver, showing the normal SPB absorption, it could also generate under certain experimental conditions, silver clusters of low nuclearity with optical absorptions below 380 nm, having stability up to ~ 1 h. It was of interest to study transient effects following the photoexcitation of polyphosphate stabilized SNPs, employing our flash photolysis system with 35 ps, 355/532 nm laser pulses. In the present work, we also studied the effect of laser irradiation, with repetitive pulses, on the long-term changes in the particle size of the SNPs.

2. Experimental

SNPs were prepared in aqueous solutions of AgClO_4 containing 2-propanol (PrOH) and sodium polyphosphate $[(\text{NaPO}_3)_6:(\text{PP})]$ using the technique of γ -radiolysis^{14–17}. A cobalt-60 gamma-source with a dose rate 12 Gy/min was used for this purpose. The ground state absorption spectra were recorded with a Shimadzu model 160-A UV-visible spectrophotometer. Characterisation of particles was carried out using a Brookhaven Instruments model BI-900 particle size analyser based on the principle of dynamic light scattering (DLS). Picosecond flash photolysis studies were carried out using either the 2nd or 3rd harmonic (10 mJ at 532 nm and 2 mJ at 355 nm) output of a Nd-YAG laser having 35 ps pulse duration. Transient absorptions were monitored using the pump and probe technique with the continuum, generated in the range 450–900 nm by focussing residual 1064 nm light on to a cell of $\text{H}_2\text{O}:\text{D}_2\text{O}$ (1:1), as the probe. The spectra were

recorded by a dual diode array based optical multichannel analyser¹⁸⁻²⁰. Solutions were deoxygenated by N₂-bubbling and flowed through a suprasil quartz flow cell (1 cm × 1 cm) and (1 cm × 0.2 cm) during the flash photolysis experiments. Nanosecond flash photolysis experiments in nanosecond time domain have been carried out using the same picosecond Nd: YAG laser for excitation and a tungsten filament lamp as the analysing light source coupled with a Bausch and Lomb monochromator, photomultiplier (Hamamatsu, R-428) and a digital oscilloscope (TDS-540, Tektronics)²⁰.

3. Results and discussion

3.1 Preparation and characterisation of Ag nanoparticles

When N₂-purged aqueous solutions of AgClO₄ containing 0.1 mM PP and 1.0 mM PrOH were irradiated by γ -rays at different times, the optical density (OD) at 390 nm due to SPB increased, reached saturation and then slightly decreased. The radiation dose was optimized to give enough OD at the desired wavelengths (355/532 nm) to carry out flash photolysis experiments. Two Ag⁺ ion concentrations and irradiation times were optimised ((I) 0.1–0.2 mM Ag⁺, 10 min and (II) 0.5 mM Ag⁺, 20 min) and these are henceforth referred to as type I and type II solutions. The absorption spectra of the surface plasmons obtained in these solutions are given in figures 1a, b, respectively. Spectra from golden-yellow coloured type I solutions are nearly Gaussian without shoulder and are comparable to those reported by Roberti *et al*⁸.

Type II solutions displayed reddish-brown colour and had a shoulder in the SPB at ~ 550 nm in addition to the absorption maximum at 390 nm. In the absence of oxygen

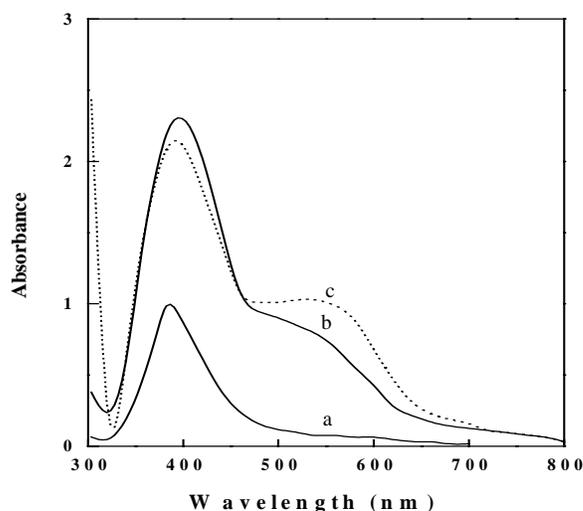


Figure 1. Ground state optical absorption spectra of silver nanoparticles produced on γ -radiolysis of aqueous solutions. The absorbance values are normalised for path length = 1.0 cm. Initial composition of solutions and duration of gamma irradiations: (a) 0.1 mM AgClO₄, 0.1 mM polyphosphate and 1 mM iso-propanol, 10 min irradiation (type I solution); (b) 0.5 mM AgClO₄, 0.5 mM polyphosphate and 5 mM iso-propanol, 20 min irradiation (type II solution); (c) addition of 10% (v/v) acetone to the radiolytically prepared type II solution (b).

they were stable for 4–5 days. When exposed to ambient air the reddish-brown solutions were stable for at least a day. It may be mentioned here that the experimental conditions were somewhat critical for the stability of the solutions. It was found that the reddish-brown solutions turned pale yellowish-green and ODs at 550 nm decreased at higher γ -doses. The yellowish-green solutions were found to be unstable and precipitation started in a few hours. Skillman and Berry have measured the absorption spectra of SNP produced in gelatin by photographic exposures and concluded that only one band (~ 390 nm) is apparent for nearly spherical particles²¹. Mode splitting occurs for elongated particles with one band moving towards the red region and the other slightly towards the blue. For average axial ratio (a/b) ~ 2.5 they observed that the red band appears at ~ 800 nm. On comparison with these results, it can be extrapolated in the present case that for type II solutions the a/b ratio is ~ 2 ^{21,22}. All the experiments were carried out on freshly prepared SNPs.

Particle size determinations were carried out in terms of volume average size employing the dynamic light scattering (DLS) technique. The solutions were filtered through 0.2 micron size filters to eliminate dust particles or microcrystals thrown out of the solution, if any, before taking the DLS measurements. Before the γ -radiolysis however, the solutions did not give any measurable photon counts and hence did not contain particles with diameters > 6 nm; which was the minimum resolution of the unit. The estimated volume average sizes were ~ 49 nm for type I and ~ 78 nm for type II solutions (table 1). Type II solutions clearly have larger particles as compared to type I solutions. It may be noted that the particle size measurements by DLS show larger particle diameters for a similar plasmon band spectrum, as compared to those by transmission electron microscopy (TEM) measurements⁸. This could be due to the fact that samples for TEM are evaporated to dryness and measured particle sizes are for bare metal particles. In contrast, DLS measures translational diffusion coefficient which is dependent on the solvation shell around the nanoparticle which possibly includes the stabilizer molecules and hence is expected to give higher values for the particle sizes. In another work, Yamamoto *et al* prepared SNP by the reduction of aqueous AgNO_3 in presence of

Table 1. Volume average size of silver nanoparticles before and after irradiation with laser pulses to a circulating 50 ml volume of SNP solution. Laser wavelength = 355 nm; energy per pulse = 4 mJ.

Solutions [Ag ⁺] ₀ *	Before laser irradiation		After laser irradiation		
	Vol. average size [#] (nm)	Width of distribution [#] (nm)	Vol. average size [#] (nm)	Width of distribution [#] (nm)	Number of pulses
Type I (0.1mM)	68	51	39	22	9000
Type I (0.2mM)	49	37	29	28	9000
Type II (0.5mM)	78	75	31	20	12000

*Silver ion concentration before γ -irradiation; [#]accuracy of measurement in volume average size and width of distribution determinations in the present set of experiments is $\pm 5\%$.

NaBH_4 ²³. They measured the particle size using the DLS technique as 64 nm which is close to the DLS value for the particles prepared by us. However, in the work of Roberti *et al*⁸, the TEM values for the particle sizes were only ~ 10 nm, although their method for preparing the SNPs was similar to those of Yamamoto *et al*. The band widths of the SPB for the type I particles prepared by our method were comparable to those obtained by Roberti *et al*, suggesting similarities in the particle sizes as well.

3.2 Transient changes upon flash photolysis

Flash photolysis studies were carried out with type II solutions, having higher absorbance values as compared to the type I solutions, at the excitation wavelengths (namely 355 and 532 nm, see figure 1). On excitation with 35 ps pulses of 532 nm, in the shoulder region of the SPB, a strong bleaching signal in the spectral region of 450–600 nm and a weak absorption band in the region 600–900 nm were seen at ‘zero’ ps delay (i.e. immediately after the pulse). There was no detectable bleach recovery on increasing the delay to 5 ns of the upper limit in our pump and probe technique (see figure 2a – 1). However, by employing the nanosecond adaptation of our detection system (see §2), it was observed that the bleaching was completely recovered at 100 ns after the 35 ps pulse. The persistence of bleaching in the interval $5 \text{ ns} < t < 100 \text{ ns}$ is an additional feature that

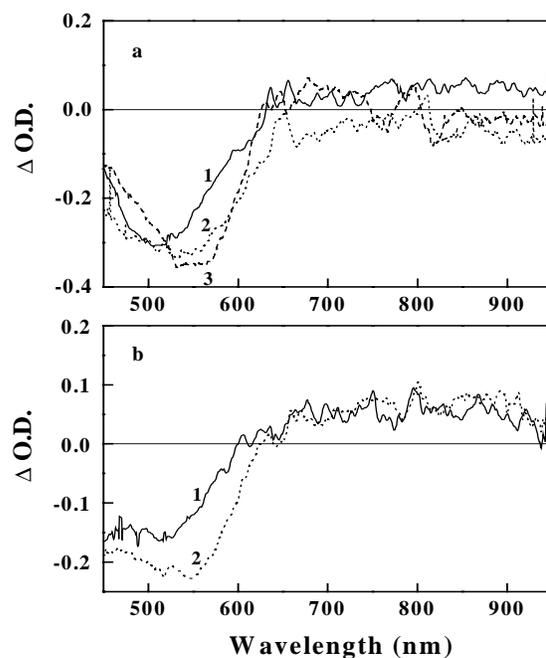


Figure 2. Transient bleaching/absorption signals between ‘zero’ to 5 ns delay after the photoexcitation of the silver nanoparticles with 35 ps laser pulse. (a) (1): Type II solutions, wavelength of excitation, $\lambda_{\text{ex}} = 532$ nm; energy = 4 mJ/pulse. (2): with 10% (v/v) acetone addition; other conditions as in (1). (3): with 10% (v/v) 2-propanol addition; other conditions as in (1). (b) (1): Type II solutions, $\lambda_{\text{ex}} = 355$ nm; energy = 2 mJ/pulse. (2): with 10% (v/v) acetone addition; other conditions as in (1).

was not observed by Roberti *et al* who found that the SPB excitations decayed with a lifetime of ~ 40 ps⁸. Also, the work of Ahmadi *et al* on gold colloids reported the time for bleach recovery, attributed to the relaxation by the phonon-cooling process, as ≥ 50 ps⁹. Both studies were carried out with nanoparticles prepared without using any stabilizer. However, our results are in line with the more recent work by Kamat *et al* on the picosecond dynamics of silver nanoparticles prepared by reduction of AgNO₃ by sodium citrate¹⁰. In their study the bleach signal was found to rise in ~ 90 ps and recover in a few ns. The bleaching was found to be a monophotonic process. A weak absorption signal was also seen by them and is attributed to the generation of hydrated electron (e^-_{aq}) during photolysis.

Flash photolysis was also carried out with addition of acetone or 2-propanol to the type II solutions. The former reacts with e^-_{aq} as well as the precursor state *viz.*, the dry or quasifree electron²⁴ while the latter is relatively inert. Addition of 10% acetone or PrOH decreases the absorption at 390 nm and increases that around the 550 nm shoulder in the surface plasmon band of type II solutions, as shown in figure 1c. On excitation with 532 nm pulses, the extent of the 450–600 nm bleaching increases at 0 ps delay, with an apparent reduction in the weak absorptions in the 600–900 nm region (figure 2a – 2

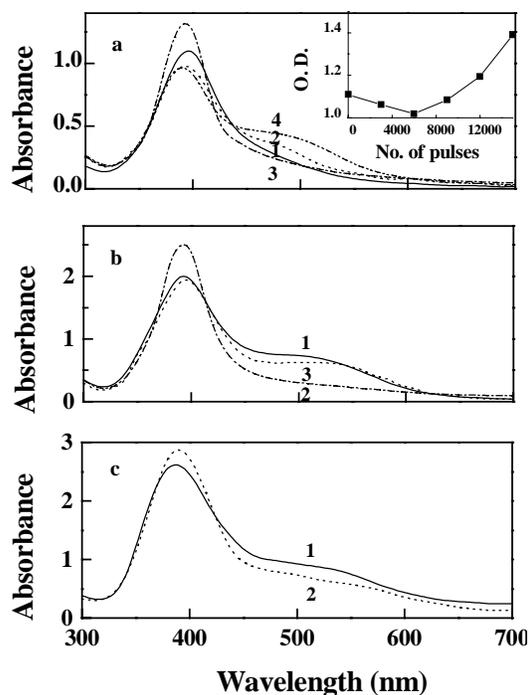


Figure 3. Changes in the optical absorption spectra of silver nanoparticles after photolysis of a circulating 50 ml solution of the SNP with repetitive laser pulses. (a) Type I solutions with $[Ag^+]_0 = 0.2$ mM, $\lambda_{ex} = 355$ nm, energy = 4 mJ/pulse. Number of pulses: (1) 0, (2) 6000, (3) 15000, (4) 15000 (after 12 h aging). Inset: Variation of OD at 390 nm with the number of pulses. (b) Type II solutions ($[Ag^+]_0 = 0.5$ mM), $\lambda_{ex} = 355$ nm, energy = 4 mJ/pulse. Number of pulses: (1) 0, (2) 12000, (3) 12000 (after 12 h aging). (c) Type II solutions ($[Ag^+]_0 = 0.5$ mM), $\lambda_{ex} = 532$ nm, energy = 4 mJ/pulse. Number of pulses: (1) 0, (2) 600.

and 3). The maximum in the bleaching signal is red-shifted by about 20 nm in the solution containing 10% acetone and by about 30 nm in that containing 10% PrOH, as compared to solutions without acetone or PrOH. The above shifts in the transient spectra could be attributed to the changes in the ground state spectra due to the presence of acetone or PrOH (see figure 1 – b and c). However, the changes in the magnitude of bleaching and absorption signals brought about by PrOH or acetone could be regarded as small. It would appear that even at the molar concentrations employed, acetone did not interfere with the 'hot' electrons produced on the excitation of SPB.

Bleaching as well as absorption signals, similar to those described above, were observed when the type II solutions were irradiated with 355 nm pulses of 35 ps duration (figure 2b – 1 and 2). The similarity in the results obtained on photoexcitation by both 355 nm and 532 nm pulses support the fact that both 390 nm peak and 550 nm shoulder arise from the same plasmon band^{19,20} i.e. from the presence of predominantly one kind of particle (i.e. similar a/b ratio) with different sizes in the type II solutions.

On excitation of type I solutions (displaying only the 390 nm band) by 355 nm laser pulses of 35 ps duration, only a very weak absorption signal in the region 500–900 nm was seen. It was not possible to study its decay due to small transient absorption intensities.

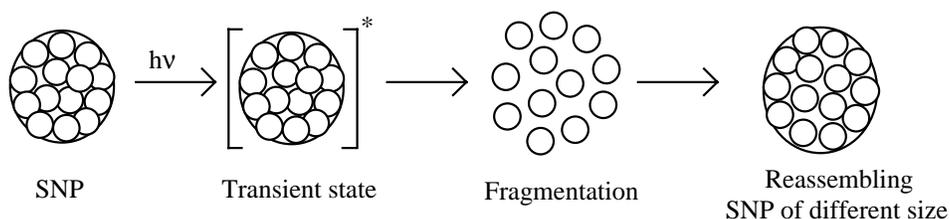
Picosecond flash photolysis experiments have been carried out earlier by Haase *et al* on CdS nanoparticles²⁵, which showed photoelectron ejection in solutions. The electrons could be scavenged by known e^-_{aq} scavengers. More relevant to our present work are the observations by Kamat *et al* on the 355 nm laser excitations of aqueous solutions of silver nanoparticles. At laser intensities higher than 1 mJ/pulse, a weak absorption signal in the red region was obtained. This was attributed to the photoejection of electrons from the silver particles by a biphotonic process, resulting in the generation of e^-_{aq} and the observed optical absorption in the visible-near infrared region. In our studies, however, the magnitude of optical absorptions in the 600–900 nm remained nearly the same between 'zero' ps and 5 ns after 355 nm excitation (2 mJ/pulse), and was not diminished by the presence of molar concentrations of acetone, which is a very efficient e^-_{aq} scavenger (see figure 2b). It thus appears that the SPB excitations of the polyphosphate stabilized silver nanoparticles do not lead to a significant photoejection of electrons into the solvent across the particle-solvent interface. We prefer to understand the bleaching and absorption signals as due to the breaking up of the particles on SPB excitation, as described in the following section.

3.3 Other effects of photolysis

In addition to the transient optical changes following the SPB excitation of the SNPs; long-term alterations in the average sizes of the particles from both the type I and type II solutions have been studied. A 50 ml solution was circulated through the flow cell which was irradiated with repeated laser pulses. On 355 nm excitation of the type I solutions (1.45×10^8 W/cm²), broadening of the SPB was observed with a decrease in optical density (OD) at 390 nm, up to 6000 laser pulses. At higher number of laser pulses, the OD at 390 nm increased beyond the pre-photolysis OD and the SPB became narrower. These changes are shown in figure 3a. The inset of figure 3a shows the effect of increasing the number of 355 nm laser pulses on the OD at 390 nm in the SPB. It is seen that as the number of pulses increases, the OD at 390 nm decreases and then increases. These results indicate that on irradiation the particles first attain a critical size and then change over to

smaller clusters, since a sharper SPB band is attributed to smaller clusters. Measurements by the DLS technique clearly showed that on laser photolysis of the solutions the volume average size of the particles decreased from 49 nm to 29 nm (9000 pulses, table 1). Further physical changes, apparently dependent on the initial Ag^+ ion concentration ($[\text{Ag}^+]_0$) were noticed on aging of the laser irradiated solutions. At $[\text{Ag}^+]_0 = 0.2$ mM, overnight aging produced a colour change from yellow to reddish-brown, while with $[\text{Ag}^+]_0 = 0.1$ mM, such changes were not observed. It may be mentioned that the unphotolysed nanoparticle solutions themselves did not show any aging effect at either concentrations of the Ag^+ ion. When the photolysis was carried out using the conventional low intensity lamps (output at ~ 350 nm) in the Rayonet photochemical reactor, neither any sharpening of the SPB nor other changes comparable to those seen on the laser photolysis were observed. In these experiments, the total number of absorbed photons was kept nearly the same as in the laser irradiations. However, the light intensity was $\sim 10^{16}$ photons $\text{cm}^{-2} \text{s}^{-1}$ as against $\sim 10^{15}$ photons cm^{-2} pulse of 35 ps duration at 10 Hz (i.e. $\sim 3 \times 10^{26}$ photons $\text{cm}^{-2} \text{s}^{-1}$) while employing the laser pulses. It was apparent from these results that the photolytic changes in the nanoparticles were intensity dependent.

Laser intensity effects on size redistribution of the silver clusters have been reported by Takami *et al*, who observe that the mode of distribution of silver particles shifts from 19 to 9 nm¹². A possible mechanism proposed by the authors is as follows. The photoexcitation of SPB results in the desorption of Ag atoms/ions from the particle surface and the atom/ion desorption results in the size reduction of the SNPs. At the same time SNPs originally aggregated separate from each other. Kamat *et al* propose that on laser excitation, the SNP lose electrons by photoejection and a transient state of the particle is formed which is the precursor for complete fragmentation of the larger particles used in their work. They also propose that the particles become charged on laser irradiation and once sufficient charge accumulates on the particle, it breaks¹⁰. Our results, however, do not support the photoejection of electrons, as the experiments with acetone, a good scavenger of electrons, would have shown different results. However, in the presence of a stabilizer like polyphosphate, the fragmented particles reassemble to give new particles with different sizes, as given below:



The particle fragments could be of such dimensions/nuclearity that they would not possess the characteristic surface plasmon band of silver nanoparticles. Therefore, during the period that the particle remains fragmented, bleaching of the plasmon band would result. The bleaching observed by us between 'zero' ps and ≤ 5 ns could represent this period. The small absorption signals in the 600–900 nm could also be the net effect of the fragmentation. However, the duration t where $5 \text{ ns} < t < 100 \text{ ns}$ could represent the slow reassembling process leading to the recovery of the plasmon band.

The metal clusters are held together with moderate to strong binding energies from 0.5–3 eV²⁶. Due to the multiphotonic nature of the excitation, the energy available with

the nanoparticle exceeds the binding energy resulting in the fragmentation of the nanoparticle as observed by us. However, the fragments are unstable as compared to the nanoparticles. Therefore, the fragments would reassemble to give another set of nanoparticles with different size distribution.

As already mentioned, continuous irradiation in the photochemical reactor does not result in sharpening of the SPB or similar changes at the same number of total absorbed photons but at drastically lower fluences, (difference of $\sim 10^{10}$ times). It can be seen that either biphotonic or multiphotonic effects are responsible for the observed particle fragmentation on laser irradiation. This observation is true for both 355 and 532 nm irradiation with laser pulses. Kamat *et al* found that plasmon bleach was dependent on intensity at intensities < 1 mJ / pulse while it became independent of intensity above this energy due to saturation effects. The transient absorption was found by them to obey quadratic dependence on the laser dose. They concluded that the primary process to break a nanocluster was biphotonic¹⁰. Our results from low intensity experiments also show that the fragmentation of SNP would involve more than one photon; with the energy input adequate to overcome the binding energy of the nanoparticles.

The influence of laser irradiation on gold nanoparticles has been recently reported by Kimura and coworkers and they observed that the stability of nanoparticles increased after laser irradiation^{27,28}. In our work, when type II solutions were irradiated continually with 355 nm or 532 nm laser pulses, sharpening of 390 nm band was seen. Furthermore, the OD of the shoulder band around 550 nm was found to decrease and that of 390 nm band increase (figures 3b and c). Simultaneously, the reddish-brown colour of the solution changed to yellow. These results would imply progressive conversion of the particles from type II to type I during the laser photolysis. In addition, the photolysis was found to decrease the volume average particle size from ~ 78 nm to 31 nm (table 1). Further changes accompanying the aging of the photolysed solutions were observed in these solutions also. On keeping the solutions overnight, the colour of the solution was found to revert from yellow to reddish-brown, and the spectrum corresponded to that typical of type II solution. Some of the intermediate stages in these post-irradiation changes might involve the familiar 'Ostwald-ripening'²⁸.

It is probable that the polyphosphate stabilizer employed in the present work had a definite role in producing the type II solutions, leading to the observed transient as well as post-photolysis changes. Radiolytic preparation of the SNP without the stabilizer did not yield clusters displaying the shoulder band and having the desired stability for further experimentation. The preparations, where sodium dodecyl sulphate (SDS) was used as the stabilizer, displayed yellow colour; however, the ODs beyond 450 nm, especially in the shoulder region were much smaller as compared to the SNP stabilization with polyphosphate.

4. Conclusions

Using the technique of γ -radiolysis, two types of silver nanoparticles (SNP) were generated, one with a near-Gaussian surface plasmon band centred at ~ 390 nm (type I) and another with a similar band and an additional shoulder at 550 nm (type II). On flash photolysis by 35 ps, 532 nm pulses, the latter showed transient bleaching signal in the 450–600 nm region. The signal was found to last longer than 5 ns. By separate nanosecond flash photolysis experiments, the lifetime for the relaxation process giving rise to bleach recovery was estimated to be less than 100 ns. A small positive transient

absorption signal was also seen at > 600 nm for the type II solutions. However, the absorption in this region could not be attributed to photoejection of electrons from the phosphate-stabilized silver nanoparticles. Photolysis of the nanoparticles with repetitive 355 nm and 532 nm laser pulses was found to narrow the surface plasmon band and decrease the particle size. It is proposed that on laser irradiation the SNP breaks down to smaller fragments which reassemble to give particles of new dimensions.

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