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Aggregated nanoplatelets: optical properties and optically induced deaggregation

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Abstract

A study of aggregation and laser-induced deaggregation of silver nanospheres and nanoplatelets in colloidal form is presented. Changes in the extinction spectrum caused by aggregation are explained using a two-particle approximation. In the case of platelets, controlled laser irradiation is shown to reverse the aggregation process.

1. Introduction

Nanoparticles suspended in liquid hosts can come close to each other due to thermal Brownian motion. Once they are close enough to interact via short-range van der Waals force and long-range columbic forces, they can form aggregates [1, 2]. At higher volume fractions of the nanoparticles in the host the probability for such aggregation increases. Aggregation changes the optical properties of the material significantly. For example, before aggregation silver nanospheres in water show only one surface plasmon resonance (SPR) peak at 400 nm, while in the aggregated form an additional peak at ~ 530 nm appears. It has been observed that aggregates have 'hot spots' where the field enhancements are huge [3]. This leads to high optical nonlinearity [4] and enhancements in Raman and hyper-Rayleigh scattering from the materials [5]. Aggregation of nanospheres and the subsequent changes in the optical properties have been widely studied [6, 2, 7].

Nanoparticles of shapes other than the spherical shape have been shown to possess higher optical nonlinearities [8–11]. Therefore, aggregates of such non-spherical particles should be very useful for nonlinear optical and sensing applications. For example an increased sensitivity in SERS has been reported for nanoplatelet aggregates [12]. These applications make it important to study the optical properties

of aggregated non-spherical particles. Ali Mahraz *et al* have shown that in nanoparticle aggregates of rod shaped particles the fractal dimension depends strongly on the aspect ratio of the particles [13]. However, they have not reported the changes in the optical properties of nanorods due to aggregation. Since the optical properties depend strongly on the way the particles are distributed within the aggregates [6], it is expected that optical properties of aggregates would be different for different nanoparticle shapes. In this paper we report the effect of aggregation on the optical properties of silver nanoplatelets. The extinction spectra of single nanoparticles and two-particle aggregates are calculated numerically. These results corroborate the trend of changes observed in the extinction spectra of the larger aggregate. For comparison we also report results on aggregated nanospheres.

As aggregation causes marked changes in the optical properties of the nanoparticle colloids which are sometimes not desirable phenomena. We show that in the case of nanoplatelet aggregates it is possible to break the aggregate back into individual platelets by using nanosecond laser irradiation. The same, however was not the case for nanosphere colloidal aggregates. The implications of these observations are discussed in section 5.

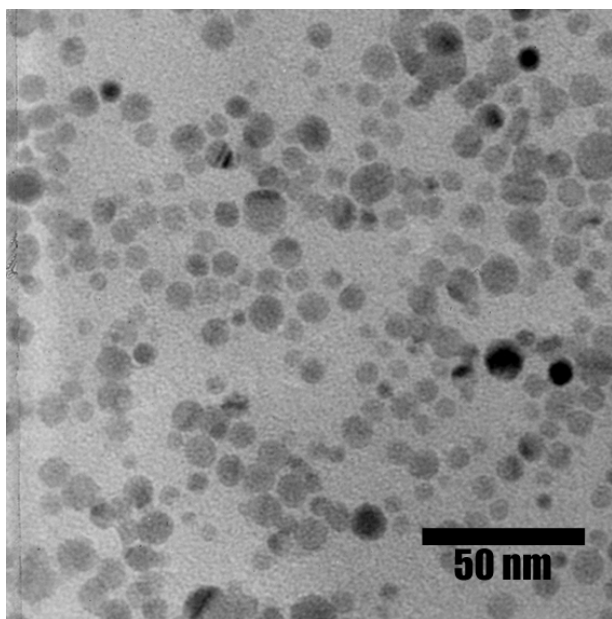


Figure 1. The TEM of the unaggregated nanosphere sample.

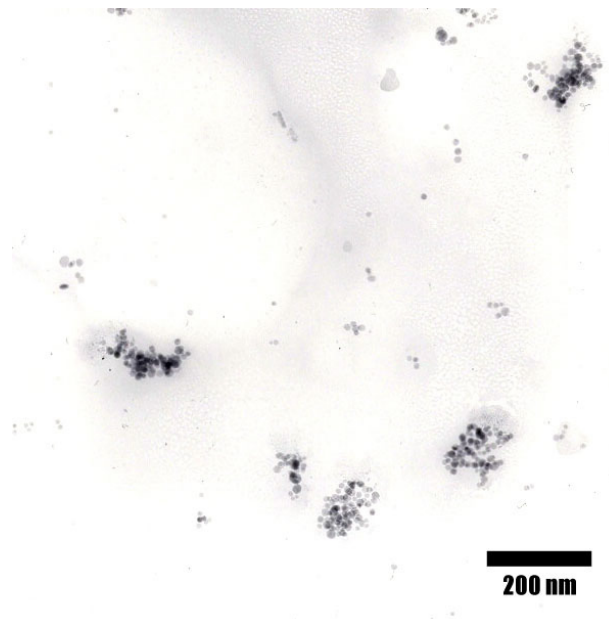


Figure 2. The TEM of the nanosphere sample after aging for a few weeks. The TEM shows the presence of aggregated nanospheres.

2. Preparation of silver nanoparticle aggregates

In this section we present the method of preparation of colloidal aggregates of platelet and spherical shaped silver nanoparticles. The nanoparticles of both spherical and platelet shapes were prepared following a method similar to that of Jin *et al* [14]. The silver nanosphere aggregates were formed by increasing the number density of silver nanoparticles in the colloidal solution, and giving sufficient time for aggregation [1]. Nanospheres, which are also the seed for nanoplatelets, were prepared by the salt reduction method. A capping agent, tri-sodium citrate (1 ml, 0.6 M) was dissolved in 100 ml deionized water kept at a temperature between 5 and 10 °C. Freshly prepared silver salt AgNO_3 solution (2 ml, 0.1 M) was added to this solution. After giving sufficient time for the silver salt to dissolve, the reducing salt NaBH_4 (1 ml, 1 M) was added. Just after the addition of NaBH_4 the solution turns to a golden yellow color, which indicates the formation of nanospheres. Further NaBH_4 solution is added in drops at regular intervals of 5 min for the next 15 min to fully reduce the AgNO_3 . At the end of the reaction another capping agent BSPP (1 ml, 0.1 M) was added to the colloidal solution. The final solution is then aged overnight in the dark. Throughout the preparation stage this solution was stirred continuously. The average diameter of the nanospheres measured by TEM (figure 1) was found to be 7.6 nm. This nanosphere solution was kept in the dark for a few weeks. During this period the color of the solution slowly changed from yellow to red. The TEM of this sample (figure 2) shows that the sample contains several aggregates of nanospheres. The diameters of the individual nanospheres forming the aggregate are nearly the same as that of the original sample indicating that coalescence, which could change the structure and size of the individual nanoparticles, has not occurred.

Nanoplatelet aggregates were prepared as follows. First the silver nanospheres were prepared as described above,

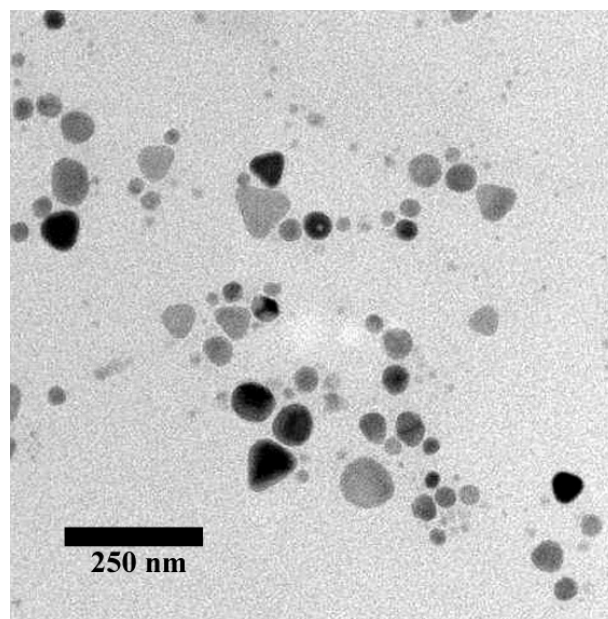


Figure 3. The TEM of the unaggregated nanoplatelet sample.

except that the concentrations were one fourth of the above mentioned values. This was governed by the previous observations that at high nanosphere concentrations, photo-induced conversion to other shapes is inhibited. After overnight aging of the nanosphere colloidal solution, it was exposed to a 532 nm nanosecond laser to convert to silver nanoplatelets at a average power density of $\sim 0.1 \text{ W cm}^{-2}$. In a few hours the color of the solution slowly turned from yellow to green then finally to blue. The TEM of the nanoplatelet sample is shown in figure 3. The TEM shows the presence of disk and prism shaped nanoparticles, i.e. nanoplatelets. The

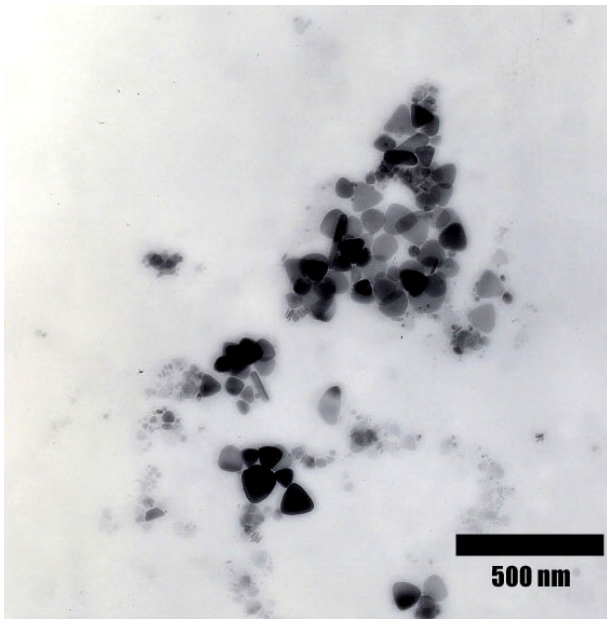


Figure 4. TEM of the sample containing silver nanoplatelets after aging in the dark for a few months. Note that almost all of the nanoplatelets touch each other showing that they are aggregated.

average diameter and side length of the disks and prisms are 71 and 79 nm, respectively. The average thickness of the platelets measured using TEM is 17 nm. This nanoplatelet sample bottle was wrapped in aluminum foil and kept in the dark for a few months. The TEM of these samples (figure 4) shows that most of the nanoplatelets touch each other to form bunches of nanoplatelets. Very few (less than 4%) of the nanoplatelets were found to be separate. The sizes of the individual nanoplatelets remain nearly the same as that in the original unaggregated sample. The TEM of the samples were taken under dilute conditions. Further dilution of the sample only increases the separation between the aggregates, the size of individual aggregate remains unchanged. In the past the process of aggregation has been induced in nanoparticle colloids using salt [1, 12] and laser light [15]. In the present case no external agent was used to induce aggregation, only the concentration of the nanoparticles in the sample was higher than normal. We believe that the aggregation could have been facilitated by either some residual impurities or by a lack of sufficient capping at high concentrations.

In an earlier report stacking of platelets was observed during drying of the sample on a TEM grid where the platelets stick to each other by the face with the largest surface area [14]. Jana *et al* also observed self-assembling of nanorods into a structure which resembles 2D smectic liquid crystal upon solvent evaporation [16]. In both the above cases the aggregation of the particles happens on the TEM grid. However, it has been shown earlier that nanoparticles can also aggregate in a liquid host due to collisions between particles. Such collisions are caused by Brownian motion of the particles within the host. The structure of such a nanoparticle aggregate and its fractal dimension strongly depend on the process of aggregation [2]. Once such an aggregate has been formed

in the colloid, its structure is already rigid. When this colloid is dried on a TEM grid we expect the aggregate to remain as a single entity and the self-assembling of individual nanoparticles will not be seen. In the present case the first indication of the aggregation occurring in the colloidal solution itself comes from the observed changes in the extinction spectra of the colloids [12]. This is discussed in section 4. As mentioned above, to exclude the possibility of the aggregation having occurred on the TEM grid, the solutions were diluted before doing the TEM. The TEM pictures of neither the unaggregated samples nor the laser irradiated (deaggregated) samples show such aggregate formation. Together these facts lead to the conclusion that the changes observed in the extinction spectra and the TEM are due to aggregation of nanoparticles in the colloidal solution.

3. Calculation of extinction spectrum of two-particle aggregates

When a uniform field is applied to a nanoparticle, the field distribution in and around the nanoparticle gets modified. For particles close to each other the field near a particle is modified by the neighboring particle. Thus the electromagnetic interaction between two nanoparticles depends strongly on the separation between them [17]. In the case of particle shapes other than a sphere the field distribution around the particle also depends on the orientation of the particle. When two particles are close together the change in the optical properties would depend not only on the size and shape of the particle but also on the orientation of the individual particles relative to one another. For multiple particle aggregates the field distribution has been shown to strongly depend on the way the particles are distributed within the aggregate [6]. As mentioned earlier the distribution of particles in an aggregate depends on the process of aggregation. For nanospheres the development of aggregates has been modeled using Monte Carlo simulation [2] and then the extinction spectrum has been calculated [6]. However, similar simulations for particles which are not spherically symmetric become computationally prohibitive for a large number of particles as the particle orientation also has to be factored in, both for modeling the aggregation and for calculation of the extinction spectrum. Hence to understand the change in extinction spectrum due to aggregation, we consider a simpler model of electromagnetic interaction between two nanoparticles. The two-particle approximation was used in the past to explain the qualitative features of multiple interactions in a collection of metal particles [18].

First let us look at the changes in the extinction spectra of two interacting and noninteracting spheres. In figure 5 we show the extinction spectrum of two noninteracting 7.6 nm diameter spheres. The extinction spectrum of the individual spheres were calculated using Mie's theory [19]. The extinction spectrum has a single peak at 387 nm which is characteristic of the spherical nanoparticle in water. For all the extinction calculations presented in this paper we have used the experimental dielectric constants of bulk silver [20]. The extinction spectrum of two such spheres touching each other (distance between the sphere centers equal to the diameter)

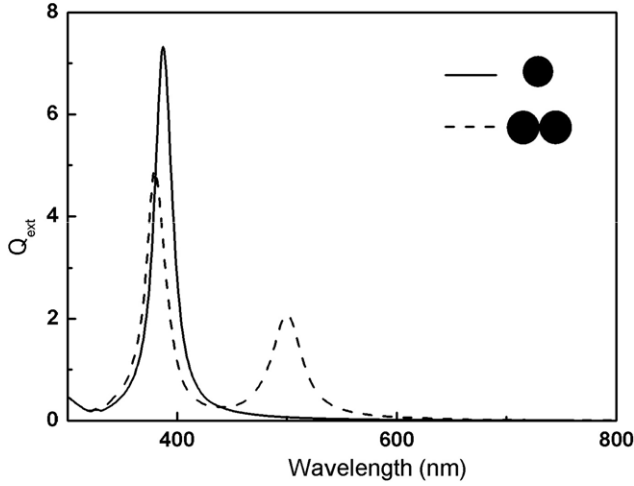


Figure 5. Calculated extinction spectra of two nanospheres having the same radius 7.6 nm. The solid line is two noninteracting spheres, the dashed line is when spheres are touching each other.

was calculated using the T -matrix method [21, 22] and is also shown in figure 5. Averaging over the random orientation of field direction with respect to the line joining the spheres (major axis of the bi-sphere) has been done. The extinction spectrum of the bi-sphere shows peaks at 380 nm and at 500 nm. The peak at 380 nm is due to the components of field perpendicular to the line joining the centers of the spheres, while the peak at 500 nm is due to the component of field along the line joining the centers. Before we compare the above results to the experimental extinction spectrum, let us turn our attention to the changes observed in the extinction spectrum of aggregated nanoplatelets.

For the calculations we consider a nanoplatelet of truncated triangular cross-section having dimensions the same as that experimentally measured. The extinction cross-sections were calculated by using the program DDSCAT of Draine and Flatau [23]. DDSCAT uses discrete dipole approximation, in which a nanoparticle is replaced by an appropriate lattice of N small spherical particles. Let \mathbf{r}_j be the location of each of those small spheres, where $j = 1, 2, 3 \dots N$. The dipole moments of each of these spherical particles are proportional to the electric fields at those places. Thus the dipole moment \mathbf{P}_j is given by

$$\mathbf{P}_j = \alpha_j \cdot \mathbf{E}_j, \quad (1)$$

where α_j is the polarizability of the j th particle and \mathbf{E}_j is the local electric field at \mathbf{r}_j . These dipole moments satisfy a system of linear equations given by

$$\sum_{j=1}^N \mathbf{A}_{lj} \mathbf{P}_j = \mathbf{E}_{0l} \quad (2)$$

where l is a dummy integer like j , \mathbf{E}_{0l} is the applied electric field and the elements of the interaction matrix \mathbf{A} are given by

$$\begin{aligned} \mathbf{A}_{lj} &= \frac{\exp(ikr_{lj})}{r_{lj}} \times \left[k^2 (\hat{\mathbf{r}}_{lj} \hat{\mathbf{r}}_{lj} - \mathbf{1}_3) \right. \\ &\quad \left. + \frac{ikr_{lj} - 1}{r_{lj}^2} (3\hat{\mathbf{r}}_{lj} \hat{\mathbf{r}}_{lj} - \mathbf{1}_3) \right], \quad \text{for } l \neq j, \\ &= \alpha_j^{-1} \quad \text{for } l = j, \end{aligned} \quad (3)$$

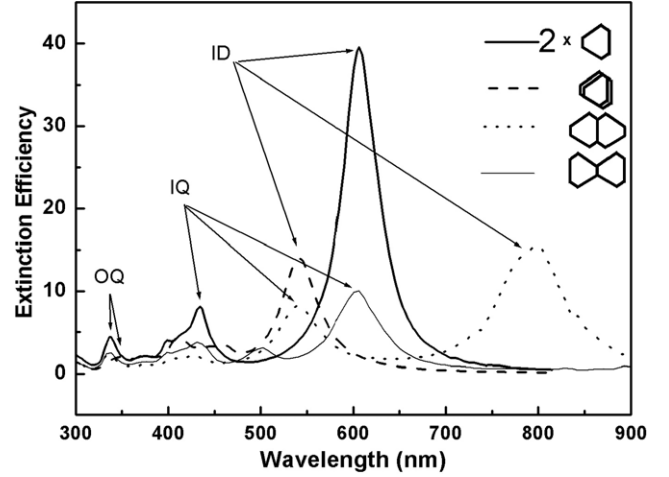


Figure 6. Numerically calculated extinction spectra of two nanoplatelets, when they are not interacting, when one is on top of the other, when touching each other at the tip and when they are touching each other along one of the base. ID, IQ, and OQ are the possible in-plane dipole, in-plane quadrupole and out-of-plane quadrupole resonances corresponding to those individual cases.

where $\hat{\mathbf{r}}_{lj} = (\mathbf{r}_l - \mathbf{r}_j)/r_{lj}$, r_{lj} is the distance between the l th and j th particles and $\mathbf{1}_3$ is the 3×3 identity matrix. By solving the system of $3N$ complex linear equations given in equation (2) the dipole moments \mathbf{P}_j can be obtained from which extinction cross-sections can be calculated. For our calculations we replace the target nanostructure by a lattice with N approximately 65 000. Since a nanoplatelet can have various orientations in a liquid host one needs to do the extinction calculation for all possible orientations of the nanoplatelets. Kelly *et al* have shown that the extinction spectrum calculated by averaging over the three Cartesian directions mimics the full calculation results [24]. We use this approximation in the calculation of the extinction spectra of the nanoparticles.

For the calculation of the extinction spectrum of double nanoplatelets we consider three configurations. These are: (a) touching on the sides (TS) i.e. stacked one over the other, (b) touching at the base (TB) and (c) touching at the tips (TT). The TS and TT are the extreme configurations for maximum and minimum contact area when two particles attach to each other, while the TB configuration is an intermediate state. All other possible configurations in a real sample would be somewhere in between the above configurations. figure 6 shows the calculated extinction spectra for the three configurations. We have also shown the calculated extinction spectrum of a single platelet. The extinction for the single platelet has been multiplied by 2 for quantitative comparison with the two platelet combination.

The calculated Q_{ext} of the single platelet shows peaks at 606 and 434 nm, which are the in-plane dipole (ID) and in-plane quadrupole (IQ) resonances. In addition to these two peaks, there are peaks at 400 and 337 nm which are the out-of-plane dipole (OD) and out-of-plane quadrupole (OQ) resonances. The OD resonance at 400 nm is very weak and it appears as a wing in the IQ resonance [24]. Let us now look

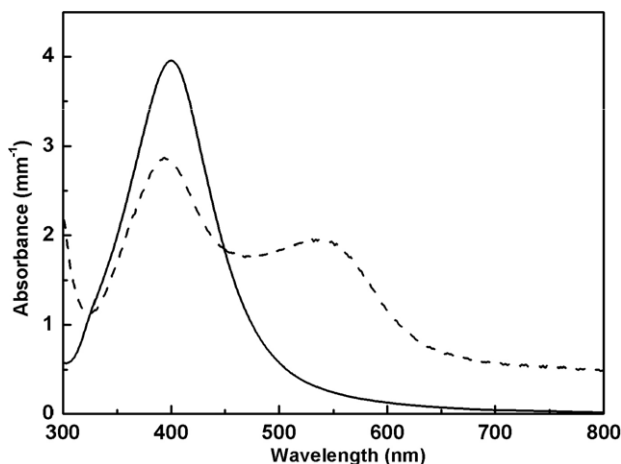


Figure 7. Linear extinction spectrum of as prepared nanosphere solution is shown as a solid line. The dashed line shows the extinction spectrum of the same sample after aging in the dark for a few weeks.

at the spectrum when two nanoplatelets touch each other. The in-plane dipole resonance peak positions for the cases of TB and TT are at 794 nm and ~ 1243 nm, respectively. While for the case when the platelets are one on top of the other the peak is at 541 nm. Note that the red shifts are very large (188 and 637 nm) for the cases TB and TT while the blue-shift shown by the TS case is relatively smaller (65 nm).

We further look at the changes observed in the quadrupole resonances (figure 6). The TB and TT cases show a sharp OQ resonance with reduced strengths. These resonances are blue shifted by 2 and 2.5 nm for the TB and TT cases, respectively, compared to the noninteracting case. The OQ resonance of the TS case is very broad and weak compared to the TB and TT cases and it shows a red-shift. For all the three possible orientations we see several new peaks around the noninteracting platelets' in-plane quadrupole resonance. Further, the overall peak heights are also smaller compared to the noninteracting case. Thus amongst the different SPR peaks the in-plane dipole resonance is the most sensitive to inter-particle interaction, and shows a strong red-shift. In section 4, the experimentally obtained extinction spectra for aggregated nanoparticles are compared with the calculated extinction spectra of two interacting particles.

4. Experimental results and discussion

The UV-visible extinction spectra of a colloidal solution of nanoparticles were measured using an unpolarized beam in a commercial spectrophotometer. The extinction spectra of the nanosphere colloidal solution, before and after aggregation, are shown in figure 7. The unaggregated nanospheres show a single surface plasmon resonance (SPR) at 400 nm, while the extinction spectrum of the aggregated nanospheres shows SPR peaks at 394 and 537 nm. These changes in extinction spectrum are in agreement with earlier reports [1]. The changes in extinction spectra of the nanosphere sample before and after aggregation show several similarities to the calculated

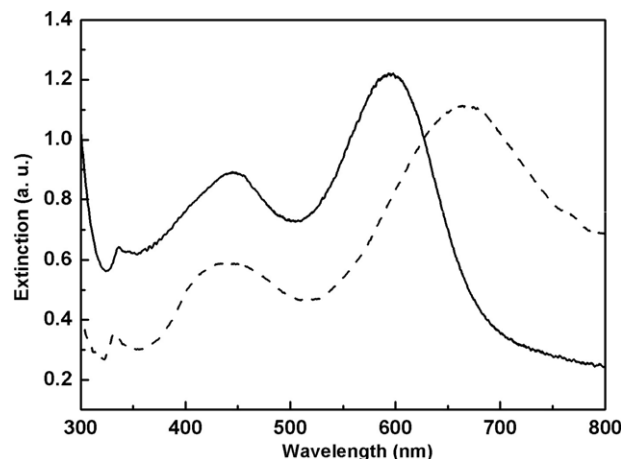


Figure 8. The solid line shows the linear extinction spectrum of silver nanoplatelets in water at the end of nanoplatelet preparation. The dotted line is the extinction spectrum of the sample after a few months of aging in the dark.

extinction spectra of single spheres and two touching spheres. Both the spectra show an appearance of a new peak at the red side of the spectrum around 500 nm. The small blue-shift of the SPR peak of the nanospheres is also seen in both the spectra. Thus without going into the detailed calculations of several aggregated nanospheres it is possible to give a qualitative explanation for the changes in the experimental spectrum of the aggregated nanospheres solution.

The extinction spectra of the nanoplatelet colloid before and after aging are shown in figure 8. The freshly prepared nanoplatelet solution has SPR peaks at 596, 445 and 336 nm. The strong SPR peaks at 596 and 445 nm are due to the in-plane dipole and the quadrupole resonance of the platelet, while the weak peak at 336 nm is due to the out-of-plane quadrupole resonance [24]. The extinction spectrum of the aggregated nanoplatelet solution shows that the in-plane dipole resonance of the nanoplatelets, which was at 596 nm for fresh sample, is now red shifted by about 69 nm to 665 nm, while the out-of-plane quadrupole resonance has blue shifted slightly from 336 to 332 nm. The peak at 445 nm has broadened substantially and it remains at nearly the same wavelength. The background extinction on the red side of the spectrum has increased compared to the nonaggregated fresh solution while the background extinction around the in-plane and out-of-plane quadrupole resonances has reduced. Similar changes in the experimental aggregated nanoplatelets have been seen earlier [12]. The presence of aggregated nanoplatelets in the sample can also be verified by dynamic light scattering measurements. However, the changes in the TEM pictures taken at dilute conditions together with the changes in the observed changes in the extinction spectrum of the platelets confirms the presence of aggregated platelets in our sample.

Let us now compare the experimental results with the calculated extinction spectra of two nanoplatelets touching each other. In the calculated extinction spectra a strong red-shift was observed for the TB and TT cases (188 nm and 637 nm respectively) while a relatively smaller blue-shift was observed for the TS case. Although TEM does not give the

exact three-dimensional structure of the aggregated platelets, it does show some platelet pairs overlapping partially in various directions. It has been shown earlier that partial overlap between two nanoplatelets leads to peak positions in between the TS and TB cases [25]. A qualitative comparison of the experimental spectrum with the numerical results suggests that a large fraction of particle pairs within the aggregates could be in the TB orientation or close to it. This is possible due to the following reason. It is known that the final shape of nanoparticles is governed by the fact that during growth the capping agents get preferentially attached to certain faces of the silver crystal and thus reduce the growth rate along those faces. In the case of nanoplatelets the growth rate is lowest along the [111] direction, therefore the growth is preferentially in the plane transverse to it. This can lead to better bonding in orientations close to TB [26]. The randomness in the possible ways of touching and overlapping will cause an increase in the width of the ID resonance and an increase in background extinction on the red end of the spectrum. The peak height of in-plane dipole resonance reduces in all the three cases, which is also seen in the experimental spectra. In the case of the out-of-plane quadrupole resonance the relatively small blue-shift observed in the experimental extinction spectrum is seen also in the calculated spectra for the TB and TT cases. The OQ resonance of the TS case is very broad and weak compared to the other two cases. Using a similar argument as above we can expect an overall blue-shift of the OQ resonance in the aggregate. In the calculated spectra a reduction of strength of in-plane quadrupole and out-of-plane dipole resonances can be seen for all the three orientations. This causes the observed reduction in the background on the blue side of the in-plane dipole resonance. Calculations also show the appearance of new peaks between the OQ and IQ resonances, which are possibly higher order resonances. This leads to the substantial broadening of the out-of-plane quadrupole resonance observed in the experiment.

5. Effect of laser irradiation on nanoparticle aggregates

The aggregate samples are found to be fairly stable under storage. However for any practical use they need to be stable under optical irradiation also. To study the stability of the aggregated nanoplatelet sample, the solutions were exposed to a 532 nm wavelength, 250 ns pulse width, 7 kHz repetition rate laser, at different power levels. Earlier during the photo-induced conversion of the nanospheres to nanoplatelets a average power density of $\sim 0.1 \text{ W cm}^{-2}$ was used. There was no change in the spectrum of the aggregated platelet sample upon exposure to irradiation levels close to 0.1 W cm^{-2} over an extended period. This leads to the conclusion that at these power levels the aggregated nanoplatelets do not deaggregate or change in shape.

However, when the power density at the sample is increased the extinction spectrum begins to show some changes. In figure 9 we show the extinction of the sample as a function of exposure time for a average power density of 10 W cm^{-2} . This was measured by a white light source

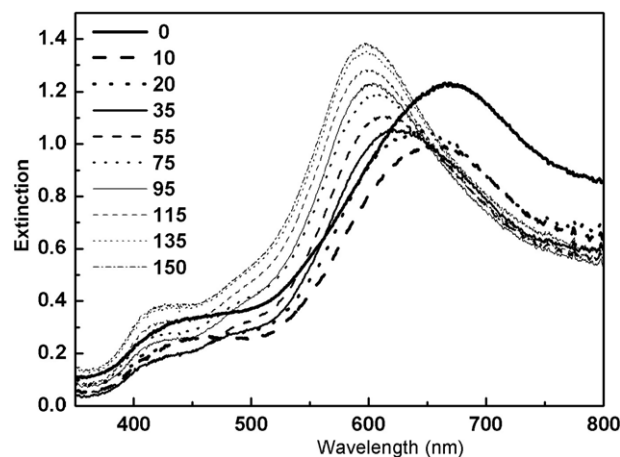


Figure 9. Extinction spectra at different times of the aggregated nanoplatelet sample during exposure to a nanosecond laser. The time in minutes is given in the legend of the plot. Note that the peak at 665 nm blue-shifts to 596 nm.

and fiber optic coupled spectrograph. Initially the peak at 665 nm reduces in strength and also blue shifts. On further exposure the peak continues to blue-shift with an increase in amplitude. After the peak reaches 596 nm there is no further shift. It has been shown earlier that when exposed to femtosecond high power lasers, the nanoplatelets break into small spheres [27]. This process of formation of nanospheres reflects in the extinction spectrum of the colloidal solution as the appearance and growth of a peak at 400 nm. In the present case even after the full peak shift the 400 nm peak does not appear. This shows that the nanoplatelets do not break into spheres during this nanosecond laser exposure. The TEM of the sample at this stage is shown in figure 10. Almost all of the nanoplatelets were separate, and only a few nanoparticles were found to be close to each other. The shape of the individual nanoparticles remains the same as that of the nanoplatelets present in the aggregated sample. The TEM and the spectral evidence shows that the sample got deaggregated during exposure to the laser. However under similar exposure conditions the aggregated nanospheres sample did not show any change in the extinction spectrum. Increasing the exposure average power densities to the order of 3 MW cm^{-2} causes the nanoplatelets to break up into much smaller spheres. Under the same intensities the aggregated nanospheres also breaks into smaller spheres. This intensity dependent deaggregation phenomena indicates that the bond strength of aggregates of nanospheres is much stronger for exposure to light.

6. Conclusions

We have prepared colloidal aggregates of silver nanoplatelets starting from a colloid of $\sim 75 \text{ nm}$ diameter platelets. Aggregation brings about significant changes in the optical extinction spectrum shifting the in-plane dipole resonance surface plasmon peak to longer wavelengths and the out-of-plane quadrupole resonance to shorter wavelengths. In addition the background of the extinction spectrum shows a substantial increase on the red side and a reduction on the

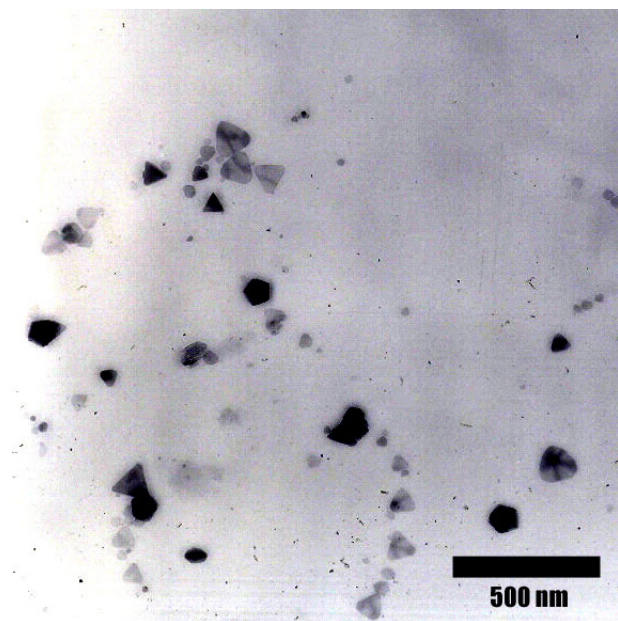


Figure 10. TEM of sample containing silver nanoplatelet aggregates after exposure to the nanosecond laser. Note that almost all of the nanoplatelets are away from each other showing that sample is deaggregated.

blue side. Similar observations on the change in background extinction had been reported earlier [12]. Our calculations clearly show that the strength of IQ and OQ reduces for all relative orientations of two neighboring nanoplatelets. This causes a reduction in the extinction on the blue end of the spectrum. Comparison of numerical and experimental spectrum show that a large number of particles present in the aggregates could be TB orientation or close it. This explains the red-shift of the in-plane dipole resonance. The observed background increase in the red side of the extinction spectrum is caused by a distribution of other possible orientations in the attachment of platelets. For comparison, aggregates of nanospheres have also been prepared and studied. The experimentally observed changes in the extinction spectrum of the nanospheres aggregates are in agreement with those predicted by the numerical calculations. Further, the stability of the aggregates against laser irradiation was also studied and a significant difference was found between the aggregates of spheres versus those of platelets. It was observed that it is possible to deaggregate platelet aggregates using a nanosecond laser of suitable power. This gives the limit of laser power which can be used for SERS or any nonlinear experiments involving nanoplatelet aggregates.

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