## L.5 Aggregation and de-aggregation of metal nanoparticle colloidal solutions

Nanoparticles start aggregating when the volume faction of nanoparticles in a nanocolloidal solution is high. In case of spherical nanoparticles, this aggregation has been reported to lead to the appearance of a new surface plasmon peak and increase in background extinction at the red end of the spectrum. We report for the first time a study of optical properties of aggregates of nanoplatelets carried out at the Laser Physics Applications Division of RRCAT. The stability of the aggregated sample against laser irradiation was also studied.

A colloidal solution of silver nanoplatelets was produced by salt-reduction method followed by photo-induced conversion using a 532 nm laser. This solution was kept in the dark for a few months. After this aging time the sample showed evidence of aggregation. Figures L.5.1 a and b show the extinction spectra of the initial (solid line) and aggregated colloid (dashed line). For the nanoplatelets, the strong peaks at 596 nm and 445 nm are from the in-plane dipole and in-plane quadruple resonance while the weak peak at 336 nm is due to the out-of-plane quadruple resonance. Comparing the extinction spectrum of the aggregated colloid with this we find that the overall extinction at the red end of the sample has increased, which is an indication of presence of random aggregations. All the SPR peaks were broadened. The out-of-plane quadruple resonance at 336 nm has blue-shifted by 4 nm, while the SPR peak at 596 nm has shifted by about 69 nm.

To understand effect of aggregation on the extinction spectra of nanoparticles we have done some preliminary calculations and compared extinction spectra of single and double truncated triangular-shaped platelets. In a colloidal solution the nanoplatelets can get attached to each other in any possible orientations. The calculations were done for few of such possible orientations of two interacting platelets. Though the amounts of shifts in various possible orientations are different, all of them show large red shift of in-plane dipole resonance and small blue shift of out-of-plane quadrupole resonance. This shows that the observed changes in the extinction spectrum are caused by aggregation. Fig.L.5.1(c) shows the TEM of the aggregated colloid.

The aggregate sample was again exposed to 532 nm, 250 ns, 7 kHz laser pulses. The average laser power was 50 W/cm$^2$. Fig.L.5.2 shows the transmission spectra of the sample during the exposure. During the initial stage the peak at 665 nm reduced in strength and also shifts to blue side of the spectrum. On further exposure the peak further blue shifts to 596 nm. The TEM of the sample at this stage is shown in Fig.L.5.3. Almost all of the nanoplatelets have separated.

Both the extinction spectrum results and the TEM show that nanoplatelets have been de-aggregated. It is interesting to note that at similar irradiation levels aggregates of silver nanospheres were unaffected. This shows that, in colloids, the aggregation of nanoplatelets is weaker as compared to nanospheres. Therefore in case of undesired aggregation, laser irradiation of suitable power can be used for de-aggregation.

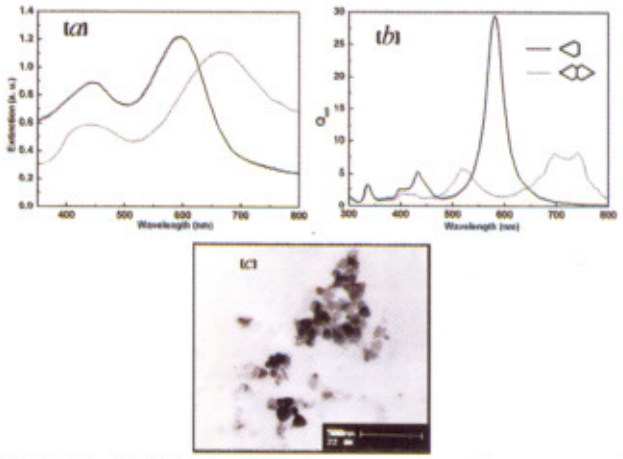


*Fig.L.5.1: (a) Calculated extinction spectra of two separated (solid line) and joined (dashed line) nanotriangles. (b) Measured extinction spectra of a nanotriangle colloid (solid line) and aggregated nanotriangles (dashed line). (c) TEM pictures of aggregated nanotriangles.*

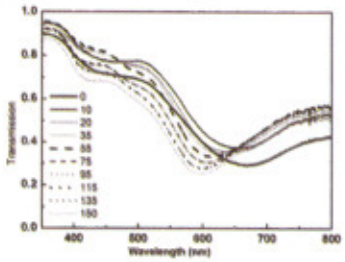


*Fig.L.5.2: The transmission of the nanoplatelet sample at various times during exposed to high power nanosecond laser. The values shown are exposure time in minutes.*

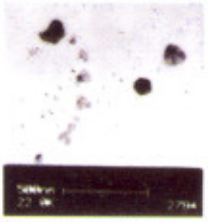

*Fig.L.5.3: TEM of the nanoplatelets after exposure to high power laser. There were very few particles that are close to each other.*

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