L.4: Tuning the Surface Plasmon Resonance of silver nanoparticles

Metal nanoparticles can enhance the applied electric or optical field in and around the nanoparticle. This enhancement of optical field increases the nonlinear optical response of the nanoparticle by several orders of magnitude. It is also widely used for enhancing the signals in optical sensing applications like Surface Enhanced Raman Scattering, fluorescence detection etc. The enhancement of field occurs at wavelengths close to the surface plasmon resonance (SPR) of the nanoparticle. Thus it is necessary to tune the SPR peak of the nanoparticle for applications at different wavelengths. Spherical nanoparticles of a given metal have a single fixed SPR peak. Nanoparticles of anisotropic shapes can have multiple SPR peaks and the peak positions depend on the aspect ratio of the particle. Thus by controlling the aspect ratio of the nanoparticle it is possible to tune the SPR peak to the required wavelength.

Fig.L.4.1: Silver nano-colloidal solutions of silver nanoplatelets of different aspect ratios. The nanoparticles in the yellow sample are spherical in shape while the particles in the magenta, orange, green, light blue and dark blue samples are nanoplatelets of increasing aspect ratio.

In the past, Laser Physics Applications Division of RRCAT has used a photochemical method for conversion of silver nanospheres to nanoplatelets. The final dimension of the nanoplatelet is determined by the laser wavelength used in photo-conversion. Thus to tune the SPR peaks a laser with the corresponding tuning range is required. This method was also found to be extremely sensitive to preparation conditions and it was difficult to control the conversion process satisfactorily. Therefore an alternate chemical method has been tried and this has given better results. In this method silver salt is reduced by H_2O_2 along with $NaBH_4$. For stabilizing, PVP polymer is used along with tri-sodium citrate. The solution containing $AgNO_3$, tri-sodium citrate and PVP in water is stirred vigorously at room temperature. A measured amount of H_2O_2 and $NaBH_4$ is added to the above solution. After the addition of the reducing salts the solution shows a series of color changes. Optimization of the preparation procedure has been done now so that it is possible to tune the color of the final solution across the visible spectrum (Fig.L.4.1).

Using the chemical method we were able to tune the in-plane dipole resonance of the nanoparticles from 506 nm to 797 nm. The extinction spectrum of these silver nanoplatelet solutions is shown in Fig.L.4.2. Spherical silver nanoparticle solution is yellow in color and has only one plasmon resonance peak at 400 nm. As the particle starts becoming anisotropic more peaks start appearing in the spectrum. The color of the solution is decided by the in-plane dipole resonance, which is the strongest peak in the visible spectrum. For example, the sample with a peak at 797 nm is blue in color, while the sample with a peak at 506 nm is magenta in color. The wavelength of this resonance is very sensitive to the aspect ratio of the nanoparticle and shifts towards red with increasing aspect ratio. The out-of-plane resonance occurs on the blue side of the sphere resonance. It shows only a small blue shift with increasing aspect ratio. For all the platelet samples shown in Fig L.4.1, the out-of plane resonance is around 330 nm.

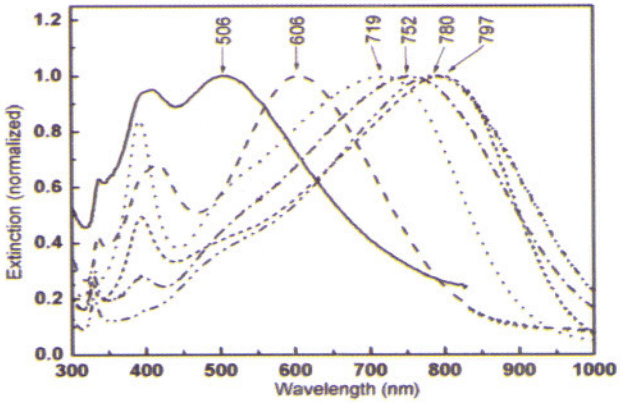

Fig.L.4.2. Extinction spectrum of nanoplatelets of different aspect ratios. The arrows indicate the in-plane dipole SPR peak positions of the silver nanoplatelets.

In addition to the flexibility of tuning the surface plasmon resonance peak position, the chemical method is found to be faster. The photochemical method takes about 8 hrs while the chemical method takes only 30 min. The repeatability of spectrum of the nanoparticle solution is as good as that obtained by the photochemical method.

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