L.5: A novel light based synthesis route for spherical and triangular silver nanoparticles

Silver nanoparticles (SNPs) are known to exhibit strong absorption and scattering of light due to collective excitation of free electrons [called "localized surface plasmon resonance (LSPR)"]. The resonance wavelength can be tuned with shape and size of nanoparticles. Anisotropic shapes like triangular and rods produce strong LSPR response tuning in entire visible to near IR regions, suggesting their potential application for solar light harvesting. Generally, a two step seed mediated growth is popular for the growth of anisotropic shapes. This involves seed nanoparticles formation with strong reducing agents like $NaBH_4$, followed by their anisotropic growth in the presence of other chemicals. As a result, these nanoparticles are associated with different extraneous species or ions used during their growth. In this respect, a complete light based growth process has been demonstrated for the synthesis of spherical and triangular shape nanoparticles. It involves synthesis of spherical nanoparticles through liquid phase pulsed laser ablation (LPPLA) followed by their photo-mediated shape transformation into triangular nanoplates through visible light irradiation. Figure L.5.1 shows schematic of LPPLA growth of SNPs (left top) with LSPR absorbance at different ablation time (left bottom) and effect of TSC concentration on morphology of SNPs and LSPR peak absorbance (right).

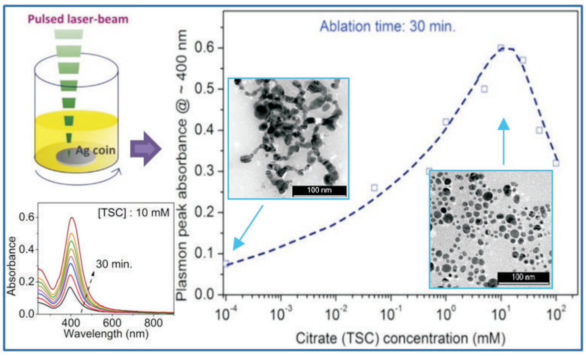

Fig. L.5.1: (Left top) Schematic of LPPLA growth of SNPs;(left bottom) LSPR absorbance at different ablation time; (right) effect of TSC concentration on morphology of SNPs and LSPR peak absorbance

Laser ablation of silver coin in aqueous trisodium citrate (TSC) solution resulted in the formation of isolated spherical nanoparticles with strong LSPR response (at ~ 400 nm) as compared to those produced in pure water. Generation of high concentration of stable nanoparticles was observed with TSC concentration of ~ 5-25 mM with pH ~ 7-10. On the basis of Mie theory calculations, the estimated concentration of the nanoparticles for 30 mins. of ablation was about 1.2 x 10^{12}/mL. It was shown that this new method has the potential to produce higher concentration of nanoparticles than that can be obtained through wet chemical route.

Under visible light irradiation, these LPPLA-grown SNPs were shown to transform into triangular shape nanoplates, exhibiting broad LSPR absorbance in the range of ~ 600-1000 nm. Presence of additional Ag^+ ions during light irradiation resulted in increasing the yield of triangular nanoplates. The size of these silver nanoplates is controlled by TSC concentration and solution pH. The size dispersion of the nanoplates can be reduced with subsequent centrifugation. The resultant citrate-capped SNPs, with negative surface charge, exhibited very long shelf life. Figure L.5.2 shows schematic of light irradiation (left top) with LSPR absorbance graph at different irradiation time (left bottom) and effect of light irradiation on morphology of SNPs and plasmon peak absorbance (right).

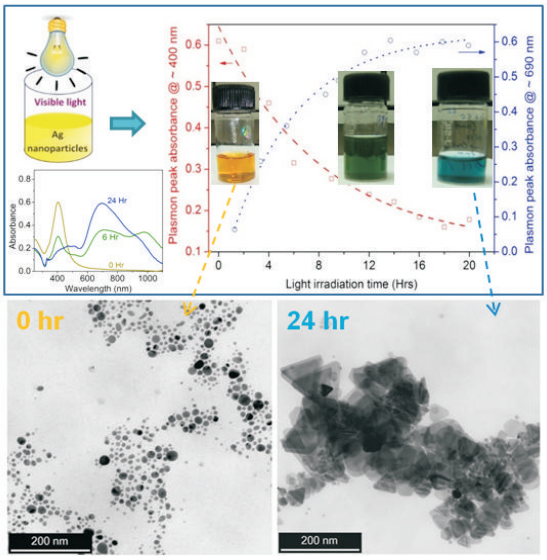

Fig. L.5.2: (Left top) *Schematic of light irradiation*; (left bottom) *LSPR absorbance at different irradiation time*; (right) *effect of light irradiation on morphology of SNPs and plasmon peak absorbance*

Notable features of the new synthesis route for spherical and triangular shaped SNPs include (i) simplified process using single reagent, (ii) high stability of generated nanoparticles, (iii) control of nanoparticle concentration with ablation time and (iv) potential to generate other metal nanoparticles. The resultant SNPs can find potential applications in colorimetric sensing of heavy metal ions in water, surface enhanced Raman scattering (SERS), photovoltaics, photocatalysis etc.

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