SYNOPSIS

Synthesis, photophysical study and simulation of surface Plasmon resonance spectra of different shaped silver nanostructures in aqueous environment

Synthesis of nanosized particles is a growing research field in chemical science, in accordance with the extensive development of nanotechnology. The size induced properties of nanoparticles enable the development of new applications such as in catalysis, optics, microelectronics and so on. Among the noble metal nanoparticles, silver nanoparticles are of great interest in a number of disciplines because of their potential use as optical labels, contrast enhancement agents, near-field optical probes, chemical and biological sensors, and substrates for surface-enhanced Raman spectroscopy (SERS). Many techniques including chemical and physical means was developed to prepare the metal nanoparticles, such as chemical reduction, electrochemical reduction, and photochemical reduction and so on. Chemical reduction is one of the commonest ways to synthesize colloidal metal particles because of its simple operation and simple equipment needed. Many solution phase synthesis produce silver nanoparticles of specific size and shape, but still there is enough scope for improvement in terms of yield, purity, monodispersity, scale of synthesis and total synthetic time etc.

In this research work, we have demonstrated the synthesis of 'native' silver hydrosol (i.e. silver hydrosol without any stabilizing agent) as well as the silver nanoparticles stabilized by two isomeric unsaturated dibasic acid salts- sodium maleate and sodium fumarate. The particles have been characterized by UV-Visible spectroscopy, fluorescence spectroscopy, transmission electron microscopy and FT-IR studies. An extensive UV-Vis

spectral studies and its comparison with the simulated curve obtained from modified Mie's theory has been done to understand the factors responsible for the shift of surface Plasmon resonance band. Though changing the size of spherical particles can induce small shifts in the LSPR peak position, in theory and in practice, changing the shape of silver nanoparticles provides more versatility. A model has been proposed using DFT based theoretical calculation for the unique size dependency of silver nanoparticles when the above two isomeric dicarboxylates are used as stabilizer.

Efforts have also been made for the synthesis of tunable coloured silver sols having different morphologies. The procedure is based on the seed-mediated growth approach where methyl cellulose (MC) has been used as soft-template in the growth solution. Nanostructures of varying morphologies as well as colour of the silver sols are controlled by altering the concentration of citrate in the growth solution. These nanostructures are characterized using UV–Vis and TEM spectroscopic study. Simulation of the UV–Vis extinction spectra of our synthesized silver nanostructures has been also carried out using discrete dipole approximation (DDA) method.

Similarly, we applied the concept of above seed-mediated growth method using a new soft template, hydroxylpropyl methyl cellulose i.e. HPMC, instead of MC. Again with the variation of concentration of tri-sodium citrate in growth solution, two different dimensional Ag nano was obtained: one is rod-like (1D) and other is disc-like (2D). Actually, the central to the concept of seed-mediated growth of nanoparticles is that small nanoparticle seeds serve as nucleation centres to grow nanoparticles to a desired size and shape. It is found that the additional citrate ions in the growth solution play the pivotal role in controlling the size of Ag nanorods and nanodiscs. Similar to the polymers in the solution, citrate ions could be likewise dynamically adsorbed on the growing silver nanoparticles and promote the one-dimensional (1D) and two-dimensional (2D) growth of nanoparticles. Morphological,

structural, and spectral changes associated with the seed-mediated growth of the nanoparticles in the presence of HPMC are characterized using UV–Vis and TEM spectroscopic studies. Metal nanoparticles have received increasing attention for their peculiar capability to control local surface plasmon resonance (LSPR) when interacting with incident light waves. The silver nanodiscs and nanorods also exhibit interesting optical features that can be simulated using the DDA based calculations. Simulated UV-Vis extinction spectra using DDA method is verified by comparing the results with the well-known exact analytical solutions of Maxwell's equation derive from Mie's theory for a sphere. A comparison between the experimental and theoretical extinction spectra have been done for anisotropic AgNPs. Our present simulation of extinction spectra using DDA method suggests the potentiality of DDA method while computing the extinction spectra of anisotropically grown silver nanoparticles.

We also synthesize salicylate anion-stabilized spherical silver nanoparticles by sodium borohydride reduction. These AgNPs are characterized by UV-Vis spectroscopy, TEM, XRD analysis and fluorescence spectroscopic technique. Emission of salicylate anion in free state and attached to AgNPs are being discussed. Fluorescence emission of salicylate functionalized silver nanoparticles reveals that salicylate anions are primarily absorbed on the surface of silver nanoparticles. It has been further demonstrated using 1, 4-dioxane as surface modifier that the salicylate anions are preferentially adsorbed on the surface of silver nanoparticles.