

L.10: Plasmonic nanoparticles based colorimetric detection of carcinogenic metal ions in aqueous solutions

Detection of carcinogenic heavy metal ions such as Hg in water is important for safe use of water and preserving the aquatic ecosystem. Noble metal nanoparticles display localized surface plasmonic resonance (LSPR) response in visible region depending on size, shape and degree of aggregation of the nanoparticles. These nanoparticles can be effectively exploited as cost effective real time colorimetric sensor (by monitoring plasmon response) for trace detection of heavy metal ions. An anti-aggregation based colorimetric sensing technique using gold nanoparticles (GNPs) has been demonstrated with the capability of detecting about 50 ppb concentration of Hg^{2+} .

GNPs of different average sizes (~15-35 nm) and variable surface characteristics in aqueous tri-sodium citrate (TSC) solutions (1-5%) were grown using laser ablation and citrate reduction method. The aggregation characteristics of the grown GNPs were studied in the presence of different cationic species (Rh6G, CTAB) and thiol group compounds (mercaptoethanol (MEA), thioglycolic acid (TGA)) under various pH conditions. The aggregation characteristics and colorimetric changes were analyzed using UV-Vis fiber spectrograph.

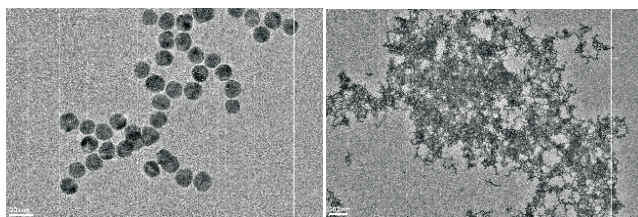


Fig. L.10.1: TEM image of (left) GNPs grown with citrate and (right) its aggregates in the presence of MEA and low $[Hg^{2+}]$ ions.

GNPs of nearly spherical shape and isolated in the presence of TSC exhibited characteristic red color with LSPR wavelength of about 530 nm. Figure L.10.1 shows TEM image of the grown GNPs in 2% citrate solution. In the presence of thiol group compounds, the inter particle separation decreases and aggregation of nanoparticles occurs, as shown in Figure L.10.1. This favors plasmon coupling resulting into change of LSPR wavelength towards longer wavelength and consequently change in the color of the solution. Figure L.10.2 shows optical absorbance of MEA-capped GNPs with different Hg concentrations. The additional peak at longer wavelengths is due to aggregation of nanoparticles caused by reduced electrostatic repulsion after surface capping by thiol

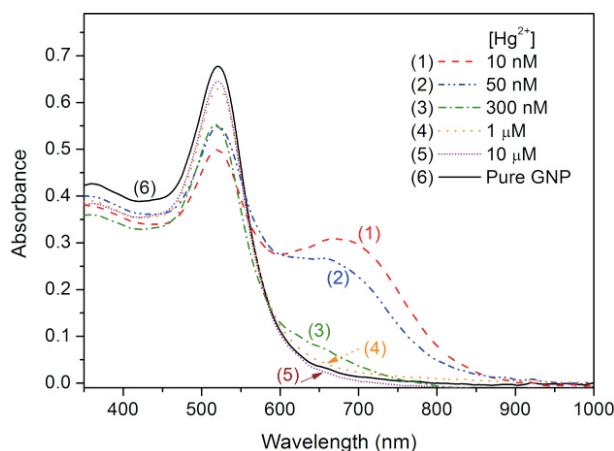


Fig. L.10.2: Optical absorption of GNPs with MEA and varying conc. of $[Hg^{2+}]$.

ligands. In the presence of Hg^{2+} having higher affinity with thiol ligand, surface capping of GNPs by MEA decreases. Hence, at higher Hg^{2+} concentration, the aggregation peak decreases with concurrent increase in peak at ~530 nm corresponding to isolated GNPs. Thus in the presence of Hg^{2+} , suppression of GNPs aggregation helped in retaining of the characteristic red color of the solution, as shown in Figure L.10.3. Capping agent concentration was varied to optimize the GNP's aggregation at varied citrate concentrations and about 5 μM MEA was found to produce naked eye detectable color change of GNPs solution grown with citrate solution.

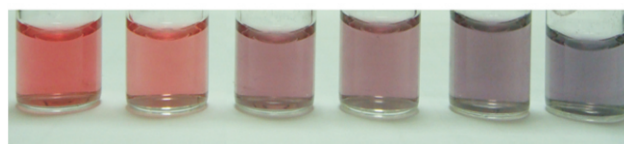


Fig. L.10.3: Colorimetric changes of GNPs with decreasing Hg^{2+} ion concentration from left: 10 μM , 1 μM , 300 nM, 50 nM, 10 nM and without Hg^{2+} ions.

The detection limit of GNPs based colorimetric sensing technique was found to be about 50 ppb of Hg^{2+} . Further studies on ion selective detection using these nanoparticles is under progress. This method, based on wet chemical route synthesis of GNPs is a simple, versatile and cost effective route for detection of toxic heavy metal ions with ppb level of detection limit. This kind of plasmonic based colorimetric sensor will be useful in environmental, pharmaceutical and food industries.

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