Chapter VII

Conclusions

This chapter contains concluding remarks on the salient features of the work described in the thesis and future potential developments in the area.
7.1 Summary of the work:

The main emphasis of work presented in this thesis has been to demonstrate the synthesis of gold nanotriangles, core-shell nanoparticles of various compositions and shape modification using different chemical and physical means. The aspects that have been covered in this thesis are: 1) Synthesis of gold nanotriangles using undialyzed and dialyzed lemongrass extract at room temperature. 2) Synthesis of triangular Au core-Ag shell nanoparticles and spherical gold-titania core-shell nanoparticles. 3) Shape transformation of gold nanotriangles using different halide ions and surfactants. 4) Photofragmentation of gold nanotriangles using Keggin ions under UV light irradiation. 5) Effect of temperatures on the synthesis of gold nanotriangles using lemongrass extract.

Room temperature and environmentally benign approach for the synthesis of gold nanotriangles and hexagons using undialyzed lemongrass extract as reducing and shape-directing agents has been demonstrated. The yield of gold nanotriangles synthesized using lemongrass extract is found to be 45%, which is higher than the previously reported chemical and photochemical methods. The AFM analysis showed that thickness of nanotriangle was ca. 18 nm. Different cut-off dialysis bags (3, 12.5 and 30 kDa) were used for dialysis of lemongrass extract against 10^{-3} M HAuCl₄ solution. Biomolecules, which have size below pore size of the dialysis bag used, diffuse from the inside bag to the external gold ion solution in the direction of decreasing concentration and reduce gold ions to synthesize spherical and triangular nanoparticles. The concentrations of extracts inside the different bags were found to be in the following order: 3 kDa>12 kDa>30 kDa, while the concentrations of extract outside the bags were in the reverse order. Spherical nanoparticles and a small percentage of gold nanotriangles were synthesized inside 3 kDa bag due to the fast reduction of diffused gold ions inside the bag. A large percentage of triangular and cubic nanoparticles were synthesized inside 12.5 and 30 kDa bags respectively due to the slow reduction of gold ions. A varying yield and size of gold nanotriangles were also found to be synthesized outside the different cut-off bags due to different rate of reduction of gold ions by outside-diffused lemongrass extract. In another experiments, lemongrass extract was dialyzed against water using 3, 12.5 and 30 kDa cut-off bags and dialyzed extract obtained from both inside and outside bags were used for the reduction of 10^{-3} M HAuCl₄ solution. Spherical nanoparticles along with the smaller
nanotriangles were synthesized using dialyzed extract obtained from inside the 3 and 12.5 kDa bags, while the gold nanocubes were observed, when gold ions were reduced using dialyzed extract obtained from inside a 30 kDa bag. Synthesis of different size and yield of gold nanotriangles using dialyzed extract obtained from outside the different dialysis bags have also been demonstrated. FTIR analysis showed that sugar derivatives and citral molecules found in lemongrass extract act as reducing and shape-directing agent for the synthesis of nanotriangles.

Synthesis of triangular Au core-Ag shell nanoparticles using ascorbic acid as a weak reducing agent under alkaline pH has been demonstrated. It was shown that 10^{-7} M concentration of silver ions was perfect to synthesize silver shell around gold core nanoparticles. Positively charged silver ions interact with negatively charged gold nanotriangles through electrostatic interaction. The bound silver ions on the surface of gold nanotriangles were reduced by ascorbic acid under different alkaline pH to achieve varying thickness of silver shell. The thickness of silver shell synthesized at pH 12 was estimated to be ca. 5 nm. Synthesis of spherical gold-titania core-shell nanoparticles using the hydrolyzing enzyme from fungus Fusarium oxysporum has also been demonstrated. A hydrolyzing enzyme has ability to hydrolyze TiF$_6^-$ ions to titania nanoparticles. The enzyme was immobilized on the surface of aspartic acid modified spherical gold nanoparticles and subsequently exposed to TiF$_6^-$ ion solution leading to the formation of spherical gold-titania core-shell nanoparticles. XRD analysis showed that brookite and rutile polymorphs of titania were synthesized on the surface of gold nanoparticles.

Shape transformation of already synthesized gold nanotriangles using halide ions and the effect of halide ions on the growth of nanotriangles during synthesis using lemongrass extract have been demonstrated. Fluoride and chloride ions do not affect the morphology of gold nanotriangles, while bromide ions promote corrugation on the edges of nanotriangles. A drastic change in the morphology of nanotriangles after treatment with iodide ions was observed. Iodide ions transform nanotriangles into circular plate like nanostructures. Iodide ions have highest ability to chemisorb on the surface of gold nanotriangles compared to the other halide ions and thus create the highest strain on the underlying Au (111) lattice planes. The shape transformation has been attributed to the
strain developed by the adlayers of I\textsuperscript{-} ions on the (111) lattice planes of gold nanotriangles. Furthermore, the prominent effects of halide ions on the growth of nanotriangles during synthesis have been demonstrated. It was shown that fluoride ions do not affect the growth of nanotriangles, while chloride ions promote the synthesis of triangular nanoparticles. It was proposed that CI\textsuperscript{-} ions having the ability to chemisorb on the (111) lattice of fcc gold with a hexagonal closed packed structure could be responsible for the formation of \textless{111}\textgreater oriented gold nanotriangles and nanohexagons.

On the contrary, bromide and iodide ions inhibit the growth of nanotriangles due to their higher tendency to chemosorb and produce strains on the surface of initially formed gold nanoparticles. Similarly the effects of cationic surfactants such as CTAB and CTAC have also been studied. \textbf{10}^{-2}\text{ M} concentration of CTAB transforms gold nanotriangles into circular plate like structures, while lower concentrations do not have significant effect on the morphology of nanotriangles. On the other hand, CTAC does not affect the morphology of gold nanotriangles due to the presence of chloride ions. Gold ions also transform gold nanotriangles into highly branched nanostructures in the presence of \textbf{10}^{-2}\text{ M} concentration of CTAB, while modify them into nanocoral and nanoflowers like structures in the presence of \textbf{10}^{-3}\text{ M} concentration of CTAC.

Photofragmentation of gold nanotriangles into spherical and aggregated nanoparticles in the presence of Keggin ions under UV light irradiation has been demonstrated. Different concentrations of Keggin ions (\textbf{10}^{-2}\text{ M} to \textbf{10}^{-4}\text{ M}) were used to achieve the varying percentage of fragmentation of already synthesized gold nanotriangles. Keggin ions get reduce from M\textsuperscript{11+} to M\textsuperscript{10+} oxidation state in the presence of iso-propyl alcohol under the UV light irradiation and therefore show dark blue colour after reduction. The high electron density on the surface of gold nanotriangles bound with Keggin ions after UV light irradiation cause fragmentation of triangles into spherical nanoparticles due to charge repulsion. Gold nanotriangles synthesized in the presence of different concentration of Keggin ions using lemongrass extract have also been demonstrated. It is believed that high concentration (\textbf{10}^{-3}\text{ M}) of Keggin ions binds to lattice planes of initially formed gold nanoparticles and inhibits the growth of nanoparticles in the \textless{111}\textgreater direction. Gold nanotriangles synthesized in the presence of different concentrations of Keggin ions were also UV light irradiated in order to fragment...
nanotriangles into spherical nanoparticles. Synthesis of gold nanotriangles at different temperatures using lemongrass extract has been described in the last chapter. Synthesis of nanotriangles is a kinetically driven process and fast reduction at higher temperature facilitates the synthesis of nanotriangles of a low population and smaller size. It has also been shown that the NIR absorption peak of gold nanotriangles could be fine-tuned by merely varying the edge length of gold nanotriangles.

7.2 Scope for future work:

The size-controlled synthesis of gold nanotriangles is an interesting result and might have potential applications in many fields. It would be interesting to use these gold nanoparticles for hyperthermic treatment of cancerous cells due to their high absorbance in the NIR region of the electromagnetic spectrum. Since the human body tissues can sufficiently transmit light in the range from 800 to 1100 nm, irradiation of suitably surface modified gold nanotriangles with cancer cell specific antibody, which are selectively localized near the cancerous tissue, may kill the cells in the local vicinity of gold nanotriangles. Gold nanotriangles could also be used for delivery of drugs or genes. Gold nanoparticles would act as a non-viral vector for the delivery of gene inside the biological cells.

We have already studied the effect of different halide ions and cationic surfactants on the morphology of gold nanoparticles during synthesis so it is worth to studying the effect of different anionic surfactants on the growth of nanoparticles. It has been shown in previous reports that presence of silver ions enhances the population and aspect ratio of gold nanorods. Similar effect can be studied in the case of gold nanoparticles synthesize using biological means. Polyoxometallates are well known for their diverse applications such as degradation of dyes and antiviral as well as antitumor agents. Thus, it would be significant to immobilize polyoxometallates on the surface of metal nanoparticles and investigate their potential applications in biomedical areas and also in removal of waste from polluted water.