Chapter VII

Conclusions

This chapter describes the salient features of the work undertaken in this thesis and discusses the possible avenues for future work.
7.1 Summary of the work.

Nanotechnology is becoming an integral part of all application-oriented research that is being carried out in various fields. One of the important challenges is to exploit the unusual electronic, optical and surface properties of the nanostructured materials to our benefit for a variety of potential applications. The work undertaken in this thesis has emphasized on the use of some unusual properties of metal nanostructures for potential applications in chemical vapor sensing and solution based mercury ions detection. Furthermore, cytotoxicity studies of the biogenic gold nanotriangles have been performed, since they are the prime materials used for a majority of the work presented in the thesis.

The work in this thesis has been devoted towards exploitation of the electrical properties of the metal nanostructures on an insulating substrate. The electronic conduction of the material at nanoscale largely depends on the local environment in the vicinity of the particles. Thus, the presence of an electron donor or acceptor ligand in the microenvironment results in a large impact on the electrical conduction behavior of the metal nanoparticles. A part of this thesis has been focused on immobilization of biogenic gold nanotriangles on quartz substrates to fabricate conducting films of varying resistances. The electrical properties of the film have been studied as a function of number of layers of gold nanotriangles on the surface. Besides, the anisotropic nature and subsequent unique electrical property of the nanoparticulate film has been used to detect polar vapors, methanol being the vapor for case study. The film shows nine orders of magnitude increase in the electrical conductivity on exposure to the methanol vapors and a response time of 10 s. The drastic increase in the electrical conductivity of the film in the presence of the methanol vapors has been attributed to the field enhancement effect at the tips of the gold nanotriangles in the presence of vapors in the vicinity.

As an extension to the previous work, Ag-Au bimetallic film with high porosity has been fabricated on the quartz substrate by a transmetallation approach. The electrical properties of the films have been studies as a function of concentration of chloroaurate ions used for the bimetallic film fabrication. The microstructure analysis of the films had been done which reveals that the bimetallic particles formed on the surface of the substrate are interconnected with pores in between them. This film of high porosity was then utilized for detection of ammonia and carbon dioxide vapors, studying the change in the electrical conductivit
conduction behavior of the film on exposure to the vapor. The film shows excellent sensitivity to the vapors, quick response time and a very uniform cycling behavior. Thus, this film has been proposed to be a promising candidate for developing metal nanoparticle based chemiresistor to detect these gases.

Soft templates have also been exploited in this work, where the spider and silkworm silk has been used as active scaffolds for immobilization of gold nanoparticles on the surface. Spider silk and silkworm silk are two natural polymers composed largely of proteinaceous material, which have been extensively studied in the past for their mechanical properties and tensile strength. Spider silk has been known to show super-contraction in the presence of polar vapors, which has been exploited here to our benefit. Spider and silkworm silk has been used to reduce chloroaurate ions to form nanoparticles and subsequently immobilize them on their surface using free amine moieties. The gold nanoparticles-decorated spider silk bioconjugate was used for electrical measurements. Based on the prior knowledge of super contraction property of the spider silk, the bioconjugate was exposed to vapors of varying polarity to obtain a graded electrical response based on the vapor polarity. It has been observed that higher the polarity of the vapor, higher is the increase in electrical conductivity of the bioconjugate. The phenomenon has been explained based on the fact that exposure to polar vapors causes super contraction of the gold nanoparticles decorated spider silk, thereby increasing the electrical conductivity.

Besides the electrical property, the optical property of the gold nanotriangles has been exploited for the solution-based detection of mercuric ions with atto-molar level sensitivity. Gold nanotriangles show a strong absorption peak in the NIR region of the electromagnetic spectrum owing to their anisotropic nature. This NIR absorption is known to be strongly dependent on the shape of the gold nanotriangles. These triangles, synthesized by reduction of chloroaurate ions using lemon grass leaf extract, are single crystalline and extremely thin in nature with the thickness ranging between 15-25 nm. Thus, they are highly prone to damage or disintegration under slight stress in the crystal structure. The strong tendency of mercury metal to amalgamate gold is an age-old phenomenon, which forms the basis of this work. The mercuric ions present in water were reduced in presence of gold nanotriangles using sodium borohydride to form mercury metal, which subsequently amalgamates the gold nanotriangles. The amalgamation process leads to disintegration of the gold nanotriangles.
into small spherical particles, leaving a signature in the optical spectra as loss in NIR absorption intensity. It is this optical signature, which is picked up for quantitative analysis of the mercuric ion concentration in the sample. The HRTEM analysis reveals that the amalgamation process is initiated at the edges and tips of the gold nanotriangles, breaking them off into small particles by budding.

Biogenic methods for synthesizing nanostructured materials are being investigated to replace the toxic chemical methods. However, it is immensely important to analyze the cytotoxicity levels and biocompatibility of these biogenic materials before envisaging their biomedical applications. Gold nanotriangles are an integral part of this thesis from the material point of view and thus, it becomes necessary to investigate their cytotoxicity levels. Besides, the exotic properties offered by them makes them a promising candidate for various applications. Their strong NIR absorption tendency can be utilized for hyperthermic treatment of cancerous cells. With these aspects in mind, a study was undertaken to analyze the cytotoxicity levels of these nanotriangles, their tendency to elicit immunological responses and their capability to enter inside the cell without disrupting the cellular integrity. It has been shown that the biogenic gold nanoparticles are non-cytotoxic up to 800 μM concentration despite the fact that per particle load of gold will be much more due to their larger size. They are internalized inside the cells and are confined in the cytoplasmic space but fail to break through in the nucleus. The possible mechanism of entry could be by the phenomenon of phagocytosis, a process reported for uptake of particles bigger than 100 nm. Gold nanoparticles have also shown the capability to induce immunological response in the cells, though the cells are viable on exposure for 24 hours. Thus, these particles can be of immense use in the metal nanoparticles based formulation for biomedical applications.

7.1 Scope for future work.

The thesis illustrates the potential application of metal nanostructures in chemical vapor sensing. The results provided in the work show a huge promise towards the fabrication of metal nanoparticle based sensors for detecting chemical vapors. However, a key issue which could not be pursued in this work was the selectivity of these metal nanoparticle films. It would be really interesting to modify the surface of these nanoparticles prior to film fabrication to impart them selectivity towards a particular gas. Another issue of importance is
to work out the minimum detection limit of these films, which have been used for sensing various gases.

The work undertaken to fabricate spider silk bioconjugate shows great potential for detecting polar vapors based on their polarity. However, one aspect that will be interesting to pursue is the study of the force of contraction of these bioconjugates on exposure of different vapors. These bioconjugates can be used as linear motors to perform tasks based on their contraction-relaxation tendency, if these physical values are known. Besides, it would be interesting to study the minimum vapor detection limit of this system because the contraction-relaxation of the spider silk fiber is a macroscopic phenomenon.

The work performed to study the cytotoxicity limits and biocompatibility of the gold nanotriangles requires detailed study. Use of a phagocytotic and pinocytotic inhibitor during the exposure of gold nanotriangles to cells will illustrate the mechanism of entry of these nanoparticles in the cells. Besides, much more work could be done to study the immunological response of the cells in great details. A detailed account on cytokine profiling of the cell during exposure to gold nanotriangles will open up a new arena in the field of nanotechnology based biomedical research.