CHAPTER 9
SUMMARY AND SCOPE FOR FUTURE WORK

This chapter summarises main conclusions drawn from the work carried out as a part of this doctoral work. Suggestions for future work are included at the end.

9.1 Summary

It has been established through this work that green synthesis of noble metals (Ag, Au, Cu) and alloy (Ag-Cu, Au-Cu) nanoparticles is possible through rice-starch. Control over their shape, size, and chemistry may be obtained either by heat treatment or by manipulating the nucleation and growth kinetics. The resulting change in LSPR behaviour can be attributed to microstructural features at nanoscale. It is also dependent on the structural complexities at the atomic scale. Sol stabilities of Au, Ag, and Cu was observed beyond $\sim$ 24, $\sim$ 12, and $\sim$ 1 months respectively. Heat treatment of Au-Cu nanoparticles in solid state close to AuCu intermetallic phase fields have given rise to a series of one dimensional superlattice structures based on orthorhombic AuCu (oP8). Structural transformation from Pbam to $P2_12_12$ has also been observed. These structural transformations have been understood by invoking the presence of vacancies within the nano-domains of the nanoparticles.

Other polymeric processes have been used for synthesis of Au and Au-Cu nanostructures. Shape control is achieved in Au nanoparticles by seeded growth approach. Two predominant shapes namely decahedral and truncated tetrahedral shapes are seen. They have been found to be dependent on the nature of the seed crystal. The seed in this synthesis seems to be either a spherical or an icosahedral one.The pentagonal twinned morphology observed under TEM has displayed two distinct types of interfaces. They refer to diffuse and sharp interfaces. Each of the three fold orientations of rotational twins forming pentatwins possesses a common five-fold axis inherited from the seed. The truncated tetrahedral particles revealed satellite spots around main Bragg spots and appearance of reflections otherwise forbidden in FCC-Au. This has been understood in terms of intrinsic fault. The reduction of cell size vis-à-vis to that of FCC-Au could be rationalized based on intrinsic faults in the Au nanoparticles. The LSPR band could be tuned from $\sim$ 520 nm to $\sim$ 620 nm via shape control in Au nanoparticles.

The morphological changes in Au-Cu alloy nanoparticles are realized through variation of concentration of stabilizer and Cu ions. Au-Cu multipods and nanowires have been observed by changing synthesis condition. Morphological transformation observed in them have been correlated with defects developed during intial stage of growth. Nanowires, in particular grew through oriented attachment of nanoparticles. There is a preferential tendency for attachment along $\{111\}$ and $\{200\}$ crystallographic facets. The LSPR band could be modulated from $\sim$ 520 nm to $\sim$ 800 nm (near infra-red region) by changing the shape from spherical to multipods nanoparticles.

Structural changes have been demonstrated in Au-Cu alloy nanoparticles near intermetallic phase fields by heat treatment in solution phase. Three novel structural characteristics of these particles have been observed. One of them relates to modification of the AuCu tetragonal cell (tP4) mimicking cubic cell metric properties without losing tetragonal symmetry. The other two refers to vacancy ordering along $< 111 >$ directions based on an ordered $AuCu_3$ cubic phase (cP4). On one hand, statistical occupancy of vacancy on Cu site in $\{111\}$ planes lead to the reduction of cell size from ~ 3.75 Å to ~ 3.5Å whereas periodic introduction of a vacant layer on the other hand, gives rise to symmetry breaking leading to formation of a trigonal cell.

Contrast interpretation of HRTEM images acquired from elemental (Ag, Au) and alloy (Ag-Cu, Au-Cu) nanoparticles have been attempted through multislice image simulations. Images have been quantified in terms of atom column positions, local thickness variations, strains etc. Exit wave analysis from Au-Cu intermetallic nanoparticles revealed the contrast reversal in exit wave phase of Cu atom columns at every ~ 9 nm thickness unlike Au atom columns where phase was always present throughout the entire thickness (6 to 45 nm). Complexities in interpretation of structures obtained through HRTEM pertain to the difference in the channeling behaviour of electrons through the structures as well as in the nature of their atomic potentials.

9.2 Suggestion for future work

Studies to ascertain structural transformations in Au-Cu nanostructures should be taken up employing technique of *in situ* heating microscopy. One can estimate critical temperature of transformations corresponding to formation of newer phases. Such investigations correlate evolution of new phases with respect to size. Structural and thermal stabilities of Ag-rich and Cu-rich phases obtained by wet chemical routes can also be explored through aforesaid technique. A study related to composition of the grown nanostructures can be carried out at nanoscale through advanced analytical TEM such as HRSTEM to ascertain atomic level chemistry. Extensive studies to asses sol stabilities through dynamic light scattering (DLS) would be helpful in ascertaining shelf life of sol for applications.