

PREFACE

The novel physical and chemical properties of metallic nanoparticles have given lot of impetus to their utilization for a wide range of applications. The nature of applications depends on structure, shape, size, compositional homogeneity, and structural stability. It is important to carry out structural and microstructural investigations of materials at nanoscale for arriving at the possible correlation with their functional behavior. Low temperature solution methods have been shown to produce colloiddally stable nanomaterials with varied morphologies and compositions. In this thesis, wet chemical method is adopted for the synthesis of elemental and alloy nanoparticles of Ag, Au, Cu, Ag-Cu and Au-Cu with varying structures, shape, size and chemistry by changing the synthesis conditions. They have been characterized extensively at atomic scale to correlate them with the synthesis parameters. The quantitative characterization of structures, shapes, size and chemistry of the particles have been carried out extensively by transmission electron microscope (TEM), high resolution TEM (HRTEM) and high angle annular dark field (HAADF)-scanning TEM (STEM)-X-ray energy dispersive spectroscopy (EDS) coupled with multislice image simulations. Correlations of localized surface plasmon activities with structure, shape, size and chemistry of the particles have been established. The Ag-Au system is not undertaken as a part of present study as this has been investigated extensively. The thesis has **nine** chapters and a bibliographic reference.

The thesis begins with an introduction (**chapter 1**) wherein existing literatures related to this doctoral work has been reviewed thoroughly. This forms the background to carry out this research work. This is followed by experimental methods (**chapter 2**) where all the relevant details of the synthesis methods adopted and experimental techniques utilized in the present doctoral work is given. The work carried out as a part of this doctoral work will be discussed in six chapters for the clarity of presentation.

Chapter 3 demonstrates the development of a green synthesis method for synthesizing Ag, Au, and Cu nanoparticles. This investigation was undertaken with a view to examine the relationship between nanoparticles and their localized surface plasmon resonance (LSPR) behavior by varying the synthesis parameters e.g. amount of rice starch

and pH of the reaction mixture etc. Sol stabilities of Au, Ag, and Cu was observed beyond ~ 24 , ~ 12 , and ~ 1 months respectively.

Chapter 4 deals with detailed investigations of structure, shape, size and chemistry of Ag-Cu and Au-Cu alloy nanostructures. To this end, X-ray diffraction (XRD) and atomic level characterization through HRTEM as well as STEM-EDS of Ag-Cu alloy nanoparticles have been carried out. The varied solid solubility of Cu in Ag and Ag in Cu was observed with a maximum solid solubilities of ~ 11 at. % and ~ 2 at. % in Ag-rich and Cu-rich samples respectively. Both these solid solutions are found as domains in the nanoparticles when investigated with the help of HRTEM. The HAADF-STEM-EDS elemental line scans and maps also substantiated above claims of solid solution formations. Elemental maps from some of the particles displayed the presence Cu-Ag core-shell nanoparticles (NPs) as well. The UV-Vis spectra show two LSPR bands in visible range corresponding to those of Ag-rich and Cu-rich phases respectively.

The morphological and structural transformations in as synthesized and heat treated Au-Cu alloy NPs have been studied in detail pertaining to the complexity of the phase diagram especially at lower temperature and with a view to resolve some long standing questions on structural transformations and defects at lower temperature. The alloying behavior is studied through HRTEM and HAADF-STEM-EDS. Particles were examined using nano-beam diffraction (NBD) to investigate the localized structural transformations. The wire like morphology was found in as synthesized Au-rich samples. Upon examination through HRTEM, oriented attachment kinetics of the NPs leading to nanowire growth has been established. The structure of the as-synthesized nanostructures revealed FCC solid solution phase. A series of one dimensional superlattice structures have been observed, which are based on ordered orthorhombic AuCu (space group Pbam) phase after heat treatment at ~ 400 °C for 1h. This was carried out in solid form under N₂ atmosphere. Superlattice ordering was observed along $[3\bar{1}0]$, $[210]$ and $[201]$ directions. In some of the samples, structural transformation from Pbam to $P2_12_12$ was observed. The synthesis protocol adopted for all the nanoparticles here is akin to that of **chapter 3**.

Chapters 5 and **6** describe the morphological transformation in Au and Au-Cu alloy nanostructures based on synthesis protocols that are different from those of above.

Shape control is achieved in Au nanoparticles by seeded growth approach. Two predominant shapes namely decahedral and truncated tetrahedral shapes evolved and were found to be dependent on the nature of the seed crystal (cf. **Chapter 5**). The pentagonal twinned morphology observed under TEM has displayed two distinct types of interfaces. They are 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 special diffraction characteristics such as 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. This shape control of Au nanoparticles allows us to tune localized surface plasmon resonance (LSPR) band maxima from ~ 520 nm to ~ 620 nm.

The morphological changes in Au-Cu alloy nanoparticles are realized through variation of concentration of stabilizer and Cu ions (**chapter 6**). Grown nanostructures such as multipods and nanowires have been characterized through HRTEM and HAADF-STEM-EDS for their structure and chemistry. The TEM and STEM-EDS results showed the formation of homogeneous Au-Cu alloy nanostructures. An attempt has been made to understand the growth pathways of nanowires by investigating the reaction products at different time intervals. The HRTEM analyses revealed oriented attachment of Au-Cu alloy NPs led to the formation of nanowires. There is a preferential tendency for attachment along $\{111\}$ and $\{100\}$ crystallographic facets. The mechanism of growth of Au-Cu multipods has also been discussed. Multiply-twinned Au seed generated in-situ followed by attachment of Cu atoms at the high energy interface sites and their diffusion have been attributed to the formation of Au-Cu multipods. The LSPR band could be modulated from ~ 520 nm to ~ 800 nm (near infra-red region) by changing the shape from spherical to multipods nanoparticles showing strong anisotropy in growth process. These multipods can be used for photothermal applications.

Chapter 7 demonstrates the structural changes in alloy nanoparticles near intermetallic phase fields by heat treatment in solution phase. A separate synthesis method

was adopted in this part which is different from those of the previous chapters. Heat treatments at $\sim 180^\circ\text{C}$ and $\sim 290^\circ\text{C}$ lead to the formation of Au-Cu solid solution and ordered cubic AuCu_3 (cP4) as well as tetragonal AuCu (tP4) phases respectively. The HAADF-STEM-EDS line scan along single particle show uniformly varying chemistry. Nano-beam diffraction (NBD) was conducted to decipher structural details at the particle level. Two predominant NBD patterns were observed during the investigation from several particles. Analyses of NBD patterns revealed the presence of bi-crystals in the particle with a fixed orientation relationship i.e. $\text{AuCu} [1\bar{1}0]//\text{AuCu} [1\bar{1}1]$; $\text{AuCu}(110)//\text{AuCu}(110)$ and AuCu_3 [I] $[1\bar{2}1]//\text{AuCu}_3$ [II] $[010]$; AuCu_3 [I](111)// AuCu_3 [II]($\bar{1}01$). From the extensive investigation of NBD and HRTEM from single nanoparticles, 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 $\langle 111 \rangle$ 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 $\sim 3.75 \text{ \AA}$ to $\sim 3.5 \text{ \AA}$ whereas periodic introduction of a vacant layer on the other hand, gives rise to symmetry breaking leading to formation of a trigonal cell.

Chapter 8 deals with interpretation of contrast obtained from HRTEM images. Attempts have been made to quantify some of the high resolution phase contrast images acquired from nanoparticles of Ag, Au, Ag-Cu, Au-Cu along $\langle 011 \rangle$ and AuCu intermetallic NPs along $[001]$ zone axes respectively. The Multislice image simulations performed with varying thickness and defocus values displayed complicated contrast patterns. Simulated images were matched with the experimental images. The bright and dark dots correspond to Ag and Au atom column respectively for the Ag and Au samples. For the interpretation of images from Ag-Cu and Au-Cu nanoparticles, it was possible only to identify the heavier atoms like Ag and Au. The thickness of the quantified regions was found to be $\sim 7 \text{ nm}$ and $\sim 8 \text{ nm}$ for Ag and Au NPs respectively. The uniform contrasts across the image could be attributed to strain free regions. The difference in the contrasts at the edges and at the center of the particles was ascribed to the polyhedral shape of the

particles. To understand the alloying behavior and underlying chemistry of AuCu intermetallic NPs, attempts have been made to quantitatively understand the contrast and its interpretation in terms of atom column positions of Au and Cu of high resolution phase contrast images. The close match was found at defocus ~ -80 nm and thickness ~ 30 nm between simulated and experimental image. This comparison allowed to ascertain the chemistry of atom columns individually. The atom columns corresponding to Au and Cu atom columns located at one of the face centered positions could be imaged. This has been understood by invoking concept of atomic potentials. Single atom potential of Au and Cu has been calculated by custom written code in Matlab. Exit wave analysis 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). Preferential imaging of Cu atom columns could be attributed to its potential and the channeling behavior of the electron wave.

In conclusion (**chapter 9**), it has been established through this work that green synthesis of pure metals and alloy nanoparticles in Ag, Au, Cu, Ag-Cu and Au-Cu is possible and control over their morphologies may be obtained either by heat treatment or by manipulating the nucleation behaviour. The resulting change in LSPR behaviour cannot only be attributed to its shape and size. Additionally, it is strongly dependent on the structural complexities. A distinct correlation between the structural complexity and the phase diagram could be drawn as the structure changes locally over nanodomains. The structural characteristics in such domains have been established through extensive transmission electron microscopy studies. They have also been understood through image simulation in conformity with experimental observations.