CHAPTER 4

Simulated Study of Plasmonic Coupling in Noble Bimetallic Alloy Nanosphere Arrays

4.1 Introduction

In Chapter 3, the noble bimetallic alloy nanosphere (BANS) of $\text{Ag}_{1-x}\text{Cu}_x$ at a particular composition of $x = 0.50$ was optimized to be the best material of choice for its possible use in thin-film solar cells. In order to enhance the efficiency, the alloy NPs is embedded directly on the top of a thin-film semiconductor absorber layer. The metal nanoparticles are deposited on the thin-film substrate using several experimental techniques like thermal evaporation method (Pillai et al., 2007), Porous alumina template technique (Nakayama et al., 2008), Nano imprint lithography method (Guo, 2007) and Electro-deposition method (Kim et al., 2008). Similar experimental techniques may also be used to deposit alloy nanoparticles. In the practical applications of NPs, the interactions between the particles also needed to be studied in the form of arrays and considered an important parameter in addition to change in size, surrounding environment, and metal composition of alloy NPs. The array of metal nanoparticles gives different surface plasmon resonance (LSPR) from that of individual nanoparticle due to the plasmonic coupling among the LSPRs of individual NPs. In arrays, the plasmonic coupling between the interacting particles plays an important role to tune the LSPR peak position and full width at half maxima (FWHM) as a function of the number of nanospheres and interparticle distance (Jain & El-Sayed, 2010).

Plasmonic coupling takes place when particles are close enough to each other so that the surface plasmon resonance of each particle is affected by surface plasmon resonance
of its neighboring particle. The strength of plasmonic coupling depends on the interparticle distance, number of interacting particles and direction of polarization (Khlebtsov et al., 2006; Ma et al., 2013). Under parallel polarization i.e. when polarization direction is along the interparticle axis, as the gap between particles is reduced, red-shift in the plasmon resonance takes place along with a broadening of the peak. Under perpendicular polarization, a small blue-shift with a decrease in the gap between the particles is observed (Noguez, 2007; Jain et al., 2007). The electronic and structural properties of bimetallic arrays have been studied in the literature (Shin et al., 2012; Tafoughalt & Samah, 2012) but their optical properties also need to be optimized theoretically for their possible practical applications. To our best knowledge, no work has been carried out to study the scattering properties of BANS arrays for plasmonic solar cells. In the previous chapter, the effect of size, surrounding medium, and alloy composition on the scattering efficiency and FWHM has been reported for single BANS but for real plasmonic applications, the interactions between these BANSs also need to be studied. Therefore, in the present chapter, the scattering properties of BANS arrays have been studied from the viewpoint of cost-effective solar cell applications. The effect of particle interactions on the scattering efficiency and FWHM for the simplest form of arrays, i.e., one dimensional (1D) BANS arrays have been investigated because the coupling of two or more NPs is also a crucial parameter for plasmonic solar cells and for designing future plasmonic devices. Since, analytical methods are unable to study the plasmonic interactions in arrays, therefore, discrete dipole approximation (DDA), a numerical method is considered to be the most powerful method to study the optical properties of arrays (Jain et al., 2007; Ma et al., 2013). Hence, DDA (Draine & Flatau, 1994) is used to optimize the size of individual BANS, number of spheres in the arrays, i.e. size of arrays, the interparticle distance, and material for higher scattering efficiency
over a broad spectral region, so that the entire region of the visible and infrared spectrum is covered which is the essential condition to enhance the absorption efficiency of thin-film plasmonic solar cells.

To simulate the excitation of LSPR in BANS arrays, the radius of nanoparticles are varied from 10 nm to 50 nm, numbers of interacting particles are varied from 2 to 8 along with varying interparticle distance in BANS dimmer. In all the calculations, the polarization direction is considered to be along the interparticle axis because of the maximum EF enhancement in this direction (Ma et al., 2013). This work is the extension of Mie theory results presented in Chapter 3 to include the effect of particle interactions between the alloy nanospheres. The LSPR wavelength, FWHM, and scattering efficiency of 1D BANS arrays of earlier, optimized compositions, i.e. Ag$_{0.75}$Au$_{0.25}$, Au$_{0.25}$Cu$_{0.75}$, and Ag$_{0.50}$Cu$_{0.50}$ have been studied using DDA simulations. Here, firstly, the scattering spectra of individual BANS calculated by using Mie theory were compared with DDA simulations and further, the scattering spectra for BANS dimmer has been studied by varying the size of individual particle and their interparticle distance. Finally, the scattering spectra of BANS arrays by varying the number of interacting spheres have also been studied.

4.2 Simulation method

Numerical simulations are being performed by using discrete dipole approximation (DDA) method implemented in source code DDSCAT 7.2, (Draine & Flatau, 2012) which is freely available and obtained from (http://code.google.com/p/ddscat/). This method is able to calculate the scattering and absorption efficiencies of EM plane waves by isolated targets or periodic targets in one or two dimensions (Draine & Flatau, 2008). In this approximation, the given target is divided into the cubic array of N polarizable dipoles with lattice spacing d and each cube having a definite polarizability. The
interactions between the dipoles in each cube and with the incident EF giving rise to a system of linear equations, which are solved using fast Fourier transform (FFT) method to obtain the polarizability of each cube and hence, the optical properties of nanostructures can be calculated. In order to obtain the accurate results, the target should consist of a large number of polarizable dipoles N with minimum dipole spacing d. In present simulations, the numbers of dipoles used were nearly $\sim 8 \times 10^4$. In all simulations, the results have been calculated by considering the parallel polarization of incident light along the interparticle axis, i.e. along the y-axis and the direction of propagation along x-axis. The refractive index of 1.33 (as used in Chapter 3) has been taken as surrounding medium. The complete detail of mathematical description of the DDA can be found in (Draine & Flatau, 1994).

4.3 Results and discussion

The behavior of surface plasmons of noble metal nanostructures is described on the basis of frequency dependent complex dielectric function and is given by the sum of the dielectric function contribution from intraband transitions in the bulk material (as Drude model) (Nogues, 2007) and the interband transition of bound electrons i.e. from d to sp-band transitions which becomes important in the visible region of the EM spectrum. The experimentally obtained complex dielectric functions for Ag, Au, and Cu are given by Palik (1991) and for alloys it is calculated using average weighted method (Motl et al., 2010; Verbruggen et al., 2013). The real and imaginary parts of the metal dielectric functions and their alloys of selected compositions are shown in Figure 4.1.
Figure 4.1: a) Real ($\varepsilon_r$) and b) Imaginary ($\varepsilon_i$) parts of the dielectric functions for pure and alloy nanoparticles.

The selected alloy compositions are $\text{Ag}_{0.75}\text{Au}_{0.25}$, $\text{Au}_{0.25}\text{Cu}_{0.75}$, and $\text{Ag}_{0.50}\text{Cu}_{0.50}$, which are already optimized in Chapter 1 as the good scattering materials for their better use in plasmonic solar cells in comparison to other compositions. The real part of the metal dielectric function determines the LSPR peak position in response to the surrounding medium refractive index, whereas the imaginary part leads to the broadening of resonance spectra and also determines the relative contribution of absorption and scattering in the total extinction. Both the real and imaginary parts of the dielectric function show a decreasing trend in the order of $\text{Ag}_{0.50}\text{Cu}_{0.50} > \text{Ag}_{0.75}\text{Au}_{0.25} > \text{Ag}$ with an increase in the Ag composition. Therefore, it is expected to increase in the scattering relative to that of absorption in the extinction spectra along with narrowing the bandwidth. However, the optical properties of Au, Cu, and their alloys are more damped due to the presence of higher interband transitions in the longer wavelength region. For solar cell applications, we need more scattering efficiency over the larger bandwidth but both these parameters have to be compromised with each other because $\text{Ag}_{0.75}\text{Au}_{0.25}$ has a high scattering efficiency with narrow bandwidth and $\text{Ag}_{0.50}\text{Cu}_{0.50}$ has comparatively less scattering efficiency with reasonable bandwidth but the cost...
effectiveness of Ag$_{0.50}$Cu$_{0.50}$ nanospheres makes them useful for plasmonic solar cells. Moreover, only 25% composition of Au in Ag-Au alloy drastically improves the stability of Ag nanoparticles (Nishijima and Akiyama, 2012). However, the lower air stability of both Ag and Cu NPs affects their LSPR properties, especially of Cu nanoparticles but a synthesis of Ag, Cu, and their alloys using a suitable stabilizer or capping agent can make them oxidation free (Taner et al., 2011; Tan & Cheong, 2013). Cysteine was used as a stabilizer agent to prevent the oxidation of Ag-Cu alloy nanoparticles (Taner et al., 2011).

During the synthesis of Ag-Cu alloy nanoparticles, the main problem encountered is with the oxidation of Cu NPs that causes the formation of copper oxide Cu$_2$O layer on Ag-Cu alloy nanoparticles. However, Rodriguez & Pal (2011) reported that the plasmonic properties of Cu NPs are slightly enhanced on the formation of small shell layer thickness of copper oxide over it. Therefore, the plasmonic properties of Ag-Cu alloy nanoparticles would also be expected to enhance due to the formation of Cu$_2$O layer in the form core-shell NPs (Ag$_{0.50}$Cu$_{0.50}$-Cu$_2$O). Moreover, due to the low standard potential of Cu than that of Ag, the reduction rate of Cu nanoparticle is slower means Cu gets reduced after reduction of Ag that may lead to the formation of Ag-Cu alloy core Cu shell nanoparticles whenever the excess amount of Cu is present in Ag-Cu alloy nanosystem. Tsuji et al. (2010b) has reported the synthesis of Ag-Cu alloy core Cu shell nanoparticles using polyol method and discussed its optical properties with better stability. On the other hand, to avoid the oxidation of Ag-Cu NPs, the addition of protective layer might be done. Therefore, the control over LSPR peak position and scattering intensity parameters of Ag-Cu alloy NPs are also studied by coating them with Au as a protection layer (Ag$_{0.50}$Cu$_{0.50}$-Au). Figure 4.2 represents the effect of copper oxide (Cu$_2$O) and Au layer on the optical properties of Ag-Cu alloy NPs. Here,
the Ag-Cu alloy nanoparticle core radius was fixed at 40 nm but with a varying shell thickness (2 to 10 nm) of both Cu$_2$O and Au layers so that the total radius not exceeds above 50 nm.

**Figure 4.2:** Scattering spectra of a single Ag$_{0.50}$Cu$_{0.50}$ BANS having radius 40 nm coated with a) Cu$_2$O as oxidation effect and b) Au as the protection layer, with varying thickness (t) from 0 to 10 nm in surrounding medium refractive index of 1.33.

In case of Cu$_2$O as shell (Figure 4.2a), the comparable scattering efficiency with bare Ag-Cu NPs has been found at shell thickness of about 6 nm and further increase in shell thickness leads to enhancement in scattering efficiency with maximum at a shell thickness of 10 nm. The scattering efficiency is comparable to Ag-Cu alloy NPs in case of Au as a shell even at a shell thickness of 10 nm but with greater stability (Figure 4.2b). Hence, the effect of oxidation and protection layer on the optical properties of Ag-Cu alloy NPs has been included and found that the oxide layer with thickness in the range of 6 to 10 nm enhances the optical properties whereas comparable in case of Au NPs.
4.3.1 Single nanosphere: Comparison of DDA with Mie theory

The theoretical calculations using the DDA method have been performed to obtain the scattering spectra of a single BANS of selected composition. Figure 4.3 compares the DDA simulated scattering spectra of single $\text{Ag}_{0.75}\text{Au}_{0.25}$, $\text{Au}_{0.25}\text{Cu}_{0.75}$, and $\text{Ag}_{0.50}\text{Cu}_{0.50}$ BANSs with the results obtained using Mie theory. The same input parameters as used in Mie calculations are taken as input for DDA simulations, i.e. the radius of BANS is assumed to be 50 nm in the surrounding medium of refractive index 1.33. It can be concluded that for all the three BANSs, DDA calculations are in good agreement with the results obtained by Mie theory. A small dip near 320 nm in both the scattering spectra of $\text{Ag}_{0.75}\text{Au}_{0.25}$ and $\text{Ag}_{0.50}\text{Cu}_{0.50}$ alloy nanospheres is due to the characteristics of Ag material. The complete detailed comparison in both the calculations of Mie theory and DDA can be found in (Felidj et al., 1999; Lee & El-Sayed, 2005).

![Figure 4.3](image)

**Figure 4.3:** Comparison of scattering spectra of a single BANS having a radius of 50 nm calculated by Mie theory (solid lines) and DDA simulations (dashed lines).
4.3.2 Bimetallic alloy nanosphere arrays

An individual alloy nanoparticle shows a well-defined LSPR between the LSPRs of individual constituent particles depending upon the composition of metal (Verbruggen et al., 2013). In case of arrays, the local electric field (EF) gets modified by scattering from individual alloy NPs which results in the shifting (red or blue) and broadening (narrowing) of LSPR depending upon the size, interparticle distance, and the number of interacting particles etc. (Pinchuk & Schatz, 2008). For smaller size particles with small separations, the EF in the gap is strongly enhanced by suppressing the scattering for polarization direction along the interparticle axis but for larger particles with larger separations, the EF in the gap is reduced with increased scattering which results in the broadening of LSPR (Kottmann & Martin, 2001). To study the interactions between the particles, the chosen target is illustrated in Figure 4.4. The size of the array increases in the form of a number of identical coupled spheres (Figure 4.4a) and with different interparticle distance g (edge to edge separations) in nanosphere dimmer (Figure 4.4b). The incident EM plane wave propagates in the x-direction and polarization is assumed to be along the interparticle axis i.e. along y-axis in all the cases.

![Figure 4.4: One dimensional target of identical BANS a) array with no gap between them and varying the number of spheres from 2 to 8 b) dimmer with varying interparticle distance g.](image-url)
4.3.2.1 Nanosphere dimmer: Effect of nanosphere size

Figure 4.5 shows the scattering spectra for Ag$_{0.50}$Cu$_{0.50}$ BANS dimmer of various sizes (radius) as an example to optimize the size of individual interacting particle for higher scattering over the broad spectral region. It has been found that for smaller size particles, scattering efficiency is very less and starts to dominate over absorption as the particle size increases. This is due to the reduced value of imaginary parts of the dielectric function above wavelength regime of 500 nm. As the particle size increases, the increased separation between the charges reduces the restoring force that results in redshifts of the scattering peak position. To use them for plasmonic solar cells, larger scattering from NPs is required in comparison to the absorption which occurs at larger particle size and is optimized to be 50 nm because for too larger particles, the radiation damping and dynamic depolarization effects become dominate that dampens the calculated spectra and therefore, results in reduced scattering efficiency. Hence, in further study, the radius of the individual interacting particles is taken to be 50 nm.

![Calculated scattering spectra of Ag$_{0.50}$Cu$_{0.50}$ BANS dimmer with varying radius $r$ of the individual particle.](image)

**Figure 4.5** Calculated scattering spectra of Ag$_{0.50}$Cu$_{0.50}$ BANS dimmer with varying radius $r$ of the individual particle.
4.3.2.2 Nanosphere dimer: Effect of interparticle distance

In this section, we have studied the optical properties of all the three selected BANS dimmers with varying edge to edge gap distance. The DDA calculated scattering spectra of dimmers with varying interparticle distance from \( g = 0 \) nm (touching) to 250 nm in the surrounding medium refractive index of 1.33 has been shown in Figure 4.6.

**Figure 4.6:** Scattering spectra of a) \( \text{Au}_{0.25}\text{Cu}_{0.75} \) b) \( \text{Ag}_{0.50}\text{Cu}_{0.50} \) and c) \( \text{Ag}_{0.75}\text{Au}_{0.25} \) BANS dimmers with varying interparticle distance \( g \).

In all the three BANS dimmers, when the gap between the interacting particles is reduced from 250 nm to 150 nm, a blue shift in resonance wavelength is found with decrease in scattering efficiency. However, the shift is very small for Au-Cu dimmer as
compared to the shift in other two dimers (Figure 4.7b). A further decrease in distance between the interacting particles leads to the redshift in resonance wavelength. A strong shift as well as broadening of dipolar resonance is found when particles are nearly touching, i.e., with no gap between them (g = 0 nm). This is due to the strong coupling between the individual dipolar resonances of the interacting particles (Pinchuk & Schatz, 2008). In general, the coupling strength increases as the interparticle distance decreases. In comparison among dimers, a strong red-shift in resonance wavelength has been found for Ag$_{0.50}$Cu$_{0.50}$ BANS dimer with larger FWHM over the visible region of the EM spectrum that covers the larger intense region of the solar spectrum and hence, enhances the absorption efficiency of thin-film solar cells at lower cost when placed on the top surface of thin-films.

For the better clarification of results, the interparticle distance dependent optical parameters such as scattering efficiency, FWHM, and LSPR wavelength has been calculated from the BANS dimer spectra and are presented collectively in Figure 4.7.

![Figure 4.7: a) Scattering efficiency, FWHM, and b) LSPR wavelength of BANS dimmers as a function of the interparticle distance. The solid lines represent the scattering efficiency, whereas the dashed lines represent the FWHM. The alloy dimmers are Ag$_{0.75}$Au$_{0.25}$ (up triangle), Au$_{0.25}$Cu$_{0.75}$ (star), and Ag$_{0.50}$Cu$_{0.50}$ (square).](image)
A continued decrease in scattering efficiency along with enhancement in FWHM (Figure 4.7a) has been found for all the three BANS dimmers as the coupling between the interacting particles increases with reducing gap between nanospheres. The increased FWHM leads to cover the larger spectral region of the solar spectrum that enhances the efficiency of plasmonic solar cells but at the cost of reduced scattering. Further, the scattering efficiency can be increased by controlling the surrounding media environment as discussed in Chapter 1. In BANS dimmers, the more tunability in LSPR along with largest FWHM has been seen in case of Ag$_{0.50}$Cu$_{0.50}$ dimmer in comparison to other two and also shows a larger FWHM in comparison to single Ag$_{0.50}$Cu$_{0.50}$ alloy nanosphere of the same size in the same surrounding medium. In conclusion, the FWHM can be controlled from 120 nm to 330 nm, scattering efficiency from 3 to 7.5, and LSPR wavelength from 510 nm to 600 nm with varying interparticle distance and changing metal in the nanosphere dimmers.

4.3.2.3 One dimensional array: Effect of number of spheres

![Graphs showing scattering spectra](image)

**Figure 4.8:** Scattering spectra of a) Au$_{0.25}$Cu$_{0.75}$ b) Ag$_{0.50}$Cu$_{0.50}$ and c) Ag$_{0.75}$Au$_{0.25}$ BANS arrays with varying number of interacting particles.

The effect of a number of interacting particles on the scattering efficiency and FWHM for 1D BANS arrays has been studied. Figure 4.8 represents the scattering spectra of BANS arrays with varying number of interacting particles in the surrounding
medium refractive index of 1.33. For the maximum coupling in arrays, the particles are considered to be touched with each other i.e. with no gap between them (g = 0 nm) and the number of interacting particles are varied to 2, 4, 6 and 8.

Similarly, the number of particle dependent optical parameters obtained from the BANS array spectra is clearly presented and compared in Figure 4.9. The LSPR of arrays is blue-shifted continuously from that of isolated alloy nanoparticle with increasing number of interacting particles but shows a significant enhancement in FWHM. This is because of the increased contribution from radiation damping due to the large volume of array with increased number of interacting particles.

![Figure 4.9](image)

**Figure 4.9:** **a)** Scattering efficiency, FWHM, and **b)** LSPR wavelength of BANS arrays as a function of number of interacting particles. The solid lines represent the scattering efficiency, whereas the dashed lines represent the FWHM. The arrays are Ag$_{0.75}$Au$_{0.25}$ (up triangle), Au$_{0.25}$Cu$_{0.75}$ (star) and Ag$_{0.50}$Cu$_{0.50}$ (square).

It is also found that as the number of interacting particles are increased up to 4, the scattering efficiency reduces in each case but with further increase in number of interacting particles lead to increase in scattering efficiency with nearly similar (for 8 numbers of spheres) as for a single BANS (Figure 4.9a). Therefore, the increased FWHM with nearly similar scattering efficiency for any number of interacting spheres
from 2 to 8 may be useful for plasmonic solar cell applications because larger the FWHM, the more spectral region will be covered which implies an increase in efficiency of thin-film plasmonic solar cells.

The increase in FWHM has been found in all the three BANS arrays with increase in the number of interacting particles (Figure 4.9a). This is due to strengthening of plasmon coupling between the surface plasmon resonances of interacting particles as the number of particles increases. The higher is the coupling strength, larger the plasmon damping and hence, larger FWHM. This increased FWHM covers the large spectral region of the EM spectrum, which is needed to enhance the efficiency of thin-film plasmonic solar cells (Catchpole & Polman, 2008). As a result, the arrays made of Ag and Cu BANSs show the larger tunability of LSPR in the visible region of the spectrum (Figure 4.9b) along with comparable value of FWHM to other arrays but at the cost of reduced scattering that can further be enhanced by increasing the surrounding media environment (Jain & El-Sayed, 2008). It can be seen that FWHM of arrays can be controlled from 175 nm to 365 nm, scattering efficiency from 2.5 to 5.2, and LSPR wavelength from 460 nm to 600 nm with varying the number of interacting particles and change of metal in the array.

The LSPR tunability and scattering efficiency of Au-Cu BANS is less for both i) varying the distance between the particles in nanosphere dimmer and ii) number of interacting particles in array in comparison to the other two BANSs of selected compositions. This is due to the effect of interband transitions in both Au and Cu which results in the damping of plasmon resonance and hence, reduces scattering efficiency and broadens the plasmon resonance. However, the effect of interband transitions in Cu is large as compared to Au therefore more damping of plasmon resonance is observed in case of Ag-Cu in comparison to Ag-Au. From Figures 4.6 to 4.9, it is found that the Ag-
Cu BANS have smaller scattering efficiency in comparison to Ag-Au but larger tunability of LSPR in the broad spectral region of the spectrum makes them useful to increase the efficiency and cost effectiveness of plasmonic solar cells. The more theoretical study will be required for better understanding of light scattering from these arrays and further trapping of this scattered light into thin-film solar cells. These results, based on theoretical simulations will also help the experimentalists to synthesize the presently optimized noble metal alloy NPs on thin-film substrate.

4.4 Conclusions

The plasmon coupling in BANS arrays of selected compositions has been studied with varying the interparticle distance and number of interacting particles using DDA simulations. It has been found that the LSPR wavelength and scattering efficiency can be controlled over the large spectral region of the EM spectrum by varying these two parameters. Although the LSPR shift is smaller due to the plasmonic coupling in comparison to the shift in individual alloy particles of the same size in the same surrounding medium but their FWHM is strongly enhanced. This enhanced FWHM helps the use of arrays for the efficiency enhancement in plasmonic solar cells. In nanosphere dimmers, when particles are nearly touching with each other a strong red-shift as well as broadening in dipolar resonance is found for $\text{Ag}_{0.50}\text{Cu}_{0.50}$. Further, in nanosphere arrays, the more tunability in LSPR has been found for $\text{Ag}_{0.50}\text{Cu}_{0.50}$ with larger FWHM. Therefore, it has been found that $\text{Ag}_{0.50}\text{Cu}_{0.50}$ BANS arrays shall be useful as a cost effective material for efficient plasmonic solar cells.