Physics Letters A 379 (2015) 163–169

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Optical response of noble metal alloy nanostructures

Amit Bansal *, S.S. Verma

Department of Physics, Sant Longowal Institute of Engineering & Technology (SLIET), Longowal – 148106, District Sangrur, Punjab, India

ARTICLE INFO

Article history:
Received 16 September 2014
Received in revised form 6 November 2014
Accepted 12 November 2014
Available online 18 November 2014
Communicated by R. Wu

Keywords:
Alloys
Scattering yield
Absorption
Bandwidth
Ag–Cu
Discrete dipole approximation

ABSTRACT

The optical response, stability, and cost-effectiveness of individual noble metals can be improved by combining them to form alloy nanostructures. The present work reveals the influence of shape, size, and metal type on the optical response of alloy nanoparticles using discrete dipole approximation (DDA) simulations. It is found that sharp corner nanostructures show enhanced plasmonic properties in comparison to rounded counterpart. For all the three shapes, viz., nanocubes, rectangular, and nanobar particles, the increase in length resulted in redshifts of the longitudinal plasmon resonance alongwith enhancement in the scattering yield as well as relative efficiency parameters except for nanocubes of edge length 120 nm. The effect of size on full width at half maxima (FWHM) has also been studied and found to be maximal for nanocubes in comparison to other nanostructures.

1. Introduction

Among metal nanoparticles (NPs) which can support surface plasmons, the noble metals of size smaller than the incident wavelength exhibit fascinating optical properties due to excitation of a surface plasmon resonance in the visible to near infrared (NIR) region of the electromagnetic (EM) spectrum [1–3]. The optical properties such as absorption, scattering, and therefore, extinction are strongly enhanced at surface plasmon resonance in comparison to their geometrical cross-sections. This is due to the large electromagnetic field enhancement in the surrounding of metal NPs. The calculations of several parameters such as scattering, absorption, localized surface plasmon resonance (LSPR) in wavelength region, and its full width at half maxima (FWHM) are necessary for a particular plasmonic application. The surface plasmon resonance can be tuned from UV–visible to IR (infrared) region of the EM spectrum and said parameters can be controlled by various factors such as size, shape, surrounding medium and metal type, etc. [4–6]. The particle shape plays an important role in deciding the optical properties i.e. the materials having sharp corners and edges provide larger LSPR excitation and redshift in comparison to their spherical counterparts because of strong electric field enhancement as a result of more accumulation of charges at corners during plasmon oscillations [7–9]. Isotropic NPs (say, nanosphere) show only plasmonic peak whereas anisotropic nanostructures show several plasmon resonances associated with the polarization state of the incident light along different particles axes [8–10]. This is due to the different free electron oscillations along different axes of the anisotropic nanostructures e.g., nanorods exhibit two orthogonal plasmonic peaks, one along short-axis at shorter wavelength (transverse plasmon resonance) and another along long-axis at longer wavelength (longitudinal plasmon resonance) [11]. Depending upon LSPR wavelength, FWHM, and scattering efficiency parameters, the noble metal NPs can be used for many plasmonic applications. To enhance the efficiency of plasmonic solar cells, we require the metal NPs having high scattering efficiency in the broad region of the EM spectrum where the underlying semiconductor is weakly absorbing and/or solar spectrum is highly intense [12,13]. For better plasmon sensing, a strong shift in plasmon resonance alongwith narrower FWHM with small change in medium refractive index is desired [6]. Strong scattering and absorption efficiencies are required for the use of metal NPs in optical imaging and photo-thermal therapy treatments, respectively [14,15].

The most commonly used noble metal NPs on the active layer of thin-film solar cells to enhance its absorption efficiency and for biomedical treatments are of silver (Ag) and gold (Au). However, Ag is optimized and preferred as the better choice over Au because of its highest scattering efficiency in the broad region of the spectrum, low-cost and comparable stability in the ambient conditions. The material's cost and its availability are the most important factors while considering the metal NPs for plasmonic solar cells and biomedical purposes. The NPs of copper (Cu) and aluminum (Al)

* Corresponding author.
E-mail address: amit.bansal133@yahoo.com (A. Bansal).

http://dx.doi.org/10.1016/j.physleta.2014.11.018
0375-9601/

have also been reported in literature [16–19] towards cost-effective plasmonic applications. Cu NPs show comparable plasmonic properties with Au in the longer wavelength region and therefore, has attracted the researchers owing to its lowest cost and high abundance relative to other noble metals. Moreover, the advances in shape and size controlled synthesis of Ag and Cu NPs motivates the researchers to study their optical properties theoretically. There have been several theoretical and experimental studies [12,17–19] available in literature on calculating the shape and size dependent optical properties of noble metal NPs. Sosa et al. [4] calculated the geometry and size dependent scattering, absorption, and extinction efficiencies of silver and gold NPs using DDA method. Salzemann et al. [20] reported the optical properties of different shape copper NPs with change in plasmon resonance for spherical NPs at 560 nm to that of nanodisks at 650 nm. The optical properties of noble metals can be drastically improved by combining the individual metals to form alloys [21–23] and core–shell nanostructures [24,25]. The potential of using these nanostructures may contribute to more cost-effective applications. However, low cost, better stability, and easy synthesis of alloy nanostructures alongwith metal composition dependent improved optical response in UV–visible to IR region of the spectrum and linear relationship of plasmon resonance with the metal composition makes them most studied plasmonic materials [22,23,26]. The optical properties of alloy NPs can be tuned in between the pure metals over the wide bandwidth with change in metal composition. Many studies have been performed in literature which indicates that alloys have potential applications in plasmonic solar cells [27–30], catalytic [31], plasmon sensing [6], biomedical [21] and antibacterial applications [22, 26]. The alloying of Ag and Cu may use the advantages of both metals and will be useful for enhanced cost-effective plasmonic applications with controllable stability. Moreover, our earlier studies [32] reported that Ag–Cu alloy nanospheres have better optical properties for plasmonic solar cells in comparison to Ag–Au and Au–Cu alloys if one can control the oxidation effect. Further, as similar to the Cu oxidation [33], no significant effect of oxidation over the optical properties of Ag–Cu alloy NPs has been found [34]. Several researchers have synthesized the Ag–Cu NPs with controllable size and shapes using various experimental techniques such as microwave assisted chemical reduction method [26], one-pot method [29], chemical reduction route [35], co-complexation method [36], electrochemical codeposition method [37], galvanic replacement reaction [31], polyol method [38] and so on but no theoretical studies are performed to calculate their optical properties. Therefore, Ag–Cu nanostructures may be preferred over other alloys in cost-effective plasmonic solar cells and hence, their optical properties as a function of shape and size also need to be investigated. Similar to the other bimetallic Ag–Au and Au–Cu alloy nanostructures [22,23,39], the optical properties of Ag–Cu can also be varied over the wider region than the individual metals with size, shape, and metal composition. Therefore, in the present work, we studied the optical properties of alloy NPs of various shape and size by using DDA simulations. The main aim is to calculate the shape and size dependent scattering over absorption in the extinction, LSPR wavelength, and FWHM of the plasmon resonance with improved plasmonic applications.

2. Methodology

Analytically, it is not possible to solve Maxwell's equations for arbitrary shape NPs in order to study their optical properties. Therefore, several numerical methods like discrete dipole approximation (DDA), finite element method (FEM), and finite difference time domain (FDTD) have been developed. DDA is one of the most powerful, freely available and useful technique to calculate the optical properties of arbitrary shape NPs. In the present work we have used the DDA method to calculate the scattering and extinction spectra, FWHM, and LSPR wavelength of different shaped Ag–Cu alloy NPs of various sizes. DDA source code DDSCAT7.2 used is given by Draine and Flatau [40]. In all the simulations, the number of dipoles used are nearly $\sim 74 \times 10^3$ in order to accurately represent the target shape and for better convergence of the optical properties. All the calculations have been performed in surrounding medium having refractive index numerically equal to 1.33 (dielectric constant 1.77). Further, the direction of polarization of incident plane wave is considered to be along the long-axis of the nanoparticle because of strong electric-filed enhancement in this direction. The complete detail of the mathematical description of the DDA can be found in [41,42].

3. Results and discussion

DDA simulations have been performed to calculate the optical response of alloy NPs. The dimensions of the nanostructures are considered greater than the mean free path of the conduction electrons so as the surface scattering effects are not important and hence, no size corrections due to surface scattering are included in the bulk dielectric constants. Therefore, the same wavelength dependent dielectric constants for NPs as that of bulk metals are used as input in DDA calculations and have been obtained from Palik [43] for individual metals. Whereas for alloys it has been calculated by average weighted method, given as $\varepsilon_{\text{alloy}}(\omega) = (1-x)\varepsilon_{\text{Ag}}(\omega) + (x)\varepsilon_{\text{Cu}}\ (\omega)$ [23,34,44], x represents the metal composition in Ag–Cu NPs. The behavior of surface plasmons of noble metal nanostructures can be described on the basis of complex dielectric constants as real part of the metal dielectric function determines the LSPR peak position in response to the surrounding medium while imaginary part determines the relative contribution of absorption and scattering in the extinction alongwith the plasmon resonance linewidth (FWHM). Therefore, when individual metals are combined to form alloys, variations in dielectric constant values are responsible for the changes in optical properties of alloy NPs from that of individual metals. The organization of the paper follows as: we first address the effect of shape on the scattering spectrum and then discuss the size dependent changes in the optical properties of different shape alloy nanostructures. For instance, the results of Ag_{1-x}–Cu_x alloy with metal composition $x = 0.50$ have been shown and later the effect of metal type on the scattering spectrum is briefly addressed.

3.1. Effect of particle shape

To calculate the effect of particle shape on the optical response of alloy NPs, different shapes such as spherical ($a = b = c$), prolate ($a = b < c$), nanocube ($l = b = h$), rectangular ($l < b = h$), and nanobar ($l = b < h$) have been considered. The simulations have been performed by approximating the volume of each shape equal to the volume of 50 nm sphere radius (in other words the effective radius of all the nanostructures is assumed to be 50 nm). The prolate NPs are formed by enlarging the nanospheres along its one axis (say c). Similarly, the nanobar and rectangular particles are formed by enlarging the nanocubes along one (say h) and two (say b and h) axes, respectively. An important feature of prolate, rectangular, and nanobar particles is that their optical properties are dominated by two plasmon resonances, one in the shorter wavelength called transverse plasmon resonance and other in the longer wavelength called longitudinal plasmon resonance due to the polarization of incident light along the short and long axis, respectively. As the long-axis length of the nanostructure increases, the large change in optical properties of longitudinal plasmon resonance has been observed in comparison to the transverse plasmon