Adjustable surface plasmon resonance with Au, Ag, and Ag@Au core-shell nanoparticles

S. M. Hamidi* and M. A. Oskuei
Magneto-Plasmonic lab, Laser and Plasma Research Institute, Shahid Beheshti University, Tehran, Iran
* Corresponding author: mhamidi@sbu.ac.ir
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We report an experimental study on the synthesis of metal nanoparticles (NPs) with adjustable optical density based on surface plasmon resonance (SPR). Metal NPs prepared by laser ablation in liquid method and the effect of laser parameters on the size, distribution, wavelength of SPR of Ag, Au, and mixture of Ag-Au, and Ag core/Au shell NPs are investigated. Our results show that the adjustable SPR band can be achieved in each class of NPs which is suitable for adjustable optical window applications.

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Noble metal nanoparticles (NPs) and nanostructures are characterized by an intense and broad absorption band in the visible and near infrared range. This property is governed by the shape[1,2], size[3], background[4], composition[5], and distribution, which are described by localized surface plasmon resonance (LSPR) of NPs. LSPR is the resonance of charge density oscillations confined to metallic NPs, metal nano-clusters, and metallic nanostructures[6,7]. Have an insight to the wavelength of the LSPR in each structure has a main role in the design of plasmonic structures and as well ability to change this spectral region is a major key in the construction of tunable optical devices.

Tunable optical devices are attractive for many important operations in optical communication systems[8] and tunable wavelength filters[9]. To reach these tunable devices, the researchers have been used multilayer structures[10], optical fibers[11], chain of NPs[12], and long range surface plasmon polaritons[13].

For this purpose, single NP, mixture of NPs, and core-shell NPs have been used extensively. Since the unique wide range frequency of LSPR, core-shell NPs have been generated great interest[14]. Furthermore, preparation of these NPs can be done by the aid of many techniques such as chemical[15] and laser ablation methods[16]. In laser ablation in liquids (LAL), we can prepare single and core-shell NPs in aqueous medium which is depends on many factors such as ablation time, laser fluence, and environment aqueous medium. The study of core-shell NPs’ size and surface plasmon of double metal NPs have been reported[16,17]. But dependence of distribution of the NPs, reliance of the wavelength of LSPR in the media, and the difference between duration times of each core or shell NPs and subsequently the sizes have not been widely explored.

In this letter, we have prepared Au and Ag NPs and Ag core/ Au shell (Ag@Au) NPs by LAL method and the adjustability of the wavelength of LSPR in these structures have been investigated.

Our samples prepared as three classes based on Au NPs, Ag NPs and also Ag@Au core-shell NPs which contain 3, 3, and 6 samples, respectively. The three sets of samples prepared by LAL method by the aid of first harmonic of the Nd: YAG laser with the wavelength 1064 nm, repetition rate of 10 Hz, pulse duration of 4−6 ns, and different energy per pulse was focused on the rotating samples[18].

Metallic NPs prepared after various time and different energy per pulses from pure target in the quartz cell with 10 mL de-ionized water. After preparation of Au and Ag NPs in different steps, the solutions of these colloids mix with each other and we reach to Ag-Au mixture in water environment.

On the other hand, we used Ag target to reach Ag NPs and then we replaced Ag target with the pure gold one in the quartz cell, and we had Ag core- Au shell NPs as Ag@Au NPs.

Fig. 1. SEM images of Au NPs (a) S1, (b) S2, and (c) S3.

Fig. 2. (a) Absorption spectra of Au colloidal NPs with different sizes; (b) SPR wavelength and (c) FWHM of the absorption region as a function of NPs sizes.
We use scanning electron microscopy (SEM) to study the NPs' size and shapes and UV-visible spectrometer to record the optical absorption spectra.

Au NPs prepared by Nd: YAG laser under different conditions as: S\textsubscript{1} sample was prepared by 100 mJ energy per pulse for 1 min, and S\textsubscript{2} and S\textsubscript{3} were prepared by pulse energy of 180 mJ for 2 and 4 min, respectively. The average sizes of NPs were measured as 28.1, 21.09, and 23.44 nm for S\textsubscript{1}, S\textsubscript{2}, and S\textsubscript{3}, through the mean values of five repeated SEM images from NPs on the glass substrate. Three of these SEM images are shown in Fig. 1.

Figure 2(a) shows the UV-visible absorption of the product S\textsubscript{1} to S\textsubscript{3} which indicates that each sample has a surface plasmon resonance (SPR) absorption spectrum according to their NPs sizes. The measured SPR peak of these samples indicates that the resonance peak become stronger as NPs size increases. Adjustability of the SPR wavelength of the samples takes place from 532 to 546 nm (Fig. 2(b)).

Also the full width at half maximum (FWHM) of the absorption band of the samples which indicates the distribution of NPs size is shown in Fig. 2(c).

In fact, we have been investigated the effect of different energy per pulses and also effect of different times of ablation in the preparation of Au NPs in order to use them as an absorber in the middle of visible spectral region.

Ag NPs prepared by LAL method for 2 min under different energy per pulses as S\textsubscript{Ag\_1} with 80 mJ, S\textsubscript{Ag\_2} with 100 mJ, and S\textsubscript{Ag\_3} with 120 mJ. The absorption spectra of NPs with different sizes are shown in Fig. 3 (a). For these samples, Ag NPs' sizes were varied from 18.45 to 28.1 nm and the wavelength of SPR had a red shift by increasing in the NPs sizes (about 7 nm). SEM image of one of these samples onto glass substrate is shown in Fig. 4.

In spite of Au NPs, we see that in Ag NPs, we decrease in FWHM of SPR band as we increase the size of Ag NPs. Furthermore use of higher energy laser pulses yield to increase in the size of NPs. In fact, the average size of NPs prepared at 80, 100, and 120 mJ are 18.45, 25.78, and 28.10 nm, respectively, which indicates that when laser energy increases, the average size begins to increase and the concentration and subsequently absorption start to decrease.

As mentioned in the experiment, we have been prepared Ag-Au mixture by combining the NPs, which are prepared in different aqueous and then mix with each other, and the absorption spectra of these mixture of NPs have been recorded to establish the difference between them with core shell of Ag/Au (Ag@Au) NPs, which are prepared by the same irradiation time and the same energy per pulses.

It should be noted that silver NPs does not stay in high level in the water and we have fast and strong sedimentation of Ag NPs compare with Au NPs in the medium without any stabilizer. This fact resulting in Au fast aggregation and larger NPs compares with Ag NPs which is confirmed by Fig. 5(a). This fast sedimentation of Ag NPs yields to the larger NPs and hence gives rise in the absorption of it as compare with Au in the mixture state. But in the core shell state, Ag NPs give a stable state by the aid of Au NPs and we have very low aggregation.

Fig. 3. (a) Absorption spectra of Ag colloidal NPs with different sizes; (b) SPR wavelength and (c) FWHM of the absorption region as a function of NPs sizes.

Fig. 4. SEM image of Ag NPs (S_{Ag\_2}).

Fig. 5. Absorption spectra of (a) Ag –Au mixture and Ag@Au core shell NPs with the same irradiation time and the same laser pulses energy and (b) Ag@Au NPs as compared with each of NPs.

Fig. 6. SEM image of Ag@Au core shell NPs.
Fig. 7. (a) Absorption spectra of Ag@Au core shell NPs prepared under different energies per pulse and (b) the tuning SPR band of the first and second peaks.

Fig. 8. (a) Absorption spectra of Ag@Au core shell NPs prepared under different times of irradiation to produce Au shell NPs and (b) the tuning SPR band of the first and second peaks.

Fig. 9. (a) Absorption spectra of Ag@Au core shell NPs prepared under different irradiation times of produce each core and shell NPs and (b) the tuning SPR band of the first and second peaks.

In conclusion, the Ag, Au, Ag-Au mixture, and Ag core/Au shell colloid NPs are prepared by LAL method. The optical density spectrum of the NPs shows the peak in absorption spectra corresponds to the SPR band which is adjusted by the aid of change in the laser parameters and then in NPs size and distributions. In Ag@Au core shell NPs, two distinct peaks correspond to SPR of each of NPs. Our results show significant adjustability and absorption band for each set of NPs that is may be useful in the design of optical absorption window.

References