The Impact of Silver: Gold Nanoparticles Ratio on its Structural, Morphological and Optical Properties

M. F. A. Alias* and KH. M. Rashed
Department of Physics, College of Science, University of Baghdad,
*Corresponding author: may20131313@yahoo.com

Abstract. The rapid development of nanomaterial applications has prompted the researchers to explore the possibility of controlling their properties. In this work, synthesize of silver: gold alloys (Ag: Au) nanoparticles by pulsed laser ablation in distilled water. Changing the ratio of the used target alloys (Ag: Au) lead to control the band wavelength of the plasmon frequency resonance. Atomic analysis shows decrease in the percentage of gold than its initial values using energy dispersive x-ray spectroscopy. The absorption spectrum illustrates the plasmon peaks in the visible range changes from 404 nm to 524 nm by changing the ratio of Ag: Au from 100:0 to 0:100 using UV-VIS spectrophotometer. The scanning electron microscopy indicates a change in the size of the NPs and achieves regular volume, especially for 50:50 ratios.

Keywords: Metal nanoparticles Ag: Au, Plasmon effect, Elemental analysis, Scanning electron microscopy.

1. Introduction

Recently, nanoparticles (NPs) have been used in many bio-researches. Some researches included the use of NPs in diagnosis and treatment due to their distinctive and varied characteristics. These are due to their large surface area relative to the size of the sample, high stability and accessibility within the cell and interaction with its components. Among the applications that have been invested on their optical properties, which are characterized by plasmon resonance phenomenon, the most common nanoparticles in this field are gold and silver [1].

The optical properties of metal NPs strongly, dependent on particle size and its composition. To understand these dependences of the optical properties of metal NPs and nanostructures, one has to consider the impact of spatial plasmon resonances confinement. Metal particles are particularly interesting because they are easily formed and modified [2].

Nanoparticles can be formed by various techniques such as chemical [3], physical [4], biological [5], etc. Pulse laser ablation technique is one of the simplest techniques for the production of nanoparticles and easy control of their shape and size with different parameters, which has been of great importance in recent years [6].

In this work Ag: Au alloys and its nanoparticles were prepared by laser ablation technique in liquid. We did study the effect of Au: Ag ratio on metal nanoparticles properties using various standard
characterization techniques such as energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), scanning electron microscopy (SEM) and Uv-Vis spectrophotometer.

2. Experimental work

Five samples of metal targets were prepared from gold, silver and their alloys of both, with different ratios of Ag: Au such as 100:0, 75:25 50:50, 25:75 and 0:100. The alloys were melted in graphite crucibles at sufficient melting point for both metals, then poured molten into small molds and left to cool in air.

The metal nanoparticles were prepared by bombarding the metal target by Nd: YAG Pulsed laser with 1064 nm wavelength and 900 mJ pulses at 9 ns pulse duration and 10 Hz repetition frequency in distilled water. The nano-particles were collected by centrifuge and dropped on glass slides to dry at 353 K under 0.1 mbar vacuum for thirty minute.

The prepared nanoparticles were characterized using energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), UV-visible spectrometer and scanning electron microscopy (SEM).

3. Results and Discussion

From the elemental analysis for prepared alloys samples, shown in Fig. 1. It is observed that the silver (Ag) peaks located around 3 and 3.2 keV corresponding to $L_\alpha$ and $L_\beta$ transition respectively. The gold (Au) peaks at 2.2 and 9.7 keV belong to $M_\alpha$ and $L_\alpha$ transitions with intensities depend on their ratio in sample. The ratio of weight and atomic percentage are shown in Table 1, were calculated by the software attached to the examination device, using peak intensities for $K_\alpha$ transition for elements.

![Figure 1: EDX for Ag, Au and their alloys target at different Au ratio.](image-url)
Fig. 2 shows the elemental analysis of nano Ag: Au samples deposited on glass substrates. The same peaks observed of Ag and Au as in alloy samples, with intensities depend on Ag: Au ratios in sample, in addition to very small peaks come from glass substrate especially for silicon peak at 1.74 keV.

Table 1 displays the Ag, Au alloys values and their nanoparticles samples and composite targets for prepared at different initial Au ratio. It seems that the gold ratio in films is nearly same as in alloy samples.

Figure 2: EDX for AgNPs, AuNPs and their alloys nanoparticles at different ratio.
Table 3: Elemental analysis for Ag, Au and their composite targets and nanoparticles at different Au ratio.

| Ag: Au | Element | Alloy sample | Nano sample |
|--------|---------|--------------|-------------|
|        | Wt%     | atm%         | Wt%         | atm%         |
| Pure Ag| Ag      | 100.00       | 100.00      | 100.00       | 100.00       |
|        | Au      | 00.00        | 00.00       | 00.00        | 00.00        |
| 75:25  | Ag      | 79.22        | 87.44       | 77.29        | 86.14        |
|        | Au      | 20.78        | 12.56       | 22.71        | 13.86        |
| 50:50  | Ag      | 53.55        | 67.79       | 55.31        | 69.33        |
|        | Au      | 46.45        | 32.21       | 44.69        | 30.67        |
| 25:75  | Ag      | 35.88        | 50.54       | 34.86        | 49.43        |
|        | Au      | 64.12        | 49.46       | 65.14        | 50.57        |
| Pure Au| Ag      | 00.00        | 00.00       | 00.00        | 00.00        |
|        | Au      | 100.00       | 100.00      | 100.00       | 100.00       |

Fig.3 shows the X-ray diffraction patterns for Ag NPs, Au NPs and their composite at different ratio prepared by pulsed laser. This figure shows polycrystalline structures for all prepared samples with peaks appear at $2\theta = 37.2785^\circ$, $43.3584^\circ$ and $63.0386^\circ$ corresponding to (111), (200) and (220) planes for Ag or Au structures, whereas for Au, the peaks appears $2\theta = 37.3200^\circ$, $43.3200^\circ$ and $62.9600^\circ$ corresponding to the planes (111), (200) and (220) respectively. Ag and Au have cubic structure with small variation in their dimensions ($a=4.1720$ Å for Ag and $a=4.1450$ Å for Au) [7], which identical according standard card No. (96-901-3054 and 96-901-3045). These results are in a good agreement with reported results of Chen et al [8].

The XPowder software was used to calculate the peaks width at half maximum is shown in Fig.4. This figure shows that the peak width along (111) and (200) directions increased with increasing Au ratio, while irregular variation along (220). In general, the average crystallite size decreases with Ag decreasing in Ag: Au ratio samples. Table 1 shows the structural parameters for prepared metal nanoparticle including Bragg angle ($2\theta$), full width at half maximum (FWHM), experimental Interplanar spacing [9], crystallite size [10] and the corresponding planes.
Figure 3: X-ray diffraction patterns for AgNPs, AuNPs and their composite NPs.

Figure 4: Peaks width calculating by Lorentzian method for AgNPs, AuNPs and their composite NPs.
Table 2: Structural parameters for AgNPs, AuNPs and their composite NPs alloys

| Ag: Au ratio % | 2θ (Deg.) | d_{hkl} Exp.(Å) | hkl | FWHM (Deg.) | C.S (nm) | Average C.S (nm) |
|----------------|-----------|----------------|-----|-------------|---------|------------------|
| 100:0          | 37.2785   | 2.4101         | (111)| 0.4820      | 17.4    |                  |
|                | 43.3584   | 2.0852         | (200)| 0.4460      | 19.2    | 17.8             |
|                | 63.0386   | 1.4735         | (220)| 0.5560      | 16.8    |                  |
|                | 37.2800   | 2.4100         | (111)| 0.5895      | 14.2    |                  |
| 75:25          | 43.3600   | 2.0851         | (200)| 0.6408      | 13.3    | 15.3             |
|                | 63.0400   | 1.4734         | (220)| 0.5055      | 18.4    |                  |
|                | 37.4000   | 2.4026         | (111)| 0.8871      | 9.5     |                  |
| 50:50          | 43.3200   | 2.0870         | (200)| 0.7300      | 11.7    | 15.5             |
|                | 63.0800   | 1.4726         | (220)| 0.3693      | 25.2    |                  |
|                | 37.4400   | 2.4001         | (111)| 0.9075      | 9.2     |                  |
| 25:75          | 43.3300   | 2.0865         | (200)| 0.7027      | 12.2    | 10.5             |
|                | 63.0000   | 1.4743         | (220)| 0.9204      | 10.1    |                  |
|                | 37.3200   | 2.4076         | (111)| 1.1159      | 7.5     |                  |
| 0:100          | 43.3200   | 2.0870         | (200)| 1.2330      | 6.9     | 10.7             |
|                | 62.9600   | 1.4751         | (220)| 0.5240      | 17.8    |                  |

Fig.5 illustrates the UV-visible absorption spectra of the aqueous solution for producing AgNPs, AuNPs and their composite at different percentage ratio prepared by pulsed laser with infrared wavelength of 1064 nm ( 900 mJ ) in distilled water.

The peak appeared at 405 nm is the specific peak of AgNPs plasmon resonance, whereas the peak at 526 nm is the specific peak of AuNPs, which is due to the excitation of the quantum size confinement effect, which have resonance frequency owing to interaction between electromagnetic wave frequency with electron resonance inside a sub of wavelength dimension. These peaks confirm the formation of NPs in the solution [11].

Increasing the gold ratio leads to shift of absorbance peaks toward higher wavelength in spectra (red shift) corresponds to variation in plasmon resonance. This shift is due to the variation of the nanoparticle material which cause changing its resonance location. This result agree with previous researches reported in Ag: Au nanoparticle composites [12]. Table 3 shows the wavelength values of plasmon resonance peak for Ag: Au nanoparticles. These absorbance peaks can use as a selective absorbance peak for irradiation treatment.
Figure 5: UV-VIS spectra for AgNPs, AuNPs and their composite at different Au ratio in distilled water prepared by PLD.

Table 3: Wavelength at maximum absorbance values corresponding to plasmon resonance for AgNPs, AuNPs and their composite at different Au ratio.

| Ag: Au ratio | Plasmon peak (nm) |
|--------------|-------------------|
| 100:0        | 404               |
| 75:25        | 414               |
| 50:50        | 434               |
| 25:75        | 477               |
| 0:100        | 524               |

The typical scanning electron microscope images, for Au, Ag, and Au: Ag nanoparticles at three different ratios are shown in Fig. 6. The pure Ag sample appeared with spherical shape various in diameter from 60 to 710 nm, for this reason the plasmon peak appears with a broad feature as shown in figure 5. The bimetallic nanoparticles samples appeared as spherical shape with less average diameter. The different in diameters is smaller especially for Ag25:Au75 sample with diameters in the range 224 to 277 nm. The Au NPs sample appeared with the smallest regular shape NPs, with diameter varied from 26 to 91 nm.
4. Conclusions

Synthesize and characterize Ag: Au alloys and their nanoparticles at various ratios using pulse laser ablation in distilled water were investigated. The outcome of this study can be summarized as follows: Elemental analysis of the alloys and nanoparticles show that the result ratios of gold less than theoretical one. Polycrystalline structure with cubic phase is shown for all prepared samples. The crystallite size increased with increasing Au ratio. SEM images indicate the decrement of nanoparticle with decreasing Ag:Au ratio. UV - visible measurements showed tunable resonance peak from 404 to 524 nm by varying the Ag: Au ratio between 100:0 to 0:100.

Figure 6: SEM images for Ag, Au and their alloys nanoparticles at different Au ratio.
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