Formation of $\text{Ag}_{\text{shell}}/\text{Au}_{\text{core}}$ Bimetallic Nanoparticles by Pulsed Laser Ablation and Chemical Reduction Methods: The Effect Green Laser Wavelength and Colloidal/Solution Concentration

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Abstract

The main purpose of this experimental research is to study the effects of different silver concentrations on the optical properties of bimetallic Ag_{shell}/Au_{core} nanoparticles. The gold nanoparticles are ablated by the PLAL technique of the gold target on the bottom of the container. The container is filled with colloidal silver nanoparticles and manufactured by chemical reduction. The colloidal solution of mixed nanoparticles is irradiated by the second harmonic of the pulsed laser Nd:YAG laser at 532 nm wavelength. The peak absorption of gold nanoparticles around 530 nm is used to transfer laser energy to nanoparticles and synthesis the Ag_{shell}/Au_{core} bimetallic nanoparticles. The volumetric ratio of nanoparticle solutions are the experimental variables. Bimetallic nanoparticles are distinguished by the following: X-ray diffraction pattern (XRD), spectroscopy in the range of UV-Vis-NIR and IR, Dynamic light scattering (DLS), Energy Dispersive Spectroscopy (EDS), Photoluminescence spectrum (PL) and, Fourier transform infrared spectroscopy (FT-IR). In addition, FE-SEM and TEM images are used to investigate nanoparticle size and morphology. One of the objectives of this research is the preparation of stable bimetallic systems and the study of optical properties, in order to check the reactivity of silver nanoparticles in the bimetallic system. Moreover, the shell thickness and catalytic properties of bimetallic structure with a different silver concentration is discussed. The following, dipole mode is shown in the visible area for every samples and quadrupole mode is not detected in sample with high silver concentration.

Article Highlights

- Using two synthesis methods leads to the formation of stable structure with variety
- All samples show core-shell structure with different thickness and catalytic properties.
- Every sample has a dipole mode in the VIS area and quadrupole mode is only found in samples with low silver concentration.

1 Introduction

In recent decades, nanoscience has become an interdisciplinary domain, particularly in combination with physics. It plays an important role in advanced technology domains due to its most critical features and well-defined structures of nanoparticles (NPs). Monometallic nanoparticles (MNPs) have shown a number of properties, releasing many new paths in nanotechnology. Bimetallic nanoparticles (BNPs) compared with monometallic analogue, increased attention of researchers because of their considerable optical and magnetic properties [1]. Compared to MNPs, BNPs have more catalytic movement and a variety of electro-optical properties as heterogeneous, core-shell, or alloy catalytic structures [2]. These characteristics make them applicable to drug delivery, biomedicine, biosensors, optics, electronics, solar energy and the food industry [3–5]. Gold, silver and their nanoscale composites as a noble metal relative to magnetic metals, have the same constant and crystalline atomic lattice structure. Additionally, these noble metals have profound electronic structures, which have presented catalysis, electronic and
plasmonic characteristics. These characteristics occur because of localized surface plasmon resonance (LSPR) and optical properties, when interaction with external electromagnetic radiation [6, 7].

The LSPR characteristic of NPs can be adjusted according to the size, shape, composition, crystallization and surrounding dielectric environment [8]. AuNPs as a noble metal, contains an unsaturated 5d electron shell that induces very good catalytic activities. These NPs have outstanding applications in nonlinear optical devices, single electronic tunnel and DNA sequencing [9–11]. AgNPs as 4d metals, have many potential applications because of magnetic and optical polarization, electric conductivity and antimicrobial activity [7, 12, 13]. BNP, consisting of two individual metallic elements to introduce new magnetic-noble multifunctional structures that have specific properties by modifying their components and geometric structures [14]. Consequently, the combination of gold and silver NPs needs further investigation, which is explained by synergistic effects and the mechanism of interaction of this noble metal [15].

PLAL as a physical method is one of the best ways to synthesize BNPs because of the capacity to produce various structures and compounds without absence of uncontrolled impurities. In addition, PLAL is used to monitor the characteristics of the synthesized NPs [16, 17]. PLAL in different liquids is of great scientific interest because of the production of NP from many types of solids and the ability to control the composition [18, 19]. There are many ways to manufacture NPs, including: solvothermal [20], Photochemical method [21], plane wave pseudopotential method [22], replacement reaction method [23], catalytic reduction [24], spray pyrolysis [25], wet-chemical method [7], chemical reduction [26, 27], green synthesize [28–30], post-modification [31], electron beam deposition [32], ion implantation [33, 34], electrochemical reduction [35], solid state dewetting (SSD) [36, 37], pulse laser deposition (PLD) [38] and PLAL [39–42].

In this study, gold target ablation is carried out in silver colloidal solution by PLAL and chemical reduction method. The purpose is to find the role of the different ratio concentration of the colloidal silver solution in the preparation of BNPs systems and the characterization of optical properties. The study of the catalytic behavior and reactivity of AgNPs is also discussed.

In the next section, we consider materials and methods is applied to experiment. Section 3, shows characterization of MNPs and BNPs. In section 4, we present results and discussion. Section 5, illustrates summary and conclusion. In the final sections, acknowledgment and author contribution is written.

2 Materials and methods

To begin with the old plate (99.9%) as an ablation target is ultrasonically cleaned with ethanol, acetone and deionized water (DIW) for 10 min. The gold target is bought from Sigma Aldrich Co. As a result, the ablation target (gold plate with a weight of 0.312 grams) is located at the bottom of a cylindrical open glass container which contains 200 mL of 1000 ppm, 2000 ppm and 4000 ppm of silver colloidal solution, respectively. The thickness of the colloidal silver solution on the gold target is 10 mm. The
removed mass is determined by weighing the substrate before and after the ablation process with a precision of 0.1 mg. The ablate mass is $3 \times 10^{-4}$ grams, as can be seen in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Sample (#)</th>
<th>The weight of the gold before ablation (gr)</th>
<th>The weight of the gold after ablation (gr)</th>
<th>The amount of gold removed (gr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s4</td>
<td>0.3125</td>
<td>0.3123</td>
<td>0.0002</td>
</tr>
<tr>
<td>s5</td>
<td>0.3125</td>
<td>0.3120</td>
<td>0.0005</td>
</tr>
<tr>
<td>s6</td>
<td>0.3125</td>
<td>0.3170</td>
<td>0.0008</td>
</tr>
</tbody>
</table>

The resulting Ag/Au nanocolloid solutions are mixed in different volumetric ratios. Colloidal nano-silver solution with a concentration of 4000 ppm is purchased from Mehregan Chemical Co which is formed by the chemical reduction method. The silver colloid solution contains 4 grams of silver powder in DIW that by adding poly vinyl pyrrolidine (PVP), disperses the AgNPs in a homogeneous manner and its dimensions are kept within the nanometer range. A chemical reduction pathway, induces an increase in electrons around a single atom and leads to a decrease in its oxidation rate. In addition, the probability of synthesizing core-shell nanocrystals by chemical reduction synthesis is increased [26, 43]. Another point is that the valence electrons of AgNPs when exposed to an outer field are excited and exhibit more plasmonic properties than the AuNPs. As a result, the silver concentration is selected as a test variable for studying the optical properties of the bimetallic system. This homogeneous solution contains 4 grams of silver powder that has attained a concentration of 4000 ppm with distilled water. Therefore, we brought the 4000 ppm solution to produce the 2000 ppm, 1000 ppm and 500 ppm concentrations. As shown in Table 2, samples are taken 500 ppm Ag (500 ml of 500 ppm Ag – s1), 4000 ppm Ag (500 ml of 4000 ppm Ag – s2), 500 ppm AgAu (500 ml of 500 ppm Ag mixed with 500 ml of distilled water – s3), 1000 ppm AgAu (500 ml of 1000 ppm of Ag mixed with 500 ml of distilled water – s4), 2000 ppm AgAu (500 ml of 2000 ppm Ag mixed with 500 ml of distilled water – s5) and 4000 ppm AgAu (500 ml of 4000 ppm Ag mixed with 500 ml of distilled water – s6) in this research.
Table 2
Symbols of Ag/Au BNPs using different amounts of silver colloidal precursor.

<table>
<thead>
<tr>
<th>Symbol of Ag/Au BNPs</th>
<th>Silver amount added to 500 ml of DIW</th>
</tr>
</thead>
<tbody>
<tr>
<td>s1</td>
<td>500 ml of 500 ppm Ag</td>
</tr>
<tr>
<td>s2</td>
<td>500 ml of 4000 ppm Ag</td>
</tr>
<tr>
<td>s3</td>
<td>500 ml of 500 ppm Ag mixed with 500 ml of DIW</td>
</tr>
<tr>
<td>s4</td>
<td>500 ml of 1000 ppm Ag mixed with 500 ml of DIW</td>
</tr>
<tr>
<td>s5</td>
<td>500 ml of 2000 ppm Ag mixed with 500 ml of DIW</td>
</tr>
<tr>
<td>s6</td>
<td>500 ml of 4000 ppm Ag mixed with 500 ml of DIW</td>
</tr>
</tbody>
</table>

To form a coherent bimetallic structure, it is necessary to use an element which has more electronegativity than silver. In this research, gold (+2.54 eV) with greater electronegativity than silver (+1.92 eV) is the best option to form a stable structure with silver [44]. In fact, AuNPs is used as the core for controlled reduction of the silver ion (Ag⁺) [26]. Ablation process carried out with a Nd:YAG pulsed laser. Figure 1 provides an overview of the ablation process. In this study, the size of the laser spot on the target surface using the Gaussian beam equations is calculated to be about 30 micrometres. The target is irradiated with 5000 pulses of the second harmonic of a 532 nm pulsed Nd:YAG laser (Quantel, model Brilliant B) running at a repetitive frequency of 10 Hz and 7 ns pulse width with fluence of 0.7 J/cm². A laser beam with a diameter of 6 mm is concentrated on the surface of the target by means of a 10 cm convex lens.

In this instance, we can differentiate between our work and other studies. In most of the papers that were done for the synthesis of MNPs and BNPs by the PLAL method, NPs were synthesized using the first harmonic generation of the Nd:YAG laser [41][45–50]. In other research apart from the use of the first and second harmonics generation, the laser parameters such as repetition rate, pulse fluence and pulse duration are variable [51–53]. Research conducted by Nikov et.al. shows that several methods such as thermal evaporation, PLD and PLAL together perform to Au/Ag BNPs synthesis [54]. In other study, PLAL was combined by green synthesis to formation bimetallic structures [50]. In the search carried out by Ayman et.al., the selected pulse fluence 

\[
(1.8 \text{ J/cm}^2)
\]

is greater than our parameter

\[
(0.7 \text{ J/cm}^2)
\]

In addition, in our current study with the pulse fluency about 0.5 J/cm² and applies only one method (PLAL) to the synthesis of the bimetallic system, can form BNPs with various structures (alloy and core-shell) and sizes [42].

Valence electrons in the orbital half-filled are the result of metallic properties of noble elements and changes in their colors during the ablation process. Electronic transition in gold, responsible for absorbing level 5d to 6s, and in silver it is 4d to 5s transition. However the relativist effects in gold increase the
energy of the orbital 5d and lower the orbital 6s. As a result, the UV absorption peak has shifted to the VIS range [55, 56]. Consequently, the probably relativistic effect is due to the yellow color of the gold and is attributed to the transition 5d to 6s that is in the vicinity of 2.3 eV. In this way, AuNPs reflect red and absorb blue. In AgNPs, due to lower relativistic effects compared to AuNPs is shown absorption in the UV area around 3.5 eV [57]. AgNPs are effective for absorbing and scattering photons according to the shape and size of the particle. The LSPR properties of plasmonic metals can be easily changed through synthetic conditions [25]. For Ag/Au structures, relativistic effects occurred for the s and the p orbital and for the d orbital, non-relativistic shell-structure effects are appeared [57]. In Fig. 2, the formation and morphological change of Ag/Au BNPs (s3-s6) is observed by changing the color of the solution from sepia to brown coffee during ablation.

3 Characterization of Ag and Ag/Au Bimetallic Nanoparticles

Various analytical techniques are applied to characterise NPs. The optical spectrums of the colloidal solution are characterised by a UV-Vis spectrophotometer (T80 UV-Vis Spectrometer/PG Instrument Ltd). A transmission electron microscope (TEM, Philips EM 208) is used to determine NPs size, shape and distribution. This test is performed by placing a drop of the concentrated suspension on a grid covered with Cu Mesh 300 carbon and kept completely dry at room temperature. The characterisation of the crystalline structure is carried out using the X-ray diffraction (XRD) technique. The concentrated suspension is released on a silicon substrate and dried for ten days for the measurement of X-rays (XRD, STOE-STADI MP, λ = 0.154 nm). The superficial morphology of NPs is examined under a field-emitting scanning electron microscope (FE-SEM, KYKY-EM 3200). Dynamic Light Scanning (DLS) is used to determine the size and distribution of NPs by measuring a hydrodynamic diameter using the MALVERN ZETASIZER 3000 HSA device. For XPS analysis, the prepared NP are attached to a stainless steel. Changes in valence status and functional surface groups of monometallic and bimetallic samples are detected by a high-performance X-ray photoelectron spectroscopic spectrometer (Escalab 250Xi; Thermo Fisher Scientific, Waltham, MA, USA). Dried sampled films are characterised by a Fourier transform infrared spectroscopy (FT-IR) (Thermo Nicolet, Nexus 870). The photoluminescence (PL) properties of individual silver and Ag/Au BNPs are detected by the PERKIN ROMER PL system.

4 Results and discussion

4.1 X-ray diffraction (XRD) Studies

The XRD spectrum of the samples is given in Fig. 3. The XRD spectrum clearly indicates the crystal structure of AgNPs. ANC peak values are shown at 2Θ = 37.03°, 45.31°, 65.23°, 77.2° and 83.28° attributed to (111), (200), (220), (331) and (222) Bragg’s reflection (JCPDS No. 01-087-0717) assigned to rounded AgNPs with fcc formation and adapt to crystalline character. The Ag/Au BNPs phase of the samples is confirmed whit XRD peaks. In each spectrum, five peaks are allocated to the diffraction of (111), (200), (220), (331) and (222) corresponding to 2Θ = 37.9°, 44.07°, 63.9°, 76.7° and 81.5° with fcc structural planes (JCPDS No. 03-065-8424). The planes determined in the bimetallic phase Ag/Au are
similar to pure silver, as their lattice constants are similar (gold (0.408 nm), silver (0.409 nm)) [24, 39]. The BNPs peaks (s3-s6) are wider and also shift from the origin position due to the formation of the core-shell and suggests the expansion of the superlattice [27, 58]. Low intensity Angles near 19.33° and 23.14° with the Bragg planes (111) and (211) belong to the orthorhombic silver nitrate (AgNO₃) (JCPDS No. 01-070-0779). The findings are reviewed as part of the EDS analysis.

The spherical and hexagonal crystal structure of the bimetallic Ag/Au samples is confirmed with Au in the nucleus and Ag in the shell of the resulting nano-structure. In other studies, Mondala and colleagues illustrate various geometries such as spheroidal and hexagonal NPs [59]. In the same study, researchers by application of the epitaxy method, could cultivate Au and Ag hexagonale nanodisk on ZnO nanoroad. The gold and silver that are included in this research, have the capability to form the hexagonal structure [60]. The latest research suggests that Nudelman and colleagues may form large hexagonal Ag/Au BNPs crystals [44]. The process of formation the hexagonal structure that is shown in s4 could be defined by minimizing the total energy by changing the interface strain in BNPs [61].

It may also be claimed that the formation of hexagonal structure due to the biphasic character of chemically synthesized AgNPs [43]. Since gold and silver have nearly identical crystalline structure (Au and Ag lattice constants are 4.08Å and 4.09Å), when silver is placed around the gold atom during synthesis, the synthesized silver/gold bimetallic structure has less total energy. This also reduces the interface strain. In this case, the probability of forming a hexagonal structure may be increased [62]. In the same way, the lattice corresponds between the core (gold) and the shell (silver) in bimetallic systems, which makes their lattice fringes indistinguishable. Moreover, it may impose the interfacial strain, which has been introduced to reduce catalytic rates [26, 63].

The mean crystallite size evaluated using Debye-Scherrer's Equation (Eq. 1), where D is the average crystallite size, K is the shape factor (0.94), \( \lambda \) is the wavelength of X-ray, \( \beta \) is full width at half-maxima (FWHM) of predominant plane's peak, and \( \theta \) is the diffraction angle.

\[
D = \frac{K \lambda}{\beta \cos \theta}
\]

For noble/plasmonic metallic NPs, the FWHM and peak intensity are dependent on particle size, morphology, and interparticle spacing [25]. Clear differences for the intense peaks of s3 with s6 in Fig. 3, determining the role of silver concentration and ablation method in the refinement of morphology and crystallization of BNPs Ag/Au. Similarly, the mean crystalline size of s1-s6 are recognised at 14 nm, 17 nm, 20 nm, 33 nm, 29 nm and 27 nm, respectively. The crystalline size of the BNPs is increased up to the optical limit activity (s3 and s4). In addition, due to the lack of oxidation and the decrease in shell thickness, the crystal size is also reduced (s5 and s6) [64, 65]. The mean crystalline sizes of samples are listed in Table 3.
Table 3
Summary of XRD data.

<table>
<thead>
<tr>
<th>Sample (#)</th>
<th>FWHM</th>
<th>$2\theta$</th>
<th>Crystallite Size (nm)</th>
<th>Reference Pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>s1</td>
<td>0.6298</td>
<td>38.22</td>
<td>14</td>
<td>01-087-0717</td>
</tr>
<tr>
<td>s2</td>
<td>0.5480</td>
<td>38.16</td>
<td>17</td>
<td>01-087-0717</td>
</tr>
<tr>
<td>s3</td>
<td>0.4723</td>
<td>38.18</td>
<td>20</td>
<td>03-065-8424</td>
</tr>
<tr>
<td>s4</td>
<td>0.3149</td>
<td>38.02</td>
<td>33</td>
<td>03-065-8424</td>
</tr>
<tr>
<td>s5</td>
<td>0.3062</td>
<td>38.21</td>
<td>29</td>
<td>03-065-8424</td>
</tr>
<tr>
<td>s6</td>
<td>0.3542</td>
<td>38.25</td>
<td>27</td>
<td>03-065-8424</td>
</tr>
</tbody>
</table>

4.2 UV-Vis Spectrophotometry

Figure 4a shows the UV–Vis absorption spectra for the synthesized NPs. The absorption spectra of colloidal suspensions consisted of a strong peak around 423 nm to 460 nm due to the inter-band transition of Ag/Au BNPs. The only peak is occurs at 390 nm due to the LSPR absorption of each silver NPs. An extra intense peak has occurred for BNPs (s3-s6), indicating the excitation of longitudinal plasmon vibrations of the AgNPs [37, 66]. Examination of peak locations associated with samples, may provide valuable information on the size, morphology and composition of NPs. Consequently, the placement of peaks associated with BNPs in relation to pure gold and silver, changes due to the oscillation of electron clouds of gold atoms [41, 48].

As can be seen, the peak position of s3-s5 is between 420 nm and 438 nm. Previous studies have suggested that the LSPR of AgNPs in the order of 410 nm to 450 nm, may be related to spherical morphology and can be consistent with FE-SEM, TEM and EDS analysis [67, 68]. An increase in peak intensities indicates an increase in the number of NPs in the samples. Despite the non-linear behavior and decrease in NPs size in samples s3 and s4, the number of NPs continues to increase. Ultimately, higher concentration leads to a reduction in adhesion and production of smaller NPs [69]. This trend can show in SEM images.

In s6 where the concentration of silver nano-colloid is extremely high and the absorption has reached the saturation limit, noise is seen in the absorption peak and we will have dark colored samples. Because of this, it is impossible to accurately determine the peak absorption in these samples and only an approximate can be set for it. In fact, strong peak which revealed around 560 nm because of the increase in effective charge transfer and the formation of more active sites [31]. Of course, in similar studies, the peak transmission of hexagonal NPs was observed in the 540 nm range, which is very close to our work [70, 71]. In particular, all plasmon bands belong to $\text{Ag}_{\text{shell}}/\text{Au}_{\text{core}}$ BNPs that show a wide spectrum, indicative of the favoured synthesis of $\text{Ag}_{\text{shell}}/\text{Au}_{\text{core}}$ nanostructures [72].
BNPs (s3-s6) experiences a red shift from a typical peak absorption of individual BNPs (about 400 nm) by increasing the concentration of the silver ratio. This may be due to the different configurations of conduction electrons on the surface and the interface between Au and AgNPs [31, 72]. AuNPs are completely covered by AgNPs of different shell thickness. These results are in good agreement with the reported red shift of the LSPR band for BNPs from 423 nm to 460 nm [26, 73]. According to the peaks related to the synthesized BNPs, not only the redshift occurred with growing fractal ratio of silver nanocolloid. It may also be seen that the height of the peaks increases as the concentration of silver colloid increases. This information is consistent with the XRD and TEM analysis of the core-shell growth [41, 74, 75]. The red shift indicates an increase of shell thickness [64]. For core-shell bimetallic structures, the shell plays an efficient role in the optical properties of the BNPs [66]. It should be noted that the core-shell structure, has a stronger optical non-linearity than the monometallic structure [76, 77].

In Fig. 4b, the LSPR band intensity of s1 is considerably above that of s3. The current aggregation of BNPs at this concentration, may be attributed to the increase in the Ag\(^+\) reduction rate [29]. However, due to the individual silver produced by the chemical reduction method, neither sample is oxidized and all samples form a stable structure by electronic means. On the other hand, the gold target ablated in the silver colloidal solution may perform nanocrystalline structures [43]. Consequently, the core-shell structures formed with the crystalline structure were reported by the XRD data.

In s4 due to the achievement of the optical limit activity and the reverse saturable absorption behavior, the shell thickness reached its maximum value. The decrease in shell thickness and the growth in optical limit activity in s5, indicate a decrease in local field and non-linear scattering effect [64]. It should be noted that the observed non-linearity can control the thickness of the synthesized shell [78]. By reducing the thickness of the silver shell in s5 and s6, the catalytic properties of Ag\(_{shell}\)/Au\(_{core}\) may be manipulated. In s5 and s6 experienced an increase in AgNPs concentration, which leads to an increase in electronic effects between the shell (silver) and the core (gold). In such condition, at the surface of the shell (silver), can prepare more functional groups for chemical reaction and adsorption of reactive substrates can alter catalytic efficiency. However, as the concentration of silver and its saturation (s5 and s6) on gold as core increases, BNPs becomes partially blocked. As a result, active sites are reduced with significantly reduced catalytic activity. This may be attributed to the lower electronic effect between the core (gold) and the shell (silver), resulting from the amplification of the thickness of the silver shell [26]. Also surface of BNPs, may not work well as an electroactive surface for oxidation with a higher Ag/Au concentration [79].

This different behavior may be attributed to the non-linearity of the core-shell structure in BNPs and the minimum reduction in Ag\(^+\) [29, 66]. Consequently, it is possible to have a bimetallic system with weak reactivity with biomolecules in the environment. This bimetallic system will ultimately lead to stability, without the addition of surfactants or metallic ions. This provides an opportunity to control the toxicity of AgNPs in compounds. The synthesis of particles into nano-dimensions, leads to the creation of free electrons. In that case, the value associated with the intra-band transition and the electric dipole transition is reduced. As a result, this type of transition will not play a role in the non-linear behavior of BNPs.
Moreover, the contribution of the hot electron in the 5d to 6s and 4d to 5s inter-band transition, will play a crucial role in the non-linear optical behavior of Ag\textsubscript{shell}/Au\textsubscript{core} BNPs. The transition seen in AuNPs is due to the saturation transition. However, the transition in AgNPs has been observed because of the absorption of two photon [41]. Moreover, the photo-generated charge carriers in the conduction bands of Ag\textsubscript{shell}/Au\textsubscript{core} BNPs during the formation of the core-shell structure, contribute to the free carrier and absorption of the excited state and therefore improvement of nonlinear absorption [65]. Additionally, it will witness the non-linear behavior of Ag\textsubscript{shell}/Au\textsubscript{core} BNPs which are placed between pure gold and silver mono-metallic NPs with two different transitions. According to some theoretical studies, the linearity of the Ag/Au BNPs alloy is better than that of the core-shell models. Thereafter, the nonlinearity characteristic of the Ag\textsubscript{core}/Au\textsubscript{shell} BNPs is greater than that of the Ag\textsubscript{core}/Au\textsubscript{shell} structure. [66].

A unique feature of plasmonic NPs is their ability to reveal multipolar modes of LSPR. Multipolar modes (dipole, quadrupolar and ...) correspond to the size, composition and distribution of the surface charge [80]. It is important to note that the emergence of LSPR modes has occurred as the formation of NPs [81]. In this search due to the high concentration of the samples, the quadropolar mode is not observed in the UV region. This will indicate no ligand-metal charge transfer (π → σ*) [82]. Only in the area greater than 400 nm can reveal the peaks related to the bipolar mode. Similar values have been found in similar studies [42, 81]. The dipole three plasmon absorption bands detected in the VIS range are shown as s3-s5 (420 nm, 423 nm and 438 nm). Moreover, the silver NPs are overlapped by plasma decoupling and the bimetallic structure is formed. Improving the charge transfer in the conductive band, it may be more in samples at higher concentrations [83–85]. All samples are in dipole mode in the VIS region. The last sample (s6), which has a high concentration of silver is not quadripolar in the UV region and quadrupolar mode is only observed in low concentrations (s3-s5). As a result, the metallic structure synthesized only in the VIS region may be an appropriate biosensor for all concentrations. In high concentrations of AgNPs, it is not possible to obtain an appropriate biosensor in the UV area.

4.3 Morphology studies

4.3.1 Electron Microscope studies (FE-SEM and TEM)

Electron microscopy studies are used to characterize both AgNPs and BNPs morphology. The Ag\textsubscript{shell}/Au\textsubscript{core} BNPs which are produced by the PLAL technique, may be combinations of different forms. In fact, AgNPs is one of the most important noble metals and by chemical composition and concentration, have a variety of morphological characters that are formed by physical, chemical, and biological methods [43, 86, 87].

Figure 5 shows the SEM gold and silver NPs next their Ag\textsubscript{shell}/Au\textsubscript{core} BNPs micrographs which clearly show uniformly spherical and hexagonal structures. The SEM images revealed that the predominant feature of s3-s5 is almost spherical with an average diameter less than 100 nm. In other hands, s3-s5 presents rounded corners because of the possible intense diffusion of Au and AgNPs by irradiation of the green laser Nd:YAG [62]. Sharma and colleagues synthesize Ag/Au BNPs using clove buds in rounded
and hexagonal forms [30]. In other studies, the researchers present this morphology of AgNPs synthesized with a clearly hexagonal structure [86].

By ablating the gold target in colloidal suspension of silver leads to the expansion of the plasma plume and the synthesis of NP with a larger size [86, 88]. Application of lasers to form nanomaterials, provides better shape control. The rate of heating in pulsed laser irradiation is superior to that of continuous laser irradiation. For this reason, the control of the morphology of synthesized Ag$_{\text{shell}}$/Au$_{\text{core}}$ BNPs by pulsed laser, have less precision than the continuous laser [89]. Moreover, in s3 and s4, due to the increase in the area of AgNPs in the shell, the size of NPs will increase significantly [88]. In addition, by adding metallic ions (such as Ag$^+$), reducing agents and surfactants can be controlled by the shape and size of NPs [70]. It should be noted that because of the similarity of the BNPs lattice constants in gold and silver, the PLAL leads to an increase in crystalline size. However, smaller AuNPs are synthesized near other metals (Au/Pt and etc) [63]. In our research, because of the synthesis of AgNPs by the chemical reduction method, the chance of oxidation was reduced [26, 43]. For this reason, as mentioned in the UV analysis the reverse saturable absorption behavior and the optical limit activity leads to decrease the size in s5 and s6. The following has also been proven morphological change. TEM micrographs of the NPs are presented in Fig. 6 to investigate the morphologies and nanostructures of AgNPs next their Ag$_{\text{shell}}$/Au$_{\text{core}}$ BNPs. TEM figures report that s1-s6 have an average size of 27 nm, 26.8 nm, 30.9 nm, 64.7 nm, 56.4 nm and 43.9 nm respectively. TEM images of Ag$_{\text{shell}}$/Au$_{\text{core}}$ BNPs are taken whit different molar ratio of silver. As can be seen, the Ag$_{\text{shell}}$/Au$_{\text{core}}$ BNPs are nearly spherical in s3-s5. Moreover, in the last sample due to the agglomeration and high adhesion, distinguish the morphology of particles very difficult. Sharma and colleagues shared the same report for Ag$_{\text{shell}}$/Au$_{\text{core}}$ BNPs [30].

Following laser irradiation, AuNPs show a higher content than AgNPs in TEM images due to higher atomic numbers and more electrons to be scattered at higher angles [90, 91]. The un-uniform contrast between the different parts of a NPs, shows that the electrons density is not homogeneous and the internal areas of the samples are darker than the shell areas. This means that BNPs closely resembles the Ag$_{\text{shell}}$/Au$_{\text{core}}$ structure [59, 92, 93]. The same results as shown in the UV-Vis diagrams.

### 4.3.2 Energy Dispersive Spectroscopy (EDS)

To provide elementary information on the composition of the BNPs phases, the EDS analysis is applied. This analysis, performed in conjunction with TEM and perhaps in addition to metals, a certain amount of carbon attributed to the TEM specimen grid is determined in the samples. For each molar ratio of Ag/Au BNPs, approximately 100 particles from the copper grid are selected for analysis of their mean composition. The BNPs values of the bimetallic systems are in good agreement with the LSPR results and determine a uniform distribution of distinguishing elements in all core-shell samples. Individual AgNPs are also presented in two separate concentration reports (s1 and s2).

In Fig. 7a, s1 as a monometallic sample is contains elements with atomic percentages of 48.68% C, 37.93% O, 6.77% Ag, 3.13% Na and 3.49% Si, whereas the silver ratio concentration is less than s2. In
addition, Fig. 7b shows that s2 is composed of the same elements with atomic percentages of 12.66% C, 6.16% O, 1.95% Zn, 78.37% Ag, 0.24% Cl and 0.61% Si and it has the highest ratio of AgNPs than s1. In the case of the Ag_{shell}/Au_{core} bimetallic system in Figs. 7c and 7d, s3 illustrates the elements with atomic percentages of 48.37% C, 33.21% O, 8.86% N, 6.05% Ag, 1.97% Na and 1.54% Si, and the concentration of silver is lower than carbon in more than s3 and s4. The sample of s4, have elemnts with atomic percentages of 25.91% C, 39.29% O, 0.37% Ni, 22.53% Ag, 9.69% Na,1.43% Mg, 0.14 Au% and 0.13 Cl% which could be see the reverse relation between the percent volume of C and Ag in s3 and s4. In s3 and s4, with the increase in silver ions concentration (Ag\(^{+}\)), the quantity of silver concentration NPs in the shell is increased. Consequently, the shell thickness of the bimetallic structure is also decreases [93].

The amount of silver metallic ions (Ag\(^{+}\)) on the BNPs shell affects the absorption wavelength and the BNPs size [94, 95]. The EDS analysis of s5 synthesis of the PLAL technique in Fig. 7e illustartes the elements with atomic percentages of 2.77% Na, 16.72% O, 2.10% Mg, 69.14% Ag, 0.65% Cl, 6.45% Si, 0.00% U and 2.18% Au. In addition, the EDS data for s6 in Fig. 7f show elements with atomic percentages of 23.76% C, 13.27% O, 2.36% Na, 1.16% Yb, 4.22% Si, 0.00% K, 54.70% Ag and 0.53% Au. The concentration of gold atoms is several times lower than that of silver atoms within s3-s6. One can see that the intensity of the peak in s6 is reduced as the concentration of silver increases. In another similar research, also the size of the BNPs is diminished with the growing concentration of silver [96].

In similar studies, elements due to the presence of impurities or penetrating into the external environment have been observed. Other elements at low peak in composition such as sodium (Na), potassium (K), magnesium (Mg), silicon (Si), chlorine (Cl), ytterbium (Yb), and uranium (U), due to applying chemical reduction method [29, 63, 75, 87, 97]. Despite the creation of numerous impurities/biomolecules in the environment and the capping of Au and AgNPs, the synthesized bimetallic structures remained stable. Based on the results obtained from the Amikoro studies, the percentage of oxygen volume is higher in spherical samples, similar to the results obtained for s3-s5 [98]. The presence of oxygen (O) and silver atoms in bimetallic compounds is indicative of the formation of AgNPs. Then there is the possibility of oxidation of silver. However, because of the synthesis of AgNPs with the chemical reduction method, the probability of silver atoms reacting with oxygen is reduced [87]. Detection of nitrogen atoms (N) in bimetallic compounds can account for how the AgNO\(_{3}\) chemical is released during chemical reduction and synthesis of AgNPs [66]. Importantly, carbon (C) is detected in all samples. The peak belongs to the carbon atoms, also may be attributed to the TEM specimen grid [63, 97]. In similar research, peaks related to monometallic Au and AgNPs and bimetallic systems were detected [29, 63, 90, 95]. Primary line displacements by energy are shown in Table 4 for all XPS spectra.
Table 4

<table>
<thead>
<tr>
<th>Spectrum name</th>
<th>Ag, binding energy (keV)</th>
<th>Au, binding energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s1</td>
<td>3.00</td>
<td>Not reported</td>
</tr>
<tr>
<td>s2</td>
<td>3.00</td>
<td>Not reported</td>
</tr>
<tr>
<td>s3</td>
<td>2.97</td>
<td>2.40</td>
</tr>
<tr>
<td>s4</td>
<td>3.00</td>
<td>2.35</td>
</tr>
<tr>
<td>s5</td>
<td>3.05</td>
<td>2.23</td>
</tr>
<tr>
<td>s6</td>
<td>3.08</td>
<td>2.10</td>
</tr>
</tbody>
</table>

In all observed XPS spectra, changes in energy may have been observed for metals in bimetallic systems (s3-s6) compared to pure samples (s1 and s2). Shifts may be attributed to changes in electron density distribution, crystalline size or the formation of the core-shell [63]. In our records, Ag MNPs is detected around 3.00 keV. In similar studies, it is reported that the binding energy of AgNPs is recorded at 3.00 keV [87]. In addition, Anjum and collies reported similar results for the binding energy of AgNPs around 3.00 keV [99]. For Ag/Au BNPs (s3-s6), the peak of the silver atoms is observed at 2.97 keV, 3.00 keV, 3.05 keV and 3.08 keV respectively that the evidence of Ag/Au are uniformly distributed over all bimetallic samples. Moreover, the EDX data for Ag MNPs confirm that the bimetallic structure is synthesized in the form of core-shell [90, 98, 100, 101].

4.4 Dynamic light scattering (DLS) Studies

The size distribution and increasing thickness of the silver shell, regardless of the core size, can be measured using the DLS method. Figure 8, shows the bar chart of the size distribution. The mean hydrodynamic diameter obtained from the DLS data, revealed that the mean size of Ag$_{\text{shell}}$/Au$_{\text{core}}$ BNPs and the thickness of the silver shell are increased by the addition of the Ag$^+$ in s3 and s4 [26]. Similarly, the mean diameters in s1-s6 are recognized at 56.3 nm, 65.5 nm, 83.6 nm, 86.5 nm, 66.3 nm and 65.1 nm, respectively.

The results obtained from DLS and UV-Vis can be regarded as being in good agreement with one another. As this question is addressed in the UV-Vis analysis, with the increase in the concentration of silver and Ag$^+$ on the shell (silver), the thickness of the shell has increased (s3 and s4). In the following, due to non-oxidation and non-linear behavior of Ag$_{\text{shell}}$/Au$_{\text{core}}$ BNPs is shown decreasing in the shell thickness in the s5 and s6 (Fig. 9). The items mentioned may also be confirmed through the DLS analysis. Table 5 shows the mean particle size for the samples obtained from the XRD, TEM and DLS data.
Table 5
The size of BNPs obtained from XRD, TEM and DLS samples.

<table>
<thead>
<tr>
<th>Sample (#)</th>
<th>Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>XRD</td>
</tr>
<tr>
<td>s3</td>
<td>20</td>
</tr>
<tr>
<td>s4</td>
<td>33</td>
</tr>
<tr>
<td>s5</td>
<td>29</td>
</tr>
<tr>
<td>s6</td>
<td>27</td>
</tr>
</tbody>
</table>

Size differences in SEM and DLS analyses may be due to the fact that DLS includes the ligand shell and determines the hydrodynamic sizes of the NPs. Whereas, in TEM shows the width of MNPs (pure silver in s1 and s2) and look only at the bimetallic core-shell. Hence, the size obtained from the DLS analysis, represents the size of the whole conjugate and proves that the size of the atoms in each molecule is increased significantly compared to other analyses [100].

The hydrodynamic sizes of the synthesized BNPs are significantly larger than their actual size. It is indicated in the TEM and XRD reports due to NPs agglomeration during ablation and the presence of the hydration layer [26, 102]. Measured NPs sizes by DLS and TEM confirmed earlier results from the SEM analysis. The increase in the concentration of the silver ratio leads to an improvement in the average size of NPs. A summary of data on the hydrodynamic radius of Ag/Au GNP is presented in Table 6.

Table 6
Hydrodynamic radius of Ag/Au BNPs.

<table>
<thead>
<tr>
<th>Sample (#)</th>
<th>s1</th>
<th>s2</th>
<th>s3</th>
<th>s4</th>
<th>s5</th>
<th>s6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrodynamic radius (nm)</td>
<td>56.3</td>
<td>65.5</td>
<td>83.6</td>
<td>86.5</td>
<td>66.3</td>
<td>65.1</td>
</tr>
</tbody>
</table>

4.5 FT-IR Studies

Fourier transform infrared spectroscopy (FT-IR) is used to determine the vibrations of atoms in a molecule and the specific surface chemistry of individual Au and AgNPs and Ag/Au BNPs. To achieve this, a spectrophotometer with a range between 400 cm$^{-1}$ and 4000 cm$^{-1}$ is applied for the samples. The footprint region (500 cm$^{-1}$ to 1500 cm$^{-1}$) showed the specific properties of the synthetic NPs. FTIR spectra are used to determine what functional groups or molecules are responsible for the formation and stabilization of metal NPs [103]. Table 7 presents chemical bonds of different wavelengths for synthesized BNPs Ag/Au.
Table 7  
Chemical bonds in different wavelength for synthesized monometallic silver and Ag/Au BNPs.

<table>
<thead>
<tr>
<th>Chemical bonds</th>
<th>O-H</th>
<th>C-O</th>
<th>C-H</th>
<th>C-H</th>
<th>C-R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (cm⁻¹)</td>
<td>3400.71</td>
<td>2079.90</td>
<td>1637.22</td>
<td>696.00</td>
<td>464.37</td>
</tr>
</tbody>
</table>

As spectra in Fig. 10a, show broad band between 3000 cm⁻¹ and 3700 cm⁻¹ belong to the stretching vibration of −OH molecules that observed in similar research [104]. At about 2370 cm⁻¹ and 2320 cm⁻¹ point, the weak peak belongs to phosphidal bonds. The carbon dioxide molecules which are present in the atmosphere are revealed in nearly 2080 cm⁻¹ and belong to C = C bending vibration mode. The strong bands at 1640 cm⁻¹ point are correlated with C = C alkenes or C = O stretching amides. The weak bands near 1390 cm⁻¹ point are represented by a sulfated ester in the form of S = O. The stretching bond of the ester group is nearly 1270 cm⁻¹ point. The alkyn bonds around 636 cm⁻¹ and 698 cm⁻¹ are representative of the C-H or C = H aromatic band. S. Ravichandran and colleagues observed the same absorption peaks during the green synthesis of the Myrtaceae leaf [105].

Other functional groups representing aromatic, phosphate and alkane groups are shown in Fig. 10b. The FTIR spectrum of s1, showed a distinct peak in the range of 1460 cm⁻¹, 2070 cm⁻¹, 2360 cm⁻¹ and 2920 cm⁻¹ that represent the alkanes aromatic C-C, C = C bending vibrations, Si-H and C-H compounds stretches, respectively. The s3 has specific peaks only within the frequencies of 694 cm⁻¹, 1040 cm⁻¹, 1090 cm⁻¹, 1640 cm⁻¹ and 3410 cm⁻¹. These peaks respectively represent alkenic and alkynic compounds, stretching C-N amine, stretching C-O esters and C = C double bond alkenes, and −OH belonging to water molecules. The silica-bound group may have been included in the samples due to the use of Pyrex as a container during ablation. High intensity peaks are an indication of their effective role in reactions. The very low peaks indicate the low role played by functional groups during ablation.

As can be seen, the reduction in the intensity of the absorption bands can describe the formation of Ag/Au BNPs in solution for all samples. In addition, the decrease in the height stretching frequency of −OH between 3000 cm⁻¹ and 3700 cm⁻¹ may be attributed to the interactions between gold, silver and −OH groups in liquid medium. The intensity of peaks belonging to s1 is more intense than s3. With the formation of the core-shell structure, the reactivity with the medium is reduced and decreases the intensity of the peaks, corresponding to the bimetallic samples is obvious.

Similar peaks can be seen in Fig. 10c and the intensity of peaks attribute to s2 is more intense relative to s4. In the s2, peaks are observed at frequencies of 480 cm⁻¹, 1050 cm⁻¹, 1100 cm⁻¹, 1460 cm⁻¹, 1640 cm⁻¹, 2070 cm⁻¹, 2360 cm⁻¹, 2980 cm⁻¹, 3400 cm⁻¹ and 3750 cm⁻¹ that are most often weak and indicate that the functional groups will play a minor role in compounds. The frequencies listed are in groups C-R stretching alkyl halide, C-O stretching ester, C-C alkane and aromatic, C = C alkene and C = O stretching amide, C = C bending vibration, Si-H, C-H stretching alkane and O-H belonging to the molecule.
of water is in the ablation environment. In Fig. 10d, a significant shift is determined in the absorbance peak for s3 and s6 of 694 cm\(^{-1}\) to 688 cm\(^{-1}\). In addition, other drastic changes are seen for s1 and s2 of 461 cm\(^{-1}\) to 480 cm\(^{-1}\), respectively. The main representative functional group of this range (C-R stretching band) is effective for capping agents, controls the morphology and stabilization of NPs during synthesis [86]. The function groups mentioned are determined by the Ir. Pal2.0 software.

The form of other peaks show the interaction between Au and AgNPs as a noble metal [105, 106]. This result reveals strong interactions between Au\(_{\text{core}}\)/Ag\(_{\text{shell}}\) BNPs. The pure silver samples (s1 and s2) with wide and sharp peaks, have changed in comparison with each other as a result of the increase in silver concentration. Peaks that are assigned to s1 and s2, being more intense than those of AuNPs and Ag/Au BNPs due to high AgNPs have a greater capping effect [107].

### 4.6 Photoluminescence (PL) studies

Photoluminescence analysis is used to study the PL characteristics of silver NPs and Ag/Au BNPs. In this research, because of the high concentration of AgNPs in monometallic and bimetal samples (s2, s5 and s6) peak extraction is impossible. As a result, only three samples (s1, s3 and s4) are found in the PL analysis. In addition, the extracted peaks contain a large amount of noise, making it difficult to identify the main peaks. In the VIS area that wide and intense peaks are detected, assign to individual AgNPs (s1) and BNPs (s3 and s4) near 528 nm (\(~2.34\) eV), 530 nm (\(~2.33\) eV) and 533 nm (\(~2.32\) eV), respectively. The PL spectrum which is detected near of 528–533 nm (\(~2.34–2.32\) eV) is also recorded by R. Zakaria et al, for Au and Ag nano-flowers around 535 nm (2.31 eV) [32]. In another study, similar peaks were found in the 530–540 nm (\(~2.33–2.29\) eV) for the Au/Ag bimetallic structure [42]. The interface interaction between Au and AgNPs in PL analysis is observed as a redshift, which represents the interference in terms of LSPR of Au and AgNPs in the bimetallic system. In this way, changes in the size of BNPs can be observed. The highest peak belongs to s3, with the lowest amount of silver ratio concentration, caused by AuNPs have a high plasmonic resonance effect and a local electrical field. By gradually increasing the ratio of silver concentration (s4), the plasmonic effect of the AuNPs decreases and the peak height decreases. In this case, not only do the plasmonic resonance spectra of the AuNPs strongly depend on particle sizes, but the luminescent improvement also depends on the crystalline sizes.

Another sharp peak, which belongs to s1 with the lowest ratio concentration, is caused by the due to electron-hole recombination [25]. The electron-hole recombination, should be increased with the decrease in the concentration of the silver ratio. but because of the presence of free active molecules in the environment and impurities recorded by EDS analysis, electron-hole recombination is reduced. Therefore, the observed peaks are recorded in the VIS region [108, 109].

### 5 Summary and Conclusion

In current investigations, Ag\(_{\text{shell}}\)/Au\(_{\text{core}}\) nanostructures are successfully formed using the PLAL method of gold plate immersed in the liquid silver solution. The volumetric concentration of the AgNPs is found to
have influenced the optical properties of the Ag\textsubscript{shell}/Au\textsubscript{core} BNPs. Of course, the study found that Ag\textsubscript{shell}/Au\textsubscript{core} BNPs exhibited non-linear properties relative to single-metal AgNPs. It will look at their potential in optoelectronic systems and as a catalytic material in germicidal applications. All the analyses used agree on mentioned results of grain size, morphology, functional groups and optical properties. To better investigate the properties of non-linear optics, further analyses should be carried out.

One of the goals of this research is to prepare Ag\textsubscript{shell}/Au\textsubscript{core} NPs to control the toxicity and reactivity of silver as a NPs with high cytotoxic effects. The synthesis method applied, leads to increased stability of AgNPs in the compounds. Increasing the accumulation of silver ions means that these samples are not oxidized and toxic compounds are not created. This result is therefore the best option for microicides in food packaging. Obviously, to verify the antibacterial activity of the synthesized NPs, relevant biological analysis should be considered.

In the final analysis, we discuss the catalytic properties of the bimetallic system. Au and AgNPs have a very similar lattice constant and for that reason the core-shell structure of these two elements has an indistinguishable lattice fringe. This results in an increase in interfacial strain and a decrease in catalytic activity. In contrast, when the concentration of AgNPs is highest with the increase in electrical effects between the core and shell, catalytic activity of the bimetallic system is decreased. Every sample has a dipole mode in the VIS area. The s\textsuperscript{6} has no quadrupole mode in the UV region and quadrupole mode is only found in s\textsubscript{3}-s\textsubscript{5}.

In conclusion, the simultaneous use of two synthesis methods can significantly control the crystal size and achieve optimal stability. In addition, it is possible to synthesize BNPs with the same shell-core structure in various concentrations. The following, Ag/Au BNPs samples with a lower percentage of AgNPs, have higher catalytic properties. Moreover, the BNPs structure only in the VIS region can be an appropriate biosensor in all concentrations. In high silver concentrations, it is impossible to get an appropriate biosensor in the UV region.

The next step in the research would be to study the antibacterial actions of Ag\textsubscript{shell}/Au\textsubscript{core} BNPs and introduce the synthesized BNPs into the polymer matrix to form the nanocomposite. The necessary base nanomaterials can be supplied in food packaging.

**Abbreviations**
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPs</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>MNPs</td>
<td>Monometallic nanoparticles</td>
</tr>
<tr>
<td>AuNPs</td>
<td>Gold nanoparticles</td>
</tr>
<tr>
<td>AgNPs</td>
<td>Silver nanoparticles</td>
</tr>
<tr>
<td>Ag/Au BNPs</td>
<td>Silver/gold bimetallic nanoparticles</td>
</tr>
<tr>
<td>PLAL</td>
<td>Pulsed laser ablation in liquid</td>
</tr>
<tr>
<td>LSPR</td>
<td>Localized surface plasmon resonance</td>
</tr>
<tr>
<td>DIW</td>
<td>Distilled water</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet region</td>
</tr>
<tr>
<td>VIS</td>
<td>Visible region</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction pattern</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible spectroscopy</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Tunneling electron microscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive spectroscopy</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence spectroscopy</td>
</tr>
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</table>

**Declarations**

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**Author Contribution**

The authors confirm their contribution to this document as follows: A. H. Sari devised the project, A. H. Sari presented the main conceptual ideas, A. H. Sari encouraged E. Mohebi to investigate a specific aspect of individual AgNPs and Ag/Au BNPs and supervised the findings of this work, D. Dorrarian designed the experimental framework, D. Dorrarian contributed to laser preparation, A. H. Sari and D.
Dorranian verified the analytical methods, E. Mohebi worked out all of the experiment, Sh. AdibAmini and E. Mohebi wrote the manuscript with support from A. H. Sari and D. Dorranian, all authors contributed to the final version of the manuscript.

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**Competing Interests**

The authors have no relevant financial or non-financial interest to disclose.

**Conflict of interest**

The authors declares that there is no conflict of interest.

**References**

12. Z.C. Ma, Y.L Zhang, B. Han, Q.D.Chen, H.B. Sun: Small Methods 2, 1700413 (2018)


86. M.S. Al Aboody: Nanomedicine and Biotechnology 47, 2107-2113 (2019)
89. Z. Jiang, L. Li, H. Huang, W. He, W. Ming: Int. J. Mol. Sci 23, 14658 (2022)
90. X. Xu, T. Isik, S. Kundu, V. Ortalan: J. Name 10, 23050-23058 (2013)

Figures
Figure 1

Schematic of PLAL process to producing $\text{Au}_{\text{core}}/\text{Ag}_{\text{shell}}$ BNPs.
Figure 2

Silver 500 ppm (s1) and silver 4000 ppm (s2) beside their mixtures: 500 ppm Ag/Au (s3), 1000 ppm Ag/Au (s4), 2000 ppm Ag/Au (s5) and 4000 ppm Ag/Au (s6).
Figure 3

X-ray diffraction pattern of silver NPs (500 ppm Ag (s1), 4000 ppm Ag (s2)) beside synthesized bimetallic structures: 500 ppm Ag/Au (s3), 1000 ppm Ag/Au (s4), 2000 ppm Ag/Au (s5) and 4000 ppm Ag/Au (s6).
Figure 4

UV-Vis-NIR absorbance spectrum of (a) silver NPs (500 ppm Ag (s1), 4000 ppm Ag (s2)) beside their BNPks (s3-s6) after green laser irradiation, (b) two samples (500 ppm Ag (s1) and 500 ppm AgAu (s3)) compare with together.
Figure 5

Representative FE-SEM images of (a) 500 ppm Ag (s1), (b) 4000 ppm Ag (s2), (c) 500 ppm Ag/Au (s3), (d) 1000 ppm Ag/Au (s4), (e) 2000 ppm Ag/Au (s5), (f) 4000 ppm Ag/Au (s6) after green laser irradiation.
Figure 6

Representative TEM images of (a) 500 ppm Ag (s1), (b) 4000 ppm Ag (s2), (c) 500 ppm Ag/Au (s3), (d) 1000 ppm Ag/Au (s4), (e) 2000 ppm Ag/Au (s5), (f) 4000 ppm Ag/Au (s6) after green laser irradiation.
Figure 7

EDS spectrum of (a) 500 ppm Ag (s1), (b) 4000 ppm Ag (s2), (c) 500 ppm Ag/Au (s3), (d) 1000 ppm Ag/Au (s4), (e) 2000 ppm Ag/Au (s5) and (f) 4000 ppm Ag/Au (s6).
Figure 8

DLS plots of (a) 500 ppm Ag (s1), (b) 4000 ppm Ag (s2), (c) 500 ppm Ag/Au (s3), (d) 1000 ppm Ag/Au (s4), (e) 2000 ppm Ag/Au (s5), (f) 4000 ppm Ag/Au (s6).
Figure 9

DLS chart of individual silver (s1 and s2) and Ag/Au BNPs (s3-s6) with different ratio concentration.
Figure 10

FT-IR diagram of (a) 500 ppm Ag/Au (s3), 1000 ppm Ag/Au (s4), 2000 ppm Ag/Au (s5) and 4000 ppm Ag/Au (s6), (b) 500 ppm Ag (s1) and 500 ppm Ag/Au (s3), (c) 4000 ppm Ag (s2) and 4000 ppm Ag/Au (s6) and (d) 4000 ppm Ag (s2), 4000 ppm Ag/Au (s6), 500 ppm Ag (s1) and 500 ppm Ag/Au (s3).
Figure 11

PL diagram of 500 ppm Ag (s1), 500 ppm Ag/Au (s3) and, 1000 ppm Ag/Au (s4).