

Pulse laser ablated growth of Au-Ag nanocolloids: Basic insight on physiochemical attributes

A A Salim, S K Ghoshal, Hazri Bakhtiar*, G Krishnan, M Safwan aziz, H H J Sapongi

Laser Center & Physics Department, Faculty of Science, Universiti Teknologi Malaysia, Johor Bahru 81310, Malaysia

Corresponding Author: hazri@utm.my*, asali@utm.my

Abstract. Despite considerable research the evidence around the wide applications in the nanomedicine and nanophotonic area of gold-silver (Au–Ag) nanocolloids remains equivocal and under exploration. Due to their physical properties, enhanced permeability, high fluorescent, surface area to volume ratio, retention effect, localized surface plasmon resonance (LSPR) and controlled perfusion of drugs, made Au–Ag nanoparticles is over interested. Hence, we produced Au–Ag nanocolloids using nanosecond pulse laser ablation in liquid (NPLAL) technique. Targets of Au and Ag were submerged individually inside the cubic vessel fulfilled by 8 mL of glycol liquid media and vertically ablated with different pulse laser ablation (PLA) energy (50, 100, 150 and 200 mJ). The influence of the PLA energy (at fundamental wavelength 1064 nm) on the optical properties, morphology, particle size distribution, and chemical structure of the obtained colloidal Au–Ag NPs was established. UV-Vis and FTIR spectrophotometers have been utilized to determine the absorbance characteristics and chemical functional groups of Au–Ag nanostructures, respectively. The attained of Au-Ag nanostructure exhibits a single-surface plasmon resonance (SPR) band, positioned between SPR bands of the monometallic and a surface bonding functional group (e.g. carboxyl or hydroxy groups). The proposed technique can be a basis for the developing complex compositions/colloids with unique and optimal physical properties may use for developing future nanomedicinal and nanophotonics.

Keywords: Synthesis, Au–Ag nanocolloids; NPLAL; Absorbance characteristic; Chemical bonding

1. Introduction

In the last decades, nanoscience and nanotechnology has scientifically derived to modern development research which is dealing with synthesis, strategy and manipulation of particle's structure and morphology ranging from approximately 1 to 100 nanoscales [1,2]. Within this range, all the properties (chemical, physical and biological) change in fundamental way for both individual atom/molecule as well as their corresponding bulk counterpart. Up to now, nanoparticles (NPs) from metals exhibit fabulous advanced features based on their physiochemical and electronic properties such as morphology, tiny size, elemental compositions and chemical structure dependent [3-5]. Novel applications of NPs are growing rapidly on various fronts due to their new-fangled/enhanced properties based on their particle size distribution, high surface area, absorbance and scattering [6]. Metallic NPs particularly as colloidal nanostructures are summarily gaining renovation in a large number of electrochemistry, biomedicine, photochemical fields such as health care, cosmetics, biomedical, food and feed, drug-gene delivery, environment, mechanics, optics, chemical industries, electronics, space industries, energy science, catalysis, light emitters, single electron transistors, nonlinear optical devices and photo-electrochemical applications [5-8].

Recently, inorganic gold (Au) and silver (Ag) NPs are being explored extensively in the field of nanomedicine drug development, which have been received focused research attention. These Au and



Ag NPs have numerous platforms that can be used for pigments, sensors, electronics, solar cells, cosmetics, drugs and antimicrobials to target pathogenic and multidrug-resistant due to easy modification, high electron conductivity, high drug loading capacity, large surface area and stability [7-9]. The enhancement in permeability and retention of those NPs are needed as unique property in order to accumulate and interact with the tumour cells [10]. Earlier, The Au and Ag NPs confirmed to be the safest and much fewer toxic agents for drug delivery and antibacterial activities [11, 12]. On top, AuNPs is biologically and medically used as immunostaining marker particles for electron microscopy, and as chromophores for immunoreactions and nucleic acid hybridized [13]. Also, it can be utilized to label DNA or proteins for detection propose of biological targets with improved sensitivity.

Diverse approaches (top-down and bottom-up) are employed for the preparation of Au and Ag NPs, involved biological, physical, and chemical methods [14,15]. The common one is being the co-reduction of the corresponding metal precursor salts However, it is insufficient to produce purified NPs, requiring extra chemical purifications and use of toxic reagents in the chemical ones [15]. To overcome of those issues, the recent versatile and efficient physical method as called nanosecond pulsed laser ablation in liquid (NPLAL) of a bulk target, is well-known as a method for the preparation of NPs of different optical properties, composition and morphology [16,17]. Lee et al., [18] has reported the production of Ag-Au alloy NPs by ablation of bulk alloy metals in water. Immense growth in these expanding technologies has opened applied frontiers and novel fundamentals.

In this work Au-Ag nanocolloides were prepared by Q-switch Nd:YAG nanosecond pulse laser ablation with different ablation energies. The established results of optical properties and as the small size surface area to volume, strong surface plasmon resonance in the visible range of electromagnetic wavelength of Au-Ag nanocolloides is similar to that of biological molecules. This makes them a promising candidate for application in both *in vivo* and *in vitro* research.

2. Experimental Procedures

A gold (Au) and silver (Ag) plate (>99.99% in purity) with was used as target material. The targets were cleaned in an ultrasonic bath of acetone for 15 min each and rinsed with distilled water in order to eliminate the contaminants. Prior of ablation process, the targets were individually positioned inside the vessel filled with 8 mL of glycol liquid media. Afterward, the laser beam was irradiated vertically on each target, causing the form of plasma plume on the target surface with generation of cavitation bubble presented due to the strong confinement of liquid and the pressure. Considering the phenomenon of light refraction, the distance from laser focusing lens into the surface of target material was fixed at 18 cm. Different laser ablation energy (50, 100, 150 and 200 mJ) are used to obtain the optimal energy for NPs growth with the fundamental wavelength (1064 nm) of a pulsed Nd:YAG laser operating at 8 ns pulse duration and 8 Hz laser repetition rate. The beaker containing the Au/Ag target immersed in glycol was revolved at the speed of 12 rpm using a magnetic stirrer to evade the diffused materials aggregation onto the surface of generated NPs.

In PLAL process, the material in the form of hot plasma plume was ejected from the Au or Ag target because of the interaction of the laser beam with glycol media. The plasma was stayed optically active for few microseconds until a fast cooling and high temperature observing. Thereafter, rapid quenching of hot plasma could liberate a vapor bubble in the media, which was principally composed of the vaporized solution and enclosed a tiny portion of matter ejected from the target surface.

3. Results and discussion

This study is clarifying the influence of different pulse laser ablation energy (PLAE) on the optical properties (especially position of the SPR and chemical structure) of the AuNPs, AgNPs, nanocolloids Au-Ag produced in glycol liquid media. Figure 1 (a-c) displays the UV-visible absorption spectra of those NPs and their insets (color variations) dependent PLAE. The appearance of SPR peak in the UV-visible absorption spectra confirms the presence of the NPs. A single and strong SPR band, located in

the range of 419–553 nm, is remarked. It is obviously seen that the increment in the PLAE (photon incidents) was attributed to destruction of larger size NPs into smaller NPs, which lead to the enhancement the absorption band intensity accompanied blue shifting to the lower wavelength of electromagnetic radiation. This is due to the robust SPR transitions and the interband transitions of the NPs. Furthermore, the characteristic features and full width half maximum (FWHM) of the size, size distribution and spherical shape of NPs that obtained in the glycol solution is verified the influence of PLAE on the NPs transformation [19,20]. In the case of mixture of Au and Ag NPs, prior to laser irradiation in the Figure 1 (c), two isolated SPR peaks, corresponding to Au and Ag NPs were detected which implies the absence of formation of alloy NPs.

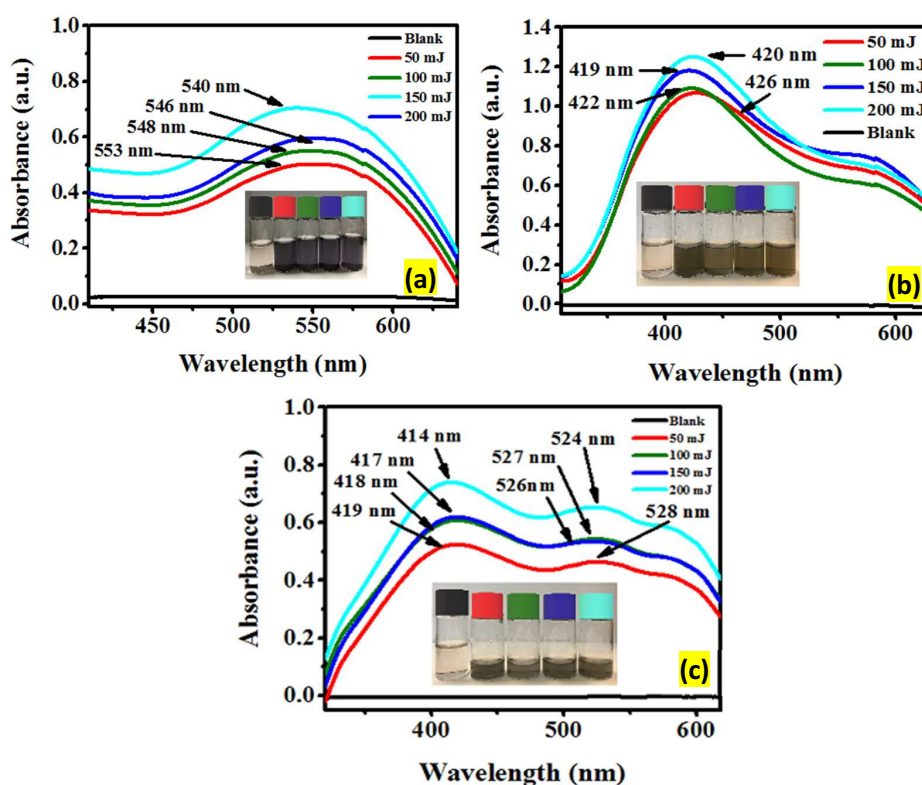
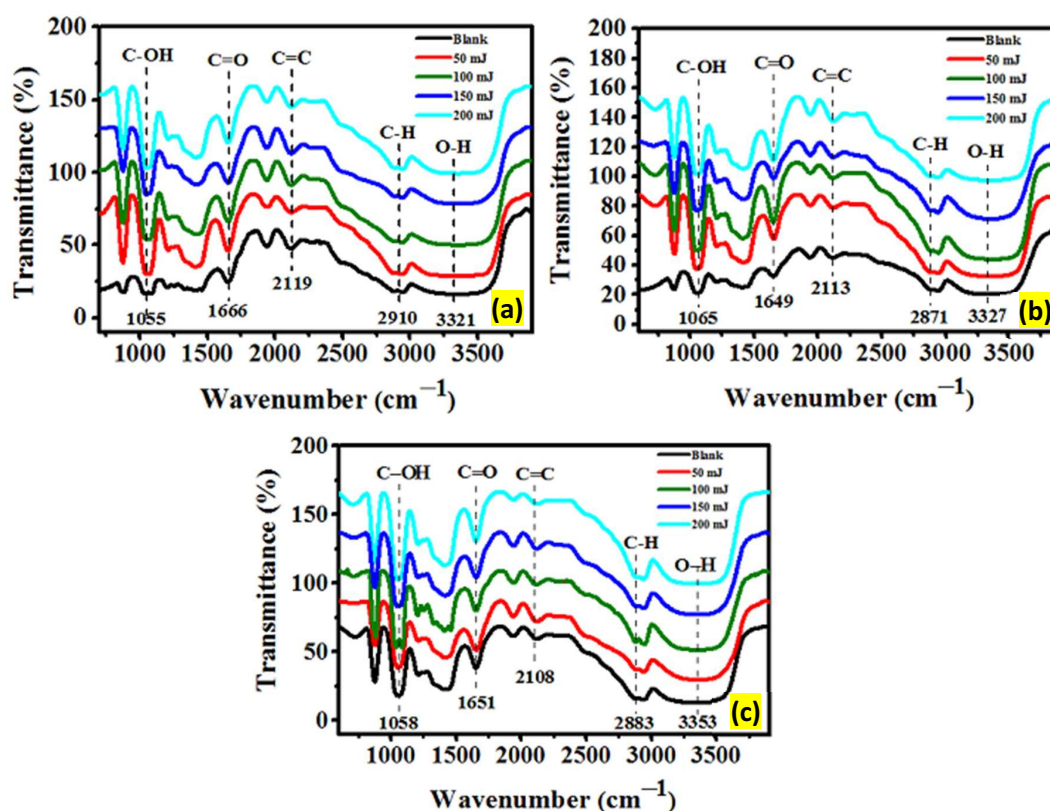


Figure 1: UV-Vis absorption spectra of as-synthesized NPs with color variation (Insets): (a) AuNPs, (b) AgNPs and (c) Au-Ag nanocolloids

Figure 2 (a-c) manifests the FTIR spectra of as-prepared AuNPs, AgNPs and Au-Ag nanocolloids in glycol liquid media. Varied functional groups of chemical bonding have been revealed and tabulated in Table 1. The detected vibration stretching groups and increased in the absorption bands accompanied different a shifting to high wavelength (low frequency) were verifying the molecules and NPs formation, all were depended PLAE. The FTIR absorption bands in the Figure 2 (a-c) located near to 3300 cm^{-1} can be assigned to the hydroxyl groups (OH) of alcohol and phenols. The bands at 2900 cm^{-1} can be accredited to carbon hydroxyl (CH) stretching of alkanes. The dominant peaks at nearly 2000 cm^{-1} , 1600 cm^{-1} and 1000 cm^{-1} can be assigned to C=C stretching of alkanes, C=O stretching vibration of alkenes and C–OH secondary alcohols, respectively [21-23]. It may be concluded from the FTIR spectroscopic study that the secondary structure of Au-Ag nanocolloids in the Figure 2 (c) are prospective candidate to catalysis applications.

Table 1. FTIR band assignments of as-prepared AuNPs, AgNPs and Au-Ag nanocolloids in glycol liquid media.

| Band Assignments | Wavenumber (cm^{-1}) | | | Vibration Modes |
|----------------------------------|---------------------------------|-----------|-----------|--------------------|
| | AuNPs | AgNPs | Au-Ag NPs | |
| O-H stretch | 3321 | 3372 | 3353 | Alcohols, phenols |
| C-H stretch | 2910 | 2871-2928 | 2883 | Alkanes |
| $\text{C}\equiv\text{C}$ stretch | 2119 | 2113 | 2108 | Alkanes |
| C=O stretching | 1666 | 1649 | 1651 | Alkenes |
| C-OH stretching | 1055 | 1065 | 1058 | secondary alcohols |

**Figure 2:** FTIR spectra of with/without NPs prepared inside glycol liquid media: (a) AuNPs, (b) AgNPs and (c) Au-Ag nanocolloids

4. Conclusions

For the first time, current study prepared the AuNPs, AgNPs and Au-Ag nanocolloids inside glycol liquid media by nanosecond pulse laser ablation in liquid (NPLAL) technique. Different spectroscopy analytical equipment was applied for the characterization of synthesized NPs such as UV-Vis and FTIR analysis. The influence of varied PLA on the optical properties, morphology, size and bonding structure of the synthesized NPs were obtained. Herein, by varying the PLAE, it is possible to control the NPs growth quantity, morphology and structure in a desired way which is useful for medicinal applications. The absorption bands of AuNPs, AgNPs and Au-Ag nanocolloids were observed in the range (540-553 nm), (419-426 nm) and ((524-528) and (414-419) nm). FTIR spectra exhibited the presence of various functional groups of the active component and the bonding structures of the AuNPs, AgNPs and Au-Ag nanocolloids. The remarkable traits of outcomes imply that Au-Ag nanocolloids with excellent optical properties that is grown in the glycol medium are potential candidate for biphotonic and biomedical development.

Acknowledgments

Authors are thankful to Malaysian Ministry of Education and RMC-Universiti Teknologi Malaysia for the financial assistance through Vote no. TDR 06G34, PDRU 04E86 and FRGS 5F050 (GUP/RU).

References

- [1] Wu, T. Duan, X. Hu, C. Wu, C. Chen, X. Huang, J. and Cui, S. (2019). *Artificial cells, nanomedicine, and biotechnology*, **47**(1), 512-523.
- [2] Salim, A. A. Bakhtiar, H. Bidin, N. and Ghoshal, S. K. (2018). *Materials Letters*, **232**, 183-186.
- [3] Nikov, R. G. Nedyalkov, N. N. Nikov, R. G. and Karashanova, D. B. (2018). *Applied Physics A*, **124**(12), 847.
- [4] Byram, C., & Soma, V. R. (2017). *Nano-Structures & Nano-Objects*, **12**, 121-129.
- [5] Salim, A. A., & Bidin, N. (2017). *Journal of Molecular Structure*, **1149**, 694-700.
- [6] Chang, C. H., Lin, R. J., Tien, C. L., & Yeh, S. M. (2018). *Advances in Condensed Matter Physics*.
- [7] Alluhaybi, H. A., Ghoshal, S. K., Shamsuri, W. W., Alsobhi, B. O., Salim, A. A., & Krishnan, G. (2019). *Nanostructures & Nano-Objects*, **19**, 100355.
- [8] Mousavi, S. M., Hashemi, S. A., Ghasemi, Y., Atapour, A., Amani, A. M., Savar Dashtaki, A., and Arjmand, O. (2018). *Artificial cells, nanomedicine, and biotechnology*, **46**(sup3), S855-S872.
- [9] Alluhaybi, H. A., Ghoshal, S. K., Shamsuri, W. W., Alsobhi, B. O., Salim, A. A., and Krishnan, G. (2019). *Nano-Structures & Nano-Objects*, **19**, 100355.
- [10] Robbins, P. D., and Morelli, A. E. (2014). *Nature Reviews Immunology*, **14**(3), 195.
- [11] Kanmani, P., & Rhim, J. W. (2014). *Food Hydrocolloids*, **35**, 644-652.
- [12] Ramasamy, M., Lee, J. H., & Lee, J. (2017). *International journal of nanomedicine*, **12**, 2813.
- [13] Chatterjee, T., Chatterjee, B. K., Saha, T., Hoque, K. M., & Chakrabarti, P. (2017). *Biochimica et Biophysica Acta (BBA)-General Subjects*, **1861**(5), 977-986.
- [14] Mafuné, F., Kohno, J. Y., Takeda, Y., Kondow, T., & Sawabe, H. (2001). *The Journal of Physical Chemistry B*, **105**(22), 5114-5120.
- [15] Agnihotri, S., Mukherji, S., & Mukherji, S. (2014). *Rsc Advances*, **4**(8), 3974-3983.
- [16] Salim, A. A., Bidin, N., Lafi, A. S., & Huyop, F. Z. (2017). *Materials & Design*, **132**, 486-495.
- [17] Byram, C., & Soma, V. R. (2017). *Nano-Structures & Nano-Objects*, **12**, 121-129.
- [20] B. Balamurugan, B., & Maruyama, T. (2005). *Applied Physics Letters*, **87**(14), 143105.
- [21] Salim, A. A., Bidin, N., & Ghoshal, S. K. (2018). *LWT*, **90**, 346-353
- [22] Abdelghany, A. M., Mekhail, M. S., Abdelrazek, E. M., & Aboud, M. M. (2015). *Journal of Alloys and Compounds*, **646**, 326-332.
- [23] Salim, A. A., Bidin, N., Ghoshal, S. K., Islam, S., & Bakhtiar, H. (2018). *Materials Letters*, **217**, 267-270.