

# **Picosecond laser fabricated Ag, Au and Ag-Au nanoparticles for detecting ammonium perchlorate using a portable Raman spectrometer**

Chandu Byram, Sree Sathya Bharathi Moram, and Venugopal Rao Soma

Citation: *AIP Conference Proceedings* **1942**, 050028 (2018); doi: 10.1063/1.5028659

View online: <https://doi.org/10.1063/1.5028659>

View Table of Contents: <http://aip.scitation.org/toc/apc/1942/1>

Published by the [American Institute of Physics](#)

---

---

# Picosecond Laser Fabricated Ag, Au and Ag-Au Nanoparticles for Detecting Ammonium Perchlorate Using a Portable Raman Spectrometer

Chandu Byram<sup>1</sup>, Sree Sathya Bharathi Moram<sup>1</sup>, and Venugopal Rao Soma<sup>1, a</sup>

<sup>1</sup>*Advanced Centre for Research in High Energy Materials (ACRHEM),  
University of Hyderabad, Prof. C. R. Rao Road, Hyderabad 500046, Telangana, India*  
<sup>a</sup> *Corresponding author: soma\_venu@uohyd.ac.in*

**Abstract.** In this paper, we present the results from fabrication studies of Ag, Au, and Ag-Au alloy nanoparticles (NPs) using picosecond laser ablation technique in the presence of liquid media. The alloy formation in the NPs was confirmed from UV-Visible measurements. The shape and crystallinity of NPs were investigated by using high resolution transmission electron microscopy (HRTEM), selected area diffraction pattern (SAED) and energy dispersive spectroscopy (EDS). The SERS effect of fabricated NPs was tested with methylene blue and an explosive molecule (ammonium perchlorate) using a portable Raman spectrometer and achieved EFs of  $\sim 10^6$ .

## INTRODUCTION

Fabrication of nanoparticles (NPs) and nanostructures (NSs) using laser ablation in liquid technique (LAL) is an effectual and simple tool because it provides pure and stable colloidal NPs devoid of any chemical precursors and/or chemical reagents making it an environmental friendly and green technique.<sup>1-4</sup> In LAL technique, pure, alloy, metal composite NPs/NSs with different shapes can be achieved by tuning the laser parameters.<sup>5,6</sup> Briefly, when an intense laser beam interacts with the target material immersed in liquid media, it generates high pressured plasma containing ionized species of ablated material. The plasma condenses, and nanoparticles were produced by nucleation and growth process.<sup>5</sup> The formed NPs were suspended in liquid as colloids. LAL fabricated NPs/NSs are successfully utilized in surface enhanced Raman spectroscopy (SERS) studies of various analyte molecules including explosives.<sup>7-9</sup> SERS is a powerful analytical tool to identify trace-level molecules due to its fingerprint nature and supported by sensitivity. In SERS technique, the Raman signal is enhanced enormously when the molecule is close to a rough (few tens of nm) metal NPs/NSs. The observed enhancement in SERS can be attributed to the higher electromagnetic field generated by the collective oscillations of surface plasmons on the metal surface as well as charge transfer between the molecule and the metal surface.<sup>10</sup> During the last two decades, metal NPs (Ag, Au, and Cu) have been widely tested as SERS substrates for identification of various analyte molecules due to their superior plasmonic nature in the visible range. Though Ag NPs demonstrate exceptional plasmonic response compared to the Au NPs (inferior plasmonic response compared to Ag), they lack stability and, therefore, many researchers focused on the synthesis of Ag-Au NPs to achieve a balance between the plasmonic efficiency and chemical stability.<sup>11-14</sup> In this study, we present our studies on ammonium perchlorate and methylene blue detection by using Ag, Au, and Ag-Au alloy NPs fabricated by picosecond ablation of bulk target immersed in liquid media

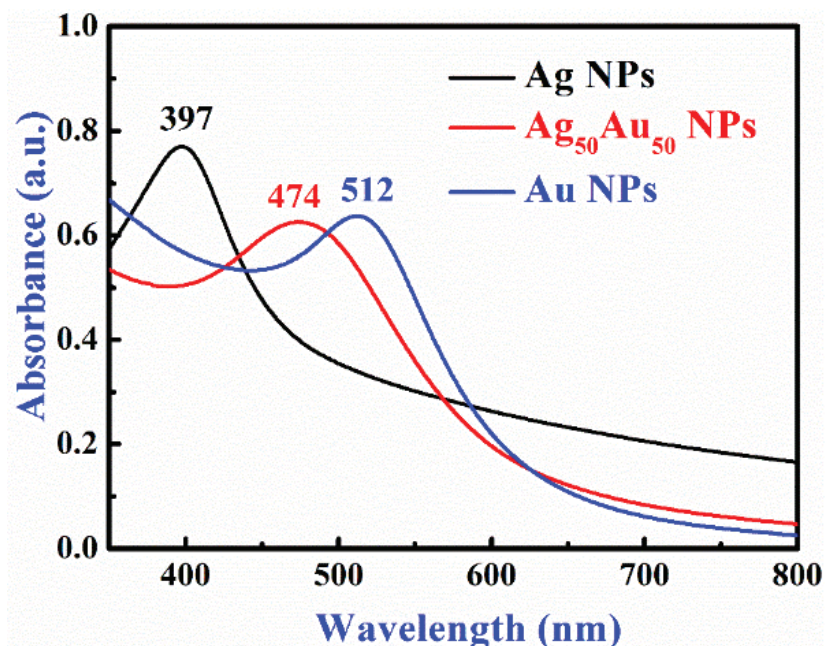
## EXPERIMENTAL DETAILS

NPs were prepared via laser ablation in liquids using a picosecond (ps) laser (EXSPLA PL-2250) delivering  $\sim 30$  ps pulses with a repetition rate of 10 Hz at a wavelength of 532 nm. For a generation of colloidal solutions, we have used silver (Ag), gold (Au), and silver-gold alloy (Au<sub>50</sub>Ag<sub>50</sub>) targets (thickness of  $\sim 1$  mm) which were immersed in

NaCl (5 mM dissolved in distilled water) solution placed in a bottom of the glass cell. The laser beam with an input diameter of ~12 mm was focused with the 100 mm focal length of convex lens normally on to the target surface dipped in NaCl solution. The liquid layer height above the target surface was ~6 mm and quantity of liquid used as 5 ml in each case. The experiments were carried out at the pulse energy of ~15 mJ and the time of ablation was ~30 minutes. The use of NaCl is to promote aggregation among the generation NPs, which is helpful in enhancing the signal in SERS studies. After a particular time, the colour of the liquid changed and this confirmed the formation of NPs in colloidal solution. The prepared colloidal solution was collected and stored in an air tightened bottles to prevent oxidation from the surrounding atmosphere. Further, the colloidal solutions were characterized by UV-Visible absorption spectroscopy, transmission electron microscopy (TEM), selected area diffraction pattern (SAED) and energy dispersive spectroscopy (EDS). The prepared NPs were utilized for detection of an explosive molecule (ammonium perchlorate), and dye (methylene blue) using portable Raman spectrometer (B&W Tek, USA) operated at a wavelength of 785 nm.

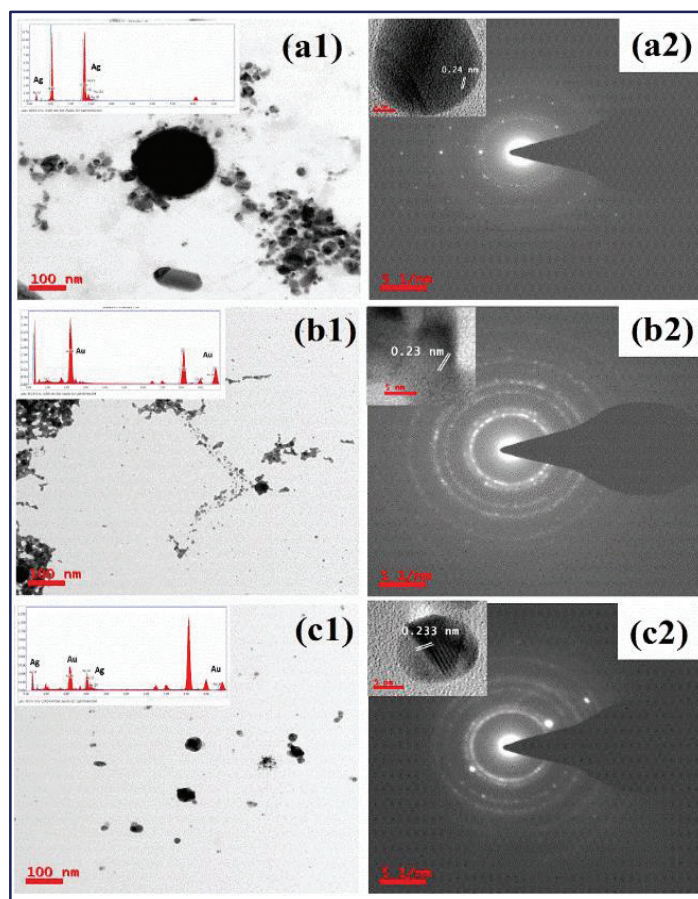
## RESULTS AND DISCUSSIONS

Figure 1 shows the absorption spectra of Ag, Au and Ag<sub>50</sub>Au<sub>50</sub> NPs obtained in NaCl solution. From the presented data it is evident that the surface plasmon peaks were observed at 397 nm, 512 nm for pure Ag and Au NPs. In case of alloy (Ag<sub>50</sub>Au<sub>50</sub>) NPs, the single plasmon peak (~474 nm) was observed within the range of pure individual metallic NPs (Ag and Au), which clearly demonstrated the formation of alloy/bimetallic NPs without any core shell structure. The plasmon peak position of alloy NPs mainly depends on the weight proportions of Ag/Au and always lies between the individual metals NPs peaks.<sup>11,13</sup>



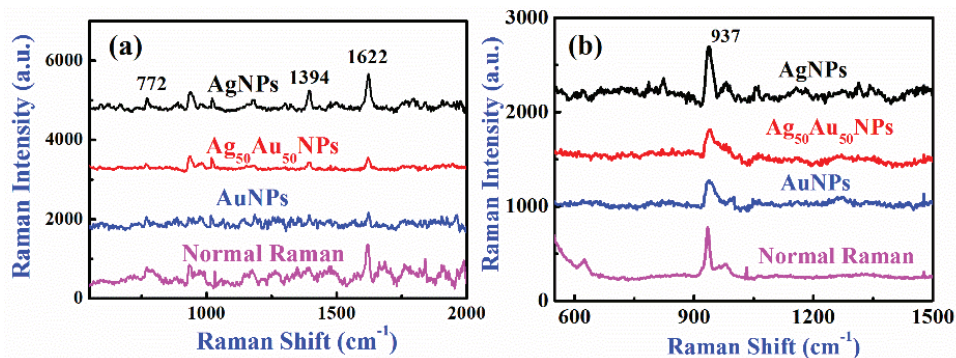
**FIGURE 1.** UV-Visible spectra of Ag (black one), Au (blue one), and Ag<sub>50</sub>Au<sub>50</sub> alloy (red one) NPs

Figure 2 presents the TEM images, their corresponding SAED patterns while the insets show their HRTEM and EDS images of Ag NPs [figure 2 (a1 and a2)], Au [figure 2 (b1 and b2)], and Ag<sub>50</sub>Au<sub>50</sub> [figure 2 (c1 and c2)] respectively. Inset of figure 2(a2) depicts the lattice image of Ag NPs with interplanar separation of 0.24 nm corresponding the first ring of Miller indices (111). Figure 2(b2) depicts the Au NPs SAED pattern and insets show the high-resolution image with a lattice spacing of 0.23 nm. Inset of figure 2(c1) presents the EDS spectra of Ag<sub>50</sub>Au<sub>50</sub> NPs which demonstrated the presence of the both elements (Ag and Au) with an observed inter planar spacing of 0.233 nm [Insets of figure 2 (c2)]. The observed lattice spacing for Ag<sub>50</sub>Au<sub>50</sub> NPs is closer to the Ag and Au NPs due to their similar lattice constants ( $a_{Au} = 4.08\text{\AA}$ ,  $a_{Ag} = 4.09\text{\AA}$ ).<sup>15,16</sup>



**FIGURE 2.** TEM images of NPs insets show their EDS and HRTEM images (a1 and a2) Ag and corresponding SAED pattern, (b1 and b2) Au NPs and corresponding SAED pattern, (c1 and c2) Ag<sub>50</sub>Au<sub>50</sub> NPs and corresponding SAED pattern, respectively.

Figure 3 (a) shows the SERS spectra of MB (50 nM) obtained on Ag (black), Au (blue) and Ag<sub>50</sub>Au<sub>50</sub> (red) NPs films (NPs were drop casted on a Si substrate). From the presented results it is observed that the major modes of MB were located at 772, 1394 and 1622 cm<sup>-1</sup> and are assigned to the in-plane bending of C-H, C-N symmetric stretching and C-C ring stretching respectively, which are consistent with the previous reports.<sup>9</sup> The normal spectra of MB (0.1 M) were recorded on a silicon substrate (spectra presented in pink color of figure 3 (a)).



**FIGURE 3.** SERS spectra of (a) MB (50 nM) (b) AP (10 μM) recorded from Ag (black one), Ag<sub>50</sub> Au<sub>50</sub> (red one), Au NPs (blue one), and normal spectra of MB (0.1 M), AP (0.1 M) recorded on silicon (pink one) substrate respectively.

The enhancement factors (EFs) were estimated by choosing the 1621 cm<sup>-1</sup> mode of MB observed the NPs films with the normal Raman spectra (same mode) obtained from Si substrate by using the following formula (1).<sup>17</sup>

$$EF = \frac{I_{SERS} C_{HC}}{I_{RAMAN} C_{LC}} \quad (1)$$

Where  $I_{SERS}$  and  $I_{RAMAN}$  are the intensities of is highly elevated Raman band of analyte molecule from the NP film and silicon substrate.  $C_{HC}$ ,  $C_{LC}$  is higher and lower concentrations of analyte molecule generating the Raman signals. The estimated EFs are  $1.38 \times 10^6$ ,  $7.48 \times 10^5$ , and  $5.8 \times 10^5$  for Ag, Au and  $Ag_{50}Au_{50}$  NPs, respectively. The SERS studies also performed for ammonium perchlorate (AP) by utilizing these NPs. SERS spectra of ammonium perchlorate (10  $\mu$ M) acquired from Ag, Au and  $Ag_{50}Au_{50}$  NP films are depicted in figure 3(b). The predominant mode of AP was observed at 937  $cm^{-1}$ , corresponding to the symmetric stretching vibration.<sup>18</sup> The calculated EFs are  $1.1 \times 10^4$ ,  $5.3 \times 10^3$ , and  $7.5 \times 10^3$  for Ag, Au, and  $Ag_{50}Au_{50}$  NP films, respectively. In the detection of both analytes, Ag NPs provided the superior enhancement factors compared to the other NPs and this could be attributed to the selective support of analyte molecule to the particular NPs surface. Further aggregation also plays an important role and effects the SERS signals, which is evident from the TEM images. In the earlier report, a similar type of result was demonstrated for Ag NPs compared to alloy NPs fabricated through the LAL technique but they achieved the detection of MB up to  $10^{-10}$  M when the NPs were fabricated in diluted solutions of MB. In the present study, we detected up to  $10^{-8}$  M when MB drop casted over the NP films and, furthermore, demonstrated the detection of an explosive molecule ( $\sim 10^{-6}$  M) using portable Raman spectrometer.

## CONCLUSION

Pure Ag, Au, and  $Ag_{50}Au_{50}$  alloy NPs were fabricated using picosecond ablation by immersing bulk target in NaCl solution. TEM and SAED patterns revealed the crystallinity of NPs, whereas alloy formation of  $Ag_{50}Au_{50}$  NPs was confirmed from the position of the plasmon peak in the absorption spectra. The SERS effect of these NPs was tested with MB and explosive molecule (ammonium perchlorate) and achieved the EFs of  $\sim 10^6$  and  $\sim 10^4$ , respectively.

## ACKNOWLEDGEMENTS.

We acknowledge DRDO for financial support.

## REFERENCES

1. V. Amendola and M. Meneghetti, *Phys. Chem. Chem. Phys.* **11** (20), 3805 (2009).
2. G. K. Podagatlapalli, S. Hamad, S. P. Tewari, S. Sreedhar, M. D. Prasad, and S. Venugopal Rao, *J. Appl. Phys.* **113** (7), 073106 (2013).
3. G. K. Podagatlapalli, S. Hamad, M. A. Mohiddon, S. Venugopal Rao, *Appl. Surf. Sci.* **303**, 217 (2014).
4. S. Hamad, G. K. Podagatlapalli, M. A. Mohiddon, V. R. Soma, *Appl. Phys. Lett.* **104** (26), 263104 (2014).
5. D. Zhang, B. Gökce, and S. Barcikowski, *Chemical Reviews* **117** (5), 3990 (2017).
6. B. Tangeysh, K. M. Tibbetts, J. H. Odhner, B. B. Wayland, and R. J. Levis, *Langmuir* **33** (1), 243 (2017).
7. F. Bertorelle, M. Ceccarello, M. Pinto, G. Fracasso, D. Badocco, V. Amendola, P. Pastore, M. Colombatti, and M. Meneghetti, *J. Phys. Chem. C* **118** (26), 14534 (2014).
8. S. Venugopal Rao, G. K. Podagatlapalli, and S. Hamad, *J. Nanosci. Nanotechnol.* **14** (2), 1364 (2014).
9. C. Byram, S. S. B. Moram, A. K. Shaik, and V. R. Soma, *Chem. Phys. Lett.* **685**, 103 (2017).
10. M. Moskovits, *Journal of Raman Spectroscopy* **36** (6-7), 485 (2005).
11. I. Lee, S. W. Han, and K. Kim, *Chem. Commun.* (18), 1782 (2001).
12. I. Srnová-Šloufová, B. Vlčková, Z. Bastl, and T. L. Hasslett, *Langmuir* **20** (8), 3407 (2004).
13. G. C. Papavassiliou, *Journal of Physics F: Metal Physics* **6** (4), L103 (1976).
14. G. K. Podagatlapalli, S. Hamad, and S. Venugopal Rao, *J. Phys. Chem. C* **119** (29), 16972 (2015).
15. M. Vinod and K. Gopchandran, *Prog. Nat. Sci.* **24** (6), 569 (2014).
16. R. Intartaglia, G. Das, K. Bagga, A. Gopalakrishnan, A. Genovese, M. Povia, E. Di Fabrizio, R. Cingolani, A. Diaspro, and F. Brandi, *Phys. Chem. Chem. Phys.* **15** (9), 3075 (2013).
17. E. Le Ru, E. Blackie, M. Meyer, and P. G. Etchegoin, *J. Phys. Chem. C* **111** (37), 13794 (2007).
18. C. Ruan, W. Wang, and B. Gu, *Analytica Chimica Acta* **567** (1), 114 (2006).