

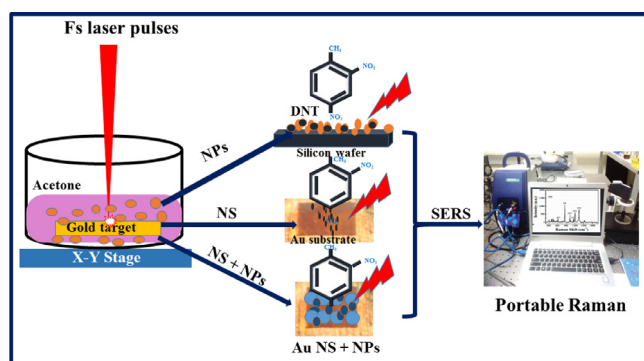
2,4-dinitrotoluene detected using portable Raman spectrometer and femtosecond laser fabricated Au–Ag nanoparticles and nanostructures



Chandu Byram, Venugopal Rao Soma*

Advanced Centre for Research in High Energy Materials (ACRHEM), University of Hyderabad, Prof. C.R. Rao Road, Hyderabad 500046, India

GRAPHICAL ABSTRACT



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ABSTRACT

We report results from our studies on the fabrication of bimetallic nanoparticles (NPs) and nanostructures (NSs) using femtosecond (~ 50 fs) laser ablation technique. The NPs and NSs were achieved by immersing bulk targets with different Au–Ag compositions in acetone followed by ablation. We demonstrate their application towards detection of an explosive molecule of 2, 4-Dinitrotoluene, DNT ($25 \mu\text{M}$) using a portable Raman spectrometer (785 nm). A tuneable surface plasmon peak observed in the UV-Visible absorption spectra with varying Au proportions confirmed the formation of bimetallic NPs. The size, shape and crystallographic phases were investigated by transmission electron microscope (TEM) and selected area diffraction pattern (SAED). The surface morphology of fabricated NSs was characterized using field emission scanning electron microscope (FESEM). Both NPs and NSs were employed as Surface Enhanced Raman Scattering (SERS) substrates for sensing Methylene Blue (MB) and DNT. From the results obtained in this investigation we concluded that $\text{Au}_{70}\text{Ag}_{30}$ NPs/NSs exhibited superior SERS performance compared to pure Ag, Au and other compositions. A detection limit of $\sim 10^{-9}$ M for MB and $\sim 10^{-6}$ M for DNT was achieved with corresponding enhancement factors of $\sim 10^7$ and $\sim 10^4$. Furthermore, we have also observed a 'factor of 3' increase in the SERS intensity by simply drop casting Ag NPs on the gaps of $\text{Au}_{70}\text{Ag}_{30}$ NSs. This clearly demonstrates that individual NPs, NSs and NPs on NSs (hybrid SERS targets) can be achieved in a single experiment and in combination provide efficient means of detecting trace quantities of explosive molecules.

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* Corresponding author.

E-mail address: soma_venu@uohyd.ac.in (V.R. Soma).

1. Introduction

During the last decade Surface Enhanced Raman Scattering (SERS) technique has proven to be an efficient analytical tool for recognition of various analyte molecules, owing to its finger print nature, sensitivity and selectivity. SERS has bounteous applications in the fields of explosive detection [1–4], chemical detection [5] and bio-sensing [6,7] etc. Over the last couple of decades, noble metal nanoparticles (NPs)/nanostructures (NSs) with diverse shapes or sizes have been exploited efficaciously as SERS substrates for sensing of variety of molecules due to their strong optical properties in the visible spectral region [7–9]. Gold (Au) and silver (Ag) are widely used as SERS substrates for detection of various molecules. The stability of Ag NPs is inferior compared to Au NPs but Ag NPs provide superior SERS enchantments due to their surface plasmon peaks and near field inter-particle coupling effects. However, Ag NPs are prone to oxidation effects reducing their efficacy. Au NPs are not susceptible to oxidation and, therefore, an approach of combining Ag and Au metals was realized to conglomerate the advantages of Ag with enhanced optical properties and Au with stable chemical properties. The alloy formation of Ag and Au is a viable process with less surface segregation due to similarities between the lattice parameters ($a_{\text{Au}} = 4.08 \text{ \AA}$, $a_{\text{Ag}} = 4.09 \text{ \AA}$). To fabricate Ag–Au bimetallic NPs, a variety of methods have been proposed during the past years such as co-reduction of metal salts [10] galvanic replacement method [11] and evaporation of bulk alloys [12], which exhibit superior optical [13] and catalytic [14,15] properties compared to monometallic NPs. Xu et al. demonstrated the enhancement in the efficiency of a solar cell by tuning the molar ratio in the composition of Ag–Au alloy NPs when compared to individual NPs [16]. More recently, Chaffin et al [17], demonstrated theoretically, the electromagnetic enhancements of Ag–Au alloy NPs by considering the Mie theory and the discrete dipole approximation [17]. Many of the chemical methods are sometimes time-consuming, offers lower purity of NPs (presence of surfactants and other toxic chemicals) and needs sophisticated instruments.

Compared to the aforesaid methods, ultrafast laser ablation in liquids (ULAL) is a simple and green technique for simultaneous fabrication of NPs and NSs in a single exposure [18–22]. ULAL offers pure and stable NPs without a necessity of reducing agents or chemicals. In ULAL, a high energy laser pulse interacting with target material immersed in liquid media penetrates the target surface up to a certain depth (nm) followed by the ejection of electrons because of high electric field offered by the laser source. The ejected electrons then oscillate along with the electromagnetic field and collide with atoms of bulk material transferring some of the energy to surrounding lattice. The ablated surface of target heats up suddenly and vaporizes, leading to a plasma formation on a target surface (at the focal point). The generated plasma plume contains atoms, clusters, electrons, ions, etc. The generated plasma plume expands continuously with a creation of shockwave below and above the target surface. As the time progresses, plasma plume cools down and produces cavitation bubble. The cavitation bubble expands up to a maximum radius and then it collapses followed by the generation of NPs [18,20,23]. In one of the earlier studies, Lee et al. demonstrated fabrication of Ag–Au alloy NPs by ablating bulk alloy target in water and they observed a redshift in the plasmon peak with increasing Au proportion [24]. Oscar et al. also synthesized Ag–Au alloy NPs through LAL technique and utilized these NPs for sensing of methylene blue (MB) [25]. Besides these works several composite materials combined with noble metals such as Au–Fe, Ag–graphene etc. were fabricated and utilized for SERS studies [26–31].

In this study, we report results from our efforts on the fabrication of bimetallic nanoparticles (NPs) and nanostructures (NSs)

using femtosecond (fs) pulses by ablating the immersed bulk Au–Ag targets in acetone with different Ag/Au compositions. The size, shape and crystallographic phases of the obtained NPs were investigated using TEM and SAED techniques. The surface morphology of the NSs was characterized using FESEM data. The fabricated Ag–Au NPs and NSs were subsequently tested as SERS substrates for sensing a common dye (methylene blue MB, 5 nM) and an explosive molecule (2, 4-dinitrotoluene DNT, 25 μM) using a portable Raman spectrometer (B&W Tek, USA). The goal of our efforts is to achieve uniform enhancement factors for all the common explosive molecules from the in-house prepared SERS targets combined with simple detection methodology of using a portable Raman spectrometer.

2. Experimental details

Bulk Au–Ag targets were prepared by mixing the gold and silver with different weight percentages (Ag, Au₂₀Ag₈₀, Au₃₀Ag₇₀, Au₅₀Ag₅₀, Au₇₀Ag₃₀, and Au₈₀Ag₂₀, Au). After the preparation, the samples were cleaned thoroughly and cut into small pieces of 1 cm \times 1 cm dimensions. The complete experimental procedure was reported in our earlier reports [3,19,32]. Briefly, ablation experiments were performed with a femtosecond amplifier (Ti:sapphire, LIBRA) delivering \sim 50 fs pulses with a repetition rate of 1 kHz and at a wavelength of 800 nm. The laser beam pulse energy (\sim 500 μJ) was focused normally onto the Au–Ag (bulk) target immersed in acetone using a convex lens of 100 mm focal length. The liquid layer height was \sim 10 mm above the target surface. The focal point was adjusted by listening to the cracking sound and the plasma formation at the target surface. During the ablation, an X–Y (ESP 300, Newport, USA) motorized stage was utilized to draw the periodic lines on the substrate with a line spacing of 100 μm and the scanning speeds of 500 $\mu\text{m/s}$ along both directions (X and Y direction). The ablation time was typically 10 min and each line length was \sim 5 mm on the target surface. All the ablation experiments were performed under same conditions such as liquid layer thickness, stage parameters, pulse energy, and time of exposure. Post ablation the colloids were collected and preserved in glass bottles and utilized for characterization and SERS studies. The absorption spectra of colloids were recorded with UV-Visible (PerkinElmer Lambda 750) spectrometer. The shape, size, and crystallinity of the nanoparticles (NPs) were investigated using high-resolution transmission electron microscope (HRTEM, FEI Tecnai G2 S-Twin) and selected area diffraction (SAED) by dropping the tiny drop of colloidal solution on carbon coated copper grid then dried at room temperature. Surface morphology of nanostructures (NSs) was characterized by field emission scanning electron microscope (FESEM, Carl Zeiss). The probe molecules of DNT (dissolved in acetone) and MB (dissolved in methanol) were prepared in stock solution ($1 \times 10^{-1} \text{ M}$) and diluted successively to attain the different lower concentrations of (10^{-9} to 10^{-4} M). For the Raman measurements initially nanoparticles (NPs) were dropped on a Silicon substrate and dried. Later 2,4-dinitrotoluene (DNT) (25 μM) solution was dropped on NP/NS surface followed by the acquisition of the Raman spectra using portable Raman spectrometer (B&W Tek, USA) with a laser operating at 785 nm wavelength and using an integration time of 5 s.

3. Results and discussions

3.1. UV-visible spectra and characterization

Fig. 1 depicts the normalized UV-visible absorption spectra of Au–Ag colloids obtained in acetone. The surface (SPR) plasmons peaks of obtained Au–Ag NPs were located at 432, 437, 459, 492 and 501 nm for Au₂₀Ag₈₀, Au₃₀Ag₇₀, Au₅₀Ag₅₀, Au₇₀Ag₃₀,

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