Ag Nanoparticles Coupled with Ag Nanostructures as Efficient SERS Platform for Detection of 2, 4-Dinitrotoluene

B. Chandu, M.S.S. Bharati, S. Venugopal Rao[#]

*Advanced Centre of Research in High Energy Materials (**ACRHEM**),*
University of Hyderabad, Hyderabad 500046, Telangana, India
Corresponding author e-mail: **soma_venu@uohyd.ac.in**

Abstract—**Ag nanoparticles (NPs) and nanostructures (NSs) were fabricated in single step using femtosecond laser ablation in liquids technique. A significant increment of one order in the SERS intensity was achieved by depositing the Ag NPs in the gaps of Ag NSs compared to that obtained with individual Ag NPs/NS.**

Keywords: **Laser ablation, Femtosecond, nanoparticles, SERS, DNT**

I. INTRODUCTION

Surface enhanced Raman scattering (SERS) as a promising analytical tool to obtain molecular signatures from hazardous chemical and/or biological molecules [1, 2]. The high sensitivity associated with the technique and finger print nature raises it potential in detection of explosives, chemical and biological molecules at trace levels. [2-5] Since it discovery in 1972 by Fleischmann et al. [6] numerous efforts have been devoted to fabricating robust and facile SERS substrates with high sensitivity, reproducibility, and low cost along with recyclable capability. In general, two fundamental mechanisms play a vital role in SERS phenomenon: electromagnetic (EM) and chemical enhancement effect. [7] The EM effect results from the high local electric field due to the excitation of surface plasmon resonance of roughened metallic surfaces while the chemical effect is due to the interaction between the adsorbed molecule and metal surface. In overall SERS enhancement, the EM effect contribution is several orders of magnitude more than the value of chemical effect.[7] Most of the SERS substrates can be fabricated using metallic nanoparticles/nanostructures with various shapes due to their tunable plasmonic nature from the visible to NIR spectral regime. A variety of methods has been reported to fabricate the conventional SERS substrates based on the deposition of metallic films on Si/glass substrates, [8] lithographic methods, [9] self-assembled nanoparticles [10] and electrochemically roughened metal surfaces. More recently, few reports have been demonstrated to achieve higher SERS enhancements with reproducibility by grafting NPs in the gaps of ordered NSs.[11-13] Kalachyova et al. reported the multi branched Au NPs coupled with Ag gratings provided superior SERS enchantments for the probe molecule of R6G with higher reproducibility.[14] However, these techniques involve multiple and complex steps in fabrication and are laborious.

A simple top down approach is ultrashort laser ablation of bulk target dipped in liquid media (ULAL), which was introduced to fabricate NPs and NSs simultaneously with diverse shapes.[3, 5, 15, 16] The achieved NPs through ULAL are highly pure, less toxic and does not require any chemical precursors.[16] Briefly, in ULAL process a high energy laser pulse interacts with target material immersed in liquid media, which penetrates through the target surface with certain penetration depth (nm) then ejection of electrons takes place because of high electric field offered by the laser source. The ejected electrons then oscillate along with the electromagnetic field and can collide with atoms of bulk material and transform some of the energy to surrounding lattice. The plasma plume expands followed by generation of shockwave. As the time progresses, plasma plume cools down and produces cavitation bubble. The cavitation bubble expands and collapses after certain time interval followed by generation of NPs through the nucleation and growth process.[16, 17]. In this report, NPs and NS were fabricated in a single experiment (and exposure) with the aid of ULAL technique. We have introduced the simple approach of depositing Ag NPs in the gaps of Ag NS to achieve higher SERS intensities, especially for detecting explosive molecules at the trave levels. The observed SERS enhancement was superior to that of the SERS enhancements due to individual Ag NPs /NS.

II. EXPERIMENTAL DETAILS

Ablation experiments were performed using a femtosecond (Ti: sapphire) laser system delivering ~50 fs pulses at a wavelength of 800 nm. The laser beam was focused with convex lens of 100 mm focal length normally on to the target surface submerged in acetone (placed in glass vessel). The height of the liquid layer above the target surface was typically 10 mm. The glass beaker was mounted on X-Y motorized stage and translated with scanning speeds 500 µm/s in both directions. The typical ablation time was ~10 minutes and the used pulse energies was 500 µJ. The extinction spectra were recorded for obtained colloids using UV-visible absorption spectrometer (PerkinElmer Lambda 750) in the wavelength range of 250-800 nm with 10 mm path length quartz cuvette. Morphological studies of prepared NPs were characterized by transmission electron microscopy (TEM) (FEI Tecnai G2 S-Twin) operated at 200 KV by placing Ag suspensions on a carbon coated copper

grid and letting it to be evaporate at room temperature. Surface morphology of the nanostructures was characterized by field emission scanning electron microscope (FESEM) (Ultra 55 from Carl ZEISS). Surface enhanced Raman studies (SERS) of 2, 4- dinitrotoluene were carried with portable Raman spectrometer (B&W Tek, USA) operated at a wavelength of 785 nm and acquisition time for each spectra is 5 s.

III. RESULTS AND DISCUSSIONS

Figure 1(a) depicts the TEM image of Ag NPs and inset shows their UV-visible spectra. The surface plasmon peak (SPR) was observed at 420 nm, which revelled the spherical nature of formed NPs. Figure 1 (b) presents the size distribution of Ag NPs with average size of ~15.1 nm, was estimated by considering more than 250 particles with diameters in the range of 5-60 nm.

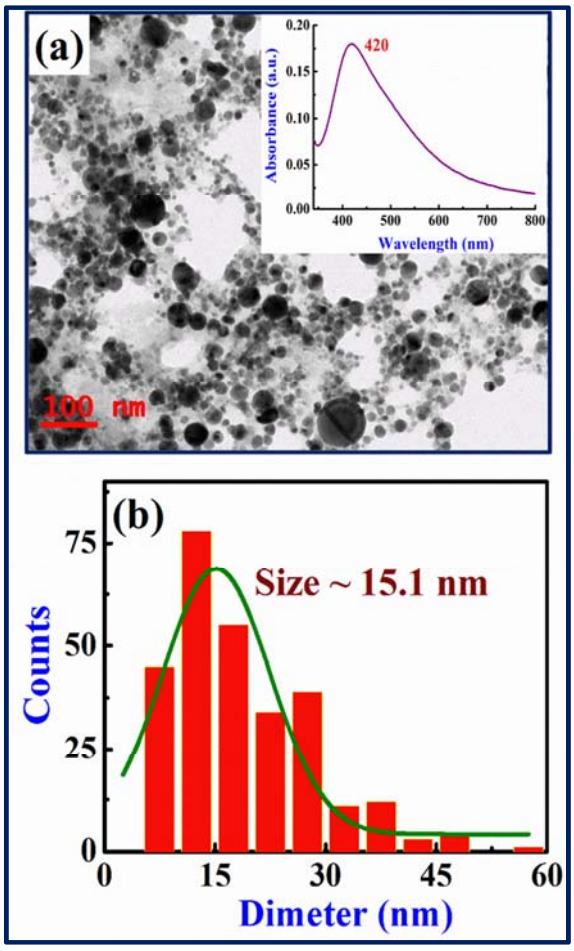

Figure 1 (a) TEM image of Ag NPs and inset shows the absorption spectra (b) size distribution of Ag NPs.

Figure 2 (a) illustrates the FESEM image of the femtosecond fabricated Ag NSs in acetone with pulse energy of 500 µJ. The surface topography of Ag NS shows the microgrooves with deepening cavities, which could be attributed to the effect of electron-phonon coupling when the metal was irradiated with femtosecond pulses.[18] The groves type morphology plays a vital role in enhancing the Raman signal when the analyte molecule is close to it.

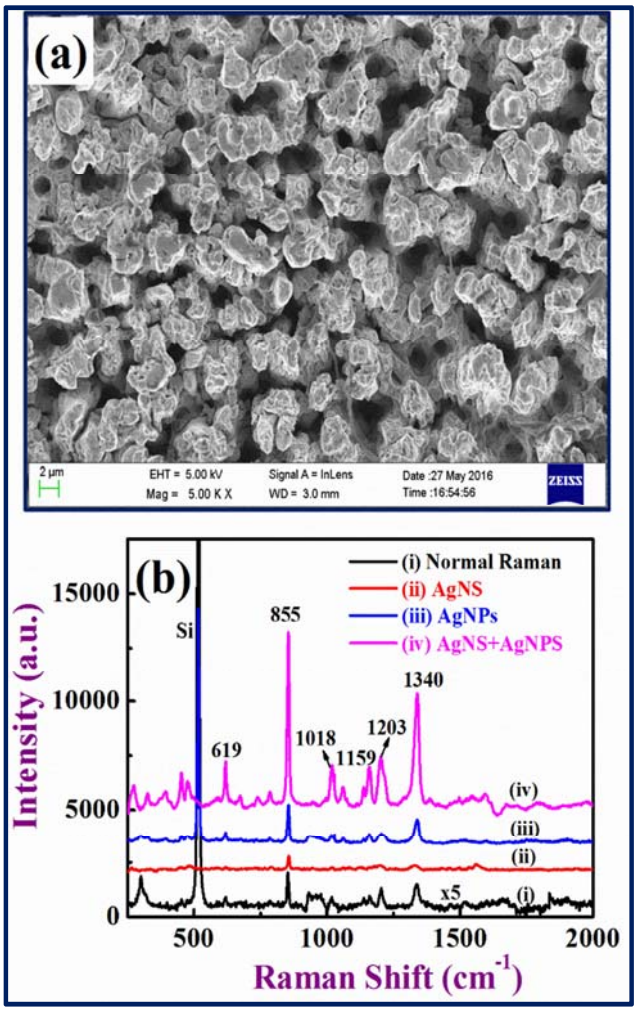

Figure 2(a) FESEM image of Ag NS (b) SERS spectra of DNT recorded on (i) silicon (ii) Ag NS (iii) Ag NPs (iv) AgNPs embedded on the AgNS (AgNS+AgNPs) using portable Raman spectrometer operated at 785 nm wavelength.

The SERS performance of fabricated Ag NPs and NS was tested with 2, 4- dinitrotolune (DNT). Before the SERS measurements, a tiny drop of DNT was deposited on top of the Ag NPs film/NS and dried. Figure 2 (b) indicates the SERS spectra of DNT (25 µM) acquired on (ii) Ag NS (iii) Ag NPs and (iv) Ag NPs were embedded on the Ag NS. The normal Raman spectra of DNT (0.1 M) were recorded on a Silicon surface [shown in figure 2(b), (i)]. The prominent modes of DNT were observed at 855, 1159, 1203 and 1340 cm^{-1}, which are attributed to the NO_2 out-of-plane mode, methyl H–C–H asymmetric bend, H–C–C in plane bending and NO_2 symmetric stretching, respectively.[13] When the DNT was deposited on Ag NPs film or Ag NS, only few modes were noticed with higher intensity. The estimated enhancement factors are 2.3×10^4, 8.1×10^3 for Ag NPs and Ag NS, respectively. From the data presented in figure 2 (b),

(iv), it is evident that a significant increase of the Raman intensity with distinguishable modes was observed for DNT, when the Ag NPs were grafted on the Ag NSs. It is also noted that the AgNS+AgNPs substrate provided at least one order of increment in the enhancement factor (EF of ~1×10^5) compared to the individual Ag NPs or NS substrates. The observed EFs could be associated with the effect of coupling between the nanoparticles localized on the nanostructured surface, which probably generated higher number of hotspots compared to individual NPs or NSs.[11, 13]. Further detailed studies are in progress to test this methodology for different molecules of interest. Further, the capability of this methodology will also be tested by repeatedly placing higher concentration of nanoparticles on the nanostructures.

IV. CONCLUSIONS

In a single step, both Ag NPs and NS were fabricated using ULAL technique. The SERS activity of Ag NPs, Ag NS, and Ag NPs grafted on Ag NS for the identification of 2, 4-dinitrotoluene was presented. With the simple approach of depositing Ag NPs on the gaps Ag NS, we achieved the one order increment in the Raman intensity for DNT molecule compared to the Ag NPs/NS substrates. The obtained enhancement factor for AgNPs+AgNS substrate is 1×10^5.

V. ACKNOWLEDGEMENTS

We acknowledge DRDO for financial support.

VI. REFERNECES

[1] C. Ruan, W. Wang, and B. Gu, "Detection of alkaline phosphatase using surface-enhanced Raman spectroscopy," *Analytical chemistry,* vol. 78, pp. 3379-3384, 2006.

[2] S. Lee, S. Kim, J. Choo, S. Y. Shin, Y. H. Lee, H. Y. Choi*, et al.*, "Biological imaging of HEK293 cells expressing PLCγ1 using surface-enhanced Raman microscopy," *Analytical chemistry,* vol. 79, pp. 916-922, 2007.

[3] G. K. Podagatlapalli, S. Hamad, and S. V. Rao, "Trace-level detection of secondary explosives using hybrid silver–gold nanoparticles and nanostructures achieved with femtosecond laser ablation," *The Journal of Physical Chemistry C,* vol. 119, pp. 16972-16983, 2015.

[4] S. Hamad, G. K. Podagatlapalli, M. A. Mohiddon, and V. R. Soma, "Cost effective nanostructured copper substrates prepared with ultrafast laser pulses for explosives detection using surface enhanced Raman scattering," *Applied Physics Letters,* vol. 104, p. 263104, 2014.

[5] C. Byram, S. S. B. Moram, A. K. Shaik, and V. R. Soma, "Versatile gold based SERS substrates fabricated by ultrafast laser ablation for sensing picric acid and ammonium nitrate," *Chemical Physics Letters,* vol. 685, pp. 103–107, 2017.

[6] M. Fleischmann, P. J. Hendra, and A. J. McQuillan, "Raman spectra of pyridine adsorbed at a silver electrode," *Chemical Physics Letters,* vol. 26, pp. 163-166, 1974.

[7] M. Moskovits, "Surface-enhanced spectroscopy," *Reviews of modern physics,* vol. 57, p. 783, 1985.

[8] S. Kubo, Z.-Z. Gu, D. A. Tryk, Y. Ohko, O. Sato, and A. Fujishima, "Metal-coated colloidal crystal film as surface-enhanced Raman scattering substrate," *Langmuir,* vol. 18, pp. 5043-5046, 2002.

[9] L. Lu, I. Randjelovic, R. Capek, N. Gaponik, J. Yang, H. Zhang*, et al.*, "Controlled fabrication of gold-coated 3D ordered colloidal crystal films and their application in surface-enhanced Raman spectroscopy," *Chemistry of materials,* vol. 17, pp. 5731-5736, 2005.

[10] H. Wang, C. S. Levin, and N. J. Halas, "Nanosphere arrays with controlled sub-10-nm gaps as surface-enhanced Raman spectroscopy substrates," *Journal of the American Chemical Society,* vol. 127, pp. 14992-14993, 2005.

[11] Z. M. Jin, W. Gu, X. B. Shi, Z. K. Wang, Z. Q. Jiang, and L. S. Liao, "A Novel Route to Surface‐Enhanced Raman Scattering: Ag Nanoparticles Embedded in the Nanogaps of a Ag Substrate," *Advanced Optical Materials,* vol. 2, pp. 588-596, 2014.

[12] H. Ko, S. Singamaneni, and V. V. Tsukruk, "Nanostructured surfaces and assemblies as SERS media," *Small,* vol. 4, pp. 1576-1599, 2008.

[13] H. Ko and V. V. Tsukruk, "Nanoparticle‐decorated nanocanals for surface‐enhanced raman scattering," *Small,* vol. 4, pp. 1980-1984, 2008.

[14] Y. Kalachyova, D. Mares, V. Jerabek, P. Ulbrich, L. Lapcak, V. Svorcik*, et al.*, "Ultrasensitive and reproducible SERS platform of coupled Ag grating with multibranched Au nanoparticles," *Physical Chemistry Chemical Physics,* vol. 19, pp. 14761-14769, 2017.

[15] S. Venugopal Rao, G. K. Podagatlapalli, and S. Hamad, "Ultrafast laser ablation in liquids for nanomaterials and applications," *J. Nanoscience and Nanotechnology,* vol. 14, pp. 1364-1388, 2014.

[16] D. Zhang, B. Gökce, and S. Barcikowski, "Laser synthesis and processing of colloids: fundamentals and applications," *Chemical Reviews,* vol. 117, pp. 3990-4103, 2017.

[17] V. Amendola and M. Meneghetti, "Laser ablation synthesis in solution and size manipulation of noble metal nanoparticles," *Physical chemistry chemical physics,* vol. 11, pp. 3805-3821, 2009.

[18] A. Y. Vorobyev and C. Guo, "Direct femtosecond laser surface nano/microstructuring and its applications," *Laser & Photonics Reviews,* vol. 7, pp. 385-407, 2013.