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Introduction

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During the last couple of decades, plasmonic nanoparticles (NPs) (e.g. Ag, Au, and Cu) have gained serious attention due to their inimitable optical properties¹ resulting in a wide range of applications including optical imaging, catalysis, and surface enhanced Raman scattering (SERS).²⁻⁷ The optical properties of plasmonic NPs can be tuned in a broad spectral range (UV-visible-near infrared region) by varying their size and shape.8-10 With the advantage of tunable optical properties, plasmonic nanoparticles are widely tested for several applications in SERS based detection. In recent years, the technique of SERS has been developed into a promising analytical tool due to its fingerprinting capability and high sensitivity combined with its non-destructive nature, and has found many applications in several areas.¹¹⁻¹⁵ Typically, the enhancement in SERS measurements using plasmonic metal NPs/ nanostructures (NSs) results from the combination of two mechanisms: (i) electromagnetic enhancement (EM),¹⁶ which is caused by surface plasmon resonance, and (ii) chemical

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SERS based detection of multiple analytes from dye/explosive mixtures using picosecond laser fabricated gold nanoparticles and nanostructures[†]

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Surface enhanced Raman spectroscopy (SERS) is a cutting edge analytical tool for trace analyte detection due to its highly sensitive, non-destructive and fingerprinting capability. Herein, we report the detection of multiple analytes from various mixtures using gold nanoparticles (NPs) and nanostructures (NSs) as SERS platforms. NPs and NSs were achieved through the simple approach of laser ablation in liquids (LAL) and their morphological studies were conducted with a UV-Visible absorption spectrometer, a high resolution transmission electron microscope (HRTEM) and a field emission scanning electron microscope (FESEM). The fabricated NPs/NSs allowed the sensitive and selective detection of different mixed compounds containing (i) rhodamine 6G (Rh6G) and methylene blue (MB), (ii) crystal violet (CV) and malachite green (MG), (iii) picric acid (explosive) and MB (dye), (iv) picric acid and 3-nitro-1,2,4- triazol-5-one (explosive, NTO) and (v) picric acid and 2,4-dinitrotoluene (explosive, DNT) using a portable Raman spectrometer. Thus, the obtained results demonstrate the capability of fabricated SERS substrates in identifying explosives and dyes from various mixtures. This could pave a new way for simultaneous detection of multiple analytes in real field applications.

enhancement,17 which results from the charge transfer between the analyte and the roughened metal surface. The SERS signal primarily relies on the generated EM fields near the roughened metal surface and the so-called 'hotspots' formed at the closely packed NPs or in the vicinity of sharp edges present in the NSs. The SERS technique has the advantage of quick analysis (real time) and with recent developments in Raman spectrometers resulting in portable and hand-held versions which could be transported easily to the point of interest for inspection/investigation. There is an imperative, present-day requirement for preparing simple, flexible, robust, recyclable, cost-effective SERS substrates for a variety of applications in the fields of hazardous material detection. Numerous techniques have been introduced to design and fabricate various SERS substrates with metal NPs such as nanoscale lithography,18 electrochemical deposition19 thermal decomposition,²⁰ honeycomb patterns via breath figure technique,²¹ etc. Although these techniques have certain advantages in terms of SERS measurements, they often require multiple fabrication steps and procedures and are cumbersome. Furthermore, there is a possibility of the presence of impurities while implementing the preparation procedures. Compared to the aforesaid methods, laser ablation in liquids (LAL) has great potential for the fabrication of various NPs/NSs of metals, alloys, semiconductors, etc.5,22-26 This technique has been widely implemented by various research groups to

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fabricate pure NPs and NSs simultaneously in a single experiment.^{22,27} In particular, the size and shape of NPs/NSs can be controlled by varying the input laser parameters (*e.g.* laser energy, wavelength, pulse width, and pulse shape) and the surrounding liquid medium.²⁸ However, it is worth mentioning that in the LAL process, the laser pulse duration can significantly alter the productivity of NPs because of the difference in ablation mechanisms associated with each one of them.

In the case of nanosecond (ns) or picosecond (ps) pulses, NPs are generated via a thermal mechanism with higher productivity whereas in the case of femtosecond (fs) pulses, the synthesis occurs via thermal-free ablation at lower fluences. Barcikowski and co-workers studied the effect of pulse width on the fabrication of NPs/NSs and achieved a higher production rate with ps pulses compared to fs pulse ablation.²⁹ González-Rubio et al. demonstrated reshaping, fragmentation, and self-assembly of Au NPs using ns and fs pulses.³⁰ Tangeysh et al. have reported the fabrication of Au nanotriangles using fs laser irradiation and the post reduction process.³¹ In recent years, laser fabricated gold (Au) or silver (Ag) NPs have been frequently utilized in SERS experiments due to their ubiquitous plasmonic properties.^{25,32,33} Gopala Krishna *et al.*^{5,34} have efficaciously demonstrated the trace level detection of various explosive molecules using Ag and Ag-Au bimetallic NPs/NSs achieved by fs ablation. Amendola et al. have also successfully utilized the laser fabricated Au-Fe or Ag-Fe NPs in cell imaging and SERS.^{35,36} Recently, a few reports have demonstrated the trace level detection capability of chemicals with composite/alloy NPs and graphene/MoS₂ decorated with metal NPs. 37-41

To date, a majority of the SERS studies using various substrates reported in the literature have demonstrated only the detection of an individual target molecule (either explosives or dyes) with high sensitivity and good reproducibility.⁴²⁻⁵⁰ There are only a few reports that have established the identification of target molecules from complex mixtures.⁵¹⁻⁵³ The complexity in simultaneous detection of multiple analytes is due to the overlapping of spectral signatures of individual molecules and analyte dominance possessing higher Raman cross-sections. White et al. utilized the chromatic separation technique with SERS substrates for the detection of analytes from complex mixtures.⁵⁴ Liu et al. demonstrated the detection of mixture compounds containing CV (10^{-8} M) and Rh6G (10^{-9} M) by utilizing a grooved silver nanoplate assembly as a SERS substrate.⁵⁵ Chen et al. reported a rhodamine B (RhB) and dopamine (DA) mixture using the cellulose nanofiber SERS substrate.⁵⁶ The identification of explosives from complex mixtures is essential to sojourn the transport of explosives in a disguised form and, consequently, to dissolve anti-social activities. However, to the best of our knowledge, until now, there are no reports on the identification of explosives in various matrices or mixtures. In our earlier studies, we have demonstrated the SERS based detection of various analytes in their pure form [AN (50 µm), PA (5 µm), Rh6G (150 nm) and MB (50 nm)] on Au NSs and NPs with a portable Raman spectrometer.25

In the present work, we used the ps laser fabricated Au NSs and NPs as SERS substrates for the detection of various mixed compounds: (i) rhodamine 6G (Rh6G, 5 µM) and methylene blue (MB, 50 nM), (ii) crystal violet (CV, 5 µM) and malachite green (MG, 5 µM), (iii) picric acid (PA, explosive, 5 µM) and MB (500 nM), (iv) PA (10 µM) and 3-nitro-1,2,4-triazol-5-one (NTO, explosive, 10 µM), and (v) PA (10 µM) and 2,4-dinitrotoluene (DNT, explosive 10 µM). PA, NTO and DNT are nitro-rich aromatic explosives where (a) PA is highly unstable and regularly used in improvised explosive devices, (b) NTO has a similar performance to RDX and is insensitive *i.e.* relatively less sensitive to external stimuli such as heat and shock and (c) DNT (an industrial impurity present in TNT) can be used as a marker for the identification of TNT-based landmines.⁵⁷ Moreover, these explosives can be synthesized easily even at the laboratory level. Therefore, the development of simple and rapid techniques for the detection of these explosives either in a pure form or in mixtures is important. The SERS technique combined with efficient (capable of detecting very low concentrations) and versatile (capable of detecting a variety of molecules) substrates and portable/hand-held spectrometers offer a convenient solution for the detection of such materials in the field/at the point of interest.

Experimental section

Synthesis of NPs/NSs

Au NPs and NSs used in the present study were achieved by ablating an Au target immersed in distilled water (DW) using a picosecond (ps) laser delivering ~30 ps pulses at 10 Hz with a wavelength of 532 nm. The laser beam was focused using a plano-convex lens (f = 80 mm). The input beam was aligned to impinge vertically on to the Au target (a thickness of ~1 mm), which was dipped in 5 mL of DW placed in a glass cell and the measured liquid height was 6 mm above the target surface. During ablation, the sample was translated along the X and Y directions with a speed of 0.1 mm s^{-1} to draw the lines on the target surface. Typical ablation time was ~40 minutes. The experiments were performed at pulse energies of 10, 15, 20 and 25 mJ and the obtained NPs and NSs were labelled as AuN10, AuN15, AuN20, and AuN25, and AuS10, AuS15, AuS20, and AuS25, respectively. The measured spot size on the target surface (from FESEM data) was ~280 µm using the method proposed by Barcikowski et al.29 The schematic of the experimental setup is presented in Fig. 1.

Characterization studies

The absorption properties of the obtained colloids were investigated using a UV-Visible absorption spectrometer (PerkinElmer Lambda 750). The size, shape and crystallinity of NPs were investigated using a high-resolution transmission electron microscope (HRTEM, FEI Tecnai G2 S-Twin) operating at 200 kV. Field emission scanning electron microscopy (FESEM, Carl Zeiss) was used to study the surface morphology of the laser textured portions on Au substrates. Explosive moleAnalyst



Fig. 1 Schematic of the experimental setup depicting the preparation of gold nanoparticles and nanostructures using picosecond laser pulses.

cules, namely 2,4-dinitrotoluene (DNT) (dissolved in acetone), 3-nitro-1,2,4-triazol-5-one (NTO) (dissolved in water), and 2,4,6trinitrophenol (picric acid, PA, dissolved in methanol), and dyes, namely rhodamine 6G (Rh6G, dissolved in methanol), methylene blue (MB, dissolved in methanol), crystal violet (CV, dissolved in water) and malachite green (MG, dissolved in water), were prepared in stock solutions and then diluted to achieve various concentrations (5 mM-5 nM). The mixtures were prepared by adding individual analyte solutions in equal ratios (1:1). For SERS substrate preparation, silicon (5 mm^2) samples were cleaned with acetone and deionized water in an ultra-sonication bath. Later, the fabricated NPs (20 µL) were deposited on Si wafer and dried on a hotplate. Subsequently, a tiny drop of analyte (20 µL) was dropped over the NP film (where NPs dropped on Si) and dried. After drop casting, the substrate was rinsed with distilled water to remove the molecules which are not adsorbed. SERS data were recorded using a portable Raman spectrometer (B&W Tek, I-Raman plus, USA) operating at a wavelength of 785 nm and possessing a maximum power of 300 mW (the utilized power was ~90 mW in the present study). Each SERS spectrum is an average of 3 accumulations with an integration time of 5 s in each accumulation.

Results and discussion

UV and TEM analysis

Fig. 2 illustrates the achieved Au NP absorption spectra at different laser energies. From the absorption spectral data, it is obvious that most of the particles are spherical in nature with a striking surface plasmon resonance (SPR) peak near 519 nm. The abrupt shift in the SPR peak position was not observed with increasing pulse energy, which is in agreement with an earlier report by Barcikowski *et al.*⁵⁸ With increasing pulse energy, the intensity of the SPR peak also increased as expected, which is due to the increase in the NP production. For TEM analysis, 10 μ L of NP solution was deposited on the carbon coated Cu grid and dried under ambient conditions. The shape, size and crystallinity nature were investigated by analysing the TEM data. The TEM micrographs of the fabri-



Fig. 2 UV-visible absorption spectra of Au NPs: (a) AuN10, (b) AuN15, (c) AuN20 and (d) AuN25 achieved with input pulse energies of 10, 15, 20, and 25 mJ, respectively.

cated NPs and their respective histograms obtained at four different pulse energies are depicted in Fig. 3. At lower energy, most of the observed NPs are spherical in shape with diameters ranging from 5 to 15 nm as shown in Fig. 3(a1). However, with increasing pulse energy, most of the NPs are found to be elongated structures with branches like nanochains/nanowires, which are composed of many small NPs having diameters ranging from 5 to 25 nm [data presented in Fig. 3(b1), (c1), and (d1)]. The probable reason to observe such elongated nanochains could be due to the generation of a high-pressure plasma at the target water interface during the laser ablation, which can induce strong interactions between the ejected Au ions and the liquid present in their vicinity. Furthermore, laser sintering and collision induced aggregation³² could also favour such structures. The average NP sizes were found to be ~8, ~10, ~14 and ~15 nm for AuN10, AuN15, AuN20 and AuN25, respectively. The insets of Fig. 3(a1), (b1), (c1) and (d1) illustrate the size distribution histograms. The HRTEM images of the synthesized NPs depict the d-spacing values of ~0.235, ~0.234, ~0.233, and ~0.235 nm, which correspond to the Au (111) plane [Fig. 3(a2), (b2), (c2) and



Fig. 3 TEM and HRTEM micrographs of Au NPs: (a1 and a2) AuN10, (b1 and b2) AuN15, (c1 and c2) AuN20 and (d1 and d2) AuN25. The insets show their corresponding size distributions obtained at pulse energies of 10, 15, 20, and 25 mJ, respectively.

(d2)]. Earlier, Shafeev and co-workers reported the formation of elongated aggregates using ps irradiation of Au NPs.⁵⁹ Chen et al. have demonstrated the Ag-Au alloy nanochain formation during the ablation of the Ag target in distilled water mixed with HAuCl₄.⁶⁰ He et al. also have reported the formation of Au nanochains in water obtained using ns laser ablation.³² Previously, several reports have demonstrated the ps ablation to be preferential (when compared to ultrafast or fs ablation) due to the high rate (and yield) of NP production.^{61,62} We have repeated the experiment for the second time for a single energy (~25 mJ) after a few weeks. The TEM micrograph [(Fig. S1, ESI[†])] depicts the morphology of AuN25 NPs with a similar shape and elongated features as obtained in the previous case. Likewise, the size distribution of new NPs is ~16 nm which is almost similar to that of the NPs obtained in the previous case (~15 nm). This result reinforces the reproducibility of the LAL technique towards the shape and size distribution of the fabricated NPs.

FESEM analysis

Picosecond laser textured portions on Au substrates obtained with various pulse energies are presented in Fig. 4. Mostly, spherical particles with diameters ranging from 150 to 300 nm along with few nanoprotrusions on AuS10 [Fig. 4(a)] were observed. Larger NPs (diameter ~400 nm) with nanocavities in AuS15 [Fig. 4(b)], few NPs with bigger size (diameter ~700 nm) on AuS20 [Fig. 4(c)] and many nanocavities covered with an irregular shape of NPs were randomly distributed over the AuS25 [Fig. 4(d)] substrate. As the pulse energy increased, larger NPs surrounded by a huge number of nanocavities were noticed, which could be attributed to the strong interaction between the laser and the Au surface. The variation in the morphology of NSs is mainly accompanied by the increment in the removal of the material, melting and re-deposition of the molten material during the ablation process.^{63,64} In the case of short pulse laser ablation (pulse duration <1 ns), the target melts at a higher fluence and subsequently the ejected species are dispersed into the surrounding liquid under the recoil pressure. At lower fluences, the ejected material could be redeposited on the target surface in the form of nanoprotrusions or nanocavities.⁶⁵ The laser pulse energy and the scanning parameters highly influence the morphology of laser treated portions on the target surface.

SERS activity of laser fabricated NPs

To evaluate the SERS activity of the laser-fabricated NPs, the Raman spectra of DNT (10 μ M) were acquired on AuN10, AuN15, AuN20 and AuN25 substrates (NPs deposited on Si followed by dropping the analyte) using a portable Raman spectrometer (excitation wavelength of 785 nm) and the data are shown in Fig. 5(a). The characteristic peak of DNT was



Fig. 4 FESEM images of Au NSs (post ablation): (a) AuS10, (b) AuS15, (c) AuS20, and (d) AuS25 obtained at pulse energies of 10, 15, 20 and 25 mJ, respectively.



Fig. 5 (a) SERS spectra of 2,4-dinitrotoluene (DNT, 10 μ M) recorded from Au NP films (NPs drop-casted on Si): (i) AuN10, (ii) AuN15, (iii) AuN20, and (iv) AuN25, respectively. (b) SERS intensities calculated for the 850 cm⁻¹ mode collected at 15 different sites from AuN10, AuN15, AuN20 and AuN25 substrates. a.u. stands for arbitrary units.

found at 850 cm⁻¹ and this peak can be assigned to the NO₂ out-of-plane mode (shown in Fig. 5). The enhancement factors (EFs) were estimated following the procedure reported in earlier studies. 25 The calculated EFs were found to be 3.1 \times $10^3,~8.6~\times~10^3,~6.5~\times~10^3,$ and $1.4~\times~10^4$ for AuN10, AuN15, AuN20 and AuN25, respectively. The reproducibility of substrates was evaluated by collecting the SERS spectra at 15 randomly selected different positions and their intensity variation plot for the 850 cm⁻¹ mode is presented in Fig. 5(b). The estimated relative standard deviation (RSD) values are 22.1%, 18%, 19.8% and 11.6% for AuN10, AuN15, AuN20 and AuN25, respectively. The highest SERS enhancement with superior reproducibility was found for the AuN25 substrate compared to the other substrates, which can be related to multiple factors such as (i) the size/shape of nanoparticles⁶⁶ and (ii) the available number of hotspots with which the analyte interreacts.^{67,68} In the present study, we observed the maximum number of NPs in elongated shapes compared to the other substrates [Fig. 3(d)] and furthermore, there could be a possibility of aggregation of NPs after the drop-casting process on Si (which was confirmed from the FESEM image, the data are shown in Fig. S2 of the ESI[†]) which might have resulted in the generation of a larger number of hot spots.

The NP aggregation/nanochain kind of morphology has possibly led to the observation of superior reproducibility with higher EFs for the AuN25 substrate. Even for batch to batch measurements, AuN25 exhibited superior repeatability with a RSD value of 13.9% (Fig. S3,† batch-2). Numerous reports have demonstrated the effect of NP size/shape in the enhancement of SERS intensities.⁶⁹ Hong et al. clearly demonstrated that the SERS intensity was increased with the NP size.⁷⁰ In an earlier study, Hui et al. demonstrated the superior SERS performance of laser fabricated Au nanochains assisted by electrophilic deposition in the case of Rh6G detection.³² With the observed higher enhancements combined with excellent reproducibility, the AuN25 substrate was opted to perform the Raman studies for various mixed compounds. SERS spectra were recorded for different mixed compounds containing (i) Rh6G (5 µM) and MB (50 nM), (ii) CV (5 µM) and MG (5 µM), (iii) PA (5 µM) and MB, (500 nM) and (iv) PA (10 µM) and NTO (10 µM). The SERS spectra of the Rh6G and MB mixture are depicted in Fig. 6(a). The major peaks of Rh6G and MB in the mixed spectra are located at 612, 770, 1362, and 1510 cm⁻¹ and 446, 1393, and 1622 cm^{-1} [peaks labelled with * (for Rh6G) and # (for MB) symbols in Fig. 6(a)] and their peak assignments are reported in earlier studies.25

The homogeneity of the SERS substrate was also studied by collecting the spectra of the mixed solution at 10 randomly selected sites on the same substrate. Fig. 6(b) depicts the histogram of the calculated SERS intensities for the characteristic modes of Rh6G (612, 1362 cm^{-1}) and MB (446, 1622 cm^{-1}) at various positions. The relative standard deviation (RSD) values are found to be 21.8% and 14.9% for the Rh6G peaks and 10% and 13% for the peaks of MB [see Fig. 6(b)]. Even in the case of the mixture, the AuN25 substrate exhibited good reproducibility, i.e. a low RSD, revealing the homogeneity of our SERS substrates. Even for a low concentration of MB (50 nM) used, we observed higher intensities for various modes compared to the R6G modes in the mixed SERS spectra, which could be due to the diverse Raman cross-sections of different molecules and binding affinity of molecules with NPs. Van Duyne et al. clearly demonstrated the effect of Raman scattering corrections in the SERS intensity variations for mixed analytes.⁷¹

Fig. 7(a) illustrates the SERS spectra of the CV and MG mixture recorded from the AuN25 substrate (labelled with 2, red coloured curve) along with the individual SERS spectra of CV and MG [labelled with 1 (black coloured curve) and 3 (blue coloured curve)] as a reference. The major Raman modes of CV and MG are located at 412, 733, 1176, and 1612 cm⁻¹ and 416, 737, 1172, and 1614 cm⁻¹, respectively. These modes are attributed to the out-of-plane vibrations of phenyl-C-phenyl, ring skeletal vibration of radical orientation, and in-plane bending of C–H and ring stretching of C–C, respectively. Meanwhile, CV has an additional territory group and due to this, other modes were noticed at 341 and 1534 cm⁻¹ which



Fig. 6 SERS spectra of (a) a mixed solution containing Rh6G (5 μ M, peaks labelled with *) and MB (50 nM, peaks labelled with #). Individual SERS spectra of compounds are also included as a reference. The Si peak near 520 cm⁻¹ is also shown in the spectra. (b) Calculated SERS intensity for the major modes of both compounds [Rh6G (612, 1362 cm⁻¹) and MB (446, 1622 cm⁻¹)] in the mixed spectra collected at 10 different sites from the AuN25 substrate. a.u. stands for arbitrary units.

are not observed in the MG Raman spectra shown in Fig. 7(a) (labelled with the * symbol). Similarly, the other peaks of MG at 1014, 1044, and 1585 cm⁻¹ were not observed in the CV spectra presented in Fig. 7(a) (labelled with the # symbol). The Raman modes of both compounds were clearly detected with individual characteristic peaks in the mixed spectra as shown in Fig. 7(a) [labelled with * and # symbols (2), red spectra]. Here, the observed spectral signatures of the mixed compound matched well with the earlier report by Chen *et al.*⁷² Our primary goal is to record the Raman spectra of complex mixtures achieved either by mixing of two explosive compounds or an explosive with a dye molecule with these substrates. The identification of target molecules from the complex mixtures can be challenging due to the interference and spectral overlap of different analytes. Furthermore, the SERS signal is



Fig. 7 SERS spectra of (a) a mixed solution containing CV and MG [(2) red spectra, peaks labelled with # (for MG) and * (for CV)], (b) mixed compounds containing PA and MB with various concentrations [(peaks indicated with grey (for MB) and yellow (for PA) rectangular boxes in the mixed spectra (2–5), of (b)] recorded from the AuN25 substrate. The silicon peak near 520 cm⁻¹ is also shown in the spectra. a.u. stands for arbitrary units.

mostly dominated if any fluorescent molecule is present in the mixed compounds [the dye molecule (MB) in the present case]. To implement the SERS studies for mixed compounds, we have chosen the dye (MB) and the explosive (PA) as the probe molecules and their individual SERS studies were reported in our earlier studies.25 SERS spectra were obtained for the mixture of PA and MB prepared at various concentrations using the AuNS25 substrate and are presented in Fig. 7(b). From Fig. 7[(b), 2-5], all the spectral features of MB and PA in the mixed spectra are well distinguished and are found at 448 cm⁻¹ (skeletal deformation of C-N-C), 1618 cm⁻¹ (ring stretching of C-C), 820 cm⁻¹ (C-H bending) and 1340 cm⁻¹ (NO₂ symmetric stretching), respectively. The prominent modes of PA (820 cm⁻¹ and 1340 cm⁻¹) can still be detected with the MB peaks even at a 5 µM concentration, which shows the high sensitivity of the AuN25 substrate in the detection of mixed compounds. For comparison purpose, individual SERS spectra of PA and MB are also included in Fig. 7[(b), 1 and 6]. Additionally, we have examined the efficacy of the AuN25 substrate with an explosive mixture [PA + NTO] as a probe mole12500

10000

7500

5000

2500

600

450

300

150

0

NIO (BAB)

Intensity (a.u.)

Intensity (a.u.)

(6) NTO

(3) PA

(6)

(5)

(4)

(3)

(1) 0

SSD=18%

600

(5)PA (50 μM)+NTO (10 μM)

(4)PA (10 µM)+NTO (10 µM)

(2)AuN25+applied solvent (1)AuN25 substarte

#*

#1

800

1000

Raman Shift (cm⁻¹

(a)

1400

PA

* NTO

*#

1200

(b)

Site Number

cule and the data are presented in Fig. 8(a). The major characteristic modes of NTO are located at 848 (NO₂ deformation), 1068 (ring deformation), and 1372 cm^{-1} (NO₂ symmetric stretching and deformation) as shown in Fig. 8(a) [labelled with the * symbol, (6) blue spectra].⁷³ In the mixed spectra, the major characteristic modes of both the analytes were clearly identified [labelled with * and # symbols in mixture spectra, Fig. 8(a), 4 and 5]. To investigate the reproducibility of the AuN25 substrate, SERS spectra were collected at 10 different sites for the mixture and their main mode intensity variation plot is presented in Fig. 8(b). The RSD values are found to be 18.2% for PA (822 cm⁻¹ peak) and 18% for NTO (848 cm⁻¹ peak) in the mixed spectra, which clearly represent the homogeneity of the substrate. Therefore, we can conclude that the proposed Au NP based SERS substrate has potential to detect a variety of complex mixtures containing explosives or an explosive mixed with other compounds at the same time.

SERS activity of laser fabricated NSs

The SERS performance of laser fabricated NSs was also tested with a probe molecule 2,4-dinitrotoluene (DNT). The SERS spectra were recorded by dropping 20 µL solution of DNT (1 µM) on AuS10, AuS15, AuS20 and AuS25 substrates. The DNT characteristic peak was found at 858 cm⁻¹ and is shown in Fig. 9(a).³⁸ The reproducibility measurements were also performed for all the substrates and their SERS signal variation with the position is presented in Fig. 9(b). The RSD values for the peak intensity at 858 cm^{-1} was estimated to be 46%, 20%, 36%, and 11%, and the estimated EFs were 1.41×10^4 , $1.70 \times$ 10^4 , 1.16×10^4 and 5.12×10^4 for AuS10, AuS15, AuS20 and AuS25, respectively. Though the EFs appear to be similar (in order of magnitude), the reproducibility measurements clearly show that the RSD values for the AuS25 substrate are <11%, which are superior when compared to other substrates. The observed higher EFs and good reproducibility for the AuS25 substrate could be attributed to the observed large number of nanocavities surrounded with larger spheres over the NS.



Fig. 8 SERS spectra of (a) a mixed solution containing PA and NTO [(4 and 5) red and pink spectra, peaks labeled with # (for PA) and * (for NTO)]. Individual spectra of PA [black one, 3] and NTO [blue one, 6] also included. (b) Calculated SERS intensity for the major modes of both compounds [PA (822 cm⁻¹) and NTO (848 cm⁻¹)] in the mixed spectra collected at different sites from the AuN25 substrate. a.u. stands for arbitrary units.

PABR

RSD=18.2%

Fig. 9 SERS spectra of 2,4-dinitrotoluene (1 μ M) recorded from (a) Au NSs [inset (1) AuS10, (2) AuS15, (3) AuS20, and (4) AuS25]. (b) SERS intensities calculated for the 858 cm⁻¹ mode collected at different sites from AuS10, AuS15, AuS20 and AuS25 substrates. a.u. stands for arbitrary units.

Furthermore, SERS studies were also implemented for the mixture of PA (10 μ M) and DNT (10 μ M) by re-using the NSs [Fig. 10(a), 1–4] after adapting appropriate cleaning procedures.²⁴ Earlier, our group has demonstrated the capability of detection of multiple analytes using the same NSs after appropriate cleaning of the Cu substrates.^{24,25} The major peaks of both compounds were clearly detected from all the nanostructured substrates and were labelled in Fig. 10(a). The prominent peaks were located at 822 cm⁻¹ (C–H bending) and 1334 cm⁻¹ (NO₂ symmetric stretching) for PA and 862 cm⁻¹ (NO₂ out-of-plane mode) and 1362 cm⁻¹ (NO₂ symmetric stretching) for DNT, respectively.

A variation in intensities and a small shift in the Raman peaks were noticed, which can be attributed to the orientation of the analyte as well as the generated number of hotspots. The AuS25 SERS substrate homogeneity was investigated by



Fig. 10 SERS spectra of (a) a mixed solution containing PA (10 μ M) and DNT (10 μ M) recorded from (1) AuS10, (2) AuS15, (3) AuS20 and (4) AuS25 substrates [the major Raman modes of both compounds are highlighted in the figure]. (b) Calculated SERS intensities for the major modes of both compounds [PA (822 cm⁻¹) and DNT (862 cm⁻¹)] in the mixed spectra collected from different sites of the AuS25 substrate. a.u. stands for arbitrary units.

collecting the Raman signal of the mixture at 8 randomly selected positions and their intensity variation plot with the position is shown in Fig. 10(b). The estimated RSD values for intensities of 822 cm⁻¹ (PA) and 862 cm⁻¹ (DNT) modes are 12%, and 14% [Fig. 10(b)], which again confirm the reasonable uniformity of the SERS (AuS25) substrate even in the case of the explosive mixture. The limit of detection accomplished in the present case is found to be on-par/superior when compared to those numbers reported recently.75,76 The AuN25/ AuS25 based SERS substrate exhibited reasonable detection limits with realistic reproducibility in the case of different mixtures. The detection limits (sensitivity) can be further improved by (a) fabricating different periodic/3D nanostructures,⁷⁴ (b) using these NPs at high concentration on filter paper⁷⁷ for achieving improved aggregation effects, (c) depositing pure NPs/alloy NPs⁷⁸ in the gaps of NSs^{38,79} inducing confinement effects, etc.

Conclusions

In summary, we have fabricated Au SERS substrates (NPs and NSs) using LAL, a simple and green technique, and successfully demonstrated their versatility for the instant detection of explosives (PA, DNT and NTO) and dves (Rh6G, MB, CV and MG) in various combinations (mixtures) using a portable Raman spectrometer. Active Au SERS substrates were synthesized at four different energies (10, 15, 20 and 25 mJ) using picosecond laser pulses at 532 nm. Au NS and NPs obtained at 25 mJ exhibited superior SERS EFs and high reproducibility for the detection of the DNT molecule. The aggregation resulting as a consequence of drop-casting our nanoparticles (<20 nm size) could have possibly increased the hot-spot density on the substrate and combined with the large spot size used for the Raman measurements gave rise to superior SERS enhancements observed in the case of AuN25. Consequently, these substrates (AuN25 and AuS25) were used for further examination of various mixtures involving dyes and explosives. The detection limits obtained in the case of explosive mixtures was µM while it was nM in the case of dye combinations, with high reproducibility and selectivity. Furthermore, the detection limit achieved for the mixture of two dye molecules in the present case is demonstrated to be superior to some of the results presented in the earlier reports.^{75,76} To the best of our knowledge, this is the first report to demonstrate the identification of explosive molecules in explosive + dye and explosive + explosive matrices with reasonable detection limits. The promising results obtained from these SERS substrates with a portable Raman spectrometer provide a new paradigm for the detection of explosive mixtures, which can be utilized for on-field and real-time applications such as screening at airports and public venues. Our results represent a significant advance since in most of the practical cases, the explosives are not carried in a pure form (or individually) but in a mixture form. Our goal is to optimize these structures for the detection of all well-known explosive molecules mixed with common masking materials (e.g. jaggery).

Conflicts of interest

There is no conflict of interest to declare.

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