Femtosecond Laser-patterned and Au-coated Iron Surfaces as SERS Platforms for Multiple Analytes Detection

Chandu Byram, Sree Satya Bharathi Moram, and Venugonal Rao Soma *

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

Abstract **We report a single-step approach for fabricating nanogrooves and ripple-like surface structures on iron (Fe) substrate using femtosecond laser irradiation in acetone and different laser processing conditions. Subsequently, these laser-patterned Fe surfaces were used as SERS sensors post deposition of a thin gold (Au) film. The Au coated laser-patterned Fe surface structures exhibited superior detection limits for the dye methylene blue (5 nM) and a pesticide (thiram, 10 µM) with enhancement factor (EFs) of ~10^6.**

Keywords - Surface-enhanced Raman scattering, fs laser processing, methylene blue, thiram

I. INTRODUCTION

Femtosecond (fs) laser processing of metals in a confined liquid environment has emerged as a fascinating technique for its wide range of applications in the fields of micromachining, material processing, and nanoparticles/nanostructures generation. [1-3] In contrast to the laser processing in air, ambient liquid offers superior heat sink by cooling the sample and thus minimizes the excessive heating. More importantly, fs-laser processing offers two foremost advantages over the long pulse processing: (a) high-quality surface structures with the desired accuracy that are possible because of infrequent heat effected zones (b) a net reduction in the ablation threshold at identical laser processing conditions (wavelength and focusing geometry). [3] Nowadays, fs-laser processing is wildly applied to produce diverse subwavelength structures comprising micro/nanoscale structures, 1-dimensional and 2-dimensioanl microstructures/nanostructures, cones, and laser-induced periodic surface structures (LIPSS). [3-7] These microscale/nanoscale structures have found potential applications in numerous fields including perfect light absorption, antireflective surfaces, and enhanced wetting properties. [1, 3-5] Very few studies have been established the utility of fs laser fabricated micro/nanoscale structures in surface enhanced Raman scattering/spectroscopy (SERS) based sensing of diverse probe molecules. [6, 7] In this report, we present our results from the fabrication of ripple/ nanogroove-like structures on iron (Fe) substrate by pattering with fs laser pulses. Afterward, these Fe ripple/groove-like features were coated with Au film and then used to detect methylene blue and thiram (pesticide).

II. EXPERIMENTAL DETAILS

A. Fabrciation procedure for Fe nanostrcutures

Before the ablation, the iron (Fe) plates (99.99%, Alfa-Aeser) of dimensions 1 cm^2 were cleaned with water and acetone for 10 minutes in an ultrasonic bath. Fe nanostructures (NSs) were by fabricated by using Ti: sapphire femtosecond (fs) laser system (LIBRA, M/s Coherent) possessing a pulse duration of ~50 fs at a central wavelength of 800 nm at a repetition rate of 1 kHz. The Fe plate was placed at the bottom of the glass beaker filled with acetone (5 mL) and then mounted on the X-Y stage controlled by a computer. The Fe surface was irradiated by focusing the laser beam normally through the plano-convex lens (f = 10 cm). The Fe NSs were prepared in acetone by varying the stage velocities of 0.25 mm/s, 0.5 mm/s and 1 mm/s with a line spacing of 60 µm. The experiments were conducted using an input pulse energy of ~150 µJ. The fabricated NSs were named as FeANS1, FeANS2, and FeANS3 for the scanning speeds of 0.25 mm/s, 0.5 mm/s and 1 mm/s, respectively. The laser treated Fe surfaces characterized by field emission scanning electron microscope (FESEM, Carl Zeiss) operated at 30 kV and Energy dispersive X-ray spectroscopy (EDX). SERS measurements conducted after Au coating (film thickness~20 nm) on Fe substrates. The Raman/SERS data was recorded using a portable Raman spectrometer (M/s B&W Tek, USA) having excitation wavelength of 785 nm while the integration time used was 5 seconds.

III. RESULTS AND DISCUSSIONS

B. FESEM stuidies of Fe NSs

The morphologies of fs laser fabricated Fe NSs in acetone at a pulse energy of 150 µJ with various scanning speeds (0.25 mm/s, 0.5 mm/s and 1 mm/s) was analysed by FESEM, and the data is presented in figures 1(a)-(d). Typical FESEM micrographs of groove-like structures on Fe substrate after irradiation at a scan speed of 0.25 mm/s (named as FeANS1) is depicted in figures 1(a) and 1(b). In the FESEM picture obtained with higher magnification, we can observe the nanogrooves with diameters of ~590 nm and heights of ~600 nm. Along with nanogrooves we also observed the nanocavities with diameters ranging from 420 nm to 980 nm [highlighted in the inset of figure 1(b)]. Figures 1(c) and 1(d) illustrate the different magnification FESEM images of FeANS2 after laser irradiation at a scan speed of 0.5 mm/s. Irregular ripple-like structures with a period of 106 nm-300 nm were formed on the irradiated surface. Along with nanoripples, several nanoparticles with diameters up to ~490 nm were uniformly distributed on the top of the NS. For the case of irradiation at a scan speed of 1 mm/s (FeANS3), nanorods and some arbitrary shape of nanoparticles (NPs) on top of the ripples are evident from the FESEM images of figures 1(e) and 1(f). The formation of spherical/arbitrary shape NPs could be ascribed to the recoil pressure provided by the surrounding liquid under the exposure of successive laser pulses. During the interaction of multiple pluses, material melt

is pushed from colder to a hotter region of the ripples and, consequently, NPs with arbitrary shapes could have resulted on top of the ripples. [7] The differences in the Fe NSs with the increase of scan speed from 0.25 mm/s to 1 mm/s could be attributed to the increase in pulse overlap. [5]

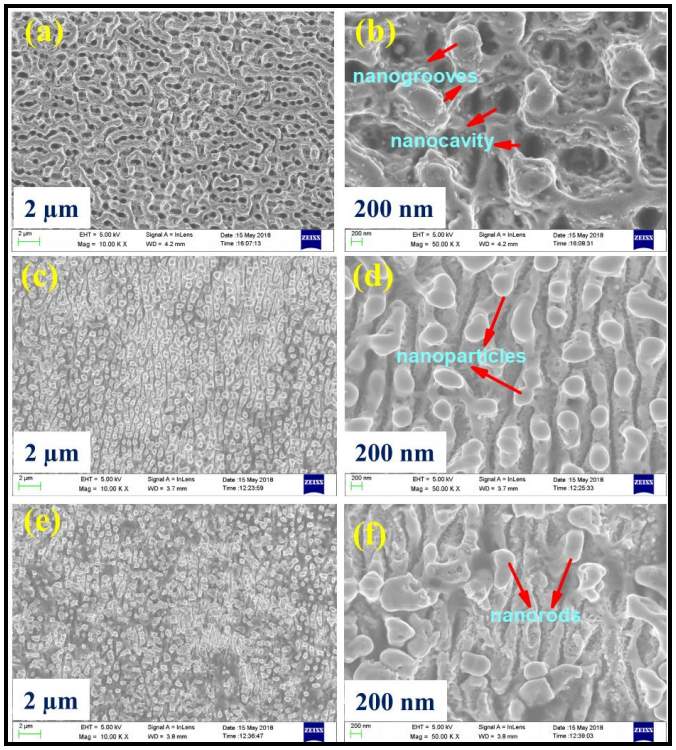

Fig. 1. Lower and higher magnification FESEM images of fs laser fabricated Fe NSs in acetone (a, b) FeANS1 (c, d) FeANS2 (e, f) FeANS3, respectivly.

C. Detection of MB and Thiram using Fe NSs as SERS susbstartes

The SERS ability of Au coated Fe NSs was initially examined with a dye molecule (MB). Figure 2(a) represents the MB (5 nM) SERS spectra recorded on FeANS1, FeANS2, and FeNS3, respectively. The Raman bands were found at 446 cm^{-1}, 605 cm^{-1}, 1391 cm^{-1}, and 1621 cm^{-1} and their assignments were reported in our earler studies. [6, 7] The peaks at 446 cm^{-1} and 1621 cm^{-1} show the most intense signals and were used as characteristic markers for MB.

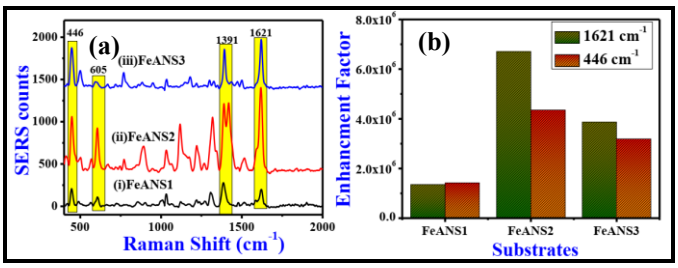

Fig. 2. SERS spectra of MB (5 nM) recorded from Au coated Fe NSs (i) FeANS1 (ii) FeANS2 (iii) FeANS3. (b) Estimated enhancement factors for by considering the major modes of MB (446, and 1621 cm^{-1}) from FeANS1, FeANS2, and FeANS3 substrates, respectivly.

The enhancment factors (EFs) were estimated by considering two most intense peaks of MB (446 cm^{-1} and 1621 cm^{-1}) observed from the laser patterned Fe surface (Fe NS) as well as from the plain Fe substrate. Figure 2(b) shows the histogram plot for the obtained enhancement factors (EFs) at 446 cm^{-1}, 1621 cm^{-1} mode intensities collected from the each Fe NS. Figure 2(b) shows the EFs histogram plot for siganl intensities at 446 cm^{-1} and 1621 cm^{-1} modes obtained on each Fe substrate. The found EFs for 446 cm^{-1} and 1621 cm^{-1} Raman bands were 1.4×10^6, 4.3×10^6, 3.1×10^6 and 1.3×10^6, 6.7×10^6, 3.8×10^6 for FeANS1, FeANS2, and FeANS3, respectivly. The reproducibility of the Raman signal over the entire SERS substrate is another paramount factor in evaluating the efficacy of SERS substrate for practical applications. In order to investigate the signal reproducibility of Fe NSs, the SERS spectra were recorded at 10 different random positions and the data is presented in figure 3.

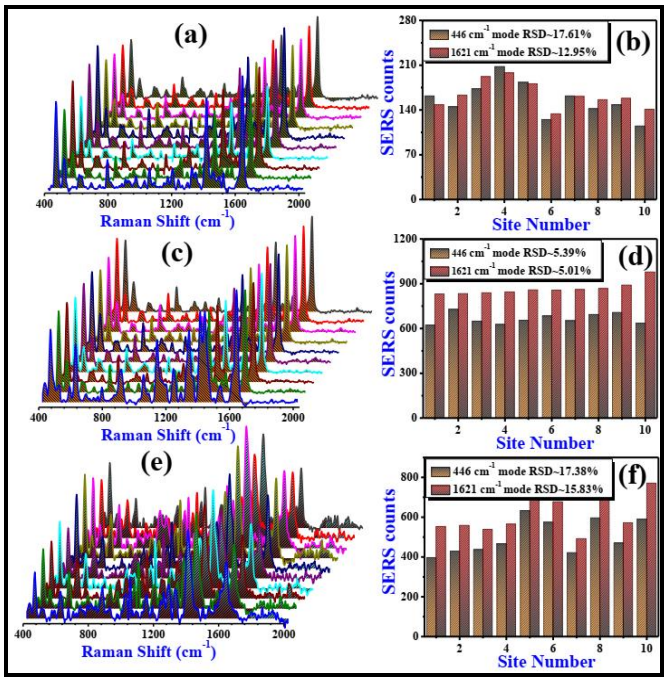

Fig. 3. Reproducibility SERS data of MB (5 nM) recoded at 10 different spots on Au coated Fe NSs and the corresponding peak intensities of 446 and 1621 cm^{-1} MB Raman modes (a, b) FeANS1 (c, d) FeANS2 (e, f) FeANS3, respectively. Calculated RSD values for the peaks of 446 and 1621 cm^{-1} are depicted in the inest of (b) (d) and (f).

The relative standard deviation (RSD) values were estimated by considering the prominent Raman peak intensities at 446 cm^{-1} and 1621 cm^{-1}. Figures 3(a) and 3(b) depict the 3D SERS plot and their corresponding intensity variation at 446 cm^{-1} and 1621 cm^{-1} Raman bands. The RSDs were found to be ~17.61% and ~12.95% for FeANS1 substrate, respectively [figure 3(a)]. Similarly, the RSDs for FeANS2, and FeANS3 substrates were calcuated to be 5.39%, 5.01% [figure 3(d)] and 17.38%, 15.83% [figure 3(f)], respectively. Even though the observed EFs differ in the only factor, an excellent reproducibility (lesser RSD value) was noticed for FeANS2 substrate among the others (FeANS1 and FeANS3). The superior reproducibility of the FeANS2 substrate can be attributed to the uniformly distributed nanoparticles on top of the ripples, which might have led to the generation of homogenous high-density hot spots throughout the patterned surface after Au caoting. Consequently, excellent reproducibility was achieved for FeANS2 (RSD <6%).

Incidentally the plain Au film also acted as SERS substrate. To check the contribution of Au film in the intensity of SERS signals, the Raman data was obtained from Au sputtered plain and laser-processed Fe surface (FeANS2). Figure 4(a) shows the recorded Raman spectra of MB (5 µM) on both these substrates. Figure 4(b) represents the histogram plot for the SERS intensities of 446 cm^{-1} and 1621 cm^{-1} MB modes obtained from Au coated plane Fe and FeANS2 substrates and the estimated Raman intensities were 791, 831 and 18967, 17982, respectivly. FeANS2 substrate exhibited ~24 times higher SERS signals than the normal plain surface which could be ascribed to the observed nano roughened surface of the laser irradiated Fe substrate. [7]

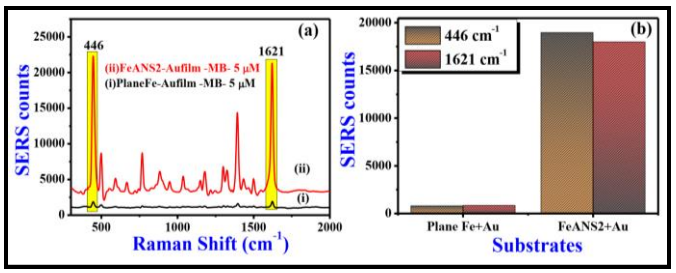

Fig. 4. (a) SERS spectra of MB (5 µM) recorded from Au coated (i) Plane Fe surface (ii) FeANS2. (b) SERS intensities at 446 and 1621 cm^{-1} MB modes obtained from plain Fe and FeANS2 substrates.

Later, we utilized the same substrates for the detection of thiram by simple cleaning procedures. Initially, the substrates were dipped in methanol solution for 20 minutes then sonicated with acetone and methanol in an ultrasonic bath for 10 minutes. [7] Subsequently, Raman data was acquired on the cleaned substrates. We did not observe any Raman bands of the previously detected molecule (MB) following which we proceeded for another analyte (Thiram) detection. Thiram is a widely used fungicide to preserve the vegetables and fruits during the storage and protecting seeds from the various crop diseases and pests. [8] Moreover, excess use of thiram to protect the vegetables and fruits could persuade the severe fetal malformations, ataxia, and convulsions, etc. Hence, there is a prime concern to detect thiram at lower concentration using available conventional methods. The cleaned Fe substrates were treated with thiram and then dried at room temperature; afterward, Raman spectra were acquired. Fig. 5(a) depicts the thiram (10 µM) SERS spectra acquired from the FeANS1, FeANS2, and FeANS3, respectively. Thiram prominent Raman bands observed at 1144 and 1379 cm^{-1} correspond to the CN stretching and symmetric CH_3 deformation mode and the data is presented in figure 5(a). As seen from the data presented in figure 5(b), the SERS spectra of thiram obtained at 10 different locations on each Fe substrate and their corresponding 1379 cm^{-1} mode intensities were considered to estimate the RSDs. The estimated RSDs were 19.1%, 8.9% and 14.9% for FeANS1, FeANS2 and FeANS3, respectively. In thiram detection also FeANS2 substrate demonstrated superior SERS EFs and reproducibility. Moreover, the detected thiram limit (2.4 ppm) in this study is lower than the maximum residue limits (7 ppm) in fruits as per the US environmental protection agency. [8] The presented results suggest that these Fe substrates could possibly be used in the detection of various other pesticide residues. Our future interest would be to detect trace explosive molecules and chemical warfare simulants.

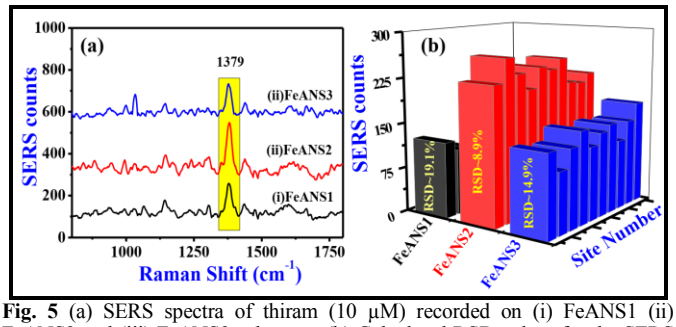

Fig. 5 (a) SERS spectra of thiram (10 µM) recorded on (i) FeANS1 (ii) FeANS2 and (iii) FeANS3 substrates (b) Calculated RSD values for the SERS intensities at 1379 cm^{-1} mode of thiram collected at 10 different locations from FeANS1, FeANS2, and FeANS3 substrates.

CONCLUSIONS

In summary, ripple and nanogroove-like structures were prepared by fs laser irradiation of Fe in acetone by altering the laser processing parameters. Subsequently, these Fe NSs sputtered with Au film and then used as SERS platforms for MB (dye) and thiram (pesticide) detection. A superior SERS performance with excellent reproducibility was noticed for FeANS2 substrate among the three NSs investigated.

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