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Gold-coated electrospun PVA nanofibers as SERS substrate for detection of pesticides

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ABSTRACT

Owing to its ability to detect Raman signals from trace amount of Raman active samples, surface enhanced Raman scattering (SERS) substrate has emerged as an interesting field of research for different areas of applications. Herein, we demonstrate a large area with good degree of reproducibility SERS substrate using PVA nanofibers. Gold (Au) coated electrospun PVA nanofibers has been used as SERS substrate in the present study. Using the designed SERS substrate, Raman signal from malachite green (MG) with concentration as low as 10 nM has been measured reliably by the Raman spectrometer. The relative standard deviation (RSD) for signature peaks of this Raman active sample at 420 cm^{-1}, 1188 cm^{-1}, 1378 cm^{-1} and 1618 cm^{-1} were found to be 6.01%, 7.38%, 5.71% and 6.50% respectively. The usability of the designed SERS substrate for detection of three commonly used pesticides namely deltamethrin, quinalphos and thiacloprid has been successfully demonstrated. It has been observed that for concentration well below the maximum residue limit as set in the Global Agricultural Information Network (GAIN) report from United States department of agriculture (USDA) foreign agricultural service, with the proposed SERS substrate one can easily estimate the concentration of the pesticide samples well below the permissible limit.

1. Introduction

Being a surface sensitive technique and its finger printing specificity along with single molecular sensitivity surface enhanced Raman scattering (SERS) has emerged as a promising technique for sensing of biomolecule, chemicals and different gases. Electromagnetic (EM) mechanism dominantly contributes in the enhancement of Raman signal intensity, which is based on coherent collective oscillations of free electrons generating the localized surface plasmon (LSP) field. Due to coupling of the incident electromagnetic field with metal nanostructures a strongly localized field can be felt in the vicinity of the nanostructure. Consequently, when a Raman active sample is brought in the vicinity of the metal nanostructures it scatters intense Raman signal and the intensity of the signal is found to be enhanced by several order with respect to the situation when normal Raman signal is recorded from the bare sample. Along with this, another phenomenon called chemical enhancement (CE) contributes to the enhancement of scattered Raman signal. In CE, surface-absorbed molecule provides higher scattering cross-sections, thus enhancing the Raman signal intensity. However, this process contributes only one or two orders of magnitude higher than that of a plane substrate. To achieve high reproducibility with good enhancement factor (EF) it is important to design proper nanostructures to maximize the LSP field coupling conditions. Therefore, development of best possible SERS substrate with high EF along with good reproducibility characteristics has been a key research interest among the researchers for last few decades.

To develop SERS substrates, primarily two main approaches are adopted - wet-chemical and top-down fabrication process. Metal nanostructures with specific patterns such as nanocubes, nanorods, nanospheres, concave nanocubes, nanostars, porous nanoparticles, etc [1–8]. Using wet-chemical approaches have been demonstrated for different SERS-based sensing studies. These substrates can be developed at low cost with high EF and sensitivity. However, such SERS substrates yield either low or moderate reproducibility. In order to achieve good reproducibility, different lithographic techniques such as electron beam lithography, focused-ion beam lithography, nano-imprint lithography, etc [9–15]. have been used, which would produce a regular patterned nanostructure on the substrate. These approaches, in general are

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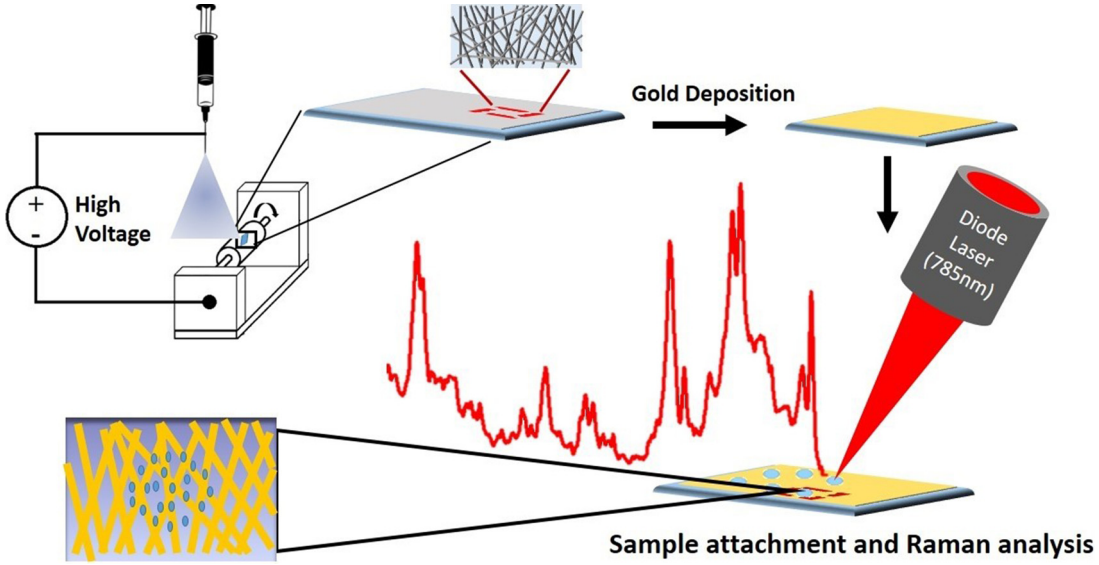

Fig. 1. Schematic representation of fabrication of proposed SERS substrate and its application to measuring of Raman signal from test samples.

expensive and time-consuming and demand sophisticated machines along with sophisticated laboratory set-up for fabrication of the substrates. Keeping these issues in mind, researchers are currently looking for alternative approaches by which SERS substrates can be obtained from naturally available patterned biological samples such as rose petals, diatom frustules, taro leaf, etc [16–26]. The use of diatom as a template for SERS-based investigations has been observed to be cost-effective and time-efficient. Of late, using inkjet printer, metal nanoparticle has been printed on paper and SERS based investigations have been performed on such paper substrate [27–31].

In this work, we demonstrate a technique to develop SERS substrate from Poly(vinyl) alcohol (PVA) nano-fiber where nano-fibers were deposited on glass substrate by electrospining technique. PVA is hydrophilic, nontoxic and biocompatible polymer and exhibits excellent physical properties such as strength, water solubility, gas permeability and thermal stability [32–34]. Using thermal evaporation technique Au nanofilm has been deposited on the crosslinked electrospun PVA nanofiber and the substrate has been used as SERS substrate in the present study. Using the designed substrate Raman signals scattered from different concentrations of MG samples has been successfully measured. For 10μM MG, the RSD of different signature peaks for this sample were found to be varying between 5–8%.

The applicability of the designed SERS substrate for quick and easy detection of some commonly used pesticides well below the permissible limits as set by USDA foreign agricultural service has been demonstrated. Use of pesticides to manage pest problems in the agricultural field has become a common practice around the world. Pesticides are not only used in agricultural fields, but also used in homes, parks, schools, buildings, forests, and roads. Few pesticides have been linked to a wide range of human health hazards, ranging from short-term impacts such as headaches and nausea to chronic impacts like cancer, reproductive harm and endocrine disruption. Acute dangers - such as nerve, skin, eye irritation and damage, headache, dizziness, fatigue and systemic poisoning can sometimes be dramatic, and even occasionally fatal. Issues related to chronic health effects may occur years even after minimal exposure to it in the environment or results from the pesticide residues [35–37]. Thus, reliable detection techniques of pesticides that contained in various food items at an affordable cost would be a relevant study for healthy and sustainable living style. Three pesticides namely deltamethrin, quinalphos and thiacloprid have been considered as test samples for detection and quantification with the proposed SERS substrate. For the considered pesticide samples, with concentrations well below the permissible level Raman signals scattered from the proposed SERS substrate can be measured reliably by the Raman spectrometer.

2. Materials and methods

2.1. Materials

Gold beads (99.999% purity), Polyvinyl alcohol (PVA) of molecular weight 145,000 and Malachite Green (MG) dye were procured from Sigma-Aldrich, India, deltamethrin, quinalphos and thiacloprid were procured from local agriculture stores. All chemicals were used as received without further processing. For detection and analysis, all the samples were prepared in deionized (DI) water.

2.2. SERS substrate fabrication and Raman signal measurement system

Fig. 1 illustrates the schematic of the experimental setup of the proposed work. The size, shape, alignment and spacing of electrospun PVA nanofibers on glass substrate play the crucial role in determining the characteristics of SERS substrate. To fabricate the SERS substrate, 8 wt% PVA solution was prepared in DI water at 80 °C under vigorous stirring condition. For deposition of PVA nanofibers we have used 1 cm x 1 cm glass slide. Prior to its use, the glass slides were cleaned in ultrasonic acetone bath followed by thorough washing with DI water. The glass slides were then allowed to dry in hot-air oven at 60 °C for 1 h. Using electrospining system (ESPIN-NANO, India) PVA nano-fibers are allowed to deposit on the clean glass substrate for 15 min. During deposition of the fibers we maintained a voltage of 16 kV between the tip of the syringe and the substrate. The flow rate of PVA was set at 0.3 ml/h and the glass slides were mounted on a rotor with its rotational speed was maintained at 1500 rpm. The distance between the tip of the needle and glass slide was kept at 15 cm. Upon completion of this step, the deposited nanofibers were allowed to cross-link at 170 °C for 2 h in the hot-air oven. Using thermal evaporation technique (Hind HiVac BC300), Au nano-film of thickness ~30 nm was allowed to deposit on the cross-linked PVA nano-fibers substrate. Fig. 2(a) shows the FESEM (Carl-Zeiss ΣIGMA VP) image of Au-coated PVA nanofibers deposited on the glass substrate. The diameters of the fibers are found to be varying between 100 nm–190 nm and the spacing among the fibers are varying between 10 nm to several 100 nm. The EDX data shown in Fig. 2(b) confirms the presence of Au in our designed SERS substrate. To study the generation of LSP field in the designed substrate the Au substrate has been illuminated with a broadband optical source (Ocean