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Synthesis and Characterization of Novel Nanomaterials for SERS Biomedical / Environmental Application

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In this study, a simple green method was used to synthesize functionalized silver nanoparticles (Ag NP) as a surface-enhanced Raman scattering (SERS) substrate for dopamine (DA) detection. In this method, polyethylene glycol (PEG) was functionalized on Ag NPs to prepare the size of the nanoparticles (NP) in a uniform and controlled manner. Optical and structural properties of functionalized nanoparticles were characterized. The Raman spectra of the prepared PEG-Ag SERS substrate clearly showed an increase in the SERS signal of DA. The improved functionalized SERS substrate could potentially be a sensitive SERS substrate for the detection of various neurotransmitters for biomedical application.

Keywords: *Surface-enhanced Raman scattering, silver nanoparticles, polyethylene glycol, dopamine*

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1. Introduction

Nanotechnology has received a great deal of attention in recent years, with the foundation being laid by Feynman in 1959 and then consolidated a decade later by Taniguchi who came up with the term nanotechnology [1]. A nanoparticle is the most central component in the buildup of a nanostructure. A nanoparticle is bigger than an atom or a simple molecule that is governed by quantum mechanics, and lies in the size range of between 1-100 nm [2]. Synthesis of these nanoparticles is carried out either through a bottom-up approach or through the top-down approach. The bottom-up approach refers to how atoms are used to build up to a nanomaterial, whereas in a top-down approach a larger material is broken down and eventually reaches a smaller sized structure.

Nanoparticles possess unique properties, especially optical, electronic and biological properties [3,4]. As they have a high surface-to-volume ratio, nanoparticles can be used as heterogeneous catalysts [5,6]. In addition, they are applied in many fields, including photonics, microelectronics, lithography and surface-enhanced Raman spectroscopy [7,8]. The exceptional plasmonic properties of silver nanoparticles leads to a great enhancement of the Raman signal. The surface-enhanced Raman scattering (SERS) is an advanced Raman technique that enhances the vibrational spectrum of molecules adsorbed on or in the vicinity of metal particles. According to previous studies, two main mechanisms, chemical and electromagnetic contribute to SERS enhancement [9]. In the electromagnetic mechanism, the laser light causes the excitation of the localized surface plasmons which causes an enhancement of the local electromagnetic field. The molecule which is near the metal surface or adsorbed to it experiences this enhancement, and as a result, the intensity of the Raman scattered light is enhanced. In the chemical mechanism, which typically occurs in those molecules with a lone pair of electrons, a charge transfer takes place between the molecule and the surface of the metal. The chemical mechanism is usually regarded as weaker than electromagnetic mechanism and occurs in concert with it. Raman signal enhancement is because of both of these mechanisms. Due to its sensitivity, readiness and minimum sample preparation requirements, SERS is being considered as a powerful technique for detection of the wide variety of analytes at very low concentrations, even down to the single molecule level [10]. A variety of materials are employed for SERS analysis. The aim while synthesizing these materials is to prepare stable, reproducible and highly active SERS substrates. Metals such as gold and silver are commonly used as part of metal hybrid nanostructures. The optical properties of silver and gold depend on their size and shape which makes it important to control these parameters, and these properties in turn influence the SERS effect. Nanoparticles can be synthesized according to various methods depending on the shape of nanoparticle needed, as the shape affects SERS enhancement. SERS substrates can be metal electrodes, colloidal metal solutions, or hybrid structures where the metal nanoparticle is chemically or electrostatically attached to other inorganic materials such as in metal island films or metal coated nanospheres [11]. These methods required complex and time consuming procedures. Therefore, in this study we opted to use easy and simple method by employing PEG as an environmental friendly surface modifier and stabilizing agent to prepare functionalized Ag NPs as SERS substrate for detection of a neurotransmitter dopamine (DA).

SERS provides a unique opportunity to detect a broader range of neurotransmitters in close proximity to neurons. DA is a catecholamine neurotransmitter that plays a significant role in the functioning of central nervous, vascular, and hormonal systems [11,12]. It is widely distributed in the brain tissues and body fluids of mammals. The abnormal variation of the DA concentration in vivo has been linked to serious neurological, renal, cardio disorders such as schizophrenia, Huntington's disease, Alzheimer's disease, and Parkinson's disease [13, 14]. Therefore, the aim of the present work is to synthesize PEG functionalized Ag NPs, through a green method, which is environmentally friendly, viable, and cost-effective to prepare an effective SERS substrate for the detection of DA through Raman spectroscopy.

2. Experimental Studies

2.1 Materials

All chemicals and reagents were of analytical grade and used as received. Silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$) and polyethylene glycol (PEG 6000) were purchased from Sigma Aldrich. Distillate was used throughout the experiments.

2.2 Synthesis of functionalized Ag NPs

Silver nanoparticles were prepared by the dropwise addition of aqueous $AgNO_3$ solution (0.01 M) to a mixture of 50 mL of PEG (0.1M) and 10 mL sodium borohydride ($NaBH_4$) (0.01M) at room temperature. The mixture was constantly stirred using a magnetic stirrer and kept in the laboratory at room temperature. Three samples were prepared with differing volumes of $AgNO_3$ in order to determine the optimum volume of $AgNO_3$ required to prepare the Ag NPs of adequate size. Three volumes of $AgNO_3$, 100, 200 and 300 μL were taken and added dropwise to the PEG and $NaBH_4$ mixture. The non-functionalized Ag NPs were synthesized with same procedure without addition of PEG.

2.3 Preparation of DA loaded SERS substrate

A volume of 100 μL of DA in phosphate buffer solution (pH 7.4, 0.05 mM) was added to the functionalized Ag NP solution and the non-functionalized Ag NP solution, respectively. The samples prepared for detection of DA (Table 1.1.) were dropped to the silica substrate as shown in Figure 1.1. The samples were dried at room temperature and used to record the Raman spectra.

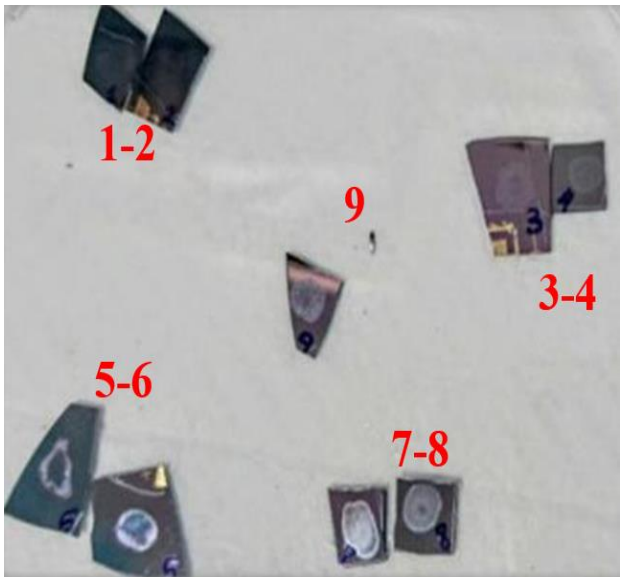

Figure 1.1. *DA incubated synthesized PEG Ag SERS substrate on silica plate*

Table 1.1: Showing DA incubated samples on silica

Sample Number	Sample Name
1-2	Non-functionalised Ag NPs without DA
3-4	Non-functionalised Ag NPs with DA
5-6	Functionalised Ag NPs without DA
7-8	Functionalised Ag NPs with DA
9	DA

2.4 Characterization of nanoparticles

UV–Visible (UV-Vis) spectroscopy is a very important technique and is the simplest way to confirm the formation of nanoparticles. The absorbance spectrum of the colloidal sample was obtained using a UV–Vis spectrometer Nanodrop 2000 (200–800 nm). X-ray diffraction (XRD) analysis was conducted using D8 ADVANCE using monochromatic Cu kα radiation (λ = 1.5406 Å) operated at a 2θ angle pattern. The scanning was done in the region of 20º–80º.Fourier-Transform Infrared (FTIR) spectra of the samples was investigated using a Thermo Scientific™ Nicolet iS™10 FTIR Spectrometer). The characterization was in the wavenumber range from 4000 to 500 cm^{-1} accumulating 64 scans. The Raman spectra were recorded by Renishaw Invia Raman microscope. Collection of the SERS spectra was performed through a 50 microscope objective using low laser power (0.5%).

3. Result and Discussion

3.1 Uv-Vis spectroscopy results

PEG functionalized Ag NPs were prepared by the dropwise addition of aqueous $AgNO_3$ solution (0.01 M) to a mixture of 50 mL of PEG (0.1M) and 10 mL of sodium borohydride ($NaBH_4$) (0.01M) at room temperature. Three different volumes of $AgNO_3$ such as 100, 200 and 300 µL were taken and added dropwise to the PEG and $NaBH_4$ mixture and respective UV absorbance responses were recorded and shown in Figure 3.1. PEG Ag NPs showed a characteristic absorption peak at around 400 nm (Figure 3.1.). Increasing the volume of $AgNO_3$ added in the reaction mixture, leads to the formation of Ag NPs of a larger size, which is shown to increase UV absorption of light as shown in Figure 3.1. For the synthesis of PEG-Ag NPs at room temperature, different volume/concentration of $AgNO_3$ solution were considered and shown in Table 3.1. At 300 µL of $AgNO_3$, a broader peak is observed due to agglomeration of the Ag NPs (Figure 3.1.).

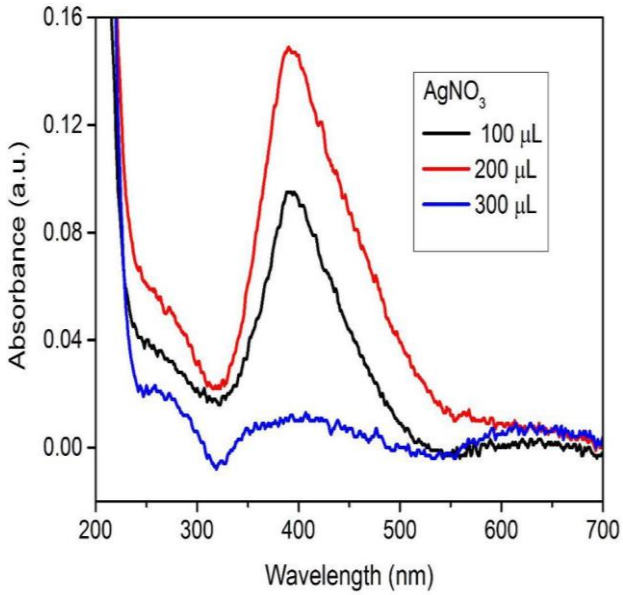

Figure 3.1. *UV-Vis spectra of functionalized silver nanoparticles using different volumes of $AgNO_3$*

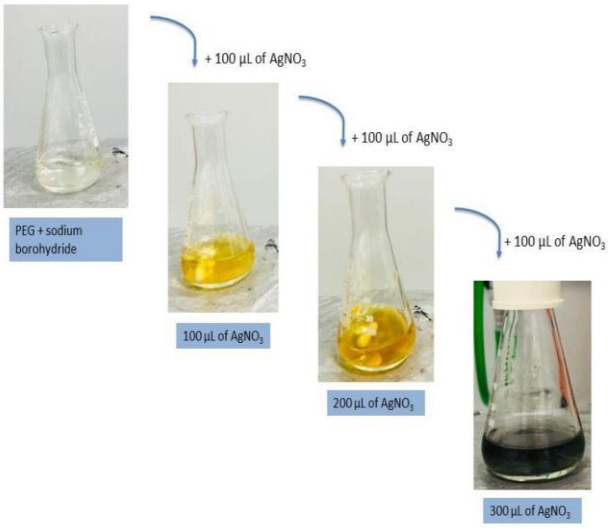

Figure 3.2. *The reaction procedure and color change with the addition of different volumes of $AgNO_3$ to a mixture of PEG and $NaBH_4$. The figure shows the appearance of a light yellow color in the reaction mixture which indicates the formation of PEG Ag NPs*

After the dropwise addition of $AgNO_3$ to a mixture of PEG and $NaBH_4$, a light yellow color solution was obtained (Figure 3.2.) and it indicates the formation of Ag NPs. The change in color of the solution was due to the surface plasmon resonance (SPR) and reduction of silver ions by PEG and $NaBH_4$. Further addition of $AgNO_3$ resulted in a darker solution being formed due to aggregation of the silver nanoparticles (Figure 3.2.).

Table 3.1: UV-Vis spectra results with optimizing parameters

Trial Number	1	2	3
Quantity of $AgNO_3$	100 µL	200 µL	300 µL
Conc. $AgNO_3$	0.01M	0.01M	0.01M
Absorbance	0.0952	0.1491	0.0130
Wavelength (nm)	388	390	408

3.2 XRD results

The X-ray diffraction (XRD) pattern of the prepared PEG Ag NPs was recorded. XRD profile was taken from 2θ range of 20° to 80° with a step of 0.02 degree and shown in three peaks at 2θ values of 38.03°, 44.22°, and 72.616° in the experimental diffractogram have been identified and corresponding to (hkl) values - (111), (200), and (311) planes of silver, respectively (Figure 3.3.). The XRD profile confirmed that the resultant particles in the prepared sample are silver NPs and having a face-centered cubic crystal structure. There is one more unidentified peak at 34.129° which may be due to $AgNO_3$, which might not have been reduced and hence remained in the sample in minute quantity.

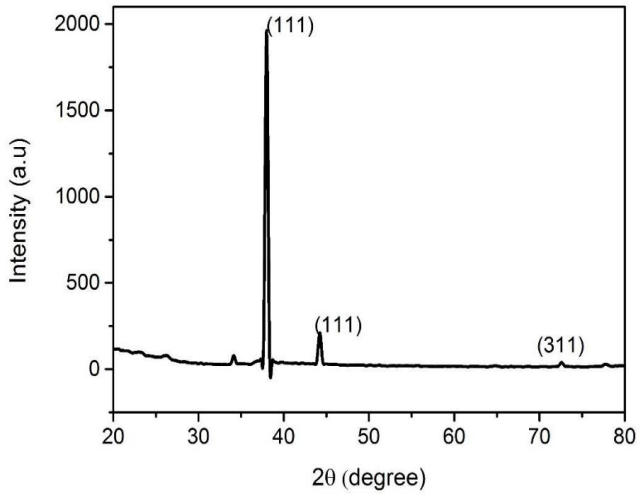

Figure 3.3. *XRD profile of functionalized Ag NPs*

3.3 FTIR results

The FTIR spectra of PEG and PEG Ag NPs were recoded and shown in Figure 3.4.

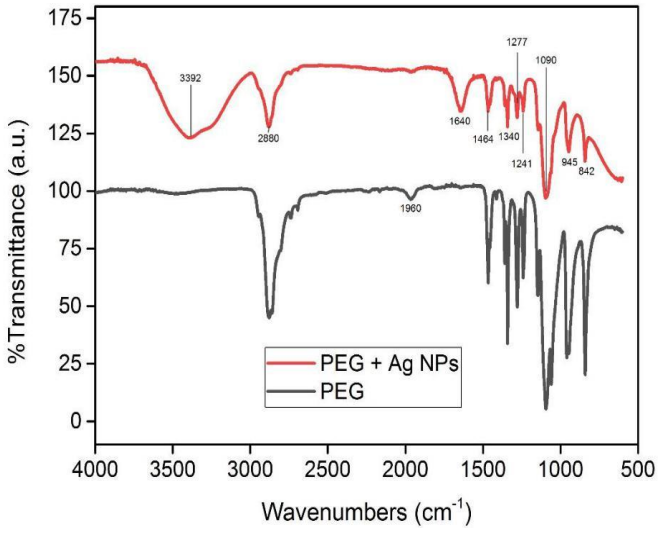

Figure 3.4. *FTIR spectra of PEG and PEG-Ag NPs*

Intense absorption bands were observed at 2880, 1640, 1464, 1340, 1277, 1090, 945 and 842 cm^{-1} for PEG Ag sample (Figure 3.4). Aliphatic C–H stretching at 1464 and 1340 cm^{-1} due to C–H bending vibrations [15], bands at 1277 cm^{-1} and 1090 cm^{-1} which were related to the stretching

vibrations of the alcoholic C–O bonds and C–O–C ether linkage ν(C–O–C) were observed in FTIR spectrum of PEG functionalized Ag NPs. Further, bands at 945 cm^{-1} ($\rho(CH_2)$) and 842 cm^{-1} ($\rho(CH_2)$) were attributed to rocking vibrations and band at 3392 cm^{-1} was attributed to the O–H stretching vibration in association with ν (CH_3^s) at ~2880 cm^{-1} in case of PEG Ag NPs. Finally, a new band was observed at ~1640 cm^{-1} which might correspond to a C=O stretching vibration and this carbonyl group formation occurred probably due to the oxidation of hydroxyl groups [16,17] in FTIR spectra of PEG Ag NPs (Figure 3.4.).

3.3. Detection of DA on synthesized SERS substrate results

The Raman Spectra of Ag NPs and PEG functionalized Ag NPs (PEG Ag) were recorded (Figure 3.5.). The Raman spectra of PEG Ag showed enhanced Raman intensities at 813, 1035, 1340 and 1600 cm^{-1} as compared with Ag NPs. These observations clearly indicated that PEG has stabilized silver nanoparticles with controlled and uniform size distribution.

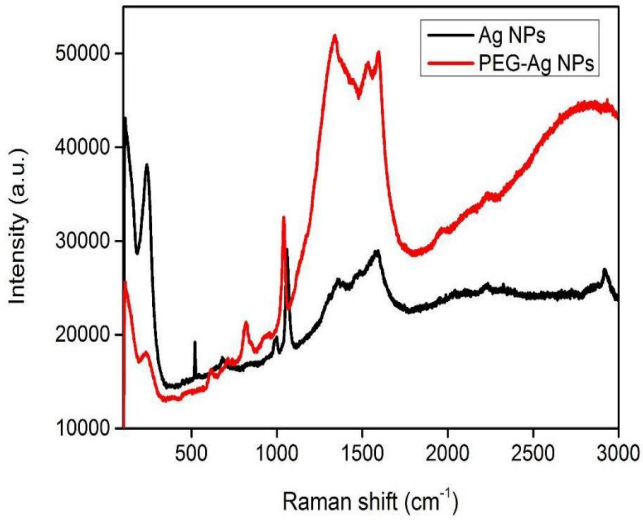

Figure 3.5. *Raman spectra of PEG Ag and Ag NPs*

Furthermore, functionalized Ag NPs were utilized for detection of DA and SERS response were recoded (Figure 3.6.). The optical image of DA incubated PEG Ag NPs SERS substrate is shown in Figure 3.7. The SERS spectra of PEG Ag NPs clearly showed enhanced peaks of DA (0.05 mM) as compared to the Ag NPs (Figure 3.6.). The band at 1480 cm^{-1} corresponds to phenyl C=C stretching has noticeably enhanced the peak signal as compared with DA peak signal. The band at 1337 cm^{-1} can be assigned to ring stretching vibration of DA. The ring stretching vibration mode of O-H bond is observed at 1395 cm^{-1} (Figure 6). The observations clearly indicated that PEG functionalized Ag NPs can enhance the SERS peak signal of DA and can be used as a sensitive SERS substrate for the detection of DA.

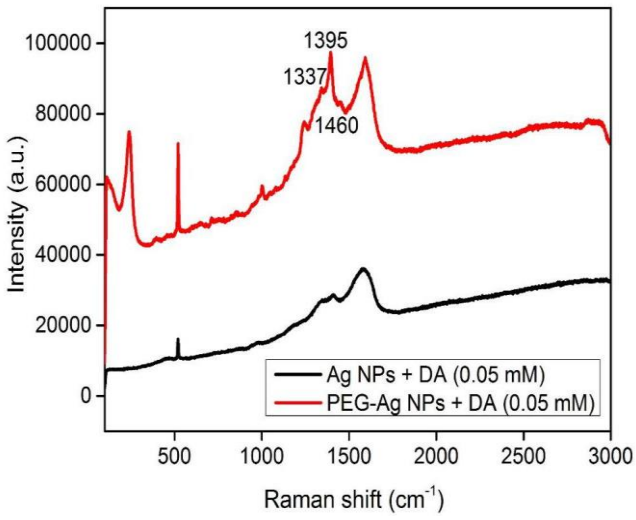

Figure 3.6. *Raman spectra of PEG Ag and Ag NPs incubated with DA (0.05 mM)*

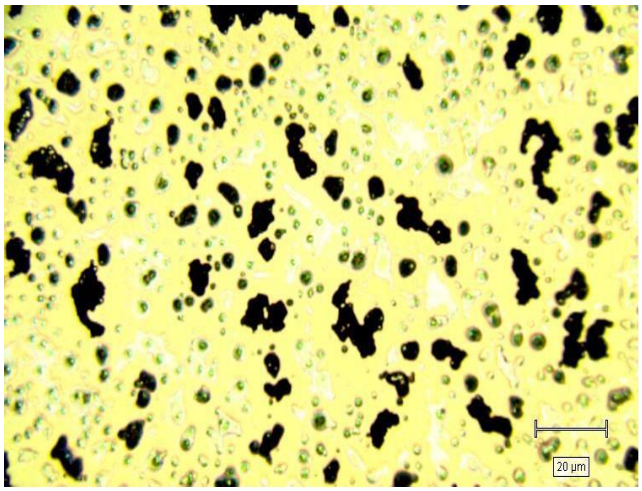

Figure 3.7. *Raman optical image of functionalized Ag NPs incubated with DA (0.05 mM)*

4. Conclusion

In this study, a simple green method was employed to prepare PEG functionalized Ag NPs as a sensitive SERS substrate for the detection of DA. The synthesized functionalized Ag NPs were successfully characterized by UV-Vis, XRD and FTIR techniques. The synthesized PEG Ag NPs showed enhanced Raman signal as compared to Ag NPs. DA was successfully detected by employing functionalized Ag NPs as a SERS substrate. The developed

method to prepare functionalized Ag SERS substrate is simple, low cost, environmentally friendly and easy to use. The developed functionalized SERS substrate in this study can be potentially used as a sensitive SERS for the detection of a variety of neurotransmitters for biomedical applications. The next step would be to study the DA concentration in human cerebrospinal fluid (CSF) samples to see if this method can quantitatively measure the amount of DA in a reliable and accurate manner. Additional investigations can be made regarding altering the chain length of PEG or using PEG as the sole reducing agent instead of $NaBH_4$.

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