Surface Enhanced Raman Spectroscopy(SERS) of TMPyP on Ag Nanoparticles.

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A R T I C L E   I N F O

A B S T R A C T

This work was aimed to study the role of interaction between silver nanoparticles, TMPyP and Graphen Oxide(GO) on surface enhanced Raman scattering (SERS) signals. Silver nanoparticles(AgNPs) prepared by chemical reduction of $AgNO_3$. SERS substrates show remarkable difference in spectral features due to the different enhancement contributions from the local chemical groups. Closely spaced NPs result in the enhancement of electromagnetic coupling between NPs leading to strong confinement of local electric field leading to large SERS enhancement. Graphene Oxide/TMPyP interaction nanostructures forming a composite with strong interaction, this came with identical results obtained in NanoPhotonics Research Group in UCD[1]. Depending on the quantum mechanics, this indicates match the energy levels between the reactants and increase the free electrons in the outer shells which enhances the surface plasmons signal.

Introduction

Solar energy is one of the most infinite source of energy. Some of this energy reaches our plant so, efforts done to save this energy in a large effective solar cells. Surface-enhanced Raman scattering (SERS) spectroscopy is a very useful detection and analytical technique thanks to the enhancement of Raman scattering for molecules adsorbed on rough metal surfaces[2,3]. The enhancement is usually up to 10^6, but selective excitation of extremely high enhancing sites ("hot spots") can give SERS enhancement of the order of 10^{12} allowing even single molecule detection[4,5,6,7].

TMPyP structure, fig.(1) is a water-soluble, tetra cationic porphyrin. TMPyP is a suitable molecule for SERS because it provides high SERS signal owing to its structure and positive charge which helps adsorption on the Ag nanoparticles surrounded by negative ions. TMPyP is a member of the porphyrin family of compounds.

Silver nanoparticle is a kind of metal silver with nano scale particle size. AgNPs are nanoparticles of silver, i.e. silver particles of between 1 nm and 100 nm in size. Silver is quite a special element. Silver is quite a special element. Combining GO with organic aggregates such as porphyrin have the potential to create organic composite materials with optoelectronic properties applicable for devices such as solar cells or sensors[8,9].

The goal of this research is to find a formula based on silver nanoparticles ,TMPyP and Graphen Oxide (GO) particles with high absorbance within visible–near infrared of spectrum to build a high efficient solar cell .The origin of these phenomena is largely due to an enhanced electromagnetic (EM) field at the metal substrate surface due to surface plasmon .

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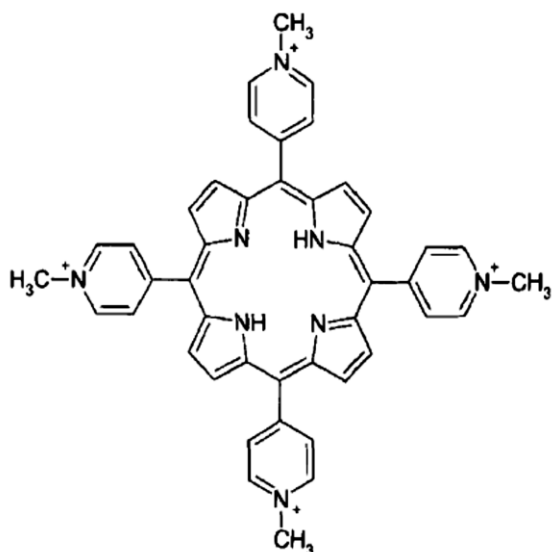.E-mail address:

Fig.(1) TMPyP structure[8].

Material and methods

  Silver colloid was prepared by chemical reduction method according to the description of Lee and Meisel[3] . Silver nitrate $AgNO_3$ (Sigma Aldrich, UK) and trisodium citrate $C_6H_5O_7Na_3$ (Sigma Aldrich, UK) of analytical grade purity, were used as starting materials without further purification.

  All solutions of reacting materials were prepared in distilled water. Fifty ml of a 0.001M silver nitrate ($AgNO_3$) solution (17 mg $AgNO_3$ in 100ml distilled water)was brought to the boil. While the solution was boiling to 100 C$^{\circ}$, 5 ml of 1% trisodium citrate ($C_6H_5O_7Na_3$) was added drop by drop using a pipette. The solution was stirred continuously during the addition of $C_6H_5O_7Na_3$. Heat continued to be applied until the solution changed from clear to pale yellow. The solution was then removed from the heat and stirred until it returned to room temperature . To make sure the particles of Ag nanoparticles are separated from each other, we rotate the solution of Ag nanoparticles by using heat-stair instrument (protected by Bio Cote) to 5 cycles/min.

  The first step is to determine whether silver nanoparticles are actually synthesized or not. Characterization of the nanoparticles, which examines with includes size and shape. The reduction of metal

ions was roughly monitored by visual inspection of the solution by the method described in chapter two . The conversion of the colorless reaction mixture to a brown color and mirror like illumination on the walls of the Erlenmeyer flask clearly indicated the formation of silver nanoparticles in the reaction mixture, as in above figure.

  The UV-VIS light spectrophotometer was used for determination of silver nanoparticles formation measuring optical absorbance spectra. The UV/Vis that was used in this work is V-650 UV-Vis Spectrophotometer.

  The silver nanoparticles were measured in a wavelength ranging from 250-900 nm with scan speed 100 nm/min and data interval 1nm. The UV-Vis spectra of the silver nanoparticles showed a well-defined surface plasmon band centered at around 450 nm, fig.(2), which is the characteristic of silver nanoparticles and clearly indicate the formation of nanoparticles in solution.
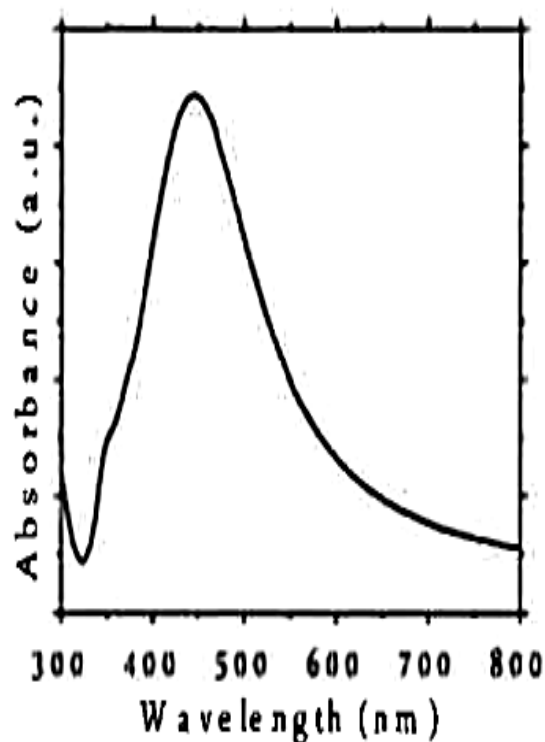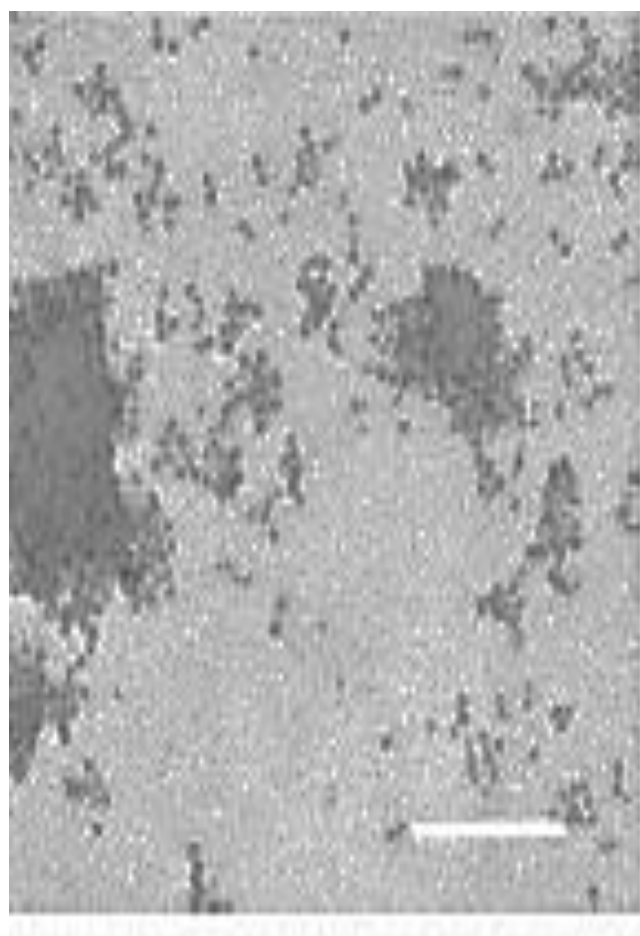

Fig. (2) UV-Vis Spectrum of Silver Nanoparticles.

With the Atomic Force Microscopy (AFM), µTA 2990 Micro-Thermal Analyzer with topographic ranges (200-500)nm, morphology and size of the silver nanoparticle was investigated. The shape obtained involved silver nanospheres of approximately 60 nm in diameter, fig(3).

2. Silver nanolayer synthesis with thickness 10nm was done by using deposition vacuum system,fig.(4). To prepare TMPyP with concentration 10-4 mol , 0.008 g from TMPyP powder, Tetrakis (N-methyi-4-pyridyl), its chemical formula is C44H38Cl4N8, was dissolved in 100 ml of distilled water. The properties of TMPyP which is used in this work, from SIGMA-ALDRICH, Co. shown in table (1). The properties of GO that was used in this work are shown in table(2).
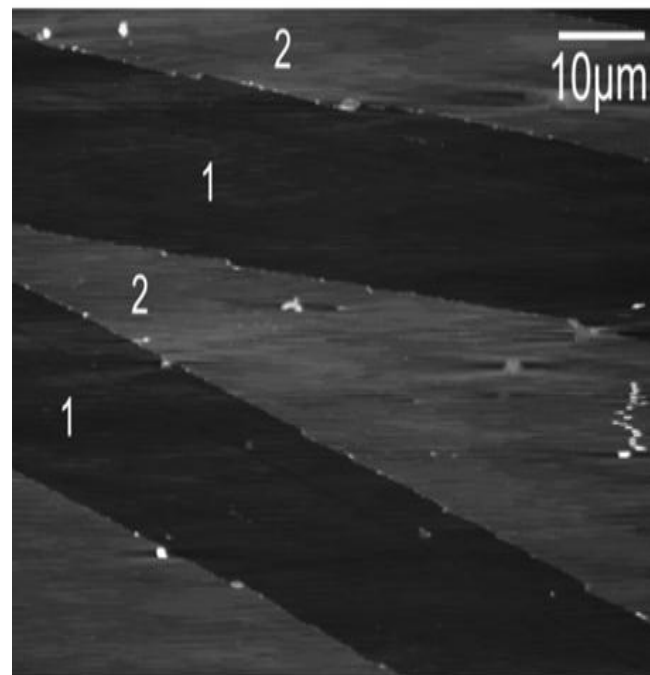
Fig(4) AFM image for Ag nano thinfilm with thickness 10nm.

Table (1) TMPyP properties

TMPyP PROPERTIES	
Chemical formula	$C_{44}H_{38}Cl_4N_8$
Appearance (Color)	Purple to Very Dark Purple
Physical State	Solid
Solubility	Soluble in water
Formula Weight	1363.60 g/mol
Storage	Store at 4° C

Table (2) Graphen Oxide properties

GO PROPERTIES	
Appearance (Color)	Brown to Very Dark Brown and Black
Physical state	Liquid
Infrared spectrum	Conforms to Structure
Carbon (Dry Basis)	42.0 - 52.0%
Sulfur (Dry Basis)	< 4.0%
Potassium (K)	< 60 ppm
Manganese) (Mn	< 60 ppm
Residue on Evaporation PH: (mg/ml)	1.9 - 2.4
Storage	At room temperature

Fig(3) AFM of Silver Nanoparticles.

Graphene oxide are novel nanomaterials that have recently attracted a great deal of consideration due to their wide variety of applications in

nanoelectronics sensors, nanocomposites, batteries, super capacitors and energy storage. In particular, the unique surface properties (oxygenated functional groups on the basal planes and edges), large surface area, layered structure, and easy exfoliation into monolayers under water mean that graphene oxide (GO) is a suitable building block for fabricating versatile functional materials via covalent or non-covalent approaches.

Silver nanostructure with thickness 10nm on the clean coverslips glass was   done by using deposition vacuum system. To prepare HCl with pH 0.5 ,used in this work, 10ml HCl (from SIGMA-AL DRICH) are added to a 90ml distilled water to produce 100ml from HCl with pH 0.5.

Sample Deposition

To prepare the required samples, 100 μmole TMPyP solution was   mixed with 50 μmole   Ag nanoparticles solution. In addition, 100 μmole TMPyP solution was mixed with 50 μ mole Ag nanoparticles and 50 μmole graphen oxide (GO)with concentration 2mg/ml dispersion in water from AL-DRICH, Co., while 100 μmole TMPyP solution was mixed with 50 μmole Ag nanoparticles and 50 μmole HCl solution, while 100 μ mole TMPyP solution was mixed with 50 μ mole Ag nanoparticles and 50 μmole HCl solution and 50 μmole graphen oxide (GO). we deposited 20 μmole from each solution on the clean coverslips glass.

Results and discussion

The SERS enhancement of TMPyP on Ag nanoparticles was studied. Ag nanostructure as a substrate and TMPyP as a probe molecule were chosen for the following reasons, TMPyP in is an organic dye with a larger extinction coefficient and highly efficient SERS and Ag nanostructure is the commonly used substrate for SERS applications. Ag nanoparticles

show unique properties due to localized surface plasmon oscillation in the Vis-infrared region . The effect of the surface plasmon oscillation of Ag nanoparticles on excitation of TMPyP molecules bound at the Ag surface is quite interesting.

In this work the solid state Nd-YAG (532 nm) green laser and a 50x objective was   used . The laser source used as a source of excitation. It is made from features of ultra compact long lifetime, low cost and easy to operate. The laser power supply model no. LD-WL206, input : 85~264V , AC , 47~ 63HZ , 0.4A with 200mW and it is counties wave(CW)   from DPSSL   DRIVER, MGL-III, 12097360.The system setup of Surface Enhance Raman Scattering, fig.(5).
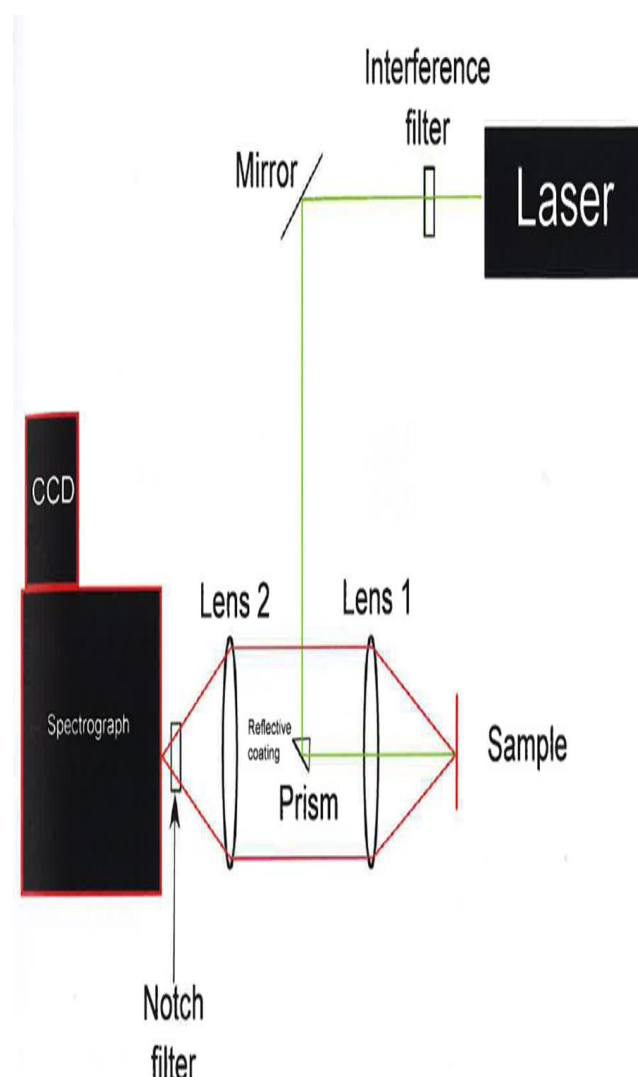
Fig(5) Schematic of SERS system.

First sample represented mixture of (100µmole TMPyP + 50µmole Ag nanoparticles) deposited in Ag nanostructure, (sample1). The enhancement of Ag nanostructure and Ag NPs to surface plasmons in this sample was very strong, with high intensities appeared in SERS spectrum, also TMPyP provides high SERS signal owing to its structure and positive charge which helps adsorption on the Ag nanoparticles surrounded by negative ions.Mix(100 µ mole TMPyP + 50 µmole Ag nanoparticles) deposited in glass without Ag nano structure, (sample 2) . Absence of Ag nanostructure did not give enough enhancement to surface plasmons with just very small peaks had low intensities. The SERS spectrum of TMPyP was in control at the SERS of this sample may be because of its high concentration.Mix mix(100 µ mole TMPyP + 50 µmole Ag nanoparticles + 50 µmole GO)deposited in Ag nanostructure, (sample3). One small peak with very low intensity for SERS spectrum, is shown in. In this sample, the graphen oxide reduced the strong coupling between Ag nanostructure and Ag NPs that we noticed it in first sample.

 Mix mix(100 µ mole TMPyP + 50 µ mole Ag nanoparticles + 50 µ mole GO)deposited in glass without Ag nanostructure, (sample 4).

The presence of TMPyP did not give any enhancement for SERS signal of GO-Ag NPs just a small peak with very intensity .The GO Raman spectra was in control, D and G bands for GO Raman spectra were very clear and there was not any effect for Ag NPs surface plasmons.

 Mix(100 µmole TMPyP + 50 µmole Ag nanoparticles + 50 µmole HCl)deposited in Ag nanostructure, (sample 5). We wanted to show if there is any effect if all previous samples mixed with acid. We chose Hydrochloric acid(HCl) with pH 0.5 and concentration 50 µmole. We chose HCl acid as common and most acid strength.

We obtained good SERS spectra with many small and approximately low intensities peaks that meant that HCl reduced the surface plasmons enhancement for Ag nanostructure and Ag NPs to SERS signals as in first sample .

 Mix(100 µmole TMPyP + 50 µmole Ag nanoparticles + 50 µmole   HCl) deposited in glass without Ag nanostructure (sample 6).

The presence of HCl reduced the GO Raman spectra, just G band peak appeared as a strongest one (peak with low intensity of SERS signal. The presence of HCl reduced the GO Raman spectra, just G band peak appeared as the strongest one.

 At last, effect of HCl on mixture (TMPyP, Ag NPs and graphen oxide) with and   without Ag nanostructure discussed. Sample (7) represented the addition of HCl on mixture(TMPyP , Ag NPs and graphen oxide) with presence of Ag nanostructure. Mix (100 µmole TMPyP + 50µmole Ag nanoparticles + 50 µmole HCl + 50 µ mole GO) deposited in Ag nanostructure.

 Presence of HCl in this mixture gave good enhancement to GO Raman peaks where these peaks clearly appeared. Also, this presence of HCl enhanced the SERS peak's value with appearance of very small peaks with this peak
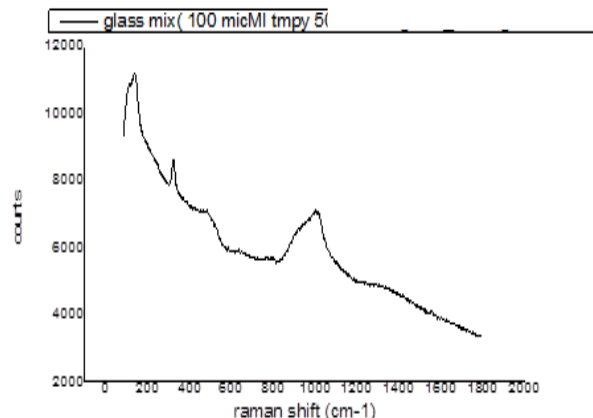
 Last sample deposited the mixture of (TMPyP-GO-HCl and Ag NPs) on glass substrate without presence of Ag nanostructure, (sample 8).
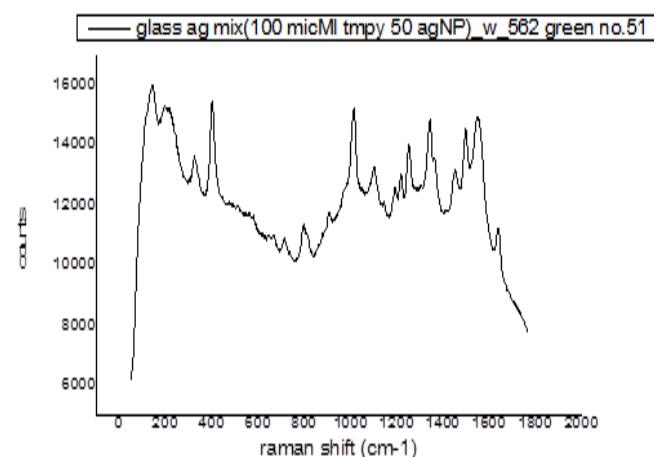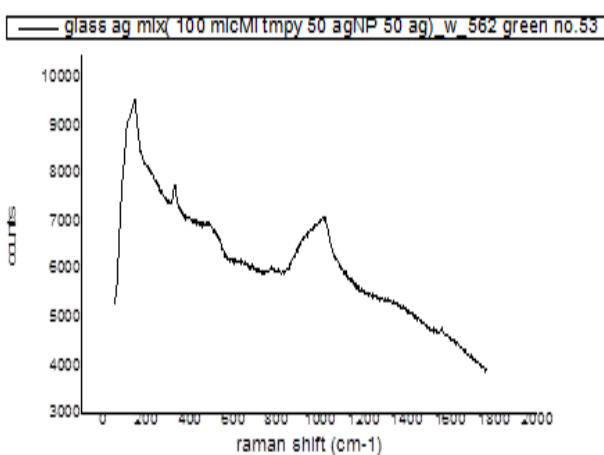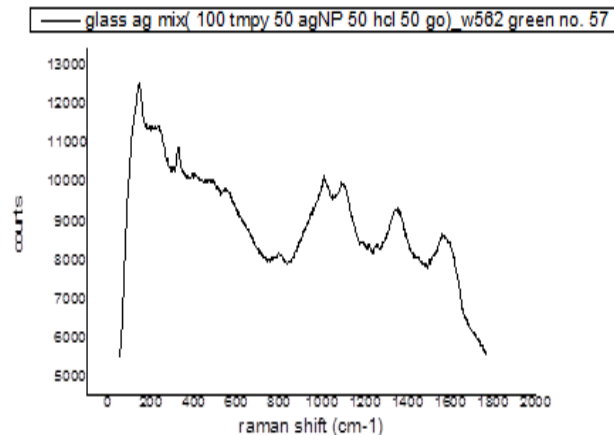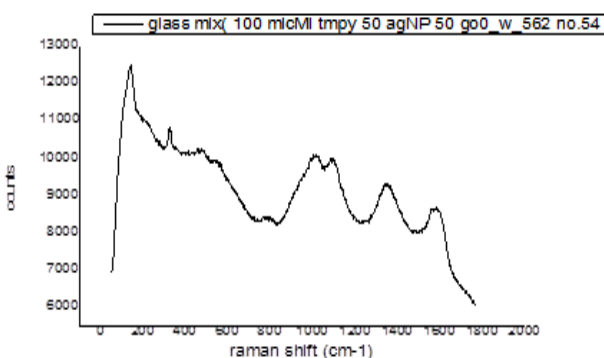

Sample (1)
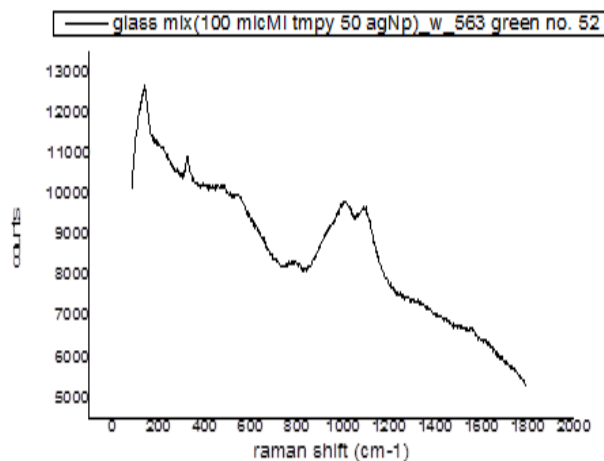
Sample (2)

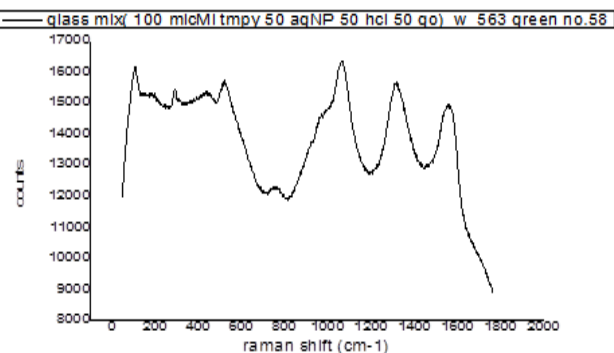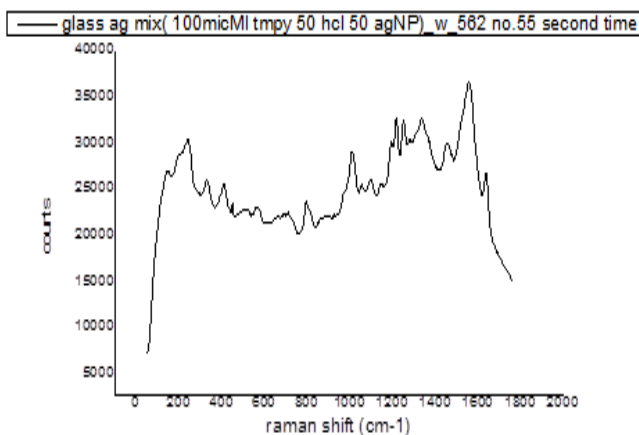**Sample(6)**

Sample (3)

Sample(7)

Sample (4)

Sample (8)

Sample (5)

SERS spectra for this sample stayed same with previous sample but with small enhancement to the one SERS peak's value and strong enhancement to GO Raman peaks.

Conclusions

The mixture of silver nanoparticles (Ag NPs) and TMPyP proved its efficiency to enhance surface

enhanced Raman scattering (SERS). That means that this mixture can be used as a good substrate in sensing and photovoltaic fields. Adding hydrochloric acid (HCl) to Ag NPs and TMPyP mixture did not give enough enhancement to SERS spectrum this might be due to the concentration used in the experiment. The plasmonic properties associated with silver nanoparticles (Ag NPs) that attached to silver nano thinfilm enabled them to be used in different applications. Given the beneficial properties of Ag NPs, as well as graphene oxide for SERS, GO-Ag NP composites should be attractive for use as a SERS substrate. GO high surface area makes it an ideal substrate for dispersion of metal NPs. Metal NPs can be grown directly on graphene oxide via a simple solution-based approach. GO itself has been used to enhance the Raman signal of target molecules.

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