Raman Scattering Enhancement by silver Nanostructures Prepared by Electrical Exploding Wire Technique

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Abstract

This project aims to fabricate nanostructures (AgNPS) using the electrical exploding wire (EEW) technique using Rhodamine 6G dye as the probe molecule, investigate the effect of AgNPS on the absorption spectra and surface-enhanced Raman scattering (SERS) activities, and advance using porous silicon as an active substrate for surface-enhanced Raman scattering (SERS). X-Ray diffraction (XRD) was used to investigate the structural properties of the nanostructures (AgNPs). Field emission scanning electron microscopy (FE-SEM) was used to investigate surface morphology. A double beam UV-Vis Spectrophotometer was used to analyze the mixed R6G laser dye(of concentration $1x\ 10^{-6}$ M) absorption spectra with the nanostructures AgNPS (of concentration $24x\ 10^{-5}$M). A sunshine Raman microscope device (the objective lens used was (50x)). was used to analyze R6G combined with nanostructures Raman spectra. All samples have shown SERS activity that increased with increasing the hot spots. The SERS enhancement factor for R6G dye(of $1x10^{-6}$ M concentration) when mixed with (AgNPS) nanostructures has reached to(2.48×10^{6}) and the lowest detection limit reached to (1×10^{-14} M) at the wave number (1652 cm^{-1}) using excited laser source (λexc. = 532nm)

Keywords: Electrical exploding cable, rough surface, surface-enhanced Raman scattering (SERS) Rh6G dye molecules, surface plasmon resonance, enhancement factor

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طيف رامان المعزز بجسيمات النانوية الفضة المحظرة بتقنية الأسلاك الكهربائية المتفجرة

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الخلاصة

يهدف هذا العمل إلى تصنيع التراكيب النانوية(AgNPs) عن طريق تقنية السلك الكهربائي المتفجر (EEW) ، دراسة التطورات في انشطة تشتت رامان المحسنة السطح (SERS) مع السيليكون المسامي الذي استخدم كركيزة نشطة , ودراسة تأثير (AgNPs) على أطياف الامتصاص وأنشطة تشتت رامان المحسنة السطح (SERS) باستخدام صبغة Rhodamine 6G كجزيئة مجس. وقد تم فحص الخصائص التركيبية للتراكيب النانوية (AgNPs) باستخدام حيود الاشعة السينية (XRD) , تم فحص مورفولوجيا السطح باستخدام field emission scanning electron microscopy. (FE−SEM) ,طيف الامتصاص لصبغة الليزرية Rh6G بتركيز(M $1x10^{-6}$) قبل وبعد ما مزج مع التراكيب النانوية (AgNPs) بتراكيز

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مختلفة تم فحصه بواسطة جهاز double beam UV−Vis Spectrophotometer. وايضا تم فحص

اطياف رامان لصبغة(Rh6G) الممزوجة مع التراكيب النانوية (AgNPs) بتركيز (M 24×10^{-5})

باستخدام جهاز A Sunshine Raman microscope system. ذي عدسة شيئية ذات تكبير (x50) .

حيث اظهرت النتائج ان SERS يزداد بازدياد النقاط الساخنة ,حيث بلغ عامل التحسين لصبغة Rh6G

(2.48×10^6) بتركيز (M 1×10^{-6}) عند عدد موجي (1652 cm^{-1}) باستخدام مصدر ليزري ذي طول

موجي (532nm) .

Introduction

There are several methods to prepare nanoscale materials by a physical technique. In this work, the electrical exploding wire technique was used because it is fast and simple in addition to its production of high purity nanoparticles. Moreover, the resulting nanoparticles have a chemical identity the same as that of the original material[1,2]. The exploding wire technique is a simple way to create metallic nanoparticles [3]. Surface-Enhanced Raman Spectroscopy (SERS) is a novel method of analysis which can quickly classify chemical and biological materials. Enormously Raman enhancement In most cases, two mechanisms can be linked: electromagnetic mechanism (EM) and chemical mechanism (CM) [4,5]. The EM improved local electromagnetic field results from resonance by surface plasmon. This mechanism happens when a metal nanoparticle reacted with incident electromagnetic field leading to the delocalization of the electron cloud. Two remarkable results are producing: provides remarkable optical properties by strong absorption band in UV –visible region and increase electromagnetic field near the nanoparticle surface. The second mechanism (CM) is processing charge transfer between chemisorbed species and substrate material[6]. Noble metal nanostructure display unparalleled optical properties because it has excitation localized plasmon[7]. The active sites found on the surface of the nanomaterial at a nanometer gap between two nanoparticles in which the electromagnetic field is present enhancement are known as hot spots [8]. It is necessary to prepare nanomaterial that contains rough surfaces and contains large numbers of hot spots that are used as a substrate to enhance the Raman spectrum. Substrates for SERS active are made from gold and other noble metals such as silver and copper. These materials have a low positive imaginary dielectric constant, which can trigger Localized Surface Plasmon Resonance (LSPR)[9,10].The porous silicon (PS) is very promising material due to its excellent mechanical and thermal properties. There are many methods for producing PS layer ; these methods are: Electrochemical etching (ECE), Photo electrochemical etching (PECE) and laser induce deep etching (LIDE)[11].

Experimental section

1-Instruments for characterization and materials

Rhodamine 6G (R6G) dye (C_28 H_31 N_2 O_3Cl, molecular weight 479.02 g/mol) was purchased from Exciton Chemical CO. INC. The dye solution was prepared using the gravimetric process, with concentrations ranging from 1x 〖10〗 ^(-6) to 1x 〖10〗 ^(-14) M. Silver wires 0.3mm in diameter, and silver plate (3cm x 2cm x 3mm)with a purity of 99.9% were purchased from local markets in Baghdad, Iraq. The nanostructures were analyzed using X-Ray diffraction (XRD), which was collected in the 2 (10–80) degree range. The morphological properties of AgNPs nanostructures were investigated using FE-SEM method. The objective lens(50x) was excited with a 532 nm laser. Raman spectra were obtained with a SunShine Raman microscope. The power of the laser used was 1mW and the integration time was 5 seconds. After combining the R6G with the AgNPs, the Raman spectra of the mixture was tested for various concentrations. Few drops of the R6G with the AgNPs mixture were placed on a porous silicon substrate, left to dry in natural light, and subsequently the nanostructures were examined with a UV-Vis double beam spectrophotometer (SHIMADZU-1800) for the absorption spectra at a concentration of (1x 〖

10⟧ ^(-6) M) in the wavelength range (300-800) nm. All samples were held at room temperature. After a few drops of AgNPs nanostructures were dried on a porous silicon .

2- The EEW technique was used to prepare AgNPs Nanostructures.

anti-shock container containing 30ml of deionized water was used to prepare the nanoparticles. Figure 1 illustrates the preparation system. AgNPs were prepared by exploding pure Ag wire (0.4 mm diameter) with an Ag plate held at 80 V relative to the wire and a current of 100 A. Contact between the wire and the plate, the electric exploding wire was completed.
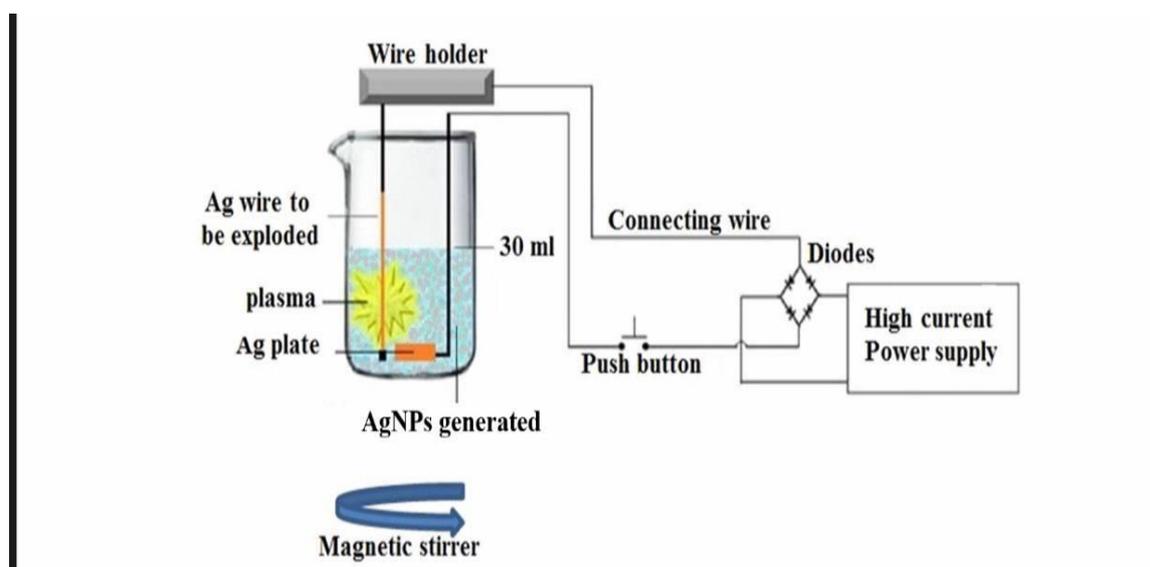
Figure 1- A diagram of the set-up for the nanoparticles preparation o the nanoparticles

3- Preparation porous silicon

n-type silicon wafer was cut to 1 cm pieces which were cleaned with deionized water and alcohol. Hf was diluted 1: 1, and these pieces were placed in the ps Preparation system for 10 minutes.

4-Preparation of SERS substrates

For Raman spectrum analysis, R6G dye, with concentrations of 1x $10^{-6}$to 10 x10^{-14} M, was mixed with the desired concentration of AgNPs nanostructures, then deposit on porous silicon substrates and allowed to dry at room temperature.

Result and discussion

1- X-ray diffraction patterns of AgNPs nanostructure

Figure 2 shows typical XRD patterns of AgNPs nanostructures. The prepared AgNPs nanostructures were found to have a face-centered cubic phase. Four peaks were observed at (2θ) degrees of 38.116 ˚, 44.227 ˚, 64.425 ˚and 77.472 ˚which was indexed to (hkl) values of (111),

(200), (220) and (311), respectively. The value of the interplanar spacing between the atoms, d, was calculated using Bragg's Law, 2dSinθ = nλ, where n is the order of diffraction pattern,. in the present case n is equal to 1. From the four data sets of the four peaks, four values of 'd' were calculated (2.3485, 2.0319, 1.4371 and 1.2284)$A^{°}$ fot the (111),(200), (220) and (311), respectively. It can be seen that the four values are nearly the same. Lattice constants were estimated using the formula, a = d*$\sqrt{(h^2+k^2 + l^2}$). The average of the four values of 'a' calculated from the four values of 'd' as obtained from the data for the four peaks was found to be 4.0676 Å. This is in fair agreement with the standard value for silver which is 4.0857 Å. From Figure 2, it can be seen that the (111) peak is sharp, which means that the nanoparticles are pure. This indicates that the EEW-prepared AgNPs nanostructures did not oxidize during

or after the process, preserving their high purity and crystalline quality. The XRD pattern peaks locations are close to that of the normal bulk silver (the same as JCPDS Card No. 4-0783).
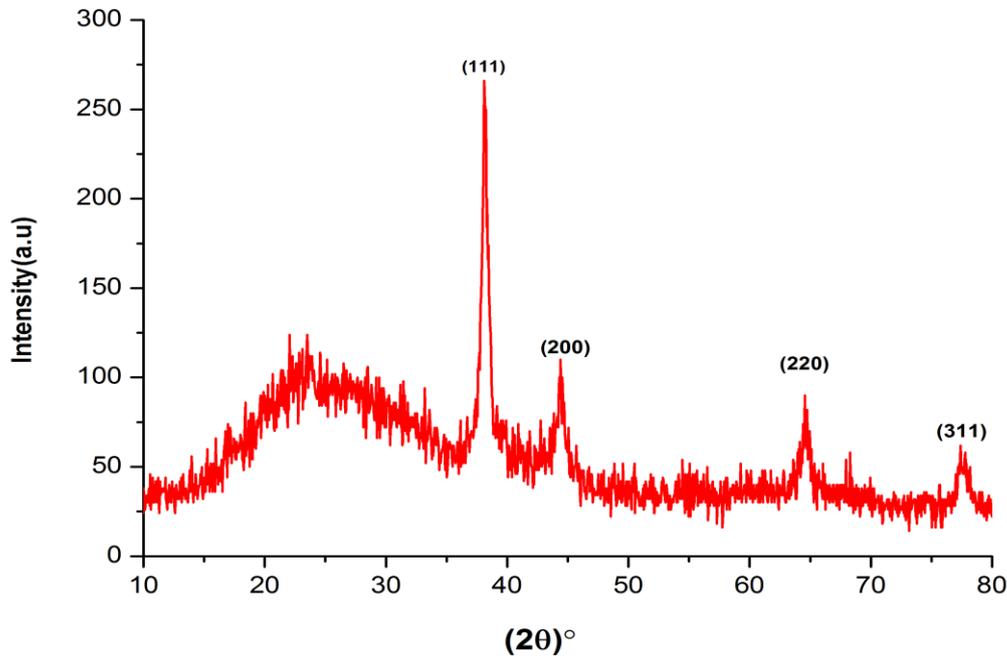
Figure 2-AgNPs X-ray Diffraction Patterns
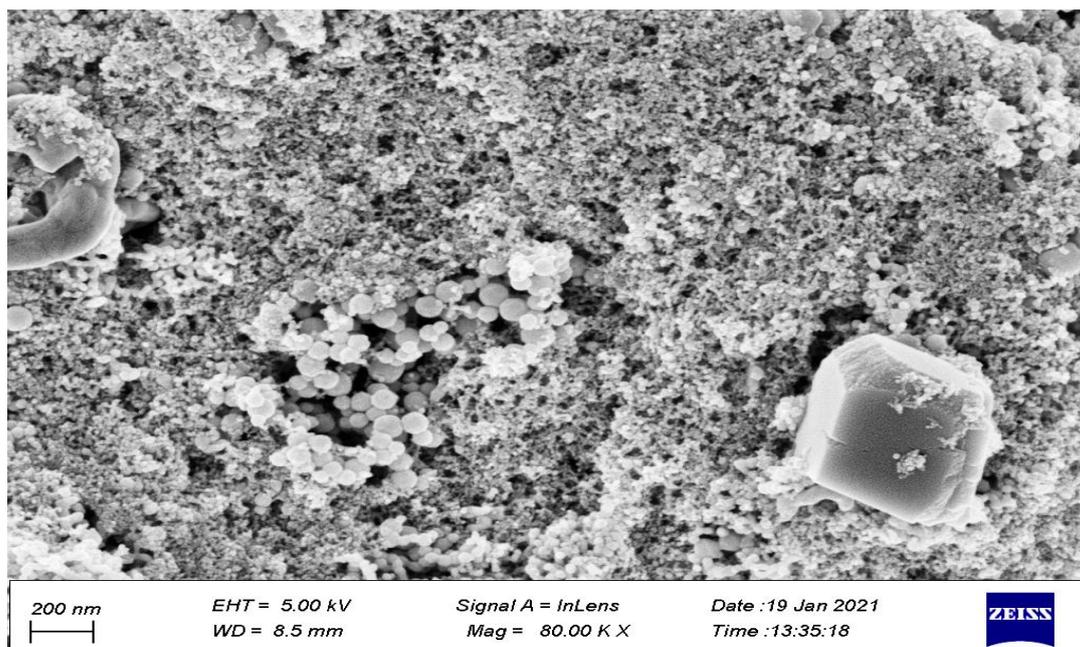
2- Absorption spectra of UV-Visible light

Figure 3 illustrates the UV–Visible absorption spectra of AgNPs of different concentrations ($96 \, X \, 10^{-5}$, $48 \, X \, 10^{-5}$, $24 \, X \, 10^{-5}$, $12 \, X \, 10^{-5}$ and $6 \, X \, 10^{-5}$M) and with a concentration of ($1x10^{-6}$ M) R6G dye. Surface plasmon resonance peaks were distinctive and their locations are almost constant. In Figure 3(a), the surface Plasmon resonance (SPR) of the AgNPs appeared at 406nm, and the SPR peak intensity increased with increasing the AgNPs concentrations. The increase in the intensity of SPR peaks is due to the increase in resonance between the collective oscillations of conduction electrons with incident electromagnetic field. On the other hand, as shown in Figure 3(b), the absorption peak position of R6G ($1x10^{-6}$ M) was at 525nm. The absorption peak of the R6G dye increased with increasing the AgNPs concentration. The intensity of the SPR peaks of the AgNPs decreased after AgNPs was mixed with the dye because the energy is transferred from the nanoparticles to the dye[12] .
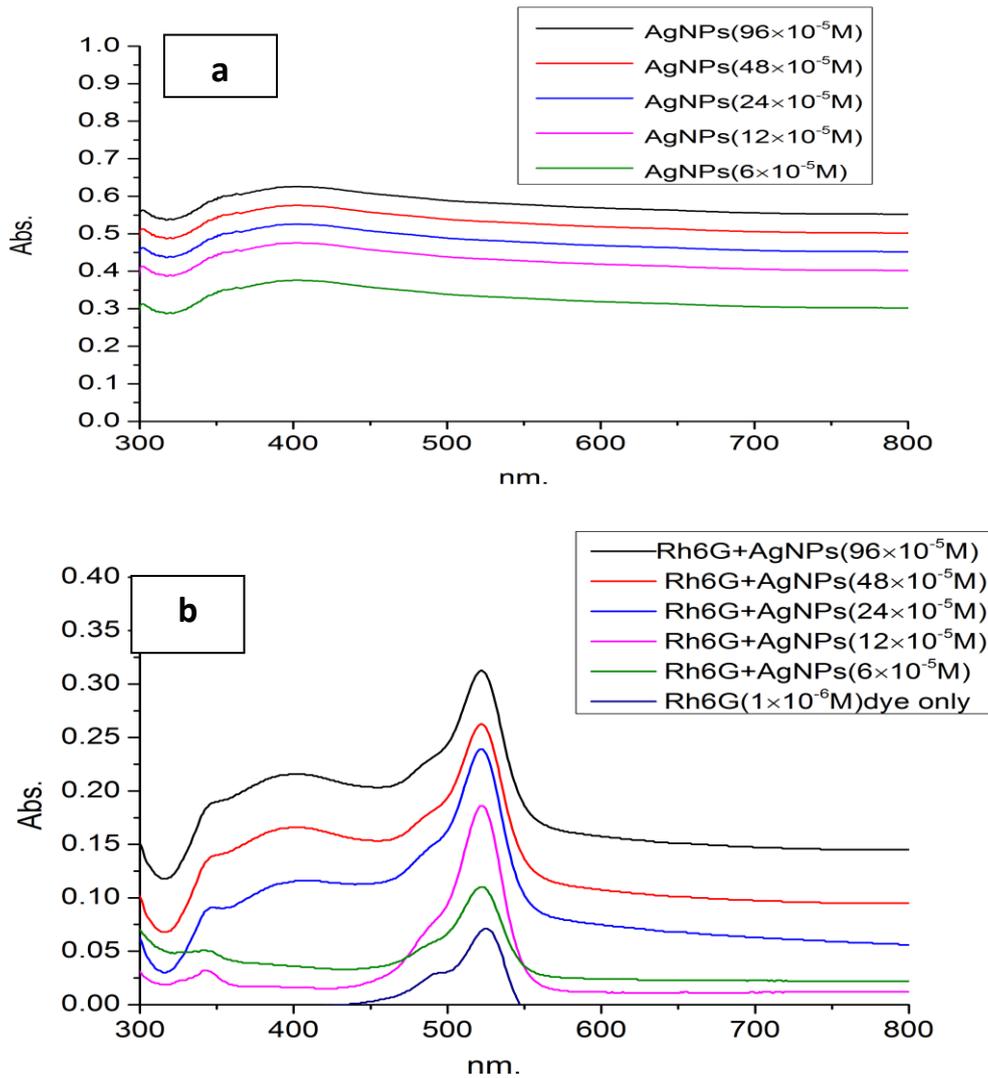
Figure 3- The UV- Visible absorption spectra of various AgNPs concentrations(a) without R6G and(b) with R6G dye $(1 \times 10^{-6} M)$

3- FESEM image analyses

Figure 4 shows FESEM images displaying the AgNPs morphology and particle size. It can be seen that the AgNPs have average size of about (44nm). The AgNPs are nearly spherical and slightly agglomerated. The process of forming nanoparticles results from the fusion and explosion of the wire. There is no nucleation and growth process, as the process is up- down.

200 nm	EHT = 5.00 kV	Signal A = InLens	Date :19 Jan 2021	ZEISS
⊢―――⊣	WD = 8.5 mm	Mag = 80.00 K X	Time :13:35:18	

Figure 4- FESEM image of AgNPs prepared by EEW technique

4- Rhodamine 6G Raman spectra

The R6G dye was used as probe molecules to prove the capability of the prepared AgNPs for enhancing SERS signals and testing its ultra-sensitivity. Figure 5 shows the Raman spectra of 1×10^{-1} M concentration R6G molecules, as well as the spectra of R6G molecules at different AgNPs concentrations (1×10^{-6} M to 1×10^{-14} M). AgNPs nanostructures with a concentration of 24×10^{-5}M were deposited and desiccated onto slides of porous silicon, then the R6G dye of different concentrations was deposited above the nanostructure. All samples have shown SERS activity and distinctive peaks of the R6G dye after being excited with 532nm wavelength and 4.5mW power laser source. The positions of the peaks were at wavenumbers (610 , 776, 1185 , 1312,1361 ,1510 ,1575 and 1652 cm^{-1}) which belong to the modes (C-C-C ring in –plane vibration) , (C-H out of –plane bend) ,(C-H in-plane bend) ,(N-H in-plane bend) ,(C-C stretching) , (C-C stretching) , (N-H in-plane bend) and (C-C stretching), respectively. Raman shift was noted in spectral range from 400 to 2000 (cm^{-1}). The AgNPs nanostructure have large number of hot spots, nanogaps and interstices. The detection limit for Rh6G ranged from 10^{-6} M to 10^{-14}M. Figure 5 shows that the peak intensity decreases with decreasing the concentration . The optimum value is the lowest detectable concentration of Raman values for R6G with resolution limit.
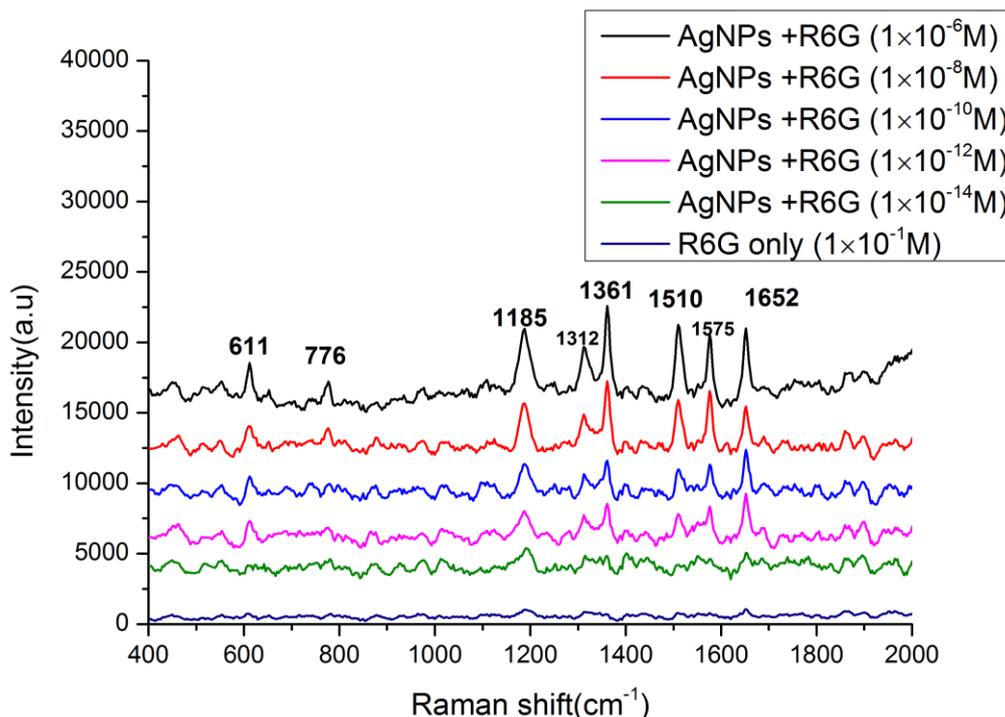
Figure 5- Raman spectra of Rh6G (10^{-1} M) on porous Si and Rh6G of 10^{-6} M to 10^{-14} M concentration of AgNPs.

The enhancement factor(EF) is one of the main aspect of characterization of SERS substrates. It can be calculated using the mathematical equation:

$$\mathbf{EF} = \frac{\mathbf{I_{SERS}}}{\mathbf{I_{bulk}}} \ \mathbf{x} \ \frac{\mathbf{c_{bulk}}}{c_{SERS}}$$

Where

I_{SERS} is the intensity of the certain Raman band of the target on nanostructure as surface enhance Raman spectroscopy substrate.

I_{bulk} is the intensity of certain Raman bulk of the target without any effect of the surface enhance Raman spectroscopy.

c_{bulk} is the concentration of target molecules is using for SERS.

c_{SERS} is the concentration of target molecules is using for non-SERS.

Figure 6 shows the highest peak for Raman signal, the value of I_{SERS} taken at the wave at (1652 cm^{-1}) and the vibration mode (C-C stretching) is equal to 20141.8. Since the fluorescence is the most prominent characteristic of the aqueous drop of Rh6G dye luminescence, it is impossible to get an adequate value to Raman signal(I_{bulk}), the maximum value of I_{bulk} is (809) in range of the detector noise. The concentration of Rh6G dye solution was (1x $10^{-1}M$) without AgNPs nanostructure and (1x $10^{-6}M$) when mixed with with AgNPs nanostructure. The enhancement factor for AgNPs nanostructure was calculated to be (2.48 x 10^{6}). It is worth noting that SERS has been improved. Intensity due to the prepared AgNPs is attributed to a well-known fact, that the properties of SERS are significantly increased when AgNPs are contiguous enough to create coupling between localized surface plasmon resonances. Plasmonic resonance coupling is thought to occur at NP-NP distances under one diameter of the nanoparticles and generates strong local excitation fields.
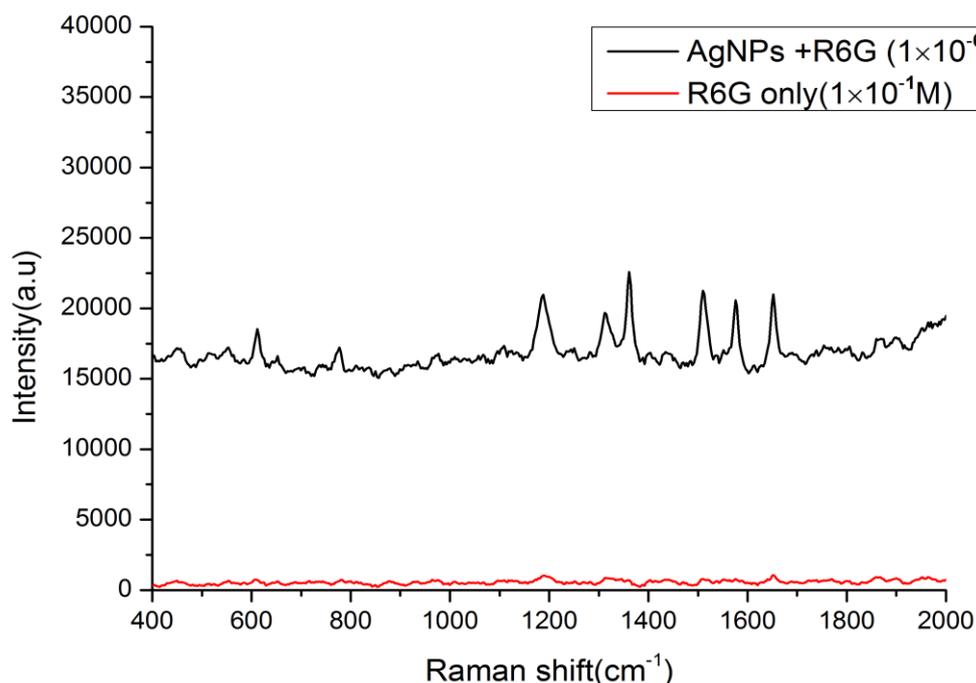
Figure 6- Raman spectra of Rh6G dye (10^{-1} M) only and Rh6G dye (10^{-6} M) mixed with AgNPs nanostructures.

Conclusions

    It can be concluded that the electrical exploding wire technique for fabricating AgNPs nanostructure is both effective and simple. The nanostructures were used as a Raman single enhancement substrate. According to the XRD patterns and FE-SEM images, the fabricated nanostructures have a rough surface with many hot spots. Since the EM field is concentrated, a larger hot spot increases the detection limit. As Rh6G dye molecules are combined with fabricated AgNPs nanostructures, many desirable optical and electronic properties are enhanced, which can be used in a variety of applications such as chemistry.

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