Enhanced Raman Scattering in Colloidal -Comparison of Surface Silver Nanostar and Colloidal Silver Nanocubes

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Abstract

Surface-enhanced Raman spectroscopy (SERS) is an extremely responsive and selective method that improves the Raman scattering signals of molecules utilizing nanomaterials as substrates. SERS enables the identification of material in very low concentrations via electrical field amplification or chemical enhancement due to the localized surface Plasmon (LSP). In this work, low concentrations of sodium sulfate (Na2SO4) were investigated as a water pollutant using liquid SERS based on colloidal Ag nanostructures. Two types of Ag nanostructures were prepared and utilized as liquid SERS substrates: nanostars (NSs) and nanocubes (NCs). A chemical reduction method was used for synthesizing Ag nanostructures from silver ions using reducing agents. An atomic force microscope (AFM) and Scanning Electron Microscope (SEM) were employed to characterize the nanosilver. The SERS actions of these nanostructures in detecting sodium sulfates were reported and analyzed concerning both shape and size using a 532 nm diode-pumped solid-state laser. We observed that nanostructures with more and more shaped corners gave stronger SERS signals. The increase in the SERS signal is related to LSP, which results from the deposition of sodium sulfate molecules in the hotspots (spaces between aggregated silver nanostructures) in the solution. Raman peaks intensify as the sulfate concentration increases. The proposed AgNS colloid provides stronger SERS activity than the AgNC colloid. This means that AgNS as liquid SERS substrates are more efficient at detecting low concentrations of analytes than AgNC. The highest sulfate analytical enhancement factor (AEF) obtained for SERS in both colloids, AgNS and AgNC, were at the lowest concentrations (7x10^-7 M), which were 2.6 x10^3 and 1.7x10^3, respectively.

Keywords: AgNps, Hotspot, Raman spectroscopy, Sodium sulfates, Surface Plasmon resonance.

Introduction

Raman spectroscopy is a vibrational spectroscopy method that can be used to analyze and identify solids, liquids, and gases, but it has only recently been utilized to investigate species in rather complex mixture1,2. It can be used to recognize various compounds since each Raman line
corresponds with a vibration mode in a specific chemical bond, so compounds with anions like \( \text{PO}_4^{3-} \), \( \text{NO}_3^- \), \( \text{NO}_2^- \), and \( \text{SO}_4^{2-} \) are capable of being identified using Raman spectroscopy\(^1,3,4\). However, according to statistics, Raman scattering was difficult to detect as only one of every 1–10 million photons that incident a sample causes Raman scattering\(^5\). Therefore Raman technology has not really been considered as a tool for routine environmental monitoring due to the weak signals of low-concentration detection.

Raman-based techniques may become more widely used because of the most recent developments in reproducible surface enhancement Raman spectroscopy (SERS) substrates and methodology. SERS, first observed in 1974, greatly increases the sensitivity of Raman spectroscopy by using noble materials such as Au, Ag, and Cu nanostructures as substrates. It is an extension of conventional Raman spectroscopy that relies on electronic and chemical interactions between the excitation laser, analyte of interest, and SERS substrate\(^5,6\). SERS is potent fingerprint spectroscopy that can in situ identify the active sites and the surface reaction intermediates during catalytic processes since it can produce surface-sensitive as well as chemical bond-specific signals at the atomic level\(^7\). By adjusting the colloidal particle sizes, shapes, and compositions, an enhancement factor of up to 14 orders of magnitude has been achieved for SERS substrates\(^8\). When molecules are adsorbed onto corrugated metal surfaces, such as silver or gold nanoparticles (NPs), the inelastic light scattering by molecules is significantly increased (by factors up to \( \times 10^8 \) or even larger, enabling single-molecule (SM) SERS in some cases), see Fig. 1. Raman signal is produced by the absorption of a photon with an incidence of frequency \( \omega_{\text{in}} \) coupling to an internal degree of freedom of the molecule, typically a molecular vibration of frequency \( \omega_{\text{vib}} \), and re-emission at different frequencies \( \omega_{\text{em}} = \omega_{\text{in}} \pm \omega_{\text{vib}} \), see Fig 1, where the sum/difference results in anti-Stokes/Stokes Raman scattering, respectively. Three inelastic transitions are therefore involved in the process (absorption vibrational, excitation, and re-emission)\(^9\). As plasmonic nanodimers, nanorods, nanotriangles, and nanostars, a huge variety of geometries have been studied\(^10\).

In SERS, localized surface plasmon resonances (LSPR) supported by metal nanostructures are excited, which significantly increases the amount of Raman scattering from molecules adsorbed on or near the metallic surface. An ultrasensitive plasmon-enhanced spectroscopic method has been created as a result of this effect, which maintains the inherent structural specificity and experimental flexibility of Raman spectroscopy\(^11\).

![Figure 1. SERS involves inelastic light scattering by molecules adsorbed\(^9\)](image)

The aim of this study is to compare liquid surface-enhanced Raman spectroscopy use on Ag colloid nanostars (NSs) and nanocubes (NCs).

**Materials and Methods**

**Synthesis of silver nanocube (AgNCs)**

A typical method for producing silver nanocubes (AgNCs) involves covering a 20 mL vial containing 5 mL of ethylene glycol (EG), and heating it for one hour in an oil bath at 140°C while stirring. 1 mL of (3mM solution in EG) of HCl was then quickly added. After 10 min, 3 mL of (94 mM solution in EG) of AgNO\(_3\) and 3 mL of 147mM of polyvinyl pyrrolidone (PVP) were added dropwise to the stirring solution. Upon adding the solution of AgNO\(_3\), the color changed to light yellow\(^{12}\). The vial was then covered and heated at 140°C.

**Synthesis of silver Nanostar (AgNS)**

Silver nitrate (AgNO\(_3\)), tri-sodium citrate (TSC), hydroxylamine (HA) solution (50 w/w in water), and sodium hydroxide (NaOH) solutions were prepared
in double-ionized water. 1mL of $6 \times 10^{-2}$ M HA was mixed with 1mL of NaOH (0.05 M) then, 20 mL of $10^{-3}$ M AgNO$_3$ was added dropwise to the first solution under agitation. After 5 min, 200 μL of $4 \times 10^{-2}$ M (1%, w/v) TSC was added to the mixture. The final suspension was shaken for 15 min before measuring a pH of 5.5. Scanning electron microscopy (SEM) images were obtained using Axia Chemi SEM, at 30 kV accelerating voltage. Atomic Force Microscope (Model TT-2 AFM workshop) was employed to examine both Ag nanocolloidals.

**Preparation of samples for SERS spectra**

Four solutions of Sodium sulfate with different concentrations were prepared in each AgNS and AgNC colloidal: $0.7 \times 10^{-3}$, $0.7 \times 10^{-4}$, $0.7 \times 10^{-5}$, and $0.7 \times 10^{-6}$ M, and one sample of $7 \times 10^{-3}$ M Sodium sulfate diluted in distilled water for comparison. The eight SERS samples and the bare one were measured in glass vials focusing the laser beam inside. Raman scattering measurements were performed using a 532 nm Pre-configured Raman Spectrometer System. Samples were excited by a 532 nm laser line provided by a frequency-doubled Nd:YAG laser achieved by using a nonlinear crystal (KTP) and a laser power of 70 mW at the sample with the integration time of 9 s. The spectral resolution was set in all cases to 2 cm$^{-1}$. SERS spectra were registered with a total acquisition of 10s for each SERS spectrum and consisted of only one scan.

**Results and Discussion**

The nanosilver colloids (NSs and NCs) were utilized as liquid SERS sensors for intensifying the Raman signal of sodium sulfate. The sodium sulfate absorbance was first measured with UV-Vis before using the liquid SERS system. The absorbance result of sodium sulfate is shown in the range of 281–330 nm, as depicted in Fig. 2. The 532 laser source in the Raman measurement is appropriate for being not close to the absorbance area of the sodium sulfate to avoid the Rayleigh scattering.

The size and shape of Ag nanostructures were examined by the scanning electron microscope (SEM) image. The presence of AgNSs and AgNCs was clearly detected. SEM images began to show the aggregated silver nanostructures with approximate sizes ranging from 33 to 178 nm for AgNSs and from 37.5 to 165 nm for AgNCs as shown in Fig. 3 a, and 3 b. We also observed other nanostructures with irregular shapes due to the aggregation of the nanostructures.

![Figure 2. The UV-Vis absorption spectra of sodium sulfate.](image-url)
AFM images with nanoparticle (NP) size distribution of AgNS and AgNC are shown in Figs. 4a, and 4b, respectively. Before samples were examined with AFM, the agglomeration in the silver nanoparticles (AgNPs) was broken up ultrasonically, so the irregular nanostructures, we have previously mentioned, were not detected in the AFM characterization. The images indicate that the cluster formations of nanosilver in the topographic distribution of both samples are uniform and the average NP diameter of the AgNPs samples was found to be 37.68 nm for AgNS and 85.61 nm for AgNC. Also the test showed the density of the two silver nano colloidal solutions which were 434 million particles/mm² for AgNS, and 384 million particles/mm² for AgNC.

The SERS spectra of sodium sulfate diluted in distilled water (0.7 x10⁻³M) compared with three samples of SERS of sodium sulfate (Na₂SO₄) diluted in AgNP colloidal are shown in Figs. 5a, and 5b. The main peak corresponds to the v₁ mode centered at 980 and 983 cm⁻¹ which refer to modes of the SO₄²⁻ ion.
Other modes detected in lower and higher wavenumber sides respectively are clearly seen in the spectra, where four characteristic peaks were found beside the main peak at 445, 620, 1121 and 1155 cm$^{-1}$ in Figs. 5a, and 463, 629, and 1153 cm$^{-1}$ in Fig. 5b. From the spectra we notice that the presence of nanosilver with (Na$_2$SO$_4$) solution improved the Raman signal for sulfate. From the results, it can be said that Ag nanostructures contribute significantly to enhancing the Raman signal.

Figure 5. SERS spectra of sodium sulfate of concentrations from 0.7x10$^{-6}$M to 0.007M diluted in: (a) AgNS solution and (b) AgNC.

When dissolved sulfate molecules in Ag nanocolloidal interact with "hotspots", which are often nanogaps between neighboring metal nanostructures or surrounding metal nanostructure tips as shown in Figs. 3a, and 3b, the electromagnetic field intensifies thus the Raman signal enhances. The colloidal NPs were purposefully made to be aggregated to form hotspots.

The SERS effect has two mechanisms: an electromagnetic (EM) and a chemical (CM) that work together to simultaneously boost the Raman signal. The localized surface plasmon resonances (LSPR) induced local rise in an electric field close to the nanoparticles has an impact on electromagnetic enhancement. The CM results from charge-transfer interactions between the surface of the nanoparticles and the electronic states of the molecules, which will also result in an increase in Raman signals. As a result, the surface plasmon resonance (SPR) is what the EM depends on, whereas the Raman-active molecule and its interaction with nanoparticle surfaces determine the CM.

We can say that our results were influenced by the high electric field of AgNPs. Based on the observation of the significant red shift of the $\tilde{\text{SO}}_4^-$ symmetric stretching frequency and the deposition of sulfate on AgNSs were better than they were on AgNCs; because the shape of the star has more arms and sharper edges than the shape of the cube and thus the hot spots are more in the NSs than those in the NCs. From the spectra we can notice that when the sulfate concentration increases, Raman intensity also increases; because the sulfate particles deposited on AgNps increase, the enhanced Raman scattering increases as well; see Figs. 6a, and 6b.
Figure 6. SERS intensity of the main peak against sodium sulfate concentration of samples with: (a) Ag Nanocubs and (b) Ag Nanostar.

The analytical enhancement factor (AEF) is one of the essential metrics that is widely used to quantify the direct SERS enhancement result from EM and CM\(^20\). AEF equation is an analytical approach to evaluate signal enhancement, relating signal intensity to analyte concentration \(C\). When it is difficult to estimate the number of analyte molecules present, this metric is useful, particularly for analytes with no particular affinity for the plasmonic surfaces.

\[
\text{AEF} = \frac{I_{\text{SERS}}/C_{\text{SERS}}}{I_{\text{NRS}}/C_{\text{NRS}}}
\]

Where; \(I_{\text{NRS}}\) and \(I_{\text{SERS}}\) refer to the counterpart intensities of normal Raman and SERS, respectively, \(C_{\text{NRS}}\) and \(C_{\text{SERS}}\) are the concentrations of the analyte in the normal Raman and SERS liquid substrates, respectively.

Figure 7. Dependence of AEF on concentration of sodium sulfate with: (a) Ag Nanocubs at highest peak of 983 cm\(^{-1}\) and (b) Ag Nanostar at highest peak of 980 cm\(^{-1}\).

The AEF versus the concentrations of sodium sulfate solution is shown in Fig 7a, and 7b. We can see a non-linear rise of the AEF with a decrease in sulfate concentration. Very low concentrations of molecules increase the probability of target molecule localization; which leads to its detection and thus increases the AEF by strengthening the SERS signal. The highest sulfate analytical enhancement factor obtained for SERS in colloidal NS was \(2.6 \times 10^3\) at \(7 \times 10^{-7}\) M (the lowest concentration), and was \(1.7 \times 10^3\) at \(7 \times 10^{-7}\) M (the lowest concentration) for SERS in colloidal NC. This means that AgNSs as liquid SERS substrates are more efficient in detecting low concentrations of analytes than AgNCs. The difference in (AEF) was mostly attributed to the variance in the overlap between the laser source and surface plasmon resonance (SPR) bands as a function of size and degree of edges. The electromagnetic mechanism of aggregated AgNS generates numerous hotspots from abundant nanogaps on AgNSs for ultrasensitive detection of sulfate molecules.
Conclusion

Sodium sulfate was investigated as a pollutant using liquid SERS based on two types of colloidal Ag NPs: star and cube. The NP's structure with more and shaper corners gave stronger SERS signals. The increase in the SERS signal is related to the deposition of sodium sulfates (Na₂SO₄) molecules in the aggregated silver nanostructure in the solution. Raman peaks were increased with the increase of the sulfate concentration. The proposed AgNS structure provides stronger SERS activity than AgNCs. The highest sulfate AEF obtained for SERS in colloidal Nanostar was 2.6×10⁴ at 7×10⁻⁷ M (the lowest concentration) and was 1.7×10³ at 7×10⁻⁷ M (the lowest concentration) for SERS in colloidal NC. This means that AgNS as a SERS substrate is more efficient in detecting low concentrations of analytes than AgNC.

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Authors’ Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

Authors’ Contribution Statement

Z S Sh. and A A D implemented, designed and built the system, conducted all practical experiments, obtained readings and results, and presented them. S K Y. undertook the general supervision of the research and the discussion of the obtained results and the method of presenting them.

References


مقارنة بين تشتت رامان المعزز بالسطح في محلول الفضة الغروي النانوي النجمي والنانوي المكعب الشكل.

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الخلاصة
بعد تشتت رامان المحسن بالسطح (SERS) طريقة سريعة الاستجابة وانتقائية للغاية تعمل على تحسين إشارات تشتت رامان للجزيئات (Na_2SO_3) التي تستخدم المواد النانوية كركاز. يتيح تحديد مادة تراكيز منخفضة جداً عن طريق تضخيم المجال الكهربائي أو التحسين Plasmon (LSP) الكيميائي بسبط السائل. في هذا العمل، تم فحص التراكيز المنخفضة من كبريتات الصوديوم من كبريتات الصوديوم (Na_2SO_3) من أجل استخدامها كركازات SERS نجمية ومكعبية الشكل، واستخدامها كمرشحات SERS سائلة. تم استخدام طريقة الاختزال الكيميائي لتركيب الهياكل النانوية من أيونات Ag من أجل التوصيف الفصمة (SEM) والمجال الماسح الإلكتروني (AFM) للفصمة باستخدام عوامل التسيير الكيميائي. تم استخدام مجهر القوة النحيلة لمتابعة التغييرات في كبريتات الصوديوم (Na_2SO_3) وتحليلها فيما يتعلق بصرف إشارات SERS. تم الإبلاغ عن إجراءات تشتت رامان النانوية في الكشف عن كبريتات الصوديوم (Na_2SO_3) بشكل من السهل والتحليل باستخدام ليزر 532 نانومتر. لاحظنا أن بيئة السطح النانوية ذات الزوايا الأكثر عددًا والأكثر حدًا أعطت إشارات SERS أقوى وأكثر ترسب كبريتات الصوديوم في النقاط الساخنة LSP مع إثراء التراكيز المنخفضة في محلول في حالة التراكيز المنخفضة (مدايا بين الهياكل النانوية للفرن النانوية) في محلول في حالة التراكيز المنخفضة. لوحظ زيادة قم رامان مع زيادة تركيز الكبريتات. يوفر هيكلاً للقضاء النانوي النجمي المحتفل نمايا في الهياكل المعبّرة النانوية. أيضًا، يلعب تركيز الكبريتات دورًا رئيسيًا في الكشف حيث تصبح إشارة رامان أقوى مع زيادة التركيز.

كان أعلى معامل تعزيز تحليل لـ SERS في محلول الفضة النانوي الغروي 10^3 × 7 عند 7 مل بـ 10^7 مل بـ 10^3 مل. كان SERS في محلول الغروي النانوي النجمي الفضة 2.6 × 10^7 عند 7 مل بـ 10^3 مل بـ 10^7 مل بـ 10^3 M. يمكن أن يعتبر هذا النتائج إشارة قوة وفعالية SERS في حقول الفضة النانوي المكعب الغروي.

الكلمات المفتاحية: دقائق الفضة النانوية، النقاط الساخنة، مطيافية رامان، كبريتات الصوديوم، الرنين السطحي البلازموني.