Effect of halide ions on the surface-enhanced Raman spectroscopy of methylene blue for borohydride-reduced silver colloid

Xiao Dong, Huaimin Gu*, and Fang Liu
MOE Key Laboratory of Laser Life Science, College of Biophotonics, South China Normal University, 510631, Guangzhou, China

Abstract. The surface enhanced Raman scattering (SERS) spectrum of methylene blue (MB) was studied when adding a range of halide ions to borohydride-reduced silver colloid. The halide ions such as chloride, bromide and iodide were added as aggregating agents to study the effects of halide ions on SERS spectroscopy of MB and observe which halide ion gives the greatest enhancement for borohydride-reduced silver colloids. The SERS spectra of MB were also detected over a wide range of concentrations of halide ions to find the optimum concentration of halide ions for SERS enhancement. From the results of this study, the intensity of SERS signal of MB was enhanced significantly when adding halide ions to the colloid. Among the three kinds of halide ions, chloride gives the greatest enhancement on SERS signal. The enhancement factors for MB with optimal concentration of chloride, bromide and iodide are $3.44 \times 10^4$, $2.04 \times 10^4$, and $1.0 \times 10^4$, respectively. The differences of the SERS spectra of MB when adding different kinds and concentrations of halide ions to the colloid may be attributed to the both effects of extent of aggregation of the colloid and the modification of silver surface chemistry. The purpose of this study is to further investigate the effect of halide ions on borohydride-reduced silver colloid and to make the experimental conditions suitable for detecting some analytes in high efficiency on rational principles.

1. Introduction

Since the phenomenon of surface-enhanced Raman scattering (SERS) was discovered by Fleischman in 1974 [1], and was explained partially by Jeanmaire in 1977 [2], SERS has excited significant interest in many research fields [3-6]. The enhancement of Raman signal in SERS is related to the so-called “SERS-active substrates” which are various metallic structures with sizes on the order of tens of nanometers. It is well known that “surface roughness” is the key factor for such enhancement in SERS. However, the mechanisms giving rise to the surface enhancement is not quite clear yet. In general, the explanation is due to two mechanisms: the electromagnetic mechanism and the charge transfer mechanism [7]. Among the various SERS-active substrates, silver colloids are the most

* Corresponding author. Tel.: +86-20-85216972, E-mail: guhm@scnu.edu.cn

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commonly used SERS active substrates due to their better enhancement effect and simple preparation.

In this paper, borohydride-reduced silver colloid were used as SERS-active substrate for its highly SERS-active features and particle stability. The halide ions such as chloride, bromide and iodide were added as aggregating agents to study the effects of halide ions on SERS spectroscopy of MB and to observe which halide ion gives the greatest enhancement for borohydride-reduced silver colloid. MB was chosen as target molecule because MB has a very strong SERS signal. The SERS spectra of MB were also detected over a wide range of concentrations of halide ions to find the optimum concentration of halide ions for SERS enhancement. The degree of aggregation and the morphology of particles in colloid could be estimated by the absorption spectra. From this study, some general principles that could be used to guide the choice of conditions which would give the result were found. The purpose of this study is to further investigate the effects of halide ions on borohydride-reduced silver colloid and to make the experimental conditions suitable for detecting some analytes in high efficiency on rational principles. In addition, this study will have a profound implication to SERS users about their interpretation of SERS spectra when obtaining these anomalous bands.

2. Experimental

2.1. Instrumentation

A 785nm Semiconductor laser was used as excitation source. The Raman system was equipped with a BX-41 Olympus microscope and 45x objective. Spectrometer system (Acton spectro@2300i, Princeton Acton, USA), was used with a 1200 gr/mm holographic grating. An air cooled CCD detector (Pixis 256, Princeton Acton, USA) was used for measuring the Raman signal by an integration method. The signals were detected at concentration of 2.5 mM. The laser power at the sample was 2mW. The concentration of aggregating agents which was added to the colloid was 0.02 M (to final concentration). The Raman spectrum and absorption spectrum were obtained at room temperature. The absorption spectra were detected by spectrophotometer (Lamda 35, PE company, USA). The data processing was operated by using Origin 7.5 software.

2.2. Materials

Silver nitrate (AgNO₃), Sodium bohohydride (NaBH₄), and Methylene blue (MB) were purchased from Sigma. Sodium chloride (NaCl), sodium iodide (NaI), and sodium bromide (NaBr) were purchased from Sangon. The tri-distilled water was used for all solution preparation.

2.3. Silver colloids and Sample preparation

The silver colloid was prepared by Dirk and Charles borohydride-reduced method [8]. a. 8.5 mg AgNO₃ was dissolved in 50 ml H₂O to yield 10⁻³ M AgNO₃ solution. b. 11.349 mg NaBH₄ was dissolved in 150 ml H₂O to yield 2×10⁻³ M NaBH₄ solution. c. 50 mL AgNO₃ solution was added dropwise to 150 mL of ice-cold NaBH₄ solution and the mixture was stirred vigorously. d. The stirring continued for one hour until glassy yellow colour was obtained. The silver colloid was stored in an amber bottle and was laid in dark place. The UV/vis absorption spectrum of the colloid has a maximum absorption band at 392 nm with a full width half-maximum (fwhm) of 50 nm. The sample that was used for Raman studies was MB. The concentration of MB solution was 1×10⁻⁴ mM (to final concentration). The solution was stored at ambient temperature. 30 µL aggregating agent and 250 µL MB solution were added to 750 µL silver colloid gradually. The mixture was left for 10 minutes and then the SERS signals were detected.

3. Results and discussion

3.1. Features of Ag colloid

The UV-vis spectra of borohydride-reduced silver colloid with different concentration of NaCl are shown in Figure 1. The absorption spectra can provide general informations on the characterization of
colloids, such as the average particle size, the shape of particles in colloid, and the aggregation degree of particles in colloid. Because the UV-vis absorption spectrum of colloids is closely related to the localized surface plasmon resonances (LSPR) which are collective metallic nanostructures. From this figure it can be seen clearly that the absorption maximum of this kind of silver colloid is at 492 nm and the full width at half maximum (FWHM) is about 50 nm. From published literature [9], the average size of silver nanoparticles is 15 nm. With the increase of NaCl concentration, the intensity of the surface plasmon absorption band decreases and the FWHM is broadened. The addition of NaCl at low concentrations (0.01 M-0.04 M) does not alter the position of the absorption band dramatically. However, the absorption band is red-shifted when adding NaCl at the highest concentration (0.05 M). It implies that the addition of NaCl at low concentration mainly causes the modification of the silver surface chemistry but causes little aggregation, aggregation occurs when the concentration of NaCl increases to 0.05 mol dm$^{-3}$. The result may be attributed to that most residual ions are displaced by Cl$^{-}$ and the repulsive force between particles is reduced, which leads to the aggregation of particles.

![Figure 1](image-url)  
**Figure 1.** UV-vis absorption spectrum of the borohydride-reduced silver colloid and the spectra when adding a wide range of concentrations of NaCl, respectively.

3.2. SERS measurements
Figure 2 shows the SERS spectra of MB on addition of different concentrations of NaCl. Noticeable enhancement is achieved on addition of NaCl at the final concentration of 0.02 mol dm$^{-3}$. As the concentration of NaCl increases, the intensity of SERS signal is reduced. It may be attributed to the reason that the addition of Cl$^{-}$ at a much lower concentration mainly causes the modification of the silver surface chemistry but causes little aggregation. The modification of silver surface caused by Cl$^{-}$ changes the binding affinity of MB and it leads to an increase in SERS intensity. When adding more Cl$^{-}$ to the colloidal system, the SERS intensity of MB drops, and it may be due to the collapse of colloidal particles. Figure 2b shows the normal Raman spectrum of 100 mM MB aqueous solution. The bands are observed at 447, 496, 598, 776, 812, 861, 907, 950, 1071, 1163, 1298, 1393, 1474,
1627 cm$^{-1}$. From figure 2a, a new band at 241 cm$^{-1}$ appears when adding Cl$^-$ to the colloid. This band is assigned to Ag-Cl bonds [10]. At the same time, the band of Ag-Cl bonds is in proportion to MB bands. The result is reflected in the 241:1627 cm$^{-1}$ ratio. It can be ascribed to that the MB molecules have positive charge and can easily adsorb on the silver surface which has been treated by Cl$^-$, and the MB molecules can’t displace Cl$^-$, which has a high affinity to the silver surface.

![Figure 2](image)

**Figure 2.** a: SERS spectra of MB when adding different concentrations of Cl$^-$ to the colloid. b: Normal Raman spectrum of 100 mM MB aqueous solution.

Figure 3 shows the SERS spectra of MB when adding different concentrations of NaBr to the colloidal system. It is observed that Br$^-$ gives lower enhancement than Cl$^-$ though it has a high affinity for silver surface. The concentrations of Br adding to the colloid are 0.02, 0.03, 0.04, and 0.05 mol dm$^{-3}$, respectively. From detecting the SERS spectra of MB, it can be observed that the concentration of 0.02 mol dm$^{-3}$ gives the least enhancement. The bands are observed at 449, 482, 598, 772, 808, 858, 905, 949, 1034, 1072, 1155, 1171, 1221, 1344, 1388, 1438, 1624 cm$^{-1}$. It can be seen that many bands in the SERS spectra have a small shift in position relative to their corresponding normal Raman bands, and some bands split in the SERS spectra. For instance, the bands at 447, 496 cm$^{-1}$ which have been assigned to C-N-C skeletal bending [11] in normal Raman spectrum shift to 449, 482 cm$^{-1}$ in SERS spectra, respectively. The bands at 1393 and 1627 cm$^{-1}$ which have been assigned to C-N stretching and C-C stretching [11] in normal Raman spectrum shift to 1388, 1624 cm$^{-1}$ in SERS spectra. The band at 1163 cm$^{-1}$ in normal Raman spectrum splits up into two bands at 1155 and 1171 cm$^{-1}$. The shift and splits of these Raman bands indicate that MB molecules may be chemisorbed on the silver nanoparticles surface and the chemical effect is the main mechanism responsible for the relative shifts. The intense band at 241 cm$^{-1}$ which is assigned to the Ag-anion bonds doesn’t appear. That implies that Br adsorbed on the silver particles can’t form the strong Ag-Br bonds.
Figure 3. SERS spectra of borohydride-reduced silver colloid when adding different concentrations of NaBr.

Figure 4 shows the SERS spectra of MB when adding NaI to the colloid. The bands are observed at 449, 489, 598, 673, 858, 949, 1032, 1068, 1338, 1385, 1435, 1621 cm⁻¹. The intensity of SERS signal is greatly reduced, compared with the SERS spectra when adding Cl⁻ or Br⁻ as aggregating agents. From these detection it can be calculated that silver colloid with appropriate concentration of anions can enhance the Raman signal several orders of magnitude. The enhancement factors for MB with optimal concentration of Cl⁻, Br⁻, and I⁻ are 3.44×10⁴, 2.04×10⁴, and 1.0×10⁴, respectively. It shows that I⁻, the most strongly binding anion, gives the least enhancement for SERS. Cl⁻ gives the greatest enhancement among the series anions. From the numerous investigations on the change of SERS signal from silver colloid on addition of different halideions at various concentrations, it is recognized that there are at least two effects occurring: the extent of aggregation of the colloid and the modification of silver surface chemistry. The differences of the SERS spectra of MB when adding different kinds and concentrations of halideions to the colloid may be attributed to the both effects.

Figure 4. SERS spectra of borohydride-reduced silver colloid when adding different concentrations of NaI.
4. Conclusion
The intensity of SERS signal of MB was enhanced significantly when adding halide ions to the colloid. The species and concentration of the halide ions determine the aggregation degree of the silver colloid. The addition of halide ions can also modify the silver surface chemistry. Among the three kinds of halide ions, chloride gives the greatest enhancement on SERS signal. The addition of NaCl at low concentration mainly causes the modification of the silver surface chemistry but causes little aggregations, aggregation occurs when the concentration of NaCl increases to a higher concentration. From the numerous investigations on the change of SERS signal from silver colloid on addition of different halide ions salts at various concentrations, it is recognized that there are at least two effects occurring: the extent of aggregation of the colloid and the modification of silver surface chemistry. The differences of the SERS spectra of MB when adding different kinds and concentrations of halide ions to the colloid may be attributed to the both effects. The purpose of this study is to further investigate the effect of halide ions on borohydride-reduced silver colloid and to make the experimental conditions suitable for detecting some analytes in high efficiency on rational principles.

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