

# An exploration of surface enhanced Raman spectroscopy (SERS) for in situ detection of sulfite under high pressure

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## ABSTRACT

In this work, silver nanoparticles film was directly fabricated on the surface of the diamond anvil as SERS active substrate for the first time by using a simple and convenient method. With this approach, the SERS spectrum of sulfite was obtained with a detection limit of 5 μmol/L in diamond anvil cell (DAC) at ~50 MPa. The SERS signal intensity of the two main vibration modes,  $\nu_{\text{sym}}\text{S}-\text{O}$  and  $\delta_{\text{sym}}\text{O}-\text{S}-\text{O}$ , showed good linearity with the  $\text{Na}_2\text{SO}_3$  concentrations in the range from 5 to 40 μmol/L under high pressure. The linear correlation coefficients were 97.67% and 96.08%, respectively. The effects of pressure on the SERS intensity and Raman shift of the two modes were also studied. The SERS intensity dropped with the increase of pressure and the two main vibration modes shifted to high wave-number when the pressure increased in the pressures ranging from 54 MPa to 330 MPa. The experiments indicate that this method is rapid, convenient and sensitive in detecting sulfite at high pressures. It can be developed as an effect in situ method to detect sulfite in the process of high pressure reaction.

## 1. Introduction

Sulfite ( $\text{SO}_3^{2-}$ ) is one of the important products and intermediates during the oxidation of reduced sulfur compounds and elemental sulfur (S) which exist in high abundance in high pressure environments such as the marine sediments at the seafloor [1,2]. Real-time monitoring of  $\text{SO}_3^{2-}$  concentration is very meaningful for understanding the migration of S element during the high pressure reaction, so it is very important for in situ monitoring of the  $\text{SO}_3^{2-}$  concentration in high pressure environments. However, in situ determination of the concentration and structure of dissolved trace substances in high pressure conditions is a great challenge for scientists and engineers in related fields, especially in hydrothermal systems at simultaneously high temperature and high pressure.

In recent years, in situ synchrotron radiation (SR) X-ray Absorption Fine Structure (XAFS) and X-ray Fluorescence (XRF) have been developed to solve this difficult problem and have made excellent achievements [3–8]. Unfortunately, these two methods are not suitable for in situ determination of  $\text{SO}_3^{2-}$  in solution. SR-XRF cannot determine the concentration of S in different valence states in solution and SR-XAFS is generally used to determine elements with atomic number not less than vanadium. Therefore, there is no suitable method for detecting low concentration  $\text{SO}_3^{2-}$  under high pressure.

Due to the wide variation in the Raman cross section of different analytes and the molecularly specific nature of the pattern of peaks obtained, Raman spectroscopy is most frequently used in high temperature and high pressure hydrothermal systems [9–12]. However, normal Raman spectroscopy is not a sensitive technique. The signal of Raman needs to be amplified in order to make this technology more useful as an effective sensor to detect some anions in the hydrothermal systems. SERS makes up for the shortcomings of normal Raman spectroscopy and has been stimulated extensive research for its application potential in chemical/biological detection and identification in many fields [13–17]. Nevertheless, only a small number of studies involved high pressure SERS.

In previous studies, researches obtained SERS spectra at high pressures by using different methods and devices. Podini and Schnur gave the first SERS spectrum at high pressure and they obtained the SERS for pyridine in a Keyes pressure cell [18]. Sandroff and his co-workers carried out the SERS experiments using a diamond anvil cell (DAC) for the first time and the substrates they used were colloids [19]. Dlott's group gave a series of excellent studies of self-assembled monolayers (SAMs) and single-molecule in a DAC combined with SERS technology [20–23]. Most of the above studies focused on the effect of pressure on the spectral information, such as intensity, Raman shift, full width at half maxima (FWHM). In situ detection of low concentration aqueous

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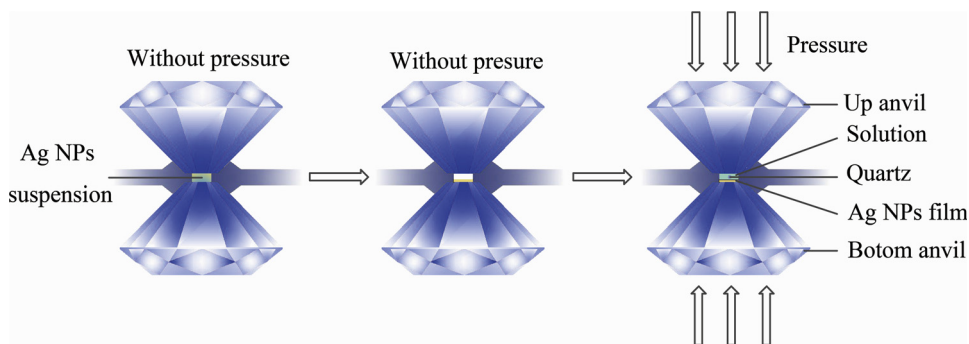


Fig. 1. Illustration of the fabrication of the Ag NPs film on the diamond anvil and the sample loading diagram in DAC.

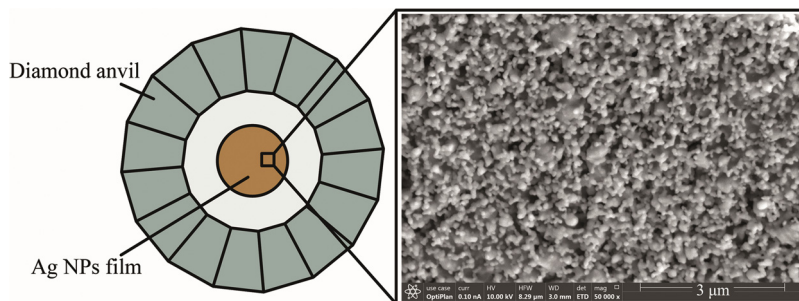


Fig. 2. SEM image of Ag NPs film on the diamond anvil.

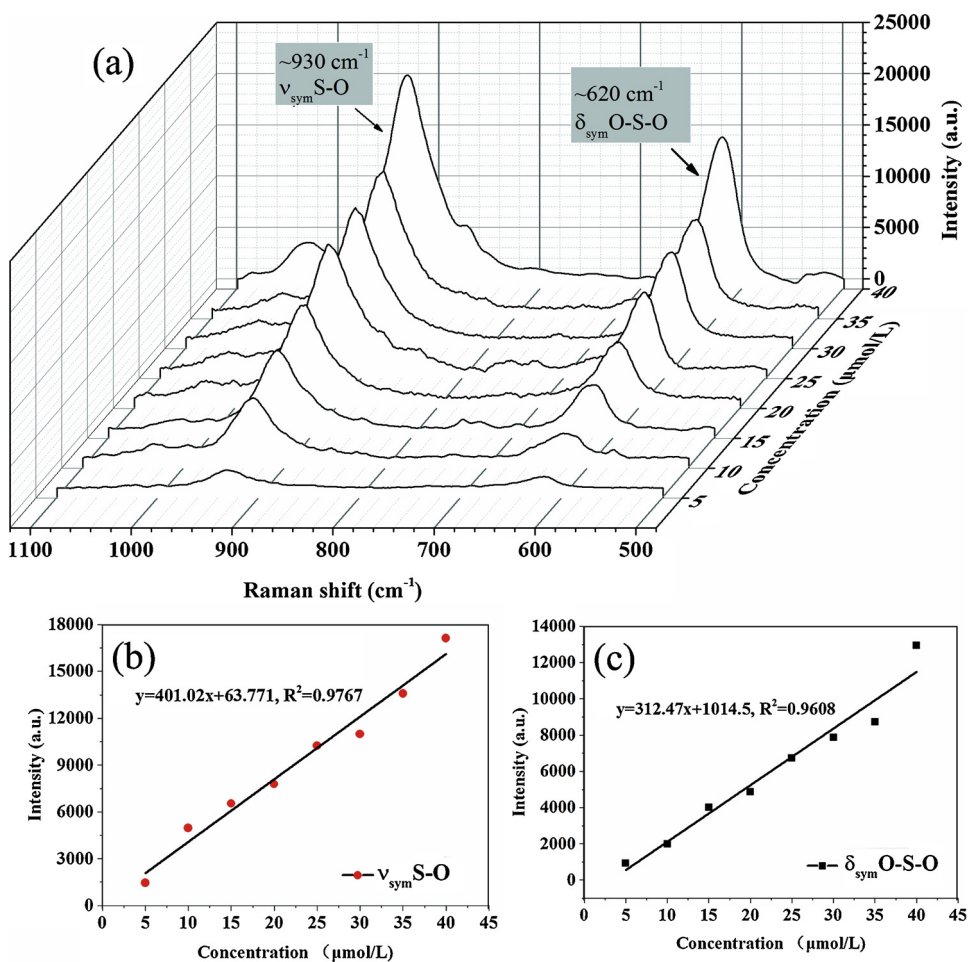


Fig. 3. (a) SERS spectra of  $\text{Na}_2\text{SO}_3$  solutions at different concentrations at  $\sim 50$  MPa; (b) and (c) simulation curve of the SERS peak intensities at  $\sim 930$   $\text{cm}^{-1}$  and  $\sim 620$   $\text{cm}^{-1}$  using different concentrations of  $\text{Na}_2\text{SO}_3$  solutions at  $\sim 50$  MPa, respectively.

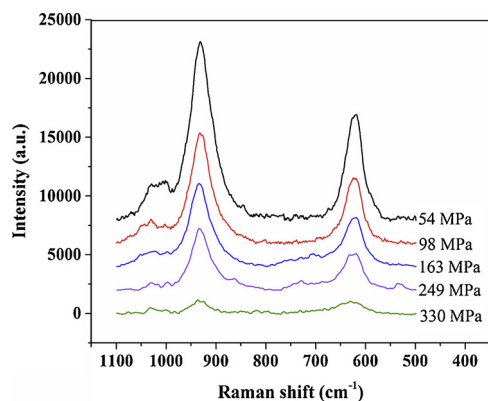


Fig. 4. SERS spectra of 35  $\mu\text{mol/L}$   $\text{Na}_2\text{SO}_3$  solution from Ag NPs film under various pressures ranging from 54 MPa to 330 MPa.

solution under high pressure was not conducted, especially the in situ SERS detection of  $\text{SO}_3^{2-}$  under high pressure.

In our previous study, we conducted the in situ SERS studies of 4-chlorothiophenol and thiocyanate ( $\text{SCN}^-$ ) in DAC at room temperature and high pressures [24,25]. The sample loading process puzzled us because of the substrates we used in our experiments were tiny and thin, which made the operation difficult and inconvenient.

In the current work, we demonstrate a convenient and rapid SERS method for in situ detection of  $\text{SO}_3^{2-}$  in DAC under high pressures. We fabricated the silver nanoparticles (Ag NPs) film on the surface of the diamond anvil by dropping the Ag NPs suspension on the surface of the diamond anvil directly. To our best knowledge, this is the first time that SERS substrates have been fabricated on the surface of the diamond anvil and applied to the in situ detection of  $\text{SO}_3^{2-}$  under high pressure. The results in this work suggest that in situ high pressure SERS detection of low concentration  $\text{SO}_3^{2-}$  using this method is feasible and sensitive.

## 2. Materials and methods

### 2.1. Materials

Hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) and sodium hydroxide ( $\text{NaOH}$ ) were purchased from Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Anhydrous sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) and silver nitrate ( $\text{AgNO}_3$ ) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Hydroxylamine hydrochloride was guaranteed reagent (GR) and the others were analytical grade. All reagents dissolved and diluted with ultrapure water.

Different concentration stock solutions of  $\text{Na}_2\text{SO}_3$  were prepared by dissolving the powdered  $\text{Na}_2\text{SO}_3$  in ultrapure water and diluting to the concentrations ranging from 5 to 40  $\mu\text{mol/L}$ . Because  $\text{SO}_3^{2-}$  is easily oxidized to sulfate ( $\text{SO}_4^{2-}$ ), all the  $\text{Na}_2\text{SO}_3$  solutions were freshly

prepared prior to the high pressure SERS experiments.

### 2.2. Synthesis of silver nanoparticles (Ag NPs)

The synthesis of Ag NPs was based on the method introduced by Leopold and Lendl [26]. The preparation procedure is briefly described. 0.034 g  $\text{AgNO}_3$  was dissolved in 180 mL ultrapure water. 0.042 g  $\text{NH}_2\text{OH}\cdot\text{HCl}$  was dissolved in 10 mL ultrapure water and 10 mL 0.1 mol/L  $\text{NaOH}$  was added to the  $\text{NH}_2\text{OH}\cdot\text{HCl}$  solution. Then, the mixture was added rapidly to the  $\text{AgNO}_3$  solution prepared before, and the resulting mixture was shaken until a homogeneous mixture was obtained. The colloids we obtained showed a milky gray color. After centrifugation for 15 min at 8000 rpm, the product was diluted with ultrapure water and the Ag NPs suspension was obtained. Since the Ag NPs synthesized by this method cannot be stored stably for a long time, they were freshly prepared before use.

### 2.3. Fabrication of Ag NPs film on the surface of the diamond anvil

Fig. 1 shows the schematic of the fabrication of the Ag NPs film on the surface of the diamond anvil. A 500  $\mu\text{m}$ -thick T 301 stainless steel was mounted on the DAC as gasket, and the sample chamber was a 200  $\mu\text{m}$  diameter hole drilled in the gasket. First, a droplet of the Ag NPs suspension was taken to the gasket, and the suspension could fill the empty space of the entire hole of the gasket in the DAC. Next, the opposed anvils were pushed toward each other, and the Ag NPs suspension was subsequently sealed in the hole of the gasket. In order to evaporate the solvent in the suspension, we did not tighten the pressure screw of the DAC. Several hours later, we obtained the Ag NPs film on the surface of the bottom anvil. Finally, the  $\text{Na}_2\text{SO}_3$  solution was loaded in the sample chamber for in situ high pressure SERS experiments.

### 2.4. Characterization

Scanning electron microscope (SEM) image of the Ag NPs film was obtained using an FEI SCIOS dual-beam system FIB SEM. The Raman experiments were carried out on a Renishaw Invia confocal micro-Raman spectroscopy system. All the SERS measurements were carried out using a 514.5 nm laser excitation line with a  $20\times$  objective, 20 mW power and 20 s accumulation time. As shown in Fig. 1, a small piece of quartz was loaded in the sample chamber as a pressure gauge. The chamber pressures in DAC were measured by 464  $\text{cm}^{-1}$  Raman peak of quartz according to the following equation [27]:

$$P \text{ (MPa)} = 0.36079 (\Delta\nu_{464 \text{ cm}^{-1}})^2 + 110.86\Delta\nu_{464 \text{ cm}^{-1}}$$

The equation is valid for  $-50 \leq T \text{ (}^\circ\text{C)} \leq 100$  and  $P < 2.0$  GPa. The accuracy of the pressure is  $\pm 50$  MPa. In this work, no additional pressure-transmitting medium was used and all of the measurements were performed at room temperature.

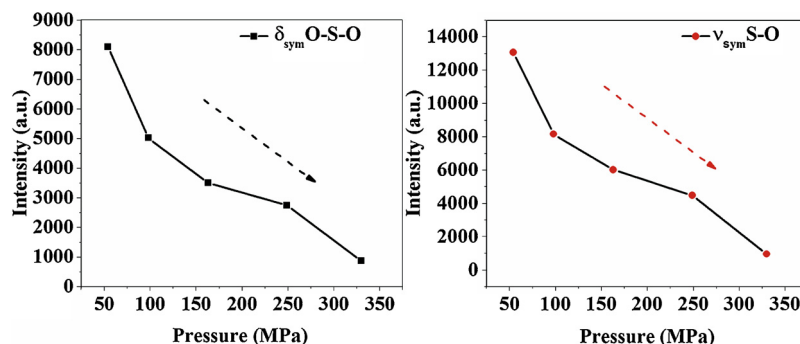


Fig. 5. Plots of the SERS intensities for  $\delta_{\text{sym}}\text{O-S-O}$  and  $\nu_{\text{sym}}\text{S-O}$  of  $\text{SO}_3^{2-}$  versus the pressure, respectively.

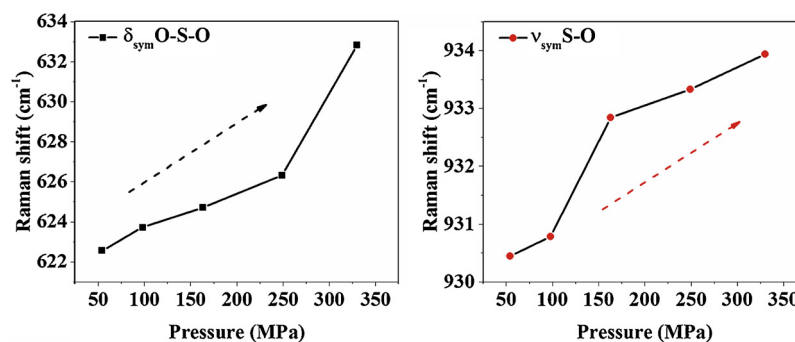


Fig. 6. Plots of the Raman shift for  $\delta_{\text{sym}}\text{O-S-O}$  and  $\nu_{\text{sym}}\text{S-O}$  of  $\text{SO}_3^{2-}$  versus the pressure, respectively.

### 3. Results and discussion

Scanning electron microscope was used to provide insight on the surface of the diamond culet and the result was shown in Fig. 2. It can be seen from the figure that a layer of Ag NPs film is formed on the surface of the diamond culet and there are many agglomerated Ag NPs. The aggregates perform a higher SERS enhance efficiency than original colloids and this phenomenon is supported by plenty of studies [28–30]. Aggregation is beneficial for producing small gap or crevice between two (or more) Ag NPs, namely, SERS-active hot spots. The SERS signal intensity is often dominated by “hot spots”, where the plasmon field is large [31,32]. If a more uniform substrate can be fabricated on the anvil surface, it will be more conducive to the quantitative detection of SERS under high pressure.

The SERS spectra obtained from different concentrations of  $\text{Na}_2\text{SO}_3$  solutions in DAC are shown in Fig. 3(a) and the pressure is about 50 MPa. The pressure was measured at once when the chamber was sealed. The primary peaks located at  $\sim 620 \text{ cm}^{-1}$  and  $\sim 930 \text{ cm}^{-1}$  were attributed to the symmetric bending vibration of O–S–O ( $\delta_{\text{sym}} \text{O-S-O}$ ) and the symmetric stretching vibration of S–O ( $\nu_{\text{sym}} \text{S-O}$ ), which are marked on the characteristic peaks [33,34]. The SERS signal of  $\text{SO}_3^{2-}$  at these two peaks could still be identified clearly even when the concentration of  $\text{Na}_2\text{SO}_3$  solution became  $5 \mu\text{mol/L}$ , which suggest that this method is sensitive and reliable under high pressure. As we know, it is impossible to achieve such a low detection limit by using normal Raman without SERS active substrate under high pressure. According to Fu et al. and our previous study, there is a dramatic drop in SERS intensity when samples are pressurized in DAC [23,24]. We think the detection limit will be lower with the developments of SERS technology in the future.

As illustrated in Fig. 3(a), the SERS signals of  $\text{SO}_3^{2-}$  at  $\sim 620 \text{ cm}^{-1}$  and  $\sim 930 \text{ cm}^{-1}$  increased with the concentrations of  $\text{Na}_2\text{SO}_3$  solutions. The intensity values of  $\nu_{\text{sym}} \text{S-O}$  and  $\delta_{\text{sym}} \text{O-S-O}$  showed good linear relationships with the  $\text{Na}_2\text{SO}_3$  concentrations in the range from 5 to  $40 \mu\text{mol/L}$ , which are shown in Fig. 3(b) and (c), respectively. The linear correlation coefficients were found to be 97.67% and 96.08%. These results suggested that this in situ high pressure SERS method could be used to simulate the concentration detection of  $\text{SO}_3^{2-}$  under high pressure and could obtain high determination sensitivity. If a stable, homogeneous and more sensitive substrate is used to ensure that the experiment can carry out the error analysis, this method will hopefully solve the problem of  $\text{SO}_3^{2-}$  detection under high pressure in practical application.

In order to study the effect of pressure on SERS spectra, we conducted the SERS experiments of  $\text{Na}_2\text{SO}_3$  solution at various pressures ranging from 54 MPa to 330 MPa. We measured the pressure as soon as the chamber was sealed and the other pressures were measured step by step as the experiment going on. The in situ SERS spectra of  $35 \mu\text{mol/L}$   $\text{Na}_2\text{SO}_3$  solution obtained inside the DAC at various pressures ranging from 54 MPa to 330 MPa are shown in Fig. 4. As we can see in the figure, the two main vibration modes of  $\text{SO}_3^{2-}$  mentioned above can be

clearly identified at the pressure up to 330 MPa, which indicated that this approach can be used to detect  $\text{SO}_3^{2-}$  in high pressure aqueous solution. And we would like to detect  $\text{SO}_3^{2-}$  in hydrothermal systems at simultaneously high temperature and high pressure in our next plan.

To further study the effect of pressure on the SERS signal and Raman shift, we plot the curves of intensity and Raman shift varying with pressure respectively, which were shown in Figs. 5 and 6. There is pressure-induced drop of SERS intensity for the two vibration modes, as shown in Fig. 5. The results indicated that the SERS intensity dropped with the increasing pressure. One of the possible reasons is the substrate. The number of SERS-active “hot spot” decreased with the pressure increasing [23] and the pressure also caused the absorption spectra of nanoparticles broad and red shift [35–37], which is negative to the SERS effect of nanoparticles. The pressure can also cause changes in refractive index and density of the solution in the chamber of DAC, which results in the decrease of Raman intensity.

Fig. 6 demonstrates the changes in Raman shift of the two vibration modes at the pressure ranging from 54 MPa to 330 MPa. The two peaks show a blue-shift with the increasing pressures. The pressure-induced blue-shift of Raman peaks is the most common phenomenon related to the increased density in molecular systems, and has been investigated in many works [38–40]. The high pressure can shorten the bond length of the molecules and increase the force constant and frequency of the corresponding peak, which caused the blue-shift of Raman peaks [41].

### 4. Conclusion

In summary, we introduced a simple and rapid approach to conduct the in situ high pressure SERS experiments in DAC, and Ag NPs film was fabricated directly on the surface of the diamond culet. The detection limit of  $\text{SO}_3^{2-}$  would reach up to  $5 \mu\text{mol/L}$  at  $\sim 50 \text{ MPa}$ , and the two main vibration modes in the spectrum could be clearly identified. To our knowledge, this is the first result reported for SERS technology applied to the  $\text{SO}_3^{2-}$  detection with concentration lower to  $5 \mu\text{mol/L}$  under high pressure. What’s more, the intensity of two main vibration modes,  $\delta_{\text{sym}}\text{O-S-O}$  and  $\nu_{\text{sym}}\text{S-O}$ , showed good linearity with the concentration in the range from 5 to  $40 \mu\text{mol/L}$  at  $\sim 50 \text{ MPa}$ . The linear correlation coefficients were 96.08% and 97.67%, respectively. The effect of pressure on SERS intensity and Raman shift were studied using the  $35 \mu\text{mol/L}$   $\text{Na}_2\text{SO}_3$  aqueous solution. Pressure-induced intensity drop and blue-shift of the two main vibration modes were found at the pressure ranging from 54 MPa to 330 MPa. The obtained results in this work show that this approach can be used to simulate low concentration  $\text{SO}_3^{2-}$  detection in high pressure environments. Considering that  $\text{SO}_3^{2-}$  exists in many high pressure reaction processes, this approach can be developed to be an effect method to detect  $\text{SO}_3^{2-}$  in situ during the high pressure reaction and to understand the reaction process of S-bearing systems under high pressures. In our next research, in situ SERS experiments in hydrothermal systems at high temperature and high pressure conditions will be explored and the detection of  $\text{SO}_3^{2-}$  in this study offer a foundation for the in situ high pressure hydrothermal



experiments.

### Conflict of interest

No conflict of interest.

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