

Full Length Article

In situ surface enhanced Raman spectroscopy detection in high pressure solution

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ABSTRACT

In situ surface enhanced Raman scattering (SERS) in solution was tested in this study at ambient temperature and high pressure (up to 978 MPa) in a diamond-anvil cell, with the intent of resolving trace detection in high pressure conditions. The 4-chlorothiophenol solution was used as the analyte in our experiments. A silver nanoparticle layer, formed by chemical reduction and assembled on a poly (allylamine hydrochloride)-modified silicon wafer, was used as the substrate. There was an obvious rise in SERS intensity when the sample chamber was pressurized for the first time in the diamond-anvil cell. But then the intensity drop occurred with increasing pressure and all peaks have pressure-induced blue shift below 700 MPa. The SERS intensity and Raman shift displayed irregular changes in the pressure range from 700 MPa to 978 MPa. The discovery of the survival of in situ high-pressure SERS in solution in the present study may make it a prospecting tool for the high-precision detection of analyte in high pressure conditions. Moreover, it could provide more information on the SERS mechanisms that have been puzzling us for decades.

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1. Introduction

Appropriate techniques for high-precision in situ chemical analyses, especially the trace-detection at simultaneously high pressure and high temperature conditions, are scarce due to technical challenges. A growing number of in situ synchrotron radiation X-ray fluorescence (XRF) studies have been conducted in ultrasensitive analysis of concentration at high temperatures and high pressures in recent years [1–5]. Although the high-pressure synchrotron radiation XRF technique can provide a sophisticated analysis method and low-detection limit, the high operating costs and non-universality limit its application.

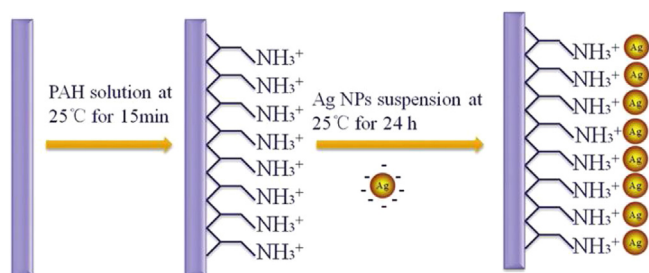
Raman spectroscopy can give specific information on molecules, but it exhibits some disadvantages [6]. One of the disadvantages is its inherently weak intensity. Another major disadvantage is the fluorescence that usually accompanies Raman scattering and can sometimes overwhelm the peaks in the spectrum, thus rendering the measurement useless. However, to date, Surface enhanced Raman scattering (SERS) has been routinely used as an

ultrasensitive and effective analytical technique for chemical/biological detection and identification [7–10] since it was first observed in 1974 [11]. Unfortunately, SERS has not been developed to be a powerful surface analysis technology as expected because of some obstacles both in its practice and theory. Specifically, the SERS mechanism on its observed effects is yet to be clearly identified, although a number of SERS mechanisms have been proposed for almost three decades. An electromagnetic enhancement and a chemical enhancement contributing to the major SERS effect have been the consensus [12]. Because of the different molecular information under high pressures, further theoretical and experimental studies combined with in situ high pressure technology are required to explain all SERS phenomena quantitatively.

Even though a few previous investigations involving SERS of adsorbed molecules under high pressures were conducted over the past few years [13–16], in situ trace-detection in liquid at high pressure using solid SERS substrate has not been studied. Dlott and Brown gave the first study of molecular monolayers in a diamond-anvil cell (DAC) with supercritical argon as pressure transmitting medium combined with SERS technology [17]. In the later studies of Dlott's Group, a series of researches on single-molecule SERS and vibrational spectroscopy of nitroaromatic self-assembled monolayers under high pressures in DAC were carried out in detail [18–20]. There is no doubt that DAC with argon as the pressure

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Scheme 1. The schematic illustration of Ag NPs suspension assembled on PAH-modified ultra-thin silicon wafer.

transmitting medium can provide hydrostatic compression up to 10 GPa [21], which has a great advantage in studying molecular vibrations. However, in situ SERS detection in solution at high pressure with solid substrate is different from the above-mentioned studies. Compared with the in situ synchrotron radiation XRF, this relatively handy way will lay the foundation for in situ ultrasensitive in high temperature and high pressure hydrothermal systems.

In the current work, we carried out the in situ high pressure experiment of SERS by taking a Zha-Bassett type DAC [22] at room temperature and high pressures (up to 978 MPa) and using 4-chlorothiophenol as the target molecule. A well-studied silver nanoparticles (Ag NPs) assembled on poly (allylamine hydrochloride) (PAH) modified ultra-thin wafer (60 μm) was used as the substrate for SERS. Atomic force microscopy (AFM) was employed to reveal the morphology of the substrate. The results in this study demonstrate that the in situ SERS detection in high pressure solution is feasible. Experiments in high temperature and high pressure hydrothermal systems will be explored in our next program.

2. Material and methods

2.1. Materials

The poly (allylamine hydrochloride) (PAH), having an average molecular weight of 900,000 Da, was purchased from Sigma-Aldrich Company. 4-Chlorothiophenol, Silver nitrate, Trisodium citrate dehydrate, and other chemicals were analytical grade and purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). 4-Chlorothiophenol was dissolved in ethanol and diluted to 1×10^{-10} mol/L with ultrapure water. The other solutions were prepared with ultrapure water. The silicon wafer was purchased from Suzhou Crystal Silicon Electronic & Technology Company (Suzhou, China).

2.2. Substrate fabrication

Scheme 1 showed the arraying mechanism of Ag NPs assembled on silicon wafer. The substrate was prepared using the chemical method [23] and assembled on PAH-modified ultra-thin silicon wafer (60 μm) similar to that described by Ociwieja et al. [24]. The preparative procedure is briefly described. 45 mg AgNO_3 was dissolved in 250 ml ultrapure water and heated to boiling. Then, 5 ml of 1% trisodium citrate dehydrate previously prepared was added drop by drop with vigorous magnetic stirring. The mixed solution was kept boiling for approximately 1 h and thereafter cooled to room temperature. After centrifugation for 30 min at 4000 rpm, the product was diluted with ultrapure water to 1/10 of the original concentration. Then, the Ag NPs suspension was obtained. Afterward, a piece of ultra-thin wafer deposited with saturated PAH monolayer was prepared as follows. The cleaned wafer was placed into the PAH solution at a concentration of 5 ppm, pH = 4 and I = 0.01 M NaCl, for 15 min. Thereafter, the silicon wafer

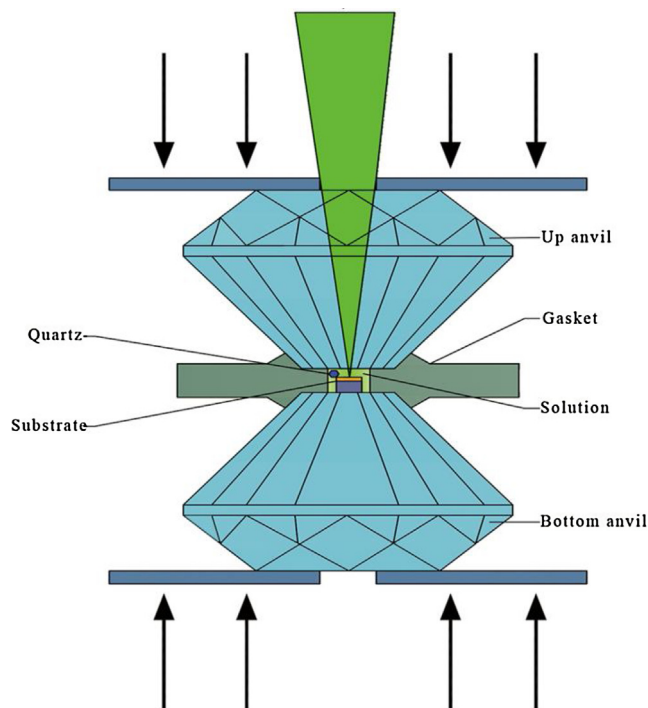


Fig. 1. The sample loading of the SERS experiments in DAC.

covered by the PAH monolayer was rinsed with ultrapure water and immersed in the Ag NPs suspension (pH = 5) for 24 h. The substrate was rinsed with ultrapure water and air dried after the deposition.

2.3. High pressure samples preparation

Fig. 1 shows the sample loading in DAC. For the high pressure measurements, a piece of substrate chip was placed into a 250 μm hole drilled in the center of a 500 μm thick copper gasket. A small piece of quartz was loaded in the DAC chamber as a pressure gauge. Then a little of 1×10^{-10} mol/L 4-chlorothiophenol solution was placed into the hole of the gasket. The sample chamber was quickly sealed with the promptly closing of the top and bottom anvils of DAC. The substrate chip was surrounded with the low concentration 4-chlorothiophenol solution in the sample chamber. No additional pressure-transmitting medium was used.

The chamber pressure in DAC was measured by 464cm^{-1} Raman peak of quartz inside the chamber on the basis of the following equation proposed by Schmidt et al. [25],

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

This equation is valid for $-50 \leq T(^{\circ}\text{C}) \leq 100$ and $P < 2.0$ GPa. The accuracy of the pressure is ± 50 MPa.

2.4. In situ SERS measurements

In situ SERS measurements were carried out by using Renishaw *in-Via* confocal micro-Raman spectroscopy system with a 514.5 nm argon laser excitation line. A laser power of 80 mW was used as an excitation source. A collection time of 20 s was used for each spectrum, and 3 spectra were accumulated for each acquisition in order to reduce noise and avoid CCD saturation and a 20 times objective was used. The Raman experiments were performed at room temperature.

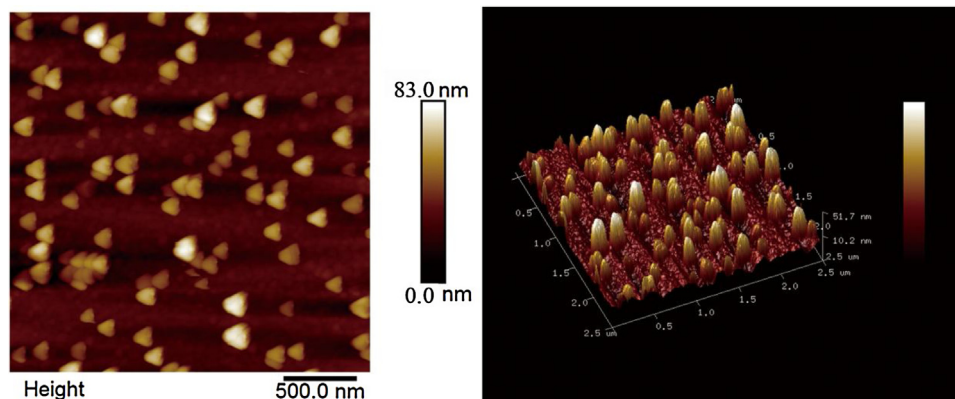


Fig. 2. AFM images of 2-dimensional view and 3-dimensional view of the Ag NPs array on the surface of the substrate.

3. Results and discussion

Atomic force microscopy was used to provide insight on the surface of the substrate and the results are shown in Fig. 2. The size distribution and morphology of Ag NPs were determined from the AFM micrographs. The substrate for SERS exhibited a rough surface distributed with Ag NPs. The particles are tapered with a 2D heart shape. The diameter is approximately 80 nm in the horizontal direction. According to Tian et al. [12], the size and morphology of the Ag NPs enable the substrate to obtain high sensitivity for SERS experiments. The high sensitivity SERS substrate is necessary because of the dramatic drop in SERS intensity when samples are pressurized in the DAC [20].

The Raman spectra of 4-chlorothiophenol (1×10^{-10} mol/L) adsorbed on Ag NPs measured in situ inside the DAC at various pressures ranging from 60 MPa to 978 MPa are shown in Fig. 3. The vibration modes are marked on the characteristic peaks [26]. The peak near 1590 cm^{-1} corresponds to the C–C symmetry stretching vibration, and the peak nearby 1080 cm^{-1} corresponds to the C–C symmetry stretching and C–S stretching vibration. The other characteristic Raman spectral bands (C–H in-plane bending vibration near 1485 cm^{-1} and 1180 cm^{-1} , C–C symmetry stretching vibration near 1380 cm^{-1} , ring in-plane deformation vibration near 621 cm^{-1} , etc.) exhibit low intensity in these spectra.

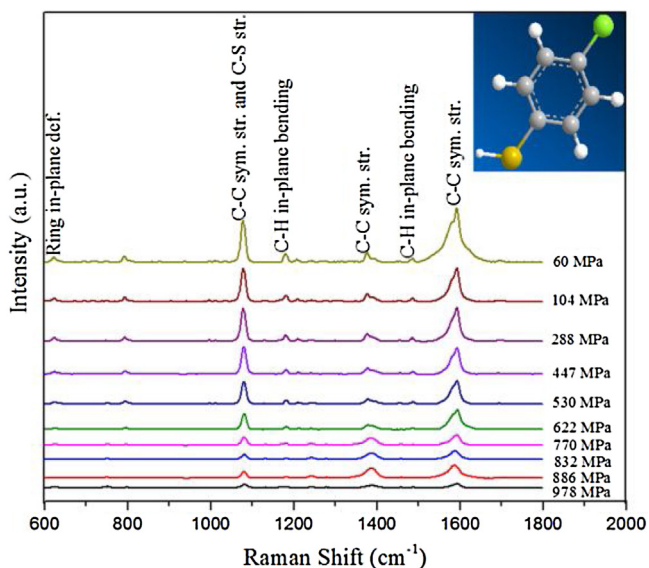


Fig. 3. SERS spectra of 1×10^{-10} mol/L 4-chlorothiophenol from self-assembled Ag NPs under various pressures ranging from 60 to 978 MPa at room temperature.

The objective of this study is to investigate in situ SERS trace detection inside the DAC under high pressure conditions. The Ag NPs arrayed substrate showed high SERS intensity under high pressures and the Raman bands of above-mentioned various vibrations can be clearly identified at up to 978 MPa. In this respect, we have successfully obtained the SERS signals of 4-chlorothiophenol (1×10^{-10} mol/L) in the DAC under high pressures.

During the experiments, we were unable to track the specific point on the surface of the substrate chip for the missing of point registration due to pressure increase process, which required the movement of DAC from the sample platform of Raman spectrometer. But the intensity generally decrease with increasing pressure. The regular pattern of the intensity changes suggested that the effects of the SERS weakened with increasing pressure in a certain pressure range. This phenomenon is likely caused by the pressure-induced destruction of SERS-active hot spots [20]. The hot spots had large enhancement factors before they were destroyed [27]. In other words, small gaps ($\sim 1 \text{ nm}$) between two or more nanoparticles that are 20–100 nm in size attribute to the largest electric field [28]. The disappearance of hot spots was likely caused by the changes of the gap junctions among Ag nanoparticles due to the increased pressures.

To further understand the effect of pressure on the intensity of SERS, we conducted experiment at ambient pressure to compare with experiment at high pressure conditions ranging from 60 MPa to 978 MPa. After the high pressure experiment, pressure in the sample chamber was decreased to 61 MPa, which was approximated to the first pressurized pressure of 60 MPa. Fig. 4(a) shows the spectrum at ambient pressure, which was conducted inside the DAC before the sample chamber was sealed. Fig. 4(b) shows the spectrum at 60 MPa, which was pressurized for the first time. Fig. 4(c) shows the spectrum at 61 MPa, which was relieved after the high-pressure experiment. The spectrum intensity at the first pressurized pressure showed in Fig. 4(b) significantly higher than the spectrum intensity at ambient pressure in Fig. 4(a). This result suggests that suitable pressures enhanced the SERS intensity. Two possible reasons are inferred to trigger the increase of SERS intensity with pressurization. On one hand, the first compression led to the decrease of the sample chamber volume, therefore, the 4-chlorothiophenol molecules free in solution were more easily adsorbed on the surface of the substrate chip. On the other hand, the pressure at 60 MPa destroyed a limited number of SERS-active hot spots, but created more new hot spots because the suitable pressure could make the gaps among nanoparticles to appropriate distance, which is more effectively for electromagnetic enhancement. When located in the hot spots, the active molecules were more effectively activated, with a significant enhancement of their Raman intensity.

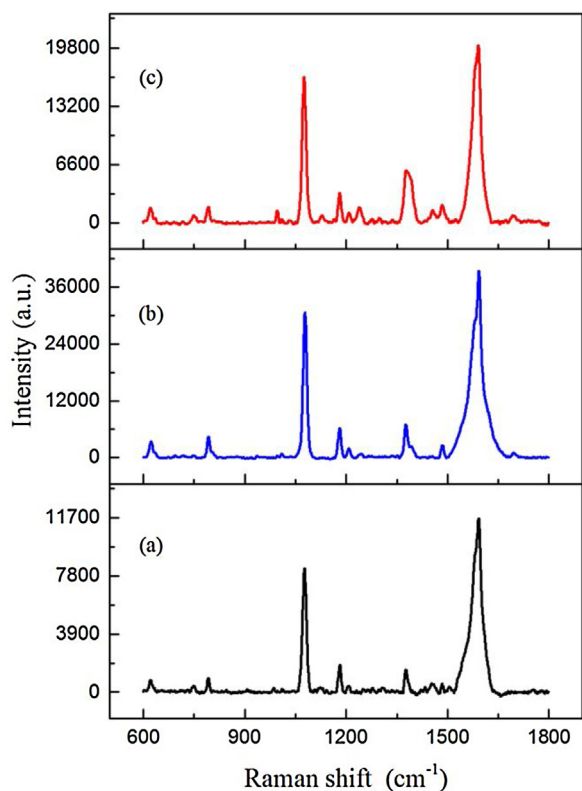


Fig. 4. SERS spectra of 1×10^{-10} mol/L 4-chlorothiophenol from self-assembled Ag NPs: (a) spectrum at ambient pressure; (b) spectrum at 60 MPa (the first pressurized); (c) spectrum at 61 MPa (pressure relieved).

By contrast, the comparison of Fig. 4(b) and (c) shows that the SERS intensity at 61 MPa (reduced from 978 MPa) is weaker than the intensity at 60 MPa (the first pressurized pressure). This observation suggests that the pressure-induced destruction of SERS-active hot spots is unable to recover completely from extreme pressure. However, SERS activity of the substrate still exists.

Fig. 5 shows the intensity of several characteristic peaks of 4-chlorothiophenol adsorbed on Ag NPs measured under different pressures ranging from 60 MPa to 978 MPa. The intensities of these peaks generally decrease from 60 MPa to 700 MPa. The pressure-induced drop of SERS intensity is similar to the previous studies [13–20]. However, these regular patterns are broken above

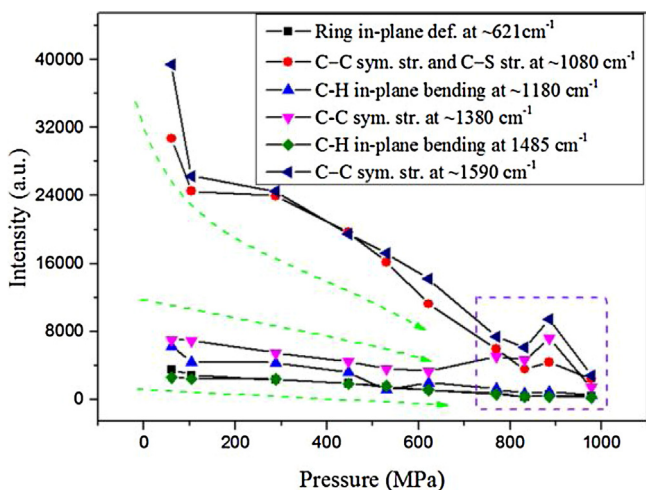


Fig. 5. The relationship between SERS intensity of 1×10^{-10} mol/L 4-chlorothiophenol and pressures at room temperature.

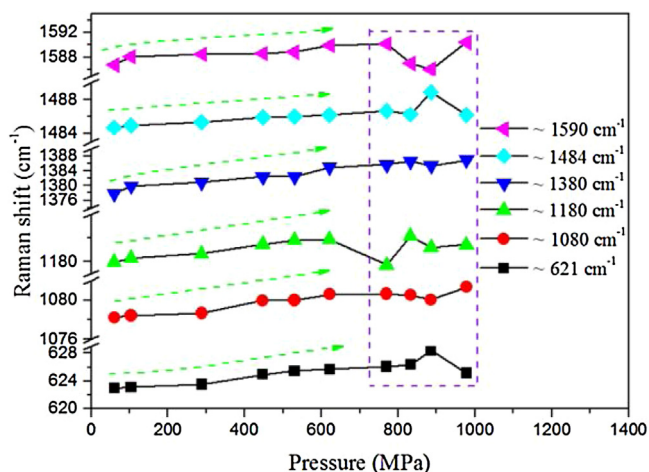


Fig. 6. The relationship between Raman shift of 1×10^{-10} mol/L 4-chlorothiophenol and pressures at room temperature.

700 MPa. According to Chou et al. [29], another H_2O phase appears at 700–12,000 MPa. The most probable reason for this outcome is that the solution prepared with water in the chamber is not a suitable pressure transmitting medium, which produced the inhomogeneous pressure. Therefore, the irregular changes occurred at 700–978 MPa are conceivable. Another possible reason should be mentioned that the structure of the substrate will be unstable under high pressure.

Fig. 6 demonstrates the changes in Raman shift of different vibrational modes from 60 MPa to 978 MPa. All peaks shifted to high wave numbers with increasing pressure to below 700 MPa. The pressure-induced blueshift of Raman peaks is the most common phenomenon to increased density in molecular systems and has been discussed in detail in many works [30–33]. Similarly to Raman intensity in Fig. 5, the plots become irregular above 700 MPa. We attribute this phenomenon to the unstable surface structure resulted from the change in vibration frequency of chemical bond because of the possible change in the adsorption directions of 4-chlorothiophenol on Ag NPs under high pressure. Moreover, the new H_2O phase mentioned above can affect the Raman shift. A third possible reason is the Fermi resonance strongly perturbed the vibrational frequency [34].

4. Conclusion

With a silver nanoparticle layer assembled on a PAH-modified silicon wafer, which provides a great enhanced intensity, we have obtained the in situ SERS of the 4-chlorothiophenol molecules in the solution at high pressure conditions in DAC. Analysis of SERS spectra of 4-chlorothiophenol at high pressures showed that the Raman intensity decreased with increased pressure below 700 MPa. In the same pressure range, the variations in the pressure-induced blueshift increased significantly with pressure. But irregular changes occurred at pressures between 700 MPa and 978 MPa, likely because of the change H_2O phase and/or Fermi resonance. The intensity between ambient pressure and the first pressurization showed that appropriate pressurization can improve the surface enhancement factor to some extent. The Raman spectroscopy at 61 MPa suggested that the pressure-induced destruction of SERS-active hot spots can recover partially when pressure relieved. Due to the above reasons, this in situ SERS technique provides a method to study the SERS mechanism in the relationship between pressure and SERS intensity or Raman shift of the characteristic peaks. The most important discovery is the detection limit could reach up to 1×10^{-10} mol/L, therefore, the

in situ SERS technique in DAC provides the possibility of detecting a low molecular concentration under high pressures and can also be used for trace detection in hydrothermal environments or other high pressure environments. With the developments of SERS technology, the in situ SERS detection under high pressure will be an important application in surface science.

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