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In-situ reversible temperature-dependent surface enhanced Raman scattering study using optical fibers

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ABSTRACT

Surface enhanced Raman scattering (SERS) spectra of Rhodamine 6G adsorbed on silver nanoparticles have been measured using an optical fiber from 22 to 85 °C. The fiber carries both the laser excitation and SERS signal, providing a convenient scheme for in-situ SERS measurement at high-temperature microscale environments. It is found that although SERS intensity generally decreases with increasing temperature, the signal is still significant and stable at high-temperature up to 85 °C. More importantly, the SERS signal is reversible with respect to the temperature change. These results are important for high-temperature SERS applications in chemical and biological detection.

1. Introduction

Surface enhanced Raman scattering (SERS) provides a promising optical sensing technique with high sensitivity and molecular specificity [1–6]. In SERS, the Raman signal can be amplified by orders of magnitude due to strong enhancement of the electromagnetic field by the surface plasmon resonance (SPR) of metallic nanostructures and surface chemical enhancement [7]. Since its discovery [8,9], SERS has attracted extensive attention and been well applied in detection and analysis of a large number of chemicals and biological molecules [10–13].

While SERS provides the high sensitivity and molecular selectivity, optical fibers offer compactness, flexibility and remote sensing capability important for practical applications. The original single multimode SERS fiber probe was demonstrated in 1991 by Mullen and Carron [14]. In subsequent studies, single fiber scheme has been widely implemented in SERS systems in which an optical fiber is used to carry both the excitation laser and Raman signal radiation [15–20].

For certain analytical applications, it is necessary to measure the SERS signal above or below room temperature. For example, SERS can be potentially used to measure local temperature involved in processes such as photothermal ablation therapy of cancer by determining the ratio of Stokes and anti-Stoke Raman scattering [21]. To date, only a few studies on elevated temperature dependence of SERS have been reported [22–27]. A recent study has shown stability and reversibility of the silver SERS substrate up to about 60 °C [28].

In this Letter, we demonstrate a simple and versatile method based on the optical fiber for measuring the temperature dependence of SERS intensities of Rhodamine 6G (R6G) adsorbed on silver nanoparticles (SNPs). Good stability and reversibility have been found in the temperature range of 22–85 °C. The results indicate that the SNPs are good SERS substrates for molecules such as R6G at relatively high-temperature and optical fibers can provide a convenient platform for in-situ high-temperature SERS measurements that are of interest for high-temperature SERS applications in chemical and biological analysis and detection.

2. Experiment

The silver (Ag) nanoparticles used in the sample solution were synthesized using the Lee and Meisel protocol [29]. Basically, silver nitrate was used as the metal precursor and sodium citrate as the reducing agent. Formation of the SNPs was monitored by UV–vis spectroscopy using a HP 8452A spectrometer with 2 nm resolution. With the average diameter of the SNPs estimated at 30 nm based on transmission electron microscope (Model JEOL JEM 1200EX), the concentration of SNPs using the Lee and Meisel method was calculated to be $\sim 3 \times 10^{-11}$ M. The sample solution in this study was prepared by mixing 400 μL of the aqueous Rhodamine 6G (R6G) solution (10^{-4} M) and 2 mL of SNPs.

The schematic of temperature-dependent SERS measurements is illustrated in Fig. 1. A 50 cm section of 100 μm core diameter optical fiber (Model F-MLD-500 from Newport) was cleaved carefully at both ends using a fiber cleaver. A 20× objective was used to focus the 632.8 nm excitation light into the fiber from one end

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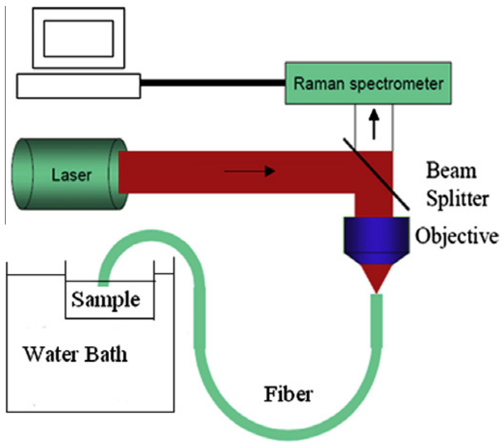

Fig. 1. Schematic of temperature-dependent SERS measurements using a single optical fiber.

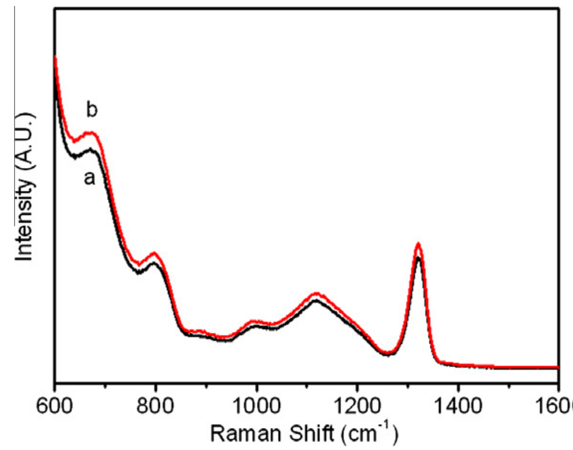

Fig. 3. Background measurement of the optical fiber without R6G molecule in the solution: (a) MilliQ water; (b) silver colloids. Both background mainly come from the fiber and the difference comes from the system itself instead of the solution.

and well confined in the fiber during the propagation to the far end of the fiber which was dipped into the sample solution. The laser power out of the fiber end was around 1 mW. The SERS signal from the sample would propagate back from the fiber and be collected by the Raman spectrometer. All the SERS signals were obtained with one accumulation of a 10 s scan. The sample solution was heated from 22 to 85 °C in a water bath and finally cooled back down to 22 °C, and the measured SERS results are reversible for a given temperature before and after heating. The water bath temperature was monitored using a mercury thermometer. The sample solution temperature should be within about 1 °C of the water bath temperature after equilibration for about 3 min for each temperature reached.

3. Results and discussion

The primary goal of this work is to demonstrate the ability of SNPs as a stable and reversible SERS substrate in high-temperature environment. Fig. 2 shows the UV–vis absorption spectrum of the SNPs used in this experiment, which exhibits a well-known surface plasmon band around 415 nm [30]. Although the absorption is not strong around 632.8 nm, it is sufficient for SERS measurement.

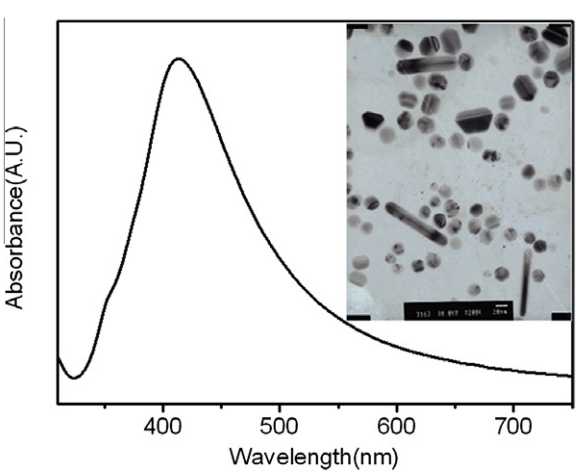

Fig. 2. Representative UV–vis absorption spectrum of 3×10^{-11} M silver nanoparticles. Although the SPR peaks at 415 nm, there is sufficient absorption around 632.8 nm for SERS measurement. Inset: TEM image of the silver nanoparticles and the average size is estimated to be 30 nm.

As shown in Fig. 3, the background of the measurements in this experimental scheme mainly came from the fiber and has been removed in the following results. Fig. 4 shows the SERS spectra of R6G adsorbed on SNPs measured through an optical fiber at different temperatures ranging from 22 to 85 °C monitored by a mercury thermometer. Although SERS signal of direct measurement by focusing the objective onto the sample surface was higher than that obtained using an optical fiber, it is difficult to get an accurate measurement of SERS intensity at high-temperature directly. The liquid would evaporate causing the surface level to change and also the vapor would condense onto and thereby blur the objective, making it challenging to focus the objective properly onto the liquid surface. Therefore, an optical fiber is employed as a more convenient platform for SERS measurements in the system and, to the best of our knowledge; this is the first time a single optical fiber has been applied for temperature-dependent SERS study. It can be seen that SERS signals collected via optical fiber are still strong and clear at various temperatures up to 85 °C. Moreover, since the signal detected by the optical fiber is mostly from the sample near the fiber tip which merely has a 100 μm diameter, the optical fiber is well suited for in-situ measurement at microscale environment in various chemical and biological systems.

Fig. 5 shows the temperature dependence of the intensity of the typical 1508 cm^{-1} peak of R6G as a function of temperature. The

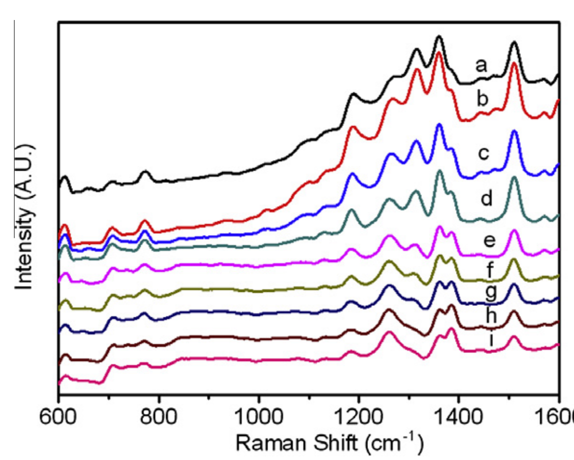

Fig. 4. SERS spectra of R6G adsorbed on silver nanoparticles at different temperatures: (a–i) spectra representing SERS substrates at 22, 30, 40, 50, 60, 70, 75, 80, and 85 °C, respectively. The spectra were offset vertically for easier visualization.

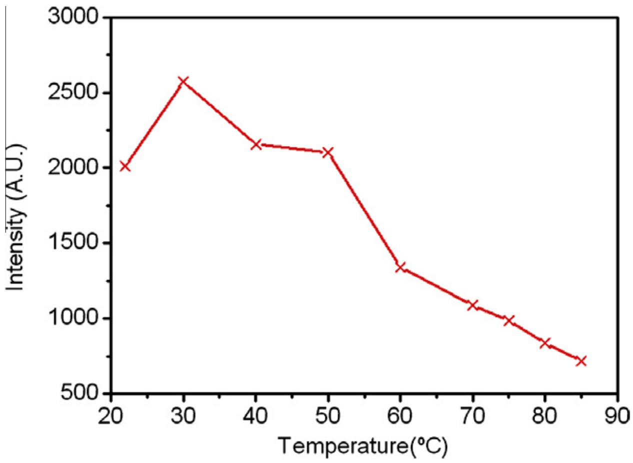

Fig. 5. Temperature dependence of SERS intensities of R6G adsorbed on silver nanoparticles measured at 1508 cm^{-1} during heating procedures.

general decrease in SERS intensity with increasing temperature is somewhat expected as some of the R6G molecules are anticipated to desorb from the SNP surface at elevated temperature. There was an unusual increase in SERS intensity from 20 to 30 °C, and the reason behind is not very clear. However, similar behavior has been observed by others recently and it was suggested that the increase in SERS signal with increasing temperature was due to an increase in chemical enhancement effect [28]. The maximum SERS signal was found to be near 50 °C in the previous study [28] while near 30 °C in our case. The difference could be due to difference in surface characteristics of the SERS substrates used.

As a control experiment, the same optical fiber was used to detect the normal Raman signal of R6G at the same concentration without using SNPs and no signal was observed. Therefore, all the signals detected were SERS signals without any contribution from normal Raman signals.

The results show that while there is some expected desorption of R6G molecules from SNP at higher temperature, a large fraction of R6G molecules are still adsorbed on the SNP surface at temperatures as high as 85 °C to generate detectable SERS signal. Fig. 6 shows the SERS spectra at different times following heating up to 85 °C and there is little change after 10 min. This result clearly demonstrates that the SNPs can be used as a good SERS substrate for applications with temperature substantially above room

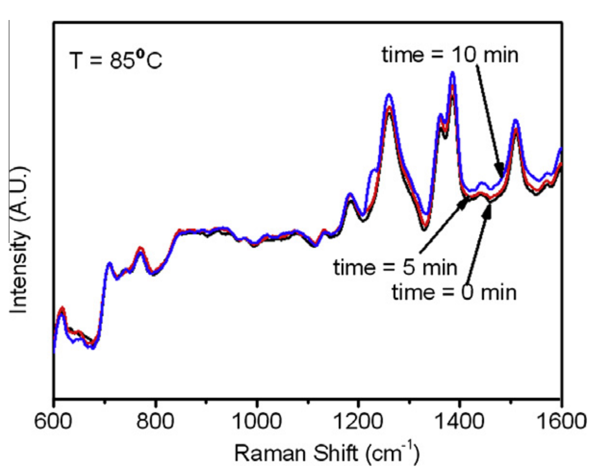

Fig. 6. SERS spectra of R6G adsorbed on silver nanoparticles at different times when the temperature was held at 85 °C.

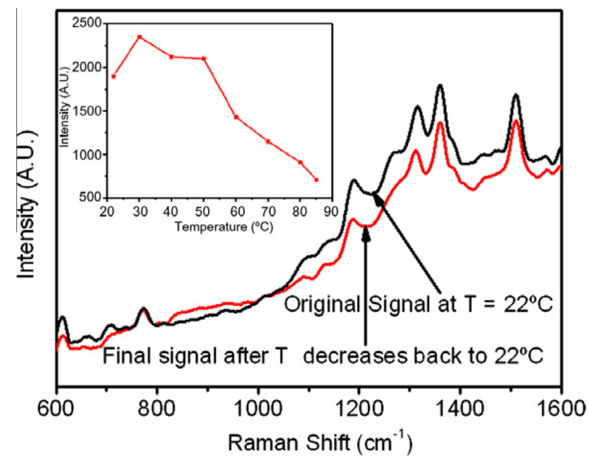

Fig. 7. The comparison between of the original R6G SERS spectrum at 22 °C and the final R6G SERS spectrum after the solution was heated from 22 to 85 °C and then cooled back down to 22 °C again. Inset: temperature dependence of SERS intensities of R6G adsorbed on silver nanoparticles measured at 1508 cm^{-1} during cooling procedures.

temperature. In a previous study, the SERS-active silver substrates was reported to be destroyed when heated up to 60 °C and when the temperature was cooled back to room temperature, the signal reduced to ca. 60% of its original intensity [28]. In our present study, the process was reversible even when the sample solution was heated up to 85 °C. As shown in Fig. 7, when the temperature of the solution was cooled back down to 22 °C again from 85 °C, the SERS intensity was essentially the same as the original signal obtained at 22 °C before heating, indicating that the SNPs were not changed. Our study demonstrates the good stability of SNPs as a SERS substrate at high-temperatures. This could have many potential applications in high-temperature environment. The reversibility observed in our study in contrast to the irreversibility reported before [28] may be due to the difference in surface characteristics of the nanoparticles since the surface is sensitive to the specific synthesis and can affect how the target analyte molecules interact with the nanoparticle.

4. Conclusion

This work successfully demonstrates that SNPs can be used a good SERS substrate for high-temperature SERS applications. It is shown that although SERS intensity in general decreases when temperature increases, the signals can be stable and reversible over 22–85 °C. Also, optical fibers can be implemented as an in-situ detection tool in high-temperature environments, carrying both the excitation laser and the SERS signal radiation. Further study will explore the SERS applications in various high-temperature chemical and biological systems.

Acknowledgments

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