Portable fiber sensors based on surface-enhanced Raman scattering

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Two portable molecular sensing systems based on surface-enhanced Raman scattering (SERS) have been experimentally demonstrated using either a tip-coated multimode fiber (TCMMF) or a liquid core photonic crystal fiber (LCPCF) as the SERS probe. With Rhodamine 6G as a test molecule, the TCMMF-portable SERS system achieved 2–3 times better sensitivity than direct sampling (focusing the laser light directly into the sample without the fiber probe), and a highly sensitive LCPCF-portable SERS system reached a sensitivity up to 59 times that of direct sampling, comparable to the sensitivity enhancement achieved using fiber probes in the bulky Renishaw system. These fiber SERS probes integrated with a portable Raman spectrometer provide a promising scheme for a compact and flexible molecular sensing system with high sensitivity and portability. © *2010 American Institute of Physics*. [doi:10.1063/1.3518957]

I. INTRODUCTION

Molecular sensors based on surface-enhanced Raman scattering (SERS) and optical fiber probes have been widely used in chemical and biological detection and sensing due to their unique advantages, such as molecular specificity, high sensitivity, flexibility, reliability, and also remote sensing capabilities.[1–16] However, the bulky spectrometer in the detection system seriously limits their practical applications outside the laboratory. In recent years, portable Raman spectrometers have been developed and are commercially available although their sensitivity still needs improvement. Fiber SERS probes integrated with a portable Raman spectrometer offer an ideal solution to a compact and flexible sensor system with high sensitivity and molecular specificity.

Previously, we have demonstrated that tip coated multimode fiber (TCMMF) (Ref. 17) and liquid core photonic crystal fiber (LCPCF) SERS probes[18–21] can achieve higher sensitivity than that obtainable by directly focusing the excitation laser light into the sample solution without using any fiber probes (direct sampling). The higher sensitivity achieved by the TCMMF SERS probe was attributed to a double substrate "sandwich" structure which utilized the strong electric field between the silver nanoparticles coated on the fiber tip and the ones in the solution.[17] The even higher sensitivity achieved by the LCPCF SERS probe was shown to be due to the confinement of the excitation light and the Raman scattered light, as well as the analyte, inside the fiber core that increased the effective interaction volume.[20,21] And recently, LCPCF SERS probe integrated with a portable Raman spectrometer was proposed and demonstrated in our preliminary studies.[22] However, the unique high sensitivity was not well preserved and the achieved sensitivity was only roughly the same as that of direct sampling.

In this paper, we experimentally demonstrate two improved approaches of integrating fiber SERS probes to a portable Raman spectrometer for higher sensitivity. The first approach is the TCMMF-portable SERS system, which can achieve 2–3 times better sensitivity than direct sampling, the same level of improvement as that achieved in the bulky Renishaw Raman system.[17] The TCMMF-portable SERS system, employing the standard ferrule connector/physical contact (FC/PC) connectors, is lens-free and does not require any optical adjustment. Moreover, the TCMMF probe can be reusable after ultrasonic washing with MilliQ water. The second approach is the highly sensitive LCPCF-portable SERS system, whose sensitivity can reach up to 59 times as that of direct sampling, comparable to the value of 100 times using the Renishaw Raman system.[20,21] The demonstration of the highly sensitive portable SERS systems offers a very promising technique for various chemical, biological, medical, and environmental detections outside the laboratory.

II. EXPERIMENTAL DEMONSTRATIONS

The optical setups based on the integration of the TCMMF and LCPCF SERS probes with a portable Raman spectrometer are shown in Figs. 1(a) and 1(b), respectively. Their corresponding schematics are shown in Figs. 2(a) and 2(b), respectively. For the TCMMF-portable SERS system shown in Fig. 2(a), a custom-designed probe box (also shown in Fig. 1(a) as the black box held in the right hand) provides the FC/PC connectors for the excitation fiber, the collection fiber, and the TCMMF SERS probe. The excitation laser source inside the portable Raman spectrometer (785 nm, 70 mW) was delivered to the probe box by a multimode fiber. A band-pass filter inside the box was used to remove the silica Raman background from the fiber and only transmit the laser light. Also a long-pass filter was employed

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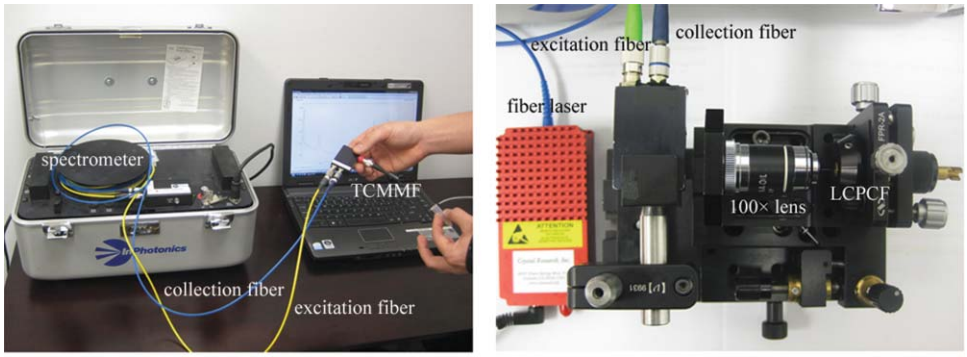

FIG. 1. (Color online) Experimental set-up: (a) TCMMF-portable SERS system; (b) LCPCF-portable SERS system (spectrometer and laptop computer not included).

to transmit only the Raman scattered signal, which was reflected by a dichroic beam splitter. And for the LCPCF-portable SERS system shown in Fig. 1(b), a compact stage was self-designed and used for the integration and alignment. A single-mode fiber laser (785 nm, 20 mW) was chosen as the excitation source, for better mode matching, which was coupled to the filter box by FC/PC connectors. And a 100× objective lens was employed for the coupling between the filter box and the LCPCF SERS probe that was mounted on an adjustable stage. For the direct sampling experiment, a small lens with 7.5 mm focal length was placed at the output port of the filter box, replacing the aspheric lens and the output FC/PC connector in Fig. 2(a), for focusing the laser beam onto the sample solution and collecting the SERS signal as well. The portable Raman spectrometer was purchased from InPhotonics.

In our experiment, silver nanoparticles (SNPs) were used as the SERS substrates and Rhodamine 6G (R6G) was used as a test molecule. SNPs used in the sample solution were synthesized using the Lee and Meisel protocol.[23] Briefly, 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. The average diameter of the SNPs was estimated to be around 35 nm based on transmission electron microscope (Model JEOL JEM 1200EX) and the concentration of SNPs was calculated to be $\sim 3 \times 10^{-11}$ M.

The sample solution was prepared as previously reported for various concentrations of R6G molecules (10^{-5} M–10^{-6} M), and sodium chloride (10 mM) was added to induce aggregation of SNPs for optimum SERS performance.[17] For the TCMMF-portable SERS system, 10^{-5} M SERS sample was measured with an integration time of 10 s. For the LCPCF-portable SERS system, 10^{-6} M sample solution was measured with an integration time of 10 s.

The multimode fiber used to build the TCMMF SERS probe was purchased from Newport (model F-MLD-500). One end of the fiber was self-packaged with a FC/PC connector while the other end was tip coated with another type of SNPs synthesized by a modified Brust method.[24] Briefly,

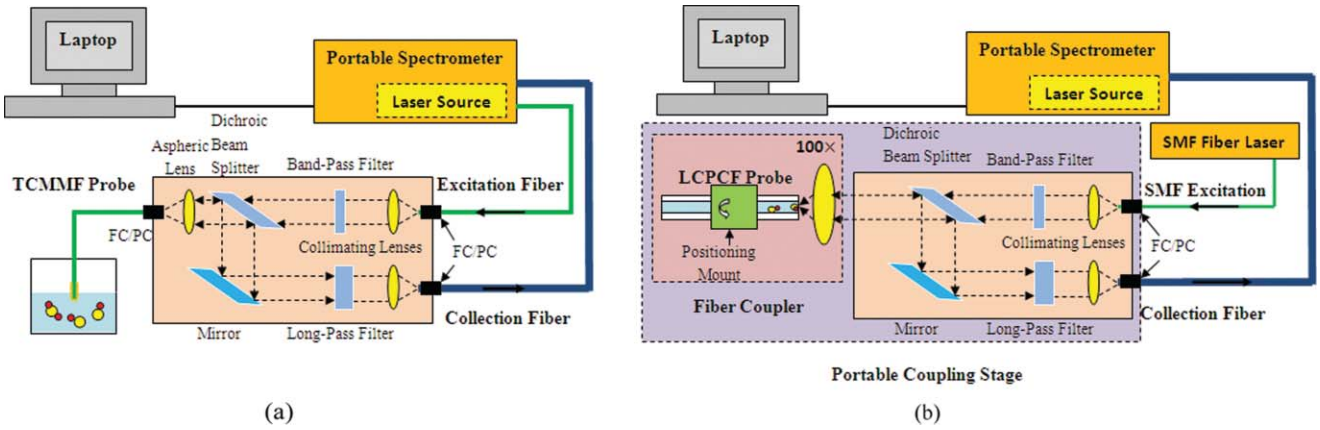

FIG. 2. (Color online) Schematics of (a) TCMMF-portable SERS system and (b) LCPCF-portable SERS system (not to scale). In (a), a custom-designed probe box provides the FC/PC connectors for the excitation fiber, the collection fiber, and the TCMMF SERS probe. The excitation laser source inside the portable Raman spectrometer is delivered to the probe box by a multimode fiber. A band-pass beam splitter removes the silica Raman background from the fiber and only transmits the laser light. A long-pass filter is used to transmit only the Raman scattered signal, which is reflected by a dichroic beam splitter. In (b), a single-mode fiber laser is chosen as the excitation source and a 100× objective lens is employed for the coupling of the box to the LCPCF SERS probe. The LCPCF SERS probe is packaged with the objective lens by a fiber coupler with 5 degrees of freedom position adjustments and the fiber coupler is fixed with the box on a compact self-designed stage.

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170 mg of $AgNO_3$ was dissolved in 5 ml of ethanol and kept under magnetic stirring; and three molar equivalents of hexanethiol were added dropwise followed by an addition of 80 ml of toluene. The solution was subsequently reduced with a 10-fold molar excess of $NaBH_4$ in 10 ml of nanopure water. The reduction was allowed to proceed overnight. Afterward, the solution was washed several times with nanopure water to remove any inorganic impurities and the toluene phase was collected and was placed under rotary evaporation. The particles were further purified with methanol. The average core size of the resulting hexanethiolate-protected silver (AgC6) nanoparticles was 5 ± 2 nm. The coating procedure was much simpler than the one used previously;[17] the tip of the fiber was dipped into the SNPs solution overnight without any complicated procedures.

The hollow core photonic crystal fiber (HCPCF) used for the LCPCF SERS probe was purchased from Crystal Fiber A/S (model AIR-6-800). The central core diameter is 6 μm, the side length of cladding holes is 0.75 μm, and the pitch distance between cladding holes is 1.6 μm. The fiber has a low transmission loss, indicating a photonic band gap, in the wavelength range of 745–853 nm and therefore is suitable for 785 nm laser excitation. To make an LCPCF SERS probe, an 8 cm long HCPCF segment was cleaved carefully at both ends, and a fusion splicer (Model FITEL S175) was used to seal the cladding holes at one end of the fiber. When the sealed end was dipped into the sample solution only the central core was filled with the liquid mixture of R6G and SNPs. Then the LCPCF was placed in the fiber holder on the coupler with the sealed end toward the objective lens. The alignment for focusing the laser beam onto the surface of the core of LCPCF was performed with adjusting screws on the fiber coupler with 5 degrees of freedom, 3 translational and 2 rotational; and a power meter was placed after the LCPCF for monitoring the transmitted power. The best SERS signal was obtained around the point with the maximum transmitted power, but not exactly at the transmission peak where a significant amount of power was coupled into the cladding.

III. RESULTS AND DISCUSSION

Figure 3 shows the SERS signals obtained from the TCMMF-portable SERS system and the direct sampling when the concentration of R6G is 10^{-5} M. Comparing the typical peak at 1358 cm^{-1}, the signal obtained with the TCMMF system is around 2.5 times that obtained from the direct sampling. Since the core size of the TCMMF is 100 μm, the same as that of the excitation fiber, the coupling is relatively easy by using a collimating lens and an aspheric focusing lens between the excitation fiber and the TCMMF. Also, a 200 μm collection fiber is chosen for better collection efficiency. Therefore, the sensitivity enhancement, defined as the ratio between the SERS signals obtained with the TCMMF and from the direct sampling, achieved by using the TCMMF-portable SERS system can be the same as that achieved by using the bulky Renishaw system.[17] Besides the higher sensitivity, the other advantage of the TCMMF-portable SERS system is the freedom from any optical adjustments. The

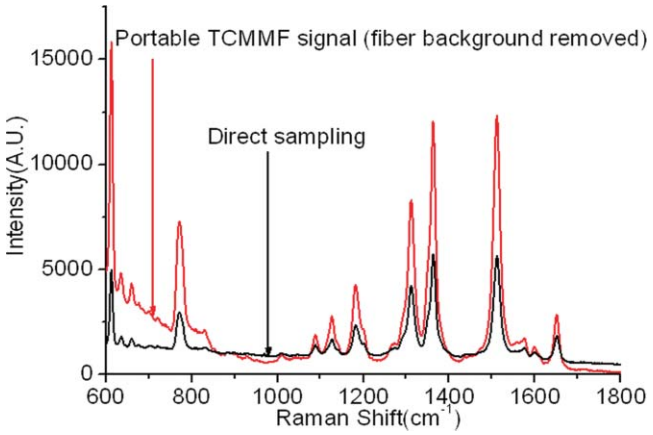

FIG. 3. (Color online) SERS signals obtained using the portable-TCMMF system and that obtained using direct sampling, when the R6G concentration is 10^{-5} M.

TCMMF SERS probe can be interfaced with the rest of the system by FC/PC connectors, and the measurement is easily performed by inserting the fiber probe into the sample solution by hand, as shown in Fig. 1(a).

In addition, we have demonstrated that the TCMMF SERS probe is reusable. Since the SNPs coated on the fiber are not dissolvable in water, the probe can be ultrasonically washed by MilliQ water. Figure 4 shows that after two washing procedures, the SERS signal is still roughly the same as before. And no SERS signal was observed with just the tip after the washing procedure, which demonstrated the molecules have been washed away. All these features of the TCMMF-portable SERS system including higher sensitivity, portability, and reusability make it well suited for various practical detection applications.

For the LCPCF-portable SERS system, since LCPCF has a much smaller core (6 μm diameter), coupling between the laser source and the LCPCF is more challenging than the TCMMF system. Misalignment or large beam size would affect the coupling and therefore degrade the performance of the highly sensitive SERS probe. In our system, a single-mode fiber laser was used to replace the excitation laser built in the portable Raman spectrometer, and a 100× objective lens was

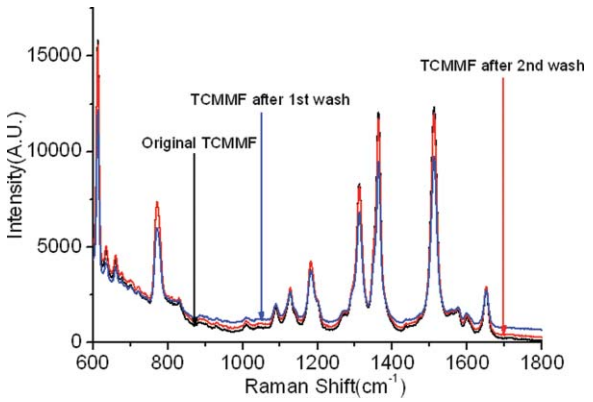

FIG. 4. (Color online) SERS signals obtained using the portable-TCMMF system after washing procedures.

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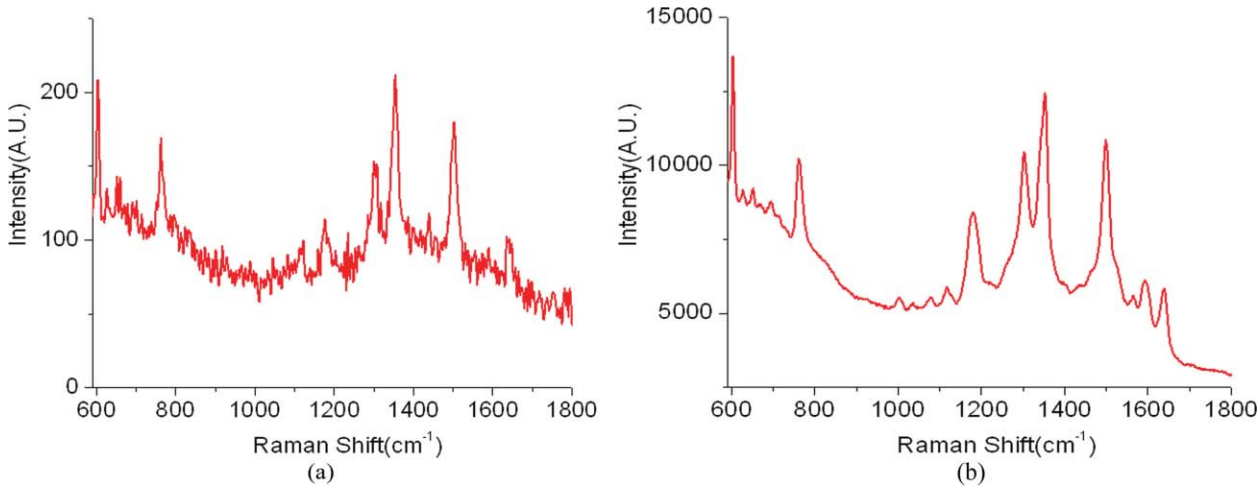

FIG. 5. (Color online) SERS signals obtained using (a) direct sampling and (b) the portable-LCPCF system, when the R6G concentration is 10^{-6} M.

employed to achieve a small enough beam size for coupling. The beam size at the focal plane can be as small as 5 μm measured by a CCD imaging system, which is well suitable for the coupling considering the core size of the LCPCF (6 μm diameter). To integrate the LCPCF SERS probe to the fiber laser and the portable spectrometer, a compact portable coupling stage with adjustment screws was employed, as shown in Fig. 1(b). All optical components, except the fiber holder, are fixed. The fiber holder can be adjusted with 5 degrees of freedom, 3 translational and 2 rotational, by using the screws on the mount.

Figure 5 shows the SERS signals obtained from the direct sampling and that obtain using the portable LCPCF SERS system. Compared to the result shown in Fig. 5(a), Fig. 5(b) shows that the portable LCPCF SERS system's sensitivity is 59 times that of direct sampling, measured based on the intensity of the 1358 cm^{-1} peak. This enhancement is comparable to the 100 times obtained when using the LCPCF SERS probe under the Renishaw system.[20,21] The difference in sensitivity enhancement between the portable system and bulky Renishaw system is attributed to the coupling between the objective lens and the LCPCF. In the portable system the adjustment was performed with the help of a power meter; while in the Renishaw system the CCD image was utilized to facilitate the alignment. Other possible factors that limit the achievement of the 100 times sensitivity enhancement include the performance of other optical parts in the portable SERS system. Better integration and packaging techniques are being explored for further improvement. At present, the 59 times sensitivity enhancement is quite significant for a portable Raman system. Future work will include expanding the testing of more complex molecules using this highly sensitive LCPCF-portable SERS system.

IV. CONCLUSION

In summary, we have successfully demonstrated two portable fiber SERS systems with higher sensitivity than direct sampling; one is the TCMMF-portable SERS system and the other is the LCPCF-portable SERS system. The TCMMF system provides 2–3 times higher sensitivity than direct sampling, is alignment-free, and uses a SERS probe that is reusable after washing. The LCPCF system provides even much higher (59 times) sensitivity than direct sampling, with proper coupling, while preserving the portability. These fiber-based portable SERS systems offer promising platforms for various applications in chemical, biological, medical, and environmental detections. Our future work will explore a more compact portable fiber SERS system with higher sensitivity and implement it as a powerful analytical tool for molecular detections outside the laboratory.

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