

Inner wall coated hollow core waveguide sensor based on double substrate surface enhanced Raman scattering

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A hollow core waveguide with silver nanoparticles coated on the inner wall has been used for molecular detection based on surface enhanced Raman scattering (SERS). With rhodamine 6G as an analyte molecule and two types of silver nanoparticles as double SERS substrates, the inner wall coated hollow core waveguide (IWCHCW) exhibits higher sensitivity than previous sampling methods with only one substrate. The improvement of sensitivity is attributed to the additional enhancement of the electromagnetic field by double substrate “sandwich” structure. The simple architecture and high sensitivity of IWCHCW make it promising for molecular detection in various analytical and sensing applications. © 2008 American Institute of Physics.

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Surface enhanced Raman scattering¹⁻⁷ (SERS) is an enabling technology for molecular sensing. Raman spectroscopy provides the unique molecular specificity while surface enhancement provides the needed sensitivity. Optical fibers have been used as SERS probes due to their compactness, flexibility, and remote sensing capability in practical applications. Various configurations such as flat,⁸ angled,⁹ and tapered¹⁰⁻¹² fibers were tested, but the small number of SERS substrate nanoparticles involved in the active region due to relatively small contact area limited their sensitivity.

In our recent study, a liquid core photonic crystal fiber¹³ (LCPCF) has been demonstrated to involve more SERS particles in the active region, leading to increased sensitivity. The measured enhancement is attributed to the confinement of both the excitation light and the liquid sample inside the microcavity. In addition, a double SERS substrate “sandwich” structure¹⁴ for fiber probes has been shown by us recently to enhance SERS sensitivity. The key idea of the “sandwich” structure is to use two types of silver nanoparticles (SNPs) as SERS substrates simultaneously. In our earlier work,¹⁴ one SERS substrate (e.g., SNPs) was coated on the tip of the normal multimode fiber and the other was mixed with analyte molecules in the sample solution. When the tip was dipped into the sample solution, the SNPs with analyte molecules would randomly bind to the SNPs on the tip to form a sandwich structure. The highly enhanced electromagnetic field between the two SNPs introduced significantly stronger SERS than those detected otherwise.

Based on the two enhancement effects due to the microcavity¹³ and the sandwich structure,¹⁴ it is of interest to test the possibility of combining the two ideas together to achieve further enhancement. In this paper, we demonstrate a SERS probe, namely, the inner wall coated hollow core

waveguide (IWCHCW), with sensitivity of two orders of magnitude higher than that of direct detection. The hollow core is for the introduction of the microcavity effect and the inner wall coating is one part of the sandwich structure (the other one is in the sample solution). Two types of hollow core waveguides (HCWs) are used in our experiments: hollow core photonic crystal fiber (HCPCF) and hollow silica waveguide (HSW).¹⁵ The advantage of the HCPCF is its low transmission loss resulting in better light confinement and hence higher sensitivity. However, the small core size (5 μm in diameter) makes light coupling challenging. As for the HSW, its relatively large core (300 μm in diameter) makes the coupling much easier and more stable. However, the radiation loss is relatively high for the HSWs due to poor light confinement at the wavelength used. This problem could be solved by using different laser wavelengths. Therefore, in our experiments carried out to date, there is a tradeoff between HCPCF and HSW. With a reduction in the transmission loss, HSWs are the most promising for high sensitivity and low cost SERS detection applications.

The schematic of the IWCHCW sensor is illustrated in Fig. 1. The inner surface of the hollow core is coated with one type of SNP. The second type of SNP is mixed with the analyte in the solution. The solution enters the hollow core from the bottom end via the capillary effect, forming random sandwich structures with the analyte molecules in between the two types of SNPs. The excitation light is coupled into the core of HCW from the top end and propagates in it. The confined light interacts with the sample solution, which contained SNPs with the analyte molecules absorbed on the nanoparticle surface. The SERS signal from the sample propagates back through the HCW and is collected by the Raman spectrometer. The light source is a 633 nm diode laser used in conjunction with a Renishaw micro-Raman spectrometer with a leica microscope and a 50 \times objective lens.

The HCPCF used in our experiments was purchased from Thorlabs, Inc. (model HC-633-01) with its cross section

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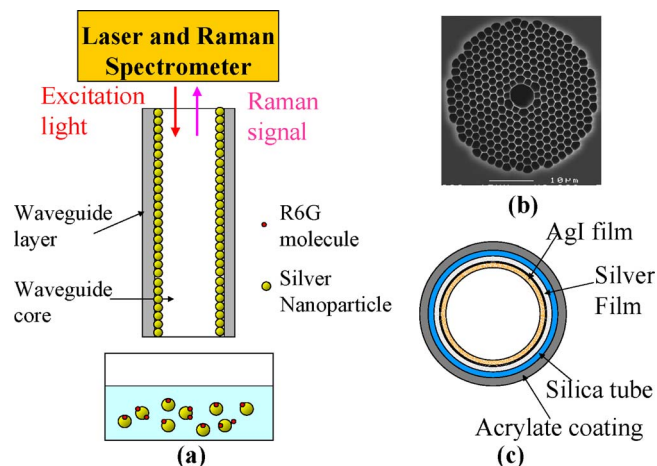


FIG. 1. (Color online) (a) Schematic of the IWCHCW sensor; (b) cross section of hollow core photonic crystal fiber; (c) cross section of HSW and four different layers of the HSW.

shown in Fig. 1(b). A fusion splicer (model FITELE S175) was used to seal the cladding holes at one end of the fiber¹⁶ in order to create a LCPCF. The HSW used was a sample from Polymicro Technologies, Arizona. As shown in Fig. 1(c), a HSW is a capillary tube containing four layers, AgI film, silver film, silica tube, and acrylate coating from the inside out. This particular HSW was designed to transmit high power laser beams for IR applications. Since the wavelength used is 633 nm, the radiation loss is relatively high. A 5 cm HSW was prepared by cutting carefully at both ends. The laser output power was 4.00 mW and at the far end of the HSW the power dropped to 0.200 mW. The light confinement was slightly improved after coating SNPs on the inner wall of HSW. The far end output power increased to 0.255 mW after the coating.

The SNPs used in the sample solution were synthesized using Lee and Meisel protocol.¹⁷ 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 is about 25 nm as determined using transmission electron microscope (Model JEOL JEM 1200EX). The nanoparticles made by this method in aqueous solution have a typical UV-vis spectrum with the characteristic broad surface plasmon band peaked around 405 nm.

The SNPs coated on the inner wall were prepared by following a literature procedure.¹⁸ Briefly, 0.25 mmol of AgNO_3 was dissolved in 5 ml of nanopure H_2O , into which was added 40 ml of toluene with 0.75 mmol of tetraoctylammonium bromide (TOABr) under vigorous stirring. Then $\sim 400 \mu\text{l}$ of dodecanethiol was added into the solution. In a separate beaker, 2.5 mmol of NaBH_4 was dissolved in 10 ml of H_2O . While the Ag-containing mixture was rapidly stirred, the reducing agent was added, and the solution turned dark brown quickly, signifying the formation of SNP. The reaction was allowed to proceed for several hours. Upon completion of the reaction, the mixture was washed with nanopure water for three times. The toluene phase was then collected, and dried under reduced pressure with a rotary evaporator. Excessive thiol and TOABr ligands were then removed by rinsing the collected black solids with copious methanol. Then the SNPs were collected by centrifugation and redispersed in

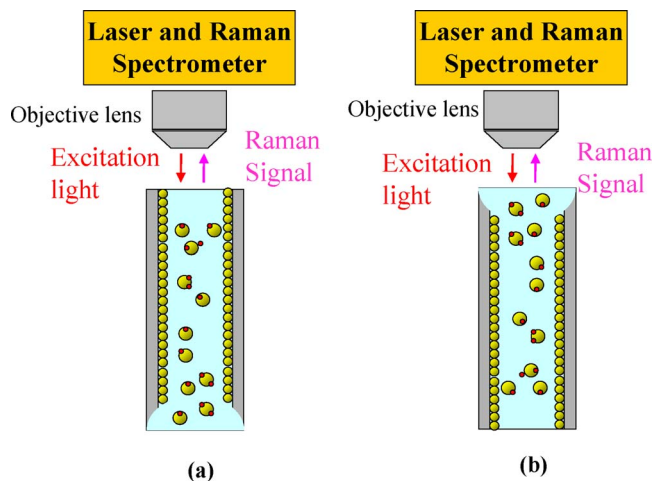


FIG. 2. (Color online) (a) Schematic of the detection by focusing light and collecting the SERS signal from the unsealed end of the coated LCPCF; (b) schematic of the detection by focusing light and collecting the SERS signal from the sealed end of the coated LCPCF.

dichloromethane for further use. The average core diameter is $5 \pm 2 \text{ nm}$.¹⁴

An injector was used to help coat the SNPs onto the inner wall of HCW. The HCW was mounted inside a syringe needle and a sticky tape was used to close the gap between the syringe needle and the HCW. After dipping the other end of HCW into the SNP solution and pulling the injector to pump the SNP solution into the core of the HCW, the hollow core was quickly filled with the SNP solution. Then the HCW was dried for 20 min to remove the organic component from the silver particles. The dipping procedure was repeated to form a multilayer of SNPs on the inner wall surface of the HCW.

The analyte solution is 10^{-6} M R6G in water and sodium chloride (NaCl , 10 mM) was added to induce SNP aggregate formation. The solutions were incubated for about 10 min at room temperature and then activated with $15 \mu\text{l}$ NaCl solution. Raman measurements were performed about 20 min after the introduction of salt.

The inner wall coated LCPCF probe was used in two different modes to detect R6G molecules. When the cladding-sealed end of the coated LCPCF was dipped into the sample solution, the sample solution would enter the central core due to the capillary effect until it reached the unsealed end of the coated LCPCF. One way to detect the sample solution is to focus light and collect the SERS signal from the unsealed end of the coated LCPCF, shown in Fig. 2(a), and the other is from the sealed end of the coated LCPCF, shown in Fig. 2(b). The experimental results are shown in Fig. 3(a). The SERS signals from both the unsealed end and the sealed end are much better than that obtained from the direct sampling method. Furthermore, the signal obtained from the unsealed end is nearly 10 times stronger than that from the direct sampling and the signal from the sealed end is around 100 times stronger than that from the direct sampling. Compared to the results of the same photonic crystal fiber and only LCPCF configuration,¹⁹ which is slightly higher than that obtained from the direct sampling, it is evident that the inner wall coating indeed further enhances the signal, which is attributed to the sandwich effect.

An extra enhancement due to the shape of the sealed end was also observed. As shown above, the SERS signal from

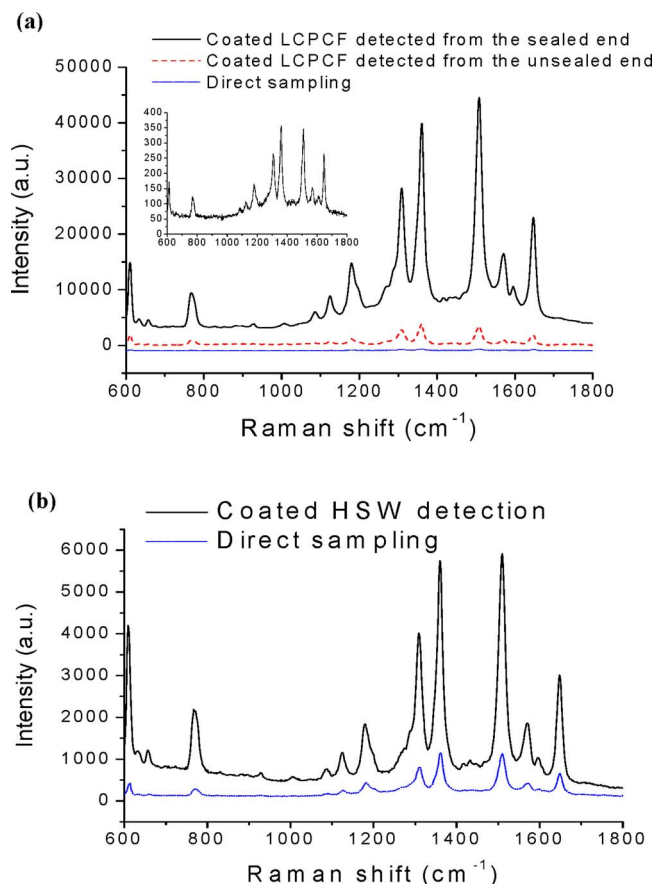


FIG. 3. (Color online) SERS spectra of R6G molecules at the concentration of $10^{-6}M$ by using different detection methods. (a) Comparison of direct sampling and using coated LCPCF; inset: the enlarged SERS spectrum of direct sampling; (b) comparison of direct sampling and using coated HSW.

the sealed end of the coated LCPCF was ten times stronger than that from the unsealed end. The only difference between the two ends was the geometrical shape. The sealed tip was concave as a result of heating in the fusion splicer, i.e., the sealed end appeared as a “bowl” shape, as shown in Fig. 13 of Ref. 16. There was more sample solution in the bowl shaped structure and another possible reason for the enhancement could be the surface plasmon resonance (SPR) of the SNPs in the bowl that helped couple more light into the core of the fiber.

The results obtained using inner wall coated HSW to detect R6G molecules are shown in Fig. 3(b). The SERS signal from the HSW is around five times stronger than that from the direct sampling. For comparison, we also calculated the effective number of molecules involved in the SERS activity from the direct sampling and the coated HSW, respectively. The laser spot was a circle with a diameter of $\sim 6 \mu\text{m}$. The sample solution was placed in a small cap for the direct sampling. The height of the solution was 0.5 cm so the ef-

fective volume of the sample solution involved in SERS is around $1.41 \times 10^{-4} \mu\text{L}$. On the other hand, the core diameter of the HSW is $300 \mu\text{m}$ and the effective length in the core is around 4 cm. Thus, the effective volume of sample solution in the core is $1.13 \times 10^{-3} \mu\text{L}$. In addition, the laser power is 4.00 mW and after passing through the HSW, it is 0.255 mW. Besides, the SERS intensity from the coated HSW is around five times stronger than in direct sampling. Taking into account the above factors, the enhancement per molecule per photon using coated HSW is about ten times that of direct sampling.

In summary, a simple IWCHCW has been proposed and demonstrated as a highly sensitive SERS probe for molecular detection. Both the LCPCF and hollow silica waveguide IWCHCW showed ten times stronger SERS than that in direct sampling using a single substrate. With a LCPCF IWCHCW, the SERS signal is around 100 times that in direct sampling. This is attributed to the additional R6G/SNPs solution in the fiber tip and increased coupling efficiency due to SPR in the SNPs. The IWCHCW is not only highly sensitive due to the sandwich structure but also low in cost, making it promising for various analytical and sensing applications.

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