A double substrate "sandwich" structure for fiber surface enhanced Raman scattering detection

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A double substrate "sandwiching" structure has been designed and tested for molecular detection using surface enhanced Raman scattering (SERS). With silver (Ag) nanoparticles as SERS substrates and rhodamine 6G (R6G) as a test molecule, the results show that the "sandwich" configuration exhibits significantly higher SERS enhancement compared to just one of the substrates or a simple sum of the signals from the two separate substrates. The improved SERS sensitivity is attributed to a stronger electromagnetic field enhancement by the double substrate sandwich structure. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2883957]

Molecular detection based on surface enhanced Raman scattering[1–7] (SERS) and optical fiber probe[8–16] has attracted extensive attention in recent years. The investigation of chemical and biological samples demand sensors with characteristics such as molecular specificity, high sensitivity, low cost, easy fabrication, reliability, and remote sensing capabilities. SERS provides the "fingerprint" information about specific molecules with highly enhanced signals while optical fibers offer the compactness and flexibility in practical applications.

The original single multimode SERS fiber probe was demonstrated in 1991 by Mullen and Carron.[17] In the following years, studies involving different kinds of fiber tips were tested, such as flat, angled, and tapered[18–20] fibers. Although they were easy to implement, the small number of SERS substrate particles in the active region limited the sensitivity of these sensors. In order to involve more particles in the SERS activity, hollow core photonic crystal fiber[21,22] (HCPCF) and liquid CPCF (Ref. 23) (LCPCF) were tested recently. High sensitivity and low fiber SERS background show a promising future of PCF sensors. However, the wavelength sensitive nature of HCPCFs limits the application of a HCPCF to a single excitation wavelength and the cost of PCFs is still high. While normal fibers are lower in cost, their sensitivities are somewhat limited, often due to the background Raman scattering from the fiber itself. Therefore, it is highly desired to improve the detection sensitivity of SERS sensors based on conventional fibers. Fiber SERS sensors with high sensitivity, remote sensing capability, and low cost will find potential applications in medical, environmental, food detection, and toxin identification.

In this letter, a configuration based on a double-substrate "sandwich" structure is designed to enhance the SERS activity using two substrates simultaneously. One simple approach to achieve this is to coat one SERS substrate, e.g., silver nanoparticles (SNPs), on the tip of a multimode fiber (MMF) and mix second substrate in solution with the target analyte molecules. Upon dipping the coated fiber probe into the solution, randomly formed structures of the two substrates will sandwich the analyte molecules in between. While this approach does not generate controllable sandwich structures, it is easy to implement. Perfect sandwich structures would be expected to show stronger enhancement than such random structures.

As shown in the simulation Xu and Kall,[24] the electromagnetic field between two closely spaced silver nanoparticles was substantially enhanced by an order of 10^{11} in hot nanojunctions.[25] Based on this huge enhancement, sandwich structures have the potential to reach greatly improved SERS sensitivity when the analyte molecules are placed between the two metal substrate nanostructures.

There are different approaches to implement such a sandwich structure. One possible simple scheme is shown in Fig. 1 based on a tip coated MMF (TCMMF). The excitation light for SERS is focused into the MMF from one end and well confined in the fiber during the propagation to the far end of the fiber where most light will be absorbed by the SERS substrate, SNPs, coated onto the fiber tip and form a strong field around the tip. The sample solution is a mixture of the analyte molecules, e.g., R6G, and SNPs with the molecules adsorbed on the nanoparticle surface. When the coated tip dips into the solution, the SNPs and analyte molecules in the solution will interact and bind to the SNPs coated on the fiber tip. Statistically, some of the molecules will be sandwiched in the junction between the two SNP substrates, where the electromagnetic field is further enhanced leading to stronger SERS signals. The SERS signal from the sample will propagate back from the MMF and be collected by the Raman spectrometer. The light source is a 633 nm diode laser inside the Renishaw micro-Raman spectrometer with a leica microscope and 50× objective.

The MMF used as a SERS probe is purchased from Newport (model F-MLD-500). The SNPs coated on the tip passivated with hexanethiol were prepared by using a modified Brust method.[26] Typically, 170 mg of $AgNO_3$ was dissolved in 5 ml of ethanol and kept under constant magnetic stirring. To that mixture, 3*M* equivalents of hexanethiol was

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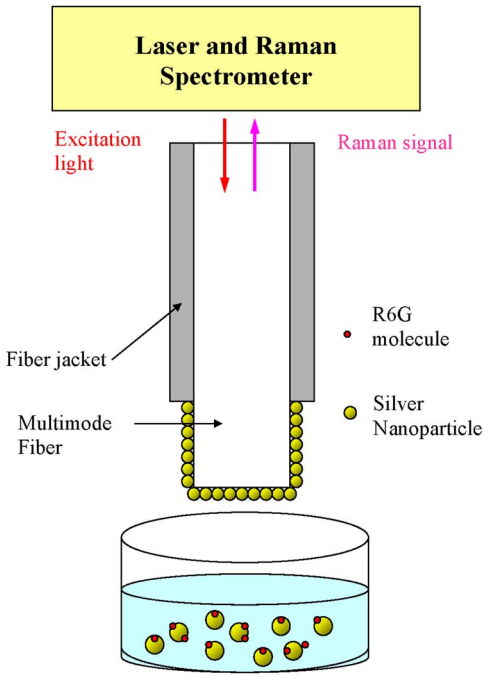

FIG. 1. (Color online) Schematic of the tip coated multimode fiber sensor.

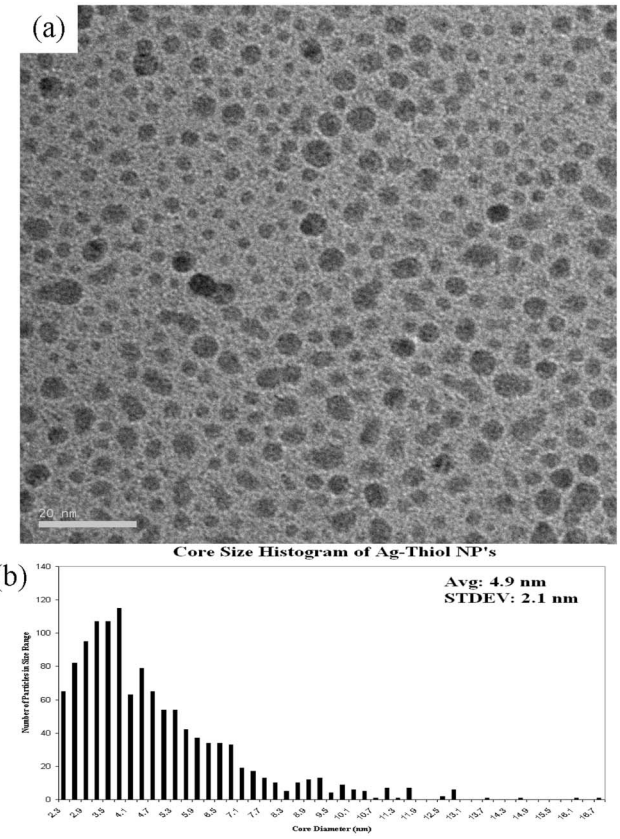

FIG. 2. TEM micrograph of AgC6 nanoparticles. (b) Size histogram with an average core size of 5 ± 2 nm.

added dropwise followed by an addition of 80 ml of toluene. The solution was subsequently reduced with a tenfold 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 and the resulting purified hexanethiolate-protected silver (AgC6) nanoparticles were collected on a glass frit. In order to determine the core size of the particles, transmission electron microscopy (TEM) was used (National Center for Electron Microscopy, Lawrence Berkeley National Laboratories). The samples were (~1 mg/ml) drop cast onto a 200 mesh carbon grid. Figure 2(a) shows a TEM micrograph of the AgC6. The average core diameter is 5 ± 2 nm, which is shown in Fig. 2(b). UV-visible spectroscopic measurements of the resulting particles in tetrahydrofuran solvent exhibited an intense absorption peak at 425 nm, a characteristic of the surface plasmon resonance of SNPs.

The coating of fiber optic cables is based on a simple dipping procedure. A concentrated solution of the silver nanoparticles (10 mg/ml) was prepared. The end of the fiber, with its protection jacket removed, was then dipped into the solution and left in the solution for 5 min. After dipping, the end of the fiber coated with the silver particles was washed with copious amounts of ethanol and then dried with a gentle stream of ultrahigh purity nitrogen. The fiber was then placed in a UVO chamber for 10 min to remove the organic component from the particles. The dipping procedure was repeated to form a multilayer[27] of particles on the surface of the optical fiber.

The SNPs used in the solution were prepared by using a different synthetic protocol from Lee and Meisel.[28] Briefly, silver nitrate was used as the metal precursor and sodium citrate as the reducing agent. The formation of the SNPs was monitored by UV-visible spectroscopy using an HP 8452A spectrometer with 2 nm resolution, and the corresponding surface plasmon absorption in the aqueous solution was observed to be at 406 nm. The average diameter of these SNPs was measured by TEM (Model JEOL JEM 1200EX) to be 25 nm. Compared to the AgC6 particles organic solvent, the nanoparticles made by the Lee and Meisel method in aqueous solution have larger average diameter but show a blueshift in the plasmon peak. The reason for this seemingly contradictory data is that the peak position depends not only on particle size but also on the media or the solvent. The larger refractive index of dielectric constant of the organic solvent causes a substantial redshift of the plamson peak compared to that of water.

The sample solution in this study was prepared for various concentrations of R6G molecules ($10^{-5}M - 10^{-9}M$) and sodium chloride (NaCl, 10 mM) was added to induce aggregate formation.[29] Starting with aqueous R6G solution ($10^{-4}M$), SNPs were added to dilute the R6G solutions. 30 μl of the R6G solution and 270 μl of the SNP colloid were mixed and, therefore, we obtained 300 μl sample with a concentration of $10^{-5}M$ of R6G molecules. Then, 30 μl of the resulting solution was added to 270 μl of the SNP colloid again to obtain a sample solution with R6G concentration of $10^{-6}M$. Solutions of various concentrations from $10^{-7}M$ to $10^{-9}M$, respectively, were prepared using the similar method. The solutions were incubated for about 10 min at room temperature and then activated with 15 μl NaCl solution. Raman tests were performed about 20 min after the introduction of salt.

Four different configurations were tested to compare the performance of the TCMMF sensors with other approaches,

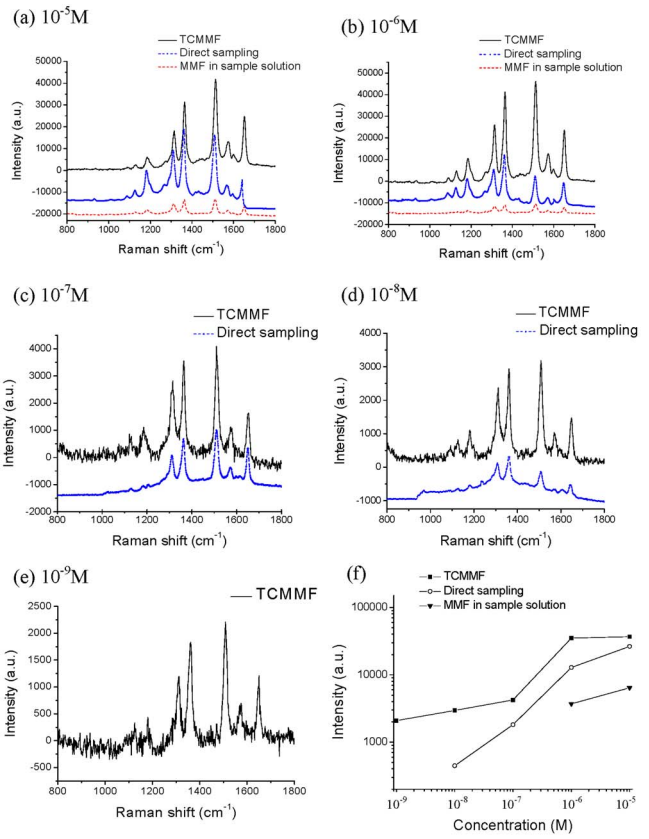

FIG. 3. (Color online) SERS spectra of R6G molecules for various concentrations by using different detection methods (TCMMF, MMF in sample solution, and direct detection). (a) $10^{-5}M$, (b) $10^{-6}M$, (c) $10^{-7}M$, (d) $10^{-8}M$, and (e) $10^{-9}M$. (f) Using the peak 1514.3 cm^{-1} as an example, the SERS intensity vs R6G concentration is plotted.

for various concentrations: (1) detection with the TCMMF probe dipped in the mixed sample solution; (2) direct detection of the SERS signal in the sample solution; (3) detection with an uncoated MMF as the probe dipped in the mixed sample solution; and (4) detection with the TCMMF probe dipped in the aqueous R6G solution. The lowest detectable concentration with the fourth approach was around $10^{-3}M$–$10^{-4}M$, which was much higher than the other three methods, therefore, was not included in the following comparison.

Figures 3(a)–3(e) compare the results obtained with the first three methods for various concentrations. For each concentration, the output power from the laser diode was 3.2 mW and at the far end of an ordinary MMF (case 3), the power was around 3.0 mW, indicating a 93.75% coupling efficiency. Whereas at the far end of a TCMMF (case 1), the power was 1.0 mW, indicating that most of the light was absorbed by the SNPs coated at the tip and the field was confined well around the tip. Using the peak 1514.3 cm^{-1} as an example, the SERS intensity versus R6G concentration was shown in Fig. 3(f).

Based on quantitative comparison of the SERS results, the lowest detectable concentration using the MMF probe, direct solution detection, and the TCMMF probe were $10^{-6}M$, $10^{-8}M$, and $10^{-9}M$, respectively. For the same concentration of R6G, the signal intensity from the TCMMF probe was consistently much higher than that from the MMF probe or direct solution detection, as well as the simple sum of the signals from MMF plus the direct solution detection. This indicates stronger SERS activity with the TCMMF due most likely to stronger electromagnetic enhancement as a result of the unique sandwich structure. Such sandwich structures formed by SNPs on the fiber probe with SNPs in solution are expected to exhibit stronger SERS due to stronger electromagnetic enhancement as compared to each substrate alone since some of the R6G analyte molecules are at the junctions of SNPs. The results in the TCMMF experiment are reproducible. These results show that sandwich structures are indeed promising for improving SERS detection.

In conclusion, a unique double substrate sandwich structure based on TCMMF has been developed as a highly sensitive SERS probe. This probe is tested using R6G molecules and the sensitivity has been found to be ten times better than that using a single SNP substrate in solution. Concentration as low as $10^{-9}M$ can be readily detected using this probe, which is not possible using one of the two single substrates alone. The improvement of SERS sensitivity is attributed to the extremely large electromagnetic enhancement between SNPs. These experiments demonstrate the potential of using such a sandwich configuration for chemical and biological sensing and detection applications.

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