

Surface-enhanced Raman-scattering fiber probe fabricated by femtosecond laser

Xinwei Lan,¹ Yukun Han,² Tao Wei,¹ Yinan Zhang,¹ Lan Jiang,³ Hai-Lung Tsai,² and Hai Xiao^{1,*}

¹Department of Electrical and Computer Engineering, Missouri University of Science and Technology, 1870 Miner Circle, Rolla, Missouri 65409, USA

²Department of Mechanical and Aerospace Engineering, Missouri University of Science and Technology, 1870 Miner Circle, Rolla, Missouri 65409, USA

³Department of Mechanical and Automation Engineering, Beijing Institute of Technology, Beijing 100081, China

*Corresponding author: xiaoha@mst.edu

Received May 5, 2009; revised June 15, 2009; accepted June 18, 2009;
posted June 29, 2009 (Doc. ID 110890); published July 21, 2009

We report what we believe to be a new method to fabricate surface enhanced Raman scattering (SERS) fiber probe by direct femtosecond laser micromachining. Direct femtosecond laser ablations resulted in nanostructures on the cleaved endface of a multimode optical fiber with a 105/125 μm core/cladding diameter. The laser-ablated fiber endface was SERS activated by silver chemical plating. High-quality SERS signal was detected using Rhodamine 6G molecules (10^{-8} – 10^{-6} M solutions) via back excitation with the fiber length of up to 1 m. The fiber SERS probe was compared with a planar fused silica substrate at a front excitation. The long lead-in fiber length and the backexcitation/collection setup make the SERS probe promising for remote sensing applications. © 2009 Optical Society of America
OCIS codes: 060.2370, 300.6450, 220.4000.

Fiber-optic surface-enhanced Raman scattering (SERS) has raised wide interests since the first demonstrations in the 1990s [1,2]. With its remote sensing capability, molecular identification, high sensitivity, and ultracompactness, the miniaturized SERS fiber probe may find a variety of applications in environmental monitoring, food safety, biochemical sensing, and explosive detection [3–5]. The preparation of fiber SERS probes commonly requires uniformly roughened surface and properly deposited noble metal thin films or particles. Various techniques have been reported to fabricate fiber SERS probes in the past. Examples include metal coating of roughened endface [6], metallic nanoparticle deposition [7–9], bioimprint aided fabrication [10], and metal coated fiber taper [11]. More recently, Yan *et al.* demonstrated an evanescent-field coupled-fiber SERS device by filling the voids of a photonic crystal fiber with metal colloids [12]. Shi *et al.* demonstrated a “sandwiched” fiber SERS probe configuration for sensitivity improvement by the combination of depositing silver nanoparticles on the fiber endface and by adding suspended silver colloids in the solution [13].

The latest advancement in femtosecond laser technology has opened a new window of opportunity for one-step fabrication of microdevices with three-dimensional (3D) configurations. Direct exposure of most solid materials (including silica glass) to ultraintense femtosecond laser pulses results in the quick establishment of free electron plasma at the focal point, leading to the ablation of a thin layer of materials [14]. Femtosecond lasers have been successfully used for directly writing optical waveguides [15] and machining microchannels/microchambers in glasses [16]. Most recently, femtosecond lasers were introduced as a tool for fast and direct fabrication of SERS substrate. Diebold *et al.* reported a SERS substrate, nanostructured by a femtosecond laser and

silver deposited by thermal evaporation on an *n*-type silicon wafer [17]. Zhou *et al.* used a femtosecond laser to write a waveguidelike microwire on Ag⁺-doped glass and then grew the photoreduced silver aggregates into SERS suitable sizes by chemical plating [18].

With fast speed, flexibility, high precision, and operation in an open atmosphere, femtosecond laser fabrication is one of the few promising methods for the direct fabrication of microstructures/nanostructures on optical fibers [19]. In this Letter, we report a high performance backexcitation/collection fiber SERS probe fabricated by direct femtosecond laser micromachining nanostructures on the cleaved endface of a multimode optical fiber (MMF) with a 105/125 μm core/cladding diameter.

A 1-m-long MMF (Fiberguide 105/125Y) segment with both ends cleaved was mounted on a home-integrated femtosecond laser 3D micromachining system, with one cleaved endface positioned perpendicular to the laser beam using a fiber holder. The repetition rate, the center wavelength, and the pulse width of the femtosecond laser (Legend-F, Coherent, Inc.) were 1 kHz, 800 nm, and 80 fs, respectively. The attenuated laser beam (0.7 nJ) was directed into an objective lens [Olympus UMPLFL 20 \times , NA of 0.46] and focused onto the cleaved fiber endface. The computer controlled stage moved the fiber endface at a speed of 1 mm/s, spacing the neighboring laser ablation points at a distance of 1 μm , considering a 1 kHz repetition rate. Upon finishing a line scan, the fiber was stepped transversely by 1 μm to start another line scan. Every single pulse produced an ablation spot with a size of ~ 1.5 μm in diameter on the fiber endface. The fast scanning technique took less than 1 min to cover the entire fiber endface. Figures 1(a) and 1(b) show a field emission scanning electron microscopic (SEM) images of the femtosecond laser-ablated

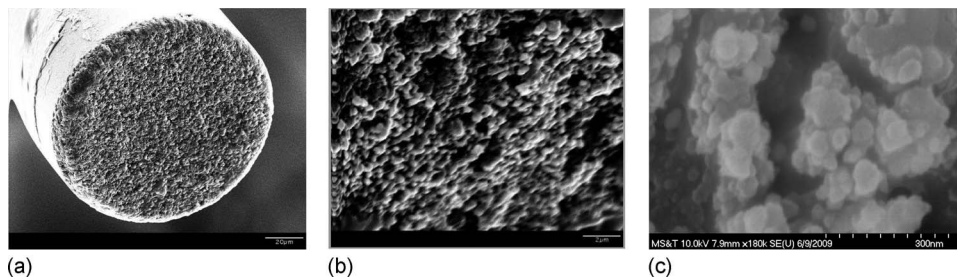


Fig. 1. SEM images of femtosecond laser-ablated fiber endface, (a) fiber tip (1500 \times), (b) surface profile (15,000 \times , 60 $^\circ$ tilted), (c) silver nanoparticles coated on structured surface (70,000 \times).

fiber endface. The laser ablation created a roughened surface with quasi-uniformly distributed features with a size of several hundred nanometers.

The formation of silver nanoparticles on a laser-ablated fiber endface proceeded as follows. A container cleaned by concentrated H_2SO_4 was well rinsed with de-ionized (DI) water. Mixing 30 ml of 0.3 M silver nitrate aqueous solution with 30 ml of 0.2 M NaOH formed a fine brown precipitate of Ag_2O . The 0.4 M ammonia solution was then added into this mixture drop by drop until the precipitate completely dissolved to form $[Ag(NH_3)_2]^+$. Then the 0.3 M silver nitrate solution was added until the solution became pale brown. After one drop of 0.4 M ammonium, the solution became transparent again. A sonicated clean femtosecond laser-ablated fiber tip was then fully immersed into the solution. We started to count the time as soon as 30 ml of 0.1 M α lactose was added into the solution. After 10 min, the fiber tip was removed from the solution, cleaned with DI water, and dried in nitrogen flow. Figure 1(c) shows the SEM image of the silver-coated laser roughened fiber endface. The coated silver appears to be isolated nanoparticles with the size ranging from 20 to 60 nm estimated from the SEM image.

The fiber SERS probe was evaluated by the Rhodamine 6G (R6G) molecule, carrying out on a commercial Raman spectroscopy system (LabRAM ARAMIS, Jobin Yvon Inc.). The SERS probe was immersed in the R6G solutions (10^{-8} – 10^{-6} M mixed with a 10 mM NaCl solution), while the other end of the fiber was vertically mounted under the microscope. The MMF has a NA of 0.22. A built-in 632.8 nm HeNe laser was focused into the core of the MMF through a 10 \times microscope objective (NA=0.25). The SERS probe was backexcited by the laser beam propagating through the MMF fiber core. Part of the SERS excitation propagated backward in the fiber and was collected by the microscope objective. The spectra were recorded by projecting the collected light onto a CCD array using a 1200 g/mm grating. A built-in 50 mW 785 nm diode laser was switched on for ~ 10 s to activate the fiber probe before testing.

Trace (a) in Fig. 2 (dashed curve at the bottom) is the Raman spectrum of a freshly cleaved fiber endface with a 1-m-long lead-in fiber. The as-cleaved fiber endface only showed the Raman signal of fiber material (fused silica). Trace (b) is the Raman spectrum of R6G (10^{-6} M) obtained by using a SERS probe with a 1-m-long lead-in fiber. The strong R6G SERS signal indicated an effective Raman amplifica-

tion through the silver-coated laser roughened surface. Trace (c) is the Raman spectrum of a planar fused silica SERS substrate fabricated via the same laser scanning and silver-coating procedures for comparison. The planar SERS substrate was front excited under the same 10 \times microscope objective. It is worth noting that the quantitative comparison between the planar SERS substrate and the fiber SERS probe is neither the intention nor trivial owing to variations in measurement conditions [7]. However, the similar signal-to-noise ratio for both the planar glass substrate and the 1 m long fiber SERS probe indicates that the backexcited fiber SERS probe is comparable with the conventional front excited SERS substrate. To qualitatively assess the contribution of the laser ablation, a freshly cleaved fiber probe was silver coated for 10 min following the same chemical plating procedures. Using the same laser power (1.7 mW) and integration time (1 s), the silver-coated unroughened probe could not pick up any noticeable Raman signature of R6G with the concentration of 10^{-6} M. When the concentration increased to 10^{-3} M, a small Raman signal appeared as shown in trace (d), where the signal intensity is multiplied by 10 for easy viewing. The above comparison indicated that it

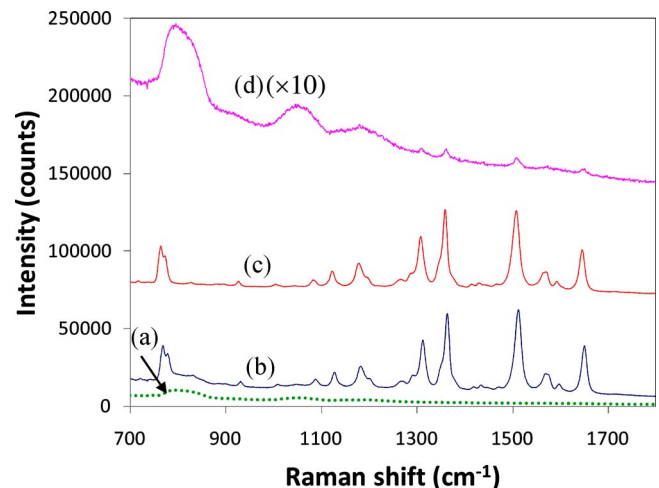


Fig. 2. (Color online) Raman spectra of R6G with a 1.7 mW HeNe laser excitation power and 1 s integration time. (a) Freshly cleaved fiber (1 m long); (b) femtosecond laser-ablated silver-coated (10 min) fiber SERS probe (1 m long) in a 10^{-6} M solution; (c) femtosecond laser-ablated silver-coated (10 min) planar fused silica SERS substrate in a 10^{-6} M solution with front excitation (shifted); and (d) silver-coated (10 min) unroughened fiber (1 m long) in a 10^{-3} M solution (multiplied by 10).

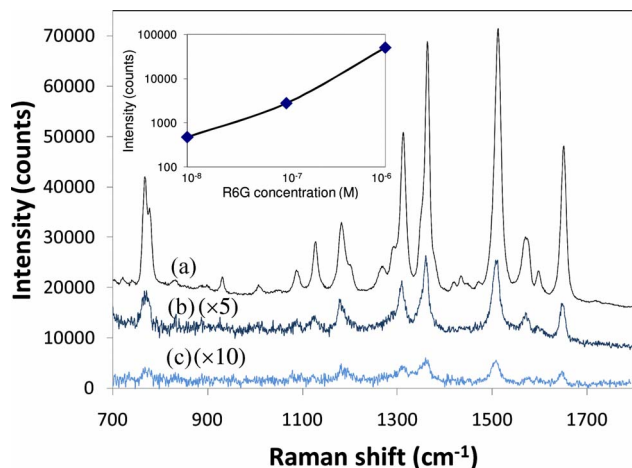


Fig. 3. (Color online) Raman spectra of R6G solutions with various concentrations obtained by the fiber SERS probe (1 m long). (a) 10^{-6} , (b) 10^{-7} (multiplied by 5 for easy viewing), (c) 10^{-8} M (multiplied by 10 for easy viewing). Inset, SERS intensity versus R6G concentration at 1511 cm^{-1} .

was the combination of the laser structured surface and the silver coating that accounted for the strong SERS signal.

Figure 3 plots the Raman spectra of R6G solutions with various concentrations (10^{-6} – 10^{-8} M) obtained by the fiber SERS probe. With a 1.7 mW laser excitation power and a 1 s integration time, the lowest detectable R6G concentration using our fiber SERS probe was about 10^{-8} M. The Raman intensity at 1511 cm^{-1} as a function of R6G concentration was also plotted in the inset of Fig. 3 for reference.

To investigate the lead-in fiber length effect on the backexcited Raman signal, we took a fiber SERS probe with a 1 m lead-in fiber and cut back every 10 cm while recording the SERS signal at each fiber length. Figure 4 plots the intensity at the Raman shift of 1312 cm^{-1} as a function of the lead-in fiber length. The SERS intensity increased by $\sim 16\%$ after the fiber length was cut to half, indicating that the SERS signal was relatively insensitive to the lead-in

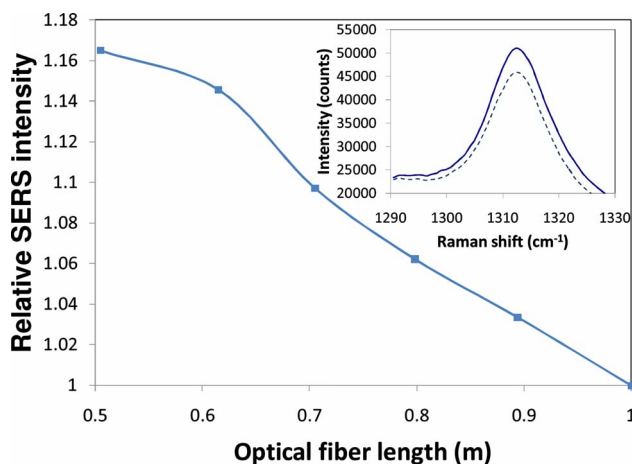


Fig. 4. (Color online) Back-excited Raman intensity as a function of lead-in fiber length at 1312 cm^{-1} . Inset: SERS spectra at 1312 cm^{-1} , solid curve: 0.5 m long lead-in fiber; dashed curve: 1 m long lead-in fiber.

fiber length. The observed dependence of the SERS signal on the lead-in fiber length may be attributed to the excess optical loss induced by imperfect light coupling from the microscope objective lens to the fiber. For example, the mismatch between the NAs of the objective lens and that of the fiber excites unguided cladding modes, whose loss is strongly length dependent at the launch section.

To summarize, a backexcited fiber SERS probe with a 1-m-long lead-in fiber was fabricated by fast femtosecond laser scanning and chemical silver plating. A high-quality SERS signal probe was observed using R6G as the probe molecule. With fast speed, flexibility, high precision, and operation in an open atmosphere, femtosecond laser fabrication may present a convenient and cost-effective way to construct high-quality fiber SERS probes. With a relative insensitivity to the lead-in fiber length, a back-excitation/collection setup, and a high sensitivity, the new fiber probe may find potential applications in remote detection and identification of various biological/chemical substances.

The research is supported by the Office of Naval Research (ONR) through the Young Investigator Program (N00014-07-0008), the National Natural Science Foundation of China (NSFC) under grant 50705009, and the 111 Project of China under grant B08043.

References

1. K. I. Mullen and K. T. Carron, *Anal. Chem.* **63**, 2196 (1991).
2. J. M. Bello and T. Vo-Dinh, *Appl. Spectrosc.* **44**, 63 (1990).
3. C. Haynes, A. McFarland, and R. Duyne, *Anal. Chem.* **77**, 338A (2005).
4. T. Vo-Dinh, *Anal. Chem.* **17**, 557 (1998).
5. C. Gu and C. Shi, *Laser Focus World* **45**, 97 (2009).
6. C. Viets and W. Hill, *Sens. Actuators B* **51**, 92 (1998).
7. D. L. Stokes and T. Vo-Dinh, *Sens. Actuators B* **69**, 28 (2000).
8. X. Zheng, D. Guo, Y. Shao, S. Jia, S. Xu, B. Zhao, and W. Xu, *Langmuir* **24**, 4394 (2008).
9. E. Polwart, R. L. Keir, C. M. Davidson, W. E. Smith, and D. A. Sadler, *Appl. Spectrosc.* **54**, 522 (2000).
10. A. Lucotti and G. Zerbi, *Sens. Actuators B* **121**, 356 (2007).
11. C. Viets and W. Hill, *J. Phys. Chem. B* **105**, 6330 (2001).
12. H. Yan, J. Liu, C. Yang, G. Jin, C. Gu, and L. Hou, *Opt. Express* **16**, 8300 (2008).
13. C. Shi, H. Yan, and C. Gu, *Appl. Phys. Lett.* **92**, 103107 (2008).
14. M. Li, S. Menon, J. P. Nibarger, and G. N. Gibson, *Phys. Rev. Lett.* **82**, 2394 (1999).
15. K. M. Davis, K. Miura, N. Sugimoto, and K. Hirao, *Opt. Lett.* **21**, 1729 (1996).
16. A. Szameit, D. Bloemer, J. Burghoff, T. Pertsch, S. Nolte, F. Lederer, and A. Tuennermann, *Appl. Phys. B* **82**, 507 (2006).
17. E. D. Diebold, N. H. Mack, S. K. Doorn, and E. Mazur, *Langmuir* **25**, 1790 (2009).
18. Z. Zhou, J. Xu, Y. Cheng, and Z. Xu, *Jpn. J. Appl. Phys.* **47**, 189 (2008).
19. T. Wei, Y. Han, H. Tsai, and H. Xiao, *Opt. Lett.* **33**, 536 (2008).