

# Synthesis and deposition of Silver nanostructures on the silica microsphere by a laser-assisted photochemical method for SERS applications

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**Abstract**—The homogeneous distribution of nano-metallic structures on the surface-enhanced Raman (SERS) substrates plays an important factor for high-sensitive Raman scattering measurement. In this paper, we present a low-cost laser-assisted photochemical method for making a SERS probe based on silver nanostructures, which are one-timely synthesized nano-silver structures, homogeneously deposited on silica microsphere surfaces. Achieved SERS-activity substrates with a homogeneous distribution of Ag-nanostructures are verified by a mapping technique on the surface of Ag-coated microsphere for the detection of low concentration of Rhodamine 6G in aqueous solutions in a range of  $10^{-4}$ - $10^{-9}$ M. The obtained results show that a SERS microsphere probe has a good repetition of SERS-activity in any space of sensing area, and large potential for application in a biochemical sensing technique.

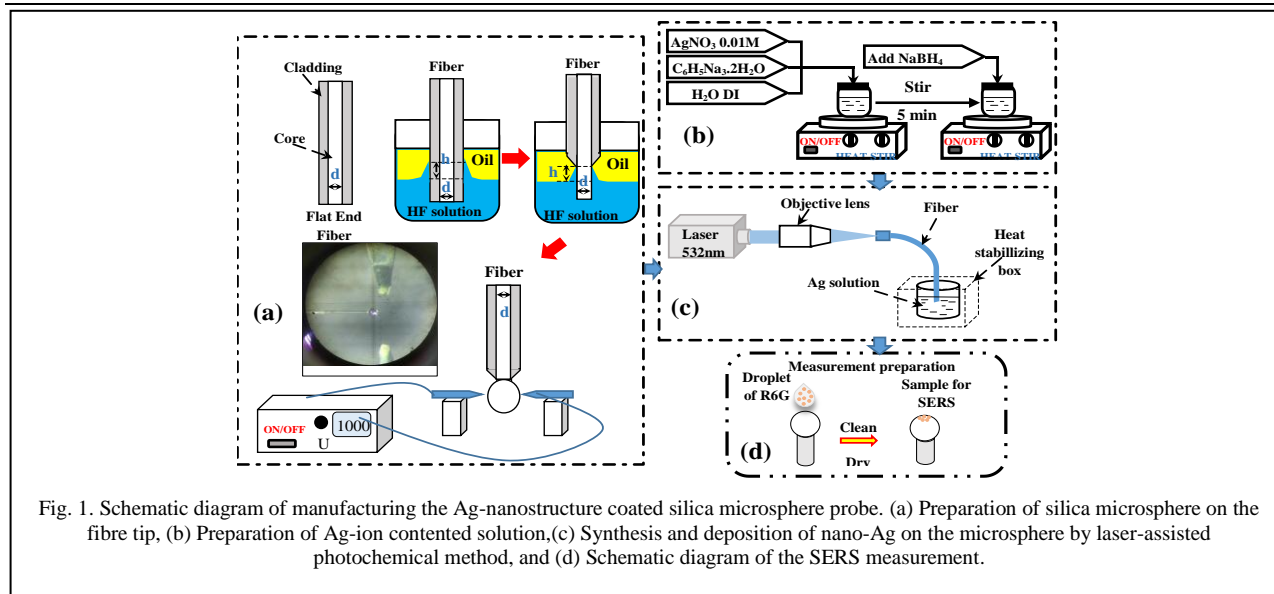
Today, our modern society makes ever-increasing technological demands for applications in environment monitoring, food safety control and health care [1–3]. Among the technologies applied in biochemical sensing, the SERS has been shown a powerful spectroscopic technique for ultrasensitive and high selective biochemical detection due to its capability of providing “fingerprint” information on biochemical molecular structures. The enhancement mechanism of SERS has been explained by a highly local enhanced electromagnetic (EM) field on the noble metal surface due to the excitation of localized surface plasmon resonances and enhanced chemical interaction between adsorbate and noble metal nanoparticles [4–6]. Recently, in the literature, there have been several studies combining SERS activity with optical fibre [7–10]. Among the noble metals such as gold, silver, palladium, and platinum, which have normally been applied in SERS substrates; the Ag-nanostructure is considered to be one of the most excellent candidates for SERS applications due to its highly desired plasmonic properties, low-cost and simple fabrication/synthesis. SERS substrates based

on Ag-nanostructure with various morphologies can be fabricated in many different ways, such as gamma irradiation, electron irradiation, electrochemical deposition, chemical vapour deposition (CVD), chemical synthesis, microwave processing, by hydrothermal or photochemical method [11]. But the homogenous distribution of Ag-nanostructure on the SERS substrate is a problem for sample preparation and repeating measurement results.

In this paper, we propose a novel low-cost laser-assisted photochemical technique, which will take one-timely synthesis and deposition of Ag-nanostructures on the silica microsphere surface, in comparison with a photochemical method using high power light emitting diodes (LED). The morphology and chemical composition of SERS probes are characterized by high-resolution scanning electron microscope (HR-SEM) and Energy dispersive X-ray spectroscopy (EDX), respectively. The achieved SERS-activity substrates on nano-Ag coated silica microsphere probes demonstrate low concentration of Rhodamine 6G in aqueous solutions in a range of  $10^{-4}$ - $10^{-9}$ M. The homogeneous distribution of Ag-nanostructures on the microsphere surface was tested by a mapping technique on the SERS surface with a different Raman signal of 2%.

The schematic diagram of the making process of SERS probes with Ag nanostructures on silica microspheres prepared in two steps is shown in Fig. 1. The silica microsphere probe on the multimode optical fibre with core/cladding diameters of 50/125 microns, supplied from Thorlabs (USA), was fabricated by wet chemical etching of the optical fibre end in the HF acid (30%) solution for 30 minutes, and then a microsphere was formed by melting the etched fibre end with electrical arc between the couple of discharge electrodes, as shown in Fig. 1a. The Ag growth solution was prepared by mixing an optimal molar concentration of aqueous  $\text{AgNO}_3$  of 0.1mM (Fisher Scientific, UK), and  $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$  of

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3mM (Merck KGaA, Germany) in a volume ratio of 1:1 with rapid stirring for 5min, then a freshly prepared 0.02mM  $\text{NaBH}_4$  solution (Kanto Chemical, Japan) was added by drop wise addition to the mixture under vigorous stirring for 15min, after which it was kept in the dark at room temperature, as shown in Fig. 1b. The growth and deposition of Ag nanostructures on surface microspheres were performed by a green laser with an emission wavelength of 532nm and optical power of about  $80\text{W}/\text{cm}^2$  (Laserlands, China), which propagated through the optical fibre to the silica microsphere attached at the end of this fibre (Fig. 1c). The growth and deposition of Ag nanostructures can be formed on a light-focused area of the microsphere surface after illumination of few minutes. In our experiment, the reaction solution was contained in a box with a stable temperature at  $3^\circ\pm 5^\circ\text{C}$  by using a Peltier thermoelectric cooler to avoid temperature effect on the growth of Ag nanostructures. After the silver growth and deposition process, the microsphere probe was taken out, carefully rinsed in deionized water and dried with a pure nitrogen gas stream. The schematic experimental setup of SERS-activity measurement using silica microsphere probes coated by Ag-nanostructures is shown in Fig. 1d.

In order to investigate the performance of the SERS-activity of microsphere probes, we used ultralow concentrations of R6G solutions. An aqueous solution of R6G (Sigma-Aldrich) was diluted in deionized water to make solutions with different R6G concentrations ranging from  $10^{-4}$  to  $10^{-9}\text{M}$ . The droplets of  $1\mu\text{L}$  of the R6G-diluted solutions were dropped on the SERS microsphere probes and naturally dried in air before SERS detection so that R6G molecules could be adsorbed onto the Ag nanostructures. The Raman scattering measurements were performed at room temperature with a laser excitation wavelength of 532nm. The Ag nanostructure coated silica microsphere probe was fixed perpendicularly to the

objective lens by the 5-stage holder (i.e., 3 stages for XYZ movement and 2 stages for angles change), and the exciting laser beam with a focused area of about  $5\mu\text{m}$  in diameter and an incident light power of 3mW has been irradiated on the top of microsphere. The typical spectrum acquisition time is 10s.

Figures 2a and 2 b show that the Ag-nanostructures are homogeneously distributed on the surface of silica microsphere and the diameter area of Ag-nanostructure deposition is about  $80\mu\text{m}$  when the core diameter of transmitting fibre is of 50 microns. Figure 2c displays the results of EDX of the Ag-nanostructures in the tiny region. The sharp peaks as Oxygen, Germanium (Ge) and Silicon (Si) indicated the components of a typical optical fibre with Ge doped into an  $\text{SiO}_2$  substrate, and the sharp peak Ag definitively showed the growth of Ag-nanostructures deposited on the silica sphere. The nano-Ag boulders of  $100\div 250\text{nm}$  formed after a laser exposure time of 10 minutes, as shown in Fig. 2d.

The SERS-activity of Ag-nanostructures was carried out with a diluted R6G solution using the Raman Microscope system (Horiba Scientific LabRAM HR Evolution). Figure 3 illustrates the SERS spectra of a R6G solution with various concentrations ranging from  $10^{-4}\text{M}$  to  $10^{-9}\text{M}$  dispersed onto Ag-nanostructure coated microsphere probes produced by the same synthesis process. It can be observed that the intensity of the SERS signal increases as the concentration of R6G increases. The Raman peak bands can be clearly observed in solutions with R6G concentrations down to  $10^{-9}\text{M}$ . The strong Raman bands of R6G-adsorbed Ag nanostructures were clearly observed with the feature characteristic peaks at around  $611.3\text{cm}^{-1}$ ,  $772.8\text{cm}^{-1}$ ,  $1181.9\text{cm}^{-1}$ , and  $1308.4\text{cm}^{-1}$ ,  $1361.3\text{cm}^{-1}$ ,  $1507.3\text{cm}^{-1}$ ,  $1573.6\text{cm}^{-1}$ , and  $1649.2\text{cm}^{-1}$ . To quantitatively estimate the Ag nanostructure-induced Raman enhancement, we calculated the enhance factor (EF) according to the formula [12]:

$$EF = \frac{I_{SERS} \times C_R}{I_R \times C_{SERS}}$$

where  $I_{SERS}$  represents the enhanced Raman intensity of R6G adsorbed on an Ag-nanostructure functionalized microsphere probe and  $I_R$  represents the normal Raman intensity (non-SERS) of R6G on the silica microsphere probe without Ag-nanostructure,  $C_{SERS}$  and  $C_R$  are the concentration of R6G in the SERS spectrum and normal Raman spectrum, respectively.

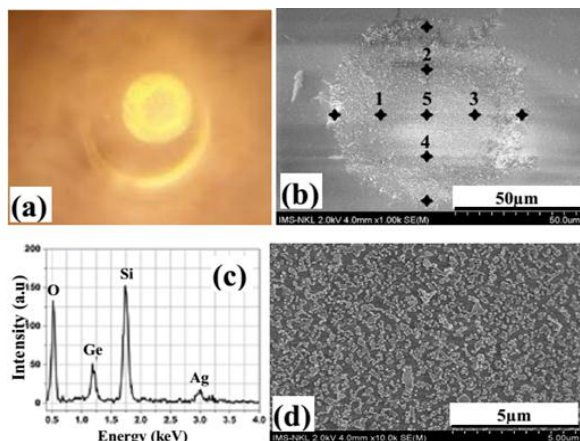


Fig. 2. (a) Optical photograph, and (b, d) the SEM images of Ag-nanostructure deposition area on the microsphere surface, and (c) EDX spectrum recorded on the Ag-deposited on the silica microsphere probe. The cross-makers in Fig. 2(b) present the mapping positions of SERS measurement.

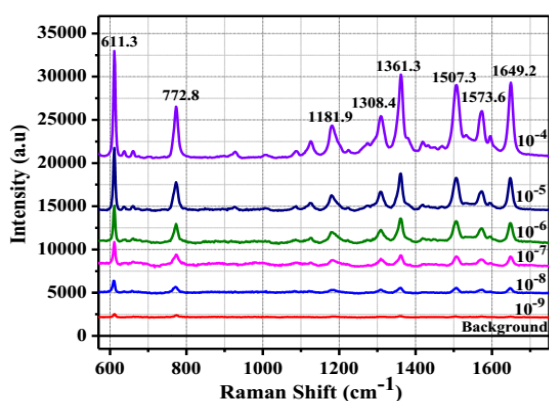


Fig. 3. SERS spectra of R6G solutions with concentrations ranging from  $10^{-4}$ M to  $10^{-9}$ M.

The Ag-nanostructure SERS exhibits excellent SERS-activity at the peak position of  $1649.2\text{cm}^{-1}$  and calculated EF value of  $6.7 \times 10^6$ . The mapping measurement of 5 positions on the nano-Ag coated silica microsphere probe indicated in Fig. 4 shows that SERS intensities of different positions at a Raman wavelength of  $611.3\text{cm}^{-1}$  for  $10^{-4}$ M of R6G varied  $\pm 2\%$ , which demonstrates that the Ag nanostructures distributed homogenously on the surface of silica microsphere.

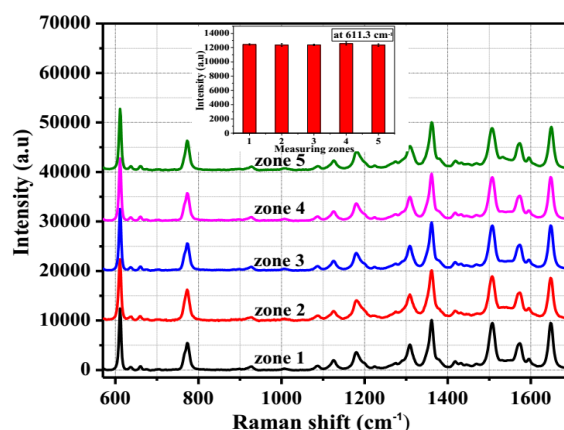


Fig. 4. Intensity of Raman spectra of R6G solutions with concentration of  $10^{-4}$ M measured by a mapping technique at 5 positions on a SERS substrate.

In summary, we have successfully grown and deposited Ag nanostructures on the surface of silica microsphere by a low-cost laser-assisted photochemical method, which can be used as a SERS-activity probe for biochemical molecular detection in a liquid environment.

The SERS-activity of an Ag nanostructure coated silica microsphere probe demonstrates its behaviour in detecting ultralow concentrations down to  $10^{-9}$ M of R6G with an enhance factor of  $6.7 \times 10^6$ . The Ag nanostructure coated silica microsphere probe has shown good repetition of SERS-activity in any space of the sensing area by homogenous distributions of Ag nanostructures and testing solutions dropped on the microsphere surface, which helps to develop a good quality SERS sensor for the detection of biochemical compounds in a liquid environment.

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