Silver Nanowire Micro-Ring Formation Using Immiscible Emulsion Droplets for Surface-Enhanced Raman Spectroscopy

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Abstract: Precise and rapid detection of biomolecules is a fast-growing research theme in the field of biomedical engineering. Based on the surface-enhanced Raman scattering, micro/nano-scale structures composed of noble metals (e.g., gold and silver) play a critical role in plasmonics. However, it is still limited to structuring nanomaterials in a specific manner. Here, we investigated a novel surface-enhanced Raman spectroscopy (SERS) application using one-dimensional nanomaterials and micro-encapsulation methods. With the immiscible nature of fluids, the nanomaterials were properly captured inside a number of droplets for encapsulation, deforming to micro-ring nanostructures. To yield uniform sizes of the silver micro-ring structures, a microchannel system was designed to characterize particle sizes via microscopic approaches. We were able to obtain printable silver nanowire micro-ring ink, and investigated the SERS substrate effect of the silver micro-ring structure. This fabrication method can be used in many other SERS-based biomedical engineering applications in the near future.

Keywords: micro-encapsulation; nanowire; immiscible solution; printing; surface-enhanced Raman spectroscopy

1. Introduction

In the past several decades, the surface plasmonics of self-assembled metallic nanostructures has been utilized for various biomedical applications such as biosensors, plasmonic filters, diagnostic devices, and photothermal-induced cancer therapy [1,2]. To precisely and rapidly detect biomolecules, micro/nano-scale structures composed of noble metals, e.g., gold (Au) and silver (Ag), play a critical role in the field of plasmonics. Surface-enhanced Raman spectroscopy (SERS) demonstrates that metal nanostructures can control the surface optical properties [3]. An ideal SERS substrate should have high uniformity and field enhancement. Such substrates can be prepared on a wafer scale, and fluctuations of SERS signals on such highly uniform, high-performance plasmonic metasurfaces can be demonstrated in label-free microscopy [4]. However, it is still difficult to structure nanomaterials due to the limitations of controlling the single nanoparticle without well-confined conditions such as atomic force microscopic (AFM) manipulation [5]. Furthermore, the fabrication cost of SERS substrates needs to be reduced via proper manufacturing techniques [6].

Among the conventional self-assembly methods for nanomaterials, the micro-encapsulation method in immiscible solution has been considered a promising technique due to its simplicity and cost-effectiveness [7,8]. For example, many researchers have tried to implement micro-encapsulation
to enclose solid or fluid materials inside a microscale membrane made of two-dimensional (2D) soluble layers, which would allow for the control of dosing frequency and prevent degradation of the pharmaceutical materials. Thanks to the benefits of micro-encapsulation, this approach to exploit the SERS effect has also been investigated [9–11]. Although these studies proposed multifunctional micro-encapsulation platforms for pharmaceutical analysis or biosensor development, there still remains an unexplored area in investigating and manipulating one-dimensional (1D) metal nanowire-based encapsulation for the SERS effect. From the perspective of material properties, 1D nanomaterials have great mechanical flexibility and high thermal or electrical conductivity [12,13]. If SERS application can be adequately explored using these nanomaterials and micro-encapsulation methods, a newly proposed approach is expected, which could be helpful in future biomedical engineering applications [14,15].

In the present study, a formation method for micro-ring materials using micro-encapsulation in immiscible solution was introduced. In order to fabricate the ring structure, metallic nanowires and emulsion liquid droplets were used. In addition, a pinched flow fractionation (PFF) microchannel was experimentally investigated to uniformly and continuously separate the Ag nanowire micro-ring structure in different sizes. Printable ink containing Ag nanowire micro-ring structures was produced through a classification process. Lastly, a printing pattern for the ring-based ink was proposed and the ring patterns were characterized.

2. Materials and Methods

2.1. Materials and Method For Emulsion Droplet Formation

Ag nanowires with a length of 25 µm and a width of 30 nm dispersed in deionized (DI) water (0.1 wt%) were purchased (N&B Corporation, Ansan, Korea). N,N-Dimethylformamide (DMF), 1,2-Dichlorobenzene (DCB), NH3·H2O, and tetraethyl orthosilicate (TEOS) were purchased from Sigma-Aldrich (Seoul, Korea). For the DMF-based Ag nanowires, a centrifuge (1248, Labogene, Seoul, Korea) was used to separate Ag nanowire solution from water at 2000 rpm for 15 min. After removing water, the separated Ag nanowires were dispersed in DMF with 0.04 wt%. To formulate a water-in-oil emulsion, 200 µL of nanowire solution and 15 µL of NH3·H2O were mixed. Afterward, 5 mL of DCB were added to the mixture at a proper ratio followed by adding 15 µL of TEOS. Before heating the solution, a sonicator (Sonics VCX-500, Sonics & Materials Inc, Newtown, CT, USA) was utilized for a short time (<1 min) to prevent the droplets from recombining. The mixture was heated at 60 °C for 30 min to form the silica shells.

2.2. Preparation of the Pinched Flow Fractionation Microchannel

Microchannel design was taken from the multi-outlet microchannel developed in a previous study [10]. A microchannel was designed with a depth of 50 µm, inlet width of 60 µm, pinched channel width of 30 µm, and outlet width of 100 µm. A microchannel mold on a silicon wafer was constructed by deep reactive ion etching (DRIE). For microchannel fabrication, silane coating on the mold substrate was conducted in a vacuum chamber. Trichloro (1 h, 1 h, 2 h, 2 h-perfluoroctyl) silane (Sigma Aldrich, Seoul, Korea) was used for silane coating, and a sufficient amount of polydimethylsiloxane (PDMS) was poured on the mold substrate. The PDMS was placed in the vacuum chamber until most of the captured bubbles in the PDMS disappeared, and then baked at 120 °C for 2 h on a hotplate. The baked PDMS channel was detached from the substrate, punched through the inlet and outlet, and connected with a Teflon tube. To attach the PDMS channels to slide glasses, oxygen plasma coating was applied to each attachment surface. Lastly, the PMDS channel attached on the slide glass was heated at 80 °C for 30 min.

2.3. Printing Process Using the Ag Nanowire Micro-Ring Ink

An electrohydrodynamic jet printing device (Enjet Inc, Suwon, Korea) was used to print the sorted Ag nanowire micro-ring ink solution. The experiment was conducted under the following conditions:
flow rate of 0.75 µL/m, working height of 500 µm, voltage of 1.5 kV, substrate temperature of 50 °C, and printing velocity of 50 mm/s.

2.4. Characterization of the Ag Nanowire Micro-Rings and the Printing Pattern

The Ag nanowire micro-ring structure and printed pattern images were characterized by optical microscopy (Eclipse Series, Nikon Instruments Inc., Melville, NY, USA) with a polarizing filter and a field emission scanning electron microscope (JEM-2100F, JEOL, Peabody, MA, USA). The optical properties were determined by dispersive Raman spectroscopy (SENTERRA Raman, Bruker, Billerica, MA, USA). The Raman spectra of the Ag nanowire micro-ring patterned substrate and bare Si wafer at a 532 nm wavelength under the same experimental conditions were measured and compared.

3. Results and Discussion

3.1. Optimization of the Ag Nanowire Micro-Ring Structure Formation

In order to make the Ag nanowire micro-ring structure, we employed an immiscible emulsion droplet formation method. Figure 1 shows that emulsion droplets could be continuously generated by tip sonication-induced vibration in DMF and DCB solution. During the process, Ag nanowires were captured in micro-scale bubbles (i.e., encapsulation) due to high surface tension force compared to the yield strength of Ag nanowires. We have previously shown that micro-rings are formed inside droplets by the force balance between the compressive force of the droplet and the restoring force of the high aspect ratio nanowire material [16]. Based on this mechanism, we investigated whether the micro-ring composed of Ag nanowire could be constructed in immiscible solution (Figure 2). The Ag nanowire micro-ring structure with a diameter in the sub-micron scale was successfully deposited on the substrate (Figure 2a,b). However, random generation of the emulsion droplets led to several entangled Ag nanowires in a single droplet. Figure 2c,d demonstrate that the entangled Ag nanowire micro-rings had a larger diameter (4–5 µm) compared to the single Ag nanowire micro-rings (<4 µm). This result led us to the next stage to sort the fabricated single and bundled Ag nanowire micro-rings with respect to droplet size using the PFF microchannel.

![Figure 1. A schematic of the coiling nanowire inside a water-in-oil emulsion droplet.](image-url)
3.2. Separation of the Droplets Using the Microchannel

Prior to sorting the Ag nanowire micro-ring structures, hollow glass particles with a diameter of 10 µm were utilized to test whether the microchannel would be suitable to efficiently sort the Ag nanowire micro-rings (Figure 3). DCB was used as a solvent for the glass particles to disperse as in the micro-ring formation process. DCB with and without glass particles was released at different flow rates (A:B = 1:1, 1:4, and 1:10) simultaneously at each inlet. In this feasibility test, almost all the glass particles were collected through outlet 1 (downstream) when the flow rate ratio was fixed to 1:10 (Figure 3d). It has been reported that moving the particle close to the wall can initiate a dispersing effect, resulting in sorting the particles by size distribution [10]. This indicates that the ratio of two different flow rates can determine the separation of particles in various sizes using a pinched channel.

Following this feasibility test with hollow glass particles, the same experimental setting was implemented to apply to the immiscible emulsion with the Ag nanowire micro-rings (Figure 4). Figure 4b demonstrates that approximately 50% of the Ag nanowire micro-ring structures with 2–3 µm diameters could be collected at outlet 1. Further detailed evaluation of the size distribution revealed that the Ag nanowire micro-rings with a relatively smaller size (<2.5 µm) could be collected in outlet 1 compared to outlet 2 (Figure 4c). Using this separation process with the micro-ring particles, we were able to collect Ag nanowire micro-ring structures of a similar size dispersed in the organic solvent.

Next, we applied this Ag nanowire micro-ring material to printing ink, and investigated a printing pattern with the Ag nanowire micro-ring structures to enhance the surface plasmonic scattering for biological applications.
3.3. Printing Pattern and Its Application

Experiments were carried out to make patterns through the electrohydrodynamic (EHD) jet printing process with the micro-ring dispersion ink (Figure 5a). First, we tried to print a line pattern containing the micro-rings through the dispensing method by heating the substrate to induce an evaporation rate of the toluene solvent. Figure 5b demonstrates the detailed pattern with the micro-ring array along the printing direction. Due to the coffee ring effect originating from the capillary flow induced by the differential evaporation rates across the drop [17], the micro-rings were concentrated at the edge of the pattern.

SERS substrates can be offered as one of the biological applications with these Ag nanowire micro-rings. The substrates are used to determine the minimum quantity of biomolecules and allow us to detect biological species in biofluids. Therefore, this technique can enhance the Raman scattering by molecules adsorbed onto metallic structures. We measured the Raman spectrum of the Ag nanowire micro-ring patterned substrate and bare Si wafer at 532 nm wavelength under the same measurement conditions, and clearly observed enhanced total surface background intensity values (Figure 5c). The shape and size of the metallic nanostructures affect the enhancement strength due to the factors influencing the ratio of absorption and scattering [18]. Moreover, self-assembled metallic nanoparticles such as Ag and Au nanostructures can actively enhance the Raman scattering. These data suggest that our Ag nanowire micro-ring structure could be utilized in SERS substrate as the Ag nanowire micro-rings have nanoscale widths (<25 nm), thus offering great printability on surfaces.

Figure 3. (a) A schematic of the pinched flow fractionation microchannel with a particle. Trajectory of 10 µm of hollow glass particles in different flow rate ratios of (b) 1:1, (c) 1:4, and (d) 1:10 (µL/min).
Figure 4. (a) A microscopic image of the sorting process in the pinched flow fractionation (PFF) microchannel, (b) Ag nanowire rings in dispersed solution from outlet 1, and (c) droplet diameters of the sorted droplets in outlets 1 and 2.

Figure 5. (a) Patterning with the micro-ring solution using electrohydrodynamic (EHD) jet printing, (b) a microscopic image of the micro-ring distribution, and (c) diagram of the Raman spectra for the Ag nanowire micro-ring structure and bare wafer.
4. Conclusions

In this study, we proposed a potential material for printing ink using ring-shaped microscale structures. A large amount of ring-shaped material was formed using Ag nanowires, immiscible emulsion solution, and silica shells. In order to utilize the micro-ring solution as printing ink, two alternatives were implemented. First, the solution was dispersed again using a sonicator to prevent the droplets surrounding the nanowire from recombination before the silica shell was formed. The size of the droplets with rings and those with bundles formed during the synthesis were determined, and the droplets were classified by size using the PFF microchannel to increase the micro-ring ratio in the solution. The Ag nanowire micro-ring solution was patterned using EHD jet printing. The optical characteristics of the micro-ring pattern fabricated by EHD jet printing were analyzed using a dispersive Raman spectrometer. This novel method to fabricate Ag nanowire micro-rings can be used in many other SERS-based biomedical engineering applications in the near future.

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