Site-Selective Deposition of Silver Nanoparticles Using Modified Silver Mirror Reaction and Surface Modification by Self-Assembled Monolayer

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We developed a set of processes for depositing silver nanoparticles on a glass substrate that involves using a modified silver mirror reaction, whereby dispersants are added to a conventional silver mirror solution. The whole set of processes was completed in 15 min in a nonvacuum environment, except the cleaning processes with oxygen plasma at 20 Pa, and at a low cost. The processes can be applied to the site-selective deposition of silver nanoparticles by modifying the surface characteristics of glass substrates using a self-assembled monolayer (SAM). We used a microcontact printing method that incorporated a non-photolithographic top-down process to pattern a SAM. The proposed processes are readily applicable to promising applications of metal nanoparticles, such as ultrasensitive sensors and catalysts.

1. Introduction

Research has been conducted on silver nanoparticles for a number of uses. These include using them for ultrasensitive chemical/biological detection because they exhibit local surface plasmon resonance[1–7] and as a catalytic material because of their extremely large surface/volume ratio.[8–10] A promising application of silver nanoparticles is for enhancing surface Raman scattering spectra. Surface enhanced Raman scattering (SERS) is a phenomenon that results in the enhancement of Raman scattering spectra by molecules adsorbed on nanoscale metal structures. Raman signals are enhanced by a factor of 3 to 6 when silver colloids are present.[11] However, recent studies have shown that the intensity of the SERS spectrum of a molecule wedged between two adjacent nanoparticles with a gap of 1 nm can be between 10^{14} and 10^{15} times higher than that of a conventional Raman spectrum owing to resonance Raman effects.[12–17] Currently, SERS is considered one of the most effective techniques for the ultrasensitive detection and analysis of materials, such as proteins, viruses, and environmental chemicals.

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The development of superior manufacturing processes of silver nanoparticles is necessary for making the above-mentioned promising applications fit for practical use. Various methods of manufacturing silver nanoparticles have been proposed: the deposition of silver on a nanostructured polymer,[1,2] the formation of Langmuir-Blodgett (LB) monolayers on silver island films,[3–5] vacuum deposition,[18–20] laser abrasion,[21] electrolysis,[6] and the reduction of silver nitrate.[21–23] After manufacturing, the silver nanoparticles are immobilized onto poly(ethylene glycol) spheres,[7] aggregated onto a glass substrate surface in solution,[24,25] or ink jet printed[26] to form SERS hot spots. To make the best use of the local surface plasmon resonance of silver nanoparticles, the optimal size of silver nanoparticles is 10–100 nm.[17] This leads to difficulties in forming silver nanostructures by top-down techniques, such as photolithography and e-beam lithography, because their formation is time-consuming and costly. Therefore, bottom-up techniques are more suitable for manufacturing silver nanoparticles.

Ultrasensitive chemical/biological sensing requires not only detection with silver nanoparticles but also sample preparation processes, such as purification and preconcentration, and leak-free sample handling. Therefore, the development of a microdevice containing silver nanoparticle sites, which requires the site-selective deposition of silver nanoparticles, as well as the formation of microfluidic components is necessary. Site-selective deposition is also effective when the nanoparticles are used as catalysts, which enables patterning of the product of the catalytic reaction to form micro/ nanostructures.

In this paper, we report on a novel site-selective deposition process for silver nanoparticles. We first present the method we developed for manufacturing silver nanoparticles that incorporates a modified silver mirror reaction, whereby dispersants are added to a conventional silver mirror solution. Silver nanoparticles with diameters of 10 –50 nm were self-assembled on a glass substrate, with the entire process completed in 15 min in an ambient environment. Second, we present a method for the site-selective deposition of silver nanoparticles. The method uses a self-assembled monolayer (SAM). SAMs capable of changing their surface properties have been widely used in microfabrication, such as for patterning polystyrene microstructures,[2] spatially defined silver mirror reactions[27] and determining the aggregation sites of silver nanoparticles.[25] To manufacture locally deposited silver nanoparticles, we used microcontact printing (µCP), which is one of the most widely used techniques for patterning SAMs.[2, 28–30] We demonstrated a microdevice including microfluidic components and silver nanoparticle sites. During manufacturing we conducted oxygen plasma treatment in a vacuum environment with a pressure of 20 Pa. Given the low vacuum level, the proposed processes are by far less time-consuming and costly.

2. Materials and Methods

2.1 *Modified silver mirror reaction*
We fabricated silver nanoparticles using a modified silver mirror reaction, whereby dispersants were added to a conventional silver mirror solution (silver nitrate solution + ammonia solution). The process we used is a bottom-up process in a nonvacuum environment.

Figure 1 shows the modified silver mirror reaction processes. (a) Ammonia solution (Wako Chemicals, 5.7%, 8 ml), DI water (20 ml), and the dispersant (BYK Additives & Instruments, Disperbyk-102, 1.5 ml) were added to a silver nitrate solution (Wako Chemicals, 5%, 5 ml) and then agitated to produce a silver nanoparticle solution. (b) Hydrazine monohydrate (Wako Chemicals, 98%, 6 ml) was added to the solution as a reducing agent and a glass substrate was simultaneously dipped into it. Silver nanoparticles were then deposited on the glass substrate surface. The substrate was extracted after a designated reaction time of 80 s, rinsed in DI water and dried using N_2 gas. The entire process was completed in only 15 min. We found that the cleanliness of the glass substrate surface was crucial to obtaining a uniform silver nanoparticle film. The glass substrate surface was cleaned with oxygen plasma at 50 W for 60 s (SAMCO, Compact Etcher FA-1) prior to the modified silver mirror reaction process. All the processes were conducted at a room temperature of 25°C and a humidity of 40%.

2.2 *Local deposition of silver nanoparticles*

We patterned silver nanoparticle sites using SAMs with a silanol group. Figure 2 shows the fabrication process for the patterned substrate. We used octadecyltrichlorosilane (OTS), which chemically adsorbs onto glass as a SAM. OTS was patterned by microcontact printing, as shown in Fig. 2(a). A polydimethylsiloxane (PDMS) (Dow Corning Toray Silpot 184) stamp was dipped into a dry toluene solution with 1 vol% OTS (Wako Chemicals) for 30 s and soft-contacted onto the substrate. The substrate was subsequently heated at 120°C for 5 min to enhance OTS adsorption. It was reported that the post-thermal treatment enhanced the adhesion of the organosilanes and silanol groups.[31] The OTS-patterned substrate was immersed in the silver nanoparticle solution (silver nitrate solution (Wako Chemicals, 5%, 5 ml) + ammonia solution (Wako Chemicals, 5.7%, 8 ml) + DI water (20 ml) + dispersants (BYK Additives & Instruments, Disperbyk-102, 1.5 ml)) as soon as a reducing agent, hydrazine monohydrate (Wako Chemicals, 98%, 6 ml), was added to the solution (Fig. 2(b)). All the processes were conducted at a room temperature of 25°C and a humidity of 40%. The silver nanoparticles were only observed on the area where OTS was not adsorbed, as shown in Fig. 2(c).
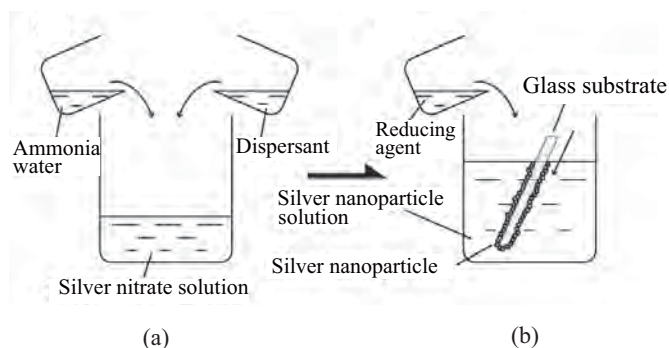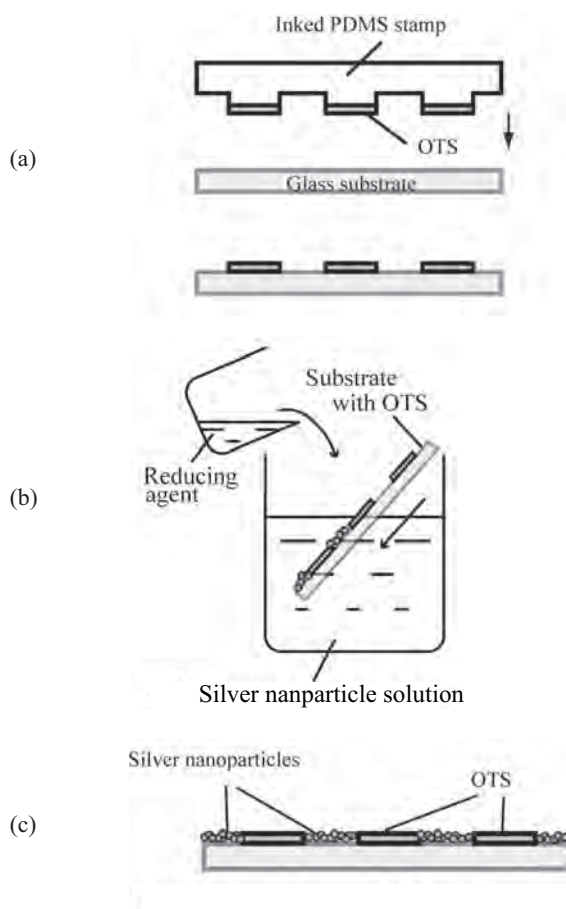

Fig. 1.   Modified silver mirror reaction.

Fig. 2.   Fabrication process of substrate patterned with SERS sites. (a) Microcontact printing of OTS, (b) modified silver mirror reaction, and (c) site-selective deposition of silver nanoparticles.

3.   Results and Discussion

3.1   *Modified silver mirror reaction*

The optimal conditions for producing silver nanoparticles on a glass substrate with respect to the concentration of silver nitrate solution, species of reducing agent, dispersant and temperature were deduced by assessing the uniformity of the silver nanoparticle film and the exerting SERS signals. The uniformity was inspected with an optical microscope and a scanning electron microscope (SEM). Silver nitrate solutions with concentrations ranging from 1 to 10% were tested. The surveyed reducing agents included formaldehyde, glucose, formic acid, sodium subsulfite, and hydrazine. A

copolymer with acidic groups (DISPERBYK®-102, BYK Additives & Instruments), a salt of a polymer with acidic groups (DISPERBYK®-106, BYK Additives & Instruments), and an alkylolammonium salt of a copolymer with acidic groups (DISPERBYK®-180, BYK Additives & Instruments) were investigated as the dispersants. The processes were conducted at temperatures of 20, 25, and 30°C. Among the foregoing reaction conditions the best result was obtained when we produced silver nanoparticles with 5% silver nitrate solution, hydrazine and copolymer with acidic groups (DISPERBYK®-102, BYK Additives & Instruments) at 25°C.

Figure 3 shows the FESEM images of the silver nanoparticles on a glass substrate, manufactured under optimal conditions at reaction times of (a) 40, (b) 80, and (c) 120 s. Figure 3(d) shows a close-up view of the silver nanoparticles at a reaction time of 80 s, which was found to be optimal by *a posteriori* analyses. These figures show that the deposition and uniformity of the silver nanoparticle film vary with the reaction time. Silver nanoparticles showing a peak uniformity with diameters of 10–50 nm were obtained at a reaction time of 80 s according to the SEM images.

Figure 4 shows the Raman spectra of 10 mM rhodamine 6G (R6G) on the manufactured silver nanoparticle substrates under optimal conditions at various reaction
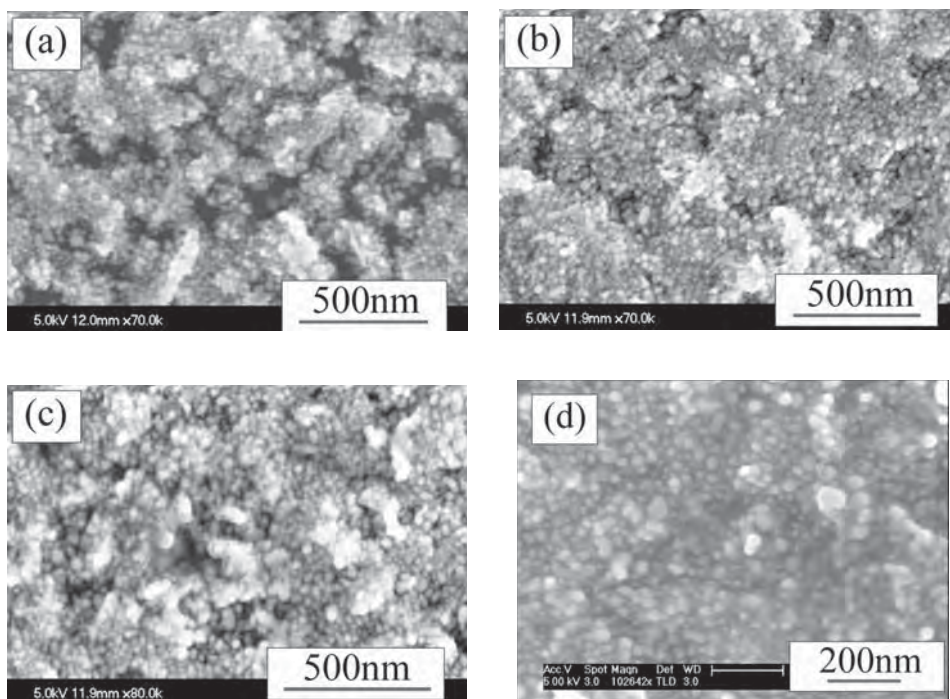

Fig. 3.   FESEM images of SERS substrates for the following reaction times of (a) 40, (b) and (d) 80, and (c) 120 s.
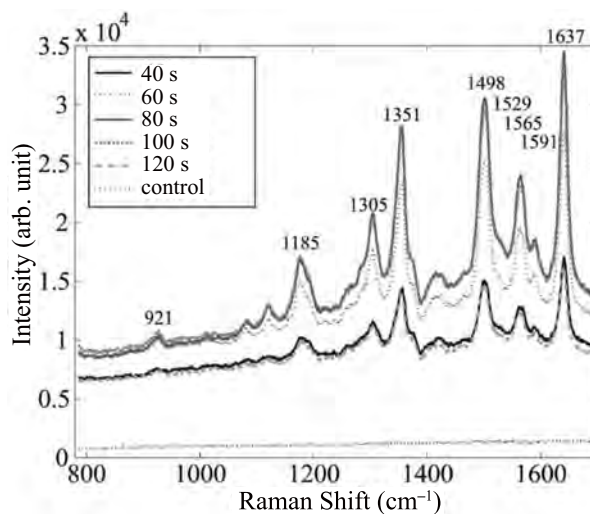
Fig. 4.   Raman spectra of 10 mM R6G on the SERS substrate for various reaction times (40, 60, 80, 100 and 120 s) and that on the pristine glass substrate (control) (Laser: Ar laser (532 nm), Spot size: 10 μm diameter, Integration time: 3 s).

times and on the pristine glass substrate (control).   The Raman signals from all the manufactured SERS substrates were found to be greatly enhanced compared with that of the control.   Amongst them, the substrate at a reaction time of 80 s exhibited the highest Raman enhancement.   The Raman enhancement strongly depends on the geometry of nanostructures.   For example, it was reported that the Raman signals were greatly enhanced when a molecule was wedged between two adjacent isolated nanoparticles with a gap of 1 nm and the enhancement decreased as the gap increased.[17]   We consider that the substrate at a reaction time of 80 s exhibited higher Raman enhancement than those at reaction times of 40 and 60 s as the density and uniformity of silver nanoparticles increased with reaction times.   At a reaction time of 120 s, silver nanoparticles aggregated and were more likely to behave as thin films than nanoparticles.   Therefore, the substrate at a reaction time of 120 s exhibited small Raman enhancement.

The size distribution of silver nanoparticles fabricated at a reaction time of 80 s is shown in Fig. 5.   The sizes of 600 nanoparticles were determined from their FESEM images and the size distributions at intervals of 5 nm were calculated.   Approximately 45% of the nanoparticles had diameters between 25 and 35 nm.   The mean diameter of the silver nanoparticles was approximately 30 nm.

3.2   *Local deposition of silver nanoparticles*

We used a PDMS stamp, as shown in Fig. 6(a), to evaluate the deposition processes of silver nanoparticles.   OTS was designed to be microcontact-printed onto a glass substrate with stripe patterns with line widths of 121 μm and silver nanoparticles
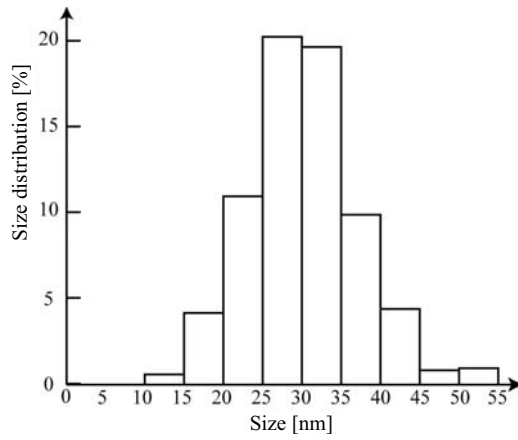
Fig. 5.   Size distribution of deposited silver nanoparticles.

(a)   (b)
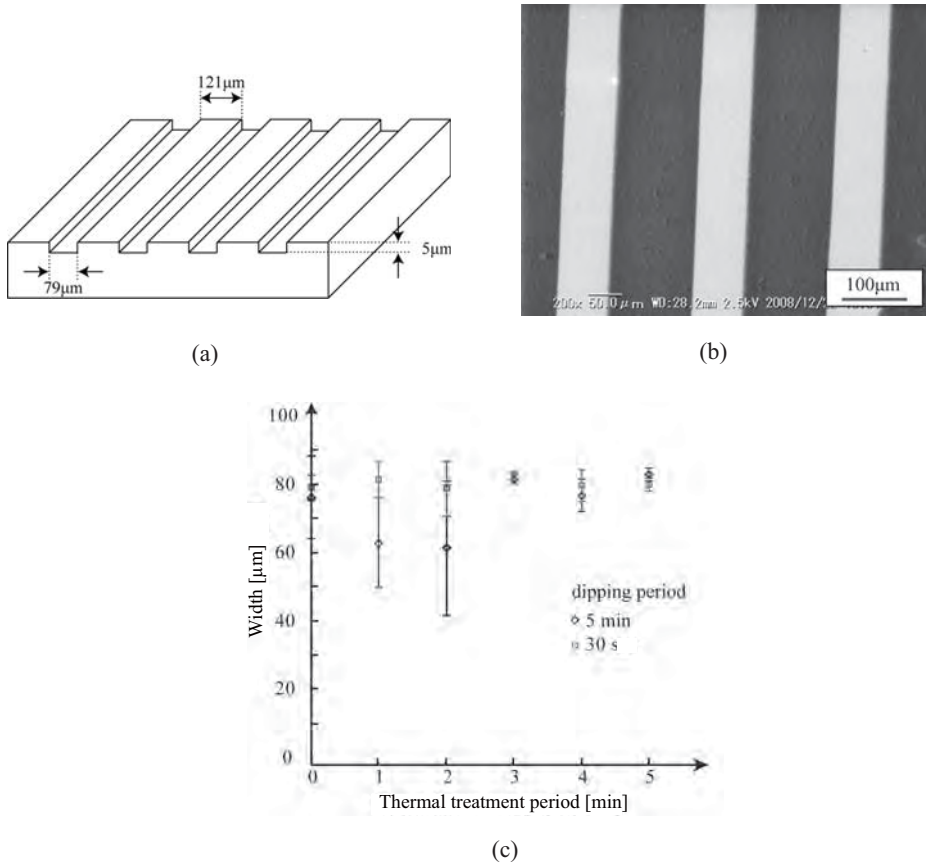

(c)

Fig. 6.   (a) Geometry of PDMS stamp, (b) SEM image of deposited silver nanoparticles with stripe patterns, and (c) patterning accuracy with respect to the microcontact printing processes.

were in turn to have 79 µm line widths. Figure 6(b) shows an SEM image of the site-selectively deposited silver nanoparticles, where the dark and bright regions represent the exposed glass and the deposited silver nanoparticles, respectively. The quality of the selective deposition of silver nanoparticles depended on the microcontact printing processes. The dipping periods of the PDMS stamp into the solution containing OTS and the thermal treatment periods after the soft contact were investigated. As shown in Fig. 6(c), the dipping period of 30 s resulted in more accurate patterns than that of 5 min. The patterning accuracy was enhanced with the post-thermal treatment periods, which was considered to be due to the augmented adhesion of OTS onto the glass substrate. A superior site-selective deposition of silver nanoparticles with a width of 79.9 µm ± 1.9 µm along 10-mm-long lines was achieved by dipping for 30 s and thermal treatment for 5 min.

The local deposition of silver nanoparticles enables the fabrication of a microdevice containing detection sites with silver nanoparticles as well as microfluidic components. We manufactured a microdevice that includes silver nanoparticle sites in microfluidic
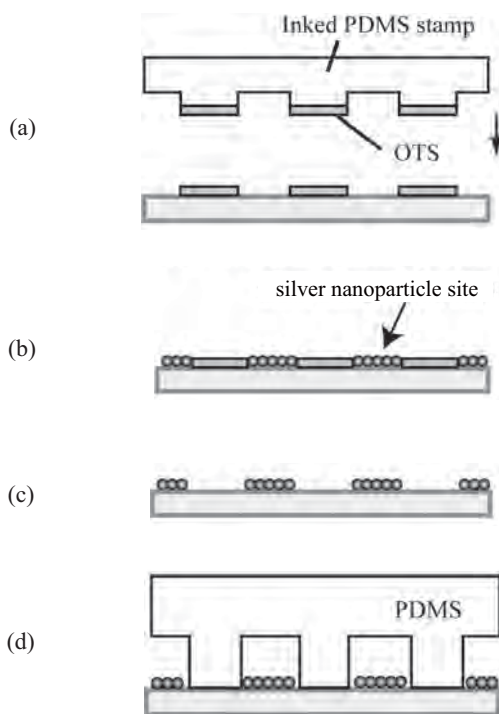

Fig. 7. Fabrication processes of a microdevice containing silver nanoparticle sites. (a) Micro-contact printing of OTS silver nanoparticle sites, (b) deposition of silver nanoparticles, (c) oxygen plasma treatment, and (d) bonding of PDMS structure.

components to verify whether the proposed local deposition processes are compatible with conventional MEMS processes (Fig 7). (a) OTS is microcontact-printed onto the substrate to prevent silver nanoparticles from depositing outside the detection site in the following modified silver mirror reaction process. (b) A modified silver mirror reaction is conducted to deposit silver nanoparticles only onto the detection site. (c) The SAMs are removed by oxygen plasma treatment at 100 W for 0.5 s since PDMS cannot bond to the OTS-patterned glass surface. (SAMCO, compact etcher FA-1) (d) A PDMS structure is bonded onto the glass substrate after the PDMS surface is activated by oxygen plasma to form microfluidic components. Figure 8 shows a photograph of the manufactured microdevice.

In the above-mentioned process (c), the silver nanoparticles were exposed to oxygen plasma, which might cause oxidation of the silver nanoparticles and thus, deterioration of the SERS sites. We detected the SERS signals produced by 10 mM R6G on silver nanoparticles before and after the plasma treatment. The silver nanoparticles exhibited a significant SERS signal even after the treatment, as shown in Fig. 9, which verified that the proposed site-selective deposition processes of silver nanoparticles are highly compatible with the fabrication processes of conventional microdevices.

Fig. 8. Photograph of a manufactured microdevice containing silver nanoparticle sites and micro-channels.
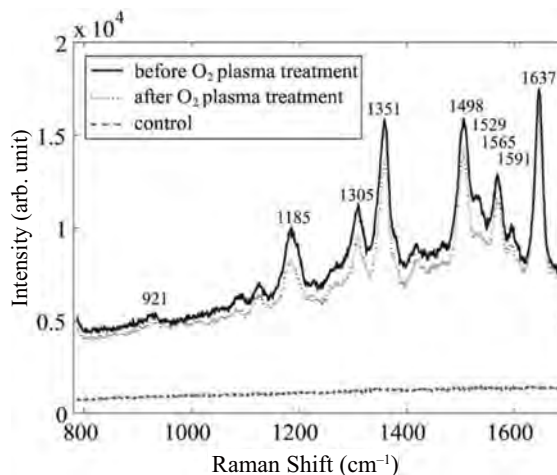

Fig. 9. SERS signals from silver nanoparticle sites before and after 0.5 s of oxygen plasma treatment.

4.   Conclusions

We developed a novel process for depositing silver nanoparticles using a modified silver mirror reaction. It is a bottom-up process conducted at ambient pressure and room temperature and is completed in only 15 min. Under optimal conditions, which we established by experiment, silver nanoparticles approximately 30 nm in diameter were uniformly deposited onto a glass substrate, which exhibited an SERS signal from R6G that was enhanced by a factor of 10^6. We demonstrated the site-selective deposition of silver nanoparticles using microcontact-printed OTS. We manufactured a microdevice that includes silver nanoparticle sites in microfluidic components using the proposed local deposition processes and verified that the proposed processes were compatible with conventional MEMS processes. Given the simplicity and low cost, the process is suitable for forming silver nanoparticles for various applications, such as ultrasensitive detection and catalysis.

Acknowledgements

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