Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

In-situ **synthesis of Au-shelled Ag nanoparticles on PDMS for flexible, long-life, and broad spectrum-sensitive SERS substrates**

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Experimental section

Materials

Silver nitrate ($AgNO_3$), gold(III) chloride hydrate ($HAuCl_4$), and 4-mercaptobenzoic acid were purchased from Sigma-Aldrich. L(+)-ascorbic acid (AA), trisodium citrate (Cit), sodium hydroxide (NaOH) and hydrogen peroxide (H_2O_2) were purchased from Wako pure chemical industries, Ltd. Silicone elastomer and silicone elastomer curing agent (Sylgard® 184 silicone elastomer kit) were purchased from Dow Corning Corporation. All chemicals were used without any further purification. Milli-Q water (Milli_Q System, Millipore) was used in all experiments.

Fabrication of polydimethylsiloxane (PDMS) film

Thin PDMS elastomers were fabricated by pouring a mixture of Sylgard® 184 silicone elastomer and curing agent (w/w = 10 : 1) on a polystyrene substrate and leaving at room temperature overnight.

Synthesis of silver nanoparticles (Ag NPs) on PDMS

The Ag NPs on PDMS was synthesized by the following method. 40 μL of AA (25 mM) and 40 μL of Na_3Ct (25 mM) were dropped onto the PDMS film and mixed by micropipette several times. Then 40 μL of silver nitrate (25 mM) was added into the solution and gently mixed. The color of the mixed solution gradually changed from colorless to dark blue. The solution was incubated for five minutes, followed by thoroughly rinsing with Milli-Q water and drying with N_2.

Au coating of silver nanoparticles (Ag NPs) on PDMS

Au coating of AgNPs on PDMS was done by the following procedure. AgNPs on PDMS film was immersed in 2 mL of aqueous solution containing 0.5 mL of 1 aM $HAuCl_4$, 1 mL of 100 mM AA, and 0.5 mL of 0.5 M of NaOH for 1 h (Final concentration of $HAuCl_4$ is 0.25 aM, AA is 50 mM, and NaOH is 125 mM). The pH of the mixed solution was adjusted pH 10. Afterwards Au coated AgNPs on PDMS was immersed in 2 mL of 2 % H_2O_2 for 3h to remove Ag which uncovered by Au.

Nanoparticle Characterization

The size and morphology of Ag NPs on PDMS film was characterized by means of scanning electron microscopy (SEM) (JEOL JSM-6700FT field-emission scanning electron microanalyzer at an accelerating voltage of 5 kV.) Prior to SEM imaging, Ag NPs on PDMS film was coated with carbon film. The phase of AgNPs was characterized by means of transmission electron microscope (TEM) (JEOL JEM-2100F accelerating voltage of 200 kV). Energy disperse X-ray spectroscopy (EDS) of AgNPs and AgNP@Au-shell was obtained by using the SEM (JEOL JSM-7600FA scanning electron microanalyzer at an accelerating voltage of 15 kV).

Optical properties of Ag NPs on PDMS film

Dark field (DF) spectroscopy was conducted using an inverted optical microscope (Ti-U, Nikon) equipped with a piezoelectric stage (P517.3CL, PI). A halogen lamp (12V/100W halogen lamp, Nikon) was used as the light source. Light of the lamp was focused on the sample through a dark field condenser (TI-DF, dry, N.A. 0.95-0.80). Scattering light at the sample was collected by an objective lens (Plan Fluor ELWD 40x, N.A. 0.60, Nikon) and passed through a confocal pinhole (100 μm diameter), then guided to a spectrograph (iHR320, Horiba) equipped with a cooled-charge coupled device (CCD) (Newton 920P, Andor). The obtained spectra were divided with the lamp spectrum taken on a clean PDMS with no Ag NPs by taking the lamp spectrum and PDMS contribution into account. To discuss the resonant wavelength statistically, at least 100 DF spectra for each sample were obtained at various sample positions (each 5 μm separation). Histograms of the main resonant wavelength are shown in figure S6. When multiple resonant peaks appeared in a DF spectrum, the largest peak was defined as the main resonant peak. The DF spectroscopy was carried out three times, after the sample was prepared (1st week), one week later (2nd week), and two weeks later (3rd week).

SERS measurements were carried out in Raman microscopy (CombiScope™ 1000, AIST-NT and RENISHAW, inVia Reflex) with the excitation line of 532 nm and 785 nm. 4-mercaptobenzoic acid was used as a sample for SERS measurements. Ag NPs, AgAu NPs, AgAu NPs treated with H_2O_2 on PDMS was immersed in 0.2 mM ethanol solution of 4-mercaptobenzoic acid overnight, followed by thoroughly rinsing with ethanol and drying with N_2.

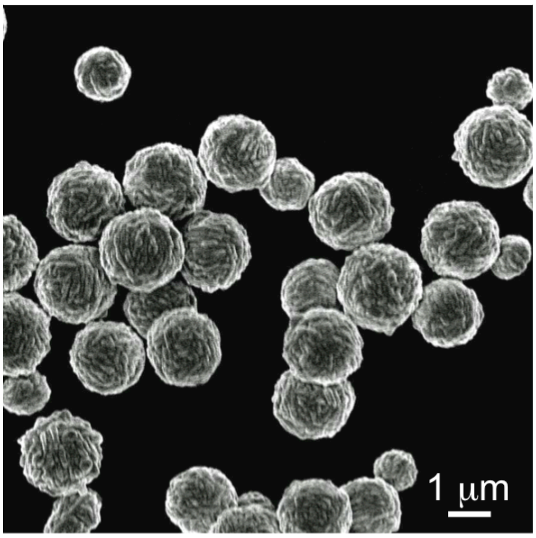


Figure S1. SEM images of AgNPs on PDMS fabricated by mixing 10 µL of ascorbic acid (100 mM) and 100 µL of $AgNO_3$ (16 mM).

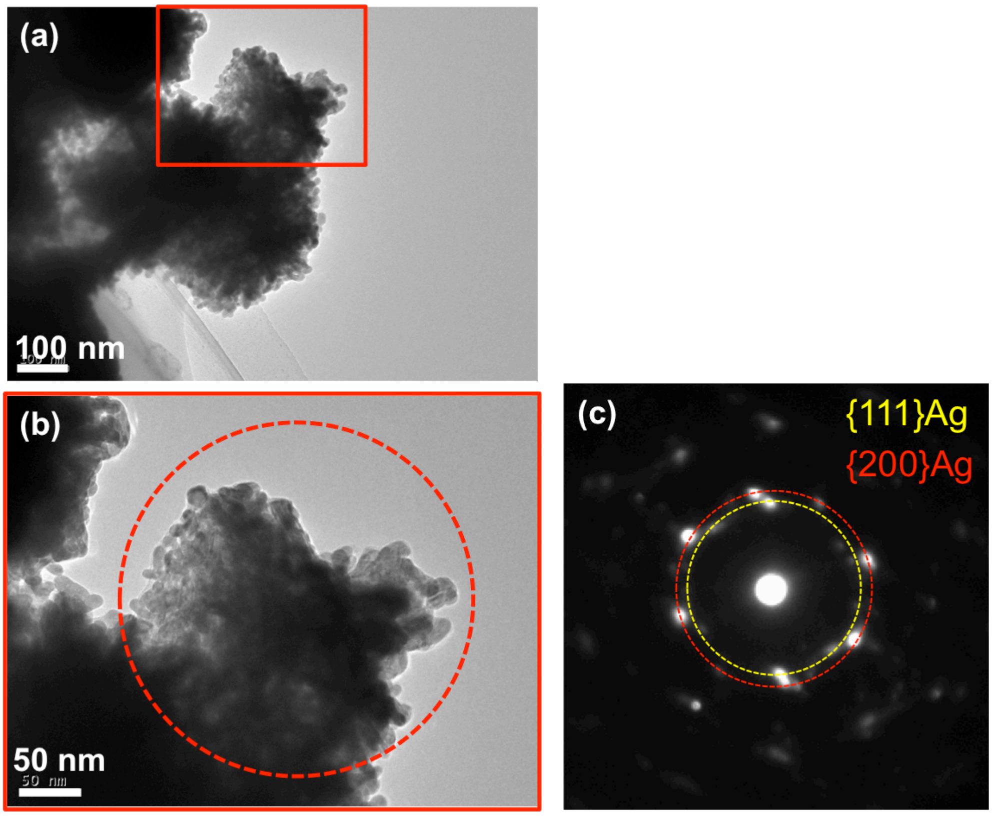
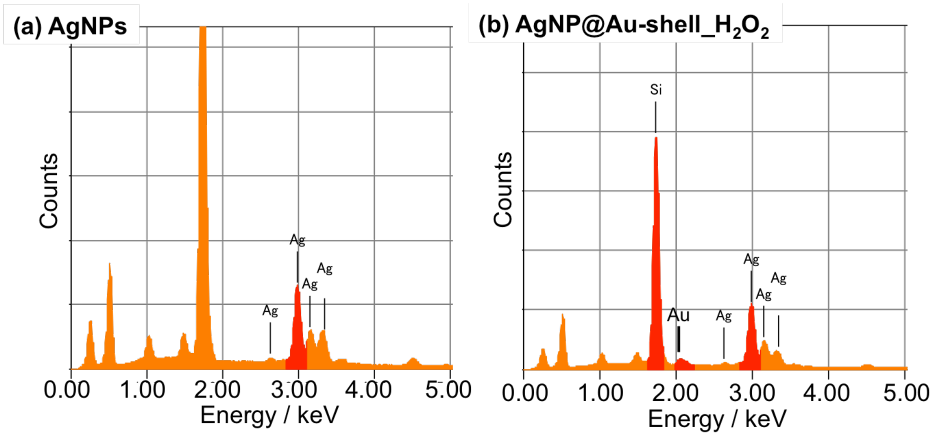
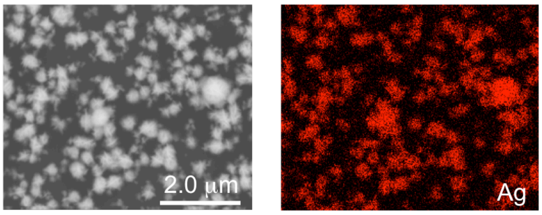


Figure S2. (a), (b) TEM images of AgNPs. (c) ED pattern that was taken from AgNPs.

Figure S3. Photograph of AgNPs on PDMS after treated with 2% of H_2O_2 aqueous solution.



(c) AgNPs



(d) AgNP@Au-shell_H_2O_2

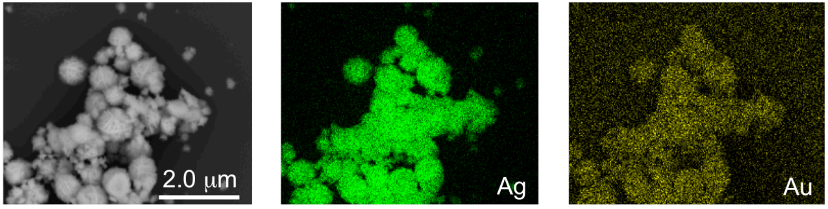


Figure S4. EDS spectra of (a) AgNPs, (b) AgNP@Au-shell_H_2O_2. EDS mapping of (c) AgNPs, (d) AgNP@Au-shell_H_2O_2.

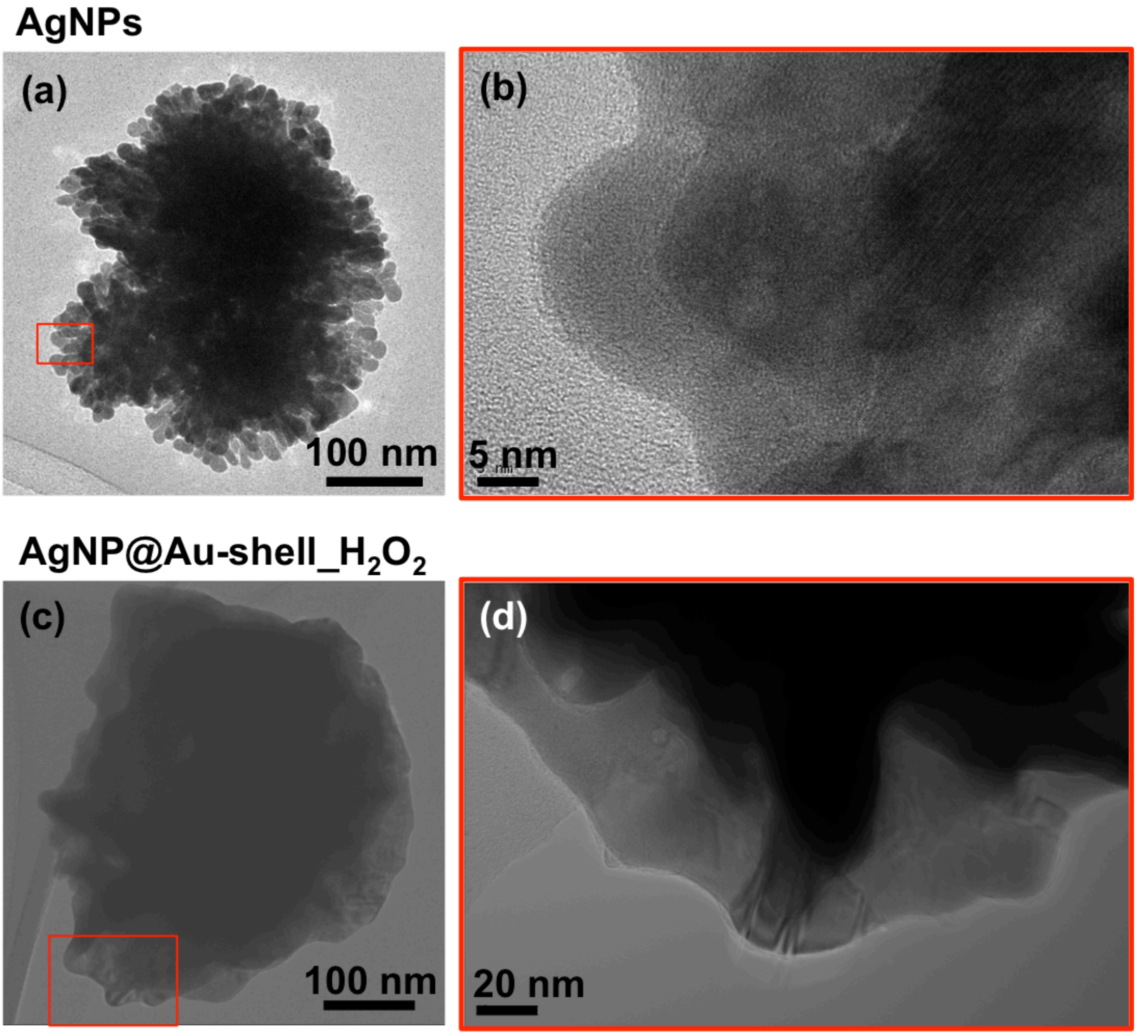


Figure S5. High resolution TEM images of (a), (b) AgNPs and (c), (d) AgNP@Au-shell_H_2O_2.

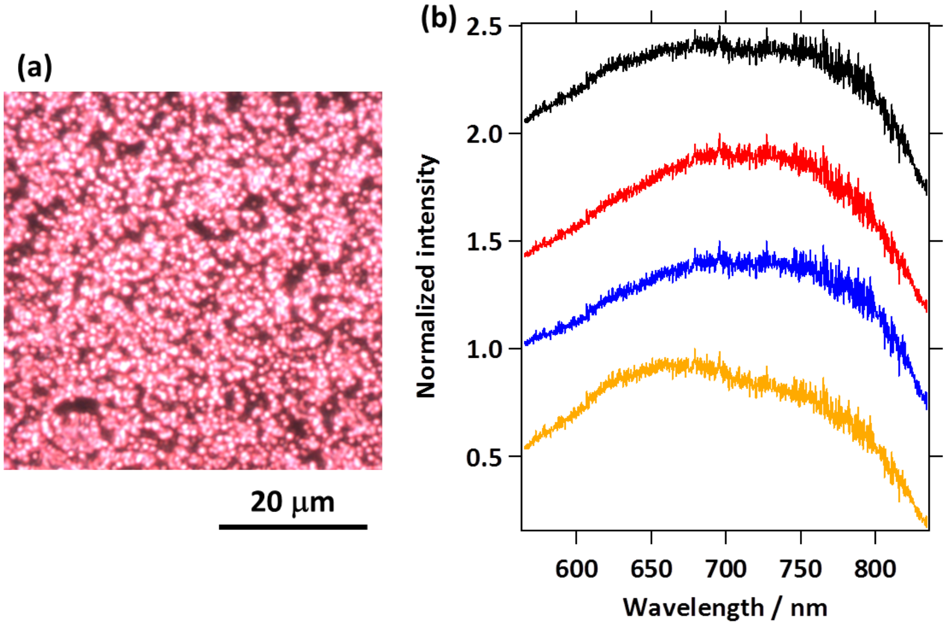


Figure S6. (a) Dark field image of AgNPs on PDMS. (b) Three typical normalized DF spectra (red, blue, and yellow) and normalized average DF spectrum of 100 spectra (black) of AgNPs.

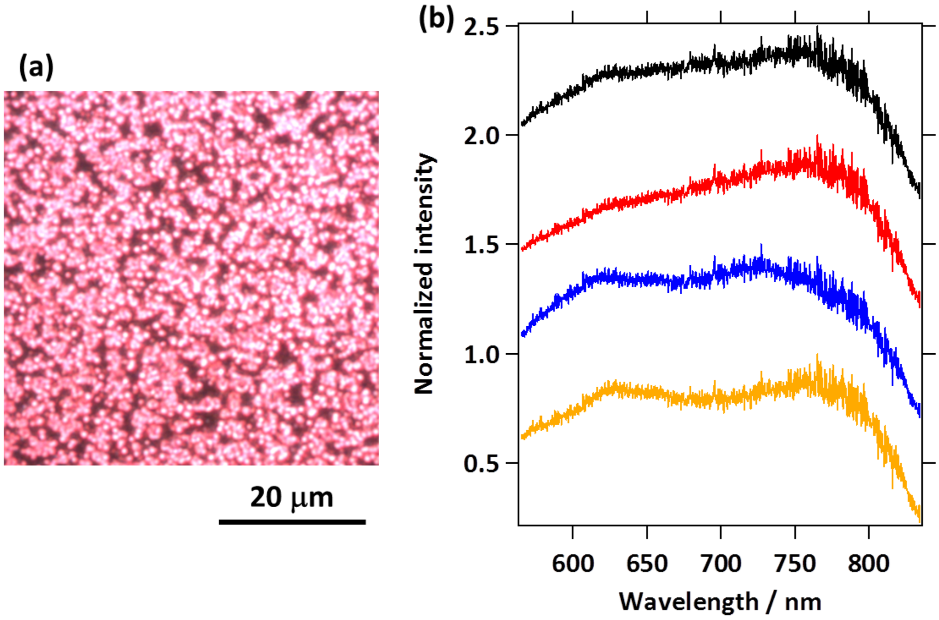


Figure S7. (a) Dark field image of AgNP@Au-shell on PDMS. (b) Three typical normalized DF spectra (red, blue, and yellow) and normalized average DF spectrum of 100 spectra (black) of AgNP@Au-shell.

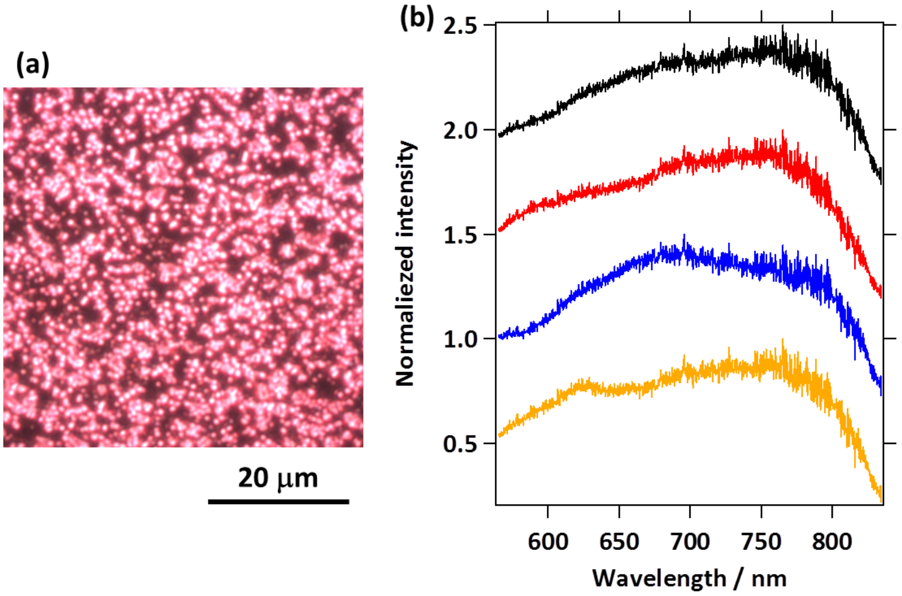


Figure S8. (a) Dark field image of AgNP@Au-shell_H_2O_2 on PDMS. (b) Three typical normalized DF spectra (red, blue, and yellow) and normalized average DF spectrum of 100 spectra (black) of AgNP@Au-shell_H_2O_2.

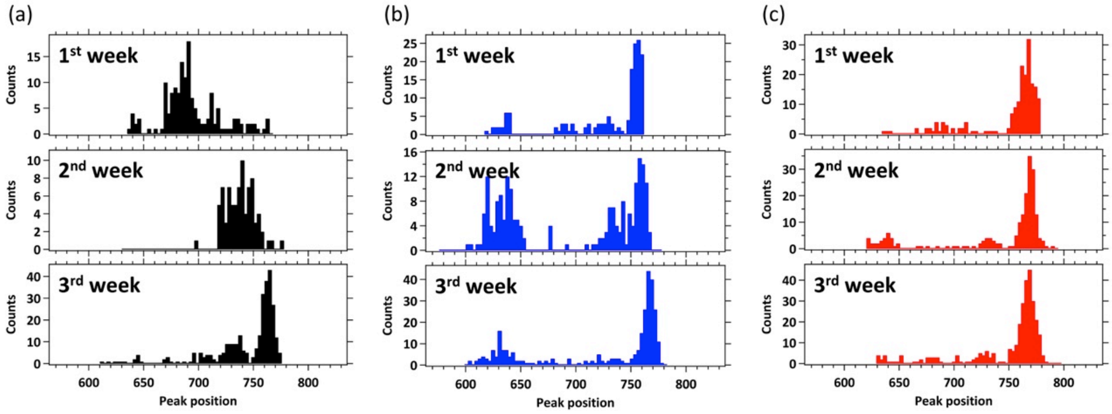


Figure S9. Histograms of the main resonant peak position of (a) AgNPs, (b) AgNP@Au-shell, (c) AgNP@Au-shell_H_2O_2.

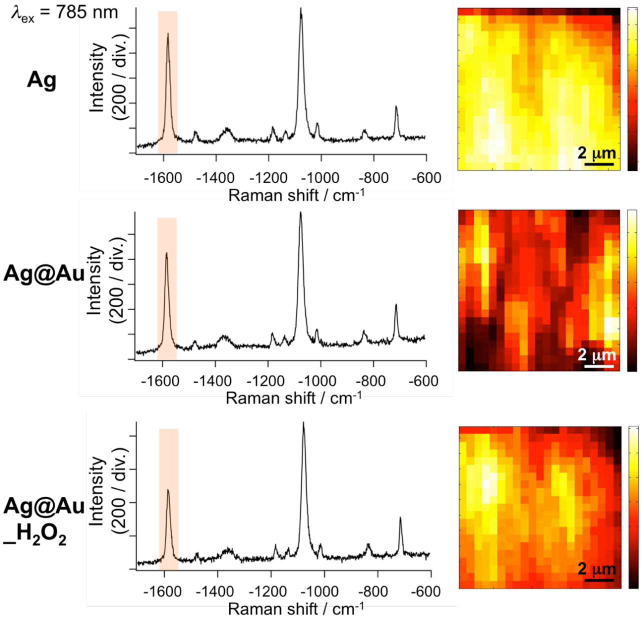


Figure S10. SERS spectra of 4-MBA-modified Ag, Ag@Au, and Ag@Au_H$_2$O$_2$ films and mapping generated for the ν(CC) ring breathing mode at 1590 cm^{-1}.

λ_{ex} = 785 nm, exposure time; 1 sec.

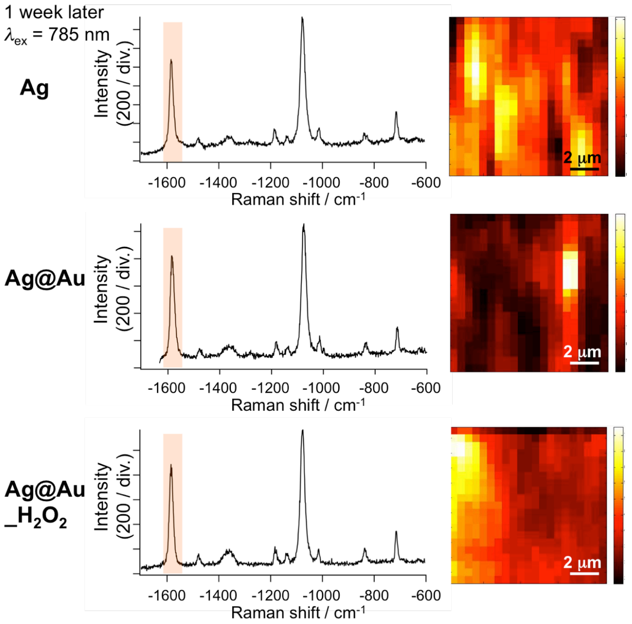


Figure S11. SERS spectra of 4-MBA-modified Ag, Ag@Au, and Ag@Au_H$_2$O$_2$ films 1 week after sample preparation, and mapping generated for the ν(CC) ring breathing mode at 1590 cm^{-1}.

λ_{ex} =785 nm, exposure time; 1 sec. The signal became extremely inhomogeneous over time though without any broad background appearing in the SERS spectrum.

Estimation of SERS enhancement factor (EF)

The SERS enhancement factor (EF) was estimated for the prepared AgNPs and AgNPs@Au-shell H_2O_2 films based on the following equation to evaluate the enhancement ability of the prepared AgNPs and AgNPs@Au-shell H_2O_2.[1-3]

$EF = (I_{SERS}/N_{SERS})/(I_{bulk}/N_{bulk})$

,where I_{SERS} and I_{bulk} are the SERS intensity of 4-MBA on the surface of AgNPs and AgNPs@Au-shell H_2O_2, and that of normal Raman scattering of the 4-MBA solution in ethanol (Fig. S10), respectively. N_{SERS} and N_{bulk} are the number of 4-MBA molecules in the confocal volume. Assuming full coverage of 4-MBA monolayers on the metal NPs with 0.8 x 0.8 nm^2 spacing per molecule[1] and one NP in the confocal volume, we estimated $N_{SERS} \sim 2.76 \times 10^6$ 4-MBA molecules. For the solution, $N_{bulk} \sim 2.33 \times 10^7$ estimated with the concentration of 4-MBA solution and the confocal volume. The measured SERS intensity for 4-MBA on AgNPs, AgNPs@Au-shell H_2O_2 and bulk 4-MBA at 1590 cm^{-1} are 1765, 1586, and 7.522, respectively. The EF was then estimated to be 1.19×10^5 and 1.07×10^5 for AgNPs and Au-shell AgNPs, respectively.

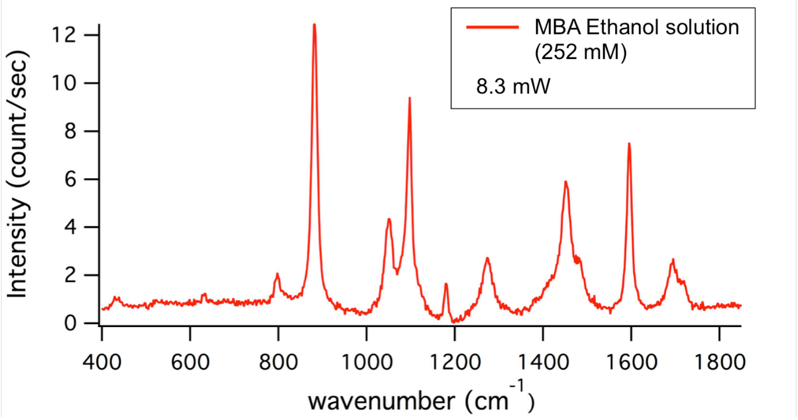
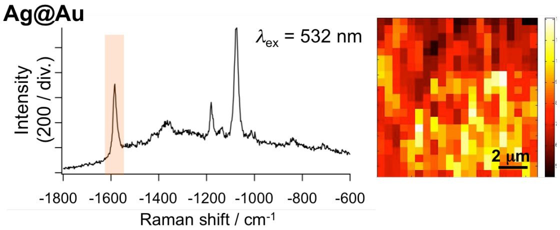


Figure S12. Raman spectrum of 4-MBA solution in ethanol (252 mM). λ_{ex} = 532 nm, laser power; 8.3 mW.

(a) Ag@Au



(b) Ag@Au: 1 week later

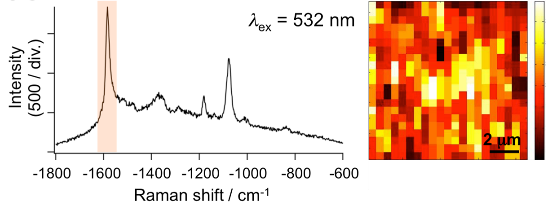


Figure S13. (a) SERS spectra of 4-MBA-modified Ag@AuNPs without H_2O_2 treatment and mapping generated for the ν(CC) ring breathing mode at 1590 cm^{-1}. (b) SERS spectra and mapping (1590 cm^{-1}) of 4-MBA-modified Ag@AuNPs 1 week after sample preparation. λ_{ex} = 532 nm, exposure time; 1 sec. The background increase after one week cannot be ignored, although two specific peaks at 1100 and 1590 cm^{-1} from 4-MBA can still be detected. The slight background increase was probably caused by oxidation of the remaining Ag NPs on the PDMS surface.

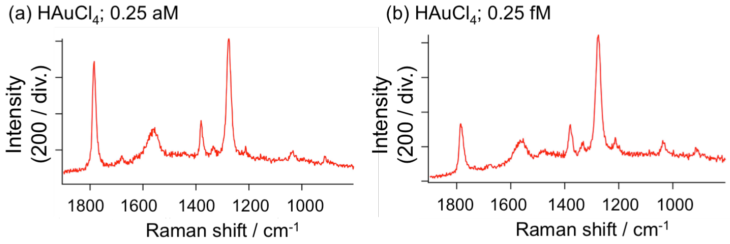


Figure S14. Comparison of SERS spectra of AgNP@Au-shell_H_2O_2 coated in solutions of different concentrations of $HAuCl_4$ (a) the solution concentration of $HAuCl_4$; 0.25 aM and (b) the solution concentration of $HAuCl_4$; 0.25 fM.

Notes and references

1 T. A. Laurence, G. B. Braun, N. O. Reich and M. Moskovits, Nano Lett., 2012, 12, 2912, 2917.

2 C. C. Kong, J. Lv, S. D. Sun, X. P. Song and Z. M. Yang, RSC Adv., 2014, 4, 27074, 27077.

3 A. Hakonen, M. Svedendahl, R. Ogier, Z. J. Yang, K. Lodewijks, R. Verre, T. Shegai, P. O. Andersson and M. Kall, Nanoscale, 2015, 7, 9405, 9410.