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Solution based On Chip Direct growth of three-dimensionally wrinkled gold nanoparticles for SERS Active Substrate

Suseung Lee,[a1] Hyeon Don Song,[a1] Young In Yang,[a] Gil-Pyo Kim,[a] Inhee Choi [*b] and Jongheop Yi[*a]

[a]Institute of Chemical Processes, School of Chemical and Biological Engineering, College of Engineering, Seoul National University, Seoul, 151-742, Republic of Korea.
E-mail: jyi@snu.ac.kr; Tel: +82-2-880-7438
[b]Department of Life Science, University of Seoul, Seoul 130-743, Republic of Korea
E-mail: inheechoi1@uos.ac.kr; Tel: +82-2-6490-2675

Supporting Information

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I. Experimental Details

Chemical and Materials. Gold(III) chloride trihydrate ($HAuCl_4$, ≥49.0%, Sigma-Aldrich), hexadecyltrimethylammonium bromide (CTAB, ≥98%, Sigma), sodium borohydride (99%, Aldrich), silver nitrate (≥99.0%, Sigma-Aldrich), *L*-ascorbic acid (≥99%, Sigma-Aldrich), (3-Mercaptopropyl)trimethoxysilane (MPTMS, 95%, Aldrich), rhodamine 6G (R6G, 99%, Aldrich) were purchased and used without any further pretreatment. All glassware were cleaned by soaking in piranha solution (98% H_2SO_4 : 30% H_2O_2 = 7:3 v/v) for 60 minutes, and copiously rinsed with deionized water and ethanol, and dried in the oven at a temperature of 65℃.

Preparation of seed and growth solution. Wrinkled gold nanoparticles (WGNPs) were synthesized based on the typical seed-mediated growth approach. The solution of seed nanoparticles was prepared by following a previously reported method[1]. 100 μl of 5.0×10^{-2} M $HAuCl_4$ was added to 40 ml of 1.50×10^{-1} M CTAB prepared in a piranha-cleaned 80-ml vial with continuous stirring. Then 2.5 ml of 1.0×10^{-2} M sodium borohydride cooled in an ice bath was added and the color of solution quickly changed to brownish red. After keeping stirring for 2 minutes, solution of seed nanoparticles was successfully synthesized and it was used after storage for 3 hours at room temperature.

Growth solution for the synthesis of WGNPs was prepared as followed. 40 ml of 5.0×10^{-2} M CTAB in a piranha-cleaned 80-ml vial with 200 μl of 5.0×10^{-2} M $HAuCl_4$ and 1.2 ml of 7.0×10^{-3} M $AgNO_3$ was prepared, then 300 μl of 1.0×10^{-1} M *L*-ascorbic acid was added. The color of solution changed immediately from dark yellow to colorless, and synthesized growth solution was used freshly made.

Direct growth of WGNPs on the glass substrate. Two types of glass substrate were used for the growth of nanostructure; slide glass (76×26×1 mm, Marienfeld-Superior, German) for the analysis of dark-field microscopy and cover glass (18×18×0.13~0.16 mm, Marienfeld-Superior, German) for the analysis of Raman spectroscopy. All glass substrate was cleaned with piranha solution (98% H_2SO_4 : 30% H_2O_2 = 7:3 v/v) for 60 minutes, and rinsed with deionized water and ethanol several times and dried with nitrogen gas.

For the functionalization of substrate with mercaptosilane monolayers, cleaned glass substrates were treated with 5 mM MPTMS ethanolic solution for 12 hours at room temperature, then rinsed with absolute ethanol to remove excess molecules and dried with nitrogen gas. The MPTMS-functionalized glass substrates were soaked into the prepared solution of seed nanoparticles for 1 hour at 30℃ for the immobilization of seed nanoparticles, then rinsed with deionized water and dried with nitrogen gas.

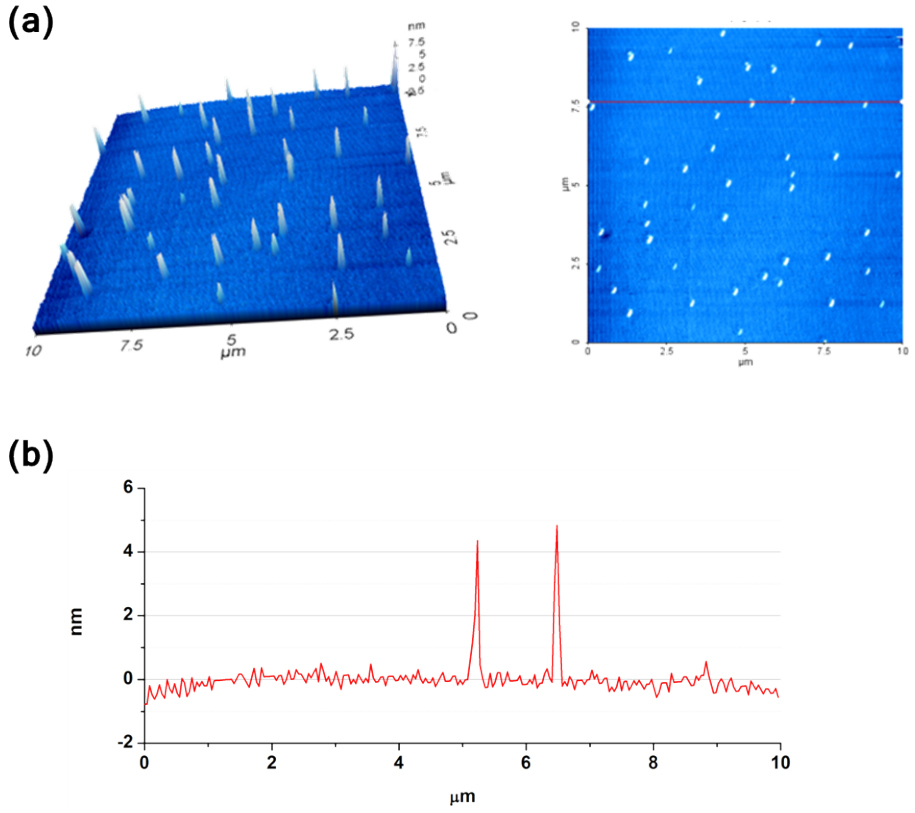
Finally, for the growth of seed nanoparticles to the WGNPs, seed-immobilized substrates were immersed in growth solution upto 5 hours at 30℃. After growth procedure, they were rinsed with deionized water several times and dried with nitrogen gas.

Rayleigh scattering microscopy and spectroscopy. Dark-field microscope system, consisting of an Axio observer Z1 inverted microscope equipped with dark-field condenser (Carl Zeiss, Germany) was used for the observation of the Rayleigh scattering images.[2] The source of illumination was halogen lamp with the 100 W power, and the Rayleigh scattering images were directly collected to a color CCD camera. The spectrum of Rayleigh scattering was collected using a line-imaging spectrometer (Monorai320i, Dongwoo Optron Co., Korea) coupled with a 1024×256 pixel cooled spectrograph CCD camera (Andor Technology PLC, UK). In this study, the spectrum was acquired via full vertical binning method, meaning that all spectrums at each pixel on CCD columns were integrated and displayed as a single spectrum.

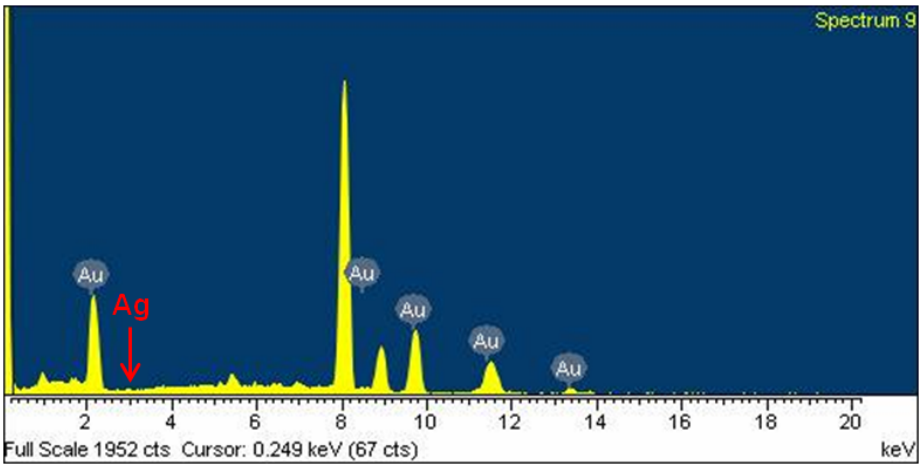
Raman spectroscopy on the wide-area region. The Raman spectrum was collected at ambient temperature using a QE65-Pro-Raman spectrometer (Ocean Optics, Dunedin, FL, USA) with a coupled fiber probe. The laser excitation wavelength was 785 nm (54.4 mW) and beam was focused to a spot size of 158 μm at the substrate. The scattered Raman signal was integrated for

1 second and measured over a spectral range of 0 to 2000 cm^{-1}. For each measurement, it performed at least 5 times with randomly selected region, and collected spectrum was averaged.

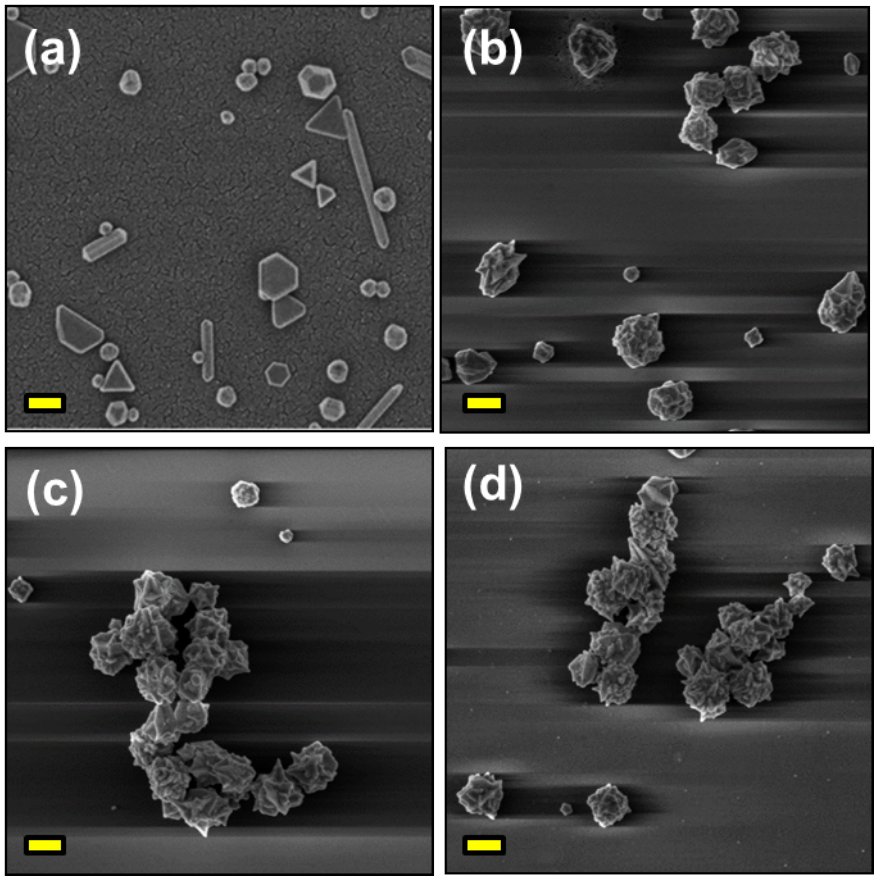
For the Raman-active molecules for SERS, rhodamine 6G was chosen as an analyte because it has been well characterized by SERS and by resonance Raman spectroscopy. From the various Raman shift of R6G, the band at 1510 cm^{-1} was selected as representative Raman shift due to its strong intensity.



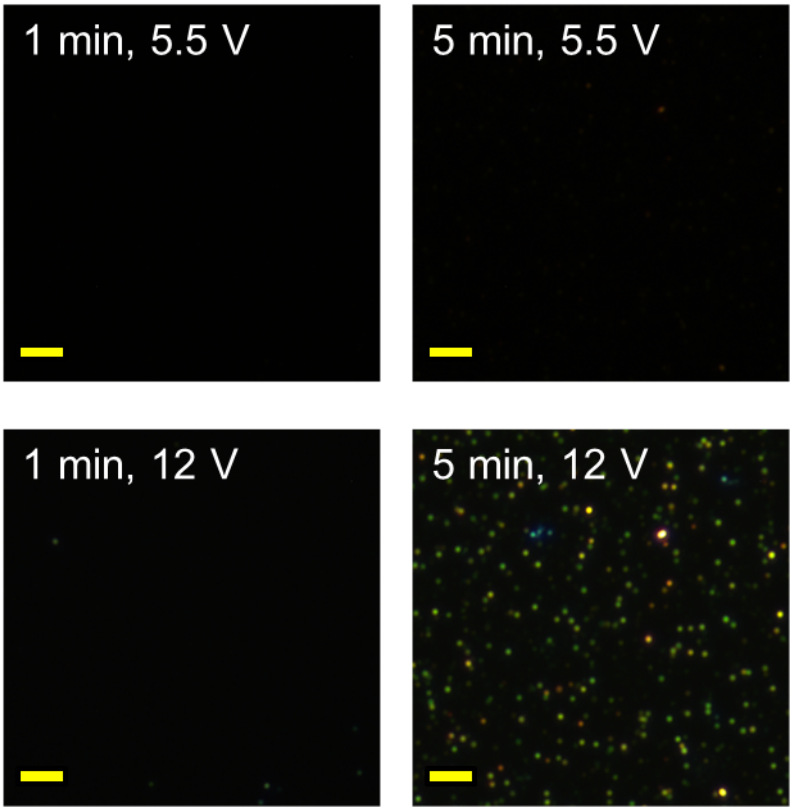
Supplementary Fig. 1 (a) Representative topographical AFM images and (b) line profile of the seed gold nanoparticles; the diameter of seed nanoparticles are about 4~5 nm.



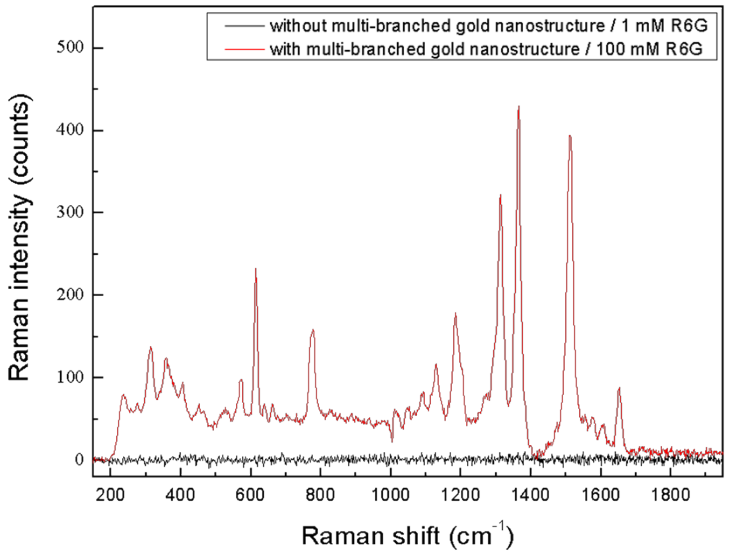
Supplementary Fig. 2 Energy Dispersive X-Ray Analysis of the fabricated wrinkled nanoparticles.



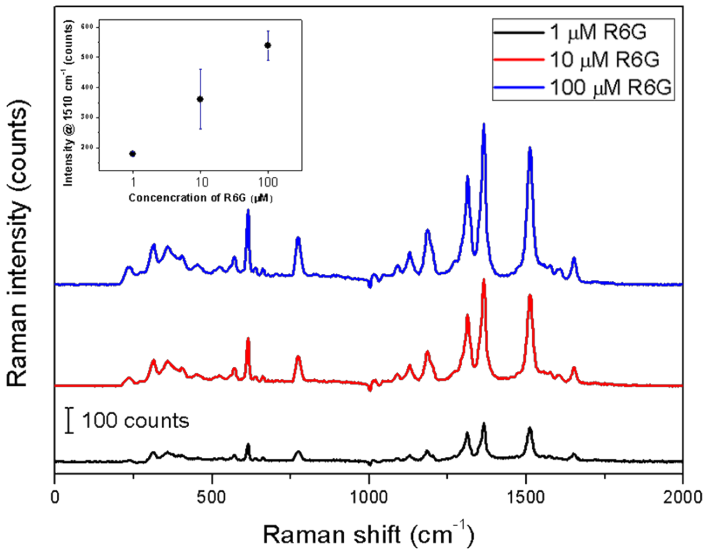
Supplementary Fig. 3 Scanning electron microscopy images of synthesized gold nanoparticles with respect to $AgNO_3$ concentration; (a) 0 μM, (b) 70 μM, (c) 140 μM, (d) 210 μM. Bar is 200 nm.



Supplementary Fig. 4 Dark-field scattering images of synthesized gold nanoparticles at an early growth stage of 1 min and 5 min; Upper images were obtained under low light illumination (5.5 V) and lower images were obtained under higher illumination (12 V).



Supplementary Fig. 5 Comparison of R6G Raman spectrum with and without the WGNPs; before measurement of Raman spectrum, WGNPs-immobilized substrate was exposed to 100 μM R6G (red line), and clean substrate exposed to 1 mM R6G (black line), respectively.



Supplementary Fig. 6 Raman spectra at lower R6G concentration. Inset shows a Raman intensity plot at 1510 cm^{-1} as a function of concentration. The laser excitation wavelength was 785 nm. The scattered Raman signal was integrated for 1 second. For each measurement, it performed at least 5 times with randomly selected region.

References

1. X. Huang, I. H. El-Sayed, W. Qian and M. A. El-Sayed*, J. Am. Chem. Soc.*, 2006, **128**, 2115-2120.
2. H. D. Song, I. Choi, Y. I. Yang, S. Hong, S. Lee, T. Kang and J. Yi, *Nanotechnology*, 2010, **21**, 145501.