Supporting Information

Title : Centrifuge-Based Stepwise Chemical Loading Disc for the Production of Multiplex Anisotropic Metallic Nanoparticles

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EXPERIMENTAL SECTION

Preparation of materials: Gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, ≥99.9%), sodium borohydride ($NaBH_4$, ≥98%), L-ascorbic acid, cetyltrimethylammonium chloride solution (CTAC, 25 wt. in H_2O), hexadecyltrimethyl ammonium bromide (CTAB, ≥98%) were purchased from Sigma Aldrich. All the reagents were prepared in Millipore water (Milli-Q1 Academic A101, France). Polycarbonates (PC, 1mm and 2mm thick) were ordered from Lexantech (Korea), and the polyolefin sealing foils were obtained from HJ BIOANALYTIK GmbH (Germany). The 30 μm thick double-sided PSA tapes were purchased from Bora industrial company (Korea).

Preparation of seed Au NPs: Seed particles were synthesized using a modified procedure of a previous report.[1] Firstly, 250 μL of $HAuCl_4 \cdot 3H_2O$ (0.01 M) was mixed with 10 mL of CTAB (0.1 M). Then, 600 μL of an ice-cold $NaBH_4$ solution (0.01 M) was injected into the mixture for synthesizing small seed particles. The solution was stirred for 1 min and left undisturbed for 1 hr. To increase the diameter in a range of 13 to 17 nm, a growth solution was prepared by stepwise addition of 1.6 mL of CTAC (0.1 M), 200 μL of $HAuCl_4 \cdot 3H_2O$ (0.01 M), and 40 μL of ascorbic acid (0.1 M) into 8 mL H_2O. Then, the growth solution was mixed with a 1/10 diluted small seed particle solution. The mixture was immediately swirled and reacted for 10 hr, producing the seed Au NPs whose diameter was 13–17 nm.

Microfabrication: All the micropatterns were designed by AutoCAD (Autodesk, Inc., San Rafael, CA) and the patterned PC disks were fabricated by a CNC modelling machine (NBS-2025 CNC Machine, Mnicnc, Korea). A PSA layer was patterned using a cutting plotter (Graphtec FC 4500-50, Yokohama, Japan). For the assembly, the polyolefin sealing foil was attached to the PC bottom layer, and both PC layers were bonded by a double-sided PSA layer. All layers are bonded using a pressure adhesive film, so we can easily disassemble the chip by pulling each layer and can remove the adhesion layer. The separate layers are washed with isopropanol and dried with nitrogen gas. Thereafter, the top and bottom layer can be bonded again in order to reassemble a microdevice for the next synthesis.

Microfluidic Au NP synthesis: A growth solution was prepared by adding 250 μL of $HAuCl_4 \cdot 3H_2O$ (0.01 M) into 10 mL of CTAB (0.02 M). The ascorbic acid was used as a control solution, and the concentration was tuned from 0.001 M to 0.2 M. To transform the typical seed-mediated Au NP synthesis from the on-batch to the on-chip platform, we accordingly scaled down the concentrations and volumes of the reagents, while keeping the reagent ratio constant. After the microdevice was exposed to UV ozone (UVO cleaner, Ahtech LTS, Korea) for 15 min, 100 μL of the 1/10 diluted seed solution and 190 μL of the growth solution were injected to the inner and outer continuous Y-shaped channels through one injection hole on the top PC layer, respectively. 5 μL of a designated control solution was individually injected into thirty control solution reservoirs in the bottom PC layer by manual pipetting. With the reagents loaded, the microdevice was mounted on the rotary stage, and then the rotation process consisting of 400 RPM for 10 s, 600 RPM for 20 s, and 1500 RPM for 20 s was followed for the successive loading of the growth, control, and seed solution to the microreactor. Total volume of the reaction was 15 μL (5 μL of a control solution, 6 μL of a growth solution, and 3 μL of a seed solution). After shaking the microdevice for 180 sec, the microdevice was sealed with a polyolefin sealing foil on the top to prevent evaporation from the microreactors, and incubated for 2 hr to complete the reaction.

Sample collection and characterization: The synthesized Au NPs were collected from the ventilation hole by using a pipettor for further characterization. Centrifugation and resuspension of the recovered Au NP products were repeated in 20 μL H_2O twice to remove the impurities. The purified Au NPs were analysed by a field emission transmission electron microscope (Tecnai G2 F30, FEI, Netherlands) operated at an accelerating voltage of 300 kV. The absorption spectra were measured by a UV-Vis spectrometer (Shimadzu UV-2450, Japan). The surface analysis of the PC layer was performed by an XPS (Thermo VG Scientific, USA).

Reference

[1] M. R. Langille, M. L. Personick, J. Zhang, C. A. Mirkin, *J. Am. Chem. Soc.*, 2012, **134**, 14542−14554

Table S1. Rotational procedure for the multiplex anisotropic AuNP synthesis

Procedure no.	Rotational procedure and its operation		
	Speed (RPM)	**Time (s)**	**Operation**
1	500	10	Growth solution loading and distribution
2	1500	20	Seed solution loading and distribution
3	2500	20	Control solution (AA) loading
4	+960 ~ -960	180	Shaking mode for mixing
5	—	—	Reaction for 2 hr

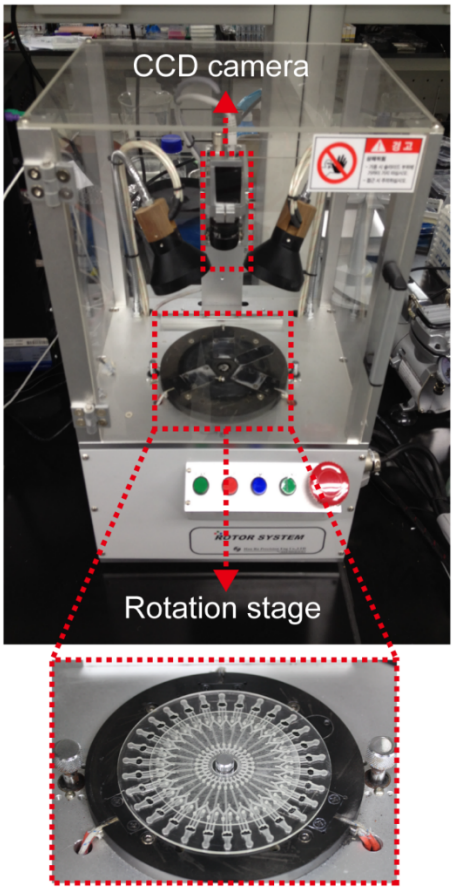


Figure S1 Digital images of the rotary stage and the rotary microfluidic device.

Theoretical critical rotational speed

We adopted a simple model to predict the burst RPM for sample loading by balancing the pressure induced by a centrifugal force with the pressure induced by a capillary force that is given the Young-Laplace equation.

$$\Delta P = \rho\omega_c^2\bar{r}\Delta r\ (Centrifugal\ pressure)$$

$$= \gamma\left(\frac{cos\theta_1 + cos\theta_2}{d} + \frac{2cos\theta_2}{w}\right)(Capillary\ pressure)$$

Table S2 Parameters of the capillary pressure

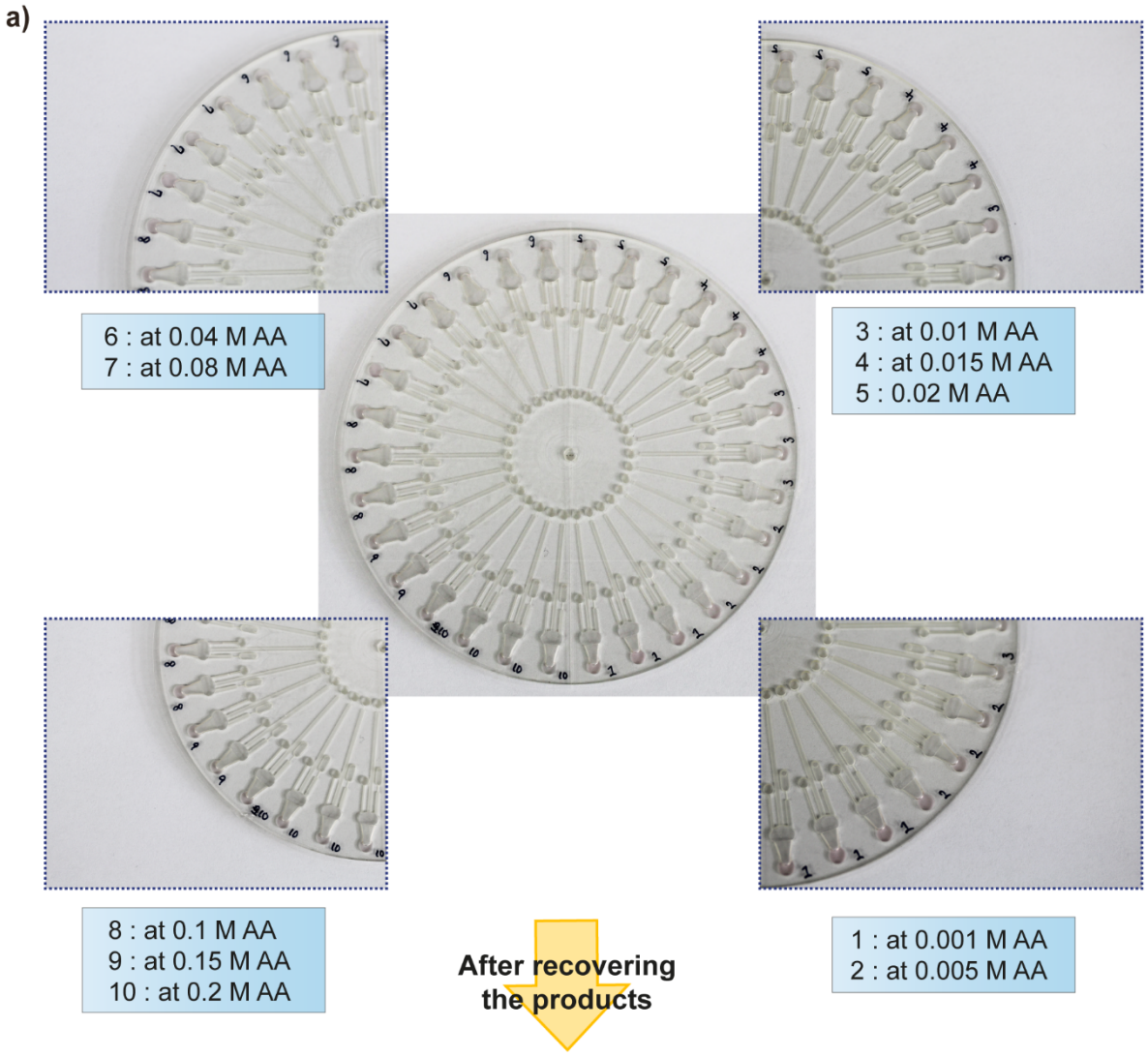
	$\gamma\ (N/m)$	$\theta_1\ (degree)$	$\theta_2\ (degree)$	$d\ (\mu m)$	$w\ (\mu m)$	$\Delta P\ (N/m^2)$
Growth solution	0.021	67	21	800	500	104.6
Control solution	0.072	105	30	300	100	852.9
Seed solution	0.028	70	29	150	100	667.2

γ = surface tension of the reagent, θ_1 = contact angle of liquid on a polyolefin sealing layer, θ_2 = contact angle of liquid on a UV ozone treated PC layer, d = depth of a microchannel, w = width of a microchannel.

Table S3 Parameters of the centrifugal pressure

	$\Delta P\ (N/m^2)$	$\rho\ (kg/m^3)$	$\bar{r}\ (\mu m)$	$\Delta r\ (\mu m)$	$\omega_c\ (rad/s)$	***Theoretical burst RPM***	***Experimental burst RPM***
Growth solution	104.6	1000	40284	8493	17.5	167	400
Control solution	852.9	1000	6470	35358	61	583	600
Seed solution	667.2	1000	16371	2015	142	1356	1500

Δr = length of a liquid plug, $\bar{r}$ = mean radial position of a liquid plug, ρ = the density of water, and the unit of ω_C (rad/s) is converted to RPM (rotation/minute) by multiplying a conversion factor (1 rad/s = 9.55 RPM).



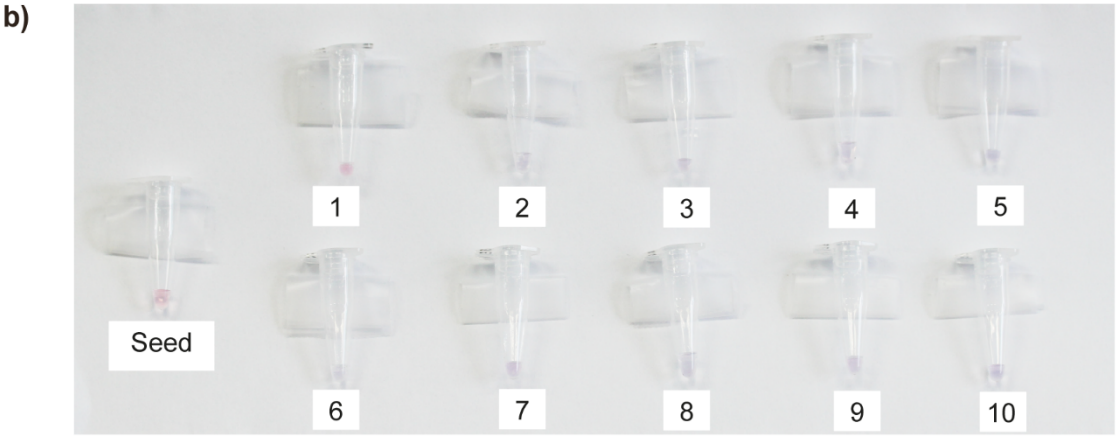


Figure S2 a) Digital images of the microreactors in which the gold nanoparticles were synthesized at different concentrations of ascorbic acid (AA), b) Digital images of the recovered Au NP products in a 0.2 mL PCR tube. The color of the Au NPs changed from pink to blue-purple as the concentration of AA increased.

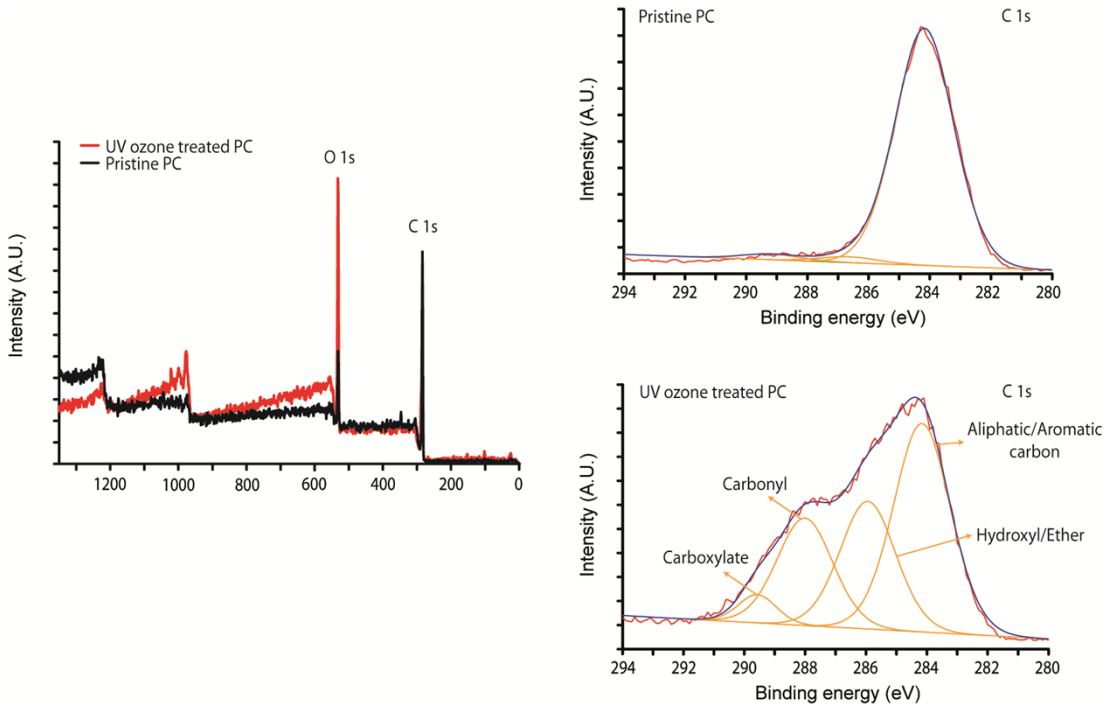


Figure S3 XPS data before and after the UV ozone treatment on the PC layer.

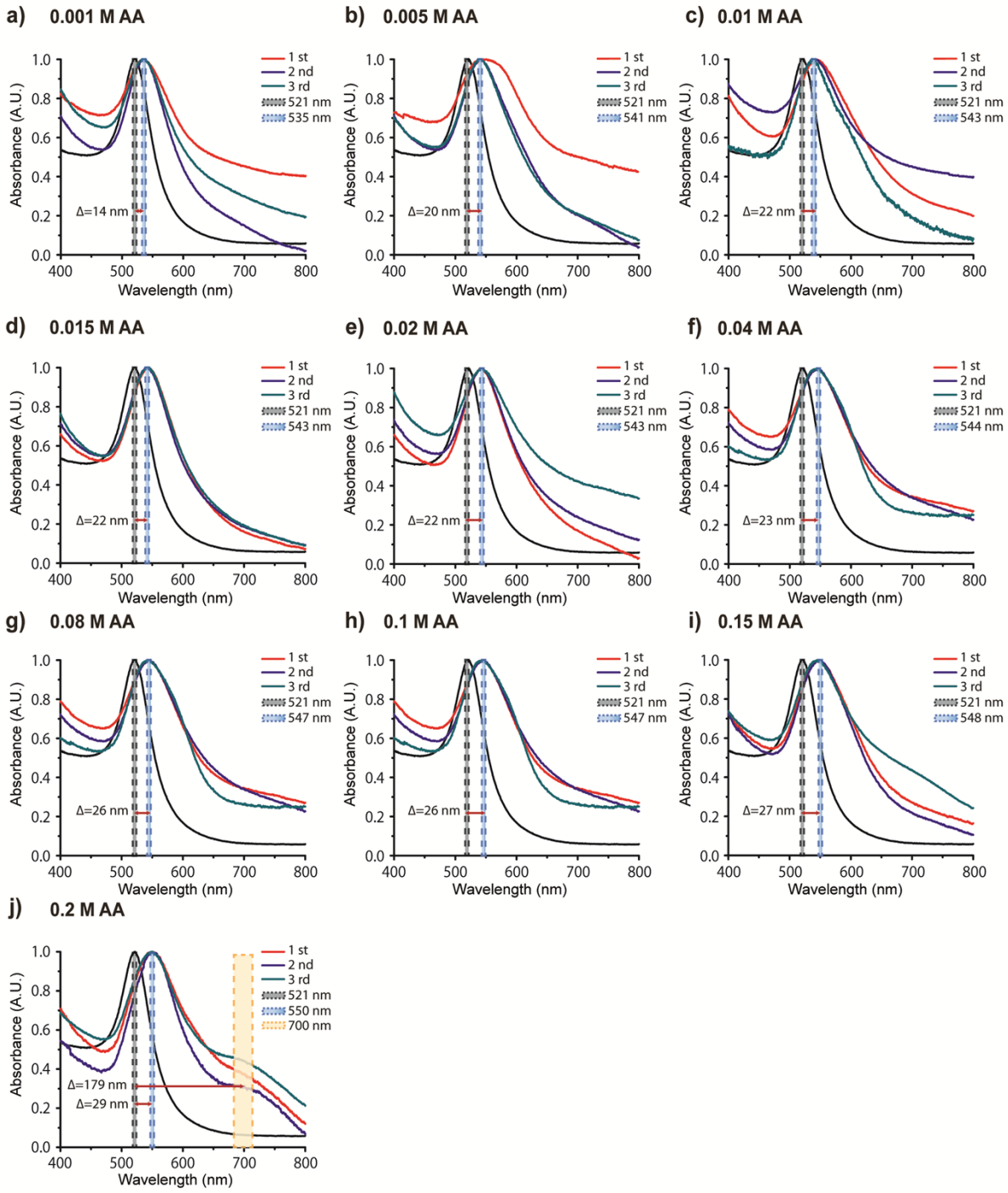


Figure S4 UV-Vis absorption spectra of the triplicate Au NPs synthesized at different concentrations of ascorbic acid: a) at 0.001 M, b) 0.005 M, c) 0.01 M, d) 0.015 M, e) 0.02 M, f) 0.04 M, g) 0.08 M, h) 0.1 M, i) 0.15M, and j) 0.2 M.