Supplementary Information for

Aerosol-based soft lithography to fabricate nanoscale silver dots and rings for spectroscopic applications

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EXPERIMENTAL PROCEDURE

Aerosol Pd nanoparticles were produced via spark discharge and carried by N_2 gas to a substrate [*N*-type Si (100), resistivity of 10^{-2}-10^{-3} Ω cm], as shown in Fig. S1. The substrate was cleaned with a 3:1 mixture of H_2SO_4 (Sigma-Aldrich, US) and 30% H_2O_2 (Merck, Germany), rinsed, and sonicated in deionized water. A spark was formed between two identical Pd rods (diameter: 3 mm, length: 100 mm, PD-342561, Nilaco, Japan) inside a chamber under a pure N_2 environment (>99.99% purity) at standard temperature and pressure. The flow rate of the N_2 gas was controlled by a mass flow controller (Tylan, US). The electrical circuit specifications were as follows: resistance 0.5 MΩ, capacitance 1.0 nF, loading current 2.0 mA, applied voltage 3.0 kV, and frequency 667 Hz.

In order to fabricate nanodots (Fig. S1a), the temperature of the particle-laden flow was maintained at 19°C with a tube heater, and the temperature of the Si substrate was maintained at -10.5°C with a Peltier cooler, thereby enhancing deposition of the particles onto the substrate *via* thermophoresis. While the temperature of the shadow mask (thickness of mask: 10 μm from chemical etching, Youngjin Astech, Korea) was maintained at 30°C by a resistive heater to prevent unwanted deposition of the Pd particles on the mask since aerosol nanoparticles tend to deposit on colder surfaces (Byeon and Roberts, Silver deposition on a polymer substrate catalyzed by singly charged monodisperse copper nanoparticles. *ACS Appl. Mater. Interfaces* 2012, **4**, 2515), similar to a stencil lithography (Villanueva et al. All-stencil transistor fabrication on 3D silicon substrates. *J. Micromech. Microeng.* 2012, **22**, 095022). The thermophoretic force was calculated based on the following equation,

$$F_T = -\frac{6\pi D_p \mu_g^2 C_s \left(K + C_t Kn\right)}{\rho_g \left(1 + 3C_m Kn\right)\left(1 + 2K + 2C_t Kn\right)} \frac{1}{T_g} \nabla T \tag{S1}$$

where μ_g is the gas viscosity, C_s, C_t, and C_m are the dimensionless constants, K is the ratio of the gas and particle thermal conductivities, Kn is the Knudsen number, ρ_g is the gas density, and T_g is the gas temperature. The substrate was then separated from the stainless steel shadow mask and annealed at 240°C for 10 min in N_2 atmosphere to prevent the detachment of the particles from the substrate. After

annealing, the Pd-patterned substrate was immersed into an electroless Ag bath, resulting in the deposition of Ag on the Pd particles of the substrate.

In order to fabricate nanoscale ring patterns as seeds (Fig. S1b), the spark discharge was also used to produce Pd nanoparticles, and the particle-laden flow was employed as the operating gas for the collison atomizing diluted EG solution. The Pd nanoparticles passed over the atomizer orifice, where they mixed with atomized EG droplets to form hybrid droplets, i.e. Pd-deposited EG droplets. The droplets then passed through a tubular chamber for solvent extraction of the droplets *via* a heated tubular reactor. The hybrid nanoparticles were size classified using a nano differential mobility analyzer (3085, TSI, US) and then the singly positively particles injected into a deposition chamber with an electric field. After annealing at 250^{o}C to remove EG from the hybrid nanoparticles, the ring-shape Pd-patterned substrate was immersed into an electroless Ag bath, resulting in the deposition of Ag on the ring patterns of the substrate.

Two solutions were mixed and used for the ELD solution. Solution A contained 1 g of $AgNO_3$, 60 g of Na_2EDTA, 88 mL of isopropyl alcohol, 12 mL of acetic acid, and 400 mL of NH_4OH in 1 L of deionized water. Solution B contained 3 mL of hydrazine, 2 mL of mercerine, and 400 mL of ethyl alcohol in 1 L of deionized water. 50 mL of solution A and 30 mL of solution B were mixed together, and the activated substrates were then immersed into this mixture at 20°C so that the electroless Ag particles would be deposited on the Pd-patterned substrates. Ag nuclei, which are formed on the surface of Pd particles in the reaction, act as the active sites for further deposition of the Ag species. The substrate was rinsed with deionized water after it was removed from the bath to remove the residual and then set aside to dry in a clean booth.

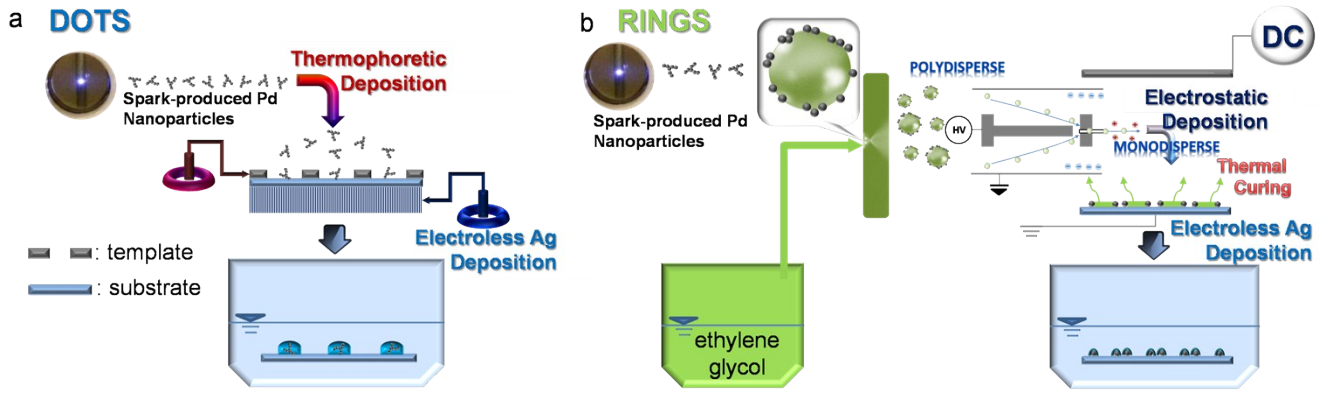

Fig. S1. Schematic diagram of site-selective Ag deposition apparatus used for preparing (a) Ag dots and (b) Ag rings on substrates.

SERS EHHANCEMENT FACTOR

The total SERS enhancement factor (E_F) can be estimated by

$$E_F = \frac{e_F}{\sigma} \quad \text{(S2)},$$

where e_F and σ the raw enhancement factor and the relative Ag coverage of a substrate, respectively, and can be calculated as follows:

$$e_F = \frac{I_{SERS}}{I_{Bulk}} \frac{M_{Bulk}}{M_{SERS}} \quad \text{(S3)},$$

$$\sigma = \frac{2\pi\left(\frac{D}{2}\right)^2}{L\sqrt{(2L)^2 - L^2}} \quad \text{(S4)},$$

where I_{SERS} is the Raman intensity measured on the nanostructured sbustrates, I_{Bulk} are the Raman intensity measured in solution, M_{Bulk} is the number of molecules probed in solution, M_{SERS} is the number of molecules probed on the nanostructured substrates, D is the diameter of the nanodots, and L

is the center-to-center interdistance between the nanodots. The number of molecules probed depends on the concentration (10^{-3} mol L^{-1}) and the probed volume.

Pd XRD PROFILE

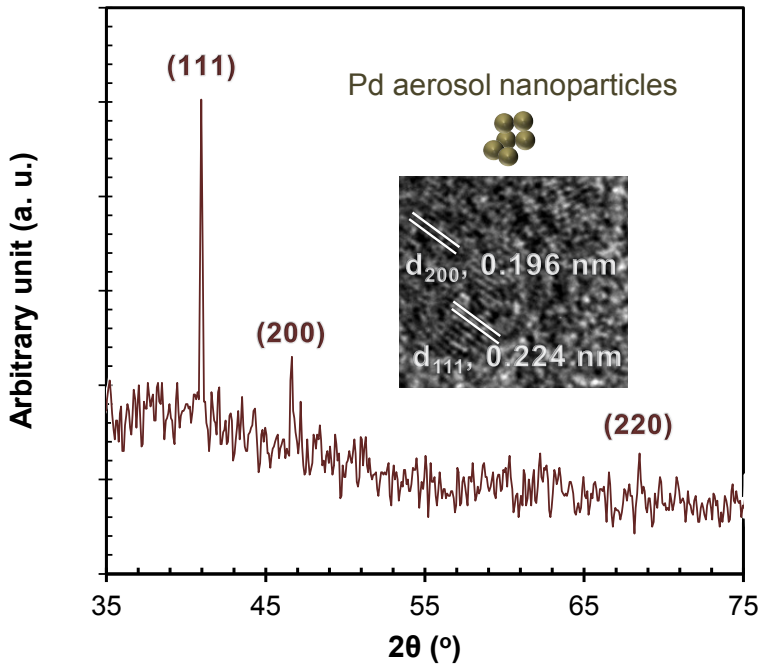

Fig. S2. XRD profile of Pd aerosol nanoparticles with a high-magnification TEM image showing the lattice indices (111) and (200).

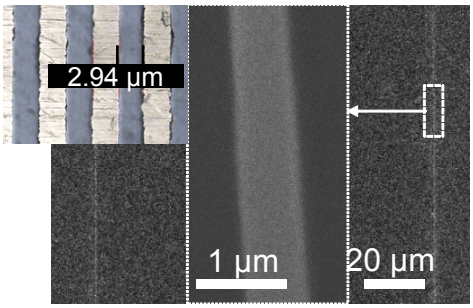

Fig. S3. Optical microscope image of "line holes" stainless steel shadow mask. The width of the hole is 2.94 μm. Low- and high-magnification SEM images of the Ag "line" patterns (~860 nm line width, ~320 nm line height) from the ELD are also shown. A resistivity (ρ) of the Ag pattern without sintering was calculated through the relationship $\rho = RA/L$, where R, A, L are the resistance, cross-sectional area, and length of the pattern, respectively. The average value of the resistivity for the Ag line patterns was approximately 8.8 μΩ cm. The value is close to the theoretical resistivity of bulk Ag (1.6 μΩ cm), which implies that the aerosol lithography assisted ELD of Ag may also be a viable option to fabricate highly conductive nanoscale line patterns.

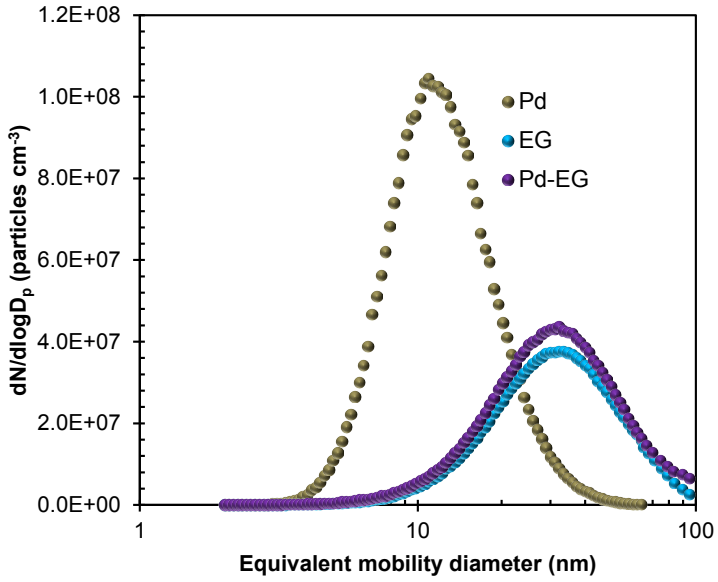

Fig. S4. Size distributions of the spark produced Pd, collison atomized EG, and merged particles. Standard deviations are described in Table SII.

TABLE SI Details of the size distribution of spark-produced Pd particles under N_2 flow environment

Case	GMD (nm)	GSD (-)	TNC (× 10^7 particles cm^{-3})
Pd	12.0	1.54	4.76

TABLE SII Details of the size distribution of collison atomized EG, and merged (Pd-EG) particles

Case	GMD (nm)	GSD (-)	TNC (× 10^7 particles cm^{-3})
EG	40.1	1.65	2.08
Pd-EG	46.4	1.66	2.69