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Tuning the Fast Generation of Luminescent Silver Nanodots on the Surface

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Experimental Procedures

Materials

Poly acrylic acid (MW~1,800 or 15,000) (PAA), silver nitrate (99.9999%), 3-(2-amino ethyl amino) propyl dimethoxy methyl silane, (3-amino propyl) trimethoxy silane, (3-glycidyloxy propyl) trimethoxy silane, isobutyl(trimethoxy)silane, trimethoxy[2-(7-oxabicyclo[4.1.0]hept-3-yl)ethyl]silane, anhydrous methanol, sodium hydroxide, sodium borohydride, boric acid, sodium tetraborate dehydrate were purchased from Sigma-Aldrich and used as received, hydrogen peroxide, hydrochloric acid, glycerol and acetone were purchased from Dae Jung and used as received. Ammonia solution was purchased from Sam Chun and used as received. ssDNA were synthesized by Integrated DNA Technologies; Deionized water (DIW) was obtained on a Millipore Direct-Q 3 ultrapure water system with a resistivity of 18.2 MΩ cm. Sylgard 184 poly(dimethyl siloxane) (PDMS) kit was purchased from DOW Corning.

Instrumentation

Emission and excitation spectra were obtained on a PTI QuantaMasterTM 40 fluorimeter. Samples were concentrated by a solvent evaporation method using an ilshin ® Freeze dryer; pH was adjusted on a Eutech, SG/PH510 pH meter. Images were obtained on an Olympus IX81 microscope with an Andor Luca^{EM} S 658M camera. Spin coating was conducted on an SC-100RPM spin coater.

Synthesis of Poly acrylic acid-stabilized Ag nanodots

Silver-silane stock solution (14 mM)) was prepared by mixing silver nitrate (12 mg) and 3-(2-aminoethylamino) propyldimethoxymethylsilane at an amino silane/Ag^+ ratio of two in anhydrous methanol (5 mL) for 2 hrs. PAA stock solution (1.8 KDa, 30 µL of 8.1 mM pH 8) was added into DIW or borate buffer (968 µL), followed by the addition of the silver-silane solution (17 µL) with a final ratio of 1:2 between silver and silane, and 1:3 between polymer and silver. The mixture was then reduced with fresh sodium borohydride stock solution (4.60 µL, 52.87 mM) and stirred overnight in the dark.

Transferring PAA AgNDs to ssDNA AgNDs on glass surface

DNA (2 mM in 20% glycerol solution) was spin coated for 30 s at 3000 rpm with a SC-100RPM spin coater on a glass coverslip. The hydrophilic stamp was slightly pressed onto the above DNA coated coverslip for 30 s, dried with nitrogen gas for 40 s, and then strongly pressed onto coverslip (APTES and acetic acid modified coverslip/ IBTMS modified coverslip/ unmodified coverslip) for 30 s. Ten minutes later, a PAA AgND solution was sprayed to the above surface twice, with an interval of three minutes.

Preparing ssDNA AgNDs on glass surface by direct preparation method

DNA (2 mM in 20% glycerol solution) was spin coated for 30 s at 3000 rpm with SC-100RPM spin coater on a glass coverslip. The hydrophilic stamp was slightly pressed onto the above DNA coated coverslip for 30 s, dried with nitrogen gas for 40 s, and then strongly pressed onto APTES and acetic acid modified coverslip for 30 s. Ten minutes later, silver nitrate (1.4 mM/ 0.14 mM) solution was sprayed to the above coverslip surface twice, with an interval of three minutes. Sodium borohydride solution (52.87 mM) was sprayed on the above glass surface once.

Transferring ssDNA AgNDs to the glass surface

ssDNA AgNDs (in 20% glycerol solution) were spin coated on the APTES modified coverslip (3000 rpm, 30 s). The hydrophilic modified PDMS stamp was pressed onto the glycerol film. Then the stamp was slightly pressed to an APTES modified coverslip.

Ratio between yellow and near-IR emitters depending on PAA Ag concentration

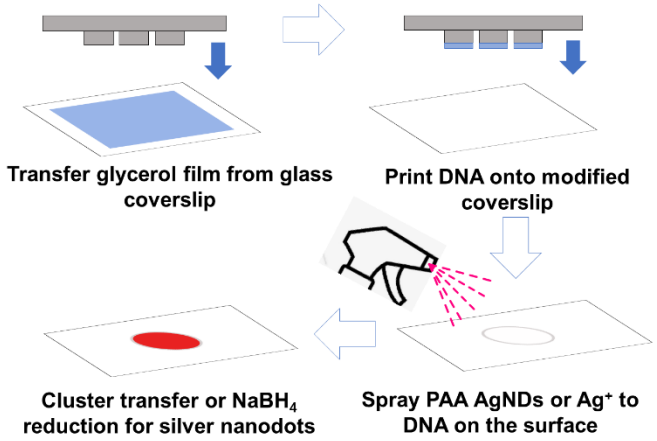
The ssDNA modified was sprayed with a PAA AgND solution (0.24 mM /0.12 mM/0.05 mM, respectively) twice, with an interval of three minutes. The emission channels were examined with a 420–460 nm excitation filter, a 545–580 nm bandpass filter, and a 665 nm long pass emission filter, respectively.

Ratio between yellow and near-IR emitters depending on surface pH

DIW washed coverslip were spin coated by PAA (15,000 Da, 5 mg/mL, 500 µL, pH5, 6, 7, 8, 9, 10, respectively) at 1500 rpm for 120 s. The coverslip was dried in the dark for 24 hr. DNA (1 mM DNA in 20% glycerol solution) was spin coated (3000 rpm, 30 s). PAA AgNDs (0.243 mM) was sprayed to the above coverslip with an interval of three minutes. The emission channels were examined with a 420–460 nm excitation filter, a 545–580 nm bandpass filter, and a 665 nm long pass emission filter, respectively.

Spectrum calibration based on microscopic images

Yellow silver nanodots (5 mL, 5 mM, DNA: 5'-CCCCACCCACCCACCCT-3) was dropped on the coverslip surface and imaged on a microscope. Emission intensities of images of ssDNA AgNDs obtained with an excitation bandpass filter of 420-460 nm and emission bandpass filter of 510-550 nm, 545-580 nm, 585-625 nm, 600-660 nm, and 665-700 nm, respectively, were plotted against the middle wavelengths of the bandpass filters. The corresponding dots were compared with the emission spectrum of this yellow emitter obtained on a fluorometer (**Figure S8**).



Scheme S1. Scheme showing microcontact printing of ssDNA molecules with PDMS stamps and visualization of these DNA molecules by silver cluster transfer or chemical reduction.

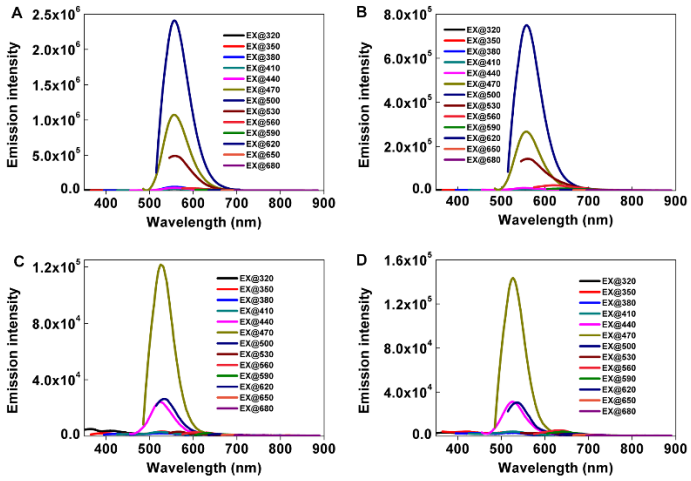


Figure S1. Emission spectra of silver nanodots in solution. A and B, Emission spectra of CCCCACCCACCCTCCCA-stabilized silver nanodots prepared in solution by direct chemical synthesis (A) and cluster transfer (B). C and D, Emission spectra of CCCCCCCCCCCCCCCCCCCC-stabilized silver nanodots prepared in solution by direct chemical synthesis (C) and cluster transfer (D). Spectra were obtained after the spectra peaked respectively. Ex@*xxx* stands for the excitation wavelength for a specific emission spectrum.

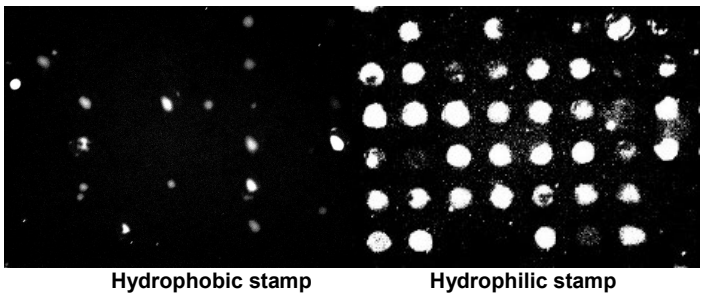


Figure S2. Impact of the hydrophilicity of PDMS on the efficiency of ssDNA. DNA sequence: 5'-CCCCACCCACCCTCCCA-3' (1 mM) was spin-coated with 20% glycerol on a coverslip, and then transferred to a new APTES-modified glass surface with the hydrophobic or hydrophilic stamp. When a hydrophobic stamp was used, only a few dots were formed.

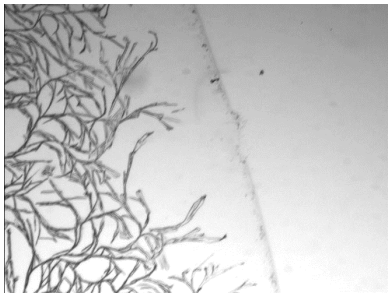


Figure S3. ssDNA forms dendrimer-like aggregates on the glass surface after spin coating. 5'-CCCCACCCACCCTCCCA-3' (1 mM) in aqueous solution.

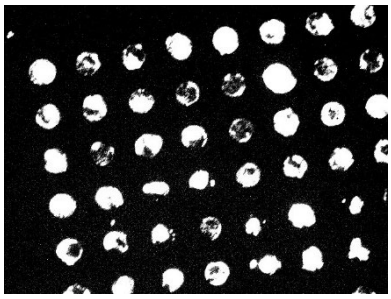


Figure S4. Microcontact-printed DNA-AgNDs (Ex467/Em563) to glass surface. DNA-AgNDs concentration: 0.53 mM. Emission was monitored with an excitation bandpass filter of 420–460 nm and emission bandpass filter of 545–580 nm.

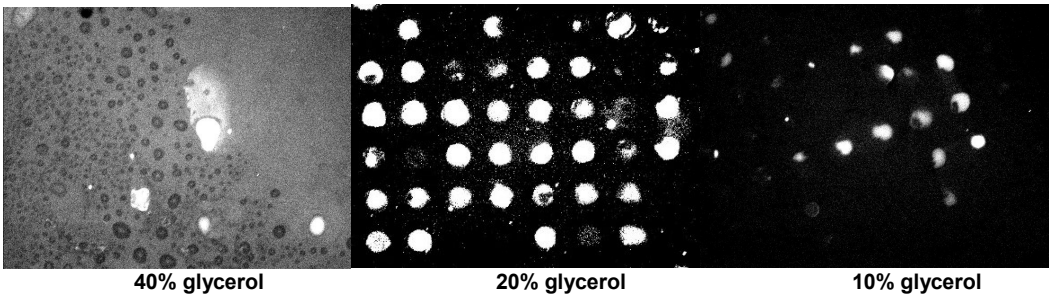


Figure S5. Influence of glycerol concentration on the transfer efficiency of ssDNA. The hydrophilic stamp was pressed to a DNA-glycerol spin-coated film for 30 s and then dried for 40 s with nitrogen gas. The stamp was then pressed to a new hydrophilic coverslip, followed by the spray of PAA-AgNDs. DNA sequence: 5'-CCCCACCCACCCTCCCA-3'. Emission was monitored with an excitation bandpass filter of 420–460 nm and emission bandpass filter of 545–580 nm.

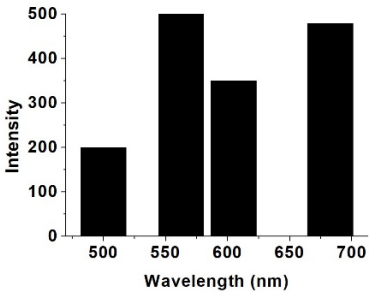


Figure S6. Emission intensity of silver nanodots at various channels on a washed glass surface. DNA sequence 5'- CCCCCCCCCCCCCCCCCCC -3' was transferred to the specific glass surface by microcontact printing, followed by cluster transfer for silver nanodot generation. Emission channels were monitored with an excitation bandpass filter of 420–460 nm and emission bandpass filters of 480–520 nm, 545–580 nm, 585–625 nm, 600–660 nm, and 665–700 nm, respectively.

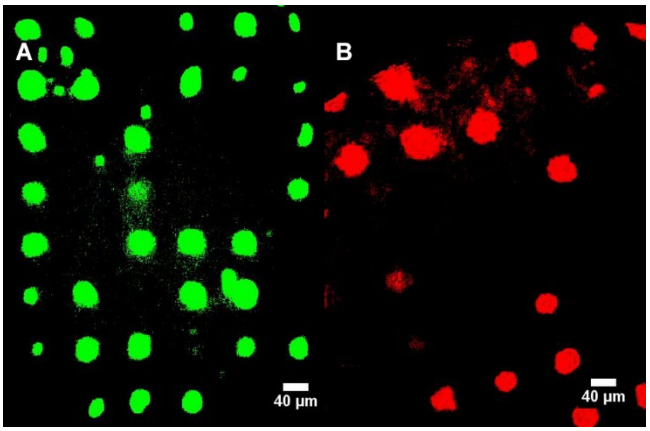


Figure S7. Color emission images of silver nanodots on the surface. Emission images of the silver nanodots on the surface with a cellular phone camera viewed from the eyepiece of the microscope. DNA sequence 5'- ATATC$_{12}$ATAT -3' (A) or 5'- CGCGC$_{12}$CGCG -3' (B) was transferred to the specific glass surface by microcontact printing, followed by cluster transfer for silver nanodot generation. Emission channels were monitored with an excitation bandpass filter of 420–460 nm and emission bandpass filters of 545–580 nm (A) or 510-550 nm bandpass excitation filter and 610–700 nm emission filter (B), respectively. Scale bar: 40 μm.

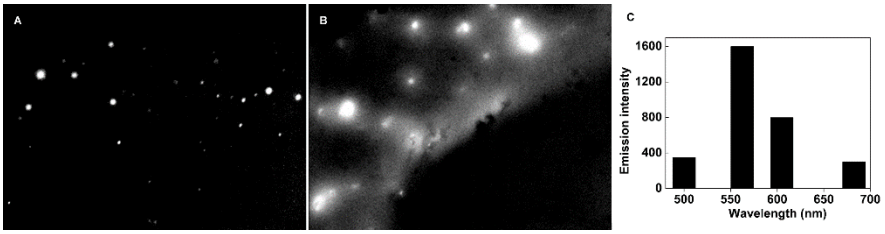


Figure S8. Impact of surface polymer coating on the generation of silver nanodots. A. and B. Silver nanodot generation on PVA (A) and PAA (MW 15,000 Da) coated surface (B), respectively. C. Emission intensity of silver nanodots at various channels on the PAA-coated surface. DNA sequence 5'- CCCCCCCCCCCCCCCCCCC -3' was transferred to the specific glass surface by spin coating, followed by cluster transfer for silver nanodot generation. The emission channels were monitored with an excitation bandpass filter of 420–460 nm and emission bandpass filters of 480–520 nm, 545–580 nm, 585–625 nm, and 665–700 nm, respectively.

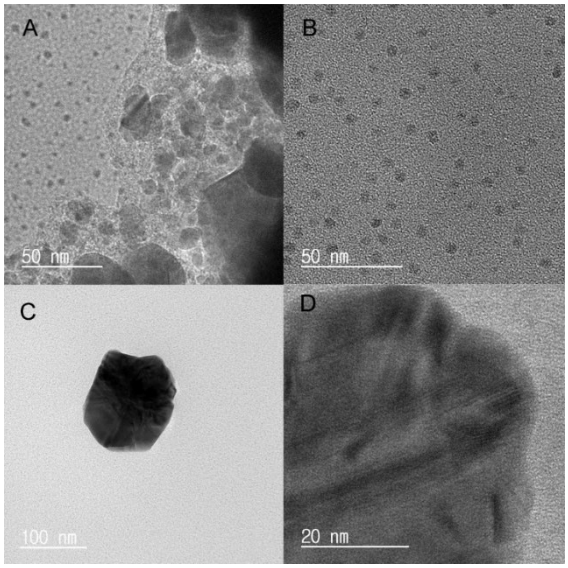


Figure S9. TEM images of PAA-AgNDs at varied concentration. TEM images of PAA-AgNDs at 2430 μM.(A and B) and 12150 μM (C and D), respectively. At lower PAA-AgNDs, some small aggregates are observed, but at higher concentration, only large aggregates are observed. The research shows that the aggregation of PAA-AgNDs increases as the concentration of PAA-AgNDs increases.

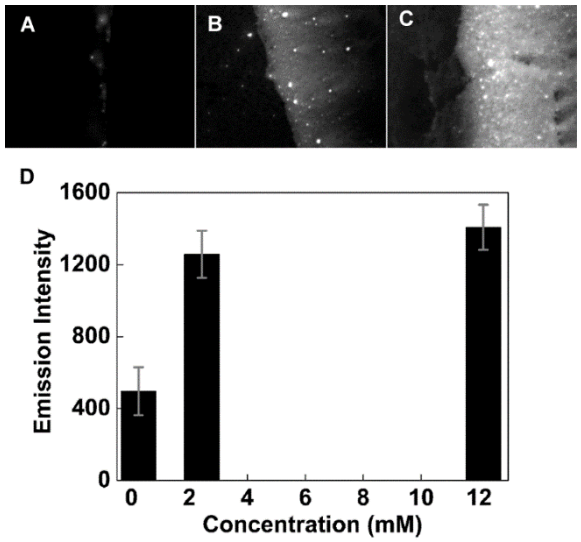


Figure S10. Brightness of PAA-AgNDs on the surface. A to C, Emission images of PAA-AgNDs spread on the glass surface at concentrations of 243 μM, 2430 μM, and 12150 μM, respectively. D, Brightness of individual spots on the surface. The research shows that the brightness of individual spots increases as the concentration of PAA-AgNDs increases, suggesting that PAA-AgNDs form aggregates as its concentration increases.

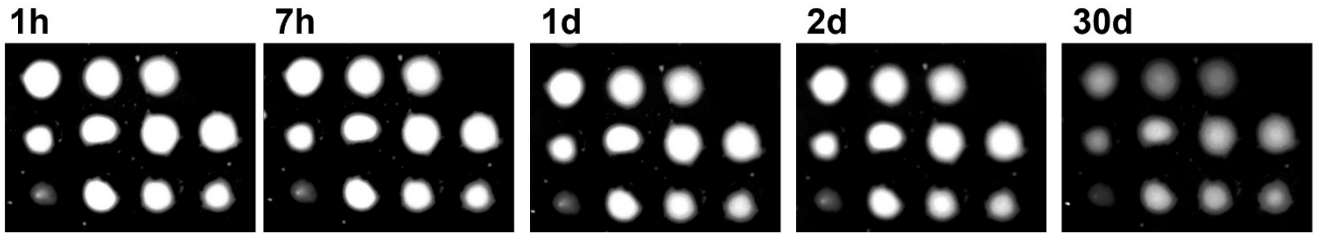


Figure S11. Photostability of the near-IR emitter on the surface. The DNA 5'-CCCACCCACCCTCCCA-3'-stabilized silver nanodot was monitored with an excitation bandpass filter of 420–460 nm and emission longpass filter of 665–700 nm at various time delays after cluster transfer.

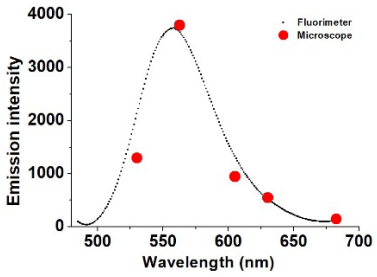


Figure S12. Calibration of the emission spectrum obtained on a microscope. Emission spectrum obtained on a microscope (red dots) is compared to that obtained on a fluorimeter (short dots). Emission intensities of images of ssDNA AgNDs obtained with an excitation bandpass filters of 420–460 nm and emission bandpass filter of 510–550 nm, 545–580 nm, 585–625 nm, 600–660 nm, and 665–700 nm, respectively, were plotted against the middle wavelengths of the bandpass filters.