Supporting Information

In-situ synthesis of large-area single sub-10 nm nanoparticle array by polymer pen lithography

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Materials and Methods

1. Materials

$HAuCl_4 \cdot 3H_2O$, $AgNO_3$, CF_3COOAg, $Fe(NO_3)_3 \cdot 9H_2O$, ethylene glycol (99%, $C_2H_6O_2$, M_n = 62.07 g.mol^{-1}), glycerol (99%, $C_3H_8O_3$, M_n = 92.09 g.mol^{-1}) , octadecyltrimethoxysilane, toluene, n-butylamine and acetone were purchased from Sigma-Aldrich. Hydrophobic silicon nitride membranes (membrane thickness = 15 nm) were purchased from Ted Pella, Inc. Silicon wafers were purchased from Silicon Valley Microelectronics. Inc. Silicon slides were soaked in a Piranha solution (H_2SO_4/H_2O_2 (70/30)) at 70 degree for 1 hour, then rinsed with water, and dried with nitrogen. The slides were washed with toluene and then acetone several times under ultrasonication. To ensure the hydrophobicity of the silicon slides, the cleaned slides were subsequently placed vertically in a 5% solution (v/v) of octadecyltrimethoxysilane in toluene with 0.5% n-butylamine at room temperature for 1 hour without touching each other.

2. Polymer pen lithography process

Polymer pen tip arrays with 80-μm spacing between tips were prepared as previously reported.[1] The polydimethylsiloxane (PDMS) tip array was treated with oxygen plasma for 1 min to make it hydrophilic before inking. The ink solution of metal precursor/ ethylene glycol or glycerol was spun cast onto the PDMS tip array (20 μL, 1500 rpm, 60 s). PPL experiment was carried out on an AFM work station (Park, Inc.) with a PPL head, using XEP software. The humidity was controlled between 80%-90% and temperature was between 25-29°C during the experiment. The polymer pen array was leveled to the underlying substrate optically with an optical microscope. The dwell time of the tips was controlled to be 2 s and the Z piezo extension of the AFM scanner was 2 μm if these parameters were not specially pointed out.

3. Nanoparticle synthesis

After PPL, Ag nanoparticles can be synthesized by two methods. The first method is thermal annealing the samples of patterned Ag precursor at 70°C for 4 h. The samples can also be exposed to halogen light (Fiber-lite Illuminators MI150, Dolan-Jenner) for 4 h to obtain Ag nanoparticles. Au nanoparticles can be obtained by two ways from Au precursor. The first way was using oxygen plasma to deal with the samples at a plasma power of high for 5 min in a plasma cleaner ((Plasma Cleaner, PDC-32G, Harrick) with the oxygen flow of 200 millitorrs. The samples can also be subjected to thermal annealing at 70°C for 4 h to obtain Au nanoparticles. After patterning Fe_2O_3 precursor, the samples were subjected to oxygen plasma (the same experimental condition as synthesis of Au nanoparticles) to obtain single Fe_2O_3 nanoparticle array.

4. AFM and Optical Microscopy

AFM measurements were performed using Park Systems Co. to obtain the topographic images of the patterned nanoreactors and the synthesized nanoparticles. The optical images were taken from a Zeiss Axiovert 200M (Carl Zeiss, Inc., Germany) optical microscope.

5. TEM, SEM, EDX and XPS

After particles synthesis, samples prepared on 15-nm-thick silicon nitride membranes were imaged with a JEOL JEM 2100F at an accelerating voltage of 200 kV. Samples prepared on hydrophobic silicon wafers were imaged with a scanning electron

microscope JEOL JSM-7600 field-emission SEM with an accelerating voltage of 5 kV. Energy-Dispersive X-Ray Spectroscopy of the samples were obtained from INCA (INCA 4.15; Oxford Instruments) equipped on the JEOL JSM-7600 field-emission SEM, which allows the elemental analysis of samples. X-ray photoelectron spectroscopy. (XPS) measurements were performed on a Kratos-Axis spectrometer with monochromatic Al KR (1486.71 eV) X-ray radiation (15 kV and 10 mA) and hemispherical electron energy analyzer. To determine the composition of final synthesized nanoparticle, aqueous solutions of hybrid ink (metal ions /ethylene glycol) were drop-cast on Si wafers. After synthesis of the nanoparticle by thermal annealing, light reduction or oxygen plasma (the same procedure as patterned samples), EDX and XPS characterization were performed on the samples.

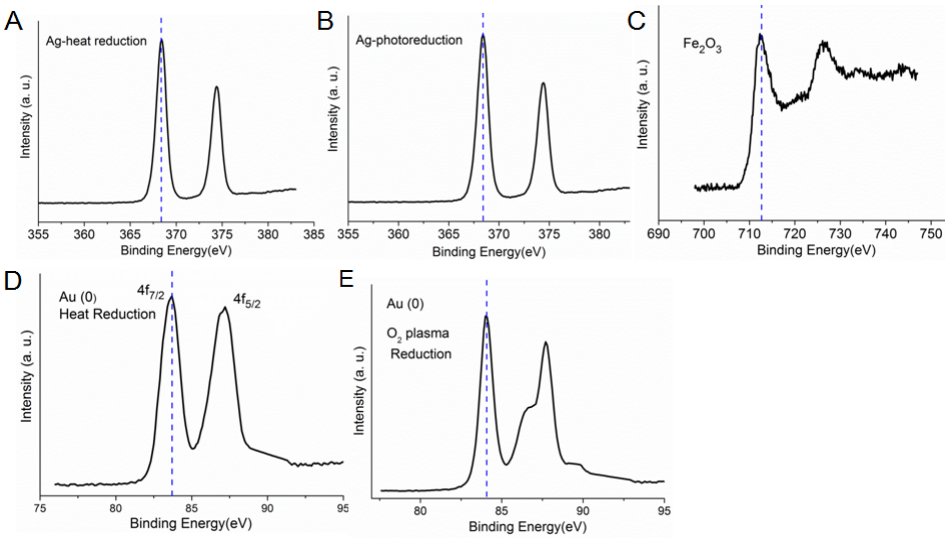
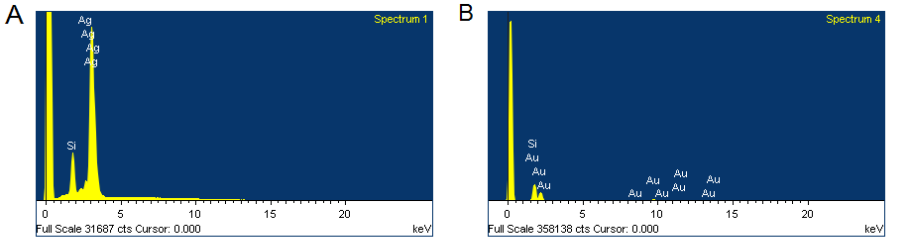


Figure S1. X-ray photoelectron spectroscopy spectras of nanoparticles consisting of Ag, Au and Fe_2O_3. All spectras shown here are for nanoparticles at the end of synthesis. All core element peak positions fall in the expected range for the corresponding compositions. The XPS results of Ag and Au nanoparticles are corroborated with results from high-resolution TEM, demonstrating Ag nanoparticles can be synthesized either by thermal annealing or photoreduction and Au nanoparticles can be synthesized either by oxygen plasma treatment or thermal annealing.



Element	Weight%	Atomic%
Si K	10.20	30.38
Ag L	89.80	69.62
Totals	100.00	

Element	Weight%	Atomic%
Si K	34.13	78.42
Au M	65.87	21.58
Totals	100.00	

Figure S2. Energy-dispersive X-ray spectras of the synthesized Ag and Au nanoparticles. Si signal comes from the silicon substrate.

References

1. F. Huo, Z. Zheng, G. Zheng, L. R. Giam, H. Zhang and C. A. Mirkin, *Science*, 2008, **321**, 1658-1660.