Electronic Supplementary Information for Chemical Communications

Synthesis and Thermal Responsiveness of Self-Assembled Gold Nanoclusters

Shenqiang Ren, Sung-Keun Lim, and Silvija Gradečak*

Department of Materials Science and Engineering, Massachusetts Institute of Technology

77 Massachusetts Avenue, Cambridge, MA 02139

E-mail: gradecak@mit.edu

(1) Experimental Details

***Gallium Arsenide**:* GaAs (111) wafers (n-type, Si doped, carrier density 1.2×10^{18} cm^{-3}, 0.0026 Ω·cm, 400 μm thickness) were cleaned in acetone for 30 min and a methanol ultrasonic bath for 30 min, and then thoroughly rinsed with methanol, DI water and dried with nitrogen.

***Block copolymers**:* Block copolymers polystyrene-block-poly(4-vinylpyridine) (PS-b-P4VP) from Polymer Source, Inc. were used without additional purification. The block copolymers PS-*b*-P4VP, with a total molecular weight of ca. 24.2 kg mol^{-1} (PS: 19 kg mol^{-1}, P4VP: 5.2 kg mol^{-1}) and a polydispersity of 1.1 (Polymer Source, Inc.) adopt a hexagonal close-packed array of vertical P4VP cylinders, surrounded by a PS matrix.

Block copolymers incorporated with Au: $HAuCl_4$ was dissolved in a toluene/ tetrahydrafuran (THF) solution of the block copolymers by vigorously stirring at least for 72 hours. The molar ratio of Au^{3+} to the pyridines in the P4VP block varies following the main text. 10 μl of the metal loaded polymer solutions were spin coated on a 10 mm^2 wafer at 4000 rpm for 1 min. After 24 hours THF solvent annealing, the thin film sample was immersed into 1% HF (aq). In 30 seconds, the samples dried under a nitrogen stream.

***Atomic Force Microscopy (AFM)*:** AFM images were obtained by a Digital Instruments Dimension 3000 microscope operated in Tapping Mode. The standard silicon nitride

probes were driven at their resonance frequencies in the range of 300 KHz. Height and phase images were taken at a scanning rate of 2 μm s^{-1}.

***Transmission Electron Microscope (TEM)*:** TEM images were recorded using a JEOL TEM 200CX at an accelerating voltage of 200 keV. For the high resolution TEM images, a field emission JEOL 2010FEG was used operating at 200 kV TEM. Chemical analysis was performed with an energy-dispersive X-ray (EDX) spectrometer, normally in Scanning TEM (STEM) mode, giving a probe size <1 nm.

(2) Figures

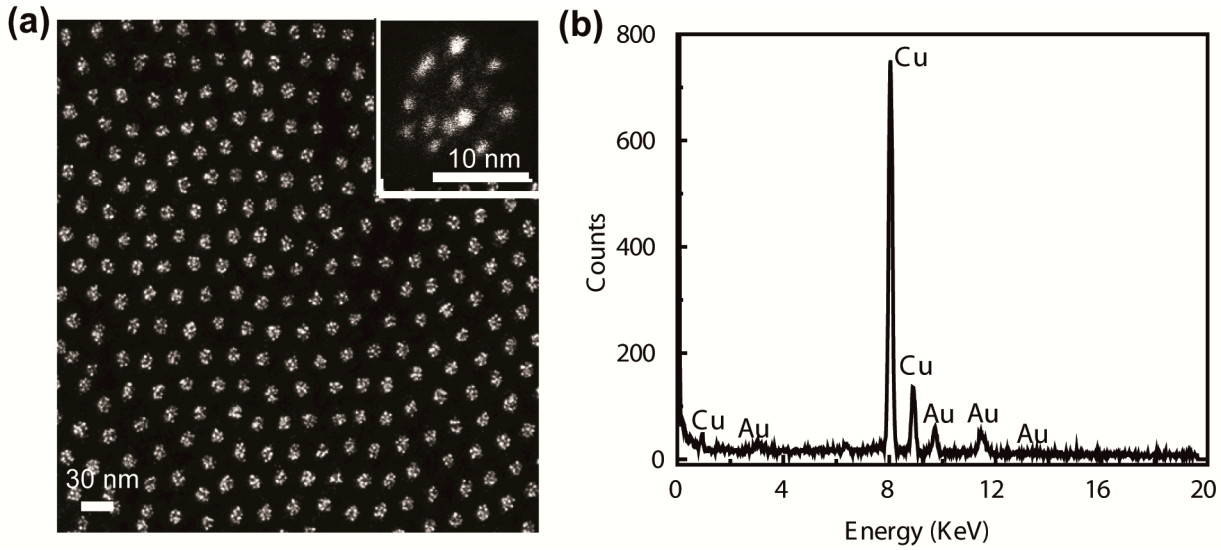

Figure S1. a, The dark-field Scanning TEM (STEM) image of Au nanocluster composite (0.5 $HAuCl_4$: P4VP ratio processed nanocomposite); One Au nanocluster diameter (bright spot) is ~1.29 nm, calibrated by STEM contrast profile. b, The EDX profile from a single P4VP Au nanocluster domain. Strong Cu signal originates from a TEM sample grid.

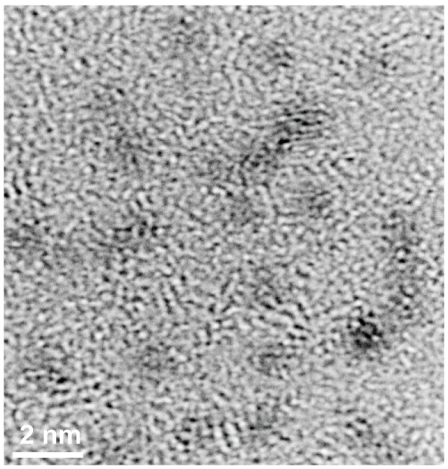

Figure S2. TEM image of single P4VP domain containing Au nanoclusters at 0.5 $HAuCl_4$: P4VP ratio. Each P4VP domain contains multiple Au nanoclusters.

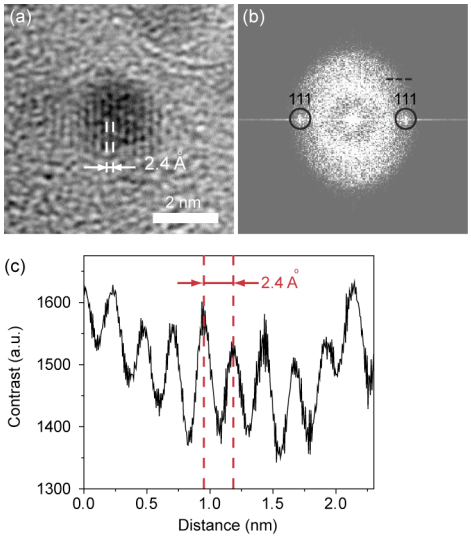

Figure S3. (a) Lattice resolved TEM images of a Au cluster at 1 $HAuCl_4$: P4VP ratio, (b) the corresponding fast Fourier-transform pattern, and (c) the intensity profile across the lattice in (a). The resolved lattice in (a) and distinct spots in (b) indicate the crystalline nature of the Au cluster. Measured interplanar spacing, 2.4 Å, of the Au cluster obtained from (c) corresponds to the (111) spacing (0.235 nm) of the face-centered-cubic crystal structure of Au.

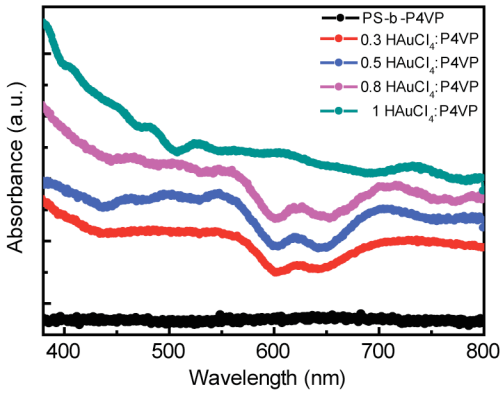

Figure S4. The normalized absorbance of a pure PS-*b*-P4VP block copolymer and the block copolymer loaded with gold nanoclusters as a function of gold complex ratio. As decreasing Au cluster sizes below 2 nm, the intensity of the surface plasmon peak at approximately 520 nm disappeared and the 640 nm and 775 nm absorption bands emerge due to the Au nanocluster quantum sized effect.

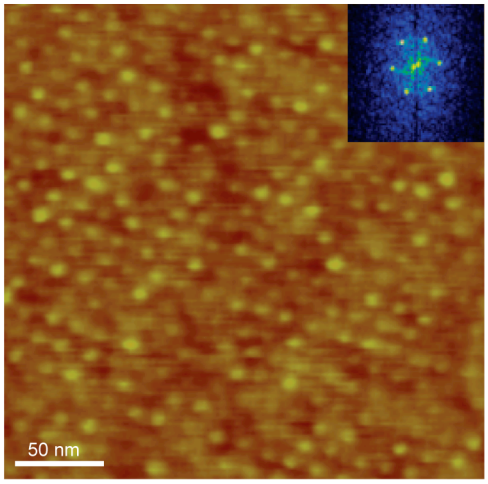

Figure S5. AFM height image and the corresponding fast Fourier transform of the self-assembled Au nanoparticles after polymer removal using oxygen plasma. The Au nanocluster arrays maintain their hexagonal assemblies on GaAs even after the removal of polymer.