Electronic Supplementary Information

IN-SITU FABRICATION OF ORDERED NANORING ARRAYS VIA THE RECONSTRUCTION OF PATTERNED BLOCK COPOLYMER THIN FILM

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Experimental

Materials

PS-b-P4VP diblock copolymer (M_n: 130 kg/mol for PS and 75 kg/mol for P4VP, $M_w/M_n = 1.25$) was purchased from Polymer Source Inc., USA. Zinc acetate dihydrate ($C_4H_6O_4Zn.2H_2O$, 98%) was purchased from Acros Organics, USA. Ferric chloride ($FeCl_3$, Anhydrous, $\geq$ 98%) was purchased from Spectrum Chemical Mfg. Corp. USA. Titanium (Ⅳ) butoxide (Ti [O $(CH_2)_3CH_3]_4$, 97%) and Chloroform (99.8%) were purchased from Sigma-Aldrich, USA. Methanol (99.9%) and Ammonium Hydroxide (29%) were purchased from Fisher Scientific, USA. Silicon wafer (P<100>, 0.001-0.005 ohm-cm, Prime Grade) was purchased from University Wafer Inc.

Preparation of PS-b-P4VP thin film

Silicon wafer was used as the substrate for preparation of block copolymer thin films. The silicon wafers were cleaned consecutively in the order of DMF (N,N-Dimethylformamide), ethanol and de-ionized water, and then heated on a hotplate at 200 ℃ to eliminate any adsorbed moisture quickly. After that, PS-b-P4VP thin films with cylindrical nanodomains were fabricated by spin-coating at room temperature on a silicon substrate, typically at 3000 rpm and 60 s using a 0.5 wt% PS-b-P4VP chloroform solution.

Preparation of ZnO nanoring arrays

PS-b-P4VP monolayer film was immersed in 0.2 M $Zn(Ac)_2$ solution with methanol as solvent for 30 min to fully load $Zn(Ac)_2$ solution in the P4VP cores. The $Zn(Ac)_2$-loaded film was then rinsed with anhydrous ethanol to remove the $Zn(Ac)_2$ that was on the film surface but not in the P4VP cores. After that, the $Zn(Ac)_2$-loaded film was exposed to a vapor of ammonium hydroxide and methanol (the volume ratio of ammonium hydroxide (29%) to methanol is 1:2) for 2 h at 40 ℃ to produce $Zn(OH)_2$ in the P4VP cores and form nanorings. Finally, the thin film with $Zn(OH)_2$ was calcined to remove the copolymer and convert the $Zn(OH)_2$ to ZnO. The thin film with $Zn(OH)_2$ was heated at 170 ^{o}C in a furnace for 1 h, and then taken out of furnace. After sample was cooled down to room temperature, it was put in a furnace previously heated to 600 ^{o}C. The sample was left in the furnace and calcined for 6 h to make sure the polymer was burnt out completely. Ordered ZnO nanoring arrays which remain the original template patterns were successfully obtained.

Preparation of TiO_2 nanoring arrays

TiO_2 nanorings were synthesized by hydrolization of titanium (Ⅳ) butoxide. PS-b-P4VP monolayer film was immersed in 0.2 M titanium (Ⅳ) butoxide solution with methanol as solvent for 30 min to fully load titanium (Ⅳ) butoxide solution in the P4VP cores. The $Ti[O(CH_2)_3CH_3]_4$-loaded film was then rinsed with anhydrous ethanol to remove the titanium (Ⅳ) butoxide that was on the film surface but not in the P4VP cores. After that, $Ti[O(CH_2)_3CH_3]_4$-loaded film was exposed into the mixture vapor of ammonium hydroxide and methanol (the volume ratio of ammonium hydroxide (29%) to methanol is 1:2) for 2 h at 40 ℃ to produce $Ti(OH)_4$ in the P4VP cores and form nanorings. Finally, the thin film with $Ti(OH)_4$ was calcinated using the calcination method discussed above to make $Ti(OH)_4$ thermal decompose to TiO_2, and in-situ transferred to silicon substrate simultaneously.

Preparation of Fe_2O_3 nanoring arrays

PS-b-P4VP monolayer film was immersed in 0.2 M $FeCl_3$ solution with methanol as solvent for 30 min to fully load $FeCl_3$ solution in the P4VP cores. The $FeCl_3$-loaded film was rinsed firstly with hexane and dry at ambient temperature, and then rinsed with anhydrous ethanol to completely remove the $FeCl_3$ that was on the film surface but not in the P4VP cores. After that, $FeCl_3$-loaded film was exposed into the mixture vapor of ammonium hydroxide and methanol (the volume ratio of ammonium hydroxide (29%) to methanol is 1:2) for 2 h at 40 ℃ to produce $Fe(OH)_3$ in the P4VP cores and form nanorings. After that, the thin film with $Fe(OH)_3$ was calcinated using the calcination method discussed above to make $Fe(OH)_3$ thermal decompose to Fe_2O_3 nanorings, and in-situ transferred to silicon substrate simultaneously.

Preparation of Au nanoring arrays

A PS-b-P4VP monolayer film was immersed in 1 mM $HAuCl_4$ solution with methanol as solvent for 30 min to fully load $HAuCl_4$ solution in the P4VP cores. The $HAuCl_4$-loaded film was then rinsed with anhydrous ethanol to remove $HAuCl_4$ that was on the film surface but not in the P4VP cores. After that, $HAuCl_4$-loaded film was exposed into methanol vapor for 2 h at 40 ℃ to form nanorings. Finally, the array of Au nanorings were obtained by the calcination method discussed above and in-situ transferred to silicon substrate simultaneously.

Characterization

The atomic force microscopy (AFM) images were taken on an Asylum Research MFP-3D AFM (Santa Barbara, CA). Imaging was performed and processed using the MFP-3D software written in the IgorPro (Wave Metrics Inc., Lake Oswego, OR) environment. Noncontact mode aluminum-coated silicon nitride cantilevers were purchased from NanoWorld. All images were taken in air under ambient conditions.

Scanning electron microscopy (SEM) images were obtained using a LEO 1530 with energy-dispersive X-ray spectroscopy (EDX).

Figure S1. XPS results and discussion: We tested the components of $Zn(Ac)_2$–loaded PS-b-P4VP thin films after exposing into the vapor mixture of ammonium hydroxide and methanol at 40 ºC for 2 h by XPS (SSX-100 X-ray photoelectron spectroscopy (XPS) with Al K Alpha source). The C1s binding energy in C-C bonds was 285.1 eV. The binding energy of the Zn2p3 core level electrons appeared at 1022.0 eV, and O 1s appeared at 531.9 eV. The binding energy of N 1s due to P4VP blocks was 399.8 eV. The XPS clearly shows the present of Zn in the thin film after $Zn(Ac)_2$ was loaded into the thin film.

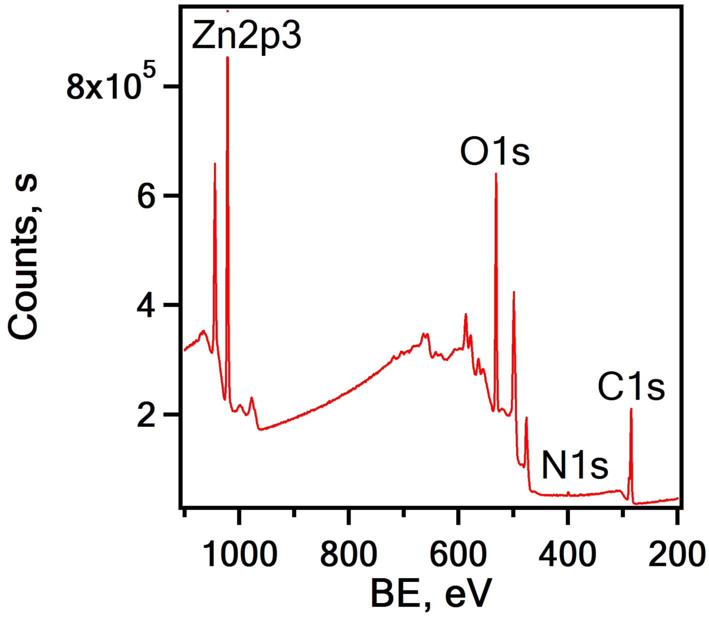


Figure S1. XPS spectra of $Zn(Ac)_2$–loaded PS-b-P4VP thin film after exposing into the vapor mixture of ammonium hydroxide and methanol at 40 ºC for 2 h.

Figure S2: Different calcination methods will affect the final nanopatterns. This was tested by calcinating patterned nanoparticles (not nanorings) by one step calcination (directly raising the temperature to 600 ºC) and a two-step method (the thin film was first heated to 170 ºC, kept for 1 h at that temperature, and finally heated to 600 ºC for 6 h). The SEM results shown in Figure S3 clearly demonstrated that the two-step calcination method is better than one-step method (these pictures were obtained for patterned nanoparticles but not for nanorings).

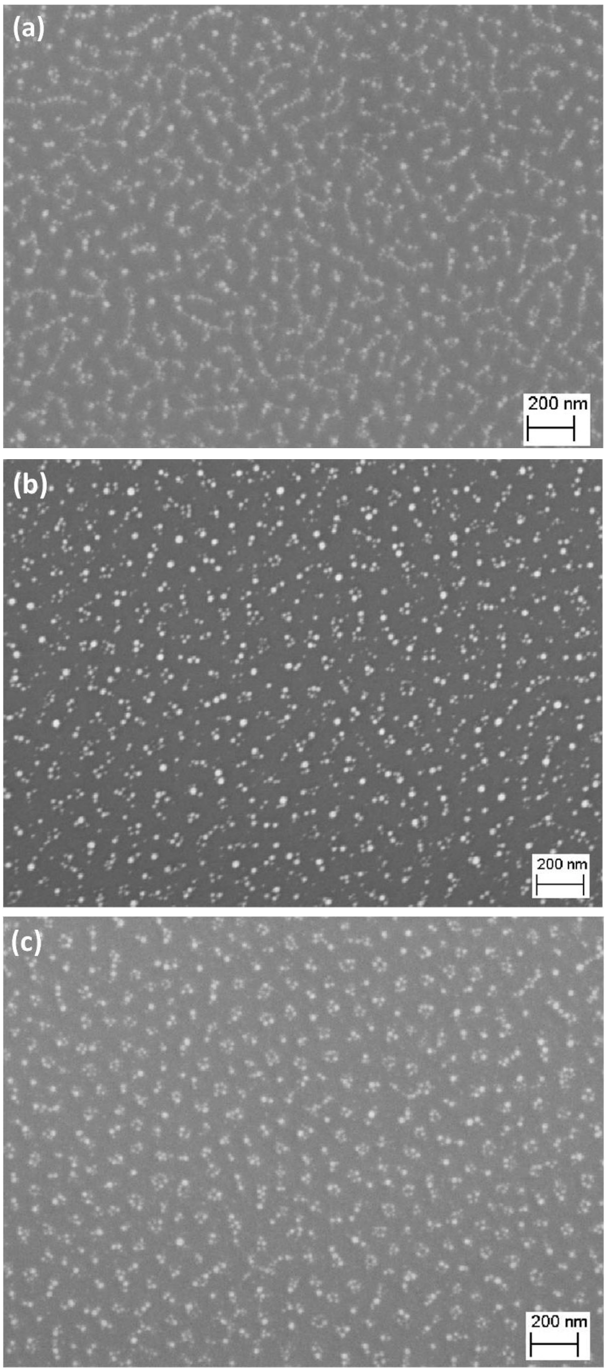
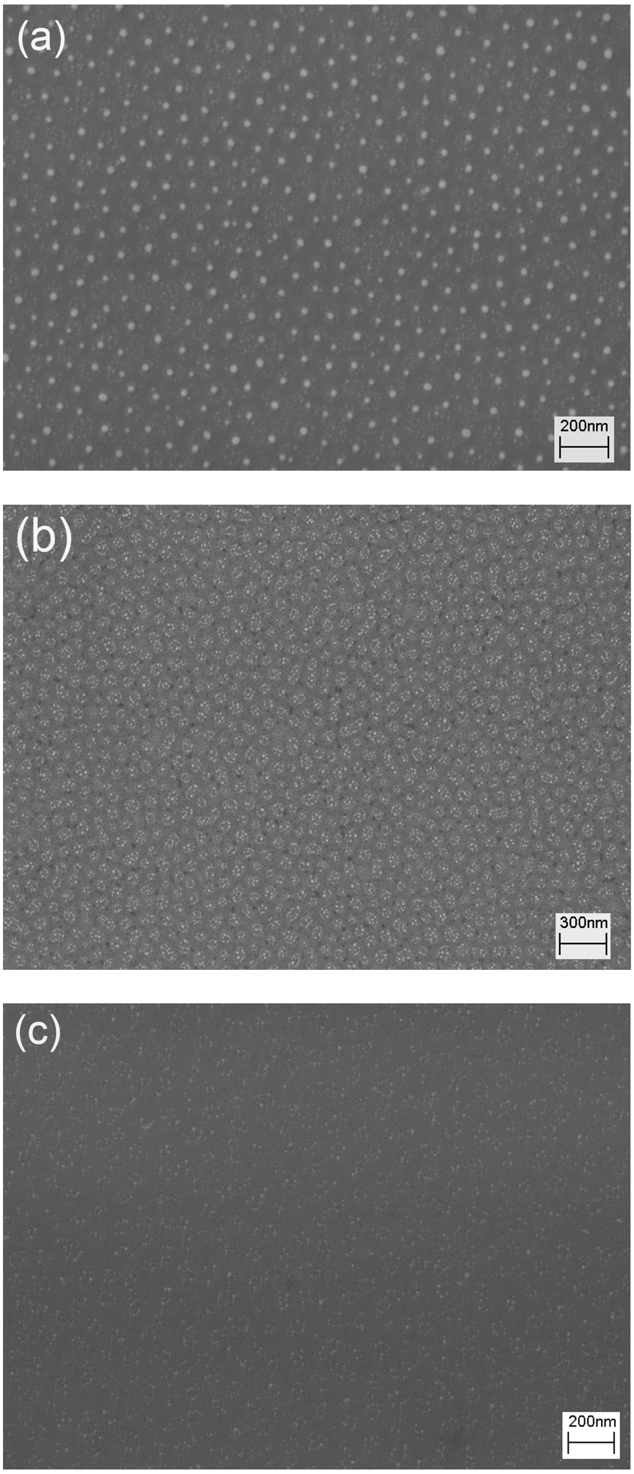


Figure S2. SEM images of Au nanoparticle arrays calcined with different temperature programs (PS-b-P4VP monolayer film as template). (a) Heat to 600 ºC at 10 ºC/min and then keep 6 h. (b) Put in furnace at 600 ºC and keep 6 h. (c) Heat to 170 ºC at 10 ºC/min and keep 1 h, then take out of the sample and put in again at 600 ºC to calcine 6 h.

Figure S3. Influence of $HAuCl_4$ concentration on arrays of Au nanorings after calcinations at 600 ºC. (a) 50 mM $HAuCl_4$, (b) 1 mM $HAuCl_4$, (c) 0.05 mM $HAuCl_4$.


(a)
200nm
(b)
300nm
(c)
200nm