Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Photochemical Fabrication of Hierarchical Ag Nanoparticle Array from Domain-selective Ag^+-loading on Block Copolymer template

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Experimental section

PS-b-P4VP diblock copolymer (Mn^{PS} = 41500 kg mol^{-1}, Mn^{P4VP} = 17500 kg mol^{-1}, Mw/Mn =1.07) was obtained from Polymer Source, Inc.. The copolymer was dissolved in chloroform to produce a 1 wt % solution. The solution, about 20 μL, was spin-coated onto a freshly cleaned silica glass or silicon substrate at about 2000 rpm for 40 seconds to form a film. To make highly oriented cylindrical P4VP microdomains in PS matrix, the film was put in a carefully sealed glass vessel for 5 hours in a saturated 1, 4-dioxane vapor environment. The temperature of the 1,

4-dioxane vapor was kept at about 25 °C. Upon annealing, PS-b-P4VP diblock copolymer films with self-assembled nanopatterns were formed. The topography of the films was scanned by an atomic force microscope (AFM) (NTEGRA Probe NanoLaboratory, NT-MDT Co.) working on semi-contact mode with a silicon cantilever (spring constant 2 N/m and resonance frequency ~98 kHZ).

$AgNO_3$ powder was dissolved in pure water and ethanol (v/v=1:1) to produce a 0.5 M solution. A drop of $AgNO_3$ solution was then dripped on the PS-P4VP diblock copolymer film surface and stayed for 30 min. Next, the Ag^+-loaded film was rinsed with pure water to remove excrescent metal ions and then irradiated immediately with UV light (254 nm line of a 2 W mercury lamp) for several hours. The morphology of the specimen was characterized with atomic force microscopy (AFM) and transmission electron microscopy (TEM). TEM measurements were performed with a FEI TECNAI F20 microscope. For TEM in plane view, the PS-b-P4VP film was floated off from the silicon substrate in a 2 wt% HF solution and collected on an amorphous carbon film of TEM grid. Optical extinction spectra of the silver-loaded films were measured with a ZLX-AS5027 UV-Visible spectrophotometer.

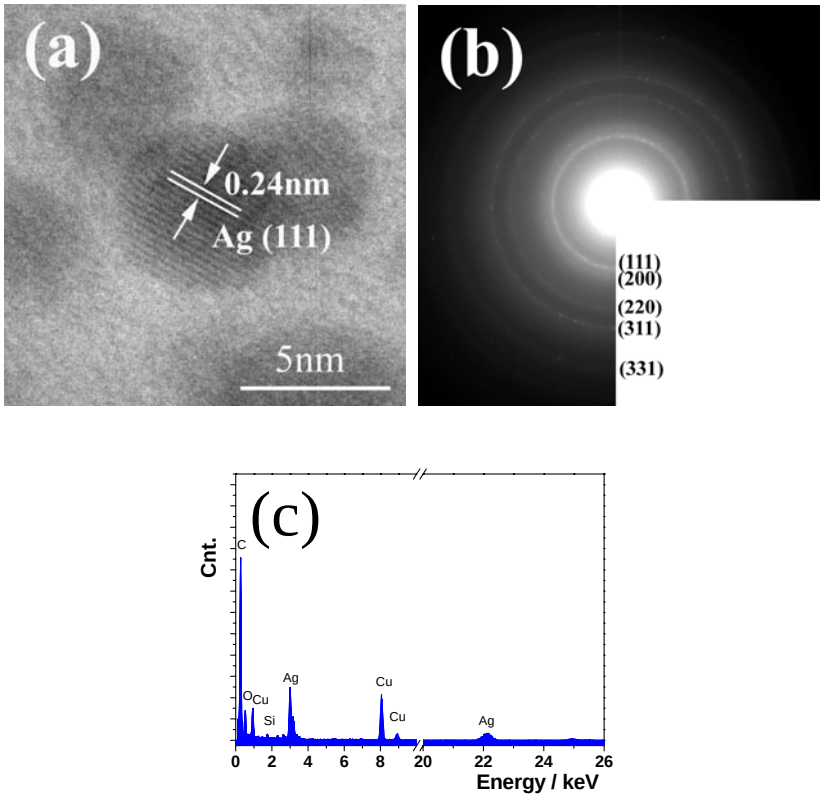

Fig. S1 (a) HRTEM image of Ag nanocrystals in the nanoparticle array. (b) SAED image of Ag nanoparticle film. (c) Energy dispersive spectrum (EDS) of Ag nanoparticle film.

Inspection with high-resolution TEM (HRTEM) shows that the nanoparticles are Ag nanocrystals. The HRTEM image of Fig. S1a displays several isolated nanocrystals in a cluster. The measured lattice-fringe distance of 0.24 nm agrees well with the spacing of the (111) planes of cubic Ag. Selected-area electron diffraction (Fig. S1b) on the film exhibits rings, which can be indexed to (111), (200), (220), (311), and (331) lattice planes of cubic Ag. The energy dispersive spectrum (EDS) of Fig. S1c also reveals that Ag is the main element of the clusters (the strong Cu intensity in Fig. S1c comes from the intrinsic background of the instrument), which further confirms the metallic silver nature of the nanoparticles composed in the clusters.