Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Material

Template-Assisted Self-Assembly of Diblock Copolymer Micelles for Non-Hexagonal Arrays of Au Nanoparticles

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1. Single-layered films of the PS-P4VP micelles

For transmission electron microscopy (TEM), copolymer films were spin-coated onto freshly-cleaved mica substrates, which were delaminated and floated off onto deionized water. The films were subsequently transferred onto carbon-coated TEM grids, followed by selective staining of P4VP cores by I_2. Then, TEM was performed on a Hitachi 7600 operating at 100 kV. Since P4VP cores were selectively stained, they appeared dark dots in TEM images (Fig. S1d~f) and showed a close-packed order without overlapping. The spacing in the TEM image was similar to that measured in the AFM image (Fig. S1a~c). If there are more than a single layer of micelles in the film, dark dots of the P4VP cores would be overlapped in through-view TEM images. Since we did not observe such overlap in TEM images (Fig. S1d~f), we concluded that each film consists of a single layer of micelles.

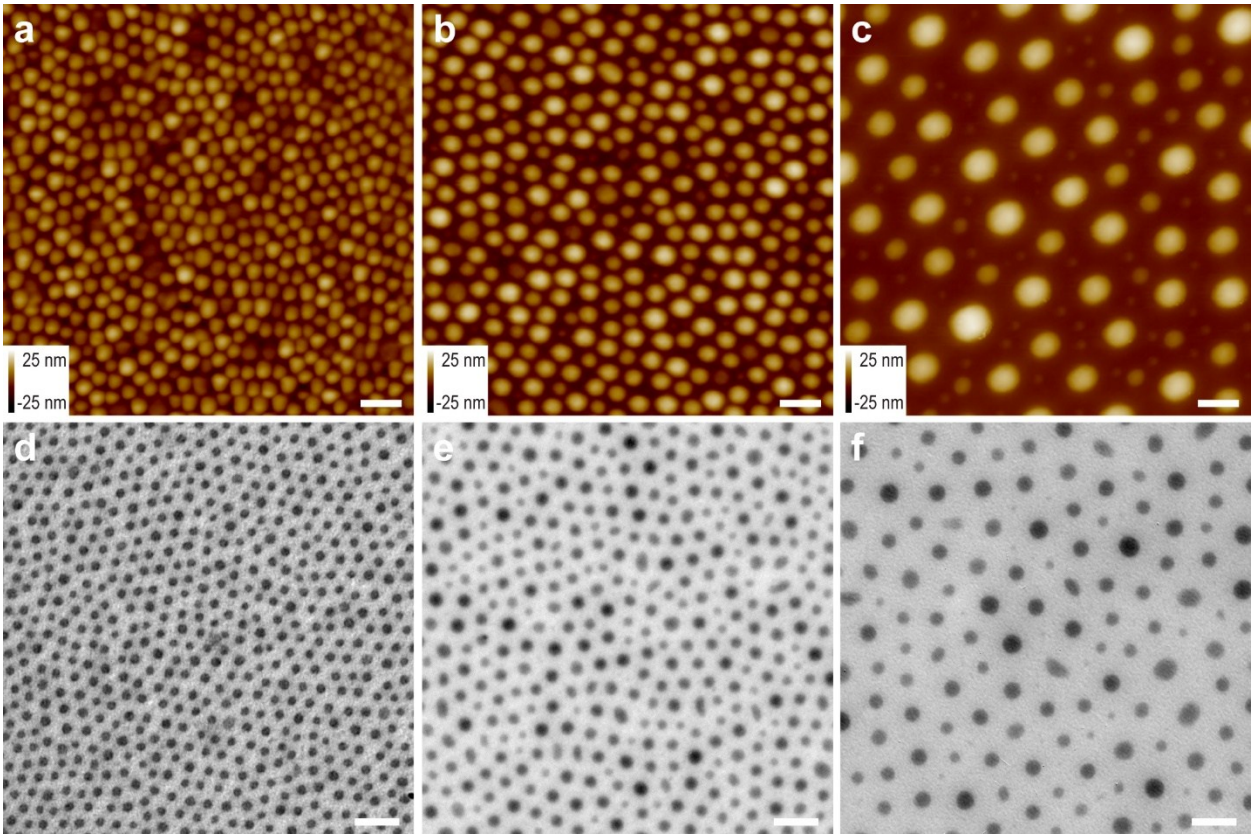

Fig. S1. AFM and TEM images of PS-P4VP micellar films: (a,d) PS(32)-P4VP(13); (b,e) PS(51)-P4VP(18); (c,f) PS(109)-P4VP(27). Scale bars are 100 nm.

2. Fabrication of the TiO_2 nanotemplates

Fig. S2a shows the AFM image of polymeric nanogroove structures, which was fabricated from the thin film of PS(80)-PMMA(80) with perpendicularly-oriented lamellar structures. The selective removal of the PMMA microdomains resulted in a fingerprint-like topographic pattern of the cross-linked PS nanogrooves with the height of ~69 nm (bright lines in AFM image of Fig. S2a). The spacing between nanogrooves (~77 nm) was calculated by performing spectral density analysis on the corresponding AFM image. These PS nanogrooves were utilized as a mold to produce nanogroove TiO_2 template (bright lines in AFM image of Fig. S2c). The spacing of the TiO_2 nanogrooves (~77 nm) is equal to that of the original PS nanogrooves, and the height of the TiO_2 nanogrooves (~37 nm), which is appropriate to guide the arrangement of the micelles in the templates, is smaller than that of the PS nanogrooves due to the loss during the reactive ion etching process for the removal of the over-coated TiO_2 layer. Fig. S2b shows the AFM image of nanoporous structures fabricated from PS(140)-PMMA(60). After the selective removal of the PMMA microdomains, we were able to discover hexagonal arrays of nanopores (dark pores in AFM image of Fig. S2b). The depth of the nanopores was ~51 nm. The same TiO_2 fabrication process was applied to PS nanoporous structures to yield nanodisc TiO_2 template (bright discs in AFM image of Fig. S2d). The spacing of the TiO_2 nanodiscs (~67 nm) is similar to that of the original PS nanoporous film. Again, CF_4 reactive ion etching led to the reduction of the height of the TiO_2 nanodiscs (~28 nm), which is less than that of the PS nanoporous structures.

In addition, we measured the diameter and spacing of the PS nanopores and the TiO_2 nanodiscs from FE-SEM images in Fig. S3 because of the distortion of the lateral size in the AFM measurement (Fig. S2b and S2d). The diameter and spacing are ~39 nm and ~60 nm, respectively. Hence, we confirmed that the final morphology and physical dimension of TiO_2 nanotemplates can be effectively controlled by polymeric nanostructures produced from the self-assembled thin films of diblock copolymers.

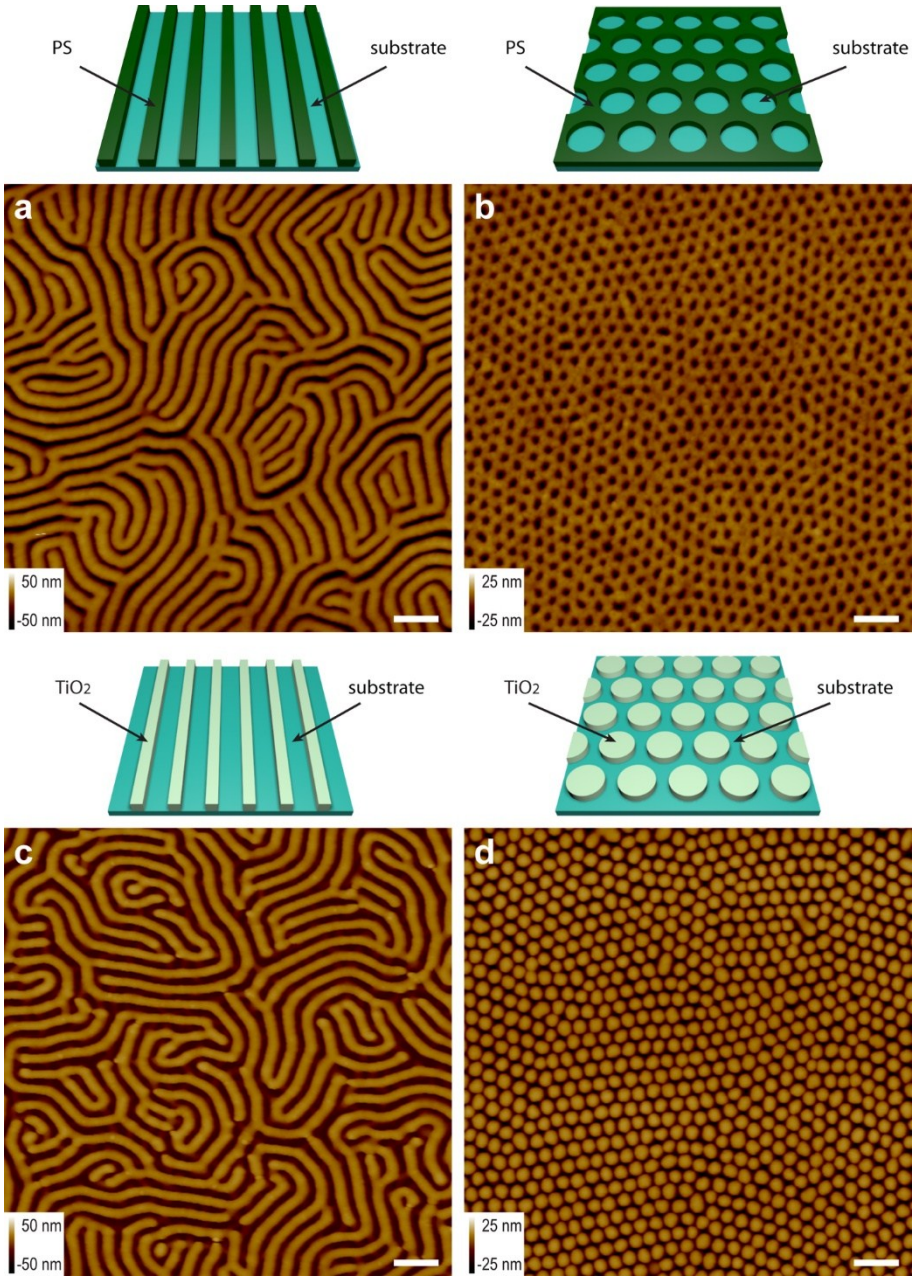

Fig. S2. AFM images of (a) PS nanogroove template from PS(80)-PMMA(80); (b) PS nanoporous template from PS(140)-PMMA(60); (c) TiO_2 nanogroove template; (d) TiO_2 nanodisc template. Schematic illustrations are depicted on the corresponding micrographs. Scale bars are 200 nm.

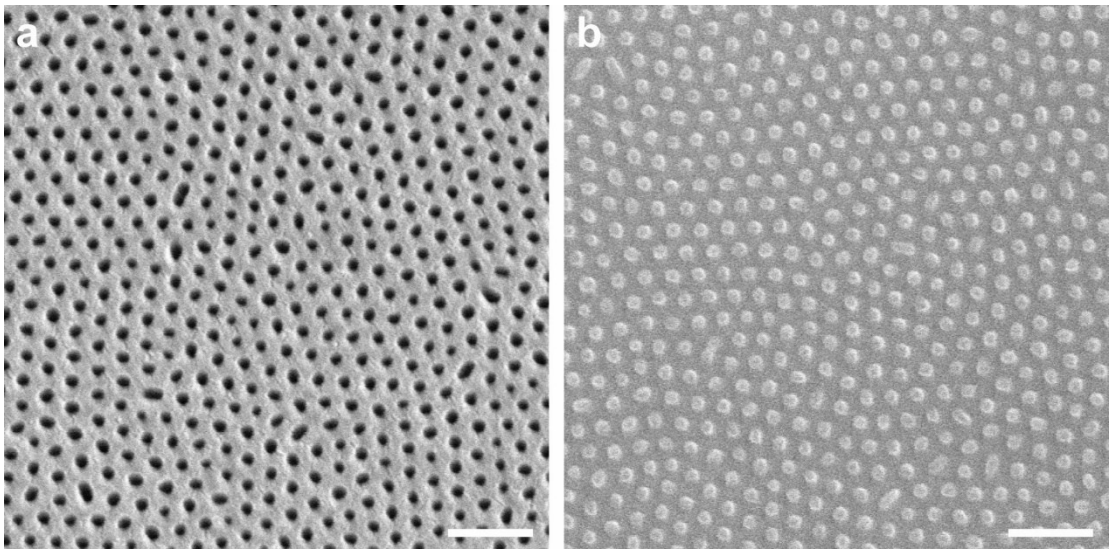

Fig. S3. FE-SEM images of (a) the PS nanopores template and (b) the TiO_2 nanodiscs. Scale bars are 200 nm.

3. AFM images of PS(109)-P4VP(27) micelles spin-coated onto the TiO_2 templates

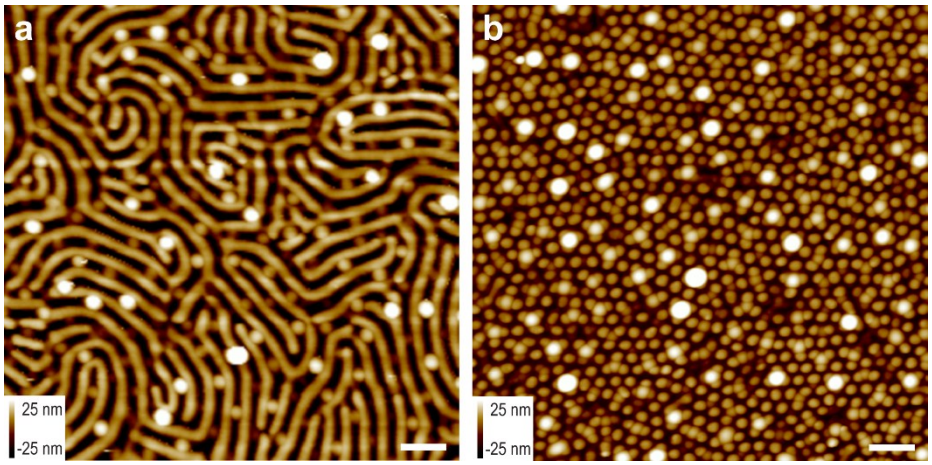

Fig. S4. AFM images of PS(109)-P4VP(27) micelles spin-coated onto (a) the TiO_2 nanogrooves; (b) the TiO_2 nanodiscs. Scale bars are 200 nm.