Electronic Supplementary Material (ESI) for Chemical Communications

Block copolymer-templated chemical nanopatterning on pyrolyzed photoresist carbon films

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Experimental details

Substrate preparation

Si(111) slice of 1.2x1.2 cm^2 was ultrasonicated by acetone, ethanol, respectively. Then the slice was cleaned in piranha solution (98%H_2SO_4:30%H_2O_2, 7/3 v/v) at 100°C for 30 min. PPF were prepared on Si(111) with AZ4620 (Clariant) followed the method described previously[1]. A micelle film was made by spin coating a 0.5 wt% toluene solution of PS-b-P4VP (Polymer Source, Inc.) on substrate at a rate of 2000 rpm.

Nitrophenyl nanopattern fabrication

In a typical procedure, a designated amount of 1% HCl solution was mixed with 10 mM 4-nitrobenzenediazonium tetrafluoroborate/acetonitrile solution. The volume ratio in the range of 1:1 to 1:10 (1% HCl : 10 mM diazonium salt) generally produces similar results. Using pure H_2O instead of HCl solution also produce chemical nanopattern, but with a typical incubation time of 3 h. Spin-coated PPF is then immersed in the above solution for a given time. After that, polymer was removed by rinsing with $CHCl_3$ and THF. In control experiment for XPS, the spin-coated sample was directly washed with $CHCl_3$ and THF without diazonium grafting step.

Characterization

Electrochemical experiments were carried out with CHI660D potentiostat using the as prepared nanopatterned PPF as working electrode, Ag/Ag^+ (0.01 M) as reference electrode, and a Pt wire as auxiliary. Samples were tested in degassed 0.1 M

tetrabutylammonium tetrafluoroborate ($TBABF_4$) in acetonitrile at a rate of 200mV/s. The results are reported against saturated calomel electrode (SCE).

X-ray photoelectron spectroscopy was conducted with an ESCALab220i-XL electron spectrometer from VG Scientific equipped with a 300 W Al Kα radiation.

Atomic force microscopy topographical measurements were performed in tapping mode using Bruker multimode 8 with a Nanoscope Ⅴ controller. The cantilever (μmasch) shares a resonant frequency of 160 kHz, and force constant of 5 N/m. Lateral force microscopy (LFM) were obtained in contact mode by Si_3N_4 tip with a force constant of 0.1 N/m.

Supplementary figures

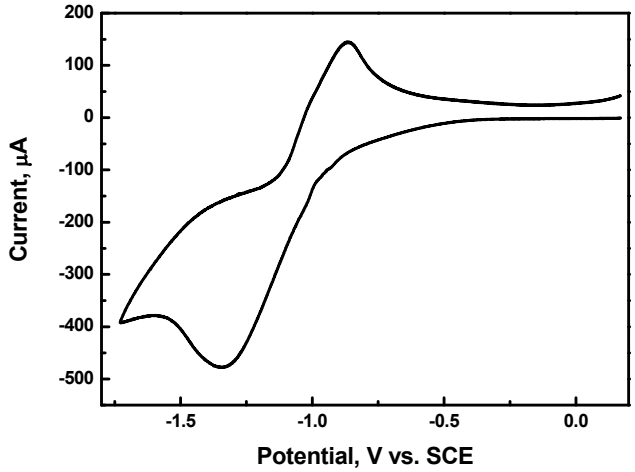

Figure S1. Cyclic voltammetry of modified PPF. The supporting electrolyte is 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile. The scan rate is 200mV/s. The curve shows the reversible redox peaks of grafted nitrobenzene.

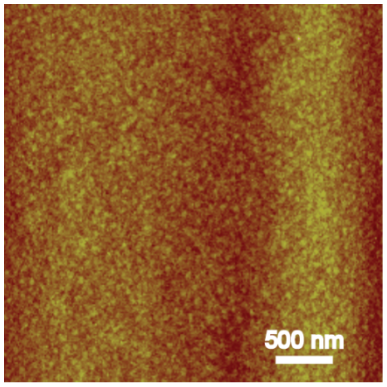

Figure S2. AFM topography images of modified PPF obtained in the mixture of water with 10 mM diazonium/acetonitrile (volume ratio is 1:9) for 3 h. Height scale of the images is 8 nm.

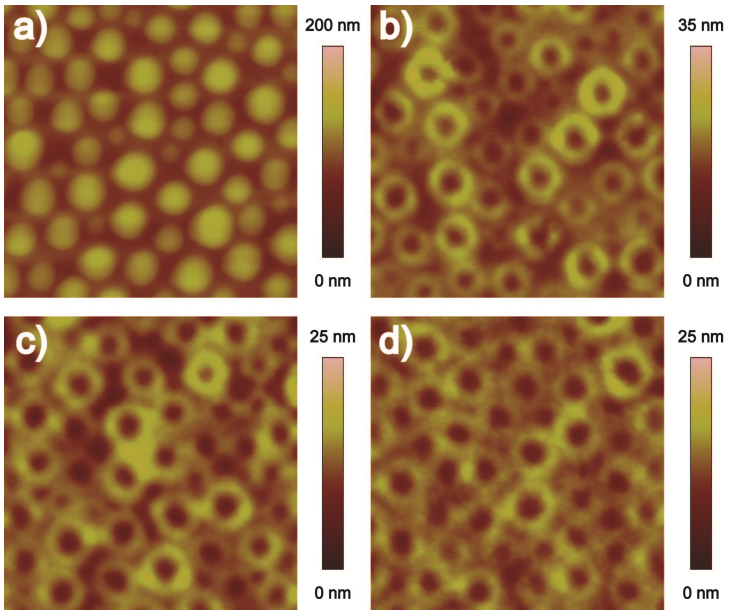

Figure S3. AFM topography images of block copolymer films on PPF before (a) and after immersion in a mixture solution of 1% HCl and 10 mM diazonium/acetonitrile (volume ratio 4:9) for 3 h (b), 10 h (c) and 20 h (d), respectively. All AFM images are 1×1 μm^2. It is noted that the flip of P4VP core occurs after immersion, which is consistent with the proposed mechanism.

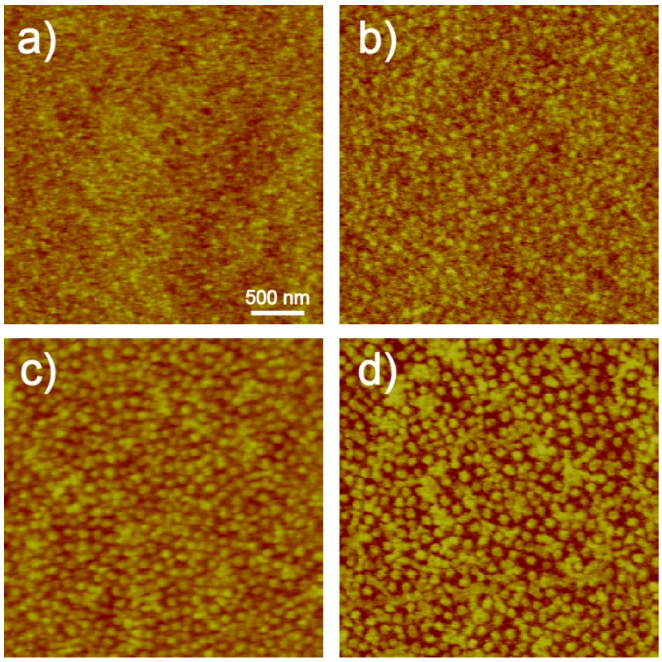

Figure S4. AFM topography images of nanopatterned PPF at different reaction time. From a to d, the reaction time is 50 min, 5 h, 10 h, 20 h, respectively. Reaction condition is the same (volume ratio of 1% HCl and diazonium/acetonitrile is 4:9). All

the height scale is 5 nm.

1. S. Ranganathan and R. L. McCreery, *Analytical Chemistry*, 2001, **73**, 893-900.