Supplementary Material (ESI) for Chemical Communications

Supplementary Information

New Responsive Property of Poly(ε-caprolactone) as the Thermal Switch from Superhydrophobic to Superhydrophilic

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Experimental

Instruments and materials:

Scanning electron microscopy (SEM) images were obtained with a field emission SEM (JEOL, JMS-6700, Japan). Morphology of the sample surfaces was also observed with atomic force microscope (AFM) (Digital Instruments, Nanoscope III A, tapping mode). Water contact angle (CA) was measured with a 2 μL water droplet at five different points of each sample on a Dataphysics OCA20 contact angle system. The temperature was controlled by a super-thermostat (Julabo F25, Germany). CAs at different temperature were measured after samples had been equilibrated for at least 10 minutes. Differential Scanning Calorimetry (DSC) was recorded with a Mettler thermal analysis DSC-822e, at a heating rate of 10 ^{o}C/min under nitrogen atmosphere.

Poly(ε-caprolactone)s (PCL) with different molecular weight (2000 g/mol, 10000 g/mol and 80000 g/mol), were purchased from Sigma-Aldrich. All other reagents are analytical-reagent (Beijing Chemical Reagents Company) and used as received. Distilled water (18.2 MΩ·cm) was obtained using a Millipore filter system.

DSC measurements:

DSC curves of a, b and c are corresponding to $PCL_{2,000}$, $PCL_{10,000}$ and $PCL_{80,000}$ respectively (Fig. S1). It shows that the phase transition temperature increases with the increase of molecular weight.

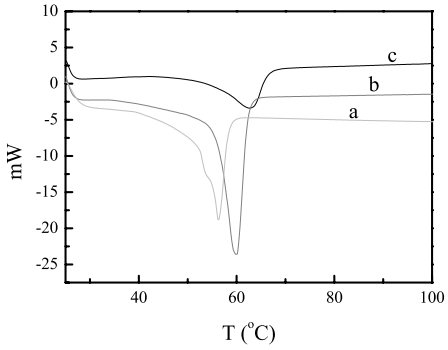

Figure S1. DSC curves of $PCL_{2,000}$(curve a), $PCL_{10,000}$(curve b) and $PCL_{80,000}$(curve c) (heating rate 10 ^{o}C /min and N_2 30 mL/min). The onset, peak and endset temperature are 52.5 ^{o}C, 56.1 ^{o}C and 58.3 ^{o}C for $PCL_{2,000}$; 55.5 ^{o}C, 59.7 ^{o}C, and 62.3 ^{o}C for $PCL_{10,000}$; 56.5 ^{o}C, 62.6 ^{o}C and 66.4 ^{o}C for $PCL_{80,000}$ respectively.

Sample preparation:

Rough silicon wafers were made by photolithography and an inductively coupled plasma deep-etching technique. Contact lithographic masks were constructed by Microelectronics R&D Center, the Chinese Academy of Science. A KARL SUSS MA6 (Germany) instrument was used to transfer the patterns of masks onto silicon wafers by a photolithographic method. A deep-etching process was completed using an STS ICP ASE (UK) instrument. The size of the square pillars is 10 μm × 10 μm in width and 30 μm in height, and the groove spacing between the nearest pillars varies from 10 μm to 60 μm.

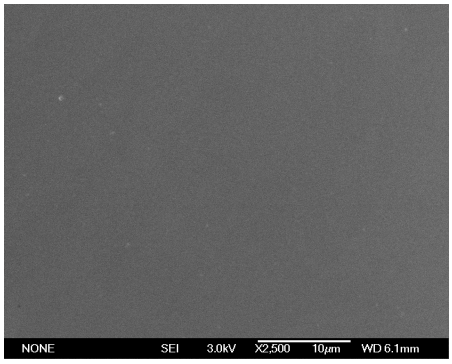

Figure S2. Typical SEM images of the $PCL_{10,000}$ modified flat surface.

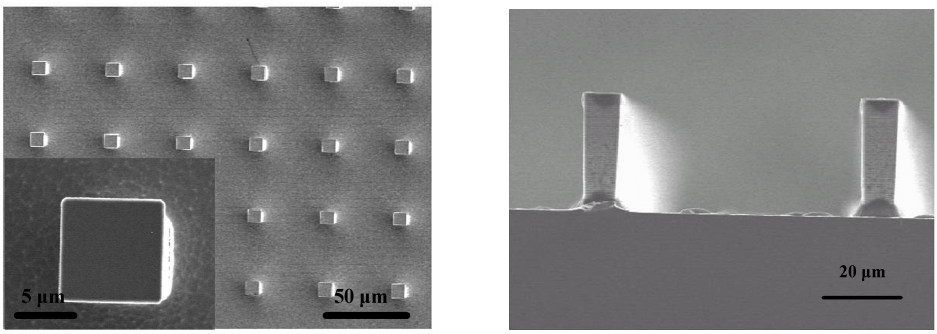

Figure S3. Typical SEM images of the $PCL_{10,000}$ modified the micro-pillar-arrayed substrate: top view (left) and side view (right). The inset is the magnified image of the top view.

The PCL films were prepared on a hydrophilic Si (1, 0, 0) substrates with flat or rough surface. The silicon wafers were washed in a mixture of H_2O:H_2O_2:H_2SO_4 = 5:1:1 (by volume) at 90 ^oC for 20 min, and rinsed with distilled water for several times; then washed again for 20 min in a mixture of H_2O:H_2O_2:$NH_3 \cdot H_2O$ = 5:1:1 (by volume) at 90 ^oC and rinsed with distilled water until pH = 7. They were dried under a flow of nitrogen. The PCL was dissolved in a mixture of methanol and chloroform (CH_3OH:$CHCl_3$ = 1:3 by volume) with the concentration of 5 mg/mL. The films were prepared by pipette a drop of solution onto the silicon substrate, and the solution spread spontaneously to form a thin film. The samples were stored in a chamber over a period of 12 h, and then kept in vacuum at 120 ^oC for 4 h to remove the solvents thoroughly.

SEM images show that the PCL films on both the flat and rough substrates are continuous and uniform (Fig. S2 and S3). The flat film and top surfaces of the pillars are smooth in micrometer scale. The magnified SEM image shows that the bottom surface of the PCL rough film is not as smooth as the pillars' top surface, but it does not affect the film's whole topography. Further AFM observation shows detail nanosized structures on the pillar's top surface (Fig. S4). The average thicknesses of PCL films are less than 200 nm according to the total spread area and the volume of the solution pipetted.

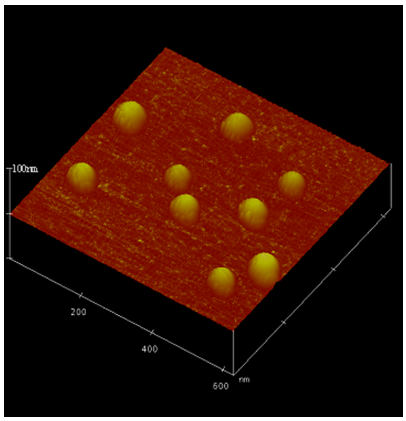

Figure S4. Typical AFM images of the $PCL_{10,000}$ on a silicon pillar surface. There are nano-sized protuberances distributing on the pillar's top surface. The protuberances are about 60 nm in diameter and 20 nm in height.