Supplementary Material (ESI) for Chemical Communications

Supporting Information:

Wettability Switching between High-Hydrophilicity at Low pH and High-Hydrophobicity at High pH on Surface based on pH-Responsive Polymer

Qiaolan Zhang,[ab] Fan Xia,[b] Taolei Sun,[b] Wenlong Song,[b] Tianyi Zhao,[b] Mancang Liu[a] and Lei Jiang*[b]

Department of Chemistry, Lanzhou University, Lanzhou 730000, and Center of Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China

E-mail: jianglei@iccas.ac.cn

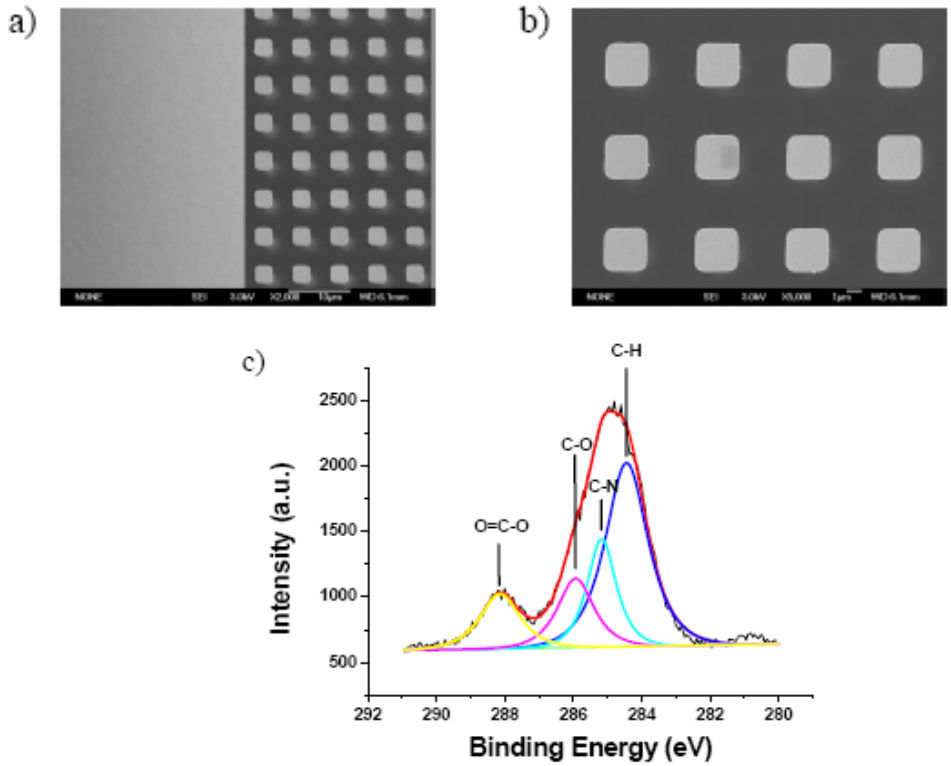

Fig S1. a) Typical SEM images of the flat (left) and the rough (right) substrate (50 μm high, 3 μm long, and with a spacing of 3 μm between the silicon pillars). b) Magnified image of the rough substrate. c) XPS spectra of the C1s signals of the PDMAEMA thin film.

Experimental

Materials

N, N'-Dimethyl aminoethyl methacrylate (DMAEMA) (99%, Acros) was distilled under reduced pressure and stored in a refrigerator before use. Silicon wafer (Grinm Semiconductor Materials Co. Ltd, China), Sodium hydroxide, nitric acid, anhydrous methanol, dichloromethane, aminopropyl trimethoxysilane (ATMS, Fluka, Switzerland), pyridine, α-bromoisobutyryl bromide (BIB) (Fluka, Switzerland), and *N, N, N', N', N''*-pentamethylene triamine (PMDETA, Aldrich, Germany), and Cu(I)Br (99.999%, Aldrich) were used as received. Anhydrous methanol and dichloromethane were dried by molecular sieves for 24h before use.

Double-distilled water (>1.82 MΩcm, MilliQ system) was used.

Synthesis of PDMAEMA Thin Films on Silicon substrates

A clean silicon substrate was immersed in an aqueous NaOH solution (0.1 M) for 5 minutes and subsequently in HNO_3 (0.1 M) for 10 minutes to generate surface hydroxyl groups. After the substrate had been washed with an excess of water and dried under a flow of nitrogen, it was immersed in anhydrous methanol that contained 5 wt% ATMS for at least 10 hours at room temperature to obtain chemically bonded $–NH_2$ groups on the surface. The surface was rinsed with anhydrous methanol and dry dichloromethane to remove any remaining ATMS, and immersed in dry dichloromethane that contained pyridine (2% v/v). The polymerization initiator, BIB, was added dropwise into the solvent that contained silicon substrate at 0℃, and the mixture was left for 1 hours at this temperature, and then at room temperature for 12 hours. The silicon substrate was cleaned with dichloromethane and dried under a nitrogen flow. Polymerization of PDMAEMA was achieved by immersing the substrate with the initiator grafted on the surface in a degassed solution of DMAEMA (50% v/v) in a 1:1 (v/v) mixture of H_2O and MeOH (10 ml) containing CuBr (0.032 g, 0.23 mol) and PMDETA (0.14 ml) for 5 hours at 60℃. Under this condition, the film thickness was about 34.4±3.1 nm.

Instrumentation and Characterization

A filed-emission scanning electron microscope (JSM-6700F, Japan) was used to obtain SEM images of the substrate which was sputtered with platinum (Fig S1a, S1b). Compared with Fig S1a (left), which shows the flat substrate, Figure S1a (right) shows a typical SEM image of a rough surface on which geometrical structures of patterned square pillars have been introduced on a flat silicon wafer. The rough surface (50 μm high, 3 μm long, and with a spacing of 3 μm between the silicon pillars) is prepared by photolithography and an inductively coupled plasma deep-etching technique. Figure S1b shows the magnified image of the rough substrate.

CAs were measured on an OCA20 machine (DataPhysics, Germany) at ambient temperature. The materials were first placed in the solution (pH = 2) for about 5 minutes, taken out from the solution blow dried by N_2. Deionized Water (ca.1.0 μl) was dropped carefully onto the responsive surface. An average CA value was obtained by measuring the same sample at five different positions. The materials were then placed in the solutions (pH = 3, 5, 7, 9, respectively) to test the CAs of the materials.

X-ray photoelectron spectroscopic (XPS) data on PDMAEMA thin film were collected on an ESCALab220i-XL electro spectrometer from VG Scientific using 300W Al Kα X-ray source (1486.6 eV photons) with a take off angle of 90°. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. Figure S1b shows the magnified image of the rough substrate. The chemical composition of the treated surface (Fig 1c) was measured by the X-ray photoelectron spectroscopy (XPS) (measured at 90°). Using software XPSPEAK, The C1s core-level spectra of the film can be curve-fitted into four peak components with binding energy at about 284.4 eV for the C-H species, 285.2 eV for the C-N species, 285.9 eV for the C-O species, and 288.2 eV for the O=C-O species. The analytic result confirms the presence of PDMAEMA thin film on the silicon substrate.