

Supporting Information

Microfluidically mediated Atom-Transfer Radical Polymerization

Chengtao Zhang, Luxiang Wang, Dianzeng Jia*, Junfeng Yan*, Hongyi Li*

Institute of Applied Chemistry, Xinjiang University, Urumqi 830046, Xinjiang

Key Laboratory of Energy Materials Chemistry, Ministry of Education, Institute of Applied Chemistry, Xinjiang University, Urumqi 830046, Xinjiang

Qualification of Products Supervision&Inspection Institute, Xinjiang, Autonomous Region, Urumqi 830011, China

Materials

3-Sulfopropyl methacrylate potassium salt (SPMA), 2-bromoisobutryl bromide (BiBB), Cuprous bromide(CuBr), 3-aminopropyltriethoxysilane (APTES), 2, 2'-dipyridyl were purchased from Sigma-Aldrich (Weinheim, Germany). Dichloromethane (DCM) were purchased from Tianjin chemical reagent factory (99%, China). 6-inch N-type monocrystalline wafer was purchased from Sigma-Aldrich (Weinheim, Germany). Zn slice was obtained from Tianjin Fuchen Chemical Reagent Factory. Other reagents used as received. In addition, the contact angle measurement is distilled water.

Experiment

Preparation of initiator modified substrate

The 6-inch N-type monocrystalline wafer was cleaned using a (KQ-100E) type ultrasonic cleaner from Kunshan Ultrasonic Instrument Company Limited for 30 minutes in an acetone solution; it was then washed with a large amount of ultra-pure water, ethanol, and dried under nitrogen. Silicon substrates were cleaned with piranha solution (H_2O_2 : H_2SO_4 , 1:3 v/v, 90 °C, 45 min); washed extensively with distilled water, and dried by a jet of dry argon. The clean substrates were immediately amine-functionalized by immersion into a 5% (v/v) 3-aminopropyltriethoxysilane (APTES) solution in dry acetone and sonicated during the SAM formation for 45 min. After SAM formation, the samples were extensively washed with dry acetone and dried under argon. This procedure results in highly reproducible APTES monolayers. The substrate was then immersed in dry DCM (20 mL), triethylamine (0.4 mL) was added, followed by dropwise addition of 2-bromoisobutryl bromide (BiBB) (20 mL, 2% in DCM) at 0 °C; and the reaction stirred for 24 h at 20 °C. The substrate was then washed with DCM, water, ethanol, and acetone, and dried with a dry nitrogen stream.

Preparation of the monomer solution

(1) 3 g 3-sulfopropyl methacrylate potassium salt (SPMA), 70 mg bipyridyl, 12 mg CuBr, 5 mL of 2:1 (v/v) H₂O/MeOH. (2) The reaction conditions as outlined in (1) were maintained, changing only the amount of CuBr: 3 mg, 6 mg and 9 mg. (3) While maintaining the conditions described in (1), the monomer amount was varied: 2 g, 4 g and 5 g. The as-prepared solution can be drawn into a syringe, then attached to syringe-pump to microfluidically drive the solution via programming the software.

Method

Ellipsometry. Ellipsometric data was obtained on a SC620 ellipsometer from (Shanghai, China) equipped with a fixed 60° angle of incidence, a refractive index of $n=1.45$ was used to calculate polymer brushes thickness. The brushes thickness via ellipsometry as-obtained was average data of five independent points.

Atomic force microscopy (AFM). Atomic force microscopy (AFM) studies were performed on a Multimode 8 microscope (Bruker, Germany) with tapping-mode to image the surface morphology of the brushes. The height determination and calculation of the surface roughness was performed with the software.

Infrared Spectroscopy (IR). Attenuated Total Reflection Infrared Spectroscopy (ATR-IR) were acquired using a STA449F3-QMS403C IR (NETZSCH Germany) spectrometer equipped with a transmission accessory, and the wavelength of the infrared spectrometer ranges from 7500 cm^{-1} -370 cm^{-1} .

X-ray photoelectron spectra (XPS). X-ray photoelectron spectra (XPS) was obtained on a multi-functional XPS system (American, Model ESCALab220i-XL, ThermoElectric.Inc.) by using Al K α radiation (pass energy of 30 eV).

Contact angle measurement. Static water contact angle measurements were performed on a Interfacial tension (JJ-2000B) with distilled water, and the contact angles (θ) were obtained using the tangent method fitting.

Method for SI-ATRP

Preparation of gradient polymer brushes

Initially, an APTES-BiBB-SAMA-silicon substrate (1.5 cm * 2.0 cm) was sandwiched with a Zn slice at a constant distance of 1 mm, which sealed with tape and leaving the top side open. The syringe pump was modulated to control the solution injection rate to completely fill the space between the two substrates over the course of 15 min, 0.5 h, 1 h and 1.5 h; this resulted in controlled gradient polymer brushes. The monomer concentration was adjusted to 0.4 g/mL, 0.6 g/mL, 0.8 g/mL, 1.0 g/mL with a polymerization time of 30 minutes. Finally, the concentration of the catalyst was adjusted to 0.6 mg/mL, 1.2 mg/mL, 1.8 mg/mL, 2.4 mg/mL with a polymerization time of 1 hour and using a similar method to prepare gradient surfaces. Additionally, a step-shaped polymer brush was prepared when periodically tuning on/off syringe pump, two types of step-shaped polymer brushes were fabricated when controlling the polymerization for 8 minutes and 15 minutes with 6 cycles. The brush thickness can be fully characterized via ellipsometry equipment. Furthermore, the color change along the substrate can be used to qualitatively dictate surface gradient.

Syringe pump: The injection rate was controlled through tuning the injection rate of LD-P2020 syringe pump (Shanghai, China). Monomer (SPMA)/catalysis solution was sucked into a 10 mL syringe, then an ultra-small volume of solution was injected into the space between two substrates

with different flow rates to prepare a series of gradient polymer brushes. The experimental set-up is shown in Fig. S1.



Fig. S1 The digital device diagram for preparing gradient polymer brushes.

The gradient polymer brushes can be further proved by AFM scratch measurements, which agrees well with ellipsometric thickness (Fig. S2). We selected five areas for independent measurement, the distance between each neighbor area is equally(4 mm), then five scratch thickness can be obtained as shown in Fig. S2. When the injection rate was controlled at 0.6 mL/h, the five scratch thicknesses obtained from the atomic force microscope(AFM) were 11 nm, 46 nm, 85 nm, 113 nm, and 154 nm, respectively(Fig. S2(a)); When the injection rate was 0.2 mL/h, the five scratch thicknesses were 37 nm, 86 nm, 141 nm, 198 nm and 293 nm, respectively (Figure S2(b)), which can confirm the polymer brushes with controlled gradient. ATR-IR analysis shows peaks at 1720.8 cm^{-1} (Fig. S3), which corresponds to carbonyl stretches from the PSPMA brushes.

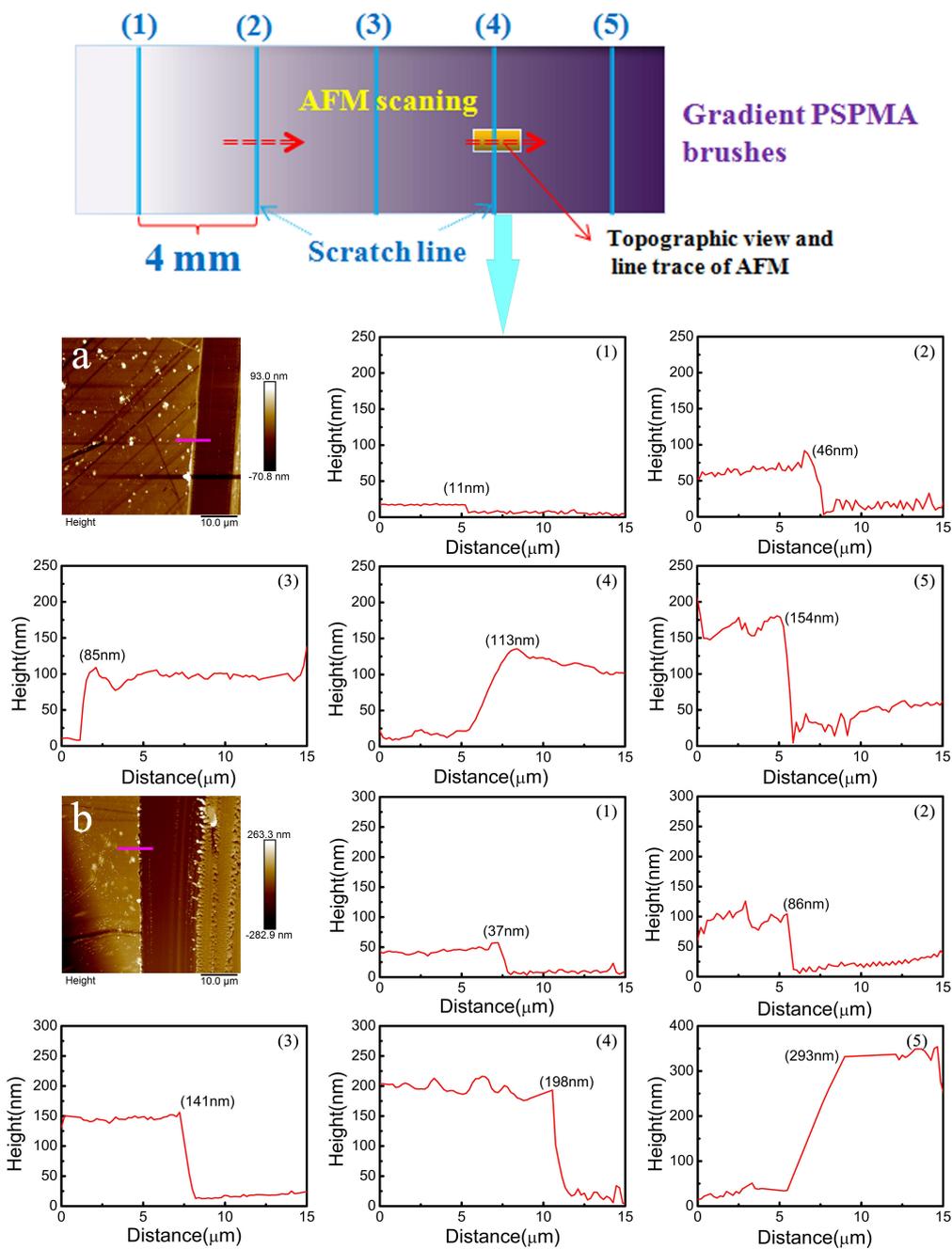


Fig. S2 Polymer thickness assessed via AFM scratch measurement. Topographic view and the cross-sectional profiles of typical AFM images each sample: (a) injection rate was 0.6 mL/h; (b) injection rate was 0.2 mL/h.

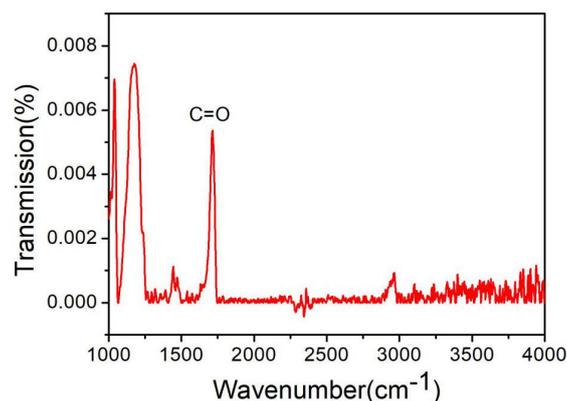


Fig. S3 The ATR-IR spectrum of PSPMA brushes, and the peaks marked is C=O stretching: 1720.8 cm^{-1} .

XPS was further conducted to confirm the surface chemical composition of Si-initiator and PSPMA-Si substrates (Fig. S4). As shown in Fig. S4(a), Br, C, N, and O elements were found in the survey scan spectrum. The two fitting peaks from Br(3d) at about 68.2 and 69.3 eV verify the existence of Br(3d5) and Br(3d3) (Fig. S4(b)), the N(1s) peak at the binding energy of about 399.8 eV(Fig. S4(c)), which all proved initiator assembled on Si substrate. After PSPMA polymer brushes were grafted, S and K elements were found in the survey scan spectrum (Fig. S4(d)). AFM topographic images in Fig. S5, and RMS roughness is 0.582 after polymer grafting. Figure S6 shows that after polymer grafting, surface becomes superhydrophilicity.

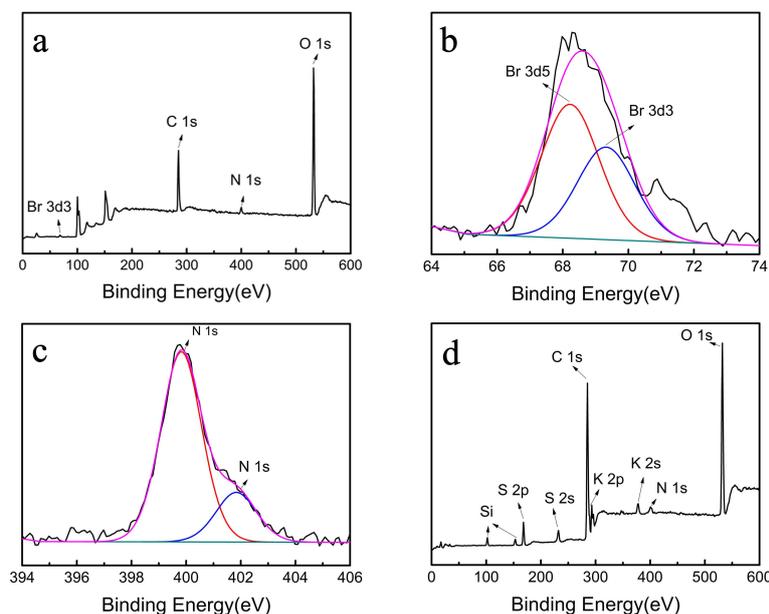


Fig. S4 (a) XPS spectrum of the BiBB initiator modified silicon surfaces. (b) Br(3d) peak indicate that the initiator for the subsequent polymerization. (c) N(1s) peak at the binding energy of about 399.8 eV. (d) XPS spectrum of PSPMA-Si substrate.

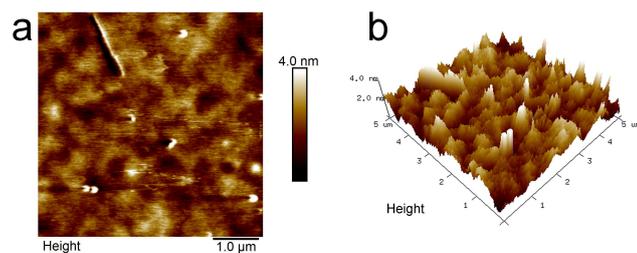


Fig. S5 AFM images of PSPMA brushes on a modified silicon wafer. (a) AFM images of surface roughness of SPMA brushes; (b) corresponding height profile of a polymer brush.

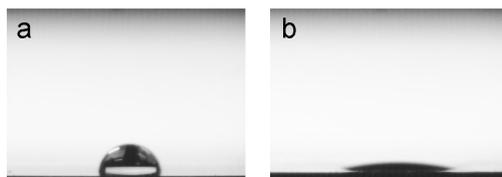


Fig. S6 The water contact angle of the BiBB initiator modified silicon surfaces and the PSPMA-Si substrate. (a) water contact angle measurements ($\theta_{\text{static}}(\text{H}_2\text{O}) = 32$); (b) water contact angle measurements ($\theta_{\text{static}}(\text{H}_2\text{O}) = 10$).

- 1 T. Zhang, Y. Du, F. Müller, I. Amin and R. Jordan, *Polym. Chem.*, 2015, 6, 2726-2733.
- 2 Y. Che, T. Zhang, Y. Du, I. Amin, C. Marschelke and R. Jordan, *Angew. Chem. Int. Ed.*, 2018, 57, 16380–16384.