Electronic Supplementary Information

Writing of nanowires via high-viscosity induced nano diffusive layer

Sifeng Mao,^{ab} Yong Zhang,^b Haifang Li,^a Hulie Zeng,^b Jin-Ming Lin^{*a} and Katsumi Uchiyama^{*b}

^a Department of Chemistry, Beijing Key Laboratory of Microanalytical Methods and Instrumentation, The Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology, Tsinghua University, Beijing 100084 (China)

^b Department of Applied Chemistry, Graduate School of Urban Environmental Sciences,

Tokyo Metropolitan University, Minamiohsawa, Hachioji, Tokyo 192-0397, Japan

**Corresponding author.*

E-mail: jmlin@mail.tsinghua.edu.cn (*J.-M. Lin*), *Fax/Tel:* +86-010-62792343; *E-mail:* <u>uchiyama-katsumi@tmu.ac.jp</u> (K. Uchiyama), *Tel:* +81-42-6772835, *Fax:* +81-42-6772821.

1. Chemicals and materials

Poly (sodium 4-styrenesulfonate) (mW ~100,000, PSS) and hexadimethrine bromide (HB) were purchased from Sigma Aldrich (USA). The XYZ stage (Sigma KOKI Co., Ltd.) served as the pen holder. In all of the experiments, the pen was maintained at its position while the XY stage was moved by an Opt Mike Controller (OMEC-2BF, Sigma KOKI Co., Ltd.). We used an Opt Mike Controller to move the XY plate moving in the X- and Y-directions, making it possible to create any desired characters. SEM (5100N, Hitachi High Technologies, Japan) was used for sample analysis.

2. Preperation of the micro chemical pen and setup of the system

Fused silica capillaries (250 μ m i.d., 350 μ m o.d.; GL Science, Japan) were cut to lengths of 10 cm long using a ShortixTM Capillary Column Cutter (Scientific Glass Technology, Singapore). We inserted three of the prepared capillaries into one 4-cm-long glass tube (800 μ m i.d., 1300 μ m o.d.; SANSYO, Japan) and then placed them on a smooth glass slide while keeping them perpendicular to the smooth surface to ensure that their ends were in the same plane. Finally, we glued the seam with an epoxy bonding agent (AR-R30, NICHIBAN, Japan) to fix the three capillaries within the glass tube. After approximately 30 min at room temperature, the glue solidified, and the pen was ready to use.

The three capillaries of the pen were connected to three 50 cm long PTFE tubes (GL Sciences, Japan) using Microtight® unions (IDEX Health & Science, WA, USA). The PTFE tubes were then connected to three syringes (Hamilton, USA), which were controlled by three independent pumps (Pump Systems Inc., USA). The pen was mounted on the XYZ positioner (Sigma Koki, Japan) and positioned parallel to the transparent substrate (glass slide) on the bottom of a petri dish which was full of surrounding medium to form a microscopic gap.

3. Viscosity adjustment of injection solutions by PVA

PVA is nontoxic to human and animal under control amount. In this experiment, we used PVA to adjust the viscosities of PSS solution and HB solution. PVA was first dissolved in water to generate a series of PVA concentrations: 0 wt%, 0.05 wt%, 0.10 wt% and 0.20 wt%. Then we used those solutions as solvent to prepare PSS solution and HB solution with desired concentrations.

4. Effect of different parameters for polymeric structure deposition

The influence of viscosity was investigated. A series couples of PSS solution (0.05 wt%) and HB (0.02 wt%) with a certain concentration of PVA (0 wt%, 0.05 wt%, 0.10 wt% and 0.20 wt%) were the two individual injection solutions, and micropatterns were confirmed under constant parameters. After that, the influences of pattern time, gaps and aspiration flow rates were optimized.

5. Nano polymer line fabrication

Under the optimized conditions (liquid viscosity, gap, patterning time, injection and aspiration flow rates), we keep the positioner stationary. At the same time, we used an Opt Mike Controller to move the XY plate moving in the X- and Y-directions, making it possible to create desired polymer line. The moving speed (V) was determined by the length of pattern (L) and desired patterning time (T).

Here, V=L/T.

6. SEM and AFM characterization of the patterned polymeric structures

The patterned polymeric structure was examined by means of an SEM system (S-3400N, Hitachi Co., Tokyo, Japan) and an AFM system. The samples of SEM and AFM were prepared after the polymer patterns were dried in room temperature. All specimens for measurements were sputtered with a layer of gold using a sputter coater (SC-701, Sanyu Electron Co. Ltd., Tokyo, Japan) at fixed conditions (time 150 s, current 10 mA).



Fig. S1 Preperation of the micro chemical pen.



Fig. S2 (a) The molecular formula of ply(sodium 4-styrenesulfonate) (PSS). (b) The molecular formula of Hexadimethrine bromide (HB).



Fig. S1 Thickness profiles of pattern (a) and reduced pattern (b) using AFM system.



Fig. S4 SEM images of multiple polymer patterns under a series of pattern time.