Electronic Supporting Information

Fabrication of Sub-100 nm Conducting Polyaniline wire on Polymer Substrate Based on Friction Nanolithography

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1. Supplementary experimental procedure:

(1) Reagents. Water was purified using a Milli-Q (Millipore Corp., Bedford MA) purification system with a resistivity of 18 MΩ cm. Aniline (ACROS, ACS grade) was used after distilling over calcium hydride and stored in the dark under a nitrogen atmosphere. HCl(aq), and (NH₄)₂S₂O₈ were obtained from commercial resources and used without further purification. PET (Poly(Ethylene Terephthalate) film (surface morphology and roughness were shown in Figure S1a) was purchased from Formosa Co. Taiwan. PDMS film on glass was prepared as described in the following paragraph.

(2) Fabrication of PDMS (Poly(DiMethylSiloxane)) film on glass. Sylgard 184A and Sylgard 184B (obtained from Silmore Co., Taiwan) in a weight ratio of 10:1 were well-mixed to make a polymer solution. The polymer solution was then evacuated under vacuum for 10 minutes to remove gases inside. Putting one drop of the polymer solution on a clean glass and let the solution coated evenly on the glass. The polymer solution coated glass was then put perpendicularly on a flask and pump under the vacuum at room temperature for 24 hours; a flat PDMS film was formed on glass. The surface morphology and roughness of PDMS film on glass were displayed in Figure S1b.
(3) Plowing a trench on a polymer substrate and measuring the morphology and friction force simultaneously of the trench. PET film (or PDMS film on glass) was put on the sample stage of the AFM (SPA400, SEIKO Inc., Japan). Contact mode with a big spring constant tip was used. The AFM tip chosen for plowing is a silicon probe with spring constant of 48 N/m obtained from Budget Sensors Co. The forces applied to the AFM cantilever were typically range from $4.8 \times 10^{-6}$ to $1.2 \times 10^{-5}$ N and the scan rate varied from $10 \sim 1000 \mu$m/s. After the trench was made, without removing the polymer film, the morphology and friction force were measured simultaneously using the applied force of 0 N. The morphology and friction force images of 150 nm trench on PET (obtained from the applied force of $4.8 \times 10^{-6}$N and scan rate of 1000 $\mu$m/s) were shown in Figure S2 and the trenches with diameter of $10 \sim 15$ nm on PDMS (obtained from the applied force of $1.2 \times 10^{-5}$ N and scan rate of $300 \mu$m/s and $600 \mu$m/s for wide and narrow trenches, respectively) were displayed in Figure S3. The trench on PET is very stable the morphology did not change after repeatedly measuring for five times as shown in Figure S4. It was found that the effect of changing the scan rate on the size of the trench on PET substrate is much larger than that of changing the applied force. This may be due to the following reasons.

(4) The shape of the AFM tip is invert pyramid. High applied force will dig a bigger trench on the substrate, since the contact area between tip and substrate increased.

(5) The effect of the plowing speed on the diameter of the trench is a little bit complicated. At low scan rate, two parameters are important: First: a shear-thinning effect, due to the plastic rheological behaviour of the polymer. An increase of scan speed will favour chains disentanglement and consequently form a wide trench. The second: a thermal effect, a higher plowing speed will induce a greater temperature on the contact area and therefore the fluidification of the transfer material. However at high scan rate (the rate we used in our experiment) when the thermal cause the substrate to melt at the contacting area, the bending of the cantilever is also very important. Higher scan rate, the cantilever bends more, lifts the tip higher, therefore smaller trench is made.

PET is a polymeric material and we used very high scan rate to plow the substrate, therefore, the effect of changing the scan rate on the size of the trench is larger than that of changing the applied force.
(6) **In-situ polymerization/deposition of polyaniline wire in the trenches on polymer substrates.** The engraved polymer substrate was removed from the AFM sample stage and dipped in C₆H₅NH₂/HCl (aq) (dissolved 0.17 g of aniline in 26 mL, 1.0 M HCl (aq)) for 20 minutes to absorb aniline molecules. After slightly rinsing the substrate with water to remove the aniline molecules adsorbed on the surface, it was then put on the bottom of a reaction box containing (NH₄)₂S₂O₈/ HCl (aq) (dissolved 0.14 g of ammonium peroxosulfate in 10 mL, 1.0 M HCl (aq)), followed by adding another aniline/HCl aqueous solution (dissolved 0.06 g of aniline and 0.01% phenol (based on aniline) in 26 mL, 1.0 M HCl (aq))³. The mixture stayed at room temperature without stirring to deposit polyaniline wire. When we observed the color of the reaction solution turned light green, the polymer substrate was removed from the reaction solution. It took 10, 12 and 13 minutes to deposit 350, 1000 and 2400 nm polyaniline wires on PET substrates, respectively. For depositing 15 nm polyaniline wire on PDMS substrate, it took 12 minute. The polyaniline wire formed on the substrate was then washed with dilute HCl (aq), dried with N₂ gas. We plowed only one trench on a substrate to insure that the polyaniline wire on the substrate grew from the trench created by the AFM tip. If the polymerization time is longer than that needed for depositing polyaniline wire, polyaniline film will start to deposit on all surface. Figure S5 displayed the morphology and current image of polyaniline film deposited on PET film with 350 nm trench for 20 minutes. Nevertheless, it formed much thicker polyaniline film on PET compared to that deposited on PDMS, since PET film has a much rougher surface as revealed in Figure S1.

(7) **C-AFM studies:** Single polyaniline wire on insulating polymer substrate for conducting Atomic Force Microscope (C-AFM) study was mounted, via silver paste, to the AFM sample holder, as shown in Figure S6. Before imaging of the PANI wire, the surface was purged by N₂ gas to minimize the effects of moisture. The contact mode AFM with a current-sensing module also called current image tunneling microscope⁸ was used to measure the topographical and current images simultaneously. The gold-coated Si cantilever (spring constant 0.11 N/m, purchased from Nanosensor Co., Germany) was used for C-AFM imaging and I-V curves measurement. The detailed experimental
procedures and data analysis can be found in the previous articles. Polyaniline wires prepared with this method (NFNL) are quite stable, after five times measurement, the morphology did not change but the average current decreased ca. 10 ~ 15 % (see Figure S7), probably due to the dedoping of the polyaniline wires. For further confirming the fact that polyaniline wire was grown from the trench, the cross-section of the trenches on substrate and polyaniline wires were measured as illustrated in Figure S8. The size of the trenches do match the diameter of the polyaniline wires.

(8) SEM studies. Scanning electron micrographs (SEM) were recorded with a Hitachi S-800 at 15 KV. The samples (polyaniline wires on polymer substrates) for SEM imaging were mounted on metal stubs with a piece of conducting tape then coated with a thin layer of gold film to avoid charging.
2. Supplementary Figures:

**Figure S1**: AFM morphology of (a) PET film. (b) PDMS film on glass. (RMS: Root-Mean Square of the surface roughness)

**Figure S2**: (a) morphology (b) frictional force of 150 nm-wide trench on PET. (Applied force on the tip is $4.8 \times 10^{-6}$N and scan rate is 1000 $\mu$m/s)
**Figure S3.** (a) morphology (b) frictional force of trenches with 11 and 15 nm diameters on PDMS. (c) the cross section analysis of the area with the rectangular white line shown in (a).

(Applied force on the tip is $1.2 \times 10^{-5} \text{N}$ and the scan rate is 600 and 300 $\mu\text{m}/\text{s}$ for 11 nm and 15 nm trenches, respectively)

**Figure S4:** AFM images of 350 nm trench on PET (a) the 1st time scan. (b) the 5th time scan.
Figure S5: (a) morphology (b) current image of polyaniline film prepared by depositing polyaniline on PET film with 350 nm trench for 20 minutes.

Figure S6. Experimental set-up for measuring the charge transport property of a single polyaniline wire. (The diameter of polyaniline wire was enlarged in the Figure.)

Figure S7: The current images of (a) 350 nm wire (the first time measured, average current 1.0 nA). (b) 350 nm wire (the 5th time measured, average current 0.85 nA). (c) 2400 nm wire (the first time measured, average current 2.0 nA). (d) 2400 nm wire (the 5th time measured, average current 1.8 nA).
Figure S8: The cross section of the trenches and polyaniline wires 
(a) 350 nm trench on PET. (b) 350 nm polyaniline wire. (c) the cross section of 350 nm trench. 
(d) the cross section of 350 nm polyaniline wire. (e) 2400 nm trench on PET. 
(f) 2400 nm polyaniline wire. (g) the cross section of 2400 nm trench on PET. 
(h) the cross section of 2400 nm polyaniline wire.
References.

