Supporting Information

Nanopatterning and Fabrication of Memory Devices from Layer-by-Layer Poly (3, 4 -ethylenedioxythiophene): Poly (styrene sulfonate) (PEDOT: PSS) Ultrathin Films

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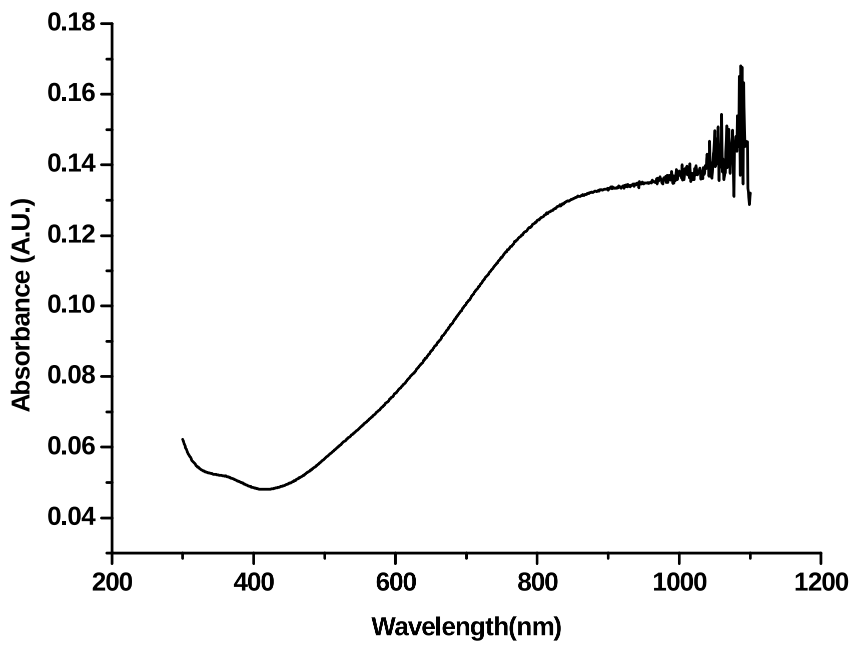
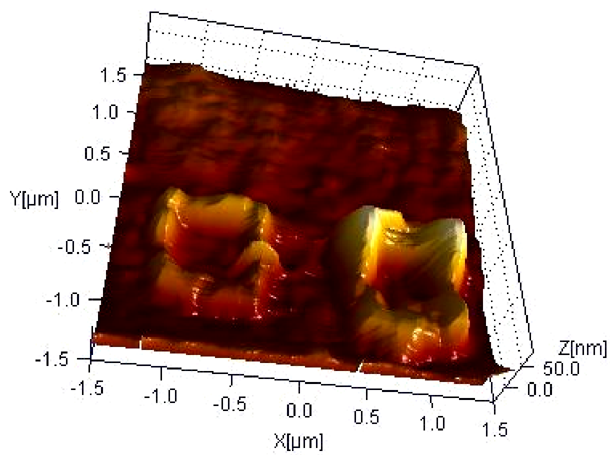
1. UV-Vis-N-IR Spectra. The initial doped state of PEDOT was studied on 10 bilayers of PDADMAC/PEDOT:PSS on BK7 glass by UV-vis-NIR absorption.



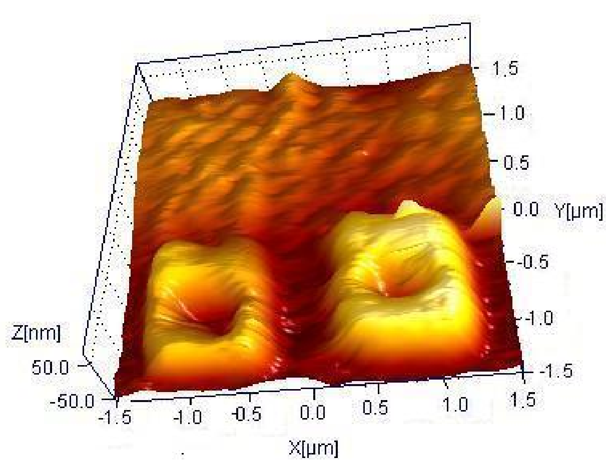
SI-Figure 1. UV-vis-NIR absortption of PEDOT:PSS in 10 bilayers.

2. Nanopatterning of 10 Bilayer Film. In order to get patterns at a constant applied voltage, we first applied different bias voltages; 4, 6, 8, and 10 V within the scanning scale at a writing speed of 0.4 µm/s. When 4V and 6 V were employed, no patterns could be obtained. However, squares were written with the applied 8 and 10 V bias voltages. Moreover, the square pattern for the 10 V bias have a noticeably higher height



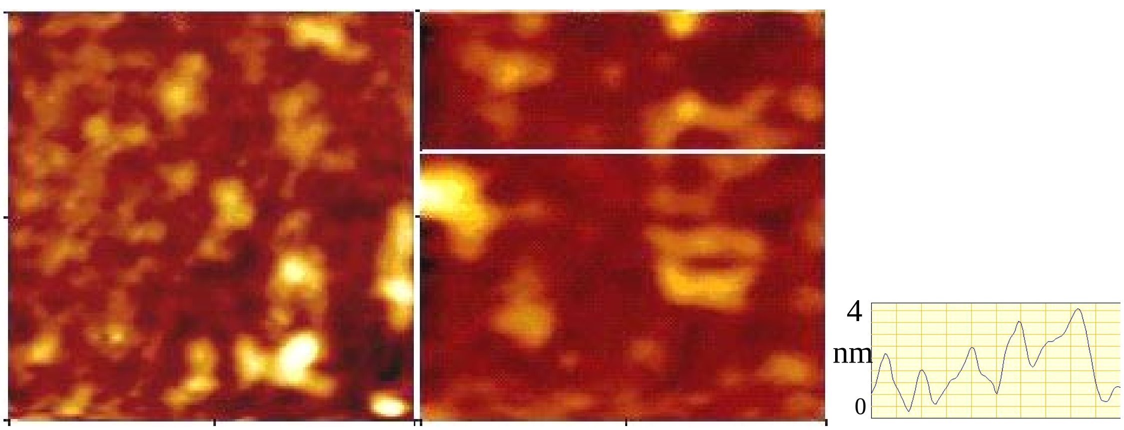
SI-Figure 2. 3D topographic image of square patterns: after nanowriting at 0.4 µm/s with applied biases of 4, 6, 8, 10 V from the top left (S1), top right (S2) (S1,S2 not obtained), bottom left (S3) and bottom right (S4).

3. Nanopatterning of 40 bilayer film. In this experiment, the sample bias was optimized again since the effects due to joule heating on the LbL film changes with a thicker film. An applied voltage bias of 4, 6, 8, and 10 V within the scanning scale at a writing speed of 0.4 µm/s were used. Similar to the 10 bilayer film, no pattern was observed with 4 and 6 V bias



SI-Figure 3. Topographic image of square patterns (a): after nanowriting at 0.4 μm/s with applied biases of 4, 6, 8, 10 V from the top left (S1), top right (S2) (S1, S2 not obtained), bottom left (S3) and bottom right (S4).

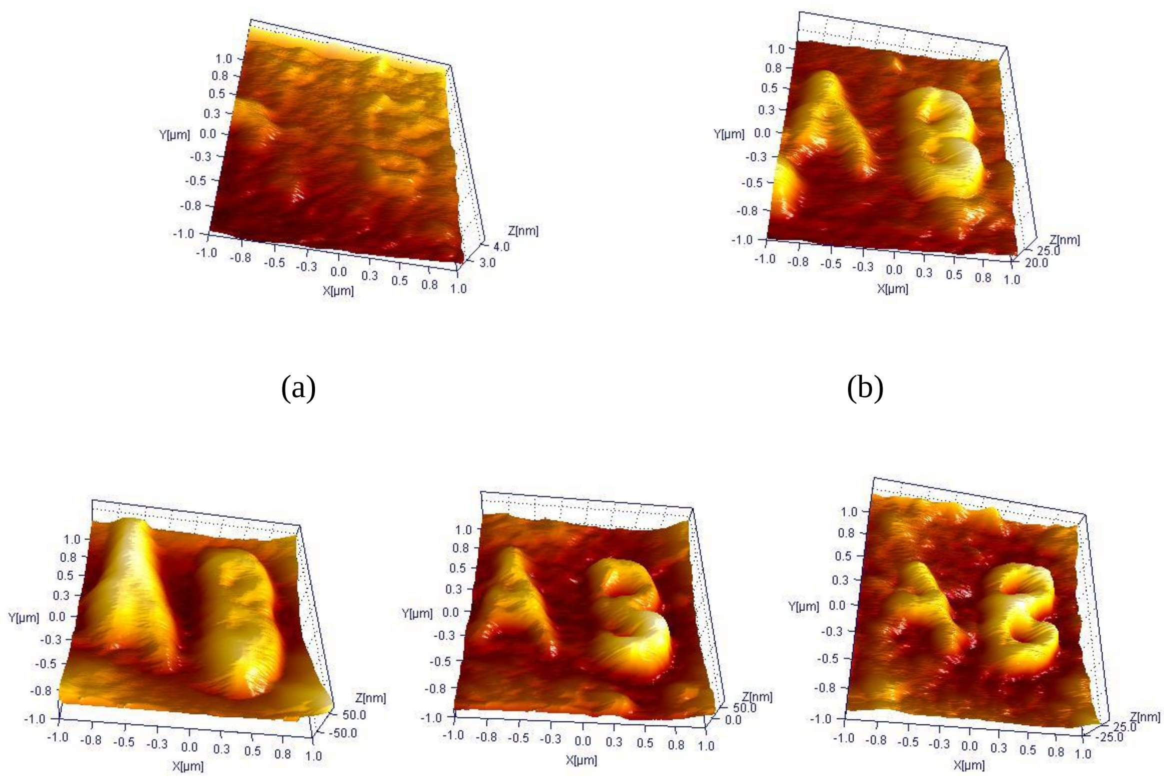
4. Thickness Dependence. To observe the effect of thickness on nanopatterning, a different pattern model was selected. SI-Figure 4(a) and (b) show the “patterns” of 4 squares and more complex pattern “AB” in each patterning area after applying 8 V. In this case, the electric field induced by applying voltage at 8 V was not strong enough to induce effectively doping of PEDOT with the 70 bilayer film. Although in SI-Figure 4(b) a faint “AB” was observed and it was very weak (averaged ~2 nm in height, which is much lower than that on 10 bilayers (24 nm) and 40 bilayers (28 nm) at 8 V with writing speed of 0.4 μm/s under the same condition (temperature =21 ºC and relative humidity=50 %). Understanding this thickness dependence is essential for successful fabrication of memory device on LbL films since a most important standard for information storage system are reliability and reproducibility.



(a) (b)

SI-Figure 4. (a) Topography of 4 squares (not obtained); (b) Topography of “AB”, and the profilemetry was obtained according to the white line.

5. AB Nanopatterning. The behavior of nanopatterning on a 70 bilayer film was studied further by writing different shapes of characters like “AB” at different applied bias and writing speeds. SI-Figure 5(a-e) shows the 3D topographical images of pattern “AB” at sample biases ranging from 8 to 10 V while the writing speed was kept from 0.3 to 0.8 μm/s. From (a), (b) and (c) the patterns were written at the same speed of 0.3 μm/s by applying voltages of 8, 9 and 10 V respectively. The height for each pattern was increased drastically as desired from 2 nm to 38 nm. In the case of (a), the pattern was too weak to be seen due to a poor electric field through the film, therefore the memory device would be poorly reproducible, while in the case of (c) the pattern lost its resolution although it’s much higher. But for the patterns of (d) and (e), lower bias with slower writing speed and higher bias with faster writing speed both provided good images, which had a medium height from 22-30 nm. Among these 5 patterns, it’s not difficult for us to expect to get good nanofeatures by applying a relatively higher bias (9 V) than the minimum value (about 8 V) which is for softening the polymer at a low writing speed <0.5 μm/s on a 70 bilayer film. The reason for the low resolution of pattern in (c) is probably due to much more anion transport during the nanopatterning process when writing slowly at 10 V. To solve this problem, we may attempt two different directons: one is to apply 9 V at a slow speed, and the other is to apply 10 V at a faster speed.

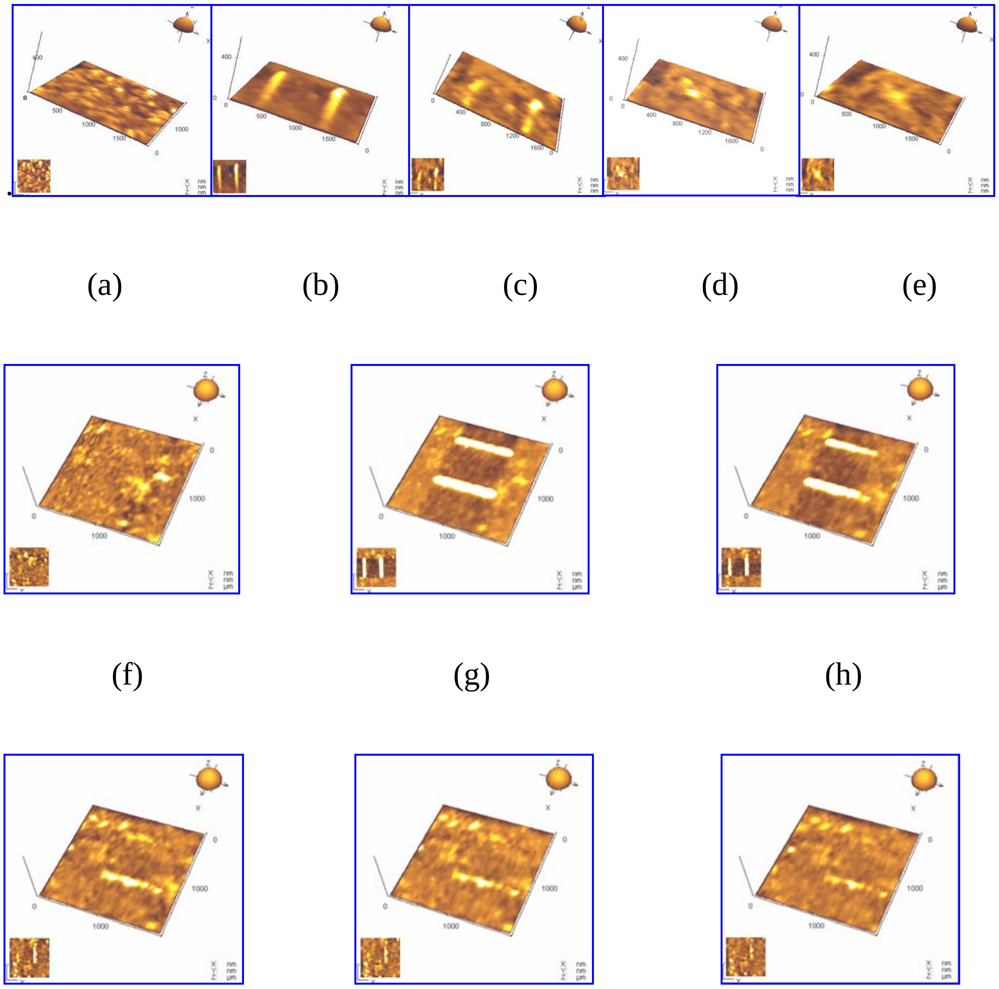


(a) (b)

(c) (d) (e)

SI-Figure 5. (a) Bias=8 V, Writing Speed=0.3 μm/s, Height=2 nm; (b) Bias=9 V, Writing Speed=0.3 μm/s, Height=30 nm; (c) Bias=10 V, Writing Speed=0.3 μm/s, Height=35 nm; (d) Bias=9 V, Writing Speed=0.4 μm/s, Height=30 nm; (e) Bias=10 V, Writing Speed=0.8 μm/s, Height=22 nm.

6. Erasability Experiments. Erasability experiments were carried out on 10 and 40 bilayers. The below images show the topography change after nanowriting and erasing.



(a) (b) (c) (d) (e)

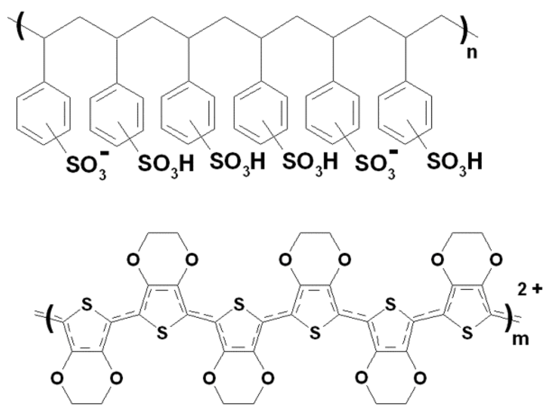
(f) (g) (h)

(i) (j) (k)

SI Figure 6. (a)-(e) 3D of topographical images (together with 2D on the bottom left corner) regarding the erasing two lines on 10 bilayers LbL film; (a) before nanowriting, (b) after nanowriting at 10 V with writing speed of 0.4(left) and 0.3 μm/s(right) respectively, (c) after first time erasing, (d) after second time erasing, (e) after third time erasing. (f)-(k) 3D of topographical images regarding the erasing two lines on 40 bilayers LbL film; (f) before nanowriting, (g) after nanowriting at 10 V with writing speed of 0.4(left) and 0.3 μm/s(right) respectively, (h)-(k) after first-fourth time erasing. All erasing were carried out by applying 0 V at an erasing speed of 8 μm/s.

7. Properties of PEDOT

Doping properties of PEDOT is related to the presence of the anion and the oxidized state of the PEDOT. PEDOT:PSS is doped and conducting. But it can be made more conducting by the addition of more anions as well as increased oxidation state (formation of radical cations).



SI Figure 6. The PEDO:PSS is doped and is in a conductive form as initially obtained as Baytron P.

A summary of the properties of Baytron P are as follows:

Synonym / Abbreviation:
PEDT/PSS, PEDOT/PSS

Form	liquid
Odour	odourless
Colour	darkblue
Surface resistance	max 1 MOhm
Conductivity	max 10 S/cm (depending on the type of coating formulation)
Solid content	1.2 to 1.4 %
Na content	max 500 ppm
Sulfate content	max 80 ppm
Viscosity	60 to 100 mPa·s
ph value	1.5 to 2.5 at 20 °C
Density	1 g/cm^3 at 20 °C
Mean particle size	d50 approximately 80 nm (swollen)
Refractive index, n	1.5228 at 589 nm (dried layer)
Surface tension	71 mN/m at 20 °C
PEDOT :PSS ratio	1 : 2.5 (by weight)
PEDOT work functn	approximately 5.2 eV
Boiling Point	approximately 100 °C
Vapor pressure	23 mbar at 20 °C