Supporting Information

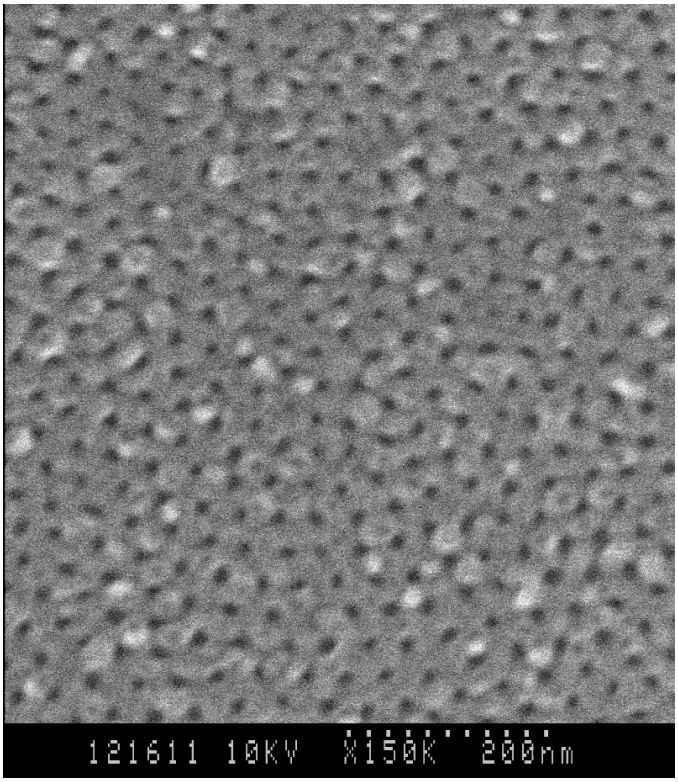

Figure S1. Field-emission scanning electron microscope (FE-SEM) image of P(S-*b*-EO) film coated on ITO substrates after immersion in a sulfolane electrolyte solution, followed by drying under vacuum. Shallow craters (ca. 10 nm according to the AFM observation) with small projections beside appeared at the PEO domains.

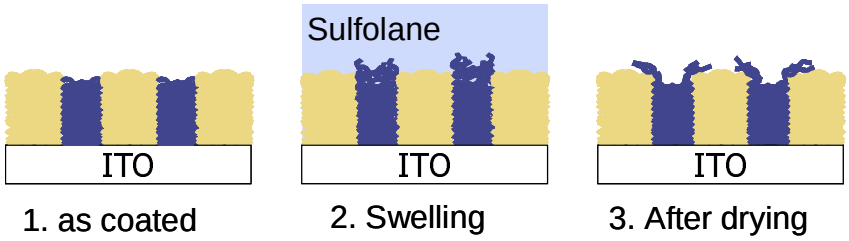

Figure S2. Schematic illustration of selective swelling of a P(S-*b*-EO) film: (a) as coated before immersion, (b) immersed in a sulfolane solution, where PEO domains were selectively swollen, (c) after drying under vacuum. Some swollen PEO chains came out from the nanodomains and were attached to the adjacent PS domains through evaporation of sulfolane.

Mathematical derivation of equation (3)

We consider a specific model of a recessed disc electrode, with the diffusion coefficient in the micropore not equal to the one in bulk solution. We shall make the approximation that the concentration of ferrocene at the mouth of the PEO nanodomain (with radius r and the length L) is a value of C_m and that there is no accumulation effect or membrane effect at the polymer/solution interface. For a steady state to exist in the PEO nanocylinder, we suppose a linear concentration profile of ferrocene, with concentration values of zero at the electrode surface and C_m at the mouth of the PEO nanodomain. Therefore

$$I_s = nFD_{PEO}C_m\pi r^2 / L \qquad \text{(A1)}$$

The diffusion from the bulk solution to the mouth of the PEO nanodomain, the steady state current is represented by the following equation, replacing the C in eq. (2) by $(C\text{-}C_m)$,

$$I_s = 4nFD_{sulfolane}(C\text{-}C_m)r \qquad \text{(A2)}$$

Those 2 equations (A1) and (A2) relate to the same current, we can solve them to find

$$C_m = 4D_{sulfolane}LC / (4D_{sulfolane}L + \pi rD_{PEO}) \qquad \text{(A3)}$$

Thus the steady state current for a single PEO nanodomain is calculated to be as follows, which gives the equation (3), multiplied by the number of nanodomain, qA_g;

$$I_s = 4\pi nFD_{PEO}Cr^2 (4L + \pi rD_{PEO}/D_{sulfolane})^{-1} \qquad \text{(A4)}$$