Electronic Supplementary Information (ESI)

In Vacuum Electropolymerization of Vapor-Deposited Source Molecules into Polymer Films in Ionic Liquid

*Keisuke Okawara[1], Tomonobu Nishimura[1], Shingo Maruyama[1], Msaki Kubo[2] and Yuji Matsumoto[1]**

[1] Department of Applied Chemistry, School of Engineering, Tohoku University,
6-6-07, Aramaki Aza Aoba Aobaku, Sendai, Miyagi 980-8579, Japan

[2] Department of Chemical Engineering, School of Engineering, Tohoku University,
6-6-07, Aramaki Aza Aoba Aobaku, Sendai, Miyagi 980-8579, Japan

*E-mail: y-matsumoto@tohoku.ac.jp

The supporting Information includes four Figures.

1. Materials.

The IL used in this experiment was 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [emim][TFSA] IL (>99.0 % in purity, IoLiTec GmbH), purchased from Kanto Chemical Co., Inc., 3T (>98.0 % in purity) was used as a monomer source for polythiophene, purchased from Tokyo Chemical Industry Co., Ltd. (TCI). All these chemicals were used as received. α-Al_2O_3(0001) of 7 mm × 7 mm in size was used as a substrate, cut from a α-Al_2O_3(0001) single crystal wafer (Shinkosha Co. Ltd.). Au (0.8 mm φ) and Ni-Cr (60:40, 1.0 mm φ) wires were purchased from The Nilaco Corporation for depositing electrodes.

2. Experimental

Elecrochemical set up.

α-Al_2O_3(0001) substrates were first cleaned ultrasonically with ethanol and acetone, respectively. Then, Au (100 nm)/Ni-Cr (5 nm) films as working, counter and reference electrodes (WE, CE and RE) were deposited on the α-Al_2O_3 (0001) substrate by a typical vacuum deposition method with a resistive heating system. A 0.5-μl droplet of [emim][TFSA] was placed on the patterned electrode substrate spreading to a total area of ~7 mm in diameter to cover all the three electrodes. The average thickness of the IL d_{IL} was then about 10 μm in this case. In fact, the IL region over the CE and RE was shielded by a Kapton tape to avoid superfluous deposition of 3T molecules on these electrodes and thereby unexpected electrochemical reactions in addition to the electropolymerization on the WE. Next, the IL-coated patterned substrate was mounted on the sample holder of the vacuum chamber with each electrode pad wire-bonded to the corresponding vacuum current feedthrough, and the chamber was evacuated down to below 10^{-6} Torr.

Electropolymerization of polythiophene Films by Vapor Deposition in Ionic Liquid.

In this study, a continuous infrared (CW-IR, $\lambda = 808$ nm, pulse width = 25 msec., frequency = 4.0 ~ 5.0 Hz) laser deposition method (Pascal Co. Ltd.) was employed for thermal evaporation of 3T. Chronoamperometry (CA) as well as cyclic voltammetry (CV) measurements (scan rate = 0.05 V/s) were performed using an potentiostat (Compact/Pocket Stat, Ivium Technologies B.V.). The vapor deposition rate of 3T was controlled by monitoring the total amount of deposited 3T by a quartz crystal microbalance (QCM: Q-pod, INFICON Co., Ltd., 6 MHz) technique. Since 3T was transparent to IR light, it was mixed with Si powder in a container in order for the Si particles to efficiently absorb the IR laser light and indirectly heat the 3T powder.

Analysis.

After the remaining IL on the sample was removed by washing out by 2-propanol or annealing in a vacuum at 200 °C, the chemical structures of the obtained deposits were examined by an attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectrophotometer (FTIR-8400 with Quest, Shimadzu Corporation). The morphology of the polythiophene films was observed by an optical microscope (ECLIPSE LV100ND, Nikon) as well as an atomic force microscope (AFM, SPA-400, Seiko Instrument).

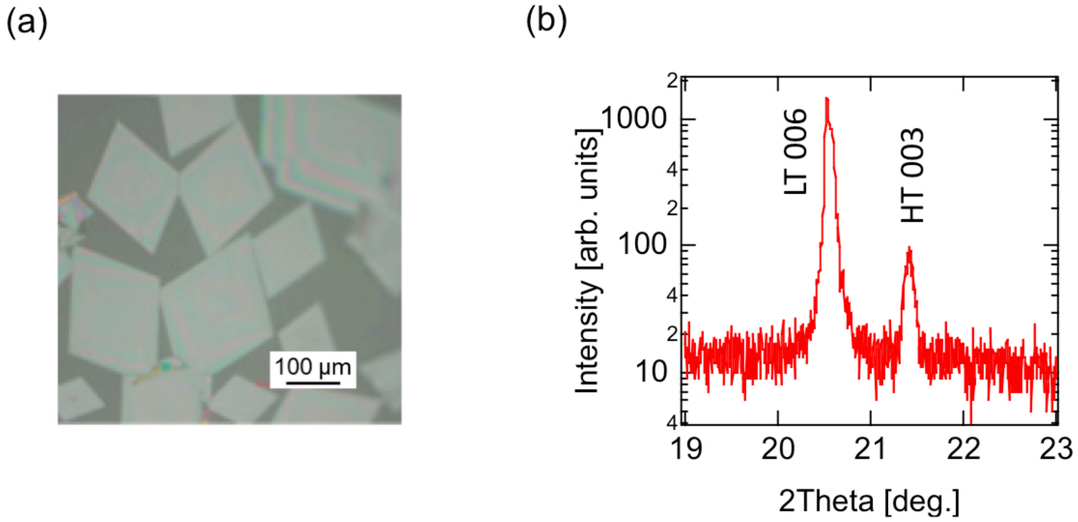

Figure S1: Typical optical microscope image (a) and XRD pattern (b) of a 1.5 µm-thick 3T deposit obtained via a bulky IL droplet at 18 °C.

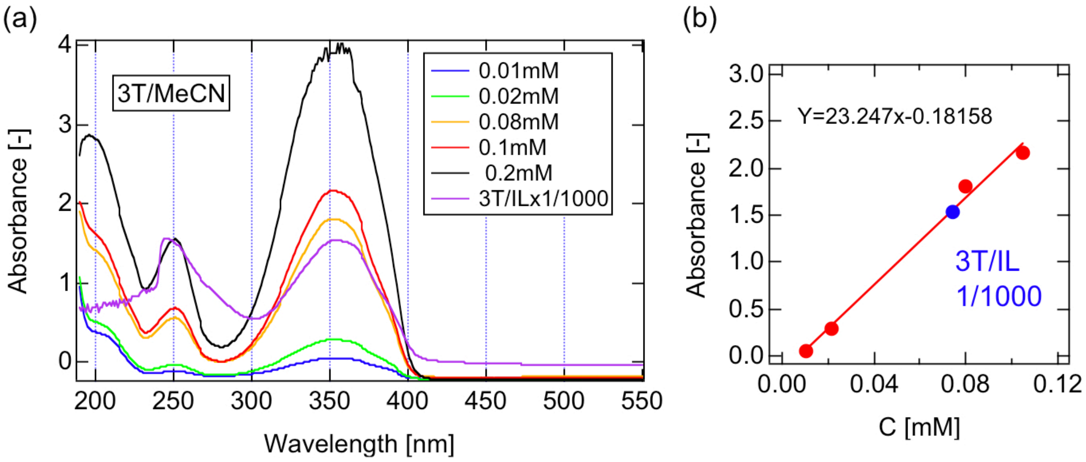

Figure S2: (a) UV-Vis spectra for 3T/MeCN solutions with different concentrations, along with that for a saturated 3T/IL solution, where the concentration was 1000 times diluted. (b) Calibration curve (red): the absorbance at λ max (~350nm) plotted as a function of the 3T concentration for estimating the saturated concentration of the 3T/IL solution (blue).

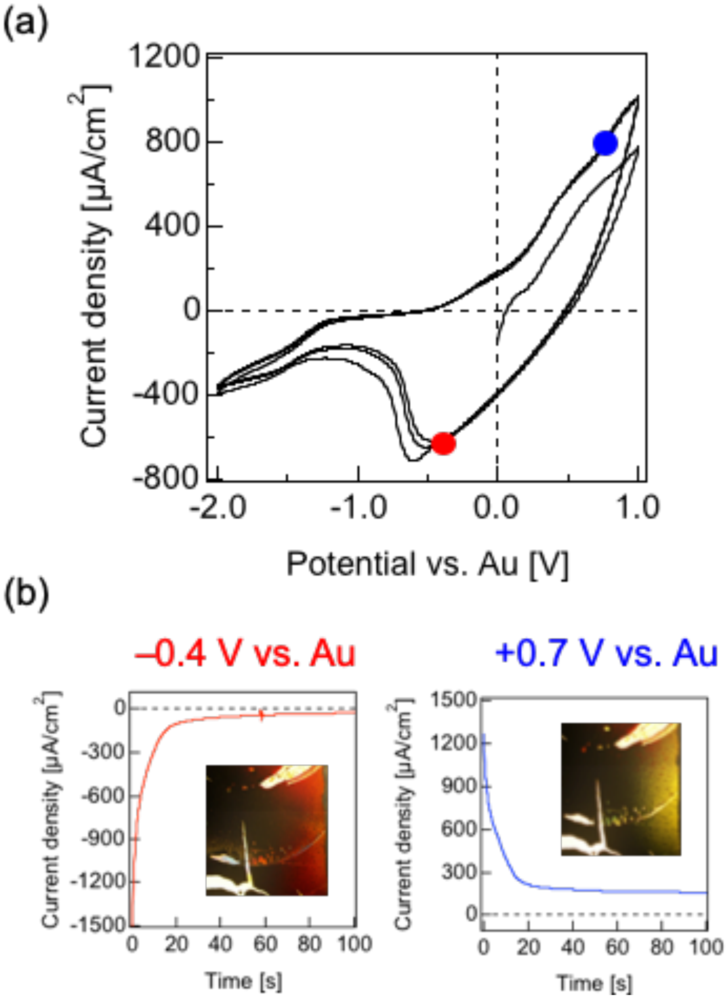

Figure S3: CV curves between –2 and +1 V vs. Au for a P3T deposit in air with IL (a), along with the optical microscope images of the deposit samples at +0.7 V and –0.4V, respectively (b). The P3T deposit was prepared by CA at 0 V vs. Au, at 40 nm/min with a thickness of 2.3 μm and it was then followed by vacuum-annealing at 200 °C for 15 min to once remove the remaining IL.

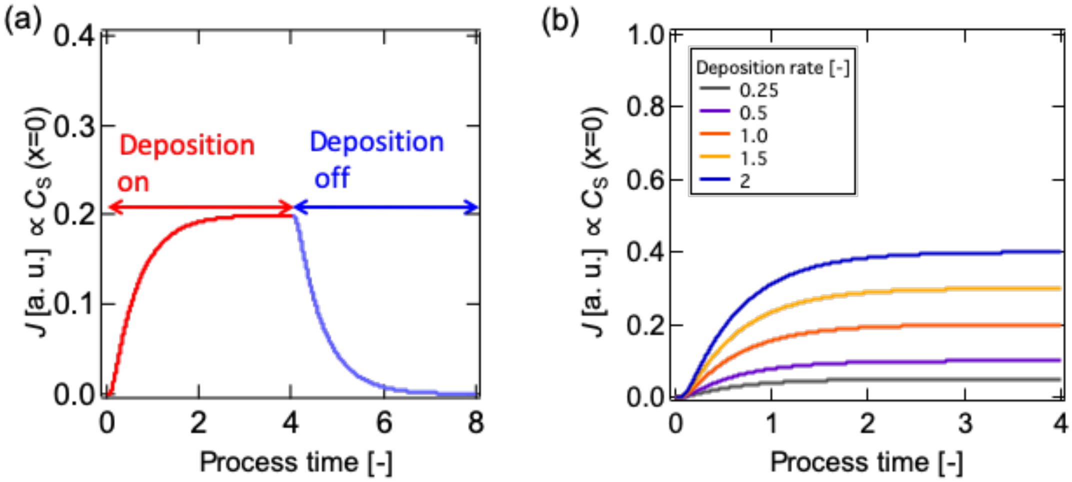

Figure S4: (a) The time-development and -decay of the concentration at x=0 C_S are able to well reproduce the time-response of the measured oxidative current density as displayed in Fig. 4(a). (b) The time-development behaviors of the concentration at x=0 C_S in IL, i.e. the time-responses of the oxidative current density for different deposition rates [-] of 0.25, 0.5, 1, 1.5 and 2, where the time required for reaching a steady-state condition does almost not change.