Supporting information

Electric-field Induced Layer-by-layer Assembly Technique with Single Component for Construction of Conjugated Polymer Films

Shiwei Wang^a, Zhuo Chen^a, Ahmad Umar^b, Yao Wang^{a*} and Peng-gang Yin^a

^aKey Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry and Environment, Beihang University, Beijing 100191, P R China.

^b Department of Chemistry, Faculty of Science and Arts and Promising Centre for Sensors and Electronic Devices, Najran University, Najran11001, P.O.Box-1988, Kingdom of Saudi Arabia

Correspondence author: E-mail: <u>yao@buaa.edu.cn</u>, <u>wswjldx2004@163.com</u>

Experiment Methods

Regular poly (3-hexylthiophene) (P3HT) was synthesized according to the literature (*J. Polym. Sci. Part A: Polym. Chem.* 2012, **50**, 2762.). Poly (9, 9-di-n-octylfluorenyl-2,7-diyl) (PFO) was purchased from Shenzhen Derthon Optoelectronic Materials Science & Technology Co., LTD (Mn=30000 by GPC). The solvent of o-dichlorobenzene (ODCB), toluene and dichloromethane were purchased from Aldrich (chromatographic pure) and used as received. Sheet resistance of Indium tin oxide (ITO) glass was 30~40 ohm per square which can be received from Normal commercial channels.

15 mg of P3HT power was dissolved in dichloromethane or ODCB solvent, ensuring the molar concentration can be kept at 0.01 M, which was dissolved completely under 70 °C. Indium tin oxide (ITO) glass was ultrasound cleaned by acetone, isopropyl alcohol and ultrapure water for 30 min respectively. The cleaned ITO glasses were dipped in H_2O_2 for 12 hours, rinsed thoroughly with Millipore water, further rinsed with pure ethanol, and then dried under a 0.55 µm filtered stream of dry N₂. Immersion of the cleaned ITO glass substrate in P3HT solution fabricated before under the 10 V DC voltage (the distances between the substrate and the counter electrode was 2 mm) for 10 min, then dried with N₂. Repetition of this procedure enables the fabrication of thin films with a large number of layers.

poly (9, 9-dioctylfluorene) (PFO) power was dissolved in toluene solvent, ensuring the molar concentration can be kept at 0.01 M. Indium tin oxide (ITO) glass was ultrasound cleaned by acetone, isopropyl alcohol and ultrapure water for 30 min respectively. The cleaned ITO glasses were dipped in H_2O_2 for 12 hours, rinsed thoroughly with Millipore water, further rinsed with pure ethanol, and then dried under a 0.55 µm filtered stream of dry N_2 . Immersion of the cleaned ITO glass substrate in PFO solution fabricated before under the 10 V DC voltage (the distances between the substrate and the counter electrode was 2 mm) for 10 min, then dried with N_2 . Repetition of this procedure enables the fabrication of thin films with a large number of layers.

Samples for atomic force microscopic (AFM) measurements were prepared by spin-coating and assembled multilayer CP films of P3HT and PFO as mentioned above. All of samples were fabricated and tested in air at room temperature. AFM images were acquired in tapping mode with a Digital Instruments Dimension 3100 Scanning Probe Microscope performed at room temperature in air using standard silicon cantilevers with a nominal spring constant of 50 N m⁻¹ and resonance frequency of ~300 kHz. The images were acquired at a scan frequency of 1 Hz in $5 \times 5 \mu m^2$ scan areas. UV–vis absorption spectra were recorded with a Shimadzu UV-3100 spectrophotometer. The crystallinity of the as-prepared P3HT films was investigated by X-ray diffraction (XRD) using Rigaku DMAX-2400 diffractometer.

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