Supporting information for:

Thickness Dependent Thermal Performance of Poly(3,4-ethylenedioxythiophene) Thin Film Synthesized via Electrochemical Approach

Shen Chen[1,2], Tian Luan[1,2], Chen Di[3], Minghui Lu, Xuejun Yan[3,], Chengyi Song[1,2,]* and Tao Deng[1, 2]*

[1]*Center of Hydrogen Science, School of Materials Science and Engineering, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, P.R.China*
[2]*Center of Hydrogen Science, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, P.R.China*
[3]*College of Engineering and applied Sciences, Nanjing University, 163 Xianlin Avenue, Qixia District, Nanjing, Jiangsu, 210093, P.R. China*

**Corresponding author: xjyan@nju.edu.cn; chengyi2013@sjtu.edu.cn*

Table of Contents

1. Materials and Instrumentations
2. Preparation of electrode substrates
3. Preparation of non-aqueous Ag/Ag^+ (0.1 M $AgNO_3$) reference electrode
4. Preparation of PEDOT:PSS film with post-treatment
5. TDTR measurements
6. The analysis on the sensitivity of Au-coated silicone by TDTR
7. Supplementary figures
8. Reference

1. Materials and Instrumentations

1.1 Materials

3,4-Ethylenedioxythiophene was obtained from Baye, and acetonitrile was obtained from Macklin. Tetrabutylammonium Hexafluorophosphate ($TBAPF_6$) was obtained from TCI. All other chemicals were purchased from Aladdin, Sinopharm Chemical Reagent Co. Ltd, and all chemicals were used as received unless mentioned otherwise.

1.2 Instrumentations

The polymer film was electropolymerized by electrochemical workstation (CHI760E, Shanghai Chenhua Instrument Co., Ltd). The surface morphology of polymer film was measured by scanning electron microscope (SEM, TESCAN MAIA3) and optical microscopy (PUDA, MM-8C). The thickness of gold (Au) film was measured by a profile meter (KLA-Tencor P7). Surface morphology of polymer and Au film was characterized by Atomic Force Microscope (AFM, Bruker multiple mode 8). The Au film coated on silicon substrate was fabricated by vacuum coating machine (JSD400, Anhui jiashuo Vacuum Technology Co., Ltd). The out-of-plane thermal conductivity of polymer film, interfacial thermal conductance, and thermal conductivity of silicon substrate were measured by homemade time-domain thermoreflectance (TDTR, Nanjing University). The doping level of PEDOT films was measured by X-ray photoelectron spectroscopy (XPS, AXIS UltraDLD, SHIMADZU).

2. Preparation of electrode substrates

Silicon substrates were carefully cut into the size of 1 cm × 2 cm to avoid scratching or polluting the polished sides. Then those silicon substrates were cleaned by sonication with acetone, ethanol and deionized water for 20 minutes, respectively, and finally blown dry under a stream of nitrogen. Before Au deposition, to strengthen

the adhesion between Au and silicon substrates, a 5 nm Ti film was firstly deposited on the cleaned silicon substrates by physical vapor deposition (JSD 400, JIASHUO Vacuum Technology). Then, a 700 nm Au layer was deposited as conducting layer on the Ti layer via the same physical vapor deposition. After Au deposition, the thickness of the Au layer was measured by profilometer.

3. Preparation of non-aqueous Ag/Ag^+ (0.1 M $AgNO_3$) reference electrode

The end of the purchased Ag/Ag^+ reference electrode (namely the part of ion permeable porous glass) was firstly immersed in the acetonitrile containing 0.1 M TBAPF6 for 1 hour. The above prepared solution, acetonitrile containing 0.1 M TBAPF6, was then injected into the internal pipe of reference electrode with a pipette and the volume of the solution is within 2/3 of the volume of the internal pipe. At last, the internal tube was blocked with the Teflon lid and sealed the joint to obtain the non-aqueous Ag/Ag^+ (0.1 M $AgNO_3$) reference electrode.

4. Preparation of PEDOT:PSS film with post-treatment

Fabrication of pristine PEDOT: PSS film: Pristine PEDOT:PSS film was prepared by a simple spin-coating method. Typically, two drops of PEDOT:PSS solution (commercial product) was dropped in a glass slide (1 × 1 ᶜm) and form PEDOT: PSS film by spin coater (WS-650MZ-23NPPB/OND). Such as-fabricated film was dried in air for overnight.

Fabrication of PEDOT: PSS film with methanol treatment: The as-prepared pristine PEDOT:PSS thin films were immersed in methonal (MeOH) for 24 hours. The

obtained films were washed by deionized water, and then dried in air. Ethylene glycol (EG) treatment of PEDOT:PSS thin films follow the same process.

5. TDTR measurement

In the TDTR measurements[1-3], a train of 170 fs long pulses at a repetition rate of 80 MHz from a mode-locked Ti:sapphire laser is split into a pump beam and a probe beam via a polarized beam splitter. A maximum delay time of ~4 ns of the probed beam can be adjusted via a mechanical delay stage. The pump beam modulated at a frequency of 9.8 MHz by an Electro-Optic Modulator will be absorbed by the aluminum transducer layer, resulting in a through-plane heat propagation in the samples. The delayed probe beam monitors the temperature-induced changes in surface reflectivity of aluminum. The reflected intensity of the probe beam is measured by a Si photo detector and a lock-in amplifier can extract amplitude and phase data from the probe beam. The measured thermoreflectance signals are then fitted to a standard two-dimensional, three-layer heat conduction model to obtain thermal transport properties of samples.

A lock-in amplifier was used to suppress undesired signals induced by the optical-thermal response and strong background noise in order to extract the useful signal at a specific frequency and amplify it. The extracted signal is composed of real part and virtual part. The in-phase signal (V_{in}) and out-of-phase signal (V_{out}) can be obtained by compared to the reference signal. And the absolute value of $-V_{in}/V_{out}$ with the delay time was used to analyze in order to balance the effect of uncertain factors on the signal.

The characterization of sensitivity in the TDTR measurement is analyzed, which represents the influence of the numerical changes of parameters involved in the experiment on the measurement results. The sensitivity of a specific parameter of interest in the TDTR measurement is defined as follows

$$S_\alpha = \frac{\partial ln(-V_{in}/V_{out})}{\partial \alpha}$$

where α is the specific parameter of interest. In the range of delay time, a larger S_α means a more accurate value of the parameter α.

6. The analysis on the sensitivity of Au-coated silicone by TDTR

The TDTR measurement of Au film coated on silicon substrate reveals the importance of sensitivity. **Figure S2** shows the atomic force microscopy (AFM) image of thickness of Au film and surface roughness measurement of Au film coated on silicon substrate. The three-layer structure composed of Au film, titanium layer and silicon substrate (**Figure S2a**). Titanium layer was used to strengthen the adhesiveness of Au film on silicon substrate. In the first trial, the thicknesses of Au film and titanium layer are ~50 nm and ~5 nm, respectively. **Figure S2b-c** show the two-dimensional and three-dimensional AFM images of the surface of Au film. The surface roughness of Au film is Ra =1.36 nm and Rq =1.90 nm, which satisfies the requirement for TDTR measurement. **Figure S3** reveals the relationship between the sensitivity and time delay of the silicon substrate coated with Au film (Si-Au) sample in the TDTR measurement, where ***C*** represents the heat capacity, ***kz*** represents the thermal conductivity, and ***h*** represents the thickness. It should be noted that ***kz1***, ***kz3*** and ***k5*** represent the thermal conductivity of the Al layer, Au film and silicon substrate, respectively. Al layer was deposited on the Au film to enhance the absorption of incident laser. ***kz2*** represents the interfacial thermal conductance between Al layer and Au film (Al-Au). ***kz4*** represents the interfacial thermal conductance between Au film and silicon substrate (Au-Si). The greater the absolute value of sensitivity in the time delay range of 200-4000 ps, the more accurate the value of parameters in the TDTR measurement[1]. Therefore, TDTR measurement of interfacial thermal conductance of Al-Au exhibits high accuracy, however, the measurement sensitivity of absolute thermal conductivity of Au film is low.

7. Supplementary figures

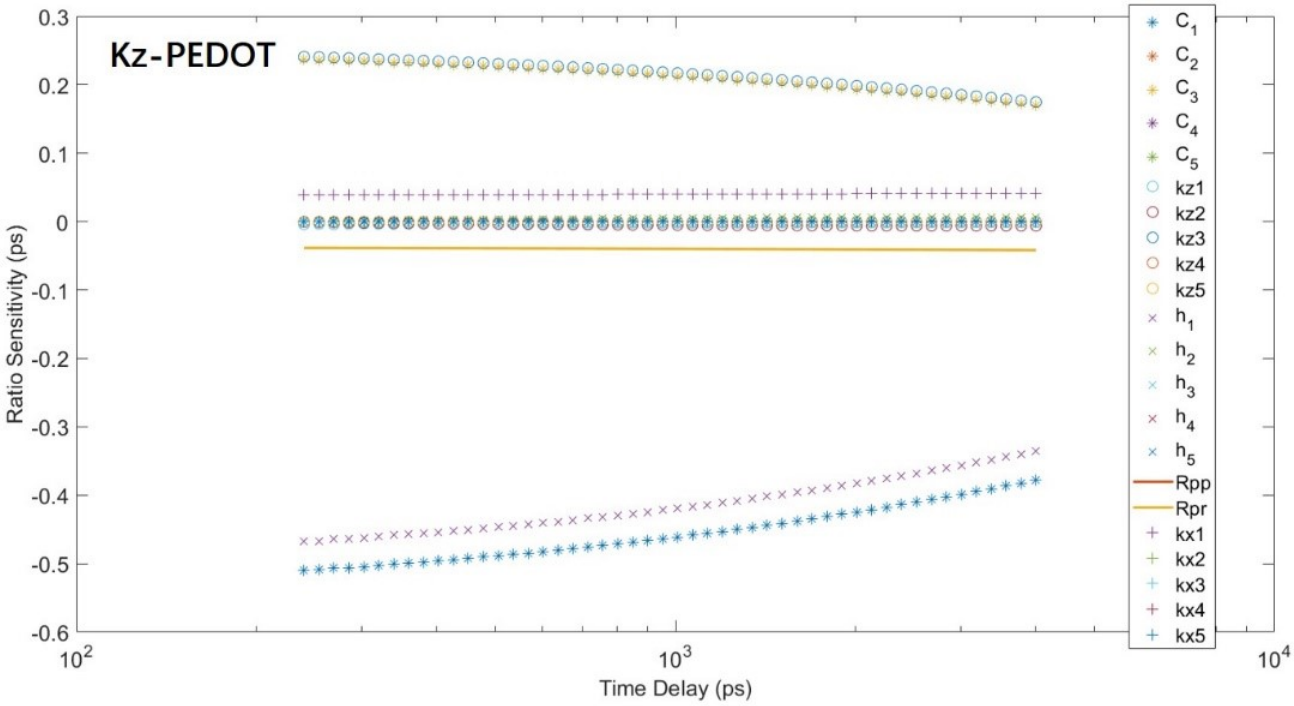

Figure S1. The relationship between the sensitivity of the parameters and the time delay in the TDTR measurement of Si-Au-PEDOT sample.

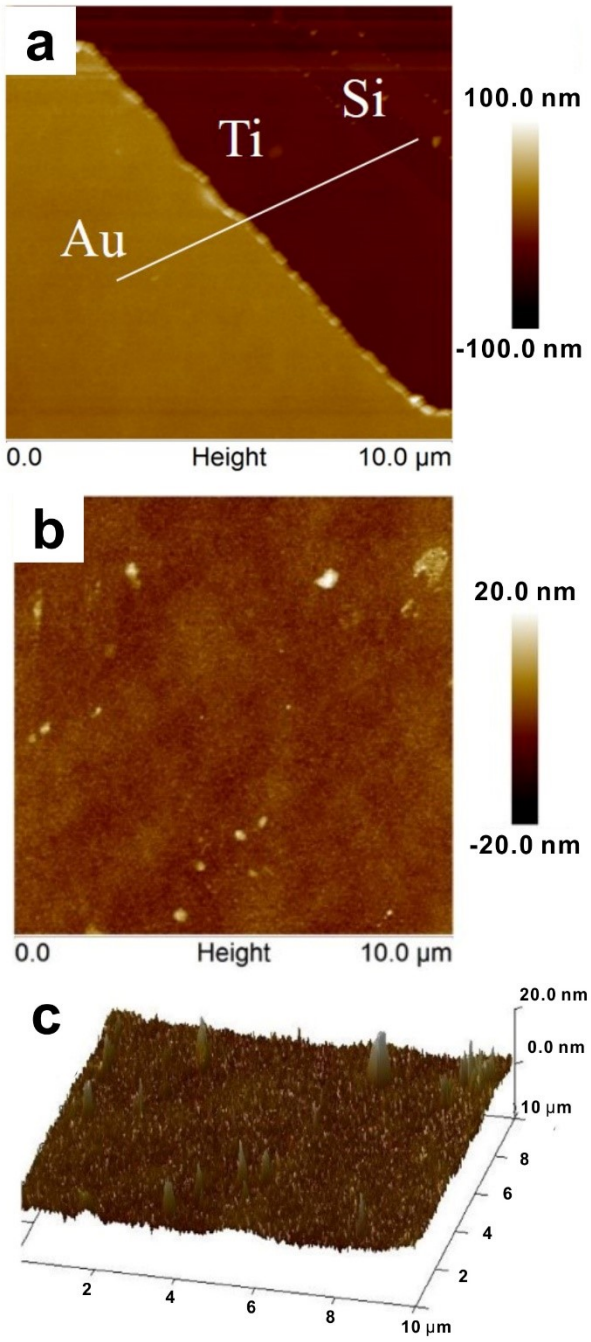

Figure S2. (a) The thickness measurement of Au film on a Au-plated silicon substrate by Atomic force microscopy (AFM). AFM image of surface roughness for Au film (b) and three-dimensional AFM image of Au film (c).

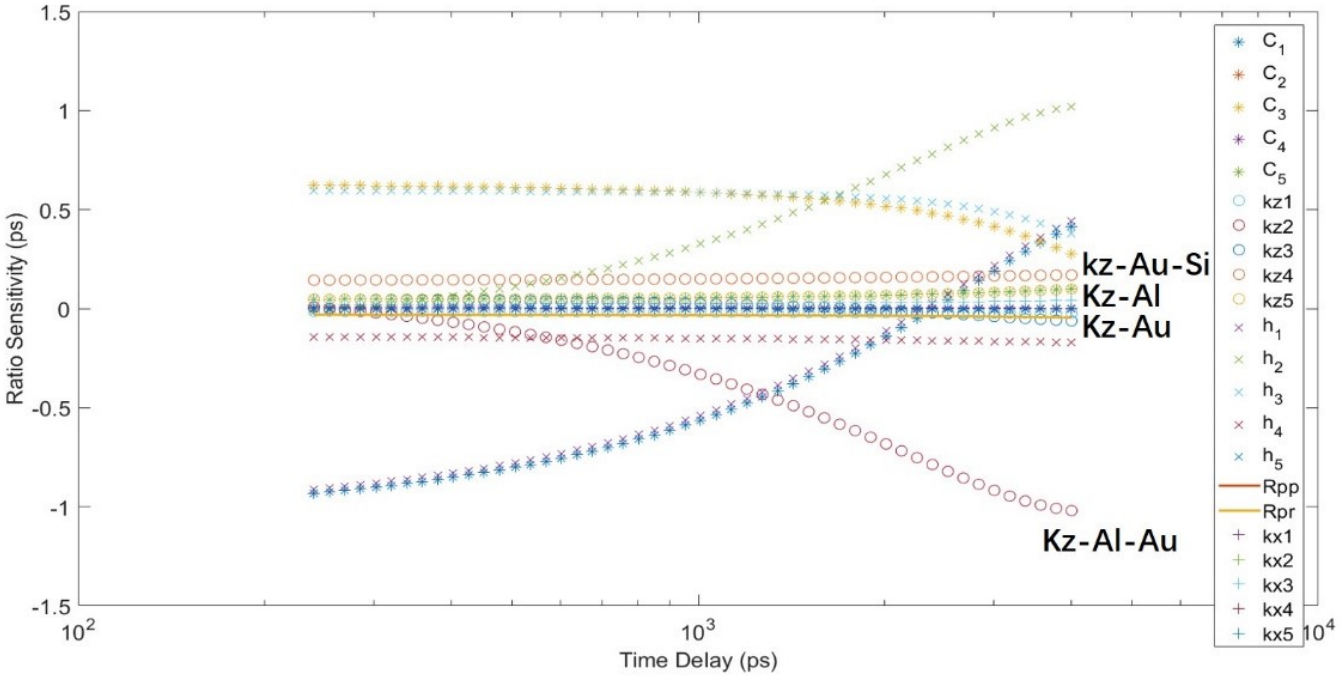

Figure S3. The relationship between the sensitivity of the parameters and the time delay in the TDTR measurement of Si-Au sample.

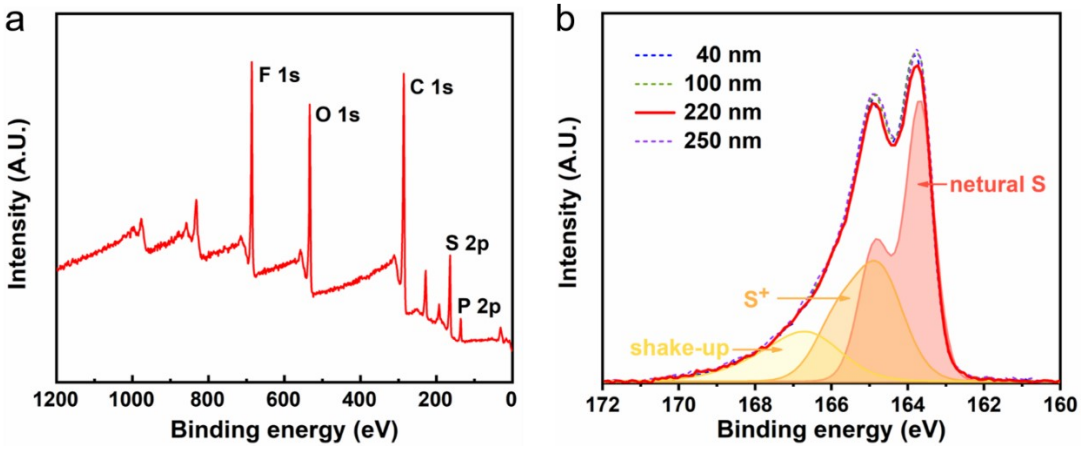

Figure S4. (a) XPS survey scan of the 220 nm PEDOT film and (b) high resolution XPS spectrum of S 2p of PEDOT films with different thickness. The fitting result of S 2p for the 220-nm PEDOT film is depicted on the Figure (b).

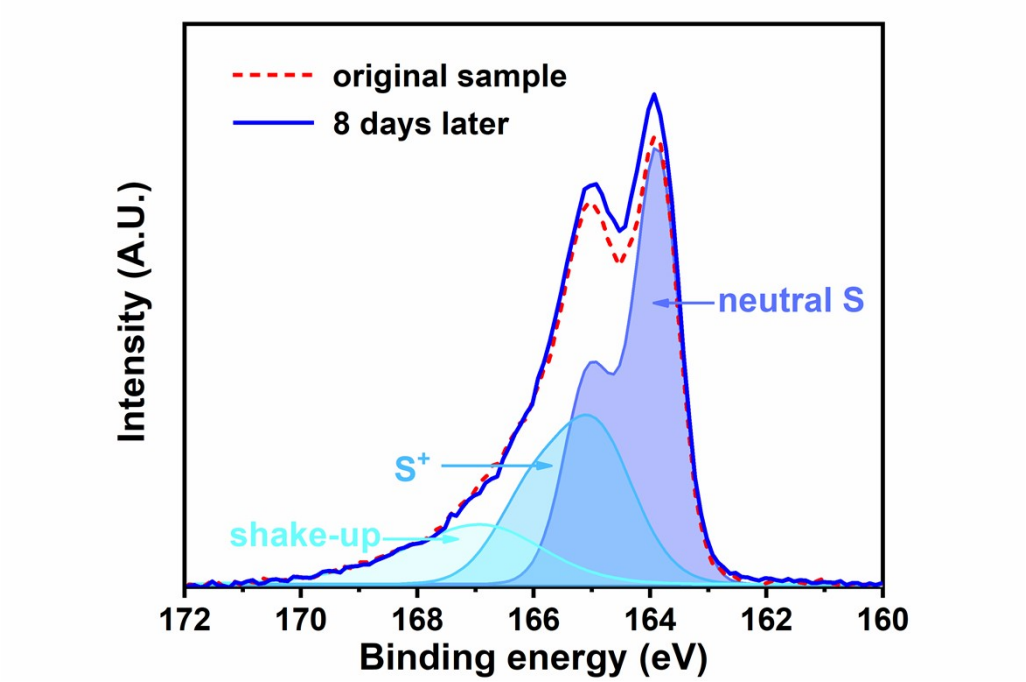

Figure S5. The high resolution XPS spectrum of S 2p of the original PEDOT film (~220 nm) and that of film kept in air for 8 days. The fitting result of S 2p for the PEDOT film after 8 days is depicted on the figure.

Reference

1. L. Cao, J. Pan, H. Zhang, Y. Zhang, Y. Wu, Y.-Y. Lv, X.-j. Yan, J. Zhou, Y. B. Chen, S.-h. Yao, Y. Pei, M.-h. Lu and Y.-f. Chen, *The Journal of Physical Chemistry C*, 2019, **123**, 27666-27671.
2. X.-J. Yan, Y.-Y. Lv, L. Li, X. Li, S.-H. Yao, Y.-B. Chen, X.-P. Liu, H. Lu, M.-H. Lu and Y.-F. Chen, *Applied Physics Letters*, 2017, **110**, 211904.
3. C. Di, J.-H. Pan, S.-T. Dong, Y.-Y. Lv, X.-J. Yan, J. Zhou, S.-H. Yao, H. Lu, V. E. Gusev, Y.-F. Chen and M.-H. Lu, *CrystEngComm*, 2019, **21**, 6261-6268.