

Synergistic Effects of Solvent Vapor Assisted Spin-coating and Thermal Annealing on Enhancing the Carrier Mobility of Poly(3-hexylthiophene) Field-effect Transistors

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Abstract Poly(3-hexylthiophene) (P3HT) thin films, obtained by normal spin-coating and solvent vapor assisted spin-coating (SVASP) before and after thermal annealing (TA), and the corresponding devices were prepared to unravel the microstructure-property relationship, which is of great importance for the development of organic electronics. When SVASP-TA films were used as the active layers of the organic field-effect transistors, a hole mobility up to $0.38 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was achieved. This mobility was one of the highest values and one order of magnitude higher than that of the normal spin-coating films based transistors. The relationship between the microstructure and the device performance was fully investigated by UV-Vis absorption spectra, grazing incident X-ray diffraction (GIXD), and atomic force microscopy (AFM). The impressive mobility was attributed to the high crystallinity and ordered molecule packing, which stem from the synergistic effects of SVASP and thermal annealing.

Keywords Poly(3-hexylthiophene); Polymer field-effect transistors; Microstructure; Polymer semiconductors

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INTRODUCTION

Conjugated polymer semiconductors have demonstrated their potential use in numerous applications such as organic light-emitting diodes (OLEDs),^[1,2] organic photovoltaics (OPVs),^[3,4] and organic field-effect transistors (OFETs)^[5,6] as well as chemical sensors and biosensors,^[7–9] due to the intrinsic properties of mechanical flexibility, thermal stability and solution processing ability. Among various conjugated polymer semiconductors, poly(3-hexylthiophene) (P3HT), as the pioneer or representative of polymer semiconductors, is by far the most studied one, on account of the simple structure and easy availability as well as its relatively high performance.^[10–15] Since it was firstly used as the semiconducting channel, the OFET devices featured a field-effect mobility of $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in 1986 and improved to 10^{-2} order of magnitude by choosing regioregular (rr) head-to-tail one in 1996,^[16,17] and P3HT was extensively investigated to unravel the self-organization behaviors and relationships between aggregation structure and performance of polymer field-effect transistors (PFETs).^[18–21] It is confirmed that the charge mobility of P3HT is depending on the intrinsic properties (degree of regioregularity and molecular weight),^[10,21,22] characteristics of the semiconductor-dielectric

interface,^[23,24] and especially the microstructure of the thin films.^[25–27] Over the years, some methods have obtained great successes in enhancing the mobility of P3HT, such as using new film preparation methods,^[28] polymer electrolyte dielectrics,^[24] and improving the crystallinity by ultrasound.^[25] However, the highest hole mobility value among the P3HT thin film PFETs using SiO_2 as the dielectric is about $0.28 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to date, which is achieved by using new functionalized self-assembled monolayers modified insulator substrate and dip-coating method with thermal treatment in 2005 and 2006, respectively.^[29,30] The value is still lower than some of its derivatives and donor-acceptor conjugated polymer.^[31,32] Therefore, it is of great challenge to obtain high mobility of P3HT and is significant to reveal the microstructure-property relationship, which is valuable for promoting its better application and is expected to provide standard guidance for other polymer semiconductors.

Noteworthy, the solvent vapor assisted spin-coating (SVASP) method was reported to improve the mobility of P3HT-based thin film transistors, which presents almost the same or even better effect to the combination of normal spin-coating and subsequent solvent vapor annealing.^[33] As we know, thermal annealing is another method frequently used to improve the polymer films' quality, involving crystallinity, orientation and surface morphology. Herein, in this report, we realized two step processes to fabricate high performance P3HT PFETs by using solvent vapor assisted spin-coating and thermal annealing (SVASP-TA). The films made by normal spin-coating (SP), normal spin-coating and thermal annealing

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(SP-TA), and SVASP were also prepared as references. The optimal hole mobility was $0.38 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for the SVASP-TA films-based transistors, which was one of the highest reported values and 10-fold higher than that of normal spin-coating one. The relationship between the microstructure and device performance was fully explored. The remarkable mobility is associated with the synergistic effects of SVASP and thermal annealing, which bring highly crystallinity of the thin films and highly ordered packing of the molecules.

EXPERIMENTAL

Materials and Instruments

The regioregular P3HT ($\geq 90\%$ head-to-tail, $M_w=87 \text{ kDa}$) was purchased from Sigma-Aldrich Co., and used as received.

Absorption spectra were recorded on a U-3900 UV-Vis spectrophotometer. Atomic force microscopy (AFM) measurements of film morphology were imaged on a SPI 3800/SPA 300HV (Seiko Instruments Inc., Japan) atomic force microscope in tapping mode. The one-dimensional (1D) out-of-plane grazing incident X-ray diffractions (GIXD) were measured using Rigaku Smartlab X-ray diffractometer equipped with a copper target (2.2 kW), CBO mirror ($\text{K}\alpha_1$ line, $\lambda=1.5406 \text{ \AA}$). The 2D-GIXD measurements were carried out at Shanghai Synchrotron Radiation Facility (SSRF) on beamline BL14B1 with $\lambda=1.24 \text{ \AA}$. The incidence angle of 0.16° was chosen to optimize the signal-to-background ratio. The image diffraction patterns were recorded using the image plate Mar345.

Device Fabrication and Measurement

The Si/SiO₂ substrates, 300 nm thermally oxidized SiO₂ layer and

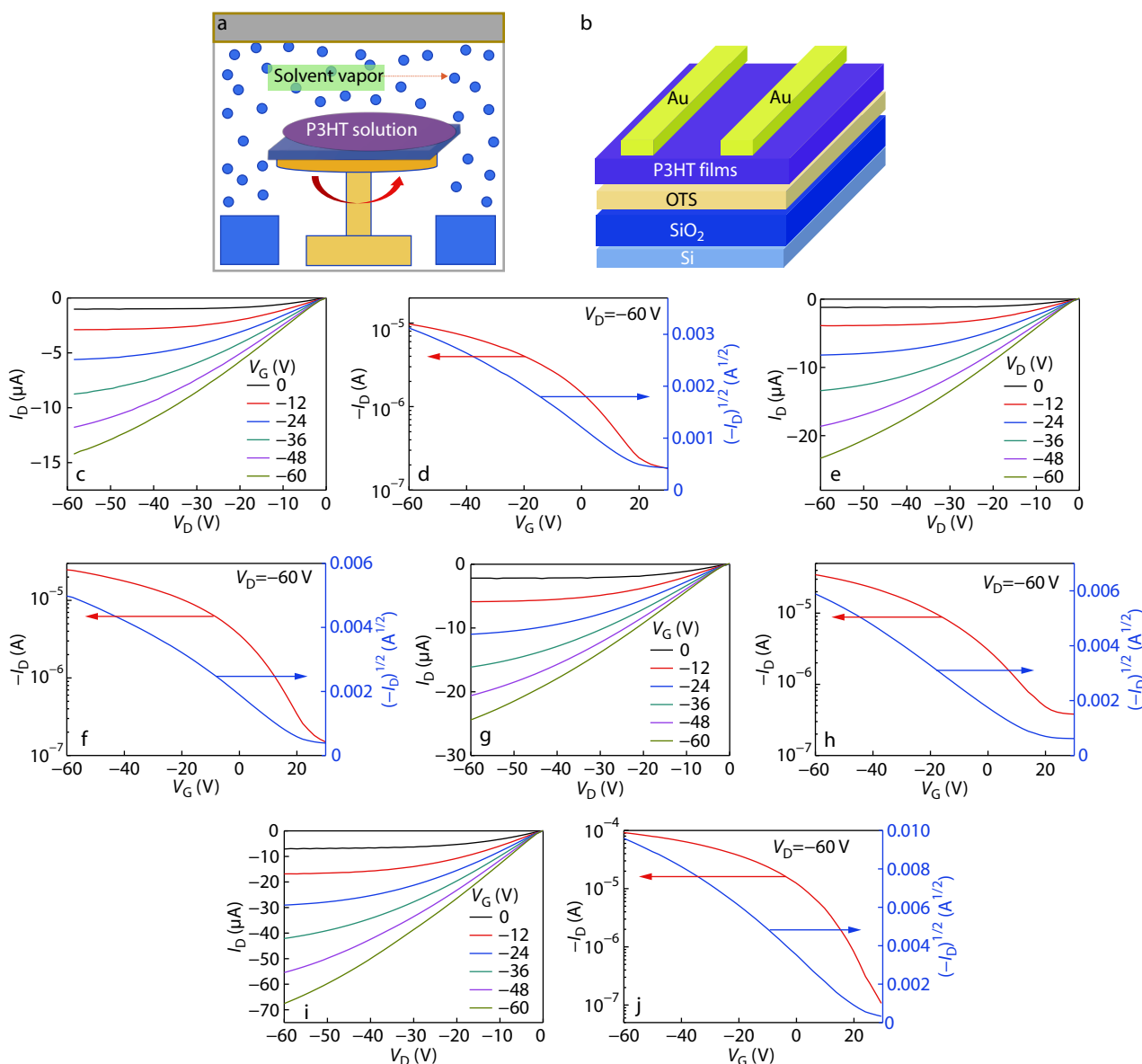


Fig. 1 (a) The schematic diagram for SVASP method; (b) the device configuration of the transistors; (c–j) typical output and transfer characteristic curves of transistors based on the P3HT thin films prepared with different conditions; (c, d) normal spin-coating; (e, f) SP-TA; (g, h) SVASP; (i, j) SVASP-TA.

its dielectric capacitance $C=10 \text{ nF}\cdot\text{cm}^{-2}$, were cleaned with deionized water and then immersed into hot sulphuric acid (98%) and hydrogen peroxide (V/V=2/1) mixed solution for 15 min to get rid of organic compounds physically absorbed on the substrate, successively cleaned with deionized water, isopropyl alcohol and acetone, and at last dried with quick purged N_2 . Before modification, the substrates were dried at 80°C for 1 h in a vacuum oven, the octadecyltrichlorosilane (OTS) modification was carried out for about 4 h at 120°C by vapor-deposition method. Then the substrates were rinsed with chloroform, *n*-hexane, isopropyl alcohol and acetone by ultrasonic cleaning. Finally, the OTS-modified substrates were dried with quick purged N_2 .

The bottom-gate/top-contact (BGTC) PFETs were fabricated as follows: the P3HT solution ($10 \text{ mg}\cdot\text{mL}^{-1}$ in chlorobenzene) was preheated at 70°C for 30 min to ensure dissolution of the materials and then cooled down to room temperature. For the normal spin-coating method, the P3HT solution was directly spin-coated ($3000 \text{ r}\cdot\text{min}^{-1}$, 60 s) onto the OTS-modified substrates. For SVASP method, twelve bottles of chlorobenzene solvent were put into the spin-coater and then the spin-coater was sealed with the lid for 15 min before spin-coating. The schematic diagram was illustrated in Fig.1(a). The spin-coating process were carried out under ambient condition. Then, the films fabricated by normal spin-coating and SVASP methods were both annealed at 160°C for 30 min in the N_2 filled glove box. Finally, 50 nm Au layer was thermally evaporated as the source-drain electrode in high vacuum. The device configuration was shown in Fig.1(b). The characteristics of the PFETs were measured using a Keithley 4200 semiconductor parameter analyzer under ambient conditions.

RESULTS AND DISCUSSION

Fig. 1 shows the typical output and transfer characteristic curves of the thin film transistors with P3HT coated with the two methods (SP and SVASP), as well as the corresponding thermally annealed films. All the devices exhibited p-type transport characteristics. The device performances of P3HT thin films fabricated by normal spin-coating and SVASP before and after thermal annealing are summarized in Table 1. The optimal saturation mobility of the thin film transistors based on the as-spun P3HT films using normal method is $0.038 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ with an average mobility of $0.031 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ and the $I_{\text{on}}/I_{\text{off}}$ ratio is 5.3×10^1 . Noting that, the mobility of the normal spin-coated films here is significantly higher than that previously reported. The mainly reason is probably due to the improvement of the modification method of OTS (solution method in the previous

report and vapor method employed here). After being thermally annealed at 160°C , the optimal mobility is greatly improved to $0.11 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ ($\mu_{\text{ave}}=0.1 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$) and the $I_{\text{on}}/I_{\text{off}}$ ratio increase to 1.6×10^2 . For the SVASP films, the optimal mobilities are up to $0.13 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ ($\mu_{\text{ave}}=0.12 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$) and $0.38 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ ($\mu_{\text{ave}}=0.35 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$), the $I_{\text{on}}/I_{\text{off}}$ ratios are enhanced from 1.1×10^2 to 8.6×10^2 before and after thermal annealing, respectively. To the best of our knowledge, the value of $0.38 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ is one of the highest mobilities for P3HT-based transistors. Combined with the results discussed below, the enhancement of the device performance based on SVASP films, comparing to the normal spin-coated P3HT films, are ascribed to the higher crystallinity of the films and better ordered molecule packing in the films. It should be noted that the on/off current ratio is relatively low due to the high off state values, which is resulted from the doping of oxygen or moisture in air during the device measurement and the active films preparation. According to the reported research,^[34] when P3HT-based transistors were characterized in air and vacuum respectively, the threshold voltage and on/off current ratio were greatly affected, while the mobilities are almost the same. Thus, it is believed that the mobilities reported here are reliable, despite of the relatively high off state current values.

To investigate changes of thin film properties, we measured the UV-Vis absorption spectra of all the P3HT films firstly and the results are presented in Fig. 2. A slight red shift of the maximum absorption peak for the SVASP films in respect to the SP films ($\lambda_{\text{max}}=556 \text{ nm}$ to $\lambda_{\text{max}}=561 \text{ nm}$) can be observed. This suggests the extent of the conjugation of P3HT film achieved from SVASP is more extended and homogeneous. In addition, the shoulder peak at around 605 nm became more pronounced by thermal annealing, SVASP, or both. The strongest intensity at around 605 nm appeared for the SVASP-TA films, the weakest for the SP films and moderate for the films prepared by normal spin-coating with thermal annealing or SVASP. The fine structure has been attributed to interchain absorption whose intensity is a measurement of the degree of the inter-chain order in microcrystalline domains.^[35–37] Thus, a best ordered microstructure existed in the SVASP-TA films. Obviously, SVASP-TA films exhibit optimal cofacial π stacking and order, the worst for the normal spin-coating films. The results agreed well with the device performance.

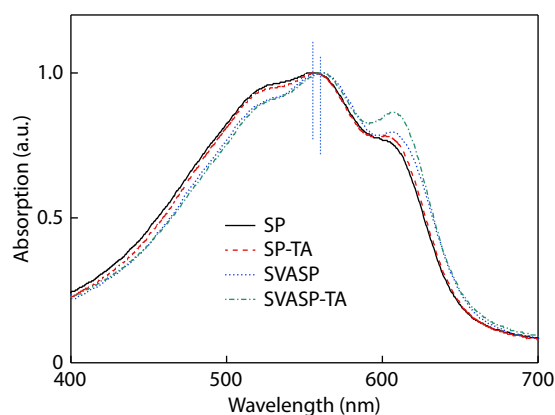


Fig. 2 UV-Vis absorption spectra of the four types P3HT thin films on quartz substrates.

Table 1 The device performances of P3HT thin films fabricated by SP and SVASP before and after TA.

P3HT thin film	μ_h^a ($\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$)	V_{th} (V)	$I_{\text{on}}/I_{\text{off}}$
SP	0.031 ± 0.005 (0.04)	24–30	5.3×10^1 – 8.2×10^1
SP-TA	0.10 ± 0.01 (0.11)	23–29	1.4×10^2 – 1.6×10^2
SVASP	0.12 ± 0.01 (0.13)	22–28	1.1×10^2 – 3.3×10^2
SVASP-TA	0.35 ± 0.02 (0.38)	19–27	8.6×10^2 – 9.6×10^2

^a Average mobilities were obtained from at least 10 transistors (the maximum mobility was shown in the blankets).

Grazing incidence X-ray diffraction (GIXD) of the thin films was performed to explore the variation of the crystallinity and orientation of the four type films. In the 1D out-of-plane GIXD patterns (Fig. 3), the previous diffraction peaks appear at 5.4° , corresponding to a d -spacing of $16.35 \text{ \AA}$, which are indexed to (100) plane. This suggests that the P3HT molecules adopt an edge-on packing mode. High order diffraction peaks of (200) and (300) appear in the four type thin films. Even though, the SVASP-TA films show the strongest intensity of (100) peak. On contrast, the SP films present the weakest diffraction peak intensity. This result indicate, undoubtedly, the film crystallinity can be enhanced by both solvent vapor and thermal annealing, and their effects on crystallinity were nearly comparable. The (100) peak intensity (I) is $I_{\text{SVASP-TA}} \approx 1.9I_{\text{SVASP}} \approx 1.8I_{\text{SV-TA}} \approx 2.9I_{\text{SP}}$. The relationship of the carrier mobility values is $\mu_{\text{SVASP-TA}} \approx 3\mu_{\text{SVASP}} \approx 3.5\mu_{\text{SV-TA}} \approx 11.3\mu_{\text{SP}}$. Apparently, it is not a linear correlation between the mobility and crystallinity of the out-of-plane films.

Furthermore, 2D-GIXD test was carried out to characterize the orientation and molecule packing motif of the four samples and the results are shown in Fig. 4. In the q_z -axis, the change trend of diffraction spot intensity was consistent well with the 1D out-of-plane result. In the q_{xy} -axis, faint (010) peak, corresponding to the π - π stacking diffraction, emerged in SVASP films, which became more pronounced in SVASP-TA films. This reflected a better regularity and order of the molecules arranged in the in-plane films. The 1D- and 2D-GIXD results demonstrated that the SVASP method can bring the enhancement of regularity and order both in the out-of-plane and in-plane films, which is also demonstrated in the UV-Vis absorption spectra. According to the reported researches,^[38,39] when P3HT films were spin-coating from higher boiling point solvent *o*-dichlorobenzene or post solvent vapor treatment, the films presented a much more ordered

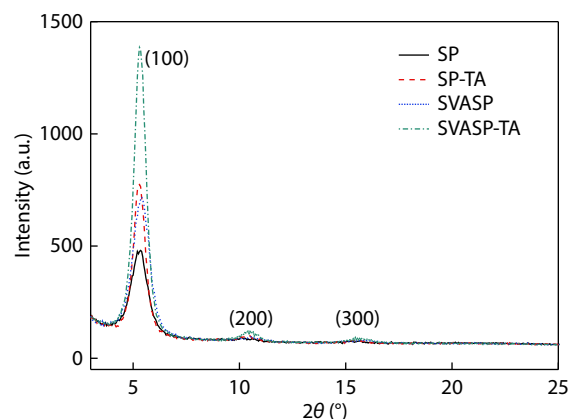


Fig. 3 1D-GIXD patterns of the P3HT films.

structure. Understandably, the mechanism of SVASP method on the structure regulation is similar to that of using higher boiling point solvent process. The solvent evaporation rate is much slower and the P3HT molecule can sufficiently self-assemble into a more ordered structure. Fig. 5 illustrates the schematic diagram for the variation of the molecule arrangement. The crystallinity and regularity could be gradually improved by post thermal annealing, solvent vapor assistant, and both processes. In addition to the crystallinity in the out-of-plane film, the efficient π - π stacking in the in-plane film also plays an important positive effect on the carrier transport, especially for the interchain transport. And consequently, the highest mobility is expected for the SVASP-TA films-based device, which is consistent with the experiment results. Combined the GIXD with the mobility values, it is inferred that the mobility can be greatly improved when the crystallinity and order are both increased to a certain extent.

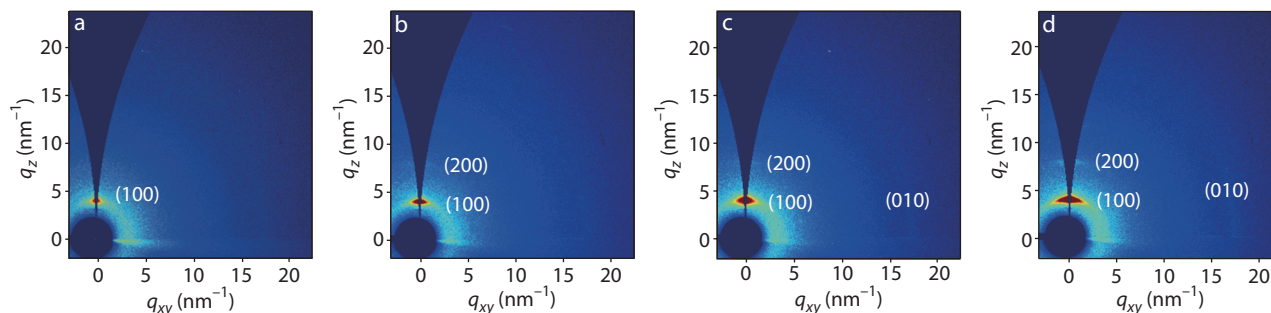


Fig. 4 2D-GIXD patterns of the P3HT films: (a) normal spin-coating (SP), (b) normal spin-coating and thermal annealing (SP-TA), (c) SVASP, (d) SVASP and thermal annealing (SVASP-TA).

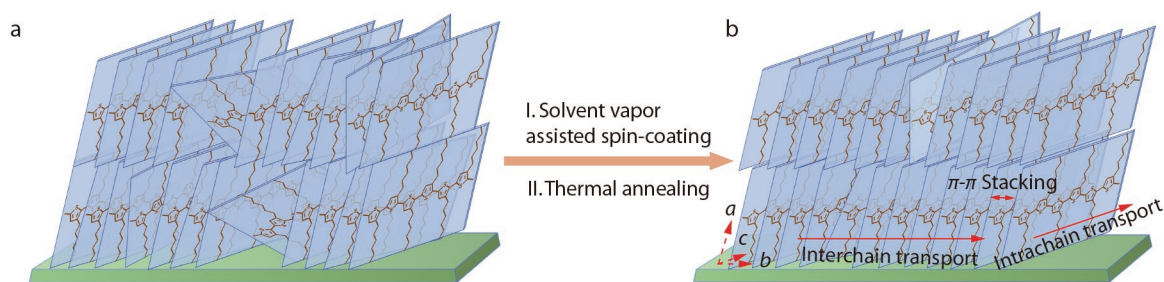


Fig. 5 Schematic diagram of the P3HT molecule arrangement of normal spin-coating films (a) and SVASP-TA films (b).

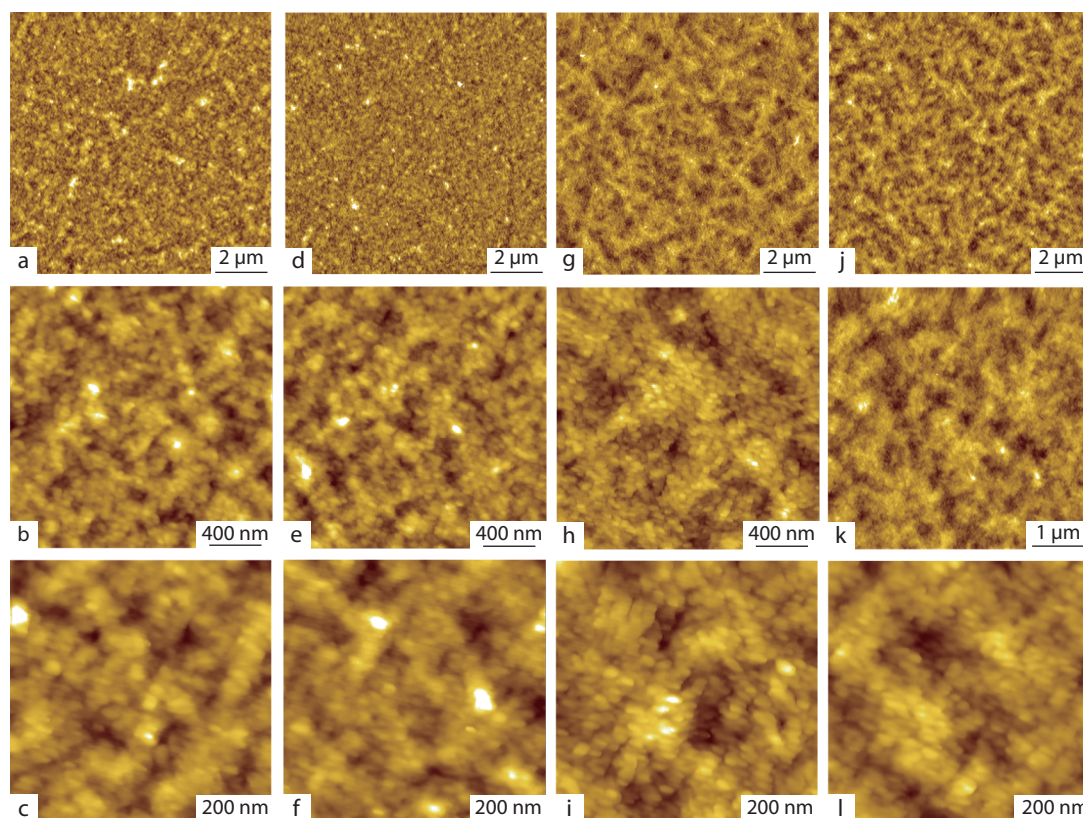


Fig. 6 Different scales of AFM images of P3HT thin films: (a–c) normal spin-coating films; (d–f) SP-TA films; (g–i) SVASP films; (j–l) SVASP-TA films.

The device performance is synergistically enhanced by SVASP and thermal annealing treatment.

To further understand the effect of solvent vapor and thermal annealing on the film morphology, AFM was used to investigate surface morphologies of the four type films and the images are shown in Fig. 6. All the films exhibit fine uniformity and continuity. It can be seen roughly that the four type films are composed of nano-grains (Figs. 6c, 6f, 6i and 6l). Nevertheless, the SVASP films before and after thermal annealing exhibit fibrous aggregation structure (Figs. 6g and 6j). This is probably resulted from the longer molecule self-assembly time during the film formation process of solvent vapor assisted spin-coating method. Due to the similar formation of the four type films, *e.g.*, nano-grains, the variation morphology is not considered as one of the main reasons for the improved performance, which stem from the ordered structures both in the out-of-plane and in-plane film.

CONCLUSIONS

In conclusion, two step processes (SVASP and thermal annealing) fabrication of P3HT films was demonstrated in synergistically enhancing the field-effect mobility. A high mobility up to $0.38 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was achieved, which is one of the highest values and 10-fold higher than that of the normal spin-coating films-based PFETs. Compared with the normal spin-coated P3HT films without and with thermal annealing, as well as their corresponding un-thermal annealing films, the SVASP-TA films exhibited the most favourable film microstructure for

the charge-carrier transport, as judged from UV-Vis absorption spectra and GIXD. The more ordered molecule packing referred to the intermolecular π - π stacking and high crystallinity were responsible for the significantly improved mobility. The research is helpful for us to understand the microstructure-property relationship. And it is believed that the solvent vapor assisted spin-coating method will be an effective strategy in enhancing the performance for other polymer semiconductors.

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