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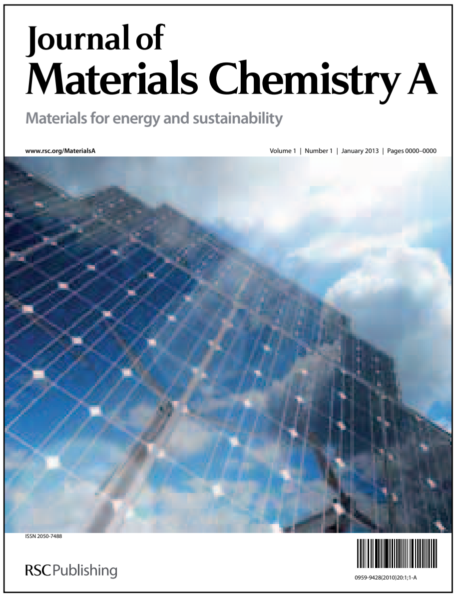

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The Synergic Regulation of Conductivity and Seebeck Coefficient in Pure Polyaniline by Chemically Changing the Ordered Degree of Molecular Chain

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Abstract

The pure polyaniline (PANI) films with different molecular chain packing state were successfully prepared by simply tuning the m-cresol content in the solvent. The SEM and AFM images display the films are dense and smooth. Vis-UV spectrum and Raman spectrum suggested that the conformation of PANI molecules changed from compacted coil to expanded coil by the chemical interactions between PANI and m-cresol, which enhanced the delocalization of π-polarons along the polymer chain. The XRD analysis indicated that the PANI molecular chain with different ordered degree formed during the solvent evaporation process. Furthermore, the measurement of temperature-dependent electrical conductivity confirmed that the ordered regions in PANI molecular structure were enhanced with increasing m-cresol content, which decreased the hopping barrier and increased the carrier mobility. Consequently, when m-cresol content increased, the electrical conductivity increased remarkably, while the Seebeck coefficient kept the same level or slight increase. The experimental results clearly reveal the intrinsic effect of molecular structure on electric transport of conducting polymers. It strongly suggests that increasing the ordered regions in the polymer molecular chain structure is an effective way to improve the thermoelectric properties of conducting polymers.

Introduction

Thermoelectric (TE) materials have great potential for applications in both power generation and solid state cooling or heating. Organic semiconductor materials offer numerous advantages over inorganic semiconductors for thermoelectric applications, such as low density, low cost due to rich resource, high toughness and elasticity. [1-2] Furthermore, organic materials inherently possess a low thermal conductivity, which increases their energy conversion efficiency in terms of the performance of a TE material evaluated by its dimensionless figure of merit $ZT= S^2\sigma T/\kappa$ (S, σ, κ and T are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively). Among the typical conducting polymers, polypyrrole (PPY), polyaniline (PANI) and poly (3,4-ethylenedioxythiophene) (PEDOT) have recently attracted wide attention as promising candidates as TE materials.[3-13] However, poor electrical transport properties of polymers, including low electrical conductivity (σ) and low Seebeck coefficient (α), have excluded them as feasible candidates for thermoelectric materials in the past. [3] Up to now, the power factor ($\alpha^2\sigma$) for most polymer thermoelectric materials is 2 or 3 orders of magnitude less than those of the state-of-the-art inorganic TE materials.[6-9] In order to explore the feasibility of using polymers for TE materials, it is urgent to find an effective way to improve the conductivity and Seebeck coefficient simultaneously.

In conventional semiconductors, adjusting the carrier concentration by doping or other methods is the common method to tune the electrical transport properties. However, σ and α often show opposite dependences on the change of carrier concentration because of the strong correlations between σ and α, which makes it difficult to improve the power factor only by optimizing doping level in a conducting polymer. [14-15] Therefore, it is a big challenge to realize the synergic regulation of conductivity and Seebeck coefficient in organic TE materials.

Generally, improving carrier mobility is the most effective way to increase both electrical conductivity and Seebeck coefficient.[6,16] For most of conducting polymers, carrier transport is primarily controlled by the inter-chain and intra-chain hopping processes and follows the variable-range-hopping (VRH) model.[17-18] According to the VRH model, the average hopping distance (mean free path) is directly related with the conformation and arrangement of polymer chains. Therefore, carrier mobility is very sensitive to the conformation and arrangement of polymer molecules. In recent years, it has been reported that increasing the ordered degree of polymer molecular chain arrangement is an effective way to improve the TE properties.[4-6,8-9] From 2009, several groups have reported the significant enhancement of power factors of PANI/carbon nanotube (CNT) composites by enhancing the electrical conductivity and Seebeck coefficient simultaneously.[4,7,8] It is conjectured that the strong π–π interactions between carbon nanotubes and aniline molecules in the composite would induce the formation of an ordered chain structure and therefore improve both the electrical conductivity and Seebeck coefficient. Similar results were reported in PANI/graphene composites subsequently.[6,9] Furthermore, in 2012 the PANI based composites with highly oriented structure at the molecular level was fabricated by a combination of PANI/CNT interfacial chemical interaction and electrical field induced aligning in electro-spinning process.[5] It was reported that the PANI chains were highly oriented in the electric field direction, which greatly enhanced the conductivity and Seebeck coefficient in the chain alignment direction. More recently, it was reported that in Te/PEDOT:PSS composite the interface interactions between Te nanowires and polymers led the formation of interface layer with a higher degree of organization of polymer molecules, which provided the simultaneous enhancement in electrical conductivity and Seebeck coefficient of the composite.[10] Although previous studies on TE properties of inorganic/conducting polymer composites revealed that the positive effect of increasing ordering degree of polymer molecular arrangement on σ and α, it is still difficult to give clear explanations for the intrinsic effect of molecular structure on electrical transport. The electrical transport in the inorganic/conducting polymer composites is complex because there are multiple factors which may influence the transport process in diverse ways, such as the distribution and structure features of the inorganic particles, interfacial layer structure, and so on. A clear understanding of the intrinsic effect of polymer chain structure on the transport properties is expected to open a new way to design high performance polymer TE materials.

In the present work, we try to tune the molecular chain alignment in pure PANI and investigate its intrinsic influence on electrical transport properties. The PANI films with different ordering degree of molecular chain alignment were successfully prepared by using solution method through changing the m-cresol content in the solvent. The combination of X-ray diffraction analysis (XRD), Vis-UV spectrum analysis and Raman Spectrum analysis revealed that, there exist ordered regions in the polyaniline film and the portion of the ordered regions increased with increasing m-cresol content. The temperature dependence of electrical conductivity and the increase of Seebeck coefficient also confirmed the strong correlation between electrical transport and order/disorder structure features. This study suggests that increasing the ordered region in the polymer molecular structure is the effective way to realize synergic regulation of conductivity and Seebeck coefficient and therefore improve the TE properties of conducting polymers.

Experimental

The polyaniline powder was synthesized by the conventional oxidation polymerization of aniline with ammonium peroxydisulfate (APS) as the oxidant and hydrochloric acid as dopant.[19] The obtained powder was put into 0.1M ammonia solution and the solution was stirred for 24h at room temperature. The suspended solution was filtered, washed with deionized water and ethanol three times each and then dried under vacuum at 60^{o}C. The obtained powder was emeraldine-based polyaniline. The polyaniline was further doped again by mixing with camphorsulfonic acid (CSA) at a mole ratio of 1:0.5 through solid state reaction.[20] 0.20g CSA-doping polyaniline powder was added into 6ml chloroform/m-cresol mixed solvent with different m-cresol content (percent by volume) , and then the solution was stirred for 8 hours at room temperature. After the process, the powder was dissolved in the solvent forming blackgreen solution. The obtained CSA-doping polyaniline solution was cast on 20×20 mm^2 glass substrates.

The morphologies of the films were characterized by scanning electron microscopy (SEM) (FEI Magellan 400) and atomic force microscope (AFM) (SPA 400, Seiko, InC. Japan). Raman spectra were recorded using Dilor LabRam-1B ($\lambda_{exp.}$ = 632.8 nm). X-ray diffraction (XRD) measurement was carried out using a diffractometer (Rigaku D/max 2550) with CuKα radiation (λ=0.15406 nm). UV-Vis absorption spectrum analysis was performed on a Perkin-Elmer UV-Vis spectrophotometer (Lambda 950, Walthan, MA) in a wavelength range of 300–1000 nm.

The electrical conductivity and Seebeck coefficient were measured following the methods previously reported.[5] The carrier concentration and carrier mobility measurements were performed in a Quantum Design Physics Property Measurements

System (PPMS).

Results and Discussions

The morphologies of the films were characterized by SEM and AFM. It was found that the film prepared from the pure chloroform (0% m-cresol) is rough and brittle. But when a few m-cresol (>5%) was added into the solvent, all the prepared films became smooth and compact. The typical SEM and AFM images of the films (prepared from 5% and 100% m-cresol content, respectively) are shown in Fig.1. The films are homogenous and smooth. No pores or particles inclusions were found in the film.The AFM images give further evidence that the roughness averages (Ra) of the films are less than 2nm.

Fig.2(a) shows the Vis-UV spectra of PANI in mixed solvent with different m-cresol content. The PANI in the solvent with pure chloroform (0% m-cresol) showed the three characteristic absorption bands 340, 440 and 750nm associated with π-π^*, polaron-π^*, and localized π-polaron band transitions of polyaniline ES.[21] With the increase of m-cresol content in the mixed solvent, the localized polaron absorption peak of PANI became weaken and the peak at 750nm obviously shifts to the high wavelength (from 750nm to 950nm). For PANI in pure m-cresol solvent, both peaks at 350nm and 750nm disappeared, while a very intense free carrier tail commencing at 1000nm was observed. The red shift and the weakening of the polaron absorption peaks (at 350nm and 752-950nm) are corresponded to the state-change of polarons from localization to delocalization and the appearance of 1000nm tailing peak corresponds to the complete delocalized polarons, which suggest the conformation of PANI changes from compacted coil to expanded coil.[21] PANI molecules show compacted coil conformation in chloroform or most other solvents because of the strong Van der Waals attractions between the functional group in the polymer chain, but when the CSA-doping polyaniline was dissolved in m-cresol an additional special interaction would take place, in which the carbonyl group in CSA forms a hydrogen bonding with the hydroxyl group of m-cresol.[22] The formation of hydrogen bond between CSA and m-cresol may result in positive ions (imine nitrogen in the polymer chain) and negative ions (CSA^-) become further apart, and therefore increased the electrostatic repulsion between imine nitrogen positive ions in polymer chain, which resulted in inner-force to overcome the Van der Waals attractions in the polymer chains, and pull the conformation of polymer from “compacted coil” to “expanded coil" and therefore promote linearity of the chains.[22] The conformation change reduced the π defects caused by ring twisting and strengthened the π-π conjugation interactions between rings and therefore lead to the delocalization of carrier along the backbone chain. Moreover, the Vis-UV spectra of PANI film prepared through the solvent method (Fig.2b) are similar with those of PANI dissolved in corresponding solvent, which suggests that the conformation of PANI molecules can be retained in the film even after the solvent was removed.

The Raman spectra further evidence the conformation changes, as shown in Fig.3. For the film prepared from the 10% m-cresol solvent, C-H bending vibration of quinoid/benzenoid ring (~1170 cm^{-1}), $C\text{-}N^+$ vibration of quinoid ring (~1335 cm^{-1}), delocalized polarons vibration in the extended polymeric conformation (~1378 cm^{-1} and ~1635 cm^{-1}) , C=N stretching vibration of quinoid ring (~1462 cm^{-1}), N-H stretching vibration (~1503 cm^{-1}) and C-C stretching vibration of benzenoid ring (~1589 cm^{-1}) were observed.[5] It was found that the $C\text{-}N^+$ vibration peak of the quinoid ring (1335 cm^{-1}) and delocalized polarons vibrations in the extended polymeric conformation (1378 cm^{-1} and 1635 cm^{-1}) increased with the increase of m-cresol content, which suggests that the increase of the m-cresol content resulted in the change of polyaniline conformation in the film from compacted coil to extend coil. The number of the effective delocalized polarons in the backbone chain was also enhanced.[27-28] Moreover, the C=N stretching vibration peak of the quinoid ring at 1462 cm^{-1} decreased with the increase of m-cresol content and vanished in the film prepared from 100% m-cresol solvent, which suggests that the chemical interactions between polyaniline and m-cresol solvent induced the chemical transformation of quinoid rings to benzenoid rings and caused the conformational changes of polyaniline from a coil-like structure to an extended one.[4,29] These results are consistent with those of the Vis-UV spectrum analysis.

The expanded molecular conformation facilitates the ordered chain packing during the solvent evaporation process because of the low steric hindrance caused by the high linearity of chains and the strong π-π interactions between polyaniline backbone chains. Fig. 4 is the XRD patterns of PANI films prepared from the mixed solvent with different m-cresol content. It was found that the films prepared from pure chloroform solvent or solvent with low m-cresol content (≦10%) show only two diffraction peaks at $2\theta = 6^{o}$ and 15^{o}, assigned to the periodic arrangement distance between the dopants and N atoms on adjacent main chains and the periodicity of the repeat unit of the PANI chain, respectively. [4,23] With the increase of the m-cresol solvent content in the mixed solvent (m-cresol≧25%), two new strong peaks at $2\theta = 20^o$ and 25^o appeared, assigned to the periodicities perpendicular and parallel to the polymer backbone chain, respectively. These two diffraction peaks became stronger and sharper with the increase of m-cresol content. These facts suggest the molecular arrangement of polyaniline became ordered with the increase of m-cresol content.

The change of electrical transport properties gives further evidence for the formation of the ordered structure in polyaniline molecules. Generally, temperature dependence of conductivity for conducting polymers shows semiconductor-like behavior ($d\sigma/dT>0$) from 0K-300K and follows the conventional variable range hopping (VRH) conduction model:

$$\rho(T) = b\cdot\rho_0 \exp\left[(T_0/T)^{1/n+1}\right] \qquad (1)$$

Where b, ρ_0, T_0 are the intrinsic constants, n is the dimensionality of the hopping (n=1, 2, 3) and T_0 is the characteristic Mott temperature that generally depends on the carrier hopping barriers.[17, 24] Fig. 5 shows the temperature dependence of conductivity of polyaniline film prepared from the mixed solvent with different m-cresol content from 20K-300K. The conductivity of PANI films increased with the increase of temperature, showing semiconductor-like behavior below 250K. However, the conductivity of films began to decrease with the temperature when the temperature is above 250K, showing metallic-like behavior, which becomes more and more obvious with the increase of m-cresol content (Fig.5a). Accordingly, the conductivity of the PANI films didn’t fit with the VRH model and the degree of deviation at high temperature became larger with the increase of m-cresol content, as shown in Fig.5b.

The change of electrical transport properties of PANI films prepared from mixed solvent with different m-cresol contents is considered to be caused by the formation of ordered regions in polyaniline’s molecular structure. Generally, conducting polymers show homogeneous disorder structure with compacted conformation and random arrangement (as shown in Fig.6a). The carriers transport by hopping in disordered regions, following the variable range hopping conduction model. For the films prepared from the solvent with m-cresol, some ordered regions with expanded conformation and aligned chains appear in the molecular packing (as shown in

Fig.6b). Thus the total resistivity ρ (T) includes the resistivity in ordered regions ρ_{ord} and the resistivity in disordered regions $\rho_{dis:}$

$$\rho (T) = a\cdot\rho_{ord} + b\cdot\rho_{dis}$$

where a and b are geometric weighting factors depending on samples.[17] Kaiser's et.al suggested that a heterogeneous model combining quesia-1D metallic conduction with hopping conduction can describe electric transport of PANI including ordered regions and disordered regions, shown as following: [17, 24]

$$\rho(T) = a\cdot\rho_m \exp(-T_m/ T) + b\cdot\rho_0 \exp[(T_0/ T)^{1/4}] \quad (2)$$

where ρ_m, T_m , ρ_0 are intrinsic constants (T_m is around 1000K for PANI[25-26]). The first contribution is related to the intrinsic quasi-1D metallic conductivity in ordered regions, and the second one comes from the 3D variable range hopping conduction in disordered regions.[18] Conductivity data of the films prepared from the solvent with m-cresol well fit with the heterogeneous model over the whole temperature, as shown in Fig.5c, which confirmed that there existed ordered regions in polyaniline molecules.

The $a\cdot\rho_m$, $b\cdot\rho_0$ and T_0 of the three samples are estimated by fitting Eq. (2) to the measured ρ data, as shown in Table 1. It appears that increasing m-cresol content leads to an increase of the relative weight of the metallic term, as evidenced by the increase of ration $b\cdot\rho_0/ a\cdot\rho_m$.[25] This strongly suggests an increase of the size of the ordered regions, which resulted in the obvious decrease of the hopping barrier, as evidence by the decrease of T_0. Thus, the carrier mobility of the film remarkably increased with the m-cresol content, as shown in Table 2. The carrier mobility of 10wt% film is only 0.6 $cm^2/V\cdot s$, but it increased to 4.4 $cm^2/V\cdot s$ for the 100% m-cresol film, while the carrier concentration kept little changes with m-cresol content. Consequently, both the conductivity and Seebeck coefficient of polyaniline film increased with the increase of m-cresol content. Especially, the electrical conductivity increased from 4.7S/cm to 220S/cm when the m-cresol content changed from 0% to 100%, as shown in Fig.7a. The power factor of polyaniline film prepared from 100% m-cresol solvent is about 60 times higher than that of polyaniline film prepared from solvent without m-cresol (Fig.7b).

Conclusions

The dense polyaniline films with smooth surface were prepared from the mixed solvent with chloroform and m-cresol. It was found that the polyaniline with expanded molecule conformation in solvent contributes to the ordered molecular chain packing during evaporation process. The increased ordered regions in molecular chain structure were confirmed by the measurement of Vis-UV, Raman spectra, XRD and temperature dependence of electrical conductivity. The increased ordering degree of molecular chain structure led to the obvious increase of carrier mobility and therefore remarkably improved the electrical conductivity with similar level of Seebeck coefficient. This study not only clearly reveals the intrinsic correlation between the electrical transport properties of conducting polymers and their molecular chain structure, but also suggests that increasing the ordered region in the polymer molecular chain structure is an effective way to realize synergic regulation of conductivity and Seebeck coefficient and therefore improve the TE properties of conducting polymers.

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References

1. O. Bubnova, Z. U. Khan, A. Malti, S. Braun, M. Fahlman, M. Berggren and X. Crispin, ***Nat. Mater.***, 2011, 10, 429.
2. Y. Du, S. Z. Shen, K. F. Cai and P. S. Casey, ***Prog. Polym. Sci.***, 2012, 37, 820.
3. D. Kim, Y. Kim, K. Choi, J. C. Grunlan, and C. Yu, ***ACS Nano***, 2011, 4, 513.
4. Q. Yao, L. D. Chen, W. Q. Zhang, S. C. Liufu and X. H. Chen, ***ACS Nano***, 2010, 4, 2445.
5. Q. Wang, Q. Yao, J. Chang and L. D. Chen, ***J. Mater. Chem.,*** 2012, 22, 17612.
6. Y. Zhao , G. S. Tang, Z. Z. Yu, J. S. Qi, ***Carbon***, 2012, 50, 3064.
7. C. Z. Meng, C. H. Liu and S. S. Fan, ***Adv. Mater.***, 2009, 21, 535.
8. R. C. Y. King, F. Roussel, J. F. Brund, C. Gorsb, R., ***Synth. Met.*** 2012. 162 1348.
9. Y. Du, S. Z. Shen, W. D. Yang, R. Donelson, K. F. Cai, P. S. Casey, ***Synth. Met.***, 2012, 161, 2688.
10. N. E. Coates, S. K. Yee, B. McCulloch, K. C. See, A. Majumdar, R. A. Segalman, and J. J. Urban, ***Adv. Mater.,*** 2013, 25, 1629.
11. Q. L. Zhang, W. J. Wang, J. L. Li, J. J. Zhu, L. J. Wang, M. F. Zhua and W. Jiang, ***J. Mater. Chem. A***, 2013, 1, 12109.
12. K. Chatterjee, M. Mitra, K. Kargupta, S. Ganguly and D. Banerjee, ***Nanotechnology***, 2013, 24, 215703.
13. H. Y. Ding, G. H. Zhou, Y. F. Zhu, Y. Zhang and L. D. Feng, ***Scripta Materialia***, 2013, 68, 957.
14. N. Mateeva, H. Niculescu, J. Schlenoff, and L. R. Testardic, ***J. Appl. Phys.***, 1998, 83, 6, 3111.
15. O. Bubnova, M. Berggren, and X. Crispin, J. Am. Chem. Soc., 2012, 134, 16456.
16. Y. Hiroshige, M. Ookawa, N. Toshima, Synth. Met. 2006, 156, 1341.
17. A. B. Kaiser and V. Skakalova, Chem. Soc. Rev., 2011, 40, 3786.
18. N. F. Mott, E. A. David, Electronic Processes in Non-crystalline Materials, Oxford University Press, Oxford. 1979.
19. P. N. Adams, P. J. Laughlin, and A. P. Monkman, ***Polymer***, 1996, 37, 3411.
20. Q. Yao, L. D. Chen, X. C. Xu and C. F. Wang, ***Chem. Lett.***, 2005, 34, 522.
21. R. Sainz, W. R. Small, N. A. Young, C. Valle´s, A. M. Benito, W. K. Maser, and M in het Panhuis, ***Macromolecules***, 2006, 39, 7324.
22. O.T. Ikkala, L. Pietila, L. Ahjopalo, H. Osterholm, and P. J. Passiniemi, ***J. Chem. Phys.***, 1995, 103, 9855.

23. Y. Yang and M. Wan, ***J. Mater. Chem.***, 2002, 12, 897.

24. A. B. Kaiser, ***Adv. Mater.*** 2001, 13, 927.

25. B. Sixou, J. P. Travers, Y. F. Nicolau, ***Synth. Met.***, 1997, 84, 703.

26. C.K. Subramaniam, A.B. Kaiser, P.W. Gilberd, C.-J. Liu, B. Wessling, ***Solid State Commun.***, 1996, 97, 235.

27. J. E. Pereira da Silva, S. I. Cordoba de Torresi, M. L. A. Temperini, D. Goncalves and O. N. Oliveira Jr, ***Synth. Met.***, 1999, 101, 691.

28. J. E. Pereira da Silva, D. L. A. de Faria, S. I. Cordoba de Torresi and M. L. A. Temperini, ***Macromolecules***, 2000, 33, 3077.

29. M. Cochet, W. K. Maser, A. M. Benito, A. Callejas, M. T. Martı´nez, J. M. Benoit, J. Schreiberb, O. Chauvet, ***Chem. Commun.***, 2001, 1450.

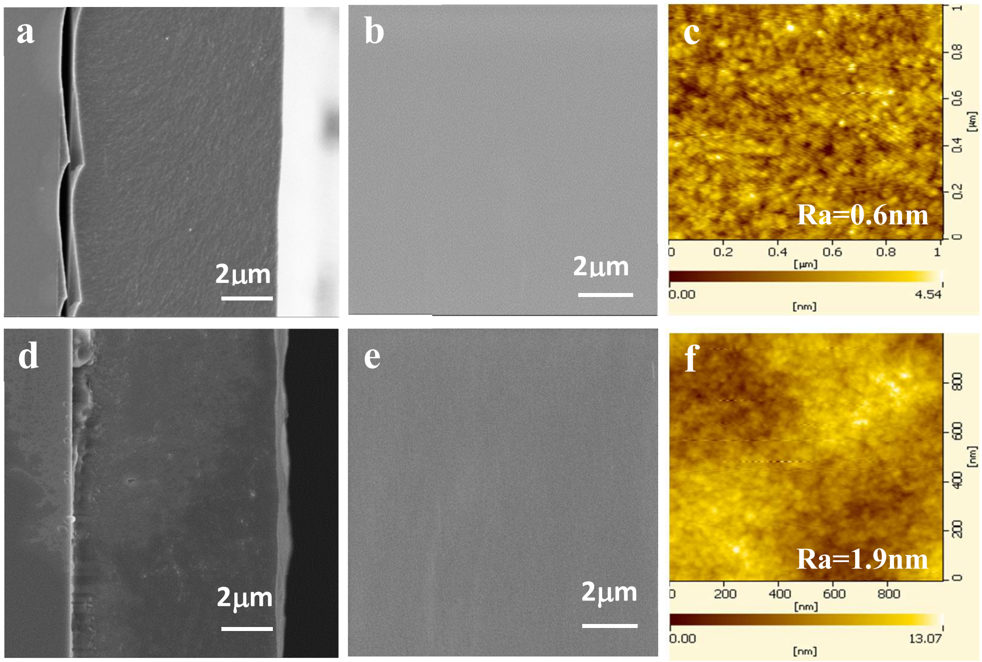


Fig.1 The SEM images (a, d: cross section; b, e: surface) and AFM surface images (c, f) of polyaniline film prepared from the mixed solvent with different m-cresol content (a, b, c: 5%; d, e, f: 100%).

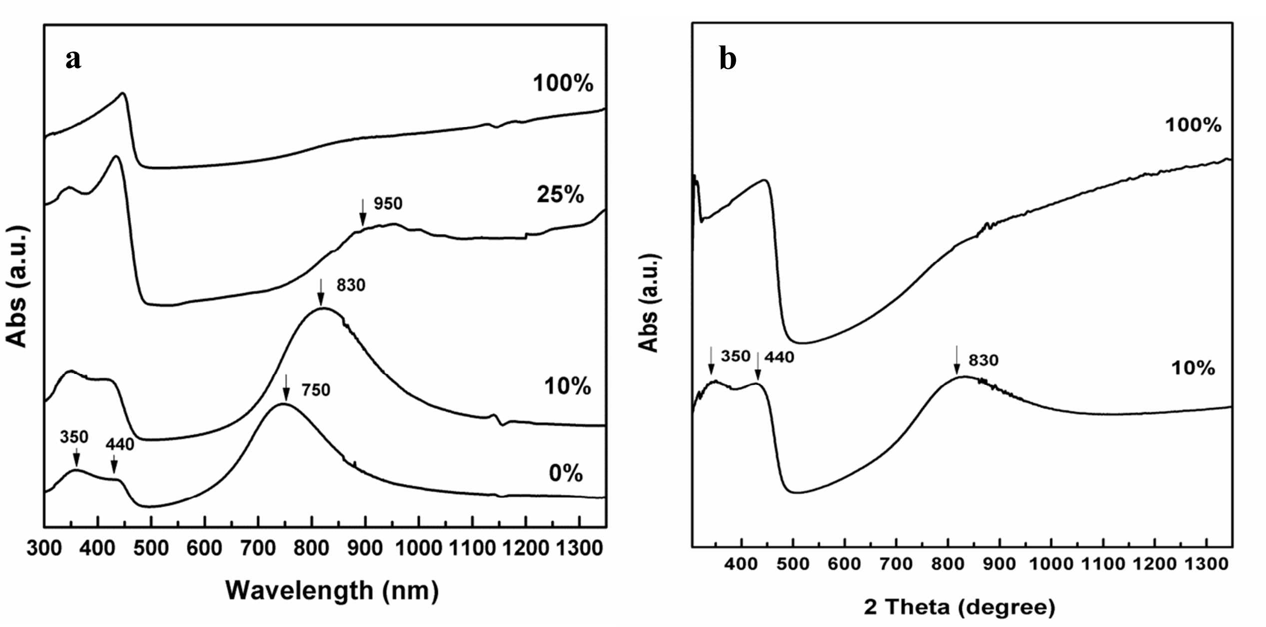


Fig.2 The Vis-UV spectra of PANI dissolved in mixed solvent with different m-cresol content (a) and PANI films prepare from mixed solvent with 10% m-cresol and from the pure m-cresol (b).

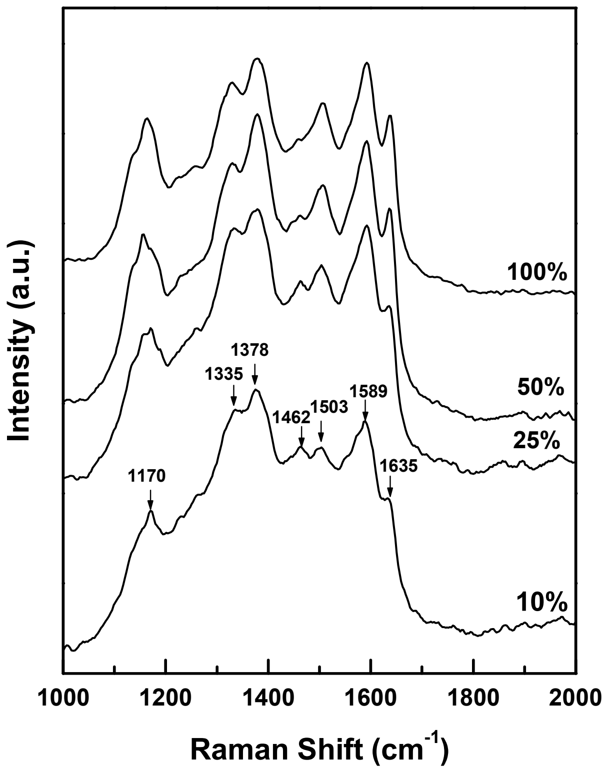


Fig.3 The Raman spectra of polyaniline films prepared from the mixed solvent with different m-cresol content.

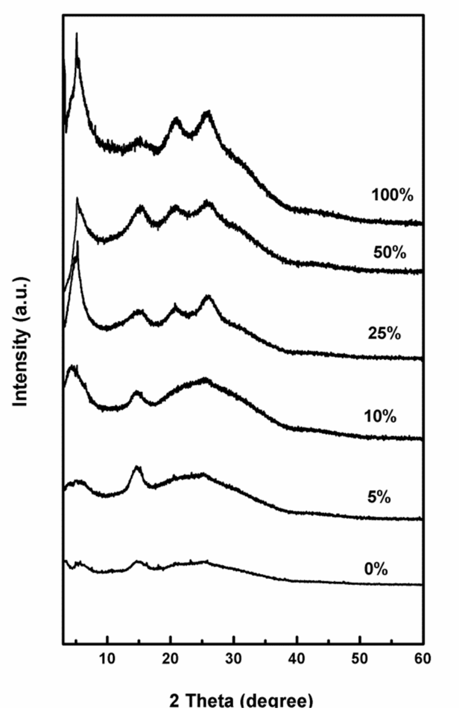


Fig.4 The XRD patterns of PANI films prepared from the mixed solvent with different m-cresol content.

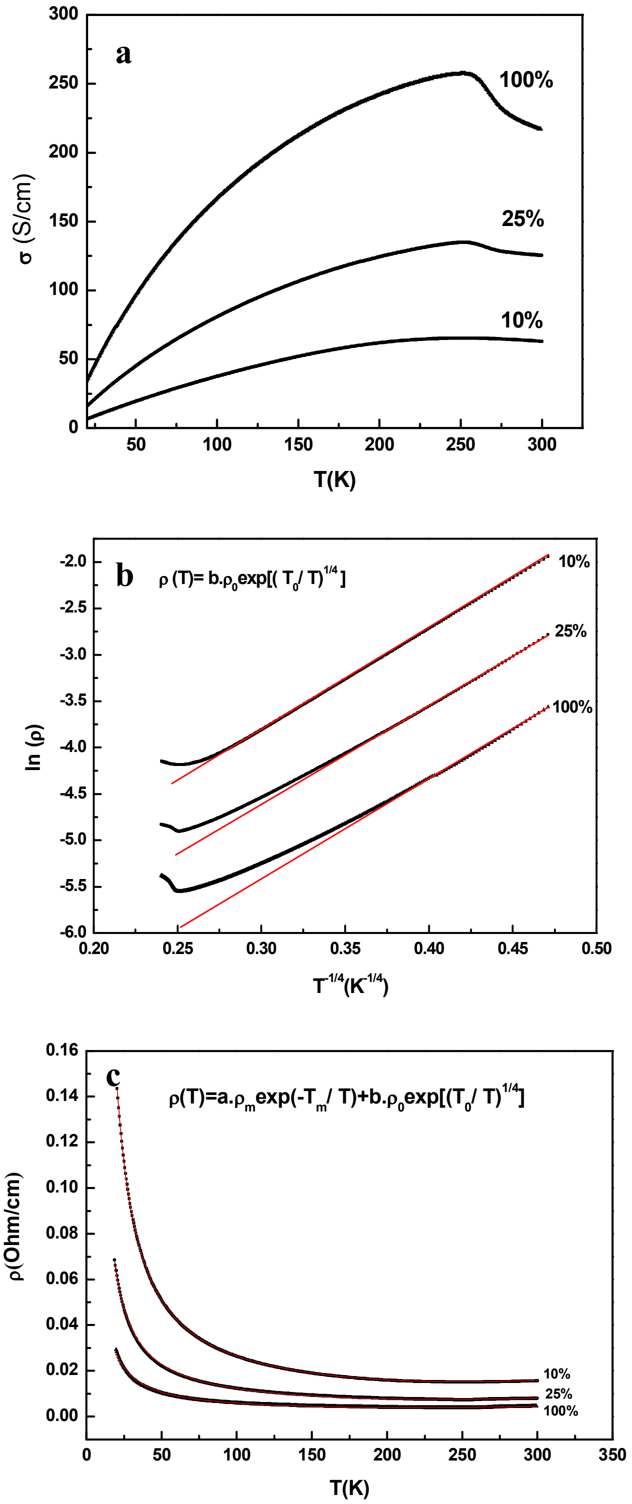


Fig.5 Temperature dependence of conductivity (resistivity): (a) σ vs T, (b) lnρ vs. $T^{-1/4}$ and (c) ρ vs. T of polyaniline film from 20-300K prepared from the mixed solvent with different m-cresol content. The black lines are the experiment values; The red lines are the fitted values respectively according to the VRH model (b) and heterogeneous model (c), respectively.

Table 1 Fitted values of $a\cdot\rho_m$, $b\cdot\rho_0$, T_0 in Eq. (2) by using measured σ for polyaniline films; the value of T_m is taken as 1000K[22-23]

Sample	**$a\cdot\rho_m$ ($10^{-1}\Omega$ cm)**	**$b\cdot\rho_0$ ($10^{-4}\Omega$ cm)**	**$b\cdot\rho_0/a\cdot\rho_m$**	**T_0 (10^4K)**
10% m-cresol	1.1	8.4	0.013	1.4
25% m-cresol	0.7	4.8	0.015	1.1
100 m-cresol	0.5	2.7	0.019	0.9

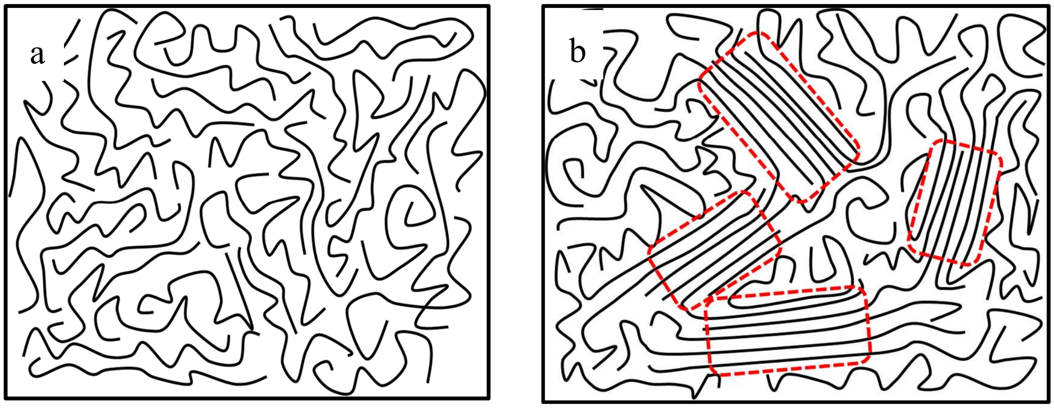
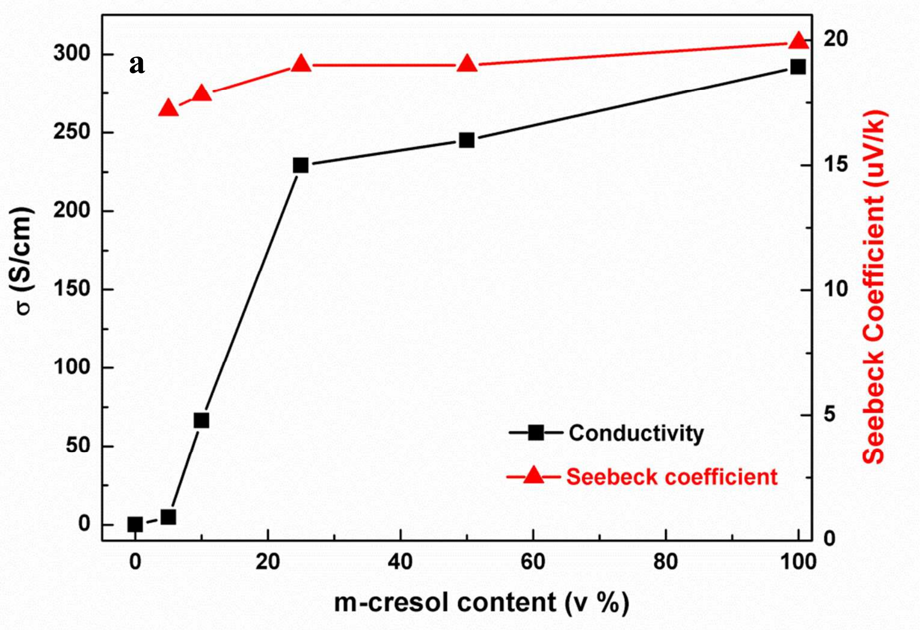


Fig.6 Schematic illustration of the packing state of polyaniline molecules with completely disordered structure (a) and with structure mixed with ordered and disordered regions (b).

Table 2 The carrier concentration and carrier mobility of PANI films prepared from the mixed solvent with different m-cresol content

m-cresol content (V/V)	10%	25%	100%
carrier concentration (1/cm^3)	7.06×10^{20}	6.12×10^{20}	4.16×10^{20}
carrier mobility (cm^2/V • s)	0.6	2.3	4.4



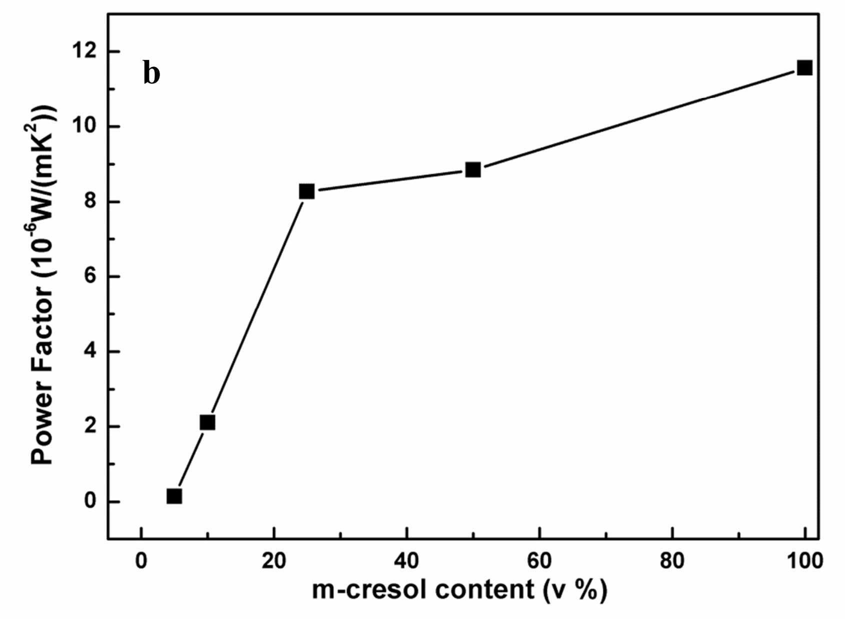


Fig.7 The electrical conductivity and Seebeck coefficient (a) and power factor (b) of polyaniline films prepared from the mixed solvent with different m-cresol content.