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Effect of addition of poly-(ethylene glycol) on electrical conductivity of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) hybrid

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Abstract **By mixing various concentrations of poly (ethylene glycol), a series of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) composite thin films were prepared. The electrical conductivity of the PEDOT-PSS/PEG thin films was measured by the four-probe method. Experimental results showed that the inclusion of poly(ethylene glycol) influenced the electrical conductivity of PEDOT-PSS film significantly. With the increase of PEG concentrations, the electrical conductivity sharply increased to reach a maximum and then slowly decreased down. Furthermore, the PEG molecular weight and environment temperature also played important roles on the electrical conductivity of PEDOT-PSS/PEG thin films. A good linear relationship was found between ln σ_{DC} and $T^{-1/2}$ within the entire temperature range detected.**

Keywords: PEDOT-PSS, poly(ethylene glycol), electrical conductivity, hybrid film, four-probe method.

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Conducting polymer has been very interesting[1,2] after being discovered due to its potential applications. Poly-(3,4-ethylenedioxythiophene)(PEDOT) has attracted much attention in the field of conducting polymer because of its high electrical conductivity, structural stability and other predominant property of its doped state. But the intrinsical state of PEDOT has a low extremely electrical conductivity and is neither soluble nor fused. Hybrid of poly(styrenesulfonate) (PSS) and PEDOT can form aqueous dispersion, and their coated films are highly stable in air. Meanwhile, the aqueous dispersion is processable, and the producing material keeps a high electrical conductivity resulting in the promotion of the application of PEDOT. Besides the favors described above, researches on the factors infecting PEDOT-PSS film electrical conductivity can also help us to solve some of the basic problems and factors on the conducting mechanism of conducting polymers. In the present work, PEDOT-PSS/PEG hybrid films were prepared by the mixing method and their electrical conductivity was measured by the four-probe method. These investigations were not reported before.

1 Experiment

(ⅰ) Reagents and instruments. PEDOT-PSS aqueous dispersion (trade name: Baytron P) was purchased from Bayer AG. Poly(ethylene glycol)s (MW= 400, 800, 2000, A.R.) were received from Merck-Schuchardt. Electrical conductivity of thin films was measured by Advantest R6142 program-mable DC potential gavanostatic generator and Keithley 196 multimeter. Films thickness was measured by thickness indicator (No.2 optics instrument company of Shanghai).

(ⅱ) Preparation of hybrid films. PEDOT-PSS dispersions were mixed by desired amount of PEG with different MW (i.e. Mn = 400, 800 and 2000). The mixtures were stirred continuously for 24 h at RT. The hybrid films were then prepared by casting those dispersions on freshly cleaned glass substrates. The coated samples were dried at 70℃ for 24 h. Films thickness was 30—50 μm.

(ⅲ) Measurements of electrical conductivity. The electrical conductivity of the films was measured by the four-probe method at various temperatures.

2 Results and discussion

(ⅰ) Effect of concentration and molecular weight of PEG on PEDOT-PSS. The mixed dispersions of PEDOT-PSS and PEG (Mn = 400, 800, 2000) of various concentrations were cast on glass substrates. Electrical conductivity of the films was measured by the four-probe method. Fig. 1 presents the curve of electrical conductivity of the above-mentioned hybrid films as a function of the concentration of PEG of various molecular weights. The electrical conductivity of PEDOT-PSS thin film in the absence of PEG was 0.1 S/cm. As shown in Fig. 1, the electrical conductivity changed significantly after the addition of PEG. Mixed by PEG400, the lowest MW one, where the concentration was below 1×10^{-2} mol/L, the electrical conductivity increased only from 0.1 to 0.24 S/cm. However, with a further increase of the PEG400's concentration, the electrical conductivity increased sharply and reached a maximum of 17.7 S/cm, which was two orders of magnitude higher than the negative sample, at a PEG concentration of 4.06×10^{-2} mol/L, and then slowly decreased down. Similarly, the electrical conductivity changed much for the PEDOT-PSS films after adding PEG800, from 0.1 S/cm to 1.7 S/cm when the concentration of PEG was below 1×10^{-2} mol/L. Whereas, it sharply increased, up to two orders of magnitude higher compared to the film without PEG, i.e. 14.2 S/cm, with the increase of PEG concentration until 3.13×10^{-2} mol/L, and again followed by a slow going down. It was noted that fine films were not obtained with a concentration of PEG2000 higher than 3.33×10^{-2} mol/L because the molecular weight of PEG2000 was relatively large. Never-

theless, the electrical conductivity of the PEDOT-PSS/PEG2000 films increased to 6.5 S/cm within a PEG concentration interval of $(0—1.25)\times10^{-2}$ mol/L, still being enhanced by one order of magnitude and then rapidly decreased. Furthermore, the molecular weight affected distinctly the electrical conductivity. At lower PEG concentration, mixing PEG of higher molecular weight resulted in a higher electrical conductivity of the hybrid film while it was opposite in the higher concentration range. In addition, the PEG concentration needed for the films to get the max electrical conductivity became lower when the molecular weight of PEG increased. And the film mixed by PEG of lower molecular weight had a higher maximum electrical conductivity value.

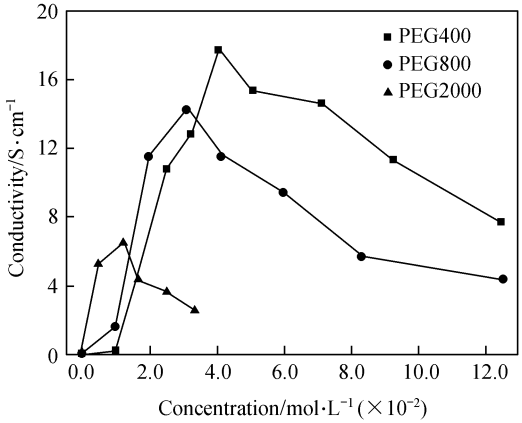

Fig. 1. Effect of PEG concentration, molecular weight on PEDOT-PSS conductivity.

(ii) The relationship of electrical conductivity of PEDOT-PSS/PEG hybrid films and the temperature. The electrical conductivity of PEDOT-PSS/PEG hybrid films was affected greatly by the environment temperature. Their relationship follows a quasi one-dimension variable range hopping model (1D-VRH)[5], which is described as

$$\sigma_{DC}(T)=\sigma_0\exp[-(T_0/T)^{1/2}], \quad (1)$$

$$T_0 = 8\alpha/ZN(E_F), \quad (2)$$

where $\sigma_{DC}(T)$ is electrical conductivity, T is temperature and σ_0 is a constant. T_0 can be interpreted as an effective energy separation of charge carrier. Relationship of T_0 and the localized length, the density of states is shown in (2), where α is the localized length, and E_F is the density of states at the Fermi level. k, Z are boltzmann's constant and the number of the neighboringest respectively. It is obtained by eq. (1):

$$\ln\sigma_{DC}(T)=-(T_0/T)^{1/2} + \ln\sigma_0. \quad (3)$$

T_0, an effective energy separation of charge carrier, can be calculated by the slope of $\ln\sigma_{DC}(T)$. The value of T_0 of the PEDOT-PSS/PEG hybrid film was calculated as ~745 K from Fig. 2, which was much lower compared to that of PEDOT-PSS film (T_0=~1700 K[5]). The results inferred that the inclusion of PEG could decrease the effective energy separation of charge carrier hopping, which resulted in the increase of the electrical conductivity.

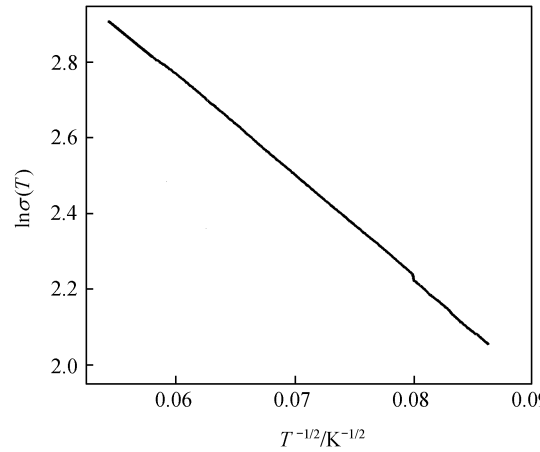

Fig. 2. Effect of temperature on PEDOT-PSS/PEG conductivity. Concentration of PEG400 is 7.18×10^{-2} mol/L.

3 Conclusion

The addition of PEG affected significantly the electrical conductivity of PEDOT-PSS film. And the effect of molecular weight of PEG on electrical conductivity presented a regular variation. The electrical conductivity of PEDOT-PSS/PEG hybrid films reached a maximum with the increase of PEG concentration. The environment temperature also played an important role in the electrical conductivity of PEDOT-PSS/PEG thin films. A good linear relationship was found between ln σ_{DC} and $T^{1/2}$ within the entire temperature range detected. By analysis, inclusion of PEG may result in the decrease of effective energy separation of charge carrier hopping, giving rise to the increase of the electrical conductivity.

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