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Research progress on the modification of organic highly conductive polymer PEDOT: PSS

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Abstract. PEDOT: PSS (poly(3,4-ethylenedioxythiophene): poly(4-styrenesulfonic acid)) is a high-profile organic conductive polymer, which is widely used because of its excellent conductivity and stability. The application of PEDOT: PSS is of great significance in the fields of energy, electronics, medical treatment and the environment. It offers an efficient, transparent, flexible, and environmentally friendly material option that drives various innovations and advancements. However, the traditional PEDOT: PSS can no longer meet the high requirements of today's electronic devices. Therefore, changing the conductivity, ductility and other properties of PEDOT: PSS through various physical and chemical methods has become an important topic. This paper reviews the progress of effectively improving the conductivity of PEDOT: PSS by reviewing PSS doping optimization, solvent doping modification (inorganic acid, organic reagent), and nanomaterial modification (CNTs, Graphene), so as to provide researchers with directions. Overall, PEDOT: PSS, as a material with excellent performance and wide application potential, has broad prospects for its application. With the continuous demand for flexible electronics, renewable energy, smart optoelectronic devices and biomedical applications, PEDOT: PSS will play an important role in these fields and promote the further development and innovation of related technologies.

Keywords: PEDOT: PSS, conductive organic polymer, modification, optimization, solvent doping, nanomaterials.

1. Introduction

In recent years, organic conductive materials, as a material with broad application prospects, have received great attention. Among them, PEDOT: PSS, as an important organic conductive polymer, Due to its excellent conductivity, transparency, and flexibility, it has been widely used in many fields such as organic solar cells, organic light-emitting diodes (OLEDs), and flexible electronic devices [1]. Therefore, PEDOT: PSS has achieved great success in the commercial field, and electronic devices such as PH1000, PH510, PH500, etc. using PEDOT: PSS as conductive electrodes have always occupied a large market share. It's estimated to be around $50 billion a year, and that number continues to grow [1]. However, the traditional PEDOT: PSS cannot meet the requirements of some high-performance devices because PSS hinders the transport of carriers and reduces conductivity [2]. Not only that, traditional PEDOT: PSS materials are sensitive to water and humidity, and are prone to problems such as water decomposition and ion migration, decreasing the material's stability as a result, which limits their

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application in some key applications [3]. Figure 1 illustrates its atomic structure. Accordingly, the modification of PEDOT: PSS composites has become the focus of research. The author reviews the research progress of effectively improving the electrical conductivity of PEDOT: PSS composites from the aspects of PSS doping optimization, solvent doping modification and nanomaterial modification.

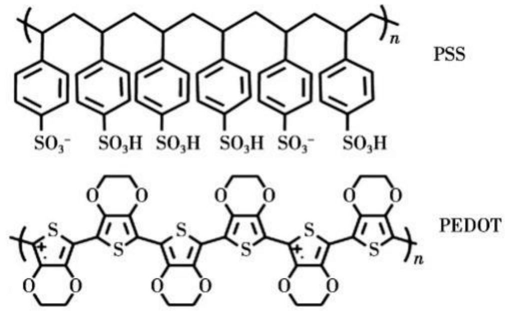

Figure 1. Molecule structures of PEDOT: PSS.

2. PSS doping optimization

PSS doping optimization refers to optimizing the conductivity of PEDOT: PSS composites by adjusting the doping process parameters of PEDOT: PSS composites, such as the PSS doping level, the PSS to PEDOT composition ratio, etc. The mechanism is: by improving the PSS doping process parameters, the formation and dispersion of conductive particles PEDOT can be promoted, and the particle size of PEDOT can be reduced, and the conductivity of the PEDOT: PSS composite material is positively related to the number of PEDOT conductive particles. Correlation, which facilitates the hopping of charge carriers between PEDOT nanocrystals.

T. Horii et al. used oxidative polymerization to obtain a PEDOT aqueous dispersion doped with PSS, and explored the influence of the composition ratio (α) of PSS and PEDOT repeating units on conductivity [4]. It has been found that PEDOT: PSS colloidal particles may achieve the highest conductivity of 700 S/cm when =2.3, and PEDOT nanocrystals are evenly dispersed in the weakly conductive PSS matrix, promoting the charge carriers in PEDOT nanocrystals. Jumping between crystals. From this, it can be concluded that PSS serves as a dopant to balance out PEDOT's positive charge and as a dispersant to evenly spread PEDOT's hydrophobic properties throughout water.

Xian Zeyu et al. looked at the impact of doping levels at PSS on PEDOT: PSS water dispersion conductivity and stability [5]. With the increase of PSS doping amount, the electrical conductivity of PEDOT: PSS decreased gradually, but the change was small; in the process of increasing PSS doping amount, the stability of PEDOT: PSS dispersion was improved well. When the mass ratio of monomer EDOT to PSS is 1:3, the electrical conductivity is 0.45 S/cm, and there is no delamination after standing still for one month, while maintaining good electrical conductivity and good dispersion stability. Although the conductivity of this doping process is very low, it cannot be directly applied in practice, but it can be used as a prerequisite for secondary doping.

3. Solvent doping modification

Solvent doping modification refers to the addition of certain solvents to PEDOT: PSS to improve the conductivity of the system. Commonly used solvents include inorganic acids, organic reagents, and ionic liquids. The conductivity improvement mechanism of solvent-doped PEDOT: PSS is mainly: (1) The solvent can change the grain size of PEDOT. The coarser the grain, the smaller the grain boundary area, thereby reducing the intergranular hopping barrier and promoting electron (2) The solvent can induce the phase separation between PEDOT and PSS, the structural transformation of PEDOT or the conformational change of the PEDOT chain, so as to promote the improvement of the conductivity of PEDOT; (3) The solvent can increase the concentration of charge carriers and enhance the charge transfer Rate.

3.1. Inorganic acid
To fabricate a film, I. Cruz-Cruz et al. added a small amount of diluted sulfuric acid to the PEDOT: PSS aqueous dispersion [6]. Since sulfuric acid will increase the viscosity of the PEDOT: PSS aqueous dispersion, thereby hindering the preparation of the film, it is necessary to dissolve sulfuric acid in deionized water first. When the volume ratio of sulfuric acid to deionized water is 1:4 and 1:3, the film has a conductivity of 103 S/cm, which is around 1400 times more than the conductivity of pure PEDOT: PSS film (which is about 0.07 S/cm). It demonstrates that the doping effect can be considerably improved by the addition of bisulfate ions (HSO4-), which can also accelerate charge transport in the system and encourage PSS enrichment on the film's surface and partial phase separation between PEDOT and PSS.

Ö. Yagci et al. prepared boric acid-doped PEDOT: PSS films by spin-coating technology, and applied them to the hole transport layer in solar cells [7]. The main role of boric acid in the device structure is to increase the open circuit voltage and fill factor. When 1.25 mg/mL boric acid was doped into PEDOT: PSS, the solar cell showed the best photovoltaic performance, with a fill factor of 46.9%, which is 8.6% higher than that without doping, and the power conversion efficiency is 2.14%, which is 0.35% higher than that without doping. Kelvin probe force microscopy (KPFM) measurements showed that boric acid-doped films increased the surface work function of indium tin oxide (ITO) compared to untreated PEDOT: PSS films, resulting in improved ITO and PEDOT: PSS. The interfacial effect between ITO and the organic active layer (P3HT: PCBM) facilitates the charge transfer.

S. M. Said et al. improved the conductivity by doping PEDOT: PSS with different concentrations of nitric acid [8]. It can be observed that as the concentration of nitric acid increases, the conductivity shows a general trend of increasing gradually. When doped with an aqueous solution of nitric acid with a volume fraction of 65%, the conductivity reaches an optimum value of 197 S/cm, which is 115.5 times higher than that of pure PEDOT: PSS film; analysis by Fourier transform infrared spectroscopy shows that the film is in Higher transparency is shown in the visible light range.

3.2. Organic reagents
Many efforts to increase the conductivity of PEDOT: PSS have been made over the past few decades with great success, as shown in Figure 2, in addition to physical methods such as heat treatment and light treatment, organic solvent treatment is the best way to improve PEDOT: PSS conductivity [9].

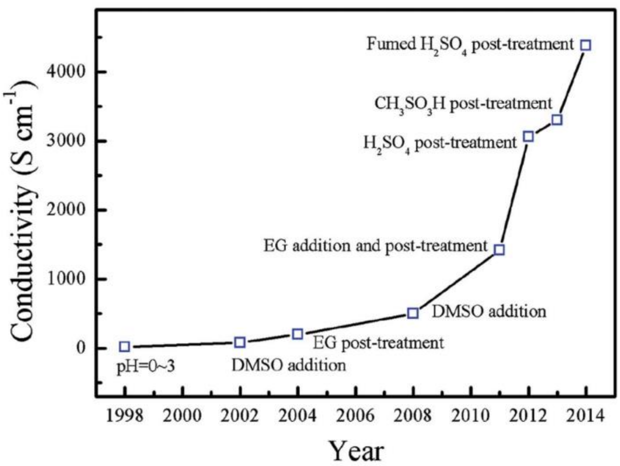

Figure 2. Timeline of conductivity values for PEDOT: PSS [10].

S. Park et al. studied the PEDOT: PSS films modified by different contents of secondary dopant sorbitol [11]. With the increase of dopant content, the work function of PEDOT: PSS thin film showed a steady decrease, while the conductivity gradually increased, especially when the mass fraction of sorbitol was 8%, and the conductivity increased to above 70 S/cm. The enhanced electrical conductivity was attributed to the intergranular size variation of PEDOT, resulting in a lowered intergranular hopping barrier.

T. Syrovy et al. studied the influence of N-methylformamide as a secondary dopant on the electrical properties, morphology and optical properties of helical rod-shaped monolayer PEDOT: PSS [12]. Through experimental tests, it was found that when doped with 5% N-methylformamide, the highest conductivity reached 78.3 S/cm, which was two orders of magnitude higher than that of pure PEDOT: PSS dispersion (0.3 S/cm). This is because the dielectric constant of N-methylformamide is very high, and the high dielectric constant will lead to an increase in electrical conductivity; N-methylformamide can also cause a conformational change in the spatial arrangement of PEDOT: PSS in the layer, optimizing the PEDOT. Alignment leads to increased conductivity

P. Wilson et al. studied the in-plane conduction mechanism of PEDOT: PSS doped with different concentrations of dimethyl sulfoxide (DMSO), and determined the electron transport model [13]. Experiments found that the in-plane conductivity increases with the increase of DMSO concentration in PEDOT: PSS. Especially when 5% mass fraction of DMSO was added, the room temperature conductivity could be increased to 130 S/cm. The variable temperature conductivity analysis showed that the variable range jump (VRH) index increased from 0.25 to 0.5; the electric field force microscope (EFM) showed that the PEDOT grain size increased by three times accordingly. Therefore, DMSO can coarsen the PEDOT grains, thereby shortening the charge jump length, resulting in an increase in conductivity

Zhang Shupeng et al. mixed several 100μL typical water-soluble vitamins into PEDOT: PSS to prepare composite films [14]. Experiments have found that when doped with 0.1 mol/L vitamin B3, the conductivity could be increased from 0.3 S/cm to more than 1 000 S/cm, especially when the solvent treatment temperature was 140 °C, the conductivity was the highest at 1285 S/cm. Studies have found that the enhancement of electrical conductivity depends on the structure of vitamins, and vitamins with multiple hydroxyl or carboxyl groups can significantly improve the electrical conductivity of composite films.

4. Nanomaterial modification

With the in-depth research on PEDOT: PSS, it is found that the combination of nanomaterials such as carbon nanotubes (CNTs), graphene and noble metal nanoparticles is the key to improving the conductivity of PEDOT: PSS. an important method of performance. However, nanomaterials have a common shortcoming, which is that they are easy to agglomerate, so that they cannot be uniformly dispersed in the system, so they cannot obviously show their outstanding performance, and even reduce the performance of the system.

4.1. CNTs

The mechanism of CNT modification is mainly as follows: (1) CNTs can provide free volume to promote ion diffusion; (2) CNTs and PEDOT: PSS matrix produce a network structure that can improve the host's conductivity; (3) The conductivity can be enhanced and the flaws in the PEDOT: PSS system can be considerably reduced by uniform CNT dispersion.

Cheng Hanlin et al. prepared PEDOT: PSS aerogels with different CNTs contents [15]. Through electrochemical tests, it was found that when the mass fraction of CNT was 10%, the PEDOT: PSS aerogel could maintain an ideal specific capacitance (30-50 F/g) within a certain range of scan rates. Therefore, a certain CNT content helped to improve the conductivity of PEDOT: PSS, and thus improve the capacitive properties of aerogel.

J. T. Illakkiya et al. prepared transparent PEDOT: PSS/single-wall carbon nanotube (SWCNT) composite film by spin coating technology [16]. It was found that the optimized loading ratio of SWCNTs in PEDOT can enhance the conductivity of the polymer without compromising the transparency of PEDOT: PSS. When 0.35% SWCNT was added, PEDOT: PSS's conductivity multiplied by six. This is because SWCNTs form a continuous network structure in the composite film to realize a conductive path for carrier flow by bridging the PEDOT dispersed in PSS.

4.2. Graphene

Combining graphene with the polymer can obtain polymer/graphene conductive composite material, which has both high conductivity and good processability [17]. The mechanism of graphene endowing PEDOT: PSS with electrical conductivity is mainly as follows: (1) Graphene provides a conductive channel by forming a strong π-π interaction with PEDOT; (2) The introduction of graphene can reduce the energy of charge transport on the PEDOT chain.

C.S. Pathak et al. studied the manufacture of PEDOT: PSS/graphite nanocomposite membranes [18]. When 0.47% graphite was added to the PEDOT: PSS solution, the nanocomposite material in the visible light region had a high-quality electrical conductivity of 60 S/cm and high-temperature transparency (>90%). Compared with the pure PEDOT: PSS film, the conductivity of the nanocomposite film increases by two orders of magnitude, and it is found that the resistivity of the PEDOT: PSS/graphite nanocomposite film decreases with the increase of temperature, which has the characteristic behavior of semiconductor. In the PEDOT: PSS solvent, the well-decomposed graphite flakes form a better conductive direction in the nanocomposite film, and at the same time reduce the energy barrier of charge transfer on the PEDOT chain.

Lin Jintang prepared PEDOT: PSS/graphene film by liquid phase exfoliation technology [19]. The conduction mechanism of the thin film was studied by means of the ultraviolet absorption spectrum and Fourier transform infrared spectroscopy; An atomic force microscope and a scanning electron microscope were used to analyze the thin film's microstructure. Experiments have found that when the concentration of graphene is 500 cm^2/mL, the film exhibits good conductivity. This is because of the π-π conjugation between graphene and PEDOT, which promotes the transfer of charges and helps to increase the degree of delocalization of carriers in the main chain of PEDOT, thereby the conductivity of PEDOT: PSS can be improved.

5. Conclusion

To sum up, the conductivity of PEDOT: PSS can be increased in a variety of ways that are efficient, and the modification effects are also different. With the in-depth study of PEDOT: PSS modification, more and more methods are recognized and used effectively. PSS doping optimization can obtain a certain modification effect; the solvent doping method can use many solvents and is the most widely used; nanomaterials can give full play to their characteristics. However, most modifications have similar disadvantages. The amount of modified dopant should be strictly controlled. Otherwise, if the amount exceeds a certain amount, the performance will not be improved, but will be deteriorated. Therefore, for PEDOT: PSS, the future modification research direction will not only be the single use of solvent doping or nanomaterials, but the combined use of various modification methods to achieve synergistic effects, so as to obtain PEDOT: PSS with excellent comprehensive properties. The material has broad application prospects in solar cells, supercapacitors, organic thermoelectric devices and other fields.

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