Exploring the Effects of Acid Fuchsin on Microscopic Morphology and Properties for Polypyrrole

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Polypyrrole (PPy) is synthesized via in situ chemical oxidative polymerization in the presence of acid fuchsin (AF) which works as both the dopant and structure-guiding agent for polymerization of pyrrole. The electronic conductivity is measured in detail, showing that the addition of AF plays a key role in regulating and even deciding the morphology and the electronic conductivity of the resulting PPy. In addition, the effects of some polymerization conditions including temperature, reaction time, kinds of doping acid and oxidant on the electronic conductivity are investigated. And the reason for the changes of performance are also explained.

Keywords: Polypyrrole, Acid fuchsin, Dopant, Electronic conductivity, Reaction conditions

1. Introduction

Conducting polymers have continuously attracted worldwide attention of researchers owing to their metallic conductivity and semiconductor properties [1-4], since polyacetylene (PA) was fabricated by H. Shirakawa, A. G. Macdiarmid, and A. J. Heeger in the 1970's [5]. Moreover, they have found a broad range of applications in sensors or electronic junctions [6], optical equipment [7], electrode materials [8], electrochromism [9], and ion transport [10]. Polypyrrole (PPy), one of the most popular polymers among the family of conducting polymers, has superior performance such as environmental stability and biocompatibility [11]. And it can be used in many potential applications including electrode materials of supercapacitors and batteries [12-14], sensors [15,16], drug delivery [17,18], biological ion detection, and electromagnetic shielding materials [19].

PPy can be prepared by chemical polymerization and electrochemical polymerization methods [20], however, ectopic PPy is in an unfavorable situation due to its poor conductivity. To overcome the problem, adding the dopant materials into solution during the reaction process is an effective approach to expand free-moving electronics in the molecular chain of PPy. There are many reports dealing with the dopant type in polymerization of pyrrole, for instance acid doping [21-23], surfactant doping [24,25], dye doping [26, 27], cyclodextrin and its derivatives doping [28].

Polar groups (-COOH, -SO3H, and -NH2) of dye dopants have unique advantages. These groups can generate p-π conjugation with the PPy backbone, giving rise to further enhanced carrier transport efficiency followed by improved conductivity [29]. Up to now, this have been demonstrated in a number of studies that azo dyes, including methyl orange (MO), ethyl orange (EO), acid red (AR), gold orange IV, orange yellow G (OYG), work as the structure-guiding agent for PPy. In particular, PPy nanotubes with the highest bulk conductivity were successfully prepared, where acid form of MO molecules serving as situ-generated solid template play a role in directing the resulting morphology of PPy [30]. Aligned PPy micro/nanotubes were synthesized via a self-assembly method using FeCl3 as oxidant, AR
as dopant, and AR-Fe (II) complex as template to realize the adjustment of PPy morphology during the reaction process [31].

However, there are relatively few studies devoted to investigate the effects of acid fuchsin (AF, C_{20}H_{17}N_{3}Na_{2}O_{9}S_{3}, Scheme 1) on the morphology and properties of PPy. To achieve a better understanding, AF, an anionic dye with a sulfonate, is used as dopant for pyrrole polymerization. In here, the following issue is focused: to identify the influences of AF on the microscopic morphology, structure and conductivity of PPy. Furthermore, it is later considered that the divergences of electrical conductivity and particles size of PPy based on the variations of reaction conditions including type and concentration of oxidant, concentration of dopant, reaction temperature, reaction time, and so forth.

Scheme 1. Molecular formula of AF.

2. Experimental procedures

2.1. Materials

Pyrrole (AR, Chemical Reagent Co.) was purified by distillation under reduced pressure prior to use. Acid fuchsin (AF, AR) was purchased from Tianjin Chemical Reagent Co., Ltd. Ferric chloride (FeCl₃, AR) was purchased from Sinopharm Chemical Reagent Company. Hydrochloric acid (HCl, 36.5%, AR, Laiyang Economic & Technological development zones Fine Chemicals Factory) were used without further purification. Deionized water was utilized throughout all the preparation procedures.

2.2. Preparation of AF doped PPy

AF doped PPy was prepared by a chemical oxidation method. The mixture of AF and pyrrole with different mole ratios were dissolved in 20 mL deionized water, separately sonicated and stirred for 30 min. FeCl₃ (the mole ratio of pyrrole to FeCl₃ = 1:1) was dissolved in 20 mL deionized water, and then added dropwise to the above solution and the reaction was conducted for 18 h. Ultimately, the AF doped PPy products were obtained by filtering and washing with deionized water until the filtrate was colorless, and drying at 60 ℃ under vacuum for 24 h.

The mole ratio of AF to pyrrole was varied from 0.05 to 0.3. Different concentrations of FeCl₃ solution (0.3 M, 0.6 M, 0.9 M) were used as oxidant. The effects of reaction time were investigated from 6 h to 18 h. In order to deeply investigate the influences of reaction temperature, a set of experiments were set up at 0 ℃.

2.3. Characterization of AF doped PPy

The morphology of PPy samples was analyzed by scanning electron microscopy (SEM, Nova Nano SEM450, FEI) at a voltage of 20 kV. The chemical composition of PPy samples was tested by Fourier transform infrared spectra (FTIR, Nicolet 380 Fourier transformation infrared spectrometer) in the region of 4000-400 cm⁻¹ and X-ray diffraction (XRD, Rigaku Dmax 2500 X-ray diffractometer) in the range of 4-70°. The resistance of PPy was measured by double testing digital four-probe tester (Suzhou Jingge Electronic Co., Ltd.). The samples were pressed into disks with diameters of 13 mm under a pressure of 15 MPa for 5 min using a powder pressing machine at room temperature before testing. The calculation method of the electric conductivity was as follows:

\[ \sigma = \frac{1}{\rho} \]  

where \( \sigma \) is the electric conductivity (S/cm), \( \rho \) is the resistivity of the samples (Ω cm).

3. Results and discussion

3.1. Morphology and characterization

SEM images of PPy samples are illustrated in Fig. 1. Figure 1 (a) shows the normal PPy particles obtained without the addition of AF, which has typical spherical shape with a diameter of about 500 nm. From Fig. 1 (b) to Fig. 1 (c), it can be clearly seen from these images that the resulting PPy samples gradually transform their morphology from spherical to nanofiber-like structure with increasing the amount of AF in the polymer polymerization process. When the mole ratio of AF to pyrrole is 0.05, in Fig. 1 (b), AF doped PPy is almost the same as normal PPy in the terms of the morphology and the diameter. However, in the case of 0.1, PPy sample begins to appear irregular globular structure and a little short rods, as shown in Fig. 1 (c). From Fig. 1 (d), along with increasing mole ratio to 0.2, the morphology of PPy has thoroughly became long and thin cylinders. Once mole ratio reaches up to 0.3, Fig.
1 (e) clearly displays that the prepared PPy becomes short and thick nanofiber-like structure. Fig. 1. SEM images of (a) normal PPy and AF doped PPy samples prepared with various mole ratios of AF to pyrrole: (b) 0.05, (c) 0.1, (d) 0.2, (e) 0.3.

The reason for forming such a one-dimensional (1D) polymer may be that AF acts as both the dopant and the structure-guiding agent for the polymerization of pyrrole. Figure 2 displays a schematic illustration of the preparation process for PPy nanofiber-like structure. AF molecules spontaneously form micellar template as skeleton in aqueous solution, which are believed responsible for the restriction of the PPy growth. Afterwards, pyrrole molecules are adsorbed on the micellar template by hydrogen bonding interaction which are formed by amino groups between AF and pyrrole. In the meantime, three sulfonic acid groups of AF have electrostatic interaction with the freshly formed PPy molecules, which is beneficial for the formation of more regular and orderly PPy molecules. The self-assembly of PPy molecules results in the appearance of 1D nanofibers due to the guidance of AF micellar template. The driving force for the maturing of the PPy molecules into high order structures is likely to the direction of the template and the minimization of surface free energy within a given system to transform the product into a more thermodynamically favorable one [32].

To further verify the preparation of PPy, FTIR spectra of PPy samples are shown in Fig. 3. Meanwhile, for the sake of comparison, the spectra of undoped PPy and AF are also included. For undoped PPy, the peaks at around 1039 and 1322 cm⁻¹ are attributed to the C-H in-plane deformation vibration of the pyrrole ring. The peak at 983 cm⁻¹ is ascribed to C=C in-plane bending vibrations of the pyrrole ring [33]. The band locates at 1077 cm⁻¹ is assigned to the C-N stretching vibration. The symmetric and anti-symmetric pyrrole ring stretching modes are separately observed at about 1556 and 1481 cm⁻¹ [34]. In the situation of AF, the peak centers at 3458 cm⁻¹ is assigned to the -OH stretching. The bands at around 3326 and 3053 cm⁻¹ belong to the stretching vibration of N-H and C-H. Besides, the C=O and -SO₃⁻ stretching can be viewed at 1623 and 1020 cm⁻¹, respectively. Out of plane bending vibration absorption peaks of C-H exists at 634 cm⁻¹ [35]. These characteristic peaks described above can be clearly found in the FTIR spectra of doped PPy samples, however, there have been a slight difference stemmed from the chemical conjugation between PPy and AF in shape and position. Furthermore, some new peaks appear for the doped PPy. For instance, it is observed that two peaks emerge at about 2912 and 1735 cm⁻¹, which interrelate with the AF functionalities. The presence of electrostatic interaction between PPy and AF is verified according to the FTIR analysis. Thus, PPy nanofibers can be considered as a nanocomposite of PPy and AF instead of a single product.

Fig. 2. Schematic illustration of the synthesis process of the PPy nanofiber-like structure.

Fig. 3. FTIR spectra of undoped PPy, AF, and PPy synthesized by doped various mole ratios of AF and pyrrole.

In order to identify the phase structure, XRD patterns of PPy samples and AF are presented in Fig. 4. With respect to undoped PPy, a typical broad peak resulting from the π-π interactions between PPy molecular units at about 20~30° is seen, indicating that normal PPy is an amorphous structure in nature [36], which is in good agreement with the previous work [37]. As for AF, a sharp peak centered at 22.5° indicates the crystallinity. The diffraction pattern of
doped PPy samples with altering mole ratios of AF and pyrrole exhibit two distinct diffraction peaks at 15.8 and 22.3°, while a weak diffraction peak of AF can be observed at 15.5°. In comparison with XRD pattern of undoped PPy, the appearance of the new peaks for doped PPy samples is attributed to the split of the peak at 25.5°, which separates into two parts situated at 15.8° and 22.3°. New sharp peaks prove that doped PPy samples have crystalline phase form. Moreover, it is found that the peak intensity of doped PPy samples gradually increases with the increase of the amount of AF. This phenomenon demonstrates that the crystal structure of PPy also gradually increases. However, when the mole ratio reaches 0.3, the inferior shape of peak testifies that the crystallization of PPy becomes worse. The enhancement of crystal structure stems from the formation intermolecular hydrogen bonds between dye molecules with sulfonic acid groups and PPy molecules. The improved intermolecular force effectively makes the growth of PPy molecule become ordered, promoting the formation of crystallization.

To analyze the impacts of the concentration of the AF on the electronic properties of PPy, the resistance of the doped PPy are tested by using double testing digital four-probe tester, and the calculated electronic conductivity are exhibited in Fig. 5. From the image, one can find that the electronic conductivity obviously increases first and then decreases with the increase of the concentration of AF. As the mole ratio of AF and pyrrole runs up to 0.2 M, a maximum electronic conductivity of 3.91 S/cm are obtained. When the mole ratios are 0.05, 0.10, 0.30 M, the electronic conductivity is 0.64, 0.79 and 1.36 S/cm, respectively. Besides, the electronic conductivity of undoped PPy is only 0.03 S/cm. It is conspicuous that the doped PPy samples show much better electrical conductivity. The change of electrical conductivity by doping is because of the difference in energy levels between the π-bonded molecular orbitals. As for undoped PPy, π-bonded molecular orbitals is impassable, which hinders the movement of electrons in the conjugated polymer chain. Nevertheless, p-π conjugation effect on the PPy backbone is formed after doping, which is in favor of the transport of electrons, resulting in the increase of electrical conductivity [31]. There was a significant drop for electrical conductivity once excess AF is employed. The fact is attributed to that the excess AF destroys conductive pathways and crystalline structure, deteriorating the electronic conductivity.

3.2. Effects of factors

Next, the influences of reaction conditions on the electronic conductivity and morphology of PPy samples are discussed when the mole ratio of AF and pyrrole is 0.2. First, various reaction time is researched including 6, 12, 18, and 24 h. The results of the electronic conductivity are shown in Fig. 6. In the image, the electronic conductivity renders a tendency of ascension first and then declines, and their values are separately 4.10, 4.83, 3.61, and 3.17 S/cm. When the reaction time is short, insufficient polymerization leads to the formation of defects against the appearance of the conductive pathway [38]. Hence, the poor electronic conductivity is obtained. But when the reaction time is excessively long, secondary growth will undoubtedly occur and leads to the formation of irregular morphology. This morphology seriously restricts electrical conductivity. Accordingly, the best electrical conductivity can be obtained only at the right reaction time, without defects or secondary growth.

In Fig. 7, SEM images reveal that PPy samples obtained at 0 and 25 °C, and their diameter and electronic conductivity are tabulated in Table 1.
Table 1. The diameter and the electronic conductivity of PPy particles synthesized at different reaction temperatures.

| Temperature | Diameter | Conductivity |
|-------------|----------|--------------|
| 0 °C        | 200 nm   | 4.13 S cm⁻¹  |
| 25 °C       | 265 nm   | 3.61 S cm⁻¹  |

From Table 1, the fabricated PPy has a smaller diameter of 200 nm and a higher electronic conductivity of 4.13 S/cm under low temperature. At high temperature, PPy sample has a diameter of 265 nm and an electronic conductivity of 3.61 S/cm. As the polymerization temperature increases, it can be seen that the electrical conductivity decreases, in accordance with the literature of conducting polymers [39,40]. The reason for the decrease is caused by the irregular arrangement of PPy molecules. It is well known that high temperature brings quick polymerization. On the basis of this case, the newly formed PPy molecules have not enough time to realize a regular arrangement. Finally, the formation of relatively large and irregular structure leads to a reduction in electrical conductivity.

When applying a mixed oxidant consisting of AF and FeCl₃, SEM images of PPy particles are shown in Fig. 8. It is found that the concentration of oxidant affects the morphology of PPy. Only the mole ratios of FeCl₃ and AF is 20%, PPy particles have a uniform size and their shape is spherical. From Table 2, the diameter of PPy particles is 165, 365, and 233 nm, respectively. At the same time, it is easily found that the electronic conductivity of PPy samples shows a similar pattern, and their value is 1.14, 4.31, 3.61 S/cm. The change of the electronic conductivity is related to the oxidation degree of PPy samples. The best property is contributed to the most appropriate oxidation degree. The increase of the amount of oxidant leads to the decrease of polypyrrole conductivity, probably due to the destruction of the conductive pathway of polypyrrole conjugate chain by peroxidation. This view has been verified in previous research work [41,42].

4. Conclusion

Doping PPy samples are synthesized in the presence of AF, in which AF acts as both the dopant and structure-guiding agent for polymerization of pyrrole. When the mole ratio of AF to pyrrole is 0.2, PPy transforms its morphology from particles to nanofibers, and displays the highest electronic conductivity of 3.91 S/cm. Researches show that more crystalline phase is formed when the mole ratio of AF to pyrrole runs up to 0.2, which is believed to be the main reason for the improvement of the electrical conductivity. In addition, the influences of different polymerization conditions on the morphology and electrical conductivity of PPy are closely researched. When the polymerization temperature is 0 °C and the reaction time is 12 h, the electronic conductivity of PPy is higher than that of other conditions. By varying FeCl₃ as oxidant, the electronic conductivity of PPy is also changed, and the reasons for this are also eliminated.

Acknowledgment

This work was supported by Scientific...
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