Preparation and Characterization of Polypyrrole-coated Wool Fabric for High Electrical Conductivity

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Abstract. In recent years, flexible electronic devices have attracted people's attention. Textiles have been used in the preparation of flexible electronic devices because of their flexibility, but how to improve their conductivity has become the key to expand their application. In this study, the wool fabric with high conductivity was prepared by plasma treatment and in-situ polymerization methods. In this paper, high conductivity wool fabric was prepared by plasma sputtering and in-situ polymerization. Firstly, the wool was descaled by plasma, and then the wool fabric was modified by in-situ polymerization of polypyrrole (PPy). The effect of polypyrrole treatment time on the high conductivity composite fabric was discussed, and a series of characterization were carried out. The results show that the resistance of PPy coated wool fabric with plasma sputtering power of 200W and polypyrrole treatment time of 1200 s is low, and the average square resistance is 67.32 Ω/ sq.

1. Introduction
In recent decades, compared with traditional electronic technology, flexible wearable electronic devices have great application potential in intelligent clothing, biomedical devices, energy conversion and storage, electromagnetic interference shielding and other fields, and have been widely concerned. Flexible electronic devices have the advantages of good flexibility, light weight, high sensitivity and strong deformation ability [1][2][3]. At present, the research on conductive textiles mainly focuses on the combination of polymer conductive materials and fabrics and the metallization of fabrics [4][5]. The common polymer conductive materials include polypyrrole, polyaniline and polythiophene. Polypyrrole has good conductivity, mechanical flexibility, biocompatibility and almost no pollution to the environment. It has a wide application prospect in the field of sensors and capacitors.

Wool fiber has good hygroscopicity and moisture regain is up to 16 %. However, due to the scale layer on the surface of wool fiber, the hydrophilicity of wool fiber is poor [6][7][8]. In the environment with high humidity, the electric charge is easy to generate before the wool fiber, which limits the application of wool fiber to a certain extent. In this paper, the plasma technology is used to pretreat wool fiber. By introducing oxygen-containing groups, the surface of wool fiber is etched [9]. The specific surface area of wool fabric is increased, which is conducive to the adsorption of pyrrole monomer and oxidant, which improves the original polymerization reaction, and finally forms a firm bond between Polypyrrole and wool.

2. Experimental details

2.1 Materials
Py (mass fraction: 98%) and ferric chloride (FeCl₃·6H₂O; molecular weight ≈ 270.3) were supplied by Sinopharm Chemical Reagent Co., Ltd (China). Black weave wool fabric [Yarn weaving100 S/2*100 S/2; gram weight: 290g/m2] used as a substrate material was provided by Shaoxing Xiqi Textile Co, Ltd (China).

2.2 Descaling of wool
The wool was descaled by plasma sputtering. Firstly, a cleaning process was carried out to remove pollutants from the wool fabric and improve the reaction between the wool fabric and the polymer. Soak the wool fabric (5 cm*5 cm) in ethanol solution for 30min and conduct ultrasonic treatment, then wash it thoroughly with deionized water, bake it for 1h at no higher than 60 °C, and treat the fabric at 200 W power and different sputtering time at 1200 s.

2.3 Preparation of PPy coated wool fabric
Polypyrrole coated cotton fabric was prepared by in-situ polymerization. The wool fabric treated by plasma for 1200 s was placed in py dispersion with mole concentration of 0.4 mol/l, 0.6 mol/l and 0.8 mol/l for 30 min, and then the initiator (FeCl₃·6H₂O) with the mole ratio of Py monomer and oxidant of 3:1 was added. The effect of sputtering time of 1200s on the electrical conductivity of PPy coated wool fabric was studied. The wool fabric with PPy coating can be obtained by rinsing with deionized water until the color of deionized water is deionized, and then drying in an oven not higher than 60 °C for 1 h.

3. Results and discussion

3.1 Surface morphology analysis
The morphologies of the wool fabric, the plasma treatment time 1200 s, and the molar concentration is 0.4 mo/l, 0.6 mol/l and 0.8 mol/l ppy/wool fabrics are observed in figures 1(a)–(e). As shown in Fig. 1 (a), wool fabric has complete scale structure and clear scale edge, and its surface is very smooth. It can be seen from Figure 1 (b) that the scale structure of wool fabric is destroyed after 1200 s of plasma treatment, and the surface depression of wool fabric becomes rough, the edge of scale disappears and the scale falls off. Figure 1 (c) when the concentration of pyrrole is 0.4 mol/l, the wool fabric after in-situ polymerization is coated with continuous polypyrrole film, but the particle size is small. As shown in Fig. 1 (d), when the concentration of pyrrole reaches 0.6 mol/l, fine polypyrrole films are arranged on the surface of wool fabrics, with local agglomeration. As shown in Fig. 1 (E), when the concentration of pyrrole reaches 0.8 mol/l, a large amount of polypyrrole is attached on the surface of wool fabric to form a continuous film. At the same time, polypyrrole molecules contact each other to form a path. The oxidation of conjugated chain and the corresponding anion doping structure make it have good conductivity. The strong intermolecular force between the two makes the conductive layer not easy to fall off, which ensures the relative stability of its conductivity in the air.
3.2 Thermal stability performance

The TG curve of conductive polypyrrole wool fabric is shown in Fig. 2. The initial decomposition of wool fabric is mainly due to the release of water and other small molecules in the fiber. After plasma treatment, the moisture content in the fiber decreases, so the weight loss is smaller than that of the original fabric. After plasma treatment, -OH and -COOH may be introduced. There are three stages: thermal decomposition stage (400 °C ~ 600 °C) and stable carbon formation stage (600 °C ~). In the first microgravity stage, the weight loss is caused by the combination of residual water and polymer. In the second stage of thermal decomposition, polypyrrole macromolecular chain is affected by high temperature, the movement speed is gradually accelerated, the molecular movement is fierce, and finally lead to the chain segment fracture, and finally form small molecular substances in the form of gas release, resulting in weight loss. In the third stable carbon formation stage, the residual mass of the PPy / wool composite fabric with the concentration of 0.4-0.6 mol / L tends to be stable, and the residual amount of the polypyrrole / wool composite fabric with the concentration of 0.8 mol / L at 600 °C is higher than that of the low concentration of pyrrole solution, and the thermal stability is good.
3.3 Electrical conductivity

Figure 3 shows the effect of pyrrole concentration on the electrical resistance of the sample. It can be seen that the conductivity of the polypyrrole wool composite fabric increases with the increase of pyrrole concentration. After conductive treatment, there are polypyrrole conductive materials attached on the surface of wool yarn, and the amount of polypyrrole conductive materials increases with the increase of pyrrole concentration. When the concentration of pyrrole is 0.4 mol / L, the surface of the fabric can be little polypyrrole; when the concentration of pyrrole is further increased to 0.6 mol / L, the polypyrrole basically completely covers the surface of the fabric and forms a continuous and uniform film with a square resistance of 145 Ω / sq; when the concentration of ferric chloride is further increased to 0.8 mol / L, the polypyrrole completely covers the surface of the fabric, The size of polypyrrole particles is larger and the conductivity is the best, which is 116 Ω / sq.
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3.4 Washing fastness
The change of the resistance of the fabric after washing is shown in Table 1. With the increase of the concentration of polypyrrole, the resistance value of the fabric gradually decreases and the conductivity becomes better. With the increase of washing time, the resistance value of the fabric with 0.4 mol / L concentration changes the most from 2.5 KΩ / sq to 57.23 KΩ / sq, and the washing resistance is the worst. With the increase of the amount and concentration of the substance, the resistance value after different washing time also decreases with the increase of the concentration. At the concentration of 0.8 mol / L, the resistance value of washing time of 0.5, 1, 1.5, 2 h is the minimum, and the washing resistance is good. This is mainly because the increase in the concentration of the amount of material ensures the perfection of the conductive network, which is more difficult to be destroyed.

Table 1 Sheet resistance (Ω/sq) of different samples after washing

| The quantity and concentration of polypyrrole | Washing time/h |
|-----------------------------------------------|----------------|
|                                               | 0  | 0.5 | 1   | 1.5 | 2   |
| 0.4                                           | 2.5| 19  | 3.5×10^6 | 4.3×10^7 | 5.7×10^7 |
| 0.6                                           | 249| 812 | 3.04×10^6 | 6.80×10^7 | 8.80×10^7 |
| 0.8                                           | 116| 582 | 2.97×10^6 | 3.75×10^7 | 5.70×10^7 |

4 Conclusion
In this work, Polypyrrole / wool composite fabrics with different concentrations were prepared by plasma technology and in-situ polymerization. The results show that polypyrrole wool composite fabric has the best electrical conductivity, the average square resistance of Polypyrrole / wool composite fabric
reaches 116 Ω / sq, and the polypyrrole coated wool fabric has high conductivity. The results show that the best conductive effect can be obtained when the polypyrrole / wool composite fabric with 0.8 mol / L pyrrole concentration is washed for 2 h and the square resistance is $5.70 \times 10^3$.

References

[1] AMIADI M, KYUNG K U, PARK I, et al. Stretchable, skin-Mountable, and wearable strain sensors and their potential applications: A Review[J]. Advanced Functional Materials, 2016, 26(11):1678-1698.

[2] EGAMIY, SUZUKI K, Tanaka T, et al. Preparation and characterization of conductive fabrics coated uniformly with polypyrrole nanoparticles[J]. Synthetic Metals, 2011, 161(3-4):0-224.

[3] PASTA M, HU L, MANTIA F L, et al. Electrodeposited gold nanoparticles on carbon nanotube-textile: Anode material for glucose alkaline fuel cells[J]. Electrochemistry Communications, 2012, 19(none):81-84.

[4] XU H, PENG S, WANG C, et al. Influence of absorbed moisture on antifelting property of wool treated with atmospheric pressure plasma[J]. Journal of Applied Polymer Science, 2009, 113(6):3687-36

[5] WANG X, SHEN X, XU W. Effect of hydrogen peroxide treatment on the properties of wool fabric[J]. Applied Surface Ence, 2012, 258(24):10012-10016.

[6] Navik R, Shafiq F, Khan A, et al. Preparation and characterizations of polypyrrole on liquid ammonia pre-treated wool fabric[J]. Fibers & Polymers, 2017, 18(6):1115-1123.

[7] Stempien Z, Rybicki T, Rybicki E, et al. In-situ deposition of polyaniline and polypyrrole electroconductive layers on textile surfaces by the reactive ink-jet printing technique[J]. Synthetic Metals, 2015, 202:49-62.

[8] Chatterjee A, Maity S. A comparative study of reaction kinetics of in-situ chemical polymerization of polypyrrole onto various textile fibres[J]. Surface and Coatings Technology, 2017, 324:569-576.

[9] Varesano A, Tonin C. Improving Electrical Performances of Wool Textiles: Synthesis of Conducting Polypyrrole on the Fiber Surface[J]. Textile Research Journal, 2008, 78(12):1110-1115.