A New Strategy of Constructing Mechanical Enhanced and Electrical Conductive Meta-aramid/Polyacrylonitrile Hybrid Fibers

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Abstract. Proper method for constructing electrical conductive m-aramid fibers without sacrificing its excellent integrated performance is still a challenge. Here a new strategy is utilized to construct electrical conductive PMIA/PAN hybrid fibers. No sensitizers or activators are needed in this method, contrast to traditional electroless plating methods. Specifically, the resulted PMIA/PAN hybrid fibers maintained a high tensile strength of 4.7 cN/dtex. Furthermore, the CuS-coated PMIA/PAN hybrid fibers (PMIA/PAN-CuS) exhibited high conductivity.

1. Introduction
Meta-aramid (PMIA) fiber, as one of the high-performance fibers, is a milestone in the field of chemical fiber preparation. In the past decades, great efforts have been made to modify PMIA, mainly including functional side groups or characteristic structural units introduced to the PMIA molecular backbone for structurally functional modification [1], blending with inorganic fillers or high polymers for composite modification [2]. Remarkably, blending for composite modification is an economically effective method for modification of PMIA compared with structural modification and copolymerization.

Due to potential applications of electromagnetic shielding, eliminating static electricity and stretchable electronics, constructing electrical conductive polymer materials has attracted great concern [3]. Specially, due to no need of expensive instruments and simple operation, electroless deposition is utilized for external metallization of insulative materials [4]. However, many factors limit the wider application of electroless plating, such as stringent PH requirements, expensive colloidal noble metal catalysts and tedious treatment of sensitization and activation [5].

In this work, we introduced a facile and easy method to fabricate PMIA/PAN hybrid fibers with more excellent integrated mechanical properties than pure PMIA fibers. What’s more, due to the superior chelation of nitrile groups (-CN) for divalent copper ions, a uniform electrically conductive CuS film could be formed on the surface of the PMIA/PAN hybrid fibers without expensive colloidal noble metal catalysts or any cumbersome activation treatment. The flexible, mechanical enhanced and electrical conductive PMIA/PAN hybrid fibers have broad application prospects.

2. Experimental Section

2.1. Materials
Polyacrylonitrile (PAN, Mw: 78000) was provided by Shanghai Petrochemical Co., Ltd. (Shanghai, China) and the weight-average molecular weight of the PAN was. m-Aramid was provided by X-FIPER
New Material Co., Ltd. (Jiangsu, China). CuSO₄, Na₂S₂O₃, and DMAc were purchased from Ling Feng Chemical Reagent Co., Ltd. (Shanghai). LiCl was purchased from J&K Chemical Technology.

2.2. Preparation of PMIA/PAN Hybrid Fibers
A series of homogeneous 15 wt % PMIA/PAN solution were subsequently prepared by mixing PMIA solution, PAN solution and 0.2 wt % LiCl, while stirring at 65 °C for 5 h. The ratio of PAN and PMIA was varied at 1/7, 1/10, 1/13 and 1/16 wt %. Then, the PMIA/PAN hybrid fibers were produced by wet spinning method.

2.3. Preparation of PMIA/PAN-CuS Composite Fibers
In detail, PMIA/PAN hybrid fibers and formulated copper sulfate (Cu₂SO₄) aqueous solution (160 g, 2 wt %) were mixed under nitrogen atmosphere. The mixture was heated to 65 °C under stirring and reacted at a constant temperature for 0.5 h. Subsequently, Na₂S₂O₃ aqueous solution (20 g, 2 wt %) was added, and then heated to 85 °C under stirring and maintained for 0.5 h. At last, another 20 g Na₂S₂O₃ aqueous solution (2 wt %) was added, the mixture was heated to 105 °C under stirring and maintained for 1.5 h. The obtained PMIA/PAN-CuS composite fibers were collected, washed with deionized water thoroughly, followed by 45 °C drying in a vacuum oven for 12 h. All of the reagents used without further purification.

2.4. Characterization
SEM was employed to evaluate the surface morphologies of PMIA/PAN hybrid fibers before and after CuS-coated (Japan, Hitachi SU8010). XRD spectra, with a 2θ range of 10−75°, was utilized to studied the crystalline Rigaku). FTIR spectra, range from 4000 to 500 cm⁻¹, was obtained. Origin 8.5 Software was used for curve fitting deconvolution of the FTIR spectra in spectral region of 1693-1620 cm⁻¹ (USA, NEXUS-670). Thermal stability of PMIA/PAN composite fibers were analyzed by means of TGA, heated from 50 to 800 °C, at a heating rate of 20 °C min⁻¹ under nitrogen atmosphere (Germany Chi Instrument Manufacturing Co., Ltd., TG 209 F1 Iris). Electronic single fiber tensile strength tester was utilized to measure the tensile properties of single PMIA/PAN hybrid fibers. Moreover, all kinds of hybrid fibers were tested for 20 times (XQ-1 tensile tester). EDS spectrum of PMIA/PAN-CuS composite fibers was studied by Energy Dispersive Spectrometer (Japan, FESEM, Hitachi SU8010). Multimeter were utilized to measure the sheet resistivity of PMIA/PAN-CuS hybrid fibers (VICTOR 86E).

3. Results and Discussion
Figure 1(a1-d1) showed the surface morphology PMIA/PAN hybrid fibers with varied jet stretch ratio. With increase in the jet stretch ratio, the fiber diameter showed an increasing trend. The surface of these PMIA/PAN hybrid fibers seemed clean, some shallow and narrow grooves were distributed in the axial direction of hybrid fibers’ surface, indicating the different degrees of double expansion between PMIA and PAN components. Comparatively, when the jet stretch ratio reached -50%, more regular morphology of hybrid fibers was observed in the high magnification SEM images. Meanwhile, similar morphologies of hybrid fibers were also observed in Figure 1(a2-d2), as these hybrid fibers were prepared with varied coagulation bath concentrations.

The mechanical properties of PMIA/PAN hybrid fibers under different jet stretch ratio, different stretch ratio of spinning and different coagulation bath concentrations were shown in Figure 1(e-g). As shown in Figure 1e, with increase in the jet stretch ratio, the mechanical properties of hybrid fibers showed an increasing trend. When the jet stretch ratio increased to -50%, the tensile strength reached the maximum value of 4.6 cN/dtex. However, a further increased jet stretch ratio allowed the blend solution to flow freely under no tension, resulting in difficult fiber formation and poor tensile strength of 2.6 cN/dtex. Figure 1g showed that both tensile strength and elongation at break reached the maximum value of 4.1 cN/dtex and 19.1%, when the coagulation bath concentration increased to 50%. Which is because that when the concentration of the coagulation bath is very low, the double diffusion
process reacts too quickly to form a brittle hard cortex, hindering the continued reaction of double diffusion. Of course, the concentration of the coagulation bath should not be too high, which will slow the fiber forming speed, and the surface of the fiber will swell severely, resulting in a decrease in fiber quality.

Figure 1 SEM images of PMIA/PAN hybrid fibers with varied jet stretch ratio of spinning (a1: -20%, b1: -35%, c1: -50%, d1: -65%) and with varied coagulation bath concentrations (a2: 35%, b2: 40%, c2: 45%; d2: 50%). And the mechanical properties of PMIA/PAN hybrid fibers under different jet stretch ratio (e), different stretch ratio of spinning (f) and different coagulation bath concentrations (g).

Figure 2 (a) WAXD patterns and (b) TGA curves of pure PMIA fiber and PMIA/PAN hybrid fibers.

The doping progress can be effectively verified by the XRD patterns, Figure 2a exhibited the WAXD patterns of pure PMIA fiber and PMIA/PAN hybrid fibers. For pure PMIA fibers, a peak at the diffraction angle (2θ) of 23°, which is its characteristic peak. In contrast, another characteristic peak at
20° = 17° was observed in XRD patterns of all the doped specimens, associating to the nitrile group (–CN) in PAN. In addition, the decreased width of full width at half maxima reflected that as the amount of PAN added increases, the degree of crystallization of PMIA decreases. And, this may also be an essential cause of increasing the toughness of PMIA/PAN blended fibers. For potential practical applications, it is essential for PMIA/PAN hybrid fibers to possess superior thermal stability. Typical TGA curves of pure PMIA were shown in Figure 2b, there was no obvious thermal decomposition below 400 °C, indicating its good thermal stability. In contrast, the PMIA/PAN hybrid fibers substantially exhibited the good thermal stability as well as the pure PMIA fibers, meeting the special application of higher temperature fields.

Table 1 The mechanical properties of PMIA/PAN hybrid fibers and pure PMIA fibers.

| Samples          | Stretch ratio |
|------------------|---------------|
|                  | 3 4 5         |
|                  | 3 4 5         |
| Strength (cN/dtex) | 3.9 4.3 4.7   |
| Elongation (%)    | 48.6 27.9 16.9 |

The elongation at break and strength of PMIA/PAN hybrid fibers were given in Table 1. The strength of both blended fibers and pure fibers increased with the increase of the stretching ratio, and the elongation at break decreased with the increase of the stretching ratio. Obviously, both the average strength and the elongation at break of PMIA/PAN hybrid fibers were much higher than that of the pure PMIA fibers under different stretch ratios. Specially, the strength of the PMIA/PAN hybrid fibers reached 4.7 cN/dtex when the stretch ratio of fibers was 5. However, pure PMIA fibers had a serious broken wire phenomenon when the stretch ratio of fibers reached 5. The excellent integrated mechanical properties of the PMIA/PAN hybrid fibers, suggesting the effect of multiple intermolecular H-bonding interactions in enhancing the mechanical properties of polymer fibers.

Figure 3 Curve-fitting FTIR spectra in the range of 1693-1620 cm⁻¹ for the prepared pure PMIA fibers (a) and PMIA/PAN hybrid fibers (b-d). Table for curve-fitting FTIR results in the range of 1693-1620 cm⁻¹ for the prepared pure PMIA fibers and PMIA/PAN hybrid fibers (g).

To verify the effect of multiple intermolecular H-bonding interactions in enhancing the mechanical performances of polymer fibers. FTIR spectroscopy was utilized to investigate the existence of H-
bonding interactions, because of its superior sensitive to the frequency shift of proton donor and acceptor at H-bonding formation [6]. The presence of the –CO-NH– groups in the PMIA/PAN hybrid fibers was expected to produce strong inter-molecular interactions especially hydrogen bonding not only with –CO-NH– groups of amide group in other PMIA molecular chains but also with –CN of the nitrile group in PAN molecular chains. Hence, as shown in Figure 3, we analyzed deconvoluted FTIR spectra range from 1620 to 1693 cm⁻¹.

Five peaks were identified separately, among which the band 5 (ca. 1735-1739 cm⁻¹) and the band 1 (ca. 1677-1680 cm⁻¹) are corresponding to the C=O symmetric stretching and asymmetric stretching, the band 2 (ca. 1662-1670 cm⁻¹) are corresponding to the “free” C=O symmetric stretching, including the effects of other interactions, the band 3 (ca. 1657-1662 cm⁻¹) are corresponding to intermolecular H-bonding on C=O symmetric stretching (e), the band 4 (ca. 1646-1651 cm⁻¹) are corresponding to intermolecular H-bonding on C=O symmetric stretching (f). All of these analyzed deconvoluted bands are summarized in the Table (Figure 3g).

Figure 4 (a, d) SEM images of PMIA/ PAN-CuS composite fibers, (b) high-resolution images of PMIA/ PAN-CuS composite fibers, (c) EDS spectrum of PMIA/ PAN-CuS composite fibers and (d, e, f) scanning SEM image and elemental mapping of S and Cu for PMIA/ PAN-CuS composite fibers, (g) the measurement of the PMIA fibers electrical resistance after nickel plated. (h) Photo of the PMIA–AgNPs–Ni composite fibers used as a part of the circuit to light the LED.

Homogeneous and dense CuS coating layers are observed in Figure 4a, as shown in Figure 4b, almost no apparent defects are found in the high-resolution images of PMIA/ PAN-CuS composite fibers. The EDS spectrum (Figure 4c) of PMIA/ PAN-CuS composite fibers confirms the presence of Cu and S.
elements. It can be seen that the atomic ratio of Cu:S was 1:1.02, which is consistent with the expected stoichiometry of 1:1. EDS elemental mapping images of PMIA/ PAN-CuS composite fibers reveal that all of its exterior constituent elements (Cu and S) had a homogeneous distribution over the investigated detection range of the CuS-coated composite fibers.

From what mentioned above, it is obvious that intact CuS coating was deposited on external of PMIA/ PAN-CuS composite fibers. And the electrically conductivity of PMIA/ PAN-CuS composite fibers were investigated. As presented in Figure 4h, several LEDs could be lighted as the PMIA/ PAN-CuS composite fibers were acted as one part of the circuit, indicating that the PMIA/ PAN-CuS composite fibers had good electrically conductivity.

4. Conclusions
We report a simple and rational design of fabricating electrically conductive PMIA/ PAN-CuS composite fibers, which has several features superior to other methods. It is worth noting that this method does not require noble metal catalysts and a lot of chemical reagents, which is in line with the development of green chemistry. Meanwhile, the CuS-coated PMIA/ PAN composite fibers show outstanding electrical conductivity and superior integrated mechanical properties compared with pure PMIA fibers.

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References
[1] Nakata, S., Brisson, J. (2001) Preparation of copolyamides based on aramid blocks with 7-9 phenylene monomer units and regularly inserted 1,6-hexanediamino units. Polymer Journal, 29: 663-669.
[2] Kim, S. S., Jeong, J., Lee, J. (2014) Antimicrobial m-Aramid/Cellulose Blend Membranes for Water Disinfection. Ind. Eng. Chem. Res., 53: 1638-1644.
[3] Jiang, S. J., Zhang, H. B., Song, S. Q., Ma, Y. W., Li, J. H., Lee, G. H., Han, Q. W., Liu, J. (2015) Highly Stretchable Conductive Fibers from Few-Walled Carbon Nanotubes Coated on Poly (m-phenylene isophthalamide) Polymer Core/Shell Structures. Acs Nano, 9: 10252-10257.
[4] Lu, Y. X. (2010) Improvement of copper plating adhesion on silane modified PET film by ultrasonic-assisted electroless deposition. Appl. Surf. Sci., 256: 3554-3558.
[5] Al-Shannaq, R., Kurdi, J., Al-Muhtaseb, S., Farid, M. (2016) Innovative method of metal coating of microcapsules containing phase change materials. Sol. Energy, 129: 54-64.
[6] Dong, H., Xin, Z., Lu, X., Lv, Y. (2011) Effect of N-substituents on the surface character-istics and hydrogen bonding network of polybenzoxazines. Polymer, 52: 1092-1101.