Highly electrically conductive silver-coated poly(p-phenylene terephthalamide) fiber prepared by poly(catechol/polyamine) surface modification

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Abstract. In this work, poly(p-phenylene terephthalamide)(PPTA) fiber was modified by catechol and tetraethylenepentamine through Michael addition and Schiff base reaction. Then the silver-coated PPTA fiber was prepared by electroless plating. The SEM images showed that the phenolic hydroxyl group of catechol has a strong adhesion effect and a metal binding ability, which can make the silver particles tightly coated on the surface of PPTA fiber. The XPS and XRD results indicate that the Ag on the surface of the PPTA fiber is elemental silver, and there is no diffraction peaks of silver halide and silver oxide. The resistivity of the silver-coated PPTA fiber prepared with the deposition time of 2h has reached 0.1mΩ·cm. This highly conductive PPTA/Ag fiber can be used in the field of flexible conductive materials and electromagnetic shielding clothing.

1. Introduction
Poly(p-phenylene terephthalamide)(PPTA) fiber has wide use in military, architecture, industry, and aerospace with the advantages of high intensity, high modulus, low density, high toughness, stable measure, and well heat resistance\textsuperscript{[1]}. Silver-coated PPTA(PPTA/Ag) combines the well mechanical properties of PPTA and high electrical conductivity of Ag, which can be used in wearable display device, light electromagnetic shielding material, and signal cable \textsuperscript{[2]}. The preparation methods of PPTA/Ag include sputtering, electron beam radiation curing spraying, electroless plating \textsuperscript{[3, 4]}. The electroless plating method is the most common method for its convenience. The surface of aramid fiber is smooth and has no catalytic active center, and its binding force to silver particles is weak, so it needs to be surface modified. The traditional surface modification method of “coarsening-activation-sensitization” has the disadvantages of weakening quality of fibers, environmental unfriendly, and complicated process. Yu et al.\textsuperscript{[5]} grafted chitosan on the surface of PPTA. The amidogen and hydroxy of chitosan can fix the Pb\textsuperscript{2+}, and the reduced palladium particles serve as the active center of the catalytic reaction. The resistivity of prepared PPTA/Ag reaches 0.38 Ω·cm. In the previous works of our team, we use polydopamine to modify the polymetaphenylene isophthalamide fiber, and prepared the high electrical conductivity PPTA/Ag through electroless plating, whose electrical resistivity is low to 0.61 mΩ·cm\textsuperscript{[6]}. 
The functional group which plays a decisive effect in dopamine is catechol structure and the terminal amino group. Inspired by dopamine, the scholars use the catechol and polyamine reactions to replace dopamine and reduce production costs. Qiu et al. [7] use the co-deposition of catechol and polyethyleneimine (PEI) on porous membrane for dye decolorization. Xu et al. [8] prepared a high-performance nanofiltration membrane by co-depositing catechol and PEI on the surface of a polysulfone ultrafiltration membrane and cross-linking with glutaraldehyde. Zhang et al. [9] used tannic acid containing a large amount of catechol groups and diethylenetriamine to co-deposit the modified polysulfone membrane, and obtained a nanofiltration membrane with a filtration rate of 98% for sodium sulfate. Wang et al. [10] used cheap catechol and polyamines (diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine) to co-deposit on polypropylene under alkaline conditions to make it change from hydrophobic to hydrophilic. Wu et al. [11] used the co-deposition method of catechol and polyamine to modify the copper sheet, and then grafted sulfhydryl groups on its surface, proving that the poly(catechol-polyamine) layer can be used as a platform for the secondary reaction. They speculated that catechol and polyamine may be co-deposited by Michael addition and Schiff base reaction. Wang et al. [12] catechol and polyamine co-deposition to modify aramid fibers, and then grafted epoxy functional groups to enhance the bonding properties of the fiber and rubber.

The methods of surface phenol-amine modification have lower cost (only 1% of the cost of method of dopamine), shorter reaction time, and versatility. It can be used as the platform of second functionalization, and suitable for industrial applications. However, to our best knowledge, there are no report yet about the use on material surface metalization of this method. In this work, we modified PPTA fiber by co-deposition of catechol and polyamine, and prepared silver-plated PPTA fiber by electroless plating. The chemical composition, crystal structure, morphology, and electrically resistivity of as-prepared samples were characterized.

2. Experimental Method

Put the PPTA in beaker, and ultrasonic clean it for 3 times with acetone and deionized water. Add 0.3 g PPTA in 50 mL deionized water and dispersed with ultrasonic cell crusher. Prepare a 50 mL catechol/tetraethylenepentamine (TEPA) solution with a concentration of 20 mM, the molar ratio of catechol and TEPA is 1:1. Adjust the pH of the solution to 9 with Tris-HCl buffer solution, then add 50 mL PPTA dispersion into it, and stir for 2-12 h. filter, wash and dry to obtain poly(catechol-polyamine) modified aramid fiber (PPTA/PCPA).

Prepare a 100 mL AgNO₃ liquid with 10 g/L concentration, and add ammonia in the liquid drop by drop until the solution is just clear. Add 0.25 g PVP into it, stir for 5 min. Then add 0.3 g PPTA/PCAPA into it, and stir for 25 min. Finally, add 100 mL glucose solution with 20 g/L concentration in it, and stir for 1 h. Filter, wash and dry to get the PPTA/PCAPA/Ag fiber.

3. Results and Discussion

Figure 1 XPS wide-scan spectra and N 1s spectra of (a, b) pristine PPTA fibers, (c, d) PPTA/PCPA fibers, (e) wide-scan spectrum and (f) Ag 3d spectrum of PPTA/PCPA/Ag fibers
The elementary composition of the PPTA, PPTA/PCPA, and PPTA/PCPA/Ag surface were represented by XPS. Comparing the Fig.1(a) and (c), there are C, O, N elements both on the wide-scan spectra of PPTA and PPTA/PCPA, but the N1s intensity of PPTA/PCPA is higher than PPTA. The reason is that there are lots of -NH$_2$ and -NH- on the PCPA deposited on the surface of PPTA, which can increase the relative amount of N element. From the Fig.1(b) we can know that the N1s peak of PPTA is only composed by -NH- bonds whose binding energy is just 399.5eV, which is introduced by the p-phenylenediamine monomer during the synthesis of PPTA. The Fig.1 (d) shows that the N1s peak of PPTA/PCPA can be divided into -N= bond with binding energy of 398.5eV, -N-H- bond with binding energy of 399.5eV, and N$^-$ proton peak with binding energy of 401eV. The -NH- bonds are come from the ursol of PPTA and the aminos and imino groups of polyamine of PCPA. -N-H- comes from p-phenylenediamine in PPTA and the amino and imino groups of polyamine in PCPA, -N= is caused by the Schiff base reaction of catechol and polyamine. The results of XPS showed that PCPA was deposited on the surface of PPTA. The Fig.1(e) proves that the characteristic peaks of Ag appear in the XPS wide-scan spectrum, and the characteristic peaks of C, O, N have significantly reduced intensities, indicating that the silver layer is covering the surface of PPTA/PCPA fiber. In Fig.1(f), the Ag 3d characteristic peak is composed by the Ag 3d$_{5/2}$ with a binding energy of 368.0eV and the Ag 3d$_{3/2}$ with a binding energy of 374.0eV, indicating that the silver on the fiber surface is in a zero-valent state.

Figure 2 SEM images of (a) pristine PPTA, (b)(c)PPTA/Ag, (d) PPTA/PCPA, (e)(f) PPTA/PCPA/Ag

The surface morphology of fibers were characterized by SEM. It can be seen from Fig.2(a) and (d) that the surface of pristine PPTA fiber is relatively smooth, while after PCPA deposition, a layer of deposition appears on the surface of PPTA fiber, and the surface of the fiber becomes Rough. In Fig.2(b) and (c), there is only a small amount of silver particles attached to the surface of the PPTA fiber after silver plating. This is because the bonding force between the PPTA fiber and the silver layer is extremely poor, and the silver particles generated by reduction are difficult to adhere to the fiber. After the deposition of PCPA, the silver layer on the surface of the PPTA/PCPA fiber became uniform and intact without falling off, as show in Fig.2(e) and (f). Catechol is oxidized to form quinone under alkaline conditions, and can undergo Michael addition or Schiff base reaction with polyamines to form PCPA. The phenolic hydroxyl group of catechol has a strong adhesion effect and a metal binding ability, which can make the silver particles tightly coated on the surface of PPTA fiber.
The crystalline state of PPTA before and after silver-plating is characterized by XRD. It can be seen from Fig.3(a) that there are diffraction peaks appear when the 2θ is 20° or 23°, which is caused by the presence of crystalline polymer in PPTA fiber. In Fig.3(b), there are similar diffraction peaks as Fig.3(a) when 2θ is 20° and 23°, but the peak intensity of (b) is slightly lower than (a), which proves that the PACA layer on the PPTA surface has no influence on the crystalline structure of PPTA, but its presence will cause occlusion and slightly reduce the peak strength. In the Fig.3(c), after silver plating, there are five crystallization peaks at 2θ of 38.3°, 44.5°, 64.6°, 77.5° and 81.6°. These five crystallization peaks correspond to the five crystal planes (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) of the face-centered cubic of silver (JCPDS Card No. 4-783). In addition, the diffraction peaks of the PPTA fiber crystal region when the 2θ is 20° and 23° almost disappear, and there is no diffraction peaks of silver halide and silver oxide in Fig.3(c). These phenomenon indicate that the Ag on the surface of the PPTA/PCPA/Ag is elemental silver. The grain size of Ag can be determined according to the equation: 

$$D = \frac{k\lambda}{\beta_{1/2}\cos\theta}$$

In the equation, k=0.89, λ=0.154 nm (Cu Kα radioactive source), β_{1/2} is the FWHM of strongest crystal face diffraction peak, θ is Bragg diffraction angle. The size of the silver particles is about 20 nm figured out by the equation.

The Figure 4 is the TG curves of pristine PPTA and PPTA/PCPA in different reaction time. Before 325 °C, the weight loss of PPTA is mainly the volatilization of water and residual solvent, and the weight loss of PPTA/PCPA also includes the decomposition of catechol and polyamine oligomers. The PPTA/PCPA prepared with reaction time of 4 h and 24 h lost more weight, indicating that more oligomers were deposited on the fiber surface. The weight loss between 520 °C and 600 °C is mainly due to the decomposition of the aramid fiber skeleton, which is caused by the dehydroxylation of the aramid fiber and the decomposition of alkoxide. At this stage, the smaller the weight loss of the sample is, the more poly(catechol-polyamine) deposited on the fiber surface exist. It can be seen from the figure that as the reaction time increases, the weight loss of the sample decreases, indicating that the deposits on the fiber surface increase. At 800 °C, the remaining substances are mainly carbon residue from the decomposition of aramid fibers and undecomposed PCPA. Therefore, the more the residual amount of the sample is, the more poly(catechol-polyamine) deposited on the fiber surface exist. When the reaction time is 2 h, the residual amount of the sample reaches 40.93%, indicating that there are more deposits on the fiber surface, and the weight loss of the sample before 325 °C is less, indicating that the deposits on the fiber surface are mainly cross-linked network polymers. With the reaction time is increased, the residual volume increases, proving that the deposition of PCPA on the fiber surface increases.
Figure 5 SEM images of PPTA/PCPA prepared at reaction time of (a) 1 h, (b) 2 h, (c) 4 h, (d) 8 h, and PPTA/PCPA/Ag prepared at PCPA deposition time of (e) 1 h, (f) 2 h, (g) 4 h, (h) 8 h.

The Figure 5 is the SEM images of PPTA/PCPA and PPTA/PCPA/Ag with different reaction time. When the reaction time is 1 h (Fig.5a), a small amount of polymer was deposited on the surface of the aramid fiber, but it is still mainly particles. As the time increases to 2 h and 4 h, a uniform and complete layer of PCPA is deposited on the surface of the aramid fiber. However, as the time continues to increase to 8 h (Fig.5d), a large amount of polymer accumulation appears on the surface of the aramid fiber, which makes the surface of the fiber uneven, which is not conducive to the subsequent silver plating. It can be seen from the Fig.5e that when the deposition time is 1 h, a small amount of the silver layer on the surface of the fiber falls off. As time increases to 2 h, the silver layer on the fiber surface becomes uniform and complete. When the deposition time reaches 8 hours, a large area of silver layer on the fiber surface appears to fall off. This is because more oligomers are accumulated on the fiber surface at this time, which increases the roughness of the fiber surface and reduces the adhesion of the silver particles.

Figure 6 Electrical resistivity of PPTA/PCPA/Ag prepared at different PCPA deposition time.

The Figure 6 shows the electrical resistivity of silver-coated PPTA prepared in different PCPA deposition time. It can be seen from the Fig.6 that the resistivity of the silver-plated aramid fiber prepared with the deposition time of 2 h is the lowest. The resistivity has reached 0.1 mΩ·cm, which is far lower than the resistivity of conductive aramid fibers reported in the existing literature. After the deposition time exceeds 4 h, the electrical resistivity increases sharply. This is because more oligomers are accumulated on the surface of the fiber, leading to the silver layer falls off. The results of resistivity of PPTA/PCPA/Ag fiber is consistent with the results of SEM, which proves that a uniform and flat PCPA layer is beneficial to the adhesion of silver particles.

4. Conclusion
In this paper, SEM, XPS, XRD, TGA were used to study the deposition of PCPA on the surface of PPTA fiber and its effect on the silver plating of PPTA fiber. It is proved that catechol and TEPA can modify the aramid fiber by co-deposition to form PCPA layer. The PCPA layer helps to improve the
adhesion of silver particles on the surface of PPTA fiber. The resistivity of the silver-coated PPTA fiber prepared with the PCPA deposition time of 2h is as low as 0.1 mΩ·cm. This highly conductive PPTA/Ag fiber can be used in the field of flexible conductive materials and electromagnetic shielding clothing.

Acknowledgments
This work was financially supported by Scientific and Technological Innovation Programs of Higher Education Institutions in Shanxi (2020L0633) and Program for the Innovative Talents of Taiyuan Institute of Technology(2020XS01).

References
[1] Zhou, Y.F., Sun, Z.H., Jiang, L., et al. (2020) Highly conductive silver nanoparticle-functionalized aramid fiber paper for electrical heaters with rapid response and chemical stability. Industrial And Engineering Chemistry Research, 59(42), 18898-18906.
[2] Zhou, Y.F., Sun, Z.H., Jiang, L., et al. (2020) Flexible and conductive meta-aramid fiber paper with high thermal and chemical stability for electromagnetic interference shielding. Applied Surface Science, 533, 147431.
[3] Li, G., Sun, Z., Gao, S., et al. (2021). The effect of plasma treatment process on the electrical conductivity and coating fastness of silver nanoparticles functionalized aramid fiber paper. Engineering Reports.
[4] Sun, Z., Zhou, Y., Li, W., et al. (2019). Preparation of silver-plated para-aramid fiber by employing low-temperature oxygen plasma treatment and dopamine functionalization. Coatings, 9(10), 599.
[5] Yu, D., S.P. Mu, L.L. Liu, et al. (2015). Preparation of electroless silver plating on aramid fiber with good conductivity and adhesion strength. Colloids & Surfaces A: Physicochemical & Engineering Aspects, 483, 53-59.
[6] Wang, W.C., Li, R.Y., Tian, M., et al. (2013) Surface silvered meta-aramid fibers prepared by bio-inspired poly (dopamine) functionalization[J]. ACS Applied Materials & Interfaces, 5(6): 2062-2069.
[7] Qiu, W.Z., Yang, H.C., Wan, L.S., et al. (2015) Co-deposition of catechol/polyethyleneimine on porous membranes for efficient decolorization of dye water. Journal of Materials Chemistry A, 3(27):14438-14444.
[8] Qiu, W.Z., Lv, Y., Du, Y., et al. (2016) Composite Nanofiltration Membranes via the Co-deposition and Cross-linking of Catechol/Polyethyleneimine. RSC Advances, 6(41):34096-34102.
[9] Zhang, X., Lv, Y., Yang, H.C., et al. (2016) Polyphenol Coating as an Interlayer for Thin-Film Composite Membranes with Enhanced Nanofiltration Performance[J]. ACS Applied Materials & Interfaces, 8(47):32512-32519.
[10] Wang, H., Wu, J., Cai, C., et al. (2014) Mussel inspired modification of polypropylene separators by catechol/polyamine for Li-ion batteries[J]. ACS Applied Materials & Interfaces, 6(8): 5602-5608.
[11] Wu, J., Cai, C., Zhou, Z., et al. (2016) Low-cost mussel inspired poly (catechol/polyamine) coating with superior anti-corrosion capability on copper[J]. Journal of Colloid and Interface Science, 463: 214-221.
[12] Wang, L., Zhang, B., Li, X., et al. (2021) Enhanced adhesion property of aramid fibers by polyphenol-metal iron complexation and silane grafting. The Journal of Adhesion. 97(4): 346-360