Research Article

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Fabrication of PANI-modified PVDF nanofibrous yarn for pH sensor

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Abstract: In recent years, with the rise of an intelligent concept, oral and maxillofacial surgery smart dressing had also attracted the interest of researchers, especially for the pH sensor with flexible medium. In this study, polyvinylidene fluoride (PVDF) nanofibrous yarn was fabricated by a conjugate electrospinning process and modified with *in situ* polymerization of polyaniline (PANI) forming a PANI/PVDF yarn. By a weaving process, these yarns could be woven into a fabric. It was found that both the PANI/PVDF yarn and the fabric showed a sensitivity to pH, about -48.53 mV per pH for yarn and -38.4 mV per pH for fabric, respectively, in the pH range of 4.0–8.0. These results indicated that the prepared PANI-modified PVDF yarn and fabric might have a potential application in intelligent oral and maxillofacial surgery dressings for monitoring wound healing.

Keywords: smart dressing, electrospinning, yarn, PANI, pH sensor

1 Introduction

The pH of a substance is one of its basic chemical properties. It was usually detected by pH value, calculated according to the concentration of hydrogen ion (H^+), $pH = -\log(H^+)$ (1). Generally, the pH value is in the range of 0–14, where $pH = 7$ is neutral, $pH < 7$ is acidic, and $pH > 7$ is alkaline. To determine the pH value of substances, different methods were used including optical and electrochemical ones (1). The optical method was based on pH-sensitive chemical dyes, which may show color changes through absorption, scattering, and luminescence, so as to calibrate the pH value (2), such as pH test paper. The electrochemical method was based on pH-sensitive potential, current, or impedance measurement (3), such as pH test pen and other tools.

The determination of pH value was of great significance in many fields, such as chemical industry, environmental monitoring, and medical care (4). It was shown that the pH value around a wound was a dynamic value during its healing process (5–10). A healthy skin was usually acidic, and the pH value ranged from 4 to 6. Once the skin was damaged, deep skin could be exposed and tissue fluid exuded, and the pH value might reach to 7.4. With the outbreak of inflammation, the pH value might reach to 8 (5). As for the chronic wounds, the pH value was in the alkaline range of 7–9 (9). Accordingly, by detecting the pH value at the wound site, one could monitor and help to manage the wound healing process (11). For the oral cavity, the nonharmful pH range was 6.0–7.5 (12,13). A pH below 5.5 was greatly harmful to both the hard and soft tissues in oral cavity (13,14). However, conventional pH measurement methods were not suitable for wound and oral and maxillofacial surgery healing monitoring, which may require a flexible pH sensing media and could be combined with wound dressing.

Recently, several flexible pH sensors had been reported (15–23). Wang et al. prepared a wearable bandage with polyaniline (PANI) conducting polymer as the pH-sensitive material and a polyvinyl butyral-based reference membrane to monitor the wound site pH (15). Rahimi et al. fabricated a

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flexible pH sensor with a screen-printed Ag/AgCl reference electrode, a carbon working electrode, and a pH-sensitive PANI film on a paper (16). Punjiya *et al.* designed a flexible yarn pH sensor based on the commercial cotton thread coating with carbon and PANI. It was found that the potential was highly sensitive to pH in an electrochemical test (17,18). Moreover, several nanofiber-based flexible pH sensors were prepared by electrospinning process with high pH sensitivity (19–23). However, it was still a challenge to integrate the flexible pH sensors into traditional textile structures (24,25).

In this communication, we proposed a yarn and fabric-based flexible pH sensor. In this context, polyvinylidene fluoride (PVDF) was electrospun into nanofibrous yarn by a conjugate electrospinning process, and then PANI was *in situ* polymerized on the yarn. Moreover, the yarn could be weaved into a fabric. The pH sensitivity of the yarn and fabric was investigated.

2 Materials and methods

PVDF powders (FR903, Shanghai Sanaifu New Material Technology Co., Ltd., China) were dissolved in *N,N*-dimethylformamide (analytical purity, Shanghai Aladdin Biochemical Technology Co., Ltd., China) at 20 wt% under 40°C water bath stirring for 4 h, and then stand for 24 h before electrospinning. During electrospinning process, an electrospinning apparatus (JDF05, Changsha Nayi Instrument Technology Co., Ltd, China) with a twisting module was used to achieve conjugate electrospinning (26–28). As suggested in Figure 1a, the prepared PVDF solution was loaded into a two 5 mL syringes with flat metal needles, and then connected to the positive and negative high voltage supply, respectively.

The voltages were set at +6 and –6 kV. The feeding rate were 0.36 mL·h^{–1}. The distance between the needles and the rotating funnel was 10 cm, and the funnel rotating speed was 200 rpm. The winding speed was 1 rpm. Cu wire with diameter 0.5 mm was used as the core of the spun yarn. Using a home-made paperboard loom, the obtained yarns could be weaved into a fabric.

To modify the obtained yarn and fabric with PANI, two solutions A and B were prepared for *in situ* polymerization. Solution A contained 50 mL deionized water, 0.01 mol (2.542 g) sulfosalicylic acid (Shanghai Aladdin Biochemical Technology Co., Ltd., China), and 0.02 mol (1.8626 g) aniline (Shanghai Aladdin Biochemical Technology Co., Ltd., China); solution B contained 50 mL deionized water and 0.02 mol (4.564 g) ammonium persulfate (Shanghai Aladdin Biochemical Technology Co., Ltd., China). When the substances in solution A and solution B were fully dissolved forming a uniform and transparent solution, they were stored in the refrigerator at 5°C for 2 h. Then, the two solutions were mixed as soon as possible to make a solution C (29), as shown in Figure 1b. The prepared PVDF nanofiber yarn and fabric could be placed into solution C until complete immersion, and then stored in a refrigerator at 5°C for 12 h. Then, PANI could be polymerized onto the PVDF yarn and fabric. For later testing, the PANI-modified PVDF yarn and fabric was washed with deionized water for two to three times and then dried at 60°C for 8 h.

The morphology of prepared yarn and fabric was examined by a scanning electron microscopy (SEM; Phenom Pro, Eindhoven, The Netherlands) at 10 kV after coating gold for 60 s. The chemical structures of the prepared samples were analyzed by a Fourier-transform infrared spectroscopy (FTIR; Thermoscientific Nicoletin 10, USA). The mechanical properties of prepared yarns (5 cm) and fabrics (2 cm × 2 cm) before and after polymerization were tested by

Figure 1: (a) Diagram of the preparation of PVDF yarn and fabric and (b) the preparation of PANI solution and the preparation of PANI/PVDF yarn.

universal tension machine (Instron 3352, US). The water contact angles of the fabrics before and after polymerization PANI were examined by an optical tensiometer (Attension Theta, Biolin Scientific, Germany) with 5 μL water drop. The prepared PANI/PVDF yarns and fabrics were put into the pH standard buffer (4.0, Leici, Shanghai Yidian Scientific Instrument Co., Ltd., China), and diluted them continuously through the pipet to increase their pH ensuring that the pH increased by 1 every time until pH = 8. The open circuit voltage with time was measured by an electrochemical workstation (CHI 660e, Shanghai Chenhua Instrument Co., Ltd, China), using Ag/AgCl as reference electrode and Cu core as working electrode.

3 Results and discussion

Figure 2 showed the morphologies of the prepared PVDF yarns and fabrics before and after PANI modification. From the comparison of Figure 2a, b, e and f, it could be found that there were obvious differences in color before and after PANI polymerization. The PVDF yarns and fabrics were white, whereas after *in situ* polymerization PANI modification, the fabrics and yarns were dark green. Through the SEM images in Figure 2c and d, it could be seen that the fibers in PVDF yarn were smooth, uniform, and arranged in a certain direction with a

certain twist showing a compact yarn structure as a whole. After *in situ* polymerization of PANI, there were obvious PANI particles on the surface of yarn and fiber and the pores between fibers (Figure 2g and h). These PANI particles blurred the original clear yarn twist, which indicated that PANI had been successfully *in situ* polymerized onto PVDF yarns and fabrics. In addition, the diameter of the yarn before PANI modification was about 324 μm , and the average diameter of the fiber was $1.55 \pm 0.61 \mu\text{m}$. Although the modified yarn diameter was about 458 μm , and the average fiber diameter increased to $2.48 \pm 0.98 \mu\text{m}$. The increases of yarn and fiber diameter were also due to the adhesion of PANI particles to the surface of fiber and yarn. Moreover, the surface wettability of the fabrics before and after polymerized PANI was also examined. As suggested in the inset images in Figure 1a and e, the water contact angles were about 120.4° and 128.6° before and after coating PANI, respectively. These prepared PVDF fabrics were both hydrophobic, and the polymerization of PANI could enhance the hydrophobicity.

Figure 3a showed the FTIR spectrum of the yarn before and after polymerization. It could be seen that the yarn after modified by PANI had new absorption peaks at the wave numbers of 1,475, 1,542, 1,582, 2,853, and 2,920 cm^{-1} . These absorption peaks correspond to the infrared absorption peaks of PANI (29). This also suggested that PANI was successfully polymerized onto a PVDF yarn.

Figure 2: Optical images of (a) PVDF fabric and (b) yarn, (c and d) the SEM images the PVDF yarn, (e and f) the optical, and (g and h) the SEM images of PANI/PVDF fabric and yarn. Inset images in (a) and (e) were the contact angles of the fabrics.

Figure 3: (a) FTIR spectra and (b) stress-strain curve of the prepared PVDF and PANI/PVDF yarns and fabrics.

From the stress-strain curve in Figure 3b, it can be found that PANI attached to the PVDF yarn might significantly improve the tensile stress and strain of the yarn. Before PANI modification, the tensile strength of the yarn was 4.56 MPa, and the elongation was about 13.95%. After PANI modification, the tensile strength of the yarn increased to 6.39 MPa and the elongation increased to 19.62%. The improvement effect was 40.1% and 40.6%, respectively. Combined with the SEM images in Figure 2d and h, after PANI modification, a large number of PANI particles were attached to the yarn, fiber surface, and the gap between fibers. These particles improved the friction coefficient between fibers, so as to improve the tensile strength and elongation of the yarn. For the fabrics, due to the fabric structure, the elongation of the fabrics

was greatly improved compared to the yarns. After coating with PANI, the tensile strength of the PANI/PVDF fabric was enhanced obviously, whereas the elongation of the PANI/PVDF fabric was reduced. It could be imagined that during the PANI *in situ* polymerization process of the fabric, PANI polymerized onto the yarn, and then enhanced the tensile strength, while for the connecting sites of the warp and weft yarns, less PANI polymerized here, and then under the high tensile force, the elongation was reduced.

To investigate the pH sensitivity of the prepared PANI/PVDF yarn and fabric, the open circuit voltages in the range of $\text{pH} = 4-8$ were measured, as shown in Figure 4. It was suggested that the open circuit voltage of PANI/PVDF yarn decreased significantly with the increase of pH value,

Figure 4: The pH response of (a) PANI/PVDF yarn and (b) PANI/PVDF fabric in the pH range of 4–8.

as displayed in Figure 4a. At pH 4, the open circuit voltage was 273 mV, whereas when pH increased to 8, the open circuit voltage decreased to 78.9 mV. The pH sensitivity was about -48.53 mV per pH. Moreover, with the increase of pH, the response of PANI/PVDF yarn to pH was increasingly faster, which was reflected in the increasingly shorter response time when pH changes. Especially, in the range of pH 6–8, the response sensitivity of PANI/PVDF yarn to pH was -50 mV per pH, and the response time was 30 s per pH.

For the PANI/PVDF fabric, the pH sensitivity was about -38.4 mV per pH in the pH range of 4–8 and -42.35 mV per pH in the pH range of 6–8, as indicated in Figure 4b. It seemed that the pH potential sensitivity of the PANI/PVDF fabric was lower than the yarn, which may result from the less PANI in the combining sites of the warp and weft yarns in the fabric. While the response time of the fabric was less than that of the yarn, which suggested the fabric may give a fast response to the pH change. These results demonstrated that the PANI-modified electrospun yarn as well as its fabric could be used as a flexible pH sensor.

4 Conclusion

In conclusion, we fabricated PANI/PVDF yarn successfully by conjugate electrospinning process and *in situ* polymerization of PANI. The prepared yarn could be weaved into a fabric for smart dressing. The SEM and FTIR spectra showed that PANI particles were uniformly attached to the surface of the as-spun yarn. And after PANI modification, the tensile strength and elongation of the yarn could be improved up to 40%, which could meet the needs of weaving. In the range of pH 4.0–8.0, the PANI/PVDF yarn and fabric showed potential sensitivity to pH about 48.53 and 38.4 mV per pH, respectively. Specific in the pH range of 6.0–8.0, the sensitivity could be 50, and 42.35 mV per pH, which may be applied as oral and maxillofacial surgery smart dressing to monitor wound healing process.

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References

- (1) Alam AU, Qin Y, Nambiar S, Yeow JTW, Howlader MMR, Hu NX, et al. Polymers and organic materials-based pH sensors for healthcare applications. *Prog Mater Sci.* 2018;96:174.
- (2) Wencei D, Abel T, McDonagh C. Optical chemical pH sensors. *Anal Chem.* 2014;86:15.
- (3) Lindfors T, Ivaska A. pH sensitivity of polyaniline and its substituted derivatives. *J Electroanal Chem.* 2002;531:43.
- (4) Chen S, Jiang S, Jiang H. A review on conversion of crayfish-shell derivatives to functional materials and their environmental applications. *J Bioresour Bioprod.* 2020;5:238–47.
- (5) Schneider LA, Grabbe AKS, Dissemmond J. Influence of pH on wound-healing: a new perspective for wound-therapy. *Arch Dermatol Res.* 2007;298:413.
- (6) Madni A, Kousar R, Naeem N, Wahid F. Recent advancements in applications of chitosan-based biomaterials for skin tissue engineering. *J Bioresour Bioprod.* 2021;6:11–25.
- (7) Yan X, Yu M, Ramakrishna S, Russell S, Long Y. Advances in portable electrospinning devices for in situ delivery of personalized wound care. *Nanoscale.* 2019;11:19166–78.
- (8) Dong W, Liu J, Mou X, Liu G, Huang X, Yan X, et al. Performance of polyvinyl pyrrolidone-isatis root antibacterial wound dressings produced in situ by handheld electrospinner. *Colloid Surf B.* 2020;188:110766.
- (9) Gethin G. The significance of surface pH in chronic wounds. *Wounds UK.* 2007;3:3.
- (10) Percival S, McCarty S, Hunt J, Woods EJ. The effects of pH on wound healing, biofilms, and antimicrobial efficacy. *Wound Repair Regen.* 2014;22(2):174.
- (11) Qin M, Guo H, Dai Z, Yan X, Ning X. Advances in flexible and wearable pH sensors for wound healing monitoring. *J Semicond.* 2019;40(11):111607.
- (12) Aframian DJ, Davidowitz T, Benoliel R. The distribution of oral mucosal pH values in healthy saliva secretors. *Oral Dis.* 2006;12:420–23.
- (13) Bardow A, Pederson AML, Nauntofte B. Saliva. In: Miles TS, Nauntofte B, Svensson P, editors. *Clinical oral physiology.* Copenhagen: Quintessence; 2004. p. 17–18, 30–33.
- (14) Aframian D, Markitziu A. Oral manifestations of bulimia nervosa. *Harefuah.* 1999;136:537–40.
- (15) Guinovart T, Ramirez GV, Windmiller JR, Andrade FJ, Wang J. Bandage-based wearable potentiometric sensor for monitoring wound pH. *Electroanalysis.* 2014;26:1345.

- (16) Rahimi R, Ochoa M, Parupudi T, Zhao X, Yazdi IK, Dokmeci MR, et al. A low-cost flexible pH sensor array for wound assessment. *Sens Actuators B*. 2016;229:609.
- (17) Punjiya M, Rezaei H, Zeeshan MA, Sonkusale S. A flexible pH sensing smart bandage with wireless cmos readout for chronic wound monitoring. In 19th International Conference on Solid-State Sensors Actuators and Microsystems (TRANSDUCERS); 2017. p. 1700.
- (18) Lyu B, Punjiya M, Matharu Z, Sonkusale S. An improved pH mapping bandage with thread-based sensors for chronic wound monitoring. In IEEE International Symposium on Circuits and Systems (ISCAS); 2018. p. 1–4.
- (19) Steyaert, I, Rahier, H, Clerck, KD. Nanofibre-based sensors for visual and optical monitoring. *Electrospinning for High performance sensors. nanoscience and technology*. Cham: Springer; 2015.
- (20) Zhao LY, Duan GG, Zhang GY, Yang H, Jiang S. Electrospun functional materials toward food packaging applications: a review. *Nanomaterials*. 2020;10(1):150.
- (21) Agarwal A, Raheja A, Natarajan TS, Chandra TS. Development of universal pH sensing electrospun nanofibers. *Sens Actuators B*. 2012;161:1097.
- (22) Schoolaert E, Steyaert I, Vancoillie G, Geltmeyer J, Lava K, Hoogenboom R, et al. Blend electrospinning of dye-functionalized chitosan and poly(ϵ -caprolactone): towards biocompatible pH-sensors. *J Mater Chem B*. 2016;4:4507.
- (23) Pan N, Qin J, Feng P, Li Z, Song B. Color-changing smart fibrous materials for naked eye real-time monitoring of wound pH. *J Mater Chem B*. 2019;7:2626.
- (24) Liu L, Xu W, Ding Y, Agarwal S, Greiner A, Duan G. A review of smart electrospun fibers toward textiles. *Compos Commun*. 2020;22:100506.
- (25) Wei DW, Wei H, Gauthier AC, Song J, Jin Y, Xiao H. Superhydrophobic modification of cellulose and cotton textiles: Methodologies and applications. *J Bioresour Bioprod*. 2020;5:1–15.
- (26) Dai Z, Yan FF, Qin M, Yan X. Fabrication of flexible SiO₂ nanofibrous yarn via a conjugate electrospinning process. *e-Polymers*. 2020;20:600–5.
- (27) Dai Z, Wang N, Yu Y, Lu Y, Jiang L, Zhang DA, et al. One-step preparation of a core-Spun Cu/P(VDF-TrFE) nanofibrous yarn for wearable smart textile to monitor human movement. *ACS Appl Mater Interfaces*. 2021;13(37):44234–242.
- (28) Jian S, Tian Z, Hu J, Zhang K, Zhang L, Duan G, et al. Enhanced visible light photocatalytic efficiency of Ia-doped ZnO nanofibers via electrospinning-calcination technology. *Adv Powder Mater*. 2021. doi: 10.1016/j.apmate.2021.09.004.
- (29) He HW, Zhang B, Yan X, Dong RH, Jia XS, Yu GF, et al. Solvent-free thermocuring electrospinning to fabricate ultrathin polyurethane fibers with high conductivity by in situ polymerization of polyaniline. *RSC Adv*. 2016;6:106945.