NANOFIBERS MEMBRANE FOR DETECTING HEAVY METAL IONS

by

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Carbon materials are promising candidates for sensors to detect heavy metal ions. This paper reported an effective method of fabricating nanofiber membrane sensor for detection of heavy metal ions by electrospinning with the carbon nanoparticles and PANi (polyaniline) as additives. The results revealed that the PANi/C/PAN nanofiber membrane was the most economical approach to adsorbing and detecting metal ions with highly sensitive property. This paper sheds a light on an economic fabrication of nanofiber membrane sensor with well-defined characteristics in electrical sensors and adsorption applications.

Key words: *carbon nanoparticles, detection, adsorption, electrospinning, nanofiber*

Introduction

Heavy metal cations, such as Fe^{3+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, and Hg^{2+}, have attracted growing concern because they are harmful to the environment and human health as well. Heavy metals are released from mining, exhaust gas, wastewater irrigation, and so on [1], and they cannot degrade in the environment, which will enter water, air, and soil and finally take a threat to humans and animals [2]. Most of the countries or districts all over the world have set strict maximum residue limits for the heavy metal ions. The accumulation of heavy metals is harmful to human health. Heavy metals are very easy to accumulate in the brain, kidney and other organs, progressive damage to the body function. The excess consumption of heavy metals will cause acute, subacute and chronic poisoning and lead to Itai-itai disease, nephropathy, Wilson's disease, and Minamata disease, respectively.

With the development of the human society technology, the adsorption of oil spills pollutions and heavy metal ions are urgently needed. Electrochemical sensors have produced as an effective tool to sensitively detecting heavy metal ions with the advantages of rapidity, low cost, facility, and portability [3]. Carbon materials are promising candidates for electrochemical sensors to detect heavy metal irons because they have good performance such as electrical conductivity, large specific surface area, and high chemical stability [4]. Carbon nanoparticles have been widely used in the field of chemical industries, energy, environment engineering and sensor due to its superior properties of low cost, chemical stability, easy preparation, excellent adsorption performance and environmentally friendly characters. Car-

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bon nanomaterials, such as MWCNT, graphene oxide, and reduced graphene oxide [5], have been successfully used to detect heavy metal ions.

Electrospinning is a simple and versatile technique for fibers fabrication with controllable diameters, compositions, and morphologies [6-16]. The nanofiber membrane's adsorption is an intrinsic property of the geometrical potential of nanoscale structure [17]. In recent years, nanofiber membrane has been widely used in oil pollution and heavy metal adsorption fields. Liu [18] prepared nanoporous fibrous mats by a one-step electrospinning process used as oil sorbents for oil-water separation. Li *et al.* [19] fabricated zirconium dioxide (ZrO_2) nanofibers by the critical bubble electrospinning, and the obtained ZrO_2 nanofibers showed excellent high temperature resistant adsorption and separation properties. To explore the heavy metals detection, herein, carbon nanoparticles and PANi were electrospun and constructed as an electronic sensor to detect Cu^{2+} ions. It seems to be imperative that carbon nanoparticles can be used as an additive material in electrospinning for fabrication of nanofibers membrane with well-defined characteristics of heavy metal ion detection.

Experiment

The PANi (Mw = 93x) was purchased from Arkpharm Company. The PAN powders (Mw =150000 g/mol) were obtained from an online shop. The solvent used for dissolving polymers was N, N-dimethylformamide (DMF, purchased from Jiangsu Qiangsheng Functional Chemical Co., Ltd.) All the materials were directly used as received without any further purification.

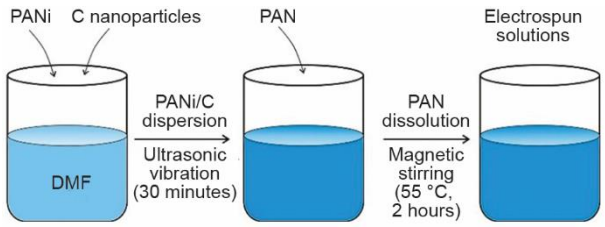

Figure 1. The scheme of solutions preparation

The solutions were prepared in two steps, fig. 1. First, the solutions of PANi/C were prepared by dispersing various amounts of PANi and carbon nanoparticles in DMF separately by using ultrasonic oscillator for 30 minutes. Second, PANi/C/PAN electrospun solutions were prepared by dissolving PAN in PANi/C/DMF solutions with using a magnetic stirrer at 55 °C for 2 hours. The proposed scheme of the two steps was given in fig. 1. The calculated PANi concentrations for each component of the various samples were listed in the tab. 1.

Table 1. Concentration of PANi, carbon nanoparticles, PAN, and DMF in the mixed solutions

Samples	PAN [g]	Carbon nanoparticles [g]	PANi [g]	DMF [g]
O	0.8	0	0	9.2
A	0.8	0.2	0.08	8.92
B	0.8	0.4	0.08	8.72
C	0.8	0.6	0.08	8.52

The electrospinning set-up was shown in fig. 2. The prepared solution was loaded into a syringe with a needle tip diameter of 0.7 mm that was positive charged. The polymer solution was electrospun at room temperature at a voltage of 18 kV. The negative collector

was 18 cm from the tip of the needle. The feeding rate of the polymer solution was 1 mL/h. Continuous nanofibers were deposited on the collector and formed a nonwoven fibrous mat.

The electrical properties of the electrospun nanofibers membrane were measured by a multimeter (NUIT UT61-A). The surface morphology of the electrospun nanofibers was examined by SEM (Hitachi S-4800, Tokyo, Japan). The mechanical property was tested by the universal material testing machine (INSTRON-3365, USA).

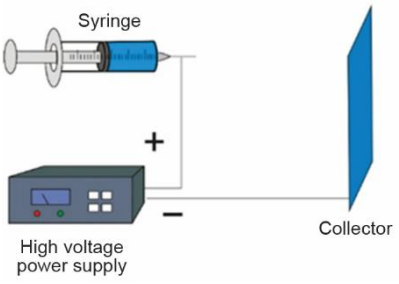

Figure 2. The electrospinning set-up

Result and discussion

Figure 3 shows SEM images and corresponding fibers diameters distribution of PANi/C/PAN nanofibers with various concentrations of PANi/C/PAN. The nanofibers exhibited cylindrical morphology with roughness surface and randomly distributed in fibrous mat with very uniform and dense structures adhered to each other. Overall, the size and morphology of the nanofibers were affected by the concentration of PANi/C in the solution. The diameters of the nanofibers increase with the concentration of PANi/C in the solution.

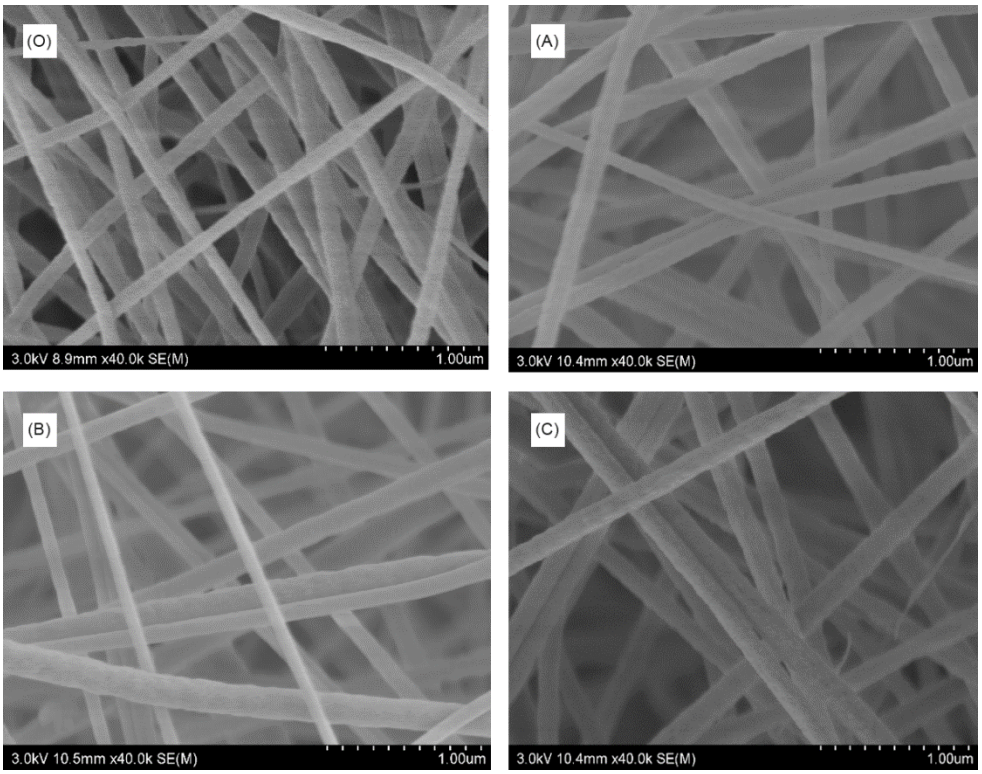

Figure 3. The SEM images for the PANi/C/PAN nanofibers; (O) pure PAN nanofibers membrane, (A) PANi/C/PAN nanofibers (PANi/C = 2:5), (B) PAN/C/PANi nanofibers (PANi/C = 1:6), (C) PAN/C/PANi nanofibers (PANi/C = 2:15)

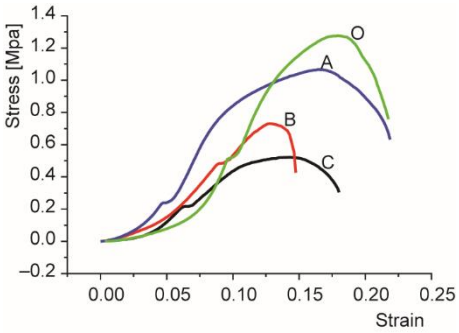

Figure 4. Stress-strain curve for PANi/C/PAN nanofibers membrane; (O) pure PAN nanofibers membrane, (A) PAN/C/PANi nanofibers (PANi/C = 2:5), (B) PAN/C/PANi nanofibers (PANi/C = 1:6), (C) PAN/C/PANi nanofibers (PANi/C = 2:15)

The mechanical property was tested by the universal material testing machine. The stress-strain curve was shown in fig. 4. It was clear that the mechanical strength of the PANi/C/PAN nanofiber membrane decreased compared with the pure PAN nanofiber membrane. With the C nanoparticles increasing, the mechanical strength of the membrane decreases. It was shown that the C nanoparticles had a negative impact on the nanofiber membrane's mechanical strength, see fig. 4.

The specimens of nanofiber membranes were cut into 3×3 cm rectangular shape and the schematic diagram was assembled in the way shown in fig. 5. The nanofiber membranes were immersed in 10 mL aqueous solution of copper acetate (the concentration of Cu^{2+} ions is 20 mol/L). Then the maximal current was recorded within 1 minure. The maximum current of the membrane in the solution within 1 minute and the thickness of the membrane were shown in the tab. 2. Sample O is the nanofiber membrane of PAN without PANi/C. Samples A, B, and C are the nanofiber membranes with different proportions of C and PANi, respectively. It was shown that the PANi/C nanofibers has a sensitivity to Cu^{2+} ions. Because the PAN membrane with PANi/C can adsorb Cu^{2+} ions, when Cu^{2+} ions were adsorbed into the membrane, it caused the change of the current. With the increasing of the carbon nanoparticles concentration in the solution, the nanofiber membrane has a more sensitive response to the aqueous solution of Cu^{2+} ions. The more adsorption of the Cu^{2+} ions on the membrane, the more the change of the current, and the PAN/C/PANi nanofiber membrane has a more sensitive response to heavy metal ions with excellent property.

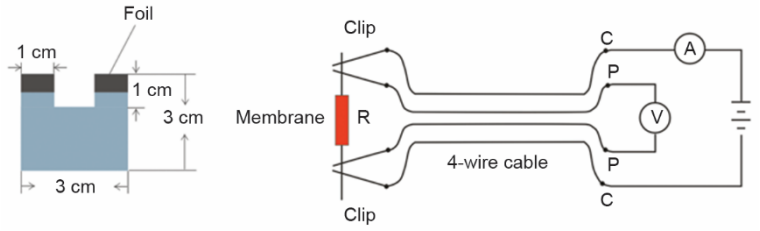

Figure 5. Schematic diagrams of test device

Table 2. The maximum current of the membrane in the solution within 1 minute and the thickness of the membrane

Membrane code	PANi/C	Maximum current in deionized water [μA]	Maximum current in aqueous solution of copper acetate [μA]
O	0	0	3.7
A	2:5	0	7
B	1:6	0.2	8.5
C	2:15	0.3	18.3

Conclusion

This paper suggested an effective method of fabricating nanofiber membrane for heavy metal ion's adsorption and detection. The PANi/C/PAN nanofiber membrane was prepared by adding the carbon nanoparticles and PANi into the solution. The nanofiber membrane was used to adsorb and detect the cupric ions in aqueous solution. It was shown that the nanofiber membrane has a great sensitive to the cupric ions. With increasing of the carbon nanoparticles' concentration and PANi in the solution, the adsorption of the cupric ions increases, and the current also increases. This method provided a facile and low cost way of fabricating nanofiber membrane for metal ion's detection, especially for micro-scale or nanoscale sensors [20].

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References

[1] Thiruppathi, A. R., *et al.*, Facile One-Pot Synthesis of Fluorinated Graphene Oxide for Electrochemical Sensing Of Heavy Metal Ions, *Electrochem Commun, 76* (2017), Mar., pp. 42-46
[2] Guo, Z., *et al.*, Simultaneous Determination of Trace Cd(II), Pb(II) and Cu(II) by Differential Pulse Anodic Stripping Voltammetry Using a Reduced Graphene Oxide-Chitosan-Poly-L-Lysine Nanocomposite Modified Glassy Carbon Electrode, *J. Colloid Interface Sci, 490* (2017), Mar., pp. 11-22
[3] El-Shishtawy, R. M., *et al.*, Development of Cd^{2+} Sensor Based on BZNA/Nafion/Glassy Carbon Electrode by Electrochemical Approach, *Chem. Eng. J., 352* (2018), Nov., pp. 225-231
[4] Wu, W., *et al.*, Sensing Nitrite with a Glassy Carbon Electrode Modified with a Three-Dimensional Network Consisting of Ni7S6 and Multi-Walled Carbon Nanotubes, *Microchim Acta, 183* (2016), 12, pp. 3159-3166
[5] Wu, W.Q., *et al.*, Sensitive, Selective and Simultaneous Electrochemical Detection of Multiple Heavy Metals in Environment and Food Using a Low Cost Fe_3O_4 Nanoparticles/Fluorinated Multi-Walled Carbon Nanotubes Sensor, *Ecotoxicology and Environmental Safety, 175* (2019), July, pp. 243-250
[6] Zhou, C. J., *et al.*, Silkworm-Based Silk Fibers by Electrospinning, *Results in Physics, 15* (2019), Dec., ID 102646
[7] Li, X. X., He, J. H., Nanoscale Adhesion and Attachment Oscillation under the Geometric Potential. Part 1: The Formation Mechanism of Nanofiber Membrane in the Electrospinning, *Results in Physics, 12* (2019), Mar., pp. 1405-1410
[8] Liu, Y. Q., *et al.*, Nanoscale Multi-Phase Flow and its Application to Control Nanofiber Diameter, *Thermal Science, 22* (2018), 1, pp. 43-46
[9] He, J. H., *et al.*, Review on Fiber Morphology Obtained by the Bubble Electrospinning and Blown Bubble Spinning, *Thermal Science, 16* (2012), 5, pp. 1263-1279
[10] Zhao L., *et al.*, Sudden Solvent Evaporation in Bubble Electrospinning for Fabrication of Unsmooth Nanofibers, *Thermal Science, 21* (2017), 4, pp. 1827-1832
[11] Liu, L. G., *et al.*, Solvent Evaporation in a Binary Solvent System for Controllable Fabrication of Porous Fibers by Electrospinning, *Thermal Science, 21* (2017), 4, pp. 1821-1825
[12] Tian, D., *et al.*, Self-Assembly of Macromolecules in a Long and Narrow Tube, *Thermal Science, 22* (2018), 4, pp. 1659-1664
[13] Peng, N. B., *et al.*, A Rachford-Rice Like Equation for Solvent Evaporation in the Bubble Electrospinning, *Thermal Science, 22* (2018), 4, pp. 1679-1683
[14] Liu, Z., *et al.*, A Mathematical Model for the Formation of Beaded Fibers in Electrospinning, *Thermal Science, 19* (2015), 4, pp. 1151-1154
[15] Tian, D., *et al.*, Macromolecular Electrospinning: Basic Concept & Preliminary Experiment, *Results in Physics, 11* (2018), Dec., pp. 740-742

[16] Li, X. X., *et al.*, The Effect of Sonic Vibration on Electrospun Fiber Mats, *Journal of Low Frequency Noise, Vibration and Active Control, 16* (2019), 3-4, pp. 1246-1251
[17] Tian, D., *et al.*, Geometrical Potential and Nanofiber Membrane's Highly Selective Adsorption Property, *Adsorption Science & Technology, 37* (2019), 5-6, pp. 367-388
[18] Liu, L. G., *et al.*, Electrospun Polysulfone/Poly (Lactic Acid) Nanoporous Fibrous Mats for Oil Removal from Water, *Adsorption Science & Technology, 37* (2019), 5-6, pp. 438-450
[19] Li, Y., *et al.*, Fabrication and Characterization of ZrO_2 Nanofibers by Critical Bubble Electrospinning for High-Temperature-Resistant Adsorption and Separation, *Adsorption Science & Technology, 37* (2019), 5-6, pp. 425-437
[20] He, J. H., From Micro to Nano and from Science to Technology: Nano Age Makes the Impossible Possible, *Micro and Nanosystems, 12* (2020), 1, pp. 1-2

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