

Synthesis, Structural and Gas Sensing Properties of Nano-branched Coaxial Polyaniline Fibers by Electrospinning

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Abstract. Polyaniline (PANI) is a promising functional polymer in the field of toxic gas detection. In this paper, nano-branched coaxial PANI fibers were grown on electrospun poly(methyl methacrylate) (PMMA) nanofibers by an *in situ* chemical oxidative polymerization method. The resultant PANI/PMMA fibers were characterized by scanning electronic microscopy and Raman spectrum analysis. The conductivity of an individual coaxial PANI/PMMA fiber is about 2.123 S/cm and that of the conducting PANI coating layer is about 21.8 S/cm. The ammonia sensing properties of the samples were tested by means of impedance analysis. The nano-branched PANI fibers can response significantly to low concentration of ammonia due to large specific surface area, and the sensitivity shows good linear relationship to the ammonia concentration of ppm level. These results indicate that nano-branched coaxial PANI fibers are promising candidate for detection of toxic ammonia gas.

1. Introduction

Extensive interests are directed toward the development of highly sensitive gas sensors using novel and nanostructured materials [1]. Till now, tremendous progress has been achieved in the area of one-dimensional (1D) nanomaterials and controllable assembly into micro-devices by top-down or bottom-up approach. However, the integration of nanosized 1D elements into electronic devices presents a big challenge of achieving reliable electrical contacts and reproducible performance. Among the different strategies, electrospinning provides some advantages including easy fabrication, versatility and mass production. With the assistance of electrospinning, organic or inorganic materials were fabricated into non-woven fiber mat, directed single fiber, and well aligned fibers or helix structures with diameter ranging from tens of nanometer to tens of micrometers [2,3].

Selection of suitable functional materials is crucial for the exploitation of electrospinning technique to fabricate electronic devices. For example, polyaniline (PANI) enjoys great popularity in new intelligent materials [4,5]. In comparison with other conjugate polymers, the price of PANI is cheap and abundant, which can be easily polymerized, with high conductivity and a broad prospect for application. But the strong polarity like other intrinsically conductive polymers with π conjugate system leads to difficult processability, which limits their application. Some researchers tried to dissolve PANI in polymer solutions and get composite fibers with relatively low electrical percolation and conductivity [6]. To solve the problem, researchers came up with an *in situ* polymerization method that grows PANI on the surface of glass [7], iron [8], textile [9], multi-walled carbon tubes [10] and even ice [11].

Here nanostructured PANI are grown on the surface of electrospun poly(methyl methacrylate) (PMMA) fibers with ammonium peroxydisulfate (APS) as oxidant and 5-sulfosalicylic acid dihydrate (SSA) as catalytic agent and dopant at 5 °C. The novel structure was characterized with Raman spectrum and scanning electronic microscopy. And the ammonia sensing property was also measured.

2. Experimental details

PMMA (average degree of polymerization is 43982) was purchased from Alfa Aesar, Tianjin. N,N-dimethyl formamide (DMF), tetrahydrofuran (THF), aniline, APS, SSA were all purchased from Sinopharm Chemical Reagent, Beijing. All the reagents were used without further purification. A dc high-voltage power supply (40 kV, Tianjin Dongwen) was employed in the electrospinning process.

The electrospinning precursor was a PMMA solution (9.1 wt%) prepared with 2 g PMMA dissolved and stirred thoroughly in 5 g DMF and 5 g THF for 3 hours. A syringe was employed as polymer solution holder and a stainless steel needle (inner diameter is 0.72 mm) was used as positive electrode connected to the power supply. Aluminum foil (5 cm×5 cm) connected to the ground was applied as negative electrode. A plastic ring with an inner diameter of 3 cm and a height of 1 cm was added to the traditional electro-spinning machine. The vertical distance from the stainless steel needle to the plastic ring was 10 cm. A 12 kV voltage was employed and kept for 3 minutes. Then the plastic ring was covered with a uniformly tight round thin porous fiber net. Fig. 1 shows the schematic illustration of the applied electrospinning setup. A piece of polyethylene with a thickness of 0.6 mm and a hole sized by 1 cm×2 cm was prepared in advance. The porous fiber net was then transformed to cover the hole and tied to the polyethylene slice with double-sided adhesive tape.

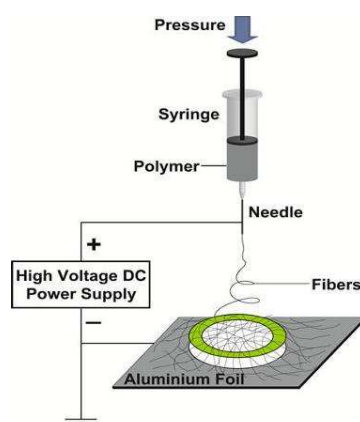


Fig. 1 Schematic illustration of electrospinning setup used in this discussion

Firstly, 0.01 mol SSA was dissolved thoroughly in 50 ml deionized water. Then 0.02 mol aniline was added and stirred to form a stable solution named by A. Secondly 0.02 mol APS was dissolved and stirred in 50 ml deionized water to form solution B. Both solution A and solution B were kept in a refrigerator of 5 °C for one hour. Thirdly, solution A and solution B were mixed, and electrospun PMMA fibers were immersed in the mixed solution C and kept steady in 5 °C for 6.5 h. PANI grew from chemical oxidative polymerization of aniline and the solution turned green, also the fibers and the plastic slice were covered by green PANI. Lastly, the fibers were taken out and washed with 50 ml water for 3 times and dried in air. The resultant PANI/PMMA fibers were characterized by scanning electron microscopy (SEM) and Raman spectrum analysis. The SEM samples were coated with gold by sputtering method for 80 seconds and the gold layer was about 10 nm. To measure electrical and gas sensing properties of the nano-branched coaxial fibers, two parallel gold electrodes with an insulating gap of 3 mm on a glass slide were fabricated, then the coaxial fiber mat was placed across the Au electrodes and fixed to the electrodes by carbon paste. The electrical and gas sensing properties of the fibers were measured by a Keithley 6517 high resistance meter and a home-made gas sensing system.

3. Results and discussion

The samples were characterized by Raman spectrum analysis with an incident light wavelength of 532.16 nm. The Raman spectrum of PANI/PMMA coaxial fibers summits matches typical PANI Raman shift peaks [12]. The micro structure of the electrospun fiber and surface features of coaxial fiber net were characterized in Fig. 2 by scanning electronic microscopy. Fig. 2a showed the non-woven web obtained from above electrospinning process. The diameter of the electrospun PMMA fiber is not uniform by nature of electrospinning technique and is about 6 μm . Fig. 2b showed the coaxial fiber after the *in situ* chemical polymerization process. The coaxial fiber was covered by some nanostructures which are characterized to be PANI. Fig. 2c-d shows the surface structure of the PANI/PMMA coaxial fiber, which indicates that PANI nanorod array and nano-clusters self-assembled on the surface of the coaxial fiber. The surface nano-stick is several micro meters long and the diameter of the stick ranges from 170 nm to 210 nm.

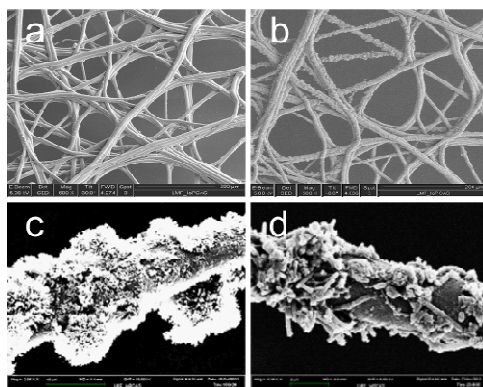


Fig. 2 SEM images of (a) as-spun PMMA fibers; (b) coaxial PANI/PMMA fibers after *in situ* chemical polymerization; (c-d) PANI nano-branches on the PANI/PMMA fibers.

It is supposed that the PANI membrane firstly grow evenly on the surface of PMMA fiber because of Interfacial compatibility of PANI to PMMA [13]. Some bumps rise up for the intrinsic non-uniformity of PANI membrane that is half amorphous and half crystallized. Then PANI grow on the chosen facet of the bumps and along preferred orientation into a PANI fiber or stick, which is much faster than the growth of PANI membrane so that the fibers are not covered by PANI membrane and several micro meters in length.

The current-voltage (I-V) curve of the sample was measured by scanning the voltage from -5 to 5 V and showed a linear relationship. The resistance of fiber mat (3 mm \times 3 mm) is about 2.5 M Ω and that of a single fiber is 1.5 M Ω . So, the average conductivity of the coaxial PANI/PMMA fiber ($\sigma=L/RS=4L/\pi\cdot R\cdot D^2$) is calculated to be about 2.12 S/cm. Since the PMMA core is insulating and the average thickness of the PANI coating layer grown for 6.5 hours is about 100 nm, the actual conductivity of the conducting PANI part ($\sigma=L/RS=4L/\pi\cdot R\cdot (D^2-d^2)$) is calculated to be about 21.8 S/cm, which is consistent with the intrinsic conductivity of one single PANI nanotube prepared by template-free self-assembly that is about 31.4 S/cm [14]. The sensing property to ammonia of the coaxial PANI fiber web sample was tested. The reversibility and repeatability of the sample were tested on 30 ppm, 50 ppm and 80 ppm ammonia concentration, as shown in Fig. 3. The period of the test cycle is 240 s. The gas dispersion process and pump process take half of the period separately. Nano-branched PANI fibers show a distinguished R/R_0 of 1.3 for 30 ppm, 2.0 for 50 ppm and 2.5 for 80 ppm, which illustrated that the PANI/PMMA microfiber gas sensors decorated with PANI nano-branches can not only detect the existence of ultra-low concentration of ammonia, but also can estimate the values of concentration in a short reverse time of tens of ppm level.

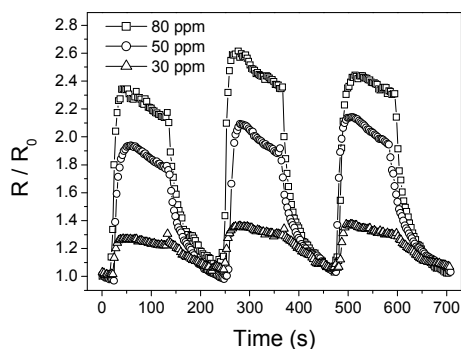


Fig. 3 The reversible response curves to 30 ppm, 50 ppm and 80 ppm concentration

4. Conclusion

In summary, novel nano-branched PANI fibers are fabricated by an *in situ* chemical oxidative polymerization method in water solution of 5-sulfosalicylic acid, APS and aniline by using electrospun PMMA fibers as hard template. The coaxial PANI/PMMA fibers coating with nano-branched PANI have a larger surface area and thus higher gas sensitivity, which can be used to detect trace level of ammonia (80 ppb). Furthermore, the 5-sulfosalicylic acid doped PANI coaxial fibers are electrically and structurally stable even after more than 120 days. These results indicate that the nano-branched PANI fibers maybe have practical usage in the alarm system and concentration determination of toxic gases like ammonia due their good environmental stability, high sensitivity and low costs.

Acknowledgments

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References

- [1] A. Rothschild and H. L. Tuller: J. Electroceram. Vol.17 (2006), p.1005
- [2] R. Kessick and G. Tepper: Appl. Phys. Lett., Vol.84 (2004), p.4807
- [3] W.E. Teo, R. Inai and S. Ramakrishna: Sci. Technol. Adv. Mater. Vol.12 (2011), p.013002
- [4] P.J. Riley and G.G. Wallace: J. Int. Mater. Syst. Struct., Vol.2 (1991), p.228
- [5] V.J. Babu, D.V.B. Murthy, V. Subramanian: J. Appl. Phys. Vol.109 (2011), p.074306
- [6] Y. Gao, S. Yao, J. Gong, L.Y. Qu: Macromol. Rapid Commun., Vol.28 (2007), p.286
- [7] X. Li, M. Zhong and S.F. Xu : J. Chromatography A, Vol.1135 (2006), p.101
- [8] M.J. Huang, C. Tai and Q.F. Zhou: J. Chromatography A, Vol.1048 (2004), p.257
- [9] J. Molina, M.F. Esteves and J. Fernández: Europ. Polym. J., Vol.47 (2011), p.2003
- [10] H.Y. Ma, Y. Gao and Y.H. Li: J. Phys. Chem. C, Vol.113 (2009), p.9047
- [11] W. Du, F.Q. Zhao and B.Z. Zeng: J. Chromatography A, Vol.1216 (2009), p.3751
- [12] M. Jain, S. Annapoorni: Synth. Met., Vol.160 (2010), p.1727
- [13] H. Bai, L. Zhao and C.H. Lu: Polymer, Vol.50 (2009), p.3292
- [14] Y.Z. Long, Z.J. Chen, N.L. Wang, et al.: Appl. Phys. Lett., Vol.83 (2003), p.1863