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Electrically Conductive Polyaniline/Polyimide Nanofiber Membranes Prepared via a Combination of Electrospinning and Subsequent In situ Polymerization Growth

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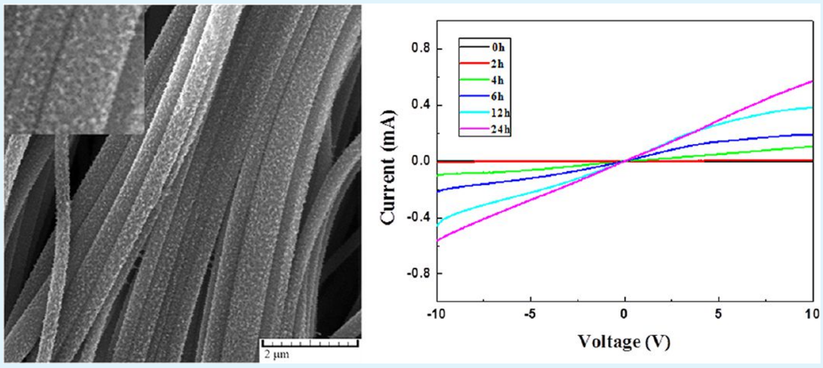
Ⓢ *Supporting Information*



ABSTRACT: Highly aligned polyimide (PI) nanofiber membranes have been prepared by electrospinning equipped with a high speed rotating collector. As the electrospun polyimide nanofiber membranes possess large surface area, they can be used as the template for in situ growth of polyaniline (PANi) by using $FeCl_3$ as the oxidant. It is found that PANi nanoparticles can be uniformly distributed on the surface of highly aligned PI nanofibers due to the low oxidization/reduction potential of $FeCl_3$ and the active nucleation sites of the functionalized PI nanofibers. The as-prepared PANi/PI composite membranes not only possess excellent thermal and mechanical properties but also show good electrical conductivity, pH sensitivity and significantly improved electromagnetic impedance properties. This is a facile method for fabricating high-performance and multifunctional composites that can find potential applications in electrical and aerospace fields.

KEYWORDS: *polyimide, polyaniline, electrospun nanofibers, in situ polymerization, alignment*

1. INTRODUCTION

Polyimide (PI), as one kind of high-performance engineering polymers, has been widely used in many advanced technology fields due to their excellent thermal stability, outstanding mechanical properties, low dielectric constants and inertness to solvent and radiation resistance.[1−3] They are distinguished from other high-performance polymers by the solubility of poly(amic acid) (PAA) precursor form, which can be prepared into uniform films and quantitatively converted into polyimide.[1−3] With the development of high technology, some of the basic properties of PI cannot satisfy the requirements in some special fields such as aerospace and electric materials. Fabrication of high-performance and multifunctional materials with excellent mechanical properties comparable with polyimide and other unique functions is of great significance.[1−5] Electrospinning is a highly versatile method based on electrohydrodynamics by applying the electrical drawing force directly on the jet body to generate continuous fibers with diameters ranging from a few nanometers to micrometer.[6−8] The solubility of the PI precursor makes it electrospinnable from solution and thus various PI nanofibers or nanofiber membranes can be produced by electrospinning. In recent years, polyimide nanofiber materials have been intensively investigated because of their diverse molecular structures, controllable fiber diameter, and degree of alignment.[5,9−11]

Conducting polymers containing conjugating π-electron systems, such as polyaniline (PANi), polythiophene, and polypyrrole, have been widely studied during the past decades. Among them, PANi has attracted special attention because of its easy polymerization, high yield with low cost, relatively high conductivities, redox reversibility, and environmental stabilities.[12−16] These properties provide its wide applications in batteries, molecular electronic devices, photoelectric cells, light-emitting diodes, electromagnetic shielding and biosensors.[16−22] However, some applications were hindered because of its poor mechanical properties and inability to be processed by

Received: August 14, 2012
Accepted: January 24, 2013
Published: January 24, 2013

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conventional methods.[14−19] It is known that PANi films are usually obtained by casting from solutions such as NMP. However, the cross-linking during the casting process and residual solvent may greatly affect the mechanical properties, resulting in the brittleness and doping capability reduction of the polymer.[13−15,23] Fortunately, the above limitations of PANi can be overcome by preparing blends or composites that combine the mechanical properties of the insulating host matrix and the electrical properties of the conductive PANi guest. However, PANi blends thus prepared usually possess high percolation threshold of electrical conductivity because it is actually a conductive material dispersed in an insulating matrix in three dimensions.[12−14] Therefore, it is difficult to prepare a conductive PANi material with high electrical conductivity and superior mechanical properties. Hence, more efforts have been devoted to the preparation of electrically conductive PANi materials with good mechanical properties through various techniques.

Nanostructured polyaniline has received great attention because of its nanometer dimension, large surface area and highly porous structure with a 3D interconnected network.[17−19] So far, different kinds of polymer nanofibers and their membranes can be prepared by electrospinning, and most of the membranes are composed of randomly distributed nanofibers. Nevertheless, when uniaxial fiber bundles are obtained, their applications can be largely expanded. In our previous studies,[9,10] highly aligned polyimide nanofiber membranes were prepared by electrospinning equipped with a high speed rotating collector and the as-prepared aligned nanofiber membranes showed excellent mechanical properties. And the nanofiber membranes can be used as homogeneity reinforcement to effectively enhance the mechanical properties of polyimide matrix.[10] By electrospinning of the precursor of polyimide, PAA, and subsequent high-temperature imidization of the collected nanofibers using a high-speed rotating collector, highly aligned PI nanofibers with uniform diameter can be obtained. As the electrospun polyimide nanofiber membranes possess large surface area, in this work, they are used as templates to in situ grow PANi to fabricate its composite materials. By surface treatment of the PI nanofiber membranes and careful control of the in situ polymerization process, nanosized PANi particles can be grown on the surface of PI nanofibers. The as-prepared PANi/PI films not only possess excellent thermal and mechanical properties but also show good electrical conductivity, pH sensitivity, and significantly improved electromagnetic impedance.

2. EXPERIMENTAL SECTION

Materials. Pyromellitic dianhydride (PMDA), 4,4′-oxidianiline (ODA), N,N-dimethylacetamide (DMAc), 98% H_2SO_4, 30% H_2O_2, and aniline were commercially obtained from China Medicine Co. Aniline was distilled under reduced pressure before use. Iron(III) chloride ($FeCl_3$) was supplied by Aldrich. All reactants were of analytical purity and used as received.

Synthesis of Electrospun Poly(amic acid) Solution. The precursor of polyimide, PAA, was synthesized from PMDA and ODA with an equivalent molar ratio. The polycondensation was performed in DMAc at about 0 °C. The solid content of the pristine PAA solution was 15 wt %. The as-prepared PAA solution was directly used as the electrospun solution for the preparation of PAA nanofibers.

Preparation of Aligned Polyimide Nanofiber Membranes. Electrospinning was carried out using a syringe with a spinneret having a diameter of 0.5 mm at an applied voltage of 20 kV at ambient temperature. The feeding rate was about 0.25 mL per hour and the spinneret-collector distance was 20 cm. The PAA nanofibers were collected using a rotating disc collector with a diameter of 0.30 m and a width of 10 mm. During electrospinning, the linear speed of the rotating collector was about 20 m s^{-1} because lower rotation speed cannot efficiently align the nanofibers and higher speed may lead to the breakage of the nanofibers. All the electrospun nanofiber membranes were dried at 60 °C for 4 h to remove the residual solvent and then thermally imidized using the following program to complete the imidization process: heating up at a rate of 3 °C min^{-1} to 100, 200, and 300 °C, followed by an annealing at each temperature stage for 30 min.

In situ Deposition of Polyaniline on PI Nanofiber Membranes. Before the growth of PANi on PI nanofiber membranes, the PI membranes were treated in a bath of H_2SO_4/H_2O_2 (3/1 by v/v) for 10 s, and then thoroughly rinsed with deionized water. PANi/PI composite nanofiber membranes were prepared by in situ polymerization of aniline on the surface of PI nanofibers. Deposition of PANi was carried out in an ice−water bath of aniline solution (1 mL of distilled aniline dissolved in 50 mL of 1 M HCl solution). First, soak the surface treated PI nanofiber membranes in 15 mL of aniline solution, and then add another 15 mL of 1 M HCl solution of $FeCl_3$. The molar ratio of aniline and $FeCl_3$ was 1:1. PANi emeraldine salt was formed after several minutes and deposited on the surface of the PI nanofibers. After deposition of PANi, PANi/PI nanofiber membranes were taken out and washed with HCl solution to remove oligomeric product loosely bound on the fibers. Finally, the membranes were washed with deionized water for several times and dried under ambient temperature.

Characterization. X-ray diffraction (XRD) experiments were conducted on a PANalytical (X′Pert PRO) X-ray diffractometer using CuKα radiation (λ = 0.154 nm) at an accelerating voltage of 40 kV and current of 40 mA. Static contact angles were measured using a commercial drop shape analysis system (Data Physics SCA20, Germany). Fourier transform infrared (FTIR) spectra were obtained in the range of 4000−400 cm^{-1} with a 4 cm^{-1} spectral resolution on a Nicolet Nexus 470 spectrometer. Scanning electron microscope (SEM, Tescan) performed at an acceleration voltage of 20 kV was used to observe the morphology of electrospun PI nanofiber membranes and PANi/PI composite nanofiber membranes. Tensile tests of the film samples were carried out using an Instron universal material testing system, and the samples were directly mounted to the sample clamps and stretched at a speed of 5 mm min^{-1}. Tensile property values reported here represent an average of the results for tests run on at least five samples. Thermogravimetric analysis (Pyris 1 TGA) was performed under nitrogen flow from 100 to 800 °C at a heating rate of 20 °C min^{-1}. For the characterization of electrical property, all I−V measurements were tested using a Keithley 4200 semiconductor characterization system at room temperature. The measurements were performed under linear sweep mode from −10 to 10 V and the separation between the electrodes was 5 mm. The electromagnetic interference (EMI) shielding effectiveness (SE) of the samples was measured at room temperature in the frequency range of 8−12 GHz using a WILTRON 54169A scalar measurement system.

3. RESULTS AND DISCUSSION

Polyimide was widely used in different fields for its high strength and good thermal and solvent stability. By controlling the electrospun polymer solution (with a solid content of 15 wt %) and the electrospinning conditions (e.g., voltage, speed), we can obtain highly aligned PI nanofibers with uniform diameter and smooth surface, as shown in Figure 1a. The diameter uniformity and absence of beads in the electrospun nanofibers are of vital importance for the fabrication of membranes with good mechanical properties.

Because of its poor solubility in common solvents, PANi nanofibers were usually prepared by coelectrospinning with other polymers, such as poly(lactic acid) or polyamide 6. Neat PANi fibers can only be obtained under harsh conditions, such

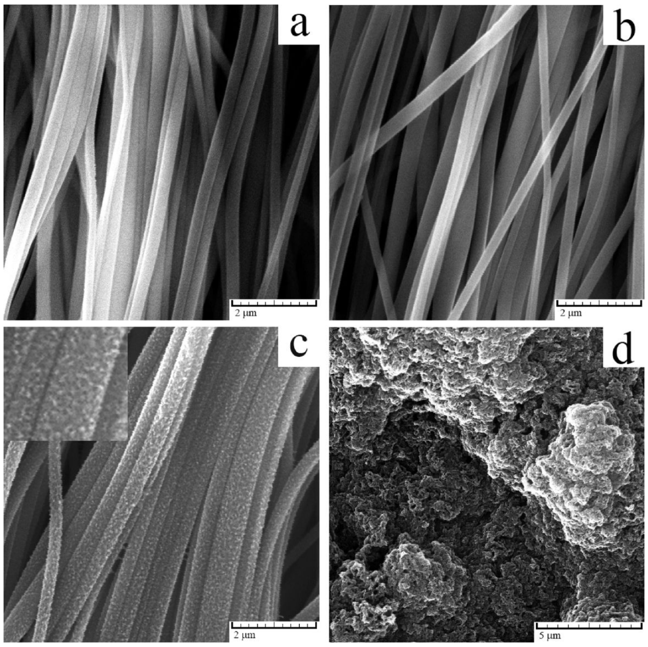

Figure 1. SEM micrographs of (a) highly aligned electrospun PI nanofiber membrane, (b) surface treated PI nanofiber membrane, (c) PANi deposited on the aligned PI nanofiber membranes prepared by $FeCl_3$ oxidization polymerization for 12 h, and (d) the as-prepared neat PANi powder.

as using hot sulfuric acid as solvent. It is very difficult to obtain neat continuous PANi nanofibers with uniform diameter and good morphology. Electrically conductive PANi/PI composite fibers were prepared by in situ deposition of PANi on PI nanofibers in this study. Prior to in situ polymerization, PI nanofiber membranes were functionalized by surface treatment in a bath of H_2SO_4/H_2O_2 (3/1 by v/v) to improve their hydrophilicity for growth of PANi. On one hand, during the high-temperature imidization process of PI, the number of functional groups on the surface of PI nanofibers decreased significantly; on the other hand, PANi can be much easily deposited on negatively charged surfaces and usually possesses higher quality compared with those grown on surfaces carrying positive charges.[19] Figure 1b shows the typical SEM micrograph of the surface-treated PI nanofibers. It can be seen that the surface of the nanofibers is smooth and no defects can be observed. Static contact angle testing results of the pristine PI nanofiber membrane and surface treated PI membrane are shown in Figure 2. It can be seen that after chemical treatment, the PI nanofiber membrane shows good hydrophilic property with the water contact angle changing from 138° for the pristine PI membrane to 0° for the surface-treated PI membrane. As the polymerization of PANi is carried out in aqueous solution, the surface treatment of PI nanofibers is crucial for the successful and complete cover of PI nanofibers by PANi.

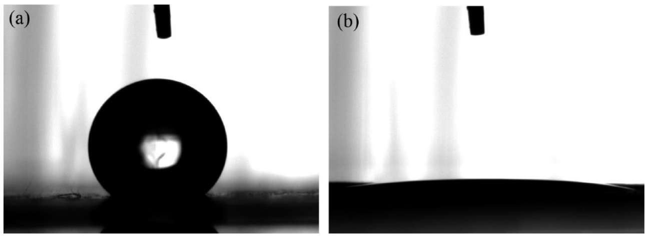

Figure 2. Contact angle testing results of (a) pristine electrospun PI nanofiber membrane and (b) surface-treated PI nanofiber membrane.

The oxidation of aniline in acidic aqueous media has become the most widely used synthetic route for the preparation of conductive PANi. As the morphology is a key factor in controlling the physicochemical properties of PANi materials,[15] recently nanostructured PANi has attracted an increasing attention due to the advantages of nanoscale systems. It has been demonstrated that the structure of the oxidant, especially the oxidation/reduction potential, affects the morphology and size of the resulting PANi.[16,19] Generally, the decrease in the oxidation potential has a favorable effect on the formation of low dimensional nanostructures because of the reduction of the probability of secondary nucleation. It is known that ammonium persulfate (APS) is usually used as an oxidant in the polymerization of PANi. However, the standard oxidation/reduction potential of $FeCl_3$ (0.77) is much lower than that of APS (2.0),[24] which suggests that the accretion or elongation process for PANi oxidized by $FeCl_3$ is much slower compared with that of PANi oxidized by APS. Therefore, $FeCl_3$ was utilized as the oxidant in the preparation of PANi in this study. Figure 1c shows the SEM micrograph of the in situ deposited PANi/PI composite nanofibers with a deposition time of 12 h. It can be seen that after in situ polymerization of aniline, a layer of ordered PANi nanoparticles are grown onto PI nanofibers. The PANi/PI cloth exhibits a hierarchical 3D micro/nano architecture, which combines the nanoscale PI nanofibers with PANi nanoparticles. The inset graph in Figure 1c shows the as-prepared PANi nanoparticles grown on PI nanofibers at higher magnification and it can be seen that PANi nanoparticles with a diameter less than 50 nm were tightly packed on the surface of PI nanofibers. Because of the low oxidation/reduction potential of $FeCl_3$, slow nucleation period and growth of polymer chains of PANi are realized during the in situ polymerization process, thus PANi nanoparticles with uniform size can be obtained. Figure 1d shows the SEM micrograph of the PANi powder obtained without PI nanofiber membranes. It can be seen that PANi particles form agglomerates during the polymerization process, whereas the surface of the functionalized PI nanofibers can act as nucleation or growth sites, thus PANI nanoparticles can be uniformly distributed on the surface of highly aligned PI nanofibers.

Because the polymerization of PANi on PI nanofibers by using $FeCl_3$ as reacting oxidant is a gradual growth process, the influence of deposition time on the morphology and properties of PANi/PI nanofiber membranes was evaluated. Figure 3a–d show the SEM micrographs of the as-prepared PANi/PI nanofiber membranes with deposition time of 6, 12, 18, and 24 h, respectively. It can be seen that after reaction for 6 h, a thin layer of PANi film can be formed on the surface of PI nanofibers. However, some inside areas of PI nanofibers cannot be fully covered by PANi nanoparticles because of the short deposition time. Further increase of deposition time may lead to the complete coverage of PI nanofibers by PANi (as shown in Figure 3b). When the polymerization time was increased to 18 h, some small agglomerates were gradually formed and became more obvious after reaction for 24 h. With increasing polymerization, the oligomers may be deposited on the surface of PI nanofibers and react with each other, thus leading to the formation of larger agglomerates (as shown in Figure 3d). The nanofibers even became interconnected with each other by the

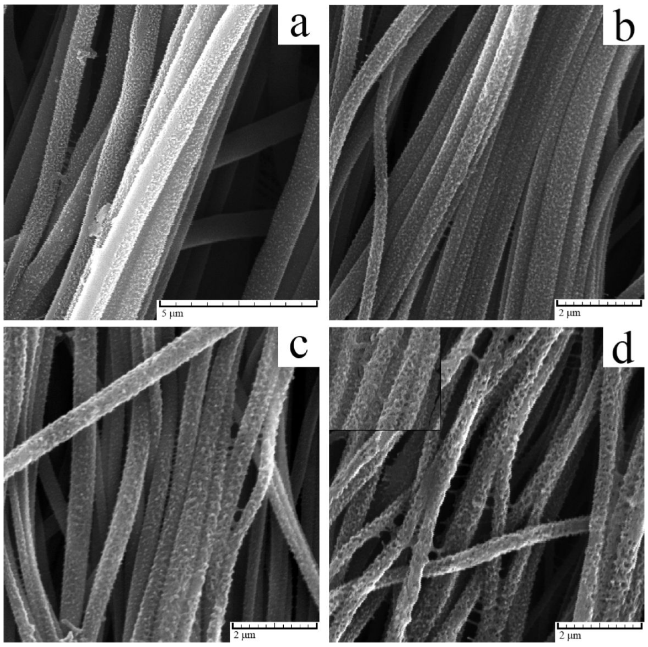

Figure 3. SEM micrographs of PI nanofiber membranes coated with PANi nanoparticles with different deposition time: (a) 6, (b) 12, (c) 18, and (d) 24 h.

large agglomerates of PANi (as shown in the inset graph of Figure 3d).

XRD was employed to characterize the as-prepared PANi/PI composite nanofiber membranes with a reacting time of 24 h. Figure 4 shows the XRD curves of neat PI nanofiber membrane, neat PANi powder and PANi/PI composite nanofiber membrane, respectively. The very broad amorphous halo in the range of $2\theta = 12{-}25°$ is the typical diffraction peak for neat PI (Figure 4a). As shown in the Figure 4c, the peaks at $2\theta = 9.8$ and 15.3° are the characteristic repeating units and doping diffraction peaks of PANi. The peak centered at $2\theta = 20.9°$ and $2\theta = 25.9°$ are ascribed to the periodicity parallel and perpendicular to PANI chains, respectively.[25,26] After depositing a thin PANi layer on the surface of PI nanofibers, the composite fibers exhibited a diffraction peak at $2\theta = 25.4°$ of PANi (Figure 4b), which demonstrated the successful in situ polymerization of PANi on PI nanofibers. FTIR spectra of neat PANi powder, PI nanofiber membrane and PANi/PI composite nanofiber membrane were obtained to further characterize the fiber surface after functionalization. As shown in Figure 5, the characteristic peaks at 1568 cm^{-1} and 1482 cm^{-1} attributed to the C−C stretching of the quinonoid (Q) and benzenoid (N) rings of PANI are clearly observed in the curve of the PANi/PI composite nanofiber membrane. The N-Q-N stretching at 1127 cm^{-1} which is the characteristic band of polyaniline salt also indicates the successful functionalization of the PI nanofiber membrane.

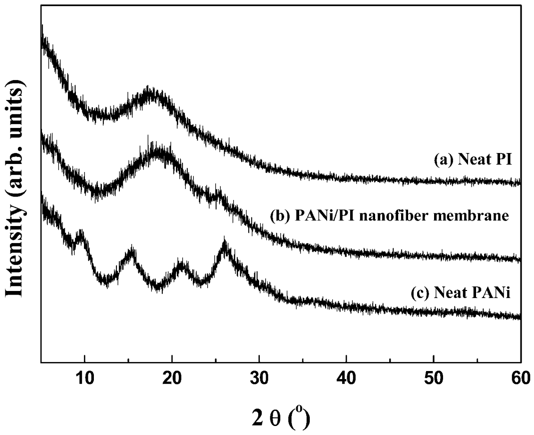

Figure 4. XRD curves of (a) neat PI nanofiber membrane, (b) PANi/PI composite nanofiber membranes, and (c) neat PANi resin.

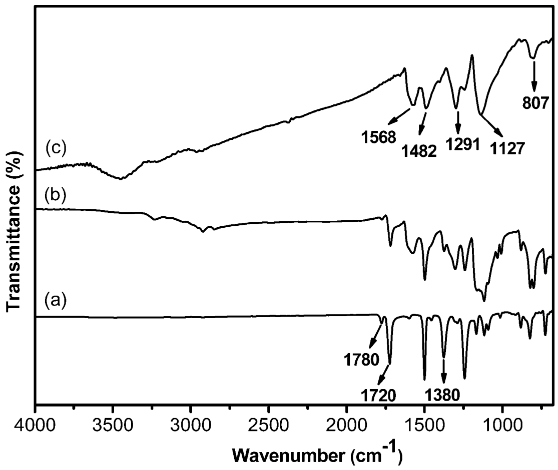

Figure 5. FTIR spectra of (a) neat PI nanofiber membrane, (b) PANi/PI composite nanofiber membrane, and (c) neat PANi resin.

PI is one kind of high performance engineering polymer materials with high thermal stability. The thermal properties of neat PI, neat PANi and PANi/PI composite nanofibers were characterized by TGA. As shown in Figure S1 in the Supporting Information, PI shows good thermal stability. Neat PI nanofiber membranes showed no weight loss until 480 °C and the residual weight of PI can reach 60% after being experienced to 800 °C. Because of the doping of HCl, PANi showed a relatively poor thermal stability with a weight loss from 150 °C. The onset decomposition temperature of the PANi/PI composite fiber membrane was decreased because of the incorporation of PANi. However, the 5% and 10% weight loss temperatures were significantly increased by about 14 and 23 °C compared with neat PI nanofiber membrane, respectively. This is probably due to the formation of a dense layer of carbon char film during the decomposition of PANi coating, which may act as a protecting layer of PI nanofibers thus preventing PI from decomposition at high temperature. Besides that, the carbon layer covered on PI nanofiber surface may promote the heat transfer of the samples and thus improve the thermal stability of the composite nanofiber membranes. By the incorporation of PANi, therefore, the thermal stability of PI nanofiber membranes can be improved significantly.

PANi is one kind of the most fascinating conductive polymers for its high π-conjugated length, unique electrical properties, reversible doping/dedoping process, and controllable chemical and electrochemical properties. When PANI is incorporated into the electrospun fiber web, its electroactive nature (i.e., the electronic, magnetic and associated properties that respond to external influences) can be enhanced due to the high surface area/volume ratio of the electrospun fiber substrate. Figure 6a shows the $I-V$ curves of PANi/PI

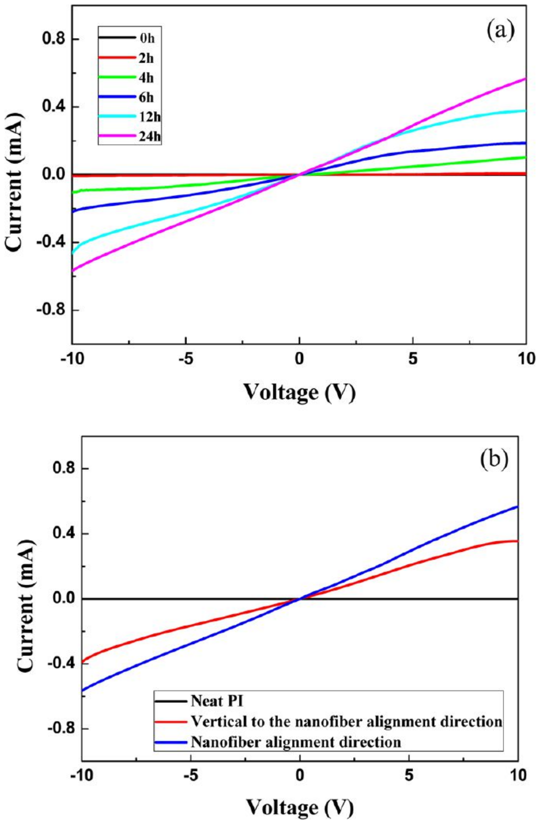

Figure 6. Current−voltage plots of PANi/PI films prepared with (a) different deposition time and (b) at different testing directions.

composite films with different deposition time along the PI nanofiber alignment direction. It can be seen that the pristine PI nanofiber membrane is electrically insulative and does not show any evident electrical signals. After in situ polymerization of PANi for 2 h, the films became electrically conductive. The electrical conductivity was increased with increasing reaction time as the in situ growth of PANi on the surface of PI nanofibers was a gradual deposition process. At the initial state, PANi nanoparticles were sparsely formed on the PI nanofibers and the surface of PI nanofibers cannot be fully covered by PANi (as shown in Figure 3a). With the increase of the deposition time, more and more PANi nanoparticles were formed and deposited on PI nanofibers. The PANi layers became more and more dense and the electrons can be easily transferred in the whole range of the composite fiber membrane, thus leading to a gradual improvement of electrical conductivity. It can be seen from the *I*−*V* curves that the conductivity (electrical current at the same voltage) of the composite membranes was increased significantly during the reaction or deposition time of 0−12 h and became insignificant after 12 h. This is probably because after in situ polymerization for 12 h, a relatively dense layer of PANi nanoparticles was formed on PI nanofibers and thus the increase of electrical conductivity was not as significant as the initial reaction period. It can be seen that after reaction for 24 h, PI nanofibers were densely covered by PANi nanoparticles (Figure 3d) and the conductivity of PANi/PI composite membrane was increased significantly compared with other samples.

Recently, anisotropic materials with different chemical or physical properties along different directions were received considerable attention[27−29] and it was found that anisotropic composite materials containing aligned carbon nanotubes in polymer matrix can be obtained by electrospinning.[27] In this study, highly aligned PI nanofiber membranes were prepared by electrospinning equipped with a high speed rotating collector. By in situ polymerization of aniline on the aligned PI nanofibers, anisotropic electrically conductive PANi/PI composite nanofiber membranes can be obtained. See Figure S2 in the Supporting Information shows the typical stress−strain curves of the pristine electrospun PI nanofiber membrane and the PANi coated PI membrane. Although the applications of PANi are hindered because of its poor mechanical property and inability to be processed by conventional methods, the composite membrane still maintains good mechanical property after deposition of PANi, which may have potential applications in electronic devices, photoelectric cells, and lightweight electromagnetic interference materials.

The electrical conductivity of PANi/PI composite nanofiber membranes was evaluated along the nanofiber alignment direction and vertical direction, respectively. Figure 6b show the *I*−*V* curves of neat PI nanofiber membrane and PANi/PI composite membrane (in situ deposited PANi for 24 h) along different directions. It can be seen that PI nanofiber membrane without PANi coating was electrically insulative. Theoretically, the difference between the electrical conductivity of the parallel and perpendicular directions of PANi/PI composite nanofiber membranes should be distinct. As shown in Figure 6b, the composite fiber membrane showed higher electrical conductivity along the nanofiber alignment direction compared with that perpendicular to the alignment direction. However, the conductivity difference between the two different directions was not as apparent as imagination. This is probably because the diameter of PI nanofibers is small and some nanofibers are connected with each other during the electrospinning process. Besides that, the in situ deposited PANi nanoparticles may form some connections with each other during the deposition process (as shown in Figure 3d), thus leading to such an insignificant difference along different directions. Such anisotropic conductive electrospun nanofiber membranes could be useful in various industrial fields because of their excellent electroactive nature, good mechanical and anisotropic properties.

Intrinsically conductive polymers can be used as chemical sensors due to the fact that their conductivity and optical properties are very sensitive to their doping level. Among various conductive polymers for sensing application, PANi is unique because it exists in a variety of forms with different degrees of oxidation and protonation and the transformations between the forms are usually accompanied by considerable changes in electrical and optical properties.[30] The response of PANi to environment originates from variation of the degree of protonation of the polymer chains which results in both color and conductivity changes of the material. This mechanism is based on the simple reversible interaction of emeraldine salt or base forms of PANi toward base or acid conditions correspondingly. It is reported that nanostructured PANi usually shows enhanced magnitude, sensitivity and response rate of these signals compared with conventional bulk materials due to a high specific surface area and enhanced accessibility of their sensitive centers. Figure 7 shows the digital photograph of the PANi/PI composite membrane (in situ polymerized for 24 h) in 0.1 M HCl, deionized water and 0.1 M NaOH solution. As shown in Figure 7, the color of the as-prepared PANi/PI composite membrane changed from green to dark green and

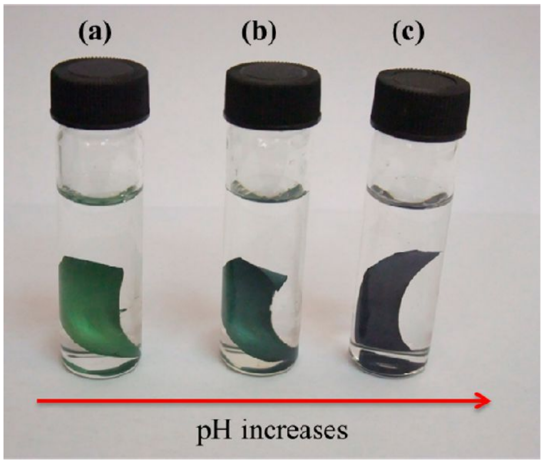

Figure 7. Digital photographs showing the pH responsive color changes of PANi/PI composite membrane soaked in 0.1 M HCl solution, deionized water, and 0.1 M NaOH solution.

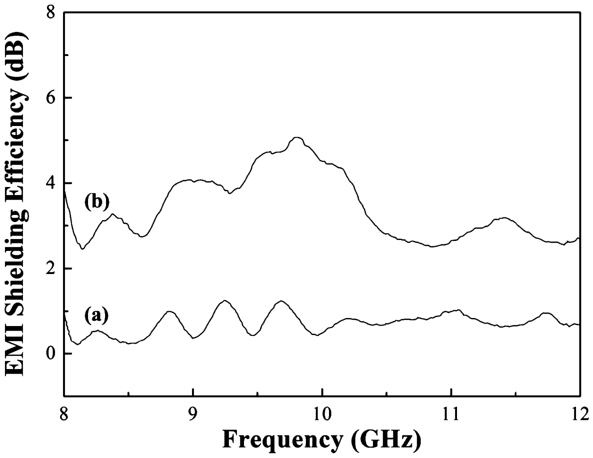

Figure 8. EMI shielding efficiency of (a) neat PI and (b) PANi/PI composite membranes.

blue by increasing the pH value of the aqueous solution. PANi is obtained as the protonated emeraldine salt, named after its green color. It can be deprotonated in alkalis to the corresponding emeraldine base, which is blue and nonconducting. Upon protonation of the imine nitrogen atoms of PANi, emeraldine base can again be converted into emeraldine salts. As the PI nanofibers and in situ polymerized PANi on PI fibers showed nanometer structure and can be protonated and deprotonated quickly and effectively, they exhibited sensitive response upon different pH environments. Because of poor mechanical properties and film-forming performance, PANi-based sensors are usually fabricated through casting or impregnating onto a solid substrate, and the lack of flexibility and stability greatly limits their practical use and sensing properties. Nevertheless, the PANi/PI composite nanofiber membranes prepared here showed good flexibility, high pH sensitivity, and repeatability, and thus can be used in different areas such as real-time pH detection.

As the use of electrical and electronic devices has rapidly grown and emissions of electromagnetic energy have increased in the same frequency range, electromagnetic interference (EMI) materials are widely investigated in recent years. Light weight is very important and favorable for the practical EMI shielding application in the areas of aircraft, spacecraft, and automobiles which can save materials and energy. Compared with metal materials, polymer materials possess lower density which makes them good candidates for the lightweight EMI materials. Figure 8 shows the EMI shielding effectiveness (SE) of neat PI nanofiber membrane and PANi/PI composite membrane determined in the microwave frequency range of 8–12 GHz. It is known that EMI SE is the sum of the reflection from the material surface, the absorption of electromagnetic energy, and the multiple internal reflections of electromagnetic radiation. The reflection is related to the impedance mismatch between air and absorber; the absorption can be regarded as the energy dissipation of the electromagnetic microwave in the absorber; and the multiple reflections are considered as the scattering effect of the inhomogeneity within the materials. It can be seen from Figure 8 that neat PI nanofiber membrane shows low electromagnetic interference due to its low thickness (about 30 μm) and electrical insulation properties. The EMI SE of a material can be expressed as SE = 10 $\log(P_t/P_{in})$ (P_t, remaining power; and P_{in}, incident power) and it can be seen that the transmittance of the electromagnetic wave can be remarkably reduced from 90 to 30% in some frequency range by the incorporation of PANi nanoparticles on PI nanofiber membranes. As the PANi/PI composite nanofiber membranes exhibit low density, good flexibility, excellent mechanical and thermal properties, they can be potentially used as lightweight electromagnetic interference materials.

4. CONCLUSIONS

Nanostructured PANi has been widely investigated in different areas due to its large surface area, high electrical conductivity, low density and reversible protonation properties. In this study, highly aligned PI nanofiber membranes were prepared by electrospinning equipped with a high speed rotating collector. By in situ polymerization of aniline in the presence of aligned PI nanofiber membrane, PANi/PI composite membranes can be obtained. $FeCl_3$ was employed as the oxidant for the oxidization polymerization of aniline for its low oxidation/reduction potential. PANi nanoparticles with size of about 50 nm were uniformly covered on the surface of PI nanofibers via an in situ deposition process. The as-prepared PANi/PI composite nanofiber membrane showed good thermal, mechanical and electromagnetic interference properties. As PI nanofibers were highly aligned, the PANi/PI composite membrane showed an anisotropic electrical conductivity along the parallel and perpendicular directions. PANi/PI composite membranes also can be protonated and deprotonated quickly and effectively, thus exhibiting sensitive response upon different pH environments. Therefore, this in situ polymerization method provides a facile way for fabricating high-performance and multifunctional composite materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

TGA curves of neat PI nanofiber membrane, neat PANi resin and PANi/PI composite nanofiber membrane, and typical stress–strain curve of neat PI nanofiber membrane and PANi/PI composite nanofiber membrane. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (51125011).

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