Electrospun PVA–PANI and PVA–PANI–AgNO₃ composite nanofibers

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Abstract Doped polyaniline (PANI) was obtained by the polymerization of aniline, using chemical oxidative polymerization in the presence of ammonium peroxodisulfate [(NH₄)₂S₂O₈]. The doped PANI was dedoped by ammonia solution. The electrospinning method was applied to solutions involving PANI–PVA, PANI–PVA–AgNO₃, where PVA = poly(vinyl alcohol) and PANI = polyaniline. Micro to nanofibers were obtained in the cases of PANI–PVA and PANI–PVA–AgNO₃. The SEM technique was used to investigate the morphology of the accumulated fibers or particles on the Al surface collector. Thermal analysis performed on PANI–PVA composite fibers indicated an endothermic peak at 280–420 °C, accompanied by 90% weight loss. The presence of Ag in the case of Ag containing composite fibers was confirmed by EDAX.

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1. Introduction
Conductive polymers, such as polyaniline and polypyrrole, have been the subject of numerous investigations in the past two decades. Among electrically conducting polymers, polyaniline (PANI) has attracted intense interest due to its environmental stability, facile synthesis, and exciting electrochemical, optical and electrical properties [1,2]. The processability of PANI to make either films or fibers is rather difficult, because it is insusible and insoluble in common solvents. Attempts have been made to overcome these setbacks, and several methods, such as blending with other soluble polymers, have been developed to turn PANI into more tractable PANI containing materials [3]. Different polymers, such as polyvinyl alcohol (PVA) [4], polymethyl methacrylate (PMMA) [5], polyethylene oxide (PEO) [6] and polysulfonated styrene (PSS) [7], have been used to prepare a PANI composite in this regard. Micro to nanofibers of polyaniline have attracted even more interest because of their properties, which make them possibly suitable for application as chemical sensors [8], batteries, light-emitting and electronic devices [9]. In recent years, considerable efforts have been made to find specific methods for the synthesis of polyaniline nanofibers, such as interfacial polymerization [10] and electrospinning [11]. Electrospinning has attracted a lot of interest as a technique that is very simple and inexpensive in the production of micro to nanofibers. It provides a potential way to fabricate infinite, continuous fibers.

A literature survey indicates that limited research studies on the preparation of PANI and PANI composite fibers have been reported [12]. To the best of our knowledge, there has been no report on PVA–PANI and PVA–PANI–AgNO₃ composite electrospun fibers. In this work, we have chosen PVA as a known soluble polymer in the preparation of electrospun fibers to prepare PANI containing fibers. Accordingly, we wish to describe the preparation of PVA–PANI and PVA–PANI–AgNO₃ composite fibers via the electrospinning method. The morphologies of these fibers are also characterized.

2. Experimental
2.1. Materials
Aniline was distilled prior to use. Ammonium peroxodisulfate (APS) 98%, hydrochloric acid 37%, 1-methyl-2-pyrrolidinone, NMP (99%), chloroform 99%, silver nitrate, and polyvinyl alcohol (PVA), with an average molecular weight (Mw) of about 50,000–80,000 g/mol, were purchased from Merck.
2.2. Instrumentation

IR and UV-Vis spectra were recorded on Perkin Elmer Gx and UV (KON) model BIO-TEK 922, respectively. To characterize the morphology of the electrospun fibers and nanoparticles, the samples were sputter coated with gold and examined at different accelerating voltages; Scanning Electron Microscope (SEM) images were obtained by a Philips XL-30. The thermal behavior of the PANI–PVA composite fibers was studied by STA 1500 from 20 to 700 °C under argon flow, at a heating rate of 10 °C/min.

2.3. Synthesis of dedoped PANI

In a typical polymerization reaction, 0.50 g aniline was dissolved in 15 mL of HCl (1 M) with stirring at room temperature. The mixture was then cooled down to below 0 °C in an ice bath. A cooled solution of 1.28 g ammonium peroxydisulfate (APS) in 15 mL of 1 M HCl to below 0 °C was added dropwise to the aniline solution. This mixture was then stirred for 4 h at −5 to 0 °C. During the polymerization process, the color changed to dark green. The resulting doped PANI precipitate was washed with deionized water several times. To prepare dedoped PANI, doped PANI precipitate was dissolved in 50 ml of 1 M aq. ammonia solution, with stirring for 24 h at room temperature, and filtered. The wet powder was washed thoroughly with deionized water and dried in vacuum (50 °C) to obtain 0.45 g emeraldine base, denoted as dedoped PANI hereafter.

2.4. Electrospinning

The electrospinning set-up consisted of a 20 mL syringe and an 18-gauge stainless steel needle that were positioned horizontally on a clamp. The metal electrode and the collector were made of copper and aluminum, respectively. Generally, viscose solutions were prepared by heating and stirring the appropriate amounts of dried dedoped PANI and additives, if needed, in solvents. The solutions were transferred into hypodermic syringes. Then, appropriate voltages were applied between two electrodes, and the webs of fibers were accumulated on the surface of the aluminum foil, which was used as the collector.

2.5. PANI solution

0.04 g dedoped PANI was dissolved in 3 ml NMP with stirring for 1 h at 50 °C. The homogeneous solution was then transferred to a syringe, and the electrospinning was tried at 18 kV with a 12 cm distance between two electrodes.

2.6. PVA solution

1.60 g PVA was dissolved in 20 ml distilled water with stirring for 2–3 h at 70 °C. Then, the viscose solution was transferred to a syringe and the electrospinning was performed at 19 kV with a 12.5 cm distance between two electrodes.

2.7. PVA–AgNO₃ solution

0.16 g silver nitrate was added to a solution containing PVA (1.06 g) in 20 ml distilled water and the mixture was stirred for 30 min until the silver nitrate was thoroughly dissolved. The resulting solution was then transferred to a syringe, and the electrospinning was performed at 15 kV with an 8 cm distance between two electrodes.

2.8. PVA–PANI solution

0.04 g dedoped PANI was dissolved in 3 ml NMP with stirring for 1 h at 50 °C. The homogeneous solution was then transferred to a syringe, and the electrospinning was tried at 18 kV with a 12 cm distance between two electrodes.

2.9. PVA–PANI–AgNO₃ electrospun composite fibers

0.10 g silver nitrate and 0.20 PVA were added separately, each in 2 ml distilled water. Then, 0.2 ml of the former solution were added to the latter and stirred to get a viscose solution containing silver nitrate and PVA. Then, 0.01 g dedoped PANI was dissolved in 1 ml NMP with stirring for 50 °C at 50 °C, and added to the previous solution. The mixture was stirred at 50 °C until a homogenous solution was achieved.

3. Results and discussion

3.1. PVA–PANI

Aniline was polymerized using chemical oxidative polymerization in the presence of ammonium peroxydisulfate \[\{(NH_4)_2S_2O_8\}\]. Then, doped PANI was dedoped by an ammonia solution. The FT–IR spectrum of doped PANI is shown in Figure 1(b). The characteristic peak around 3290 cm⁻¹ arises due to the stretching vibrations of N–H. The peaks, at about 1594 and 1504 cm⁻¹, are the absorption of quinone and
benzene rings of PANI. The peak at 1305 cm\(^{-1}\) is related to the CN stretching modes, and the peak at 832 cm\(^{-1}\) is attributable to the out-of-plane bending of C–H [13–15]. The UV-Vis spectrum of the dedoped PANI solution in NMP shows two absorption peaks at 320 and 620 nm, which are due to the \(\pi - \pi^*\) transition of benzoid rings and the excitation absorption of quinoid rings, respectively (Figure 1(a)) [6].

The electrospinning system was first operated on a 1% dedoped PANI solution in NMP solvent at room temperature. Electrospay took place, resulting in the spraying of droplets. As the jet accelerated towards the cathode and the solvent evaporated, PANI particles were deposited on the collector cathode. The morphology of the PANI particles covering the Al foil is presented in the SEM image (Figure 2). As shown, some micro to nanoparticles were accompanied by a very limited number of nanofibers. Further efforts using a modification of parameters, such as needle-Al foil distance, voltage and concentration, failed to result in the preparation of fibers. This might be due to the solubility limitation of PANI in NMP and the low viscosity of the prepared solution. To remove the problem and improve the processability of PANI, an auxiliary soluble polymer was considered for addition in order to improve the viscosity. A literature survey, as well as our experience, on the preparation of PVA electrospun fibers directed us to choose PVA as the second component. So, electrospinning was tried on a solution of a mixture of PANI and PVA. To prepare such a solution, PVA and PANI polymers were separately dissolved in water and NMP solvents, and then mixed together. The electrospinning process was applied, and fine electrospun fibers were successfully collected on the Al foil.

The morphology of PVA–PANI composite fibers was investigated by SEM. The SEM image shown in Figure 3 presents smooth fibers with several millimeters length and an average diameter, in the range of about 100 nm to 2 \(\mu\)m. The fibers contain some large size beads, indicating the resistance of the jet to extensional flow. To compare the PVA–PANI electrospun composite fibers with PVA fibers, electrospinning was also performed on a solution of PVA in water. The corresponding SEM image is presented in Figure 4. The comparison between the two SEM images obtained indicates two obvious differences: the narrower diameter range and absence of nodal in PVA electrospun fibers. So, increasing irregularities in the composite PVA–PANI composite fibers could be due to the incompatibility of the two components present in the composite.

In order to investigate the thermal behavior of the resulting composite fibers, TG and DTA analyses were performed. The corresponding curves are presented in Figure 5. As is clear, the sample is stable at about 280 °C and then an endothermic peak appears at about 380 °C, which is mostly attributed to the dehydration of PVA. The TG curve shows an overall weight loss of approximately 90% up to 420 °C. No significant weight loss occurs after 420 °C. Comparing the thermal behavior of the current PANI–PVA composite with that of pure PVA reported in the literature [16] indicates a shift of the endothermic peak from 300 to 380 °C, due to the presence of PANI.

### 3.2. Electrospin PVA–PANI–AgNO\(_3\)

Addition of AgNO\(_3\) salt to the mixture of PVA–PANI was performed to investigate the effect of silver salt on the electrospinning process and the quality and morphology of the collected composite on the Al foil. Before trying the process on
the solution containing three components, PVA–PANI–AgNO₃, it seemed logical to try the electrospinning test on the bicomponent PVA–AgNO₃ mixture. So, this was performed on an aq. solution containing 0.8% silver nitrate and 5.3% PVA. The SEM image of the resulting fibers, as shown in Figure 6(a), presents smooth fibers with a narrow diameter distribution range (300–400 nm); i.e. somewhat greater than PVA fibers. The EDAX analysis of current composite fibers, shown in Figure 6(b), confirms clearly the presence of Ag in the composite.

Considering the successful preparation of bicomponent PVA–PANI and PVA–AgNO₃ composite fibers, the electrospinning of the solution containing PVA–PANI–AgNO₃ followed in a mixture of NMP and water. The SEM image of PVA–PANI–AgNO₃ composite fibers, as shown in Figure 7(a), indicates quite a lot less nodal than in the case of PVA–PANI fibers. As observed in Figures 4 and 6, the diameter ranges in both PVA–PANI and PVA–AgNO₃ cases are greater than those in PVA fibers. The electrospun fiber diameters in tricomponent composite fibers are approximated about hundreds of nanometers to 3 μm. A careful look at every individual fiber indicates that the diameter is constantly in variation across each fiber. This is most likely due to the incompatibility of the components in the composite as mentioned earlier for PVA–PANI. EDAX analysis of PVA–PANI–AgNO₃ composite fibers, shown in Figure 7(b), demonstrates the presence of Ag in the fibers. The quantitative analysis reported by EDAX is in agreement with the original Ag weight used in the preparation of the composite.

4. Conclusion

The electrospinning of 0.036 M solution of PANI in NMP under experienced conditions results in the formation of micro to nanoparticles on the Al collector foil. This method might be used in the production of PANI film on the surface of some targets, using a rotating collector. Modification of the PANI solution composition by the addition of PVA as an auxiliary polymer altered the electrospinning behavior and resulted in the formation of fine composite electrospun fibers. When the composition is further modified by the addition of AgNO₃, three-component electrospun composite fibers are achieved.
Modification of parameters, such as solvent, auxiliary polymer, weight ratio of three components and electrospinning conditions, are under investigation to increase the contributions of PANI and silver in the composite fibers, because the main goal is preparation of composite fibers that could potentially be doped to increase conductivity. Also, the possible role of Ag⁺ as a doping agent and its influence on the conductivity of the final composite fibers are the issues of interest that are being followed and will be reported.

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