Synthetic Metals 244 (2018) 143–149

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

An investigation on the fabrication of conductive polyethylene dioxythiophene (PEDOT) nanofibers through electrospinning

Nasim Zarrin[a], Hossein Tavanai[a,b,*], Amir Abdolmaleki[c], Mehdi Bazarganipour[b], Farzaneh Alihosseini[a]

[a] Department of Textile Engineering, Isfahan University of Technology, Isfahan, 84156-83111, Iran
[b] Center of Excellence in Applied Nanotechnology, Nanotechnology and Advanced Materials Institute, Isfahan University of Technology, Isfahan, 84156-83111, Iran
[c] Department of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, Iran

ARTICLE INFO

Keywords:
Conductive polymers
3,4 ethylene dioxythiophene (EDOT)
3,4 poly ethylene dioxythiophene (PEDOT)
Electrospinning
Oxidation
Nanofibers

ABSTRACT

This article reports on the possibility of the fabrication of conductive PEDOT (3,4 poly ethylene dioxythiophene) nanofibers through electrospinning. Electrospinning of pure PEDOT nanofibers from its solution has not yet become possible. Also in this work, the efforts to electrospin pure PEDOT or pure EDOT nanofibers proved fruitless. Hence, poly(acrylic acid) (PAA)was employed to assist the electrospinning of EDOT. EDOT:PAA nanofibers were collected in an oxidation bath, where in-situ polymerization of EDOT into PEDOT occurred. After a series of experiments, PEDOT/PAA (50:50) and PEDOT/PAA (67:33) nanofibers were successfully fabricated. The lowest average diameter of the PEDOT/PAA nanofibers was around 300 nm. An electrical conductivity of 0.16 S/cm was recorded for the PEDOT/PAA (50:50) nanofibrous web which is a considerable improvement over similar products reported in the literature. X-ray analysis showed that PEDOT/PAA nanofibers have an amorphous microstructure. FTIR analysis showed no reaction or major interactions between EDOT or PEDOT and PAA. Moreover, FTIR analysis proved successful polymerization of EDOT into PEDOT. TEM images indicated a good degree of homogeneity for PEDOT and PAA in PEDOT:PAA nanofibers.

1. Introduction

Poly(1,3-ethylenedioxythiophene) (abbreviated as PEDOT) is one of the most extensively studied electroactive polymers due to excellent environmental stability and high conductivity of its polycationic (oxidized) form [1–6]. PEDOT is reported to be suitable for a wide range of applications, thanks to rather easy synthesis, relatively high electrical conductivity, electrochromic activity and biocompatibility [7,8]. Specific applications of PEDOT include synthetic muscles, battery electrodes, super capacitors, LEDs, bio-sensors and anti static [9].

As far as the electrospinning of PEDOT or PEDOT based nanofibers is concerned, the following works, dating back only to 2008, have been reported in the literature. It must be pointed out that the electrospinning of PEDOT (100%) has not yet become possible. Choi et al. [10] were the first to report the electrospinning of PEDOT: PSS/PVP nanofibers with an average diameter of about 200 nm and an electrical conductivity of 2.3×10^{-4} S/cm. PSS and PVP stand for poly (styrene sulphonate) and poly (vinyl pyrolidone), respectively. These nanofibers were employed as sensors capable to detect ethanol, methanol and tetrahydrofuran. It is worth mentioning that PEDOT: PSS indicates chemical polymerization of EDOT in the presence of PSS. In 2013 Kiristi et al. [11] reported the electrospinning of a solution of a mixture of PEDOT, plasma modified chitosan (PMCh) and PVA (poly(vinyl alcohol)) in N-methyl pyrolidone. The diameter of these PEDOT/PMCh/PVA nanofibers was 170 nm–200 nm. The conductivity of these nanofibers has not been reported. Zhao et al. [12] reported the electrospinning of PEDOT:PSS/PEO (poly(ethylene oxide)) solution in ethylene glycol in 2015. The diameter and the electrical conductivity of these nanofibers were 297–432 nm and 35.5 S/cm, respectively. Huang [13] electrospun the mixture of PEDOT: PSS and magnesium nitrate solution in distilled water and obtained nanofibers with diameter in the range of 70–100 nm which were employed as gas sensors. The electrical conductivity has not been reported in this case either. Finally in 2016, Zhang [14] electrospun the solution of PEDOT: PSS/PVP in ethanol and obtained nanofibers with diameter in the range of 600–800 nm which were employed for detecting carbon monoxide. Again, the electrical conductivity of these fibers has not been reported. It is worth mentioning that two other research groups have coated nanofibers with a layer of PEDOT as follows. In 2009, Nair et al. [15] coated a layer of porous polystyrene/ferric P toluene sulphonate nanofibers (average

* Corresponding author at: Department of Textile Engineering, Isfahan University of Technology, Isfahan, 84156-83111, Iran.
E-mail address: tavanai@cc.iut.ac.ir (H. Tavanai).

https://doi.org/10.1016/j.synthmet.2018.07.013
Received 18 December 2017; Received in revised form 17 July 2018; Accepted 20 July 2018
0379-6779/

diameter = 300 nm) with PEDOT via vapor phase deposition of EDOT, followed by polymerization. An electrical conductivity of 1 S/cm has been reported here. In a similar work carried out in 2010, Laforgue et al. [16] electrospun a solution of PVP in ethanol containing ferric P-toluene sulphonate first and then coated the nanofibers (average diameter = 350 nm) with a layer of EDOT through vapor phase deposition. This was followed by subsequent polymerization of EDOT. An electrical conductivity of 60S/cm has been reported in this case.

The following works have involved PEDOT in core shell nanofibers. Jin et al. [17] prepared core–shell PEDOT nanofibers with superior mechanical properties and biocompatibility utilizing a composition of electrospinning and in situ interfacial polymerization. Feng et al. [18] synthesized PEDOT micro tubes using aligned electrospun PEDOT shell/PLGA (poly(lactic-co-glycolic acid) core microfibers as templates. Satici et al. [19] prepared Poly(Acrylonitrile-co-Vinyl acetate)/Fe_2O_3@PEDOT core-shell by oxidative polymerization.

Considering the above mentioned literature, this research aimed at carrying out an investigation on the possibility of electrospinning PEDOT (100%) nanofibers. It must be emphasized that this work differentiates itself from the previous works by employing poly acrylic acid as a matrix for PEDOT.

2. Experimental

2.1. Materials

EDOT, anthraquinone-2-sulfonic acid sodium salt (AQSA), poly(acrylic acid) (PAA)(Mw = 450KDa) and poly(ethylene glycol) (PEG) (Mw = 400 KDa) were provided by Sigma Aldrich.

Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), ethanol (100%), dimethyl formamide (DMF), dimethyl sulfoxide, p-Toluene sulfonic acid (PTSA) monohydrate and ethylene glycol were provided by Merck. All chemicals were used as received.

2.2. Preparation of electrospinning solutions

To prepare PEDOT solutions, EDOT was first polymerized to PEDOT using FeCl3·6H2O as oxidant according to Zhao et al. [17]. EDOT was also polymerized into PEDOT in the presence of AQSA (dopant). PEDOT was then dissolved in di-methyl sulfoxide (DMSO) as well as ethylene glycol. To ensure complete dissolution, the solution was stirred for 10 h. The solution of the mixture of PEDOT in PEG and DMSO was also prepared. As, in spite of trying different conditions, the electrospinning of PEDOT solutions did not lead to the formation of proper fibers, the solution of the mixture of EDOT and PAA (as enhancer of electrospinning) in DMF was prepared after stirring at room temperature for 72 h.

2.3. Electrospinning

The electrospinning set up consisted of a high voltage supply (up to 30 kV DC output), pump (MS-2200 DAIWHA, South Korea)) with feeding capacity of 0–60 ml/h, and a 1 ml syringe with a blunt tipped needle (internal diameter = 0.5 mm). The needle tip was connected to the positive electrode. The aluminum foil collector or the oxidation bath was connected to the negative electrode depending on indirect or direct oxidation of electrospun EDOT/PAA nanofibers, respectively. In the direct process, nanofibers were collected in the oxidation bath; whereas in the indirect route, the electrospun EDOT/PAA nanofibrous web was first collected on a glass positioned on aluminum foil and then oxidized in the second stage. It is worth mentioning that a change of color from nearly white to deep black shows high degree of oxidation and hence polymerization of EDOT into PEDOT. To remove extra oxidant from PEDOT/PAA nanofibers, rinsing was carried out by ethanol first and then with distilled water.

2.4. Characterization of nanofibers

To prepare the micrographs of electrospun nanofibers, scanning electron microscope (SEM, Philips XL 30, Holland) was used. The average diameter of nanofibers (replica = 100) was measured by applying Digimizer 4.3.5 software (MedCalc Software, Belgium) to the SEM micrographs. Transmission electron microscope (TEM, PhilipsCN30, 200 kV) was employed for analyzing the distribution of PEDOT and PAA. To analyze any reaction or interaction between PEDOT and PAA, FTIR (BOMEM–MB Series, Hartmann & Braun, Canada) was used. The electrical conductivity of the samples was measured by four point probe method [18] (replica = 5). All the information concerning electrical conductivity measurement has been provided in supporting information 1.

3. Results and discussion

3.1. Electrospinning, microscopy and X-ray studies

In spite of extensive experimental work efforts to electrospin PEDOT from the solution of PEDOT in DMSO and ethylene glycol [19], even in the presence of AQSA or PEG proved unfruitful. More information is given in supporting information 2. Our research concentrated on investigating the electrospinning of EDOT followed by subsequent oxidation to obtain PEDOT nanofibers. As EDOT (liquid) alone could not be electrospun, so an auxiliary polymer capable of enhancing its electrospinnability had to be mixed with it. Literature showed the employment of poly(vinyl pyrolidone) [20] and methyl methacrylate [21] as an additive which enhanced the electrospinning of EDOT. Some of the possible choices in our work were poly(caprolactone), chitosan, poly(lactic acid), poly (lactic glycolic acid) and poly (acrylic acid) (PAA). Among these, PAA was chosen because DMF was a common solvent for PAA and EDOT. Moreover, literature showed that PAA has already been mixed with EDOT to produce PEDOT/PAA nanowires [22]. A number of electrospinning solutions with different concentrations of EDOT-PAA (50:50) and (67:33) in DMF were prepared after stirring for 72 h. However, only the solutions of EDOT-PAA (50:50) and (67:33) with concentration of 20% (w/v) could be electrospun successfully.

Fig. 1A and Fig. 2A show the SEM micrographs of the electrospun EDOT-PAA (50:50) and (67:33) nanofibers, respectively. The conditions of electrospinning (found by trial and error) experiments are mentioned at the end of the caption of each figure. Fig. 1B and Fig. 2B show the SEM micrograph of PEDOT-PAA (50:50) and (67:33) nanofibers, respectively. These PEDOT-PAA nanofibers were obtained after direct oxidation of the electrospun EDOT-PAA nanofibers in a bath containing $FeCl_3{\cdot}6\ H_2O$ solution (molarity = 2 for 50:50 and molarity = 3 for 67:33). It is worth mentioning that the molarity of 2 for $FeCl_3{\cdot}6H_2O$ in the oxidation bath led to distorted fibers in the case of 67:33 as shown in Fig. 3A. It must also be pointed out that, efforts to increase the share of EDOT in electrospun PEDOT: PAA nanofibers proved fruitless, as in spite of applying different electrospinning conditions, the solution of EDOT-PAA (83:17) with concentration of 20% (w/v) could not be electrospun successfully (Fig. 3B). Fig. 4 shows typical TEM images of PEDOT-PAA (50:50) nanofibers. Exact observation of the SEM inlay micrographs of Figs. 1 and 2 shows a rather rough surface for PEDOT: PAA (50:50) and a rather smoother surface for PEDOT: PAA(67:33). The surface of EDOT:PAA (50:50 and 67:33) are also smooth. The roughness of PEDOT-PAA (50:50) can be related to the protrusions seen on its typical TEM images (Fig. 4). It is interesting to note that the TEM images (Fig. 4) show a rather good degree of homogeneity between PEDOT and PAA.

Fig. 5 compares the average diameter of electrospun EDOT: PAA (before oxidation) and PEDOT: PAA (after oxidation) nanofibers. As can be seen, EDOT: PAA (50:50) and (67:33) nanofibers have an average diameter of about 180 nm and 245 nm, respectively. After oxidation