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Performance of electrodes synthesized with polyacrylonitrile-based carbon nanofibers for application in electrochemical sensors and biosensors

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ABSTRACT

The purpose of this work was to investigate the performance of electrodes synthesized with Polyacrylonitrile-based carbon nanofibers (PAN-based CNFs). The homogenous PAN solutions with different concentrations were prepared and electrospun to acquire PAN nanofibers and then CNFs were fabricated by heat treatment. The effective parameters for the production of electrospun CNF electrode were investigated. Scanning electron microscopy (SEM) was used to characterize electrospun nanofibers. Cyclic voltammetry was applied to investigate the changes of behavior of electrospun CNF electrodes with different diameters. The structure of CNFs was also evaluated via X-ray diffraction (XRD) and Raman spectroscopy. The results exhibited that diameter of nanofibers reduced with decreasing polymer concentration and applied voltage and increasing tip-to-collector distance, while feeding rate did not have significant effect on nanofiber diameter. The investigations of electrochemical behavior also demonstrated that cyclic voltammetric response improved as diameter of CNFs electrode decreased.

1. Introduction

Carbon-based nanomaterials have attracted increasing attentions for the application in electrochemical sensors and biosensors owing to conductivity, biocompatibility, functionality, large surface area, wide potential window, free corrosion process in positive potential and low background current [1–3]. Among these, electrospun CNFs, as one-dimensional nanostructures have been recently received considerable interest due to the fact that they can be simultaneously used both as transducers which relay the electrochemical signal and as matrixes for the immobilization of biomolecules [1,4–7].

Electrospinning is a simple and inexpensive method to fabricate polymer-based nanofibers with the diameter ranging from tens of nanometers to several micrometers [8–15]. In electrospinning process, a high voltage power source, a nozzle and a collector covered with aluminum foil are applied. The potential difference between nozzle and collector leads to stretch of solution and creates a thin jet from polymeric solution toward the collector. During stretch of solution to collector, the solvent evaporates and ultrafine nanofibers form on the collector [16–20].

CNFs prepared by electrospinning method have the high surface area, porosity, uniformity and mechanical strength [21,22]. Among the different precursors for the fabrication of CNFs, PAN is used as a current polymer owing to easy carbonization process and high carbon yield. Unlike other polymers, PAN nanofibers can be directly applied as transducer (electrode) after stabilizing and carbonizing [9,23,24]. Electrospun CNFs in comparison with other carbon materials such as glassy carbon and carbon black present edge sites which make them suitable for functionalizing [25]. Likewise, compared to other carbon materials such as graphite powder, carbon rods and same materials which need to binder, CNFs can be used without any binder, resulting in increase in electrical conductivity of electrodes [23]. Besides, Electrospun CNFs have advantages over carbon nanotubes: (1) they can be synthesized free catalyst during stabilization and carbonization, causing high purity and (2) they may enhance the facilitation of electron transfer due to more edge sites over the carbon nanotubes [26]. V. Vamvakaki et al. reported that CNFs are suitable matrix for the development of biosensors and superior to carbon nanotubes or graphite powder [27]. Electrospun CNF electrodes also have high surface area due to their small diameter to improve electrochemical performance in comparison with other carbon electrodes [23].

Totally, the selection of an efficient electrode with high surface area and excellent electrical conductivity play an important role for electrochemical sensors and biosensors and miniaturizing electrodes to nanoscale increases their efficacy due to enhancement of the signal-to-noise

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Table 1
Electrospinning data for PAN nanofibers.

NO	PAN concentration (wt.%)	Distance between tip to collector (cm)	Flow rate (mL/h)	Voltage (KV)	Mean diameter of nanofibers (nm) ± SD	Morphology
1	7	10	1	20	72.11 ± 23.20	Beaded nanofibers
2	8	10	1	20	90.70 ± 21.68	Nanofibers
3	9	10	1	20	106.76 ± 28.26	Nanofibers
4	10	10	1	20	143.00 ± 44.49	Nanofibers
5	8	15	1	20	84.70 ± 42.82	Nanofibers
6	8	20	1	20	77.05 ± 13.29	Nanofibers
7	8	10	0.5	20	102.05 ± 33.38	Nanofibers
8	8	10	1.5	20	98.41 ± 27.20	Beaded nanofibers
9	8	10	1	15	79.94 ± 22.64	Nanofibers
10	8	10	1	10	67.05 ± 8.96	Nanofibers

ratio and reduction of the sample volume [25,28]. Therefore, the design and fabrication of a nanoelectrode for the application in electrochemical sensors and biosensors is necessary. In this work, the homogenous PAN solutions with different concentrations were prepared and electrospun to acquire PAN nanofibers. The influence of electrospinning process parameters, including tip-to-collector distance, feeding rate and applied voltage on morphology and diameter of PAN nanofibers was evaluated. Electrospun CNFs were then prepared by stabilization and carbonization of PAN nanofibers, and CNFs were directly used as electrode. Then, the performances of electrospun CNFs which can be directly used as nanoelectrode were investigated.

2. Experimental

2.1. Reagents

Polyacrylonitrile (PAN) received from Polyacryl Company (Iran) with a moleculare weight of 150,000 g·mol^{-1}. Dimethylformamide (DMF) and Potassium ferricyanide were purchased from Merck Company. Sodium phosphate dibasic and potassium phosphate monobasic were bought from Sigma-Aldrich Company. Phosphate buffer solutions (PBS) were prepared by 0.1 M Na_2HPO_4 and 0.1 M KH_2PO_4. All solutions were prepared using ultra-pure water.

2.2. Electrospinning

The PAN polymer was dissolved in DMF as solvent under continuous and vigorous magnetic stirring at 40 °C for 12 h to obtain a homogenous solution. The PAN solution was electrospun using Electroris (Fanavaran Nano Meghyas Ltd., Co., Tehran, Iran). For every run, the PAN solution was put into a 10 mL plastic syringe fitted with an 18-gauge, stainless steel blunted needle as nozzle and a high-voltage power supply was used to charge the polymer solution between the syringe needle and a rotating collector. A syringe pump injected PAN solution to the tip and accelerated toward the collector and the electrospun nanofibers were collected on an aluminum foil. The effect of electrospinning variations, including polymer concentration, distance between tip-to-collector, feeding rate and applied voltage on the morphology and diameter of PAN nanofibers was investigated according to the data listed in Table 1.

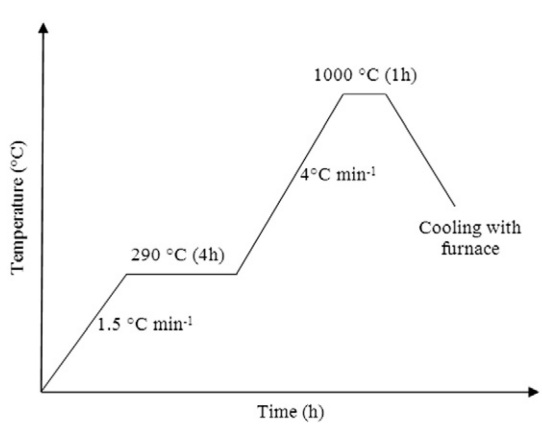

Fig. 1. Scheme of heat treatment process.

2.3. Preparation of CNFs and electrode

Electrospun PAN nanofibers were stabilized in an air atmosphere at 290 °C for 4 h with heating rate 1.5 °C min^{-1} by using a tube furnace, resulting in cyclization of nitrile groups and cross-linking between the chain molecules and hindrance from melting during carbonization step. Then, the stabilized nanofibers were carbonized at 1000 °C for 1 h in an inert atmosphere (high purity nitrogen) with heating rate of 4 °C min^{-1} (as seen in Fig. 1).

The resulted CNFs were spherically cut in size of 5 mm and inserted with copper wire for electrical contact and directly used as working electrode (Fig. 2).

2.4. Characterization of nanofibers

2.4.1. Scanning electron microscopy (SEM)

The morphology and diameter of nanofibers were carried out using SEM at an accelerating voltage of 20.0 kV (Philips XL-30) after sputtering with gold. The mean diameter of nanofibers was estimated about 50 nanofibers by SemAfore (4.01 demo, JEOL, Finland) software.

2.4.2. X-ray diffraction (XRD)

The XRD of CuKα radiation (λ = 1.54056 Å) was performed by a Philips Xpert instrument operating at 40 kV and 30 mA with at a step size of 0.08°/s over the 2θ range of 10–90°.

2.4.3. Raman spectroscopy

Raman spectra were performed with 25 mW power laser and 758 nm laser wavenumber and resolution about 3.0 cm^{-1} (Model: Senterra (2009) Bruker (Germany)). The spectra were recorded over a spectral range of 90–3500 cm^{-1} at room temperature. The measurement was taken at three various spots on the sample to realize the homogeneous nature of the CNFs.

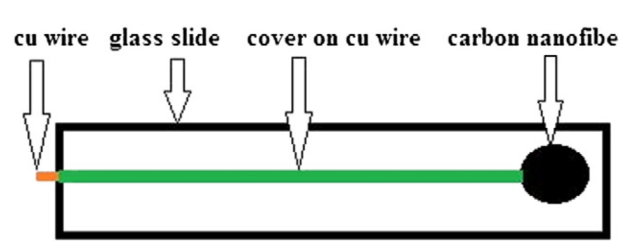

Fig. 2. Scheme of carbon nanofiber electrode.