

Electrospinning process and characterization of PVP/hematite nanofibers

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Abstract. Iron oxide (III) or also known as hematite gained their popularity of material science engineers due to its properties, including photocatalytic activity. Nowadays, some research is being carry out to confirm the potential use of Fe₂O₃ nanomaterials, in particular nanofibers and nanowires in such devices as chemical sensors, magnetic resonances, supercapacitors and transistors. Another important property of hematite is its stability, it has been proved that it is the most durable iron oxide type. Taking into consideration the above, the aim of this work was to produce composite nanofibers with polymer matrix using poly(vinylpyrrolidone) with the doping phase of α -Fe₂O₃ (30% wt.) using combining method of sol-gel technique and electrospinning process. Final fiber mats were characterized by scanning electron microscope (SEM), to determine the influence of iron oxide nanoparticles on the morphology of PVP/hematite nanofibers and UV-Vis spectroscopy to measure the optical properties of nanofibers and determine whether such obtained fibers can be used in manufacturing process of iron oxide (III) crystal nanowires.

1 Introduction

Composite nanofibers became attractive for many industrial and economic reasons. The most important property of such fibrous composites is high surface-to-volume ratio, which is successfully used

in production of chemical sensors and dye-sensitized solar cells, where the increase in surface area plays significant role in efficiency of such devices [1-3]. When it comes to another feature, the simplicity and low cost of setup and process in general is crucial for electrospinning technique success. Compared to other nanomaterials manufacturing processes, spinning in electric field is characterized by high production rates, which makes it perfect technique for industrial scale [4]. Moreover, the great attention of nanofibers is being caused by easiness of controlling the morphology and other properties of final fibers, such as pore size, structure and other physical and chemical features [5-7].

With the dynamic development of nanotechnology and techniques of producing nanomaterials, the electrospinning process also have been developed. Nowadays, there are a few kinds of composite nanofibers. It stands out polymer/polymer fibers, polymer/nanoparticles and polymer/inorganic phase fibers and combination of these. It is not surprising, that there is potential in use of fibrous mats in many areas, for example biomedical applications, where in tissue engineering nanofibers play crucial role in matrix for tissue culture cells [8], but also fibers in nano scale are used to produce novel bandages for wound healing with antimicrobial properties [9]. The convenience in such applications is



that almost every known polymer can be dissolved and used as the precursor for nanofibers process, in particular even polymers biocompatible with human body [10]. But not only biomedicine benefits from spinning in electric field technique, also the electronic industry can be revolutionized. It has been reported, that based on composite nanofibers, supercapacitors and nanogenerators can be made [11-13].

Hematite, being one of the most durable iron oxide types is widely used in metallurgy and glassmaking. But when it comes to nano scale α -Fe₂O₃, it gains some other specific features. Iron oxide (III) is typical n-type semiconductor with the width of energy band gap of 2.2 eV, chemically stable and corrosion resistant [14]. Some research has been carrying out to find its application in photocatalysis, due to visible-light responsive compound [15]. The addition of hematite nanoparticles to polymer matrix in electrospinning process results in composite nanofibers PAN/Fe₂O₃ which can be used in CO₂ gas sensors, as reported in [16]. Also, due to the increase of absorption level of PAN/hematite nanofibrous mats, such material can be used in electromagnetic radiation shields, in particular UV radiation [17].

In this paper, the Authors present the manufacturing process of PVP/ α -Fe₂O₃ composite nanofibers via combining methods of sol-gel and electrospinning techniques. The doping phase of hematite nanoparticles was set to 30% (wt.) relative to polymer mass concentration in spinning solutions. To compare structure and physical properties, pure polymer PVP nanofibers have been produced. In order to investigate the influence of iron oxide (III) nanostructures on composite nanofibers, scanning electron microscopy (SEM) was used, to examine the morphology of final mats and UV-Vis spectroscopy was used to measure the absorption of produced composites. The obtained results can testify that above described technique can be the first step to produce crystal iron oxide (III) nanowires, a novel manufacturing process of making nanowires, which was reported previously [18, 19].

2 Materials and Methodology

The spinning solutions were prepared as follows: PVP (poly(vinylpyrrolidone), Mw= 1 300 000 g/mole, purity of 99%, Sigma Aldrich) was dissolved in ethanol (EtOH, purity of 99.8%, Sigma Aldrich)

to prepare polymer solution in concentration of 10% (wt.), next the suspension of α -Fe₂O₃ nanoparticles in ethanol was subjected to sonication process for 15 minutes, after which the measured amount

of polymer granulate was added into it. After mixing for 24 hours, final suspensions: PVP/EtOH, PVP/ α -Fe₂O₃ (30% (wt.)) were electrospun on the FLOW – Nanotechnology Solutions Electrospinner 2.2.0 - 500 device using following parameters: the solution flow rate – 4.5 ml/h, the distance between the electrodes – 12.5 cm and the voltage between the syringe and collector – 15 kV. The as manufactured fibrous mats were left to dry in room temperature for 24 hours.

3 Results and Discussion

3.1 Morphology characterization of PVP and PVP/hematite nanofibers

Fig. 1 and 2 show SEM images of the obtained fibrous mats with EDX graph and histograms of fibers diameters distribution. The morphology analysis indicate that the applied electrospinning parameters allowed for the production of smooth and uniform in width polymer as well as composite nanofibers. Moreover, the entire length of fibers was characterized by the lack of any structural defects. The average value of PVP nanofibers diameter was 565 nm. However, the most values of fibers polymer width was in the range of 200 to 900 nm. EDX analysis confirm the presence of some characteristic chemical elements for poly(vinylpyrrolidone) nanofibers, carbon (C) and oxygen (O) and also aluminum (Al), which was the collector for produced fibrous mats.

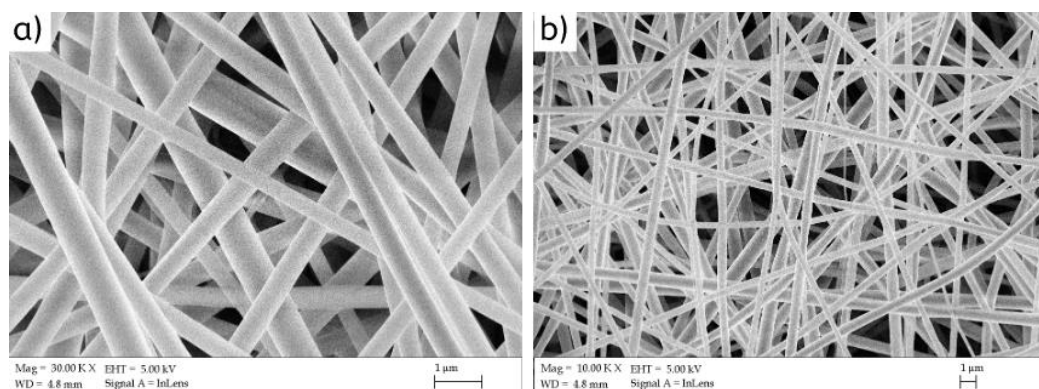


Figure 1. SEM images of PVP nanofibers: a) magnification of 30k X, b) magnification of 10k X

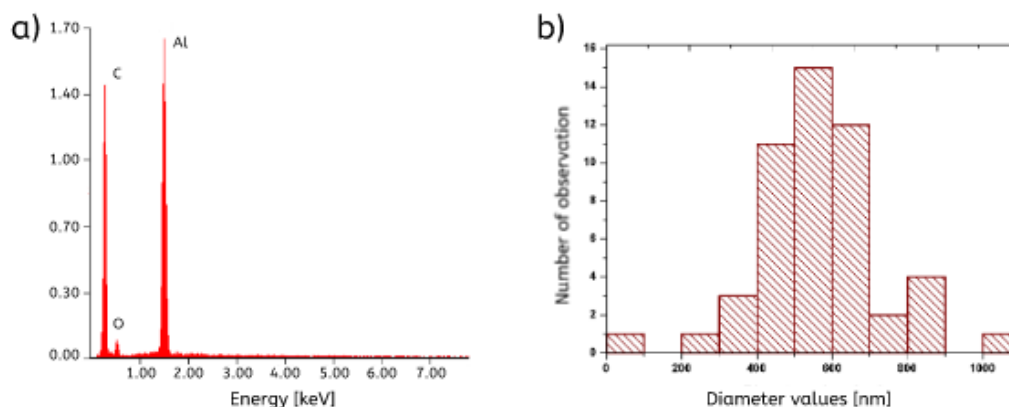


Figure 2. PVP nanofibers: a) EDX spectrum, b) histogram with fibers diameter values distribution.

Based on the histograms with diameter distribution, the addition of iron oxide (III) nanoparticles caused the decrease in fibers diameter. Scanning electron microscope images of PVP/ Fe_2O_3 are shown on Fig. 3, EDX spectra and histogram with width values fibers distribution are shown on Fig. 4.

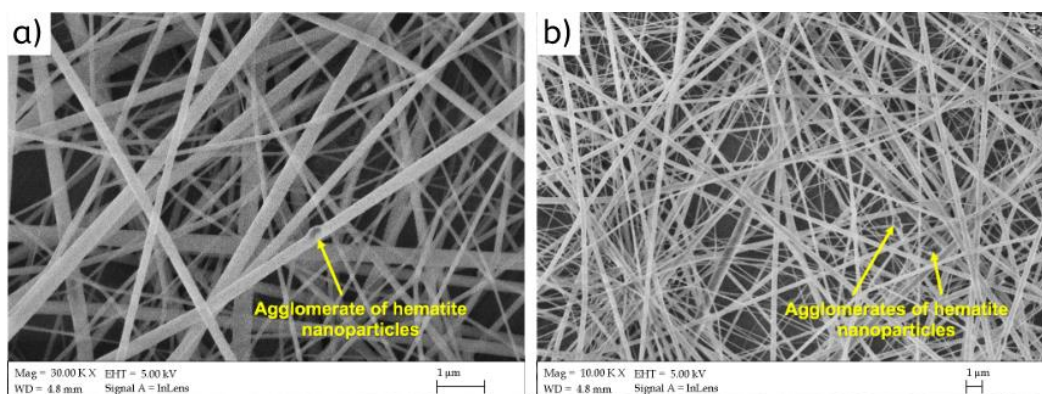


Figure 3. SEM images of PVP/ $\alpha\text{-Fe}_2\text{O}_3$ nanofibers: a) magnification of 30k X, b) magnification of 10k X.

The composite nanofibers are characterized by equal diameters along the entire fiber's length. There are single hematite nanoparticles aggregations (marked with yellow arrows in Fig. 3). The most important notable thing is that the values of composite fibers diameter increased in relation to polymer diameter nanofibers. It is caused by the addition of semiconductor doping phase, which changed the movement and elongated the jet of spinning solution. Basing on the histogram (Fig. 4 b)) the average value of PVP/iron oxide (III) diameter was 165 nm. The diameter values were distributed more evenly than those of polymer fibers diameters and were in the range of below 100 to 330 nm. Considering the above, addition of hematite nanoparticles to PVP nanofibers results in almost 3 times decrease in the fibers width values. The EDX spectrum of composite fibrous mats reveal four expected peaks corresponding to carbon (C), oxygen (O), which are attributed to chemical formula of polymer, iron (Fe) from doping phase and aluminum (Al) from aluminum foil, which was the collector for the obtained material.

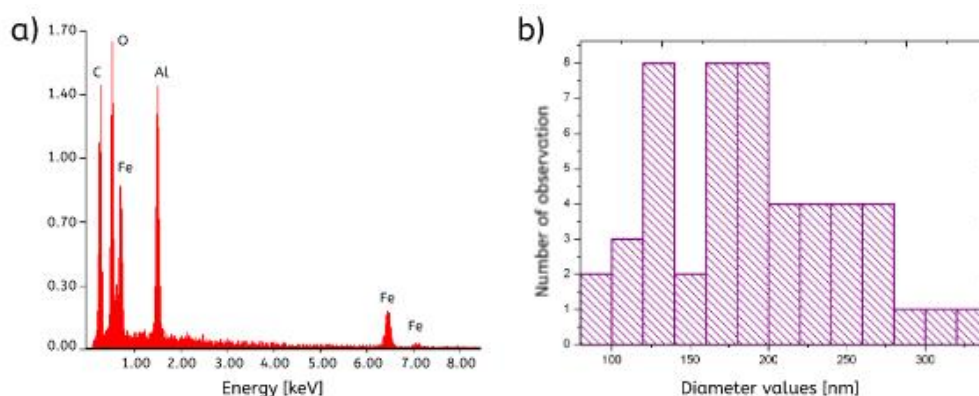


Figure 4. PVP/hematite nanofibers: a) EDX spectrum, b) histogram with fibers diameter values distribution.

3.2 UV-Vis spectroscopy

In order to determine the influence of iron oxide (III) nanoparticles on optical properties of as obtained composite nanofibers and to compare the absorption of polymer and composite nanofibers, UV-Vis spectroscopy was made (Fig. 5). Based on the absorption in the function of wavelength graphs, there can be seen slight increase in absorption level of composite nanofibers in comparison to pure polymer nanofibers. The absorption peak for PVP fibers is at 310 nm, while for PVP/hematite there is another peak at about 560 nm [17]. Such obtained results indicate, that doping phase in composite nanofibers cause higher absorption in the range of visible light wavelengths, which could be used in photocatalytic processes in such range of light [20]. Moreover, higher level of absorption in the UV radiation region indicate the use of composite nanofibers in UV light protection shields.

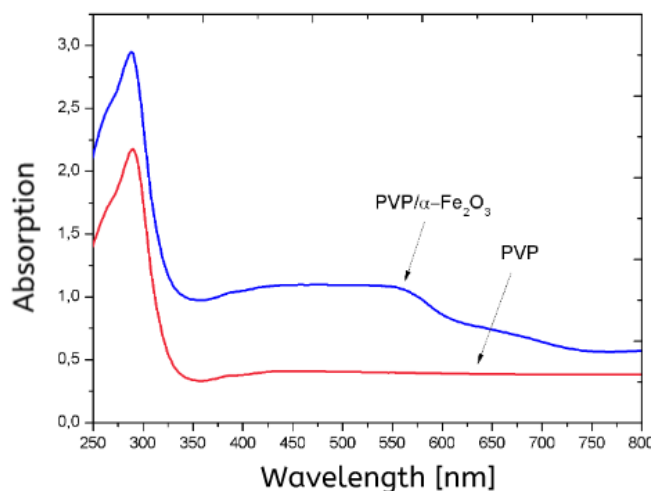


Figure 5. UV-Vis spectrum of PVP and PVP/ α -Fe₂O₃ fibrous mats.

4 Conclusions

The Authors present successfully provided manufacturing process of PVP and PVP/hematite nanofibers via combining methods of sol-gel and electrospinning techniques. Based on the morphology examination, the doping phase of iron oxide (III) nanoparticles caused almost 3 times decrease in the diameter values of composite nanofibers. Such result indicates, that the composite fibrous mats were characterized by higher surface area. With the addition of hematite particles, the absorption level of nanofibers relative to pure polymer fibers increased. The obtained nanomaterial provides the possibility of producing crystalline iron oxide (III) nanowires, with great photocatalytic features.

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