HIERARCHICAL ALIGNED ZnO NANORODS ON SURFACE OF PVDF/Fe$_2$O$_3$ NANOFIBERS BY ELECTROSPINNING IN A MAGNETIC FIELD

by

Dan TIAN$^1$, Peng LIU$^2$, Ji-Huan HE$^3$

1. School of Science, Xi’an University of Architecture and Technology, Xi’an, China
2. National Engineering Laboratory for Modern Silk, College of Textile and Engineering, Soochow University, Suzhou, China.
3. School of Mathematics and Information Science, Henan Polytechnic University, Jiaozuo, China

*Corresponding author. Email: Hejihuan@suda.edu.cn

The electrospinning was applied to fabricate aligned nanofibers in a magnetic field. Fe$_2$O$_3$ nanoparticles were added to PVDF/Zn(CHCOOH)$_2$ solution, and heat treatment of the nanofiber mats was made to produce PVDF/Fe$_2$O$_3$ nanofibers containing ZnO nanoparticles. Hierarchical composites were obtained via a facile hydrothermal growth process, where radially oriented ZnO nanorods were found. The morphology of the as-synthesized samples were investigated by using the scanning electron micrograph (SEM).

Key word: electrospinning, geometric potential, Fe$_2$O$_3$, aligned nanofibers, ZnO nanorods, wetting properties

Introduction

Composite nanofibers with some specific functions, e.g., superhydrophobic property, have attracted a lot of interest. However, a pure polymer is difficult to fabricate a functional fiber. Therefore, fabricating hybrid organic-inorganic composite fibers becomes important for advanced materials. As a kind of important inorganic materials, Fe$_2$O$_3$ has been widely doped into the various organic polymers to synthesis magnetic materials [1]. However, most of the fibers prepared by the traditional electrospinning were typically randomly oriented in the form of nonwoven mats. In comparison to randomly oriented fibers, well-aligned and highly ordered fibers have always advantages in advanced applications[2, 3].

There is much literature on preparation of aligned nanofibers by electrospinning[4-8], the general approach is to use a rotating collector, two parallel collectors or an auxiliary electrode. ZnO nanofiber composites have been widely used in photocatalytic degradation, optoelectronic devices and biological medical treatment. It was Nain [9] who first applied the hydro-thermal method to fabricate ZnO nanorods. Zheng[10] obtained highly aligned ZnO nanofibers, CdO nanofibers and abreast ZnO-CdO nanofibers. Liu[11] fabricated aligned PVP/Zn(Ac)$_2$ nanofibers and aligned ZnO nanofibers by calcining the former at 500°C.

In the present work, we give an attempt to prepare for aligned PVDF/Fe$_2$O$_3$/Zn(Ac)$_2$ nanofibers by the electrospinning[12-15] in a magnetic field. The magnetic Fe$_2$O$_3$ nanoparticles are added to PVDF/Zn(Ac)$_2$ solution in our experiment.

Experiment

In this work, 2.8g polyvinylidene fluoride (PVDF) particles were added into acetone and N-N dimethylacetamide (DMF) mixed solvent with weight ratio of 3:7, which was then magnetically stirred at 50 °C to form a homogeneous solution. 0.6 g zinc acetate (Zn(Ac)$_2$) powder was then put into the resultant solution, which was further stirred at an ambient temperature until a homogeneous solution was obtained. Meanwhile, 0.5 g maghemite iron oxide (Fe$_2$O$_3$) nanoparticles were dispersed into 4 ml DMF solvent and ultrasonically vibrated for 2 h at a room temperature. Then the dispersion was skillfully dispersed into the above solution under continuously stirring to obtain desired solution
with concentration of 10 wt % (fig. 1).

PVDF/Fe$_2$O$_3$/Zn(Ac)$_2$ nanofiber mats were fabricated using electrospinning [12-15] with an additional magnetic field. The voltage was 15 kV, the distance between the needle and the collector was 12 cm, the gap between the two parallel-positioned permanent magnets was 4 cm, the experiment was carried out under the room temperature with a relatively low humidity. Subsequently, the as-spun nanofiber mats were thermally treated at 140 °C for 24 h.

Pure zinc oxide (ZnO) nanorods were synthesized by using the hydrothermal method [16-18]. 1.36 g zinc chloride (ZnCl$_2$) and 1.41 g hexamethylene triamine (HMTA) were in turn added to 95 ml deionized water, which was then stirred at the ambient temperature for 5 min. Then 5 ml aqueous ammonia was added and a colorless transparent solution was obtained after continuous stirring. Finally, the as-prepared nanofiber mats were placed in the bottom of the beaker which was loaded with above prepared hydrothermal solution. The hydrothermal temperature was kept at 90 °C for 2h. ZnO nanorods were grown on nanofibers after the samples were taken out of the beaker and dried at 90 °C for 2 h.

Figure 1. Fe$_2$O$_3$ nanoparticles dispersed in DMF solution and electrospun solutions

**Results and discussion**

Figure 2 illustrates the fabrication process of the hierarchical aligned ZnO nanorods on surface of PVDF/Fe$_2$O$_3$ composite nanofibers. The electrospinning system with a magnetic field generated by two parallel positioned permanent magnets was used to generate aligned fibers, as shown in fig. 2(a). Then the aligned as-spun nanofiber mats, in fig. 2(b), were heated at 140 °C for 24h. Through this thermal treatment, Zn(Ac)$_2$ in the as-spun nanofibers was transferred into ZnO nanoparticles, which was used to be the seeds for the hydrothermal growth, as shown in fig. 2(c).

![Figure 2](image)

Figure 2. Schematic illustration for the preparation process of hierarchical aligned ZnO nanorods on surface of PVDF/Fe$_2$O$_3$ composite nanofiber membranes.

Figure 3b was the SEM images of the aligned PVDF/Fe$_2$O$_3$/Zn(Ac)$_2$ nanofibers at low magnifications. Figure 3c present the corresponding SEM images with medium magnification. For comparison, fig. 3a showed a typical misaligned PVDF/Fe$_2$O$_3$/Zn(Ac)$_2$ nanofiber mats via electrospinning without adding a magnetic field. A possible reason for formation mechanism of parallel fibers is that magnetic nanoparticles is subject to the magnetic force [19, 20]. The magnetic field plays a significant role in the process of spinning, which is responsible for the alignment of the magnetic nanoparticle (Fe$_2$O$_3$) doped fibers. In spite of this, all of these randomly oriented and orderly oriented PVDF/Fe$_2$O$_3$/Zn(Ac)$_2$ nanofibers have a uniform morphology with a similarly average fiber diameter.
Fig. 4(a, b) showed high magnification SEM images of the unheated and heated as-spun nanofibers, respectively. Fig. 4(a) showed unheated as-spun nanofibers with a few nanoparticles, the possible reason might be the present of Fe$_2$O$_3$ NPs in the solution. However, it was clearly observed that amounts of nanoparticles were distributed on the whole surface of the heated as-spun nanofibers from fig. 4(b). This can be explained due to the decomposition or transformation of zinc acetate in air at 140°C for 24 h.

Figure 4(c) and 4(d) respectively showed SEM images of ZnO nanorods grown around the unheated and heated as-spun nanofibers after the hydrothermal process. It was evident that ZnO nanorods desultorily arrayed around the unheated as-spun nanofibers, as shown in fig. 4(c). Figure 4(d) exhibited a very uniform coverage ZnO nanorods arrays grown onto the entire length of the heated as-spun nanofibers, which contributed the growth-induced seeds layer in the fibers surface. These results have confirmed that the heat treatment has made the parts of zinc acetate into zinc oxide. All of the ZnO nanorods have a hexagonal cross-section with a diameter in the average about 240 nm.

![Figure 3. SEM images of PVDF/Fe$_2$O$_3$/Zn(Ac)$_2$](image)

(a) misaligned, (b-c) aligned.

![Figure 4. SEM images of unheated (a) and heated nanofibers (b), respectively; after hydrothermally treated (c) and (d).](image)

### Conclusion

In summary, aligned PVDF/Fe$_2$O$_3$/Zn(Ac)$_2$ nanofiber membranes were successfully fabricated by electrospinning in magnetic field. Well-arrayed ZnO nanorods on surface of PVDF/Fe$_2$O$_3$ nanofibers hierarchical nanostructure can be prepared by heat treatment of electrospun nanofiber mats in air at 140 °C for 24 h followed by an optimized hydrothermal growth method of the obtained nanofibers. The SEM images of the composites revealed well-aligned as-synthesized products. This hierarchical structure nanocomposites has a great promising application in the area of water purification filters and oil/water separation via further chemical composition and/or morphological structures modify.

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### References


[14] He JH. On the height of Taylor cone in electrospinning, *Results in Physics, 17*(2020), June, Article number 103096


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