HIERARCHICAL ALIGNED ZnO NANORODS ON SURFACE OF PVDF/Fe_2O_3 NANOFIBERS BY ELECTROSPINNING IN A MAGNETIC FIELD

by

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The electrospinning was applied to fabricate aligned nanofibers in a magnetic field. The Fe_2O_3 nanoparticles were added to PVDF/Zn(CHCOOH)$_2$ solution, and heat treatment of the nanofiber mats was made to produce PVDF/Fe_2O_3 nanofibers containing ZnO nanoparticles. Hierarchical composites were obtained via a facile hydro-thermal growth process, where radially oriented ZnO nanorods were found. The morphology of the as-synthesized samples was investigated by using the scanning electron micrograph.

Key words: *electrospinning, geometric potential, Fe_2O_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_2O_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 non-woven 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. The ZnO nanofiber composites have been widely used in photocatalytic degradation, optoelectronic devices and biological medical treatment. It was Nain *et al.* [9] who first applied the hydro-thermal method to fabricate ZnO nanorods. Zheng *et al.* [10] obtained highly aligned ZnO nanofibers, CdO nanofibers and abreast ZnO-CdO nanofibers. Liu *et al.* [11] fabricated aligned PVP/Zn(Ac)$_2$ nanofibers and aligned ZnO nanofibers by calcining the former at 500 ^oC.

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In the present work, we give an attempt to prepare for aligned PVDF/Fe_2O_3/Zn(Ac)$_2$ nanofibers by the electrospinning [12-15] in a magnetic field. The magnetic Fe_2O_3 nanoparticles are added to PVDF/Zn(Ac)$_2$ solution in our experiment.

Experiment

In this work, 2.8 g 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. The 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_2O_3, nanoparticles were dispersed into 4 mL DMF solvent and ultrasonically vibrated for 2 hours at a room temperature. Then the dispersion was skilfully dispersed into the above solution under continuously stirring to obtain desired solution with concentration of 10 wt.%, fig. 1.

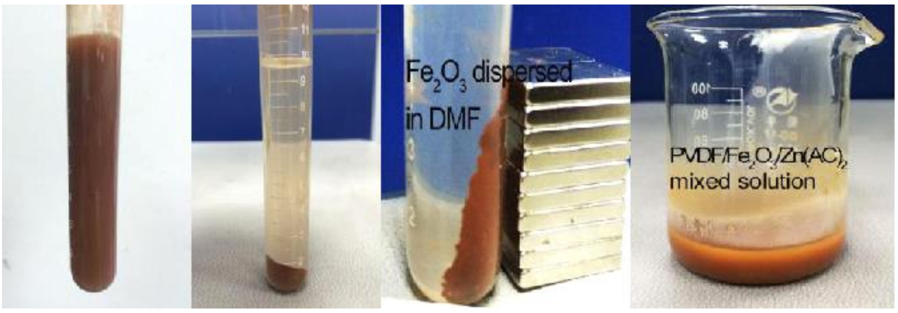

Figure 1. The Fe_2O_3 nanoparticles dispersed in DMF solution and electrospun solutions

The PVDF/Fe_2O_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 hours.

Pure zinc oxide, ZnO, nanorods were synthesized by using the hydro-thermal method [16-18]. The 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 minutes. 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 hydro-thermal solution. The hydro-thermal temperature was kept at 90 °C for 2 hours. The ZnO nanorods were grown on nanofibers after the samples were taken out of the beaker and dried at 90 °C for 2 hours.

Results and discussion

Figure 2 illustrates the fabrication process of the hierarchical aligned ZnO nanorods on surface of PVDF/Fe_2O_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 24 hours. 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 hydro-thermal growth, as shown in fig. 2(c).

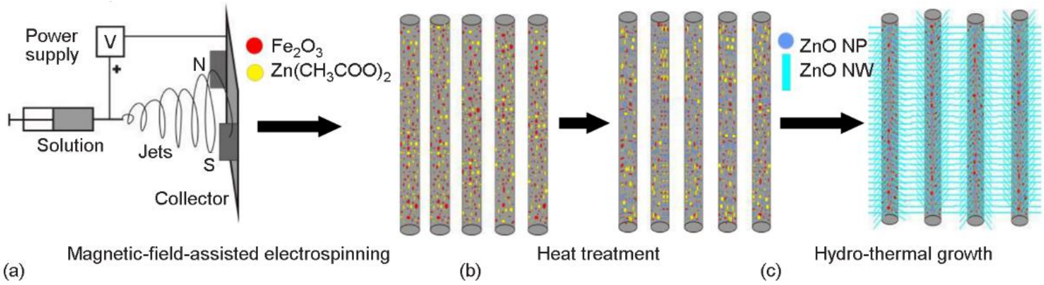

Figure 2. Schematic illustration for the preparation process of hierarchical aligned ZnO nanorods on surface of PVDF/Fe_2O_3 composite nanofiber membranes

Figure 3(b) was the SEM images of the aligned PVDF/Fe_2O_3/$Zn(Ac)_2$ nanofibers at low magnifications. Figure 3(c) present the corresponding SEM images with medium magnification. For comparison, fig. 3(a) showed a typical misaligned PVDF/Fe_2O_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_2O_3, doped fibers. In spite of this, all of these randomly oriented and orderly oriented PVDF/Fe_2O_3/$Zn(Ac)_2$ nanofibers have a uniform morphology with a similarly average fiber diameter.

Figures 4(a) and 4(b) showed high magnification SEM images of the unheated and heated as-spun nanofibers, respectively. Figure 4(a) showed unheated as-spun nanofibers with a few nanoparticles, the possible reason might be the present of Fe_2O_3 nanoparticles in the so-

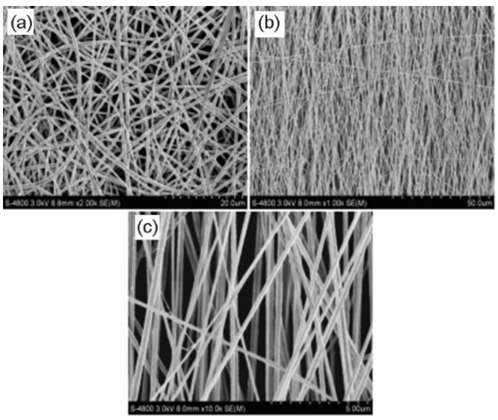

Figure 3. The SEM images of PVDF/Fe_2O_3/$Zn(Ac)_2$; (a) misaligned and (b)-(c) aligned

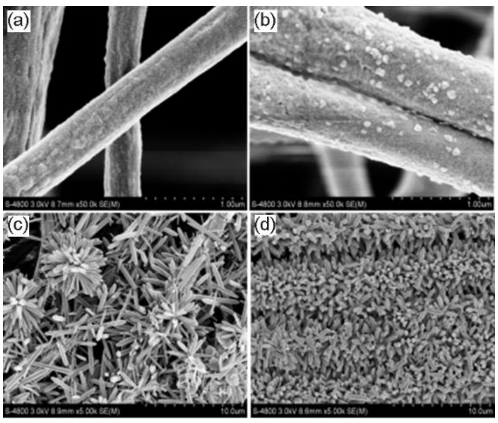

Figure 4. The SEM images of unheated (a) and heated (b) nanofibers; (a) misaligned, (b-c) aligned, after hydro-thermally treated (c) and (d)

lution. 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 ºC for 24 hours.

Figures 4(c) and 4(d) respectively showed SEM images of ZnO nanorods grown around the unheated and heated as-spun nanofibers after the hydro-thermal 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 ZnO. All of the ZnO nanorods have a hexagonal cross-section with a diameter in the average about 240 nm.

Conclusion

In summary, aligned PVDF/Fe_2O_3/Zn$(A_C)_2$ nanofiber membranes were successfully fabricated by electrospinning in magnetic field. Well-arrayed ZnO nanorods on surface of PVDF/Fe_2O_3 nanofibers hierarchical nanostructure can be prepared by heat treatment of electrospun nanofiber mats in air at 140 °C for 24 hours followed by an optimized hydro-thermal 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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