FACILE PREPARATION OF $\alpha$-Fe$_2$O$_3$ NANOBULK VIA BUBBLE ELECTROSPINNING AND THERMAL TREATMENT

by

Peng LIU$^a$, Chun-Hui HE$^b$, Fujuan LIU$^a$, Lan XU$^a$, Yuqin WAN$^c$, and Ji-Huan HE$^a$,*

$^a$National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, Suzhou, China
$^b$Nantong Bubbfil Nanotechnology Company Limited, Nantong, China
$^c$College of Textiles and Clothing, Jiangnan University, Wuxi, China

Original scientific paper
DOI: 10.2298/TSCI1603967L

In this work, $\alpha$-Fe$_2$O$_3$ nanobulk with high aspect ratio were successfully prepared via a facile bubble electrospinning technique using polyvinylidene fluoride and iron chloride hexahydrate (FeCl$_3$·6H$_2$O) as $\alpha$-Fe$_2$O$_3$ precursor followed by annealing in air at 600 °C. The products were characterized with field emission scanning electron microscope, Fourier transform infrared, X-ray photoelectron spectroscopy, and thermogravimetric analysis. The results showed that $\alpha$-Fe$_2$O$_3$ nanobulk has a hierarchical heterostructure which has an extremely broad application prospect in many areas.

Key word: $\alpha$-Fe$_2$O$_3$, bubble electrospinning, composite nanofibers, polyvinylidene fluoride

Introduction

In recent decades, transition metal oxide nanostructures have attracted considerable attention due to their widely applications. In particular, hematite ($\alpha$-Fe$_2$O$_3$) is found to be promising in a variety of applications because of its high thermal stability under ambient conditions, environmentally friendly features and low production cost. Many $\alpha$-Fe$_2$O$_3$ nanostructures, such as hollow fibers [1], nanotubes [2], and nanoporous [3], nanorods [4], and their various applications, such as gas sensors [5], catalysts [6], electrode materials [7], and adsorption materials [8] have been reported.

Compared to other means, such as chemical vapor deposition [9] and hydrothermal growth [10], bubble electrospinning [11-16] is the most effective and versatile approach for fabrication of functional nanomaterials, which using high voltage to produce ultrathin fibers with diameters ranging from a few to several hundred nanometers. For example, Liu et al. [17] have obtained electrosprun membrane with superhydrophobic-supperpleophilic performance. Liu et al. [18] developed a novel manufacturing approach which is based on bubble electrospinning technology to fabricate nanofiber yarns. Liu et al. [19] have presented a novel technique which
called needle-disk electrospinning to enhance nanofibers throughput and fabricate nanofibers from various materials with high quality.

In this research, PVDF/FeCl$_3$·6H$_2$O composite nanofibers were prepared using solution mixtures of iron(III) chloride hexahydrate (FeCl$_3$·6H$_2$O) and polyvinylidene fluoride (PVDF) via bubble electrospinning. Subsequently, the as-spun composite nanofibers were annealed in air at high temperature with an appropriate heating rate to form α-Fe$_2$O$_3$ nanobulk. The morphology, chemical, and thermal properties of the resultant α-Fe$_2$O$_3$ nanobulk were investigated through different approaches.

**Experiment**

In this work, 2.4g PVDF powder was added into acetone and dimethylformamide (DMF) mixed solvent (weight ratio = 1 : 1) and magnetically stirred for about 3 hours for 8 wt.% PVDF solution. Then different amount of FeCl$_3$·6H$_2$O was added into the previously prepared PVDF solution with magnetic stirring for 6 hours at room temperature to form a homogeneous solution. The concentration of FeCl$_3$·6H$_2$O (i.e., 2, 6, and 10 wt.%) in the mixture was calculated based on the weight of PVDF.

The bubble electrospinning set-up used in this study can be found in our previous report [11, 12]. In a typical process, the solution was loaded into a U-shape groove with a stainless steel circular ring with an inner diameter of 1 cm. The circular ring which was charged by a high direct current power supply was used as the positive electrode. A voltage of 25 kV was applied to the solution via the stainless steel circular ring. A piece of aluminum frame was grounded and used as nanofiber collector. The collecting distance between the circular ring and aluminum foil collector was 16 cm. All spinning processes were conducted at ambient temperature with a relatively low humidity.

The as-spun PVDF/FeCl$_3$·6H$_2$O composite nanofibers obtained with 2 wt.% FeCl$_3$·6H$_2$O were calcined in air at 600 °C for 3 hours with a rising rate of 10 °C per min to remove all organic residuals. After cooling to the room temperature, dark red α-Fe$_2$O$_3$ nanobulk were yield.

**Results and discussion**

The field emission scanning electron microscopy (FESEM) images and diameter distribution curves of as-spun FeCl$_3$·6H$_2$O/PVDF composite nanofibers with different contents (0, 2, 6, and 10 wt.%) are shown in fig. 1. It can be seen that pure PVDF nanofibers have a beaded morphology as show in fig. 1(a). Figure 1(b) shows that the as-spun pure PVDF nanofibers are basically smooth and relatively uniform apart from the beads.

In contrast with pure PVDF nanofibers, the composite nanofibers with different contents of FeCl$_3$·6H$_2$O are all beads free, as shown in fig. 1(c, e, g). This is due to the enhanced solution conductivity contributed by the presence of iron(III) ion. However, it is clearly observed in the fig. 1(d, f, h) that as the FeCl$_3$·6H$_2$O content increases, the surface roughness of FeCl$_3$·6H$_2$O/PVDF composite nanofibers increases. Figure 1(g) displays an interesting structure with interconnected branch-like junction.

Figure 1(A)-(D) shows the diameter distribution curves of as-spun nanofibers. The average diameters of pure PVDF nanofibers and composite nanofibers with different content of FeCl$_3$·6H$_2$O (2, 6, and 10 wt.%) are around 119.8 ± 23.9, 64.3 ± 11.8, 152.1 ± 27.1, and 215.9 ± 39.3 nm, respectively. With 2 wt.% addition of FeCl$_3$·6H$_2$O, the fibers diameter decreases. Smaller fiber diameter is desirable as it provides higher surface to volume ratio. However, the average diameter of the composite nanofibers dramatically increased as the concentration of
FeCl$_3$·6H$_2$O increased to 6 wt.% and 10 wt.%. This may be due to the increased solution viscosity caused by the high proportion of FeCl$_3$·6H$_2$O which weakened the spinnability of the solution. Among all the composite nanofibers, the composite nanofibers with 2 wt.% FeCl$_3$·6H$_2$O exhibited the smallest average diameter and narrowest scope of diameter distribution.

Figure 2 shows FESEM images of the $\alpha$-Fe$_2$O$_3$ nanobulk with 2 wt.% FeCl$_3$·6H$_2$O obtained after thermal treatment in ambient air at 600 °C for 3 hours. It is clearly observed that the nanobulk is composed of large amounts of nanoparticles about 30 nm and nanoflakes with different high aspect ratios.
The X-ray photoelectron spectroscopy (XPS) spectra was carried out to investigate the elemental composition and surface valence states of the \( \alpha \)-Fe\(_2\)O\(_3\) nanobulk, and the results are showed in fig. 3. The survey XPS curves in fig. 3(a) reveal that the sample is composed of Fe and O elements. Figure 3(b) exhibits the spectrum of Fe 2p region, in which the double individual peaks at 711.2 and 724.5 eV correspond to Fe 2p\(_{3/2}\) and Fe 2p\(_{1/2}\) respectively [1]. As shown in fig. 3(c), the characteristic peak of O1s with strong photoelectron signal at 531.6 eV, can be assigned to the Fe-O-Fe bonds. This result further proves \( \alpha \)-Fe\(_2\)O\(_3\) nanobulk was successfully synthesized.

To further verify the formation of \( \alpha \)-Fe\(_2\)O\(_3\) structure, Fourier transform infrared (FTIR) analysis was employed. Figure 4 shows the FTIR spectra of FeCl\(_3\)-6H\(_2\)O/PVDF composite fibers and \( \alpha \)-Fe\(_2\)O\(_3\) nanobulk calcined at 600 °C. A broad peak at about 3440 cm\(^{-1}\) corresponds to H-OH stretch is clearly observed in fig. 4(a) [8].

The characteristic peaks of CH symmetric and CH\(_2\) asymmetric vibration, CF\(_2\) deform-
tion and stretching vibrations corresponding to PVDF appeared at 2940 and 2850, 1400, 1180, and 883 cm$^{-1}$, respectively [20]. Those characteristic peaks disappeared and some new characteristic peaks appeared in $\alpha$-Fe$_2$O$_3$ nanobulk as shown in fig. 4(b). The two sharp peaks appearing at 478 and 573 cm$^{-1}$ are assigned to the Fe-O vibration of the $\alpha$-Fe$_2$O$_3$ nanobulk [7].

In order to elucidate the $\alpha$-Fe$_2$O$_3$ nanobulk formation process, thermogravimetric analysis (TGA) analysis was carried out on the as-spun FeCl$_3$·6H$_2$O/PVDF precursor composite nanofibers. Figure 5 shows TGA curves of the as-spun FeCl$_3$·6H$_2$O/PVDF precursor composite nanofibers in the temperature range of 50-600 °C. It is clear that the first weight loss of 12.8% occurred at around 50-250 °C resulting from the evaporation of absorbed water, residual DMF, acetone and the removal of crystal water molecules of the chlorides, which is an endothermic reaction. The second significant weight loss of approximately 31.7% from 250 °C to 360 °C can be ascribed to the partially decomposition of iron chloride and the degradation of the side chain of PVDF. These processes are accompanied by exothermic reaction. The third weight loss of 12.7% happened in the range of 360-600 °C, which could be attributed to the oxidative decomposition of the main chains of PVDF and the complete decomposition of iron chloride.

Finally, the total weight loss amounts to 57.2%, led to significant volume decrease and the formation of $\alpha$-Fe$_2$O$_3$ nanobulk.

Conclusions

The PVDF/FeCl$_3$·6H$_2$O composite nanofibers with different content of FeCl$_3$·6H$_2$O (0, 2, 6, and 10 wt.%) were successfully manufactured by bubble electrospinning technique using PVDF and FeCl$_3$·6H$_2$O. The composite fibers of PVDF/FeCl$_3$·6H$_2$O with 2 wt.% FeCl$_3$·6H$_2$O was calcined at 600 °C to form the $\alpha$-Fe$_2$O$_3$ nanobulk.

The SEM images indicates composite nanofibers with 2 wt.% FeCl$_3$·6H$_2$O exhibited smallest average diameter and the narrowest scope of diameter distribution. The formation of $\alpha$-Fe$_2$O$_3$ was confirmed by FTIR, XPS, and TGA analysis. This $\alpha$-Fe$_2$O$_3$ nanobulk can be widely used for many applications, such as gas sensors, catalysts, electrode materials, and sorption materials. This technique is applicable to preparation of other multifunctional nanomaterials as well.

Acknowledgment

The work is supported by Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), National Natural Science Foundation of China under grant No. 51203066, No. 61303236, No. 11372205, and No. 51403143 and Project for Six Kinds of Top Talents in Jiangsu Province under grant No. ZBZZ-035, Science & Technology Pillar Program of Jiangsu Province under grant No. BE2013072, Natural Science Foundation of Jiangsu Province under Grant No. BK20140398, Natural Science Foundation of the Jiangsu Higher Education Institutions of China (Grant No. 14KJA130001), Production and Research Prospective
Joint Research Project of Jiangsu Province under grant No. 2015047-09. Research and Innovation Project for College Graduates of Jiangsu Province under grant NO. SJZZ15_0162.

References


