Journal of Fluorine Chemistry 140 (2012) 38–42

Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

# Synthesis and upconversion properties of $Ln^{3+}$ doped YOF nanofibers

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ARTICLE INFO

*Article history:*
Received 17 February 2012
Received in revised form 8 April 2012
Accepted 16 April 2012
Available online 27 April 2012

*Keywords:*
Upconversion
Electrospinning
Oxyfluoride

ABSTRACT

Nanofibers of YOF doped with trivalent lanthanide ions ($Ln^{3+}$) have been synthesized successfully via an electrospinning method combining with high-temperature calcination in air. Scanning electron microscopy (SEM) observations showed that the nanofibers had uniform one-dimensional (1D) morphology. X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM) images revealed that the calcined fibers were constituted by rhombohedral phase yttrium oxyfluoride nanocrystals. Under the excitation from a 980 nm laser diode, YOF:$Yb^{3+}$,$Tm^{3+}$ and YOF:$Yb^{3+}$,$Er^{3+}$ fibers emitted blue and red light, respectively. Upconversion mechanisms of these YOF:$Ln^{3+}$ fibers were also discussed in detail.



## 1. Introduction

Recently, one-dimensional (1D) nanomaterials, such as nanotubes [1], nanorods [2] and nanowires [3], have received much attention owing to great fundamental interests and potential applications in display, data storage, optoelectronic device, etc. [4–8]. For example, material of 1D structure is expected to be of high value to the function and integration of nanoscale devices, due to its merit of efficiently transporting electrons and optical excitations. In the past decade, various methods have been employed to develop 1D materials. Among them, electrospinning is a quite facile and efficient method to produce 1D materials. It is a manufacturing approach that uses strong electric force to draw a fluid into fine filaments which have diameters ranging from several microns down to tens of nanometers [9–16].

Polymer-based 1D materials have been developed in virtue of electrospinning [17–19]. However, in polymer-based 1D materials, polymer takes a large proportion of composite fibers and, as a result, the excited $Ln^{3+}$ can be badly quenched due to the high-energy vibrations of polymers [20,21]. To improve properties of 1D materials, polymer ought to be removed. Pure inorganic 1D materials are expected to perform better fluorescent character than organic fibers.

To prepare pure inorganic 1D materials, an electrospinning method combining with an appropriate calcination process has been developed. As a classical procedure, composite fibers are prepared in advance containing polymer and the precursor of target substance; after a necessary calcination process, the organic contents are burned out and inorganic products form are yielded [22–26]. Recently, inorganic 1D materials of RE oxysalts and RE oxide such as $YVO_4$, $YPO_4$, $YBO_3$, and $Gd_2O_3$ have been synthesized successfully by the electrospinning-and-calcinate procedure [27–30]. Among upconversion (UC) materials, high efficient UC fluorescence can be obtained in $Ln^{3+}$-doped host materials with low phonon energy owing to the reduced multi-phonon relaxation rates in them [31–36]. Therefore, fluorides, which have lower phonon energy than oxides, are well known as preferable host materials for UC applications [37,38]. On the other hand, in practical applications, oxides have an advantage superior to fluorides due to their good chemical durability and excellent mechanical strength. Consequently, combining the thermal stability of oxides and the low phonon property of fluorides, oxy-fluorides have been considered in developing practical UC materials. However, many of the studies concerning $Ln^{3+}$-doped oxyfluorides have been focused on bulk materials like glasses and ceramics, and, to our best knowledge, there are no reports on oxyfluoride nanofibers. Hence, to synthesize 1D oxyfluoride fibers by using electrospinning technique remains a challenging task and is crucial to the development long inorganic nanofibers.

In this work, we report the synthesis and UC fluorescence properties of $Ln^{3+}$-doped YOF nanofibers. It is the first time to synthesize ultralong inorganic fibers of UC materials. The diameters of precursor fibers and sintered fibers were tunable from hundreds nanometers to tens nanometers. With 980 nm excitation, blue and red UC fluorescence was observed in YOF:20%Yb,0.5%Tm and YOF:20%Yb,4%Er, respectively.

## 2. Results and discussions

### 2.1. Structure and morphology

The phase evolution of the fibers sintered at different temperatures in air was evaluated by using XRD analysis. In the

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0022-1139/$ – see front matter. 
http://dx.doi.org/10.1016/j.jfluchem.2012.04.009

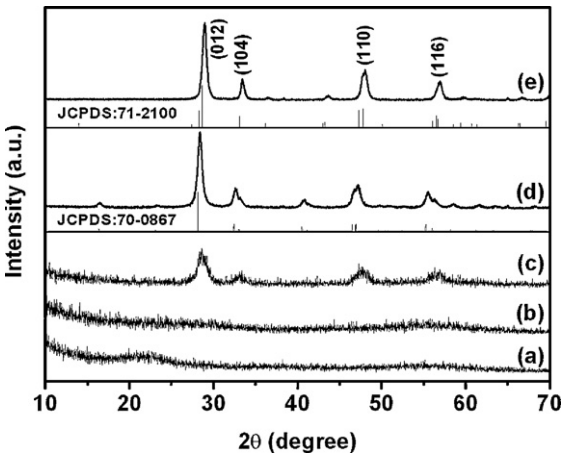


**Fig. 1.** XRD patterns of the fibers: (a) $RE(CF_3COO)_3$/PVP composite fibers; (b–e) samples which were sintered in air at 300 °C, 400 °C, 500 °C, and 600 °C, respectively.

XRD pattern of as-spun fibers, as shown in Fig. 1(a), the broad band ranging from 17° to 25° (2$\theta$) is ascribed to the amorphous PVP. No trifluoroacetate phase can be found, which means that non-crystalline $RE(CF_3COO)_3$ (RE = Y, Yb) molecules have dispersed homogeneously in the composite fibers. The broad band disappears in Fig. 1(b), implying that PVP in $RE(CF_3COO)_3$/PVP composite fibers has been decomposed at 300 °C in air. The diffraction peaks of crystalline yttrium oxyfluoride appear for the sample annealed at 400 °C in air, as shown in Fig. 1(c). The intensities of the peaks in Fig. 1(d) indicate that the sample annealed at 500 °C in air is highly crystalline in nature. The peak positions correspond closely to the standard pattern of orthorhombic $Y_7O_6F_9$ (JCPDS 70-0867). Fig. 1(e) shows the XRD pattern of the sample sintered at 600 °C in air. All these peaks can be closely indexed to the rhombohedral phase of YOF according to JCPDS card (No. 71-2100). As no additional peaks for other phases can be found, we infer that $Ln^{3+}$ ions have substituted $Y^{3+}$ ions and been effectively doped in the YOF host lattice. The XRD patterns of $Ln^{3+}$-doped samples have a shift to a large angle in comparison to the standard cards, which implies that the unit-cell parameters in the $Ln^{3+}$-doped samples have changed by a small amount. For instance, in pattern (e) the XRD peaks of the (0 1 2) and (1 0 4) planes locate at $2\theta = 28.9°$ and 33.4°, respectively. However, in the standard card, they locate at $2\theta = 28.7°$ and 33.2°. All the three $Ln^{3+}$ ions ($Er^{3+}$, $Tm^{3+}$,$Yb^{3+}$) are smaller than $Y^{3+}$ in the YOF host lattice. The calculated crystal cell parameters ($a$ = 0.378415 nm and $c$ = 1.870655 nm) for the crystalline YOF:$Ln^{3+}$ fibers are smaller than the values ($a$ = 0.379700 nm and $c$ = 1.88900 nm) of pure YOF (JCPDS 71-2100) due to the substitution of $Y^{3+}$ by $Ln^{3+}$.

The morphology and size of the precursor fibers could be influenced by various factors: voltage, distance between the tip and the collector, mass ratio of polymer in solution, relative humidity (RH), and so on. The voltage as well as the distance between spinneret tip and the collector essentially determined the electric field and therefore played a cardinal role in electrospinning process. When the electric field enhanced, the fibers became thinner. On the other hand, liquid jets would become instable and inhomogeneous fibers would be obtained in the products if the electric field was as low as 0.5 kV/cm. The average diameter of the fibers enlarged accordingly when the PVP mass ratio was increased. The PVP mass ratio of the fibers in Fig. 2(a–c) was 2.0 wt%, 2.5 wt%, and 3.0 wt%, respectively. The ideal RH for the electrospinning was less than 30%. The composite fibers in Fig. 2 were fabricated under the condition of 15 kV (voltage), 12 cm (distance), and ~20% (RH).

The $RE(CF_3COO)_3$/PVP composite fibers were calcined subsequently. Fig. 2(d) shows the SEM image of fibers calcined at 600 °C for 24 h in air. These fibers originated from the precursor fibers shown in Fig. 2(b). The annealed fibers kept their 1D morphology just like the precursor fibers presenting. Their average diameter shrank to ca. 100 nm, and their lengths were still more than hundreds of microns. In contrast, their precursor fibers had an average diameter of ca. 200 nm. In general, the use of $RE(CF_3COO)_3$

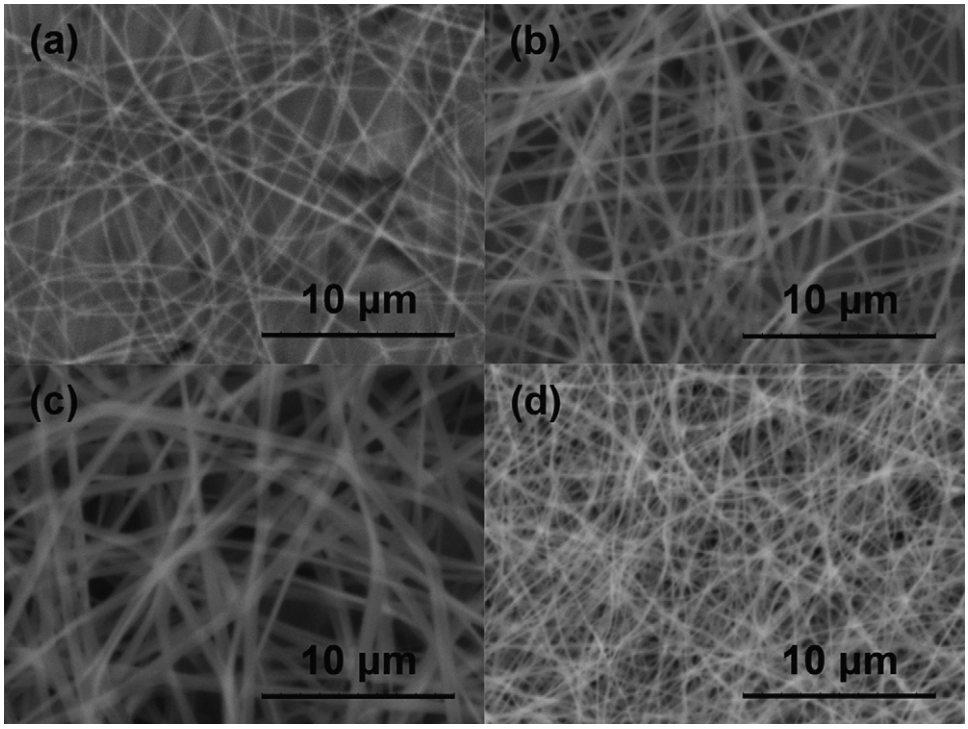


**Fig. 2.** (a–c) SEM images of $RE(CF_3COO)_3$/PVP composite fibers; (d) SEM image of calcined fibers corresponding to the precursor fibers in Fig. 1(b).