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Facile electrospinning preparation of color tunable flexible luminescent nanofiber

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A new structure of YAG:7%Tb^{3+} nanofibers/PVP flexible luminescent nanofibers has been successfully fabricated via electrospinning technology. Electrospun YAG:7%Tb^{3+} nanofibers are respectively incorporated into polyvinyl pyrrolidone (PVP) matrix and electrospun into flexible luminescent nanofibers named as YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers. The mean diameter of the flexible nanofibers is ca. 294±37.52 nm. The emission peaks of Tb^{3+} are observed under the excitation of 274-nm ultraviolet light and ascribed to the energy levels transitions of $^5D_4 \rightarrow {}^5F_6$ (489 nm), $^5D_4 \rightarrow {}^5F_5$ (544 nm), $^7D_4 \rightarrow {}^5F_4$ (590 nm) and $^5D_4 \rightarrow {}^7F_3$ (624 nm) of Tb^{3+} ions, and the $^5D_4 \rightarrow {}^5F_5$ energy levels transition at 544 nm is the predominant emission peak. The luminescent characteristics of obtained the flexible nanofibers can be tuned by adding various amounts of YAG:7%Tb^{3+} nanofibers. The possible formation mechanism of YAG:7%Tb^{3+} nanofibers/PVP flexible luminescent nanofibers is also proposed. The YAG:7%Tb^{3+} nanofibers are encapsulated in the PVP nanofibers which is expected to be used in biomedical field. The design conception and construction technology are of universal significance to fabricate other flexible nanofibers.

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1. Introduction

Electrospinning is a simple method of producing ultrafine fibers with diameters, ranging from nanometer to micrometer scales [1-6]. In particular, electrospun polymeric flexible nanofibers have been explored for their excellent performance in a variety of fields [7-9]. Most of these materials are hybrid organic-inorganic composites that are organized into different hierarchies and can perform different functions [10-13].

Flexible luminescent nanomaterials have been widely studied because of their increased applicability in many areas [14-16]. These nanomaterials play important roles in the living world. Polyvinyl pyrrolidone (PVP) is a green polymer and a surfactant usually used as a coating agent of flexible nanomaterials [17]. It has biodegradability and low toxicity, which make it useful for different application, such as medicine, food and cosmetics, etc. Tb-activated $Y_3Al_5O_{12}$ (YAG) phosphor has luminescence properties fairly insensitive to temperature variation and shows little tendency to saturate at high current excitations. Furthermore, YAG:Tb^{3+} nanomaterials have excellent luminescent properties owing to the f-f electron transition of Tb^{3+} ions, and they have received widespread attention due to their excellent performance [18-21]. Presently, researchers are mainly focused on the preparation, properties and applications of inorganic magnetic nanoparticles, nanofibers and nanobelts. In order to obtain new morphologies of magnetic nanomaterials study their performances, the fabrication of one-dimensional (1D) magnetic flexible nanomaterials is an urgent subject of study.

Herein, the flexible nanofibers were obtained from the combination of PVP and electrospun YAG:Tb^{3+} nanofibers by using electrospinning. We report a relatively simple way, where electrospun precursor was prepared by electrospun YAG:Tb^{3+} nanofibers with polymer solutions. YAG:Tb^{3+} nanofibers were incorporated into the nanofiber of PVP by with electrospinning technology. YAG:Tb^{3+} nanofibers were no agglomeration due to the special nanostructure of nanofibers and the existence of PVP. This new morphology of flexible luminescent nanofibers with adjustable luminescent properties has been obtained. The structure, morphology, luminescent properties and formation mechanism of the YAG:Tb^{3+}nanofibers/PVP flexible luminescent nanofibers were investigated in detail, and some meaningful results were obtained.

2. Experimental

2.1. Chemicals

Polyvinyl pyrrolidone (PVP, M_w=1 300 000) and N, N-dimethylformamide (DMF) were purchased from Tianjin Tiantai Fine Chemical Reagents Co., Ltd. HNO_3 was bought from Beijing Chemical Company. Y_2O_3 (99.99%), Tb_4O_7 (99.99%) and $Al(NO_3)_3 \cdot 9H_2O$ were bought from Sinopharm Chemical Reagent Co., Ltd. All chemicals were of analytical grade and directly used as received without further purification. $Y(NO_3)_3 \cdot nH_2O$ and $Tb(NO_3)_3 \cdot nH_2O$ were prepared by dissolving Y_2O_3 and Tb_4O_7 in dilute nitric acid, followed by crystallizing from the solution through evaporating the excess water and HNO_3 from the solution by heating.

2.2. Preparation of YAG:7% Tb^{3+} nanofibers

A traditional single-spinneret electrospinning instrument was used to prepare YAG:7%Tb^{3+} nanofibers. The spinning solution for preparing YAG:7%Tb^{3+} nanofibers was acquired as follows: 0.93 mmol of $Y(NO_3)_3 \cdot nH_2O$, 0.07 mmol of $Tb(NO_3)_3 \cdot nH_2O$, 1.38 g of $Al(NO_3)_3 \cdot 9H_2O$ and 2.4 g of PVP were added into 15.6 g of DMF to form uniform solution under vigorous stirring. The spinning solution was stirred for 4 h to form homogeneous mixture solutions for next-step electrospinning. Then, the spinning solution was respectively injected into a traditional single-spinneret electrospinning setup, $[Y(NO_3)_3+Al(NO_3)_3+Tb(NO_3)_3]$/PVP composite nanofibers have been prepared by electrospinning. The distance between the spinneret (a plastic needle) and collector was fixed at 18-20 cm and high voltage supply was maintained at 12-15 kV. The room temperature was 20-24 °C and the relative humidity was 60%-70%. YAG:7%Tb^{3+} nanofibers can be obtained when the relevant composite nanofibers were annealed in air at 900 °C for 8 h for 4 h with the heating rate of 1 $°C \cdot min^{-1}$.

2.3. Fabrication of YAG:7% Tb^{3+} nanofibers/PVP flexible nanofibers

The spinning solution for preparing the YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers was acquired as follows: YAG:7%Tb^{3+} nanofibers were dispersed in DMF with ultrasonication for 15 min at room temperature, then a certain amount of PVP was added into the above mixture with stirring for 6 h. The dosages of these materials were shown in Table 1.

Table 1. Compositions of the spinning solution

Compositions Samples	YAG:7%Tb^{3+}/g	PVP/g	DMF/g
I-1 (YAG:7%Tb^{3+} nanofibers/PVP=1:1)	0.200	0.200	1.338
I-2 (YAG:7%Tb^{3+} nanofibers/PVP=1:3)	0.200	0.600	4.014
I-3 (YAG:7%Tb^{3+} nanofibers/PVP=1:10)	0.200	2.000	13.38

YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers were prepared by electrospinning setup, as indicated in Fig. 1. A flat iron net used as collector was put about 18 cm away from the tip of the plastic nozzle to collect the flexible nanofibers. A positive direct current (DC) voltage of 18 kV was applied between the spinneret and the collector. The electrospinning process was carried out at ambient temperature of 22-24 °C and relative air humidity of 60%-70%.

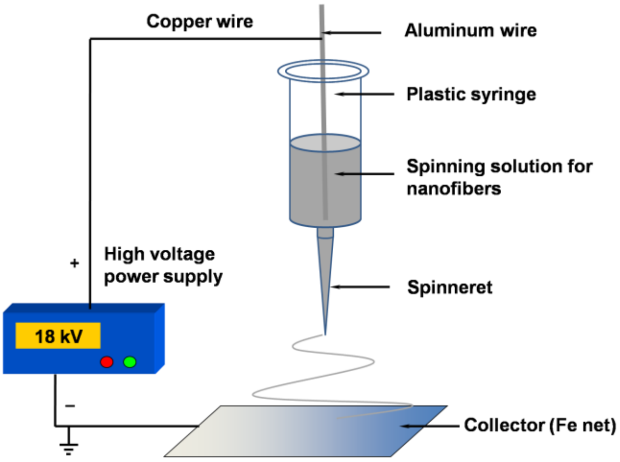

Fig. 1. Schematic diagram of the electrospinning setup

2.4. Characterization methods

The samples were identified by an X-ray powder diffractometer (XRD, Bruker D8 FOCUS) with Cu Kα radiation, and the operation voltage and current were kept at 40 kV and 20 mA, respectively. The morphology and internal structure of samples were observed by a field emission scanning electron microscope (SEM, XL-30) and a transmission electron microscope (TEM, JEM-2010), respectively. The luminescent properties of samples were investigated by a Hitachi fluorescence spectrophotometer F-7000. All measurements were performed at room temperature.

3. Results and discussions

3.1. Characterizations of structure and morphology

The phase compositions of YAG:7%Tb^{3+} nanofibers and YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers containing different mass ratios of YAG:7%Tb^{3+} nanofibers to PVP are characterized by means of XRD analysis, as shown in Fig. 2. As seen from Fig. 2a, the characteristic diffraction peaks of YAG:7%Tb^{3+} nanofibers are observed, all of which can be readily indexed to those of the cubic phase with primitive structure of YAG (PDF#33-0040). It can be seen that XRD patterns of YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers are conformed to the cubic phase with primitive structure of YAG (PDF#33-0040), and the diffraction peak of the amorphous PVP (2θ=22.2°) also can be observed, indicating that YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers contain crystalline YAG:7%Tb^{3+} and amorphous PVP, as presented in Fig. 2.

The morphology of the as-prepared [$Y(NO_3)_3$+$Al(NO_3)_3$+$Tb(NO_3)_3$]/PVP composite nanofibers and YAG:7%Tb^{3+} nanofibers are observed by means of SEM, as presented in Fig. 3a and Fig. 3b. The morphology of the as-prepared [$Y(NO_3)_3$+$Al(NO_3)_3$+ +$Tb(NO_3)_3$]/PVP composite nanofibers and YAG:7%Tb^{3+} nanofibers are observed by means of SEM, as presented in Fig. 3a and Fig. 3b. [$Y(NO_3)_3$+$Al(NO_3)_3$+$Tb(NO_3)_3$]/PVP composite nanofibers are smooth and uniform, and YAG:7%Tb^{3+} nanofibers have coarse surface, and the size distribution of the as-prepared nanofibers are almost uniform, and the diameters of [$Y(NO_3)_3$+$Al(NO_3)_3$+ +$Tb(NO_3)_3$]/PVP composite nanofibers and YAG:7%Tb^{3+} nanofibers are 249.96±32.14nm and 165.22±18.30 nm under the confidence level of 95%, respectively, as demonstrated in Fig. 4a and Fig. 4b. The morphology and structure of YAG:7%Tb^{3+} nanofibers/PVP flexible magnetic nanofibers are characterized by the combination of SEM and TEM analyses. As seen from Fig. 3c, the surface of the flexible nanofibers is smooth. The mean diameter of the flexible nanofibers is ca. 294±37.52 nm under the confidence level of 95%, as shown in Fig. 4c. The TEM image of YAG:7%Tb^{3+} nanofibers/PVP flexible magnetic nanofibers is presented in Fig. 3d. As revealed in Fig. 3d, the YAG:7%Tb^{3+} nanofibers are clearly observed in the PVP nanofibers, it can confirm that the flexible nanofiber is composed of YAG:7%Tb^{3+} nanofibers and PVP. The diameter of the YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers is 270-310 nm, which is in good agreement with results of SEM analyses. From the above SEM and TEM analysis, we can confirm that the YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers have been successfully fabricated. As seen from Fig. 3e, one can see that the YAG:7%Tb^{3+} nanofibers/PVP luminescent nanofibers are flexible nanofibers.

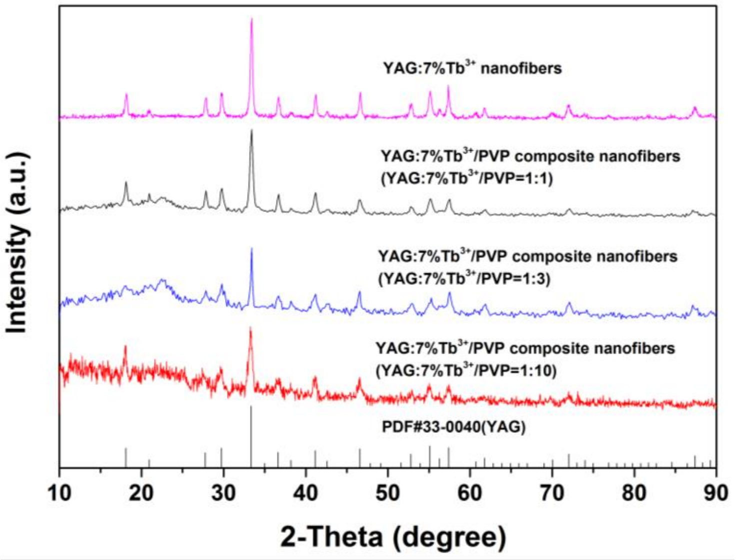

Fig. 2. XRD patterns of YAG:7%Tb^{3+} nanofibers and YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers containing different mass ratios of YAG:7%Tb^{3+} nanofibers to PVP with PDF standard card of YAG

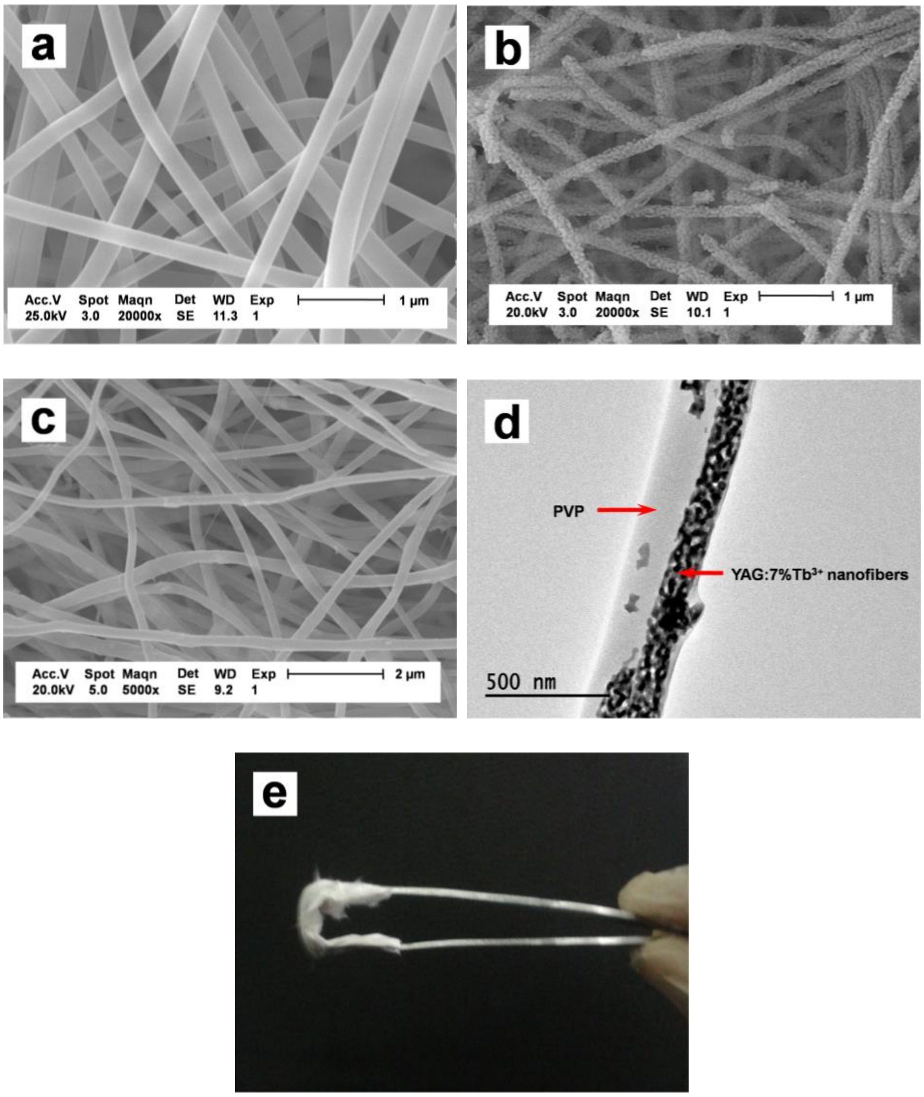

Fig. 3. SEM image of [Y(NO$_3$)$_3$+Al(NO$_3$)$_3$+Tb(NO$_3$)$_3$]/PVP composite nanofibers (a), YAG:7%Tb^{3+} nanofibers (b) and SEM image and TEM image of YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers (c and d) and photograph of YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers (e)

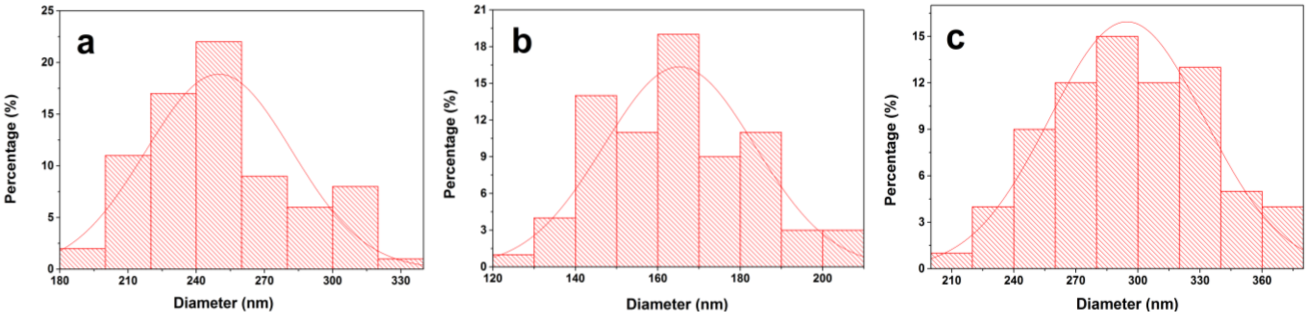

Fig. 4. Histograms of diameters distribution of [Y(NO$_3$)$_3$+Al(NO$_3$)$_3$+Tb(NO$_3$)$_3$]/PVP composite nanofibers (a), YAG:7%Tb^{3+} nanofibers (b) and YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers (c)

3.2. Luminescent properties of YAG:7% Tb^{3+} nanofibers/PVP flexible nanofibers

In order to investigate the impact of the mass ratio of YAG:7%Tb^{3+} luminescent nanofibers to PVP on the luminescent performance, a series of YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers were fabricated. In order to perform this study, the mass ratios of YAG:7%Tb^{3+} nanofibers to PVP are varied from 1:1 to 1:10. It can be observed from Fig. 5 that the excitation spectra (monitored by 544 nm) of the samples show broadband with a main peak centering at about 274 nm, which can be attributed to $4f^8\rightarrow 4f^7 5d$ energy levels transitions of Tb^{3+}. As shown in Fig. 6, characteristic emission peaks of Tb^{3+} are observed under the excitation of 274-nm ultraviolet light and ascribed to the energy levels transitions of $^5D_4\rightarrow{}^5F_6$ (489 nm), $^5D_4\rightarrow{}^5F_5$ (544 nm), $^7D_4\rightarrow{}^5F_4$ (590 nm) and $^5D_4\rightarrow{}^7F_3$ (624 nm) of Tb^{3+} ions, and the $^5D_4\rightarrow{}^5F_5$ energy levels transition at 544 nm is the predominant emission peak. It is found from Fig. 5 and Fig. 6 that the peaks have the same spectral shape with the increase of amount of luminescent substance, whereas the intensities of excitation and emission peaks are strengthened, indicating that the luminescent intensity of the flexible nanofibers can be tuned by adjusting the amount of luminescent material.

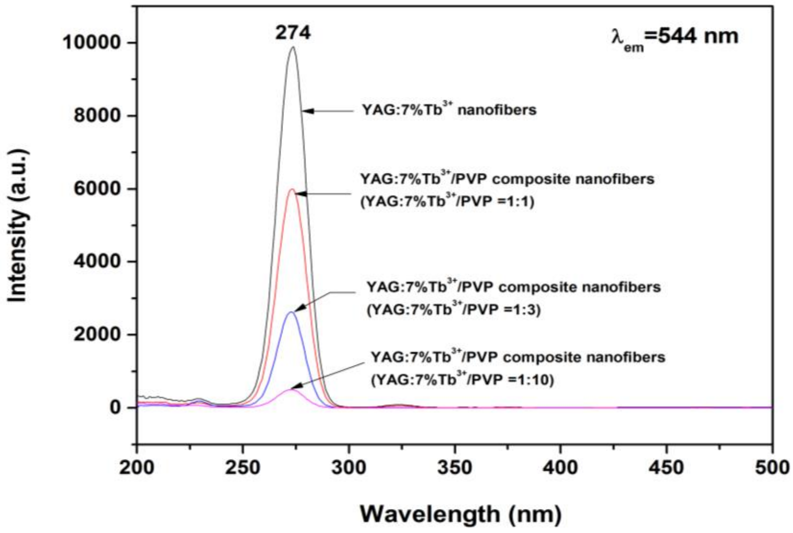

Fig. 5. Excitation spectra of YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers containing different mass ratios of YAG:7%Tb^{3+} nanofibers to PVP

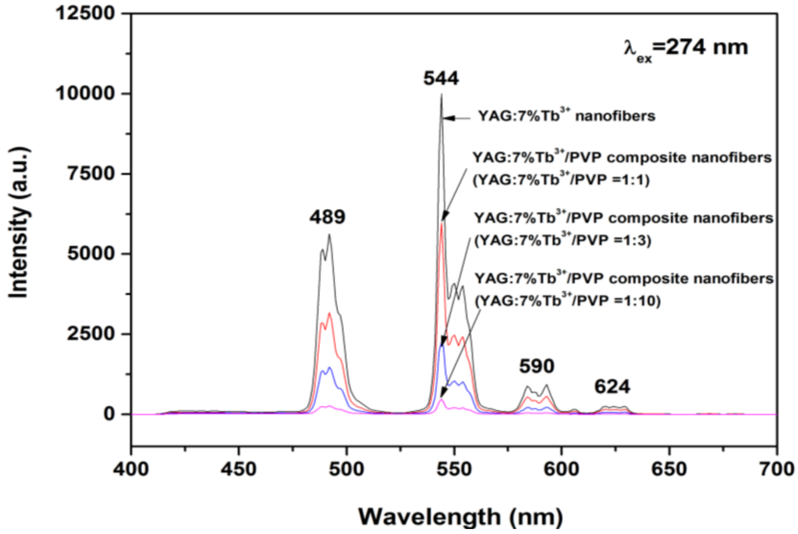

Fig. 6. Emission spectra of YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers containing different mass ratios of YAG:7%Tb^{3+} nanofibers to PVP

3.3. Formation mechanism for YAG:7% Tb^{3+} nanofibers/PVP flexible nanofibers

Formation mechanism for YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers is proposed on the basis of the above experimental results, as shown in Fig. 7. YAG:7%Tb^{3+} luminescent nanofibers is ultrasonically dispersed into DMF, then PVP is dissolved into the above solutions to form spinning solution with certain viscosity. YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers are fabricated via electrospinning using a traditional single-spinneret. PVP acted as template and matrix during the formation of YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers. YAG:7%Tb^{3+} nanofibers is mixed with or absorbed onto PVP chain and combined to generate YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers.

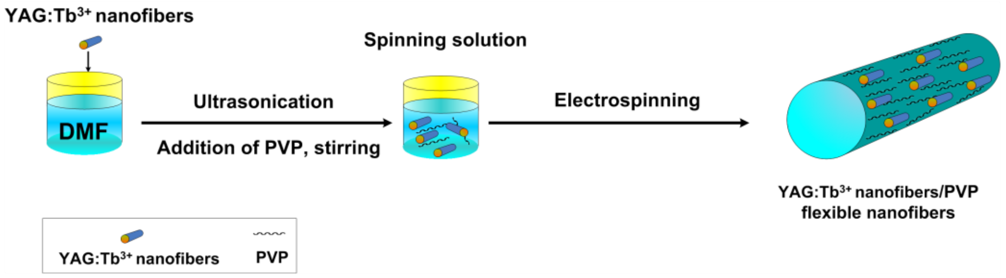

Fig. 7. Formation mechanism for YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers

4. Conclusions

In summary, YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers have been successfully synthesized by electrospinning technology. The YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers is composed of YAG:7%Tb^{3+} luminescent nanofibers and PVP. The average diameter of the flexible nanofiber is ca. 294±37.52 nm. It is very gratifying to see that the luminescent intensity of the flexible nanofibers can be tuned via adjusting the content of luminescent compounds. Besides, the design conception and preparation method of the flexible nanofibers are of universal significance to fabricate other one-dimensional multifunctional nanostructures. The new structure YAG:7%Tb^{3+} nanofibers/PVP flexible nanofibers have potential applications in the fields of medical diagnostics, drug target delivery, optical imaging, anti-counterfeiting technology and future nanomechanics.

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