Facile electrospinning preparation of tunable flexible magnetism nanofiber

FEI BI[1,*], GUANGQING GAI[1], XIANGTING DONG[2,*], SHANSHAN XIAO[1], LI ZHAO[1], LIYAN WANG[1,*]
[1]Laboratory of Building Energy-Saving Technology Engineering, College of Material Science and Engineering, Jilin Jianzhu University, Changchun 130118, China
[2]Key Laboratory of Applied Chemistry and Nanotechnology at Universities of Jilin Province, Changchun University of Science and Technology, Changchun 130022, China

A new structure of $CoFe_2O_4$ nanofibers/PVP flexible magnetic nanofibers has been successfully fabricated via electrospinning technology. Electrospun $CoFe_2O_4$ magnetic nanofibers are respectively incorporated into polyvinyl pyrrolidone (PVP) matrix and electrospun into flexible magnetic nanofibers named as $CoFe_2O_4$ nanofibers/PVP flexible nanofibers. The saturation magnetizations of obtained the flexible nanofibers can be tuned by adding various amounts of $CoFe_2O_4$ magnetic nanofibers. According to this way, we got stable magnetic fluid, which has been electrospun into magnetic nanofiber directly. The $CoFe_2O_4$ nanofibers encapsulated in the PVP nanofibers respond to an external magnetic field which is expected to be used in biomedical field. The design conception and construction technology are of universal significance to fabricate other flexible nanofibers.

1. Introduction

Electrospinning is a simple method of producing ultrafine fibers with diameters, ranging from nanometer to micrometer scales [1-8]. In particular, electrospun polymeric flexible nanofibers have been explored for their excellent performance in a variety of fields [9-11]. Most of these materials are hybrid organic-inorganic composites that are organized into different hierarchies and can perform different functions [12-17].

Flexible magnetic nanomaterials have been widely studied because of their increased applicability in many areas [18-21]. These nanomaterials play important roles in the living world, which can be used as cilia, self-propelling microorganisms etc. Polyvinyl pyrrolidone (PVP) is a green polymer and a surfactant usually used as a coating agent of flexible nanomaterials [22]. It has biodegradability and low toxicity, which make it useful for different application, such as medicine, food and cosmetics etc. Spinel cobalt ferrite ($CoFe_2O_4$) is a typical magnetic and electrical resistive ferrite material, which has moderate saturation magnetization and excellent physical and chemical stability. $CoFe_2O_4$ nanomaterials exhibit promising prospects for magnetic recording media, targeting drug delivery carriers and sensor magnetic cores [23-26]. Presently, researchers are mainly studied on the inorganic magnetic nanoparticles, nanofibers and nanobelts. In order to obtain new morphologies of magnetic nanomaterials, 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 $CoFe_2O_4$ nanofibers by using electrospinning. We report a relatively simple way, where electrospun precursor was prepared by electrospun $CoFe_2O_4$ magnetic nanofibers with polymer solutions. $CoFe_2O_4$ nanofibers were incorporated into the nanofiber of PVP by with electrospinning technology, to prepare spinel ferrites in the presence of PVP. $CoFe_2O_4$ nanofibers were no agglomeration due to the special nanostructure of nanofibers and the existence of PVP. This new morphology of flexible magnetic nanofibers with adjustable magnetism has been obtained. The structure, morphology, magnetic properties and formation mechanism of the $CoFe_2O_4$ nanofibers/PVP flexible magnetic 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. $Fe(NO_3)_3 \cdot 9H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ were bought from Sinopharm Chemical Reagent Co., Ltd. All chemicals were of analytical grade and directly used as received without further purification.

2.2. Preparation of CoFe₂O₄ nanofibers

A traditional single-spinneret electrospinning instrument was used to prepare $CoFe_2O_4$ nanofibers. In a typical procedure of preparing spinning solution for fabricating $CoFe_2O_4$ nanofibers, 1 mmol of $Fe(NO_3)_3 \cdot 9H_2O$, 0.5 mmol of $Co(NO_3)_2 \cdot 6H_2O$ and 2.4 g of PVP were dissolved into 15.6 g of DMF under continuous stirring. The spinning solutions were stirred for 6 h to form homogeneous mixture solutions for next-step electrospinning. Then, the spinning solutions were respectively injected into a traditional single-spinneret electrospinning setup, $[Fe(NO_3)_3+Co(NO_3)_2]$/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 13-16 kV. The room temperature was 20-24 °C and the relative humidity was 60%-70%. $CoFe_2O_4$ nanofibers can be obtained when the relevant composite nanofibers were annealed in air at 600 °C for 6 h with the heating rate of 1 °C·min⁻¹.

2.3. Fabrication of CoFe₂O₄ nanofibers /PVP flexible nanofibers

The spinning solution for preparing the $CoFe_2O_4$ nanofibers/PVP flexible nanofibers was acquired as follows: $CoFe_2O_4$ magnetic 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. $CoFe_2O_4$ 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%.
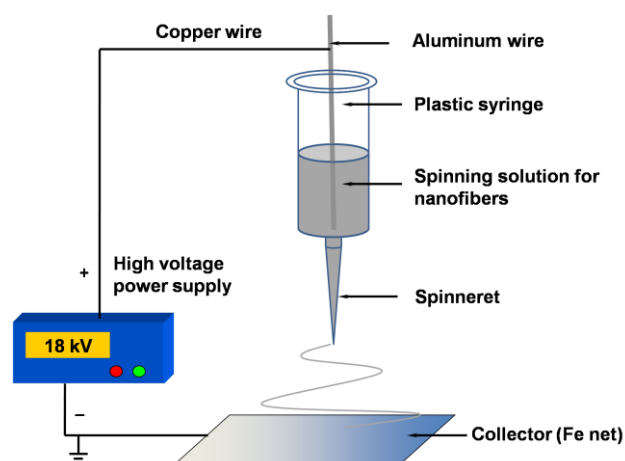

Fig. 1. Schematic diagram of the electrospinning setup (color online)

Table 1. Compositions of the spinning solution

Compositions / Samples	CoFe₂O₄ nanofibers/g	PVP/g	DMF/g
I-1 (CoFe₂O₄ nanofibers/PVP=1:1)	0.500	0.500	3.345
I-2 (CoFe₂O₄ nanofibers/PVP=1:3)	0.500	1.500	10.035
I-3 (CoFe₂O₄ nanofibers/PVP=1:5)	0.500	2.500	16.725

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 purity of the products was examined by OXFORD ISIS-300 energy dispersive X-ray spectrometer (EDX). The magnetic performance of samples was measured by a vibrating sample magnetometer (VSM, MPMS SQUID XL).

3. Results and discussion

3.1. Characterizations of structure and morphology

The phase compositions of $CoFe_2O_4$ nanofibers and $CoFe_2O_4$ nanofibers/PVP flexible nanofibers containing different mass ratios of $CoFe_2O_4$ 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 $CoFe_2O_4$ nanofibers are observed, all of which can be readily indexed to those of the cubic spinel structure of $CoFe_2O_4$ (PDF#22-1086). It can be seen that XRD patterns of $CoFe_2O_4$ nanofibers/PVP flexible nanofibers are conformed to the cubic spinel structure of $CoFe_2O_4$ (PDF#22-1086), and the diffraction peak of the amorphous PVP ($2\theta=22.2°$) also can be observed, indicating that $CoFe_2O_4$ nanofibers/PVP flexible nanofibers contain crystalline $CoFe_2O_4$ and amorphous PVP, as presented in Fig. 2b, Fig. 2c and Fig. 2d.
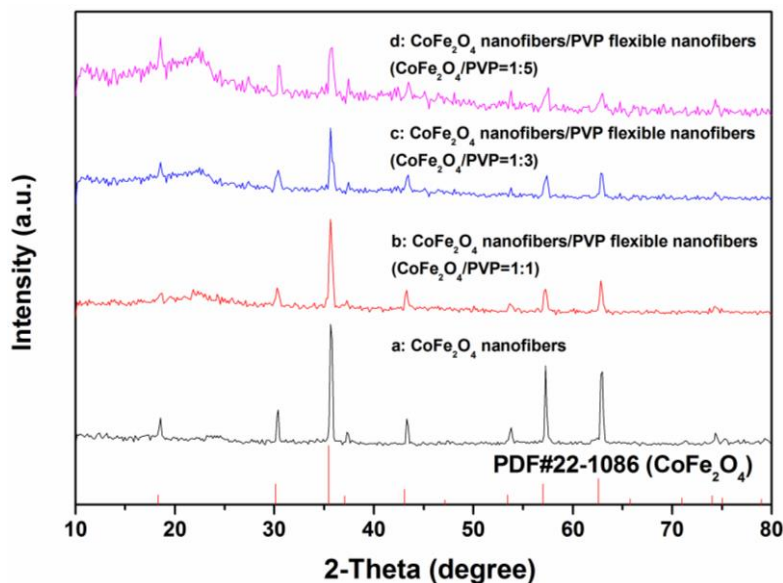
Fig. 2. XRD patterns of CoFe₂O₄ nanofibers (a) and CoFe₂O₄ nanofibers/PVP flexible nanofibers containing different mass ratios of CoFe₂O₄ nanofibers to PVP (b, c, d) with PDF standard card of CoFe₂O₄ (color online)

The morphology of the as-prepared $CoFe_2O_4$ nanofibers is observed by means of SEM, as presented in Fig. 3a. $CoFe_2O_4$ nanofibers have coarse surface, and the size distribution of the as-prepared nanofibers are almost uniform, and the diameter of the $CoFe_2O_4$ nanofibers is 86.79±9.09 nm under the confidence level of 95%, respectively, as demonstrated in Fig. 4a.
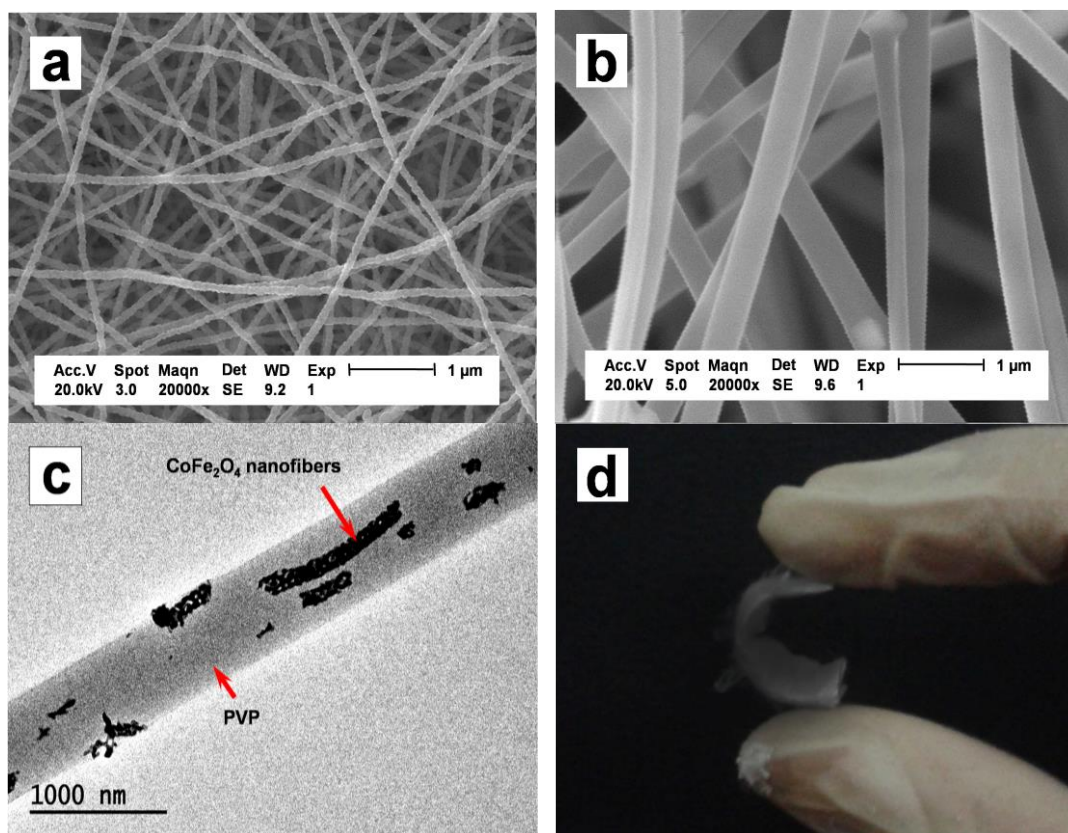

Fig. 3. SEM image of CoFe₂O₄ nanofibers (a) and SEM image and TEM image of CoFe₂O₄ nanofibers/PVP flexible nanofibers (b and c) and photograph of CoFe₂O₄ nanofibers/PVP flexible nanofibers (d) (color online)

The morphology and structure of $CoFe_2O_4$ nanofibers/PVP flexible magnetic nanofibers are characterized by the combination of SEM and TEM analyses. As seen from Fig. 3b, the surface of the flexible nanofibers is smooth. The mean diameter of the flexible nanofibers is ca. 335.68±55.71 nm under the confidence level of 95%, as shown in Fig. 4b. The TEM image of $CoFe_2O_4$ nanofibers/PVP flexible magnetic nanofibers is presented in Fig. 3c. As revealed in Fig. 3c, the $CoFe_2O_4$ nanofibers are clearly observed in the PVP nanofibers, it can confirm that the flexible magnetic nanofiber is composed of $CoFe_2O_4$ magnetic nanofibers and PVP. The diameter of the $CoFe_2O_4$ nanofibers/PVP flexible magnetic nanofibers is 320-350 nm, which is in good agreement with results of SEM analyses. From the above SEM and TEM analysis, we can confirm that the $CoFe_2O_4$ nanofibers/PVP flexible nanofibers have been successfully fabricated. As seen from Fig. 3d, one can see that the $CoFe_2O_4$ nanofibers/PVP magnetic nanofibers are flexible nanofibers.
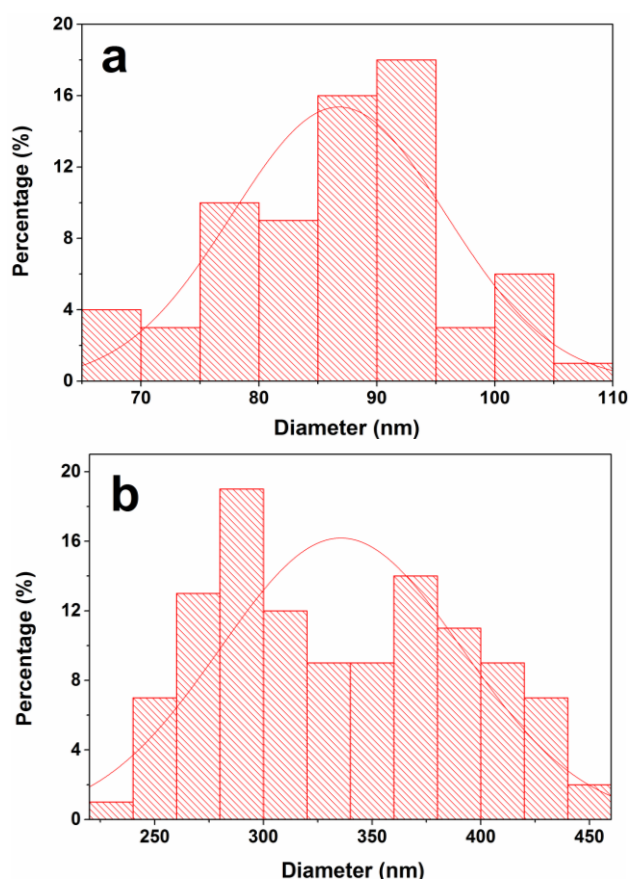

Fig. 4 Histograms of diameters distribution of CoFe₂O₄ nanofibers (a) and CoFe₂O₄ nanofibers/PVP flexible nanofibers (b) (color online)

The elementary compositions of $CoFe_2O_4$ nanofibers and $CoFe_2O_4$ nanofibers/PVP flexible magnetic nanofibers are further confirmed by energy dispersive X-ray spectrometer (EDX), as reveals in Fig. 5. EDX spectra show that O, Fe and Co are the main elements in $CoFe_2O_4$ nanofibers, and C, O, Fe and Co in $CoFe_2O_4$

nanofibers/PVP flexible nanofibers. The element of Au in the spectra comes from the Au film coated on the surface of the sample for SEM observation.
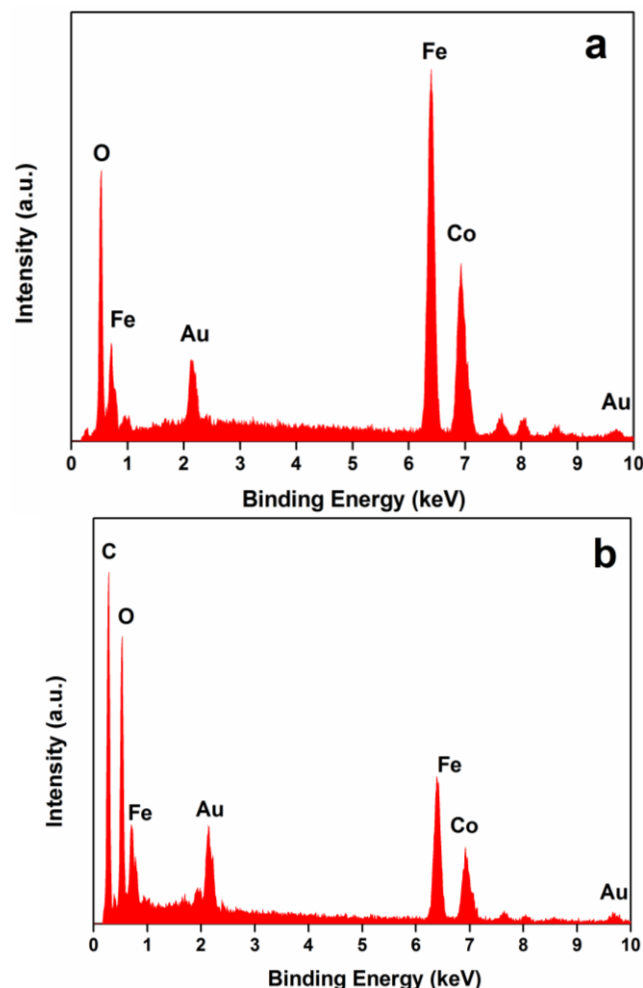

Fig. 5. EDX spectra of CoFe₂O₄ nanofibers (a) and CoFe₂O₄ nanofibers/PVP flexible nanofibers (b) (color online)

3.2. Magnetic properties of CoFe₂O₄ nanofibers /PVP flexible nanofibers

The typical hysteresis loops for $CoFe_2O_4$ nanofibers and $CoFe_2O_4$ nanofibers/PVP flexible nanofibers containing different mass ratios of $CoFe_2O_4$ nanofibers to PVP are shown in Fig. 6, and the saturation magnetizations of the samples are summarized in Table 2. It is known that the saturation magnetization of a magnetic composite material depends on the mass percentage of the magnetic substance in the magnetic composite material [16-19]. The saturation magnetization of the $CoFe_2O_4$ nanofibers is 41.3 emu·g⁻¹. Compared with the $CoFe_2O_4$ nanofibers, the saturation magnetizations of $CoFe_2O_4$ nanofibers/PVP flexible nanofibers is lower due to adding PVP into the flexible nanofibers. It is found that the saturation magnetization of the $CoFe_2O_4$ nanofibers/PVP flexible nanofibers is increased with the increase of the amount of $CoFe_2O_4$ magnetic nanofibers introduced into the PVP,

implying that the magnetism of the flexible magnetic nanofibers can be tunable by adjusting the amount of $CoFe_2O_4$ magnetic nanofibers. The saturation magnetizations of the $CoFe_2O_4$ nanofibers/PVP flexible nanofibers containing different mass ratios of $CoFe_2O_4$ nanofibers to PVP are $20.3\,emu\cdot g^{-1}$, $6.8\,emu\cdot g^{-1}$ and $3.1\,emu\cdot g^{-1}$, respectively.
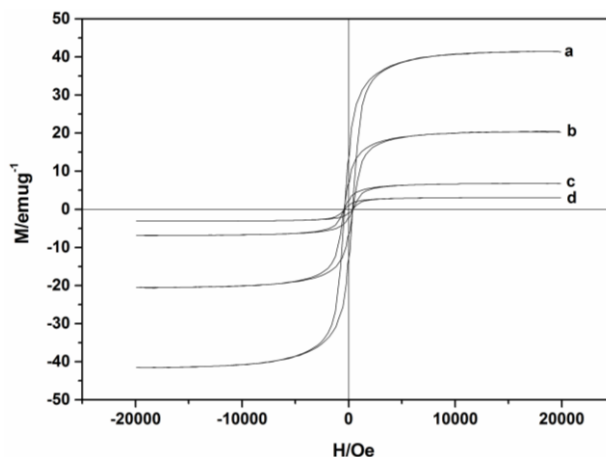

Fig. 6. Hysteresis loops of CoFe₂O₄ nanofibers (a) and CoFe₂O₄ nanofibers/PVP flexible nanofibers containing different mass ratios of CoFe₂O₄ nanofibers to PVP (b, c, d)

Table 2. Saturation magnetization of samples

Samples	Saturation magnetization $(M_s)/emu\cdot g^{-1}$
$CoFe_2O_4$ nanofibers	41.3
$CoFe_2O_4$ nanofibers/PVP flexible nanofibers ($CoFe_2O_4$/PVP=1:1)	20.3
$CoFe_2O_4$ nanofibers/PVP flexible nanofibers ($CoFe_2O_4$/PVP=1:3)	6.8
$CoFe_2O_4$ nanofibers/PVP flexible nanofibers ($CoFe_2O_4$/PVP=1:5)	3.1

3.3. Formation mechanism for CoFe₂O₄ nanofibers/PVP flexible nanofibers

Formation mechanism for $CoFe_2O_4$ nanofibers/PVP flexible magnetic nanofibers is proposed on the basis of the above experimental results, as shown in Fig. 7. $CoFe_2O_4$ nanofibers is ultrasonically dispersed into DMF, then PVP is dissolved into the above solutions to form spinning solution with certain viscosity. $CoFe_2O_4$ nanofibers/PVP flexible nanofibers are fabricated via electrospinning using a traditional single-spinneret. PVP acted as template and matrix during the formation of $CoFe_2O_4$ nanofibers/PVP flexible nanofibers. $CoFe_2O_4$ nanofibers is mixed with or absorbed onto PVP chain and combined to generate $CoFe_2O_4$ nanofibers/PVP flexible nanofibers.
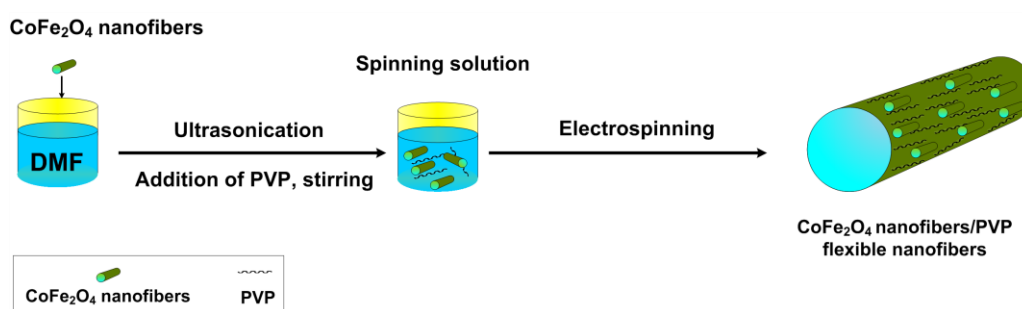

Fig. 7. Formation mechanism for CoFe₂O₄ nanofibers/PVP flexible nanofibers

4. Conclusions

In summary, $CoFe_2O_4$ nanofibers/PVP flexible nanofibers have been successfully synthesized by electrospinning technology. The $CoFe_2O_4$ nanofibers/PVP flexible nanofibers is composed of $CoFe_2O_4$ magnetic nanofibers and PVP. The average diameter of the flexible nanofiber is ca. 335.68 ± 55.71 nm. It is very gratifying to see that the magnetism of the flexible nanofibers can be tuned via adjusting the content of magnetic 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 $CoFe_2O_4$ nanofibers/PVP flexible nanofibers have potential applications in the fields of medical diagnostics, drug target delivery, optical imaging, anti-counterfeiting technology and future nanomechanics.

References

[1] Y. T. Geng, P. Zhang, Q. T. Wang, Y. X. Liu, K. Pan, J. Mater. Chem. B **5**, 5390 (2017).

[2] C. Luo, X. X. Wang, J. Q. Wang, K. Pan, Compos. Sci. Technol. **133**, 97 (2016).

[3] N. Lv, J. L. Zhang, G. M. Li, X. Wang, J. Z. Ni, J. Phys. Chem. C **121**, 11926 (2017).

[4] J. Zhang, X. B. Hou, Z. Y. Pang, Y. B. Cai, H. M. Zhou, P. F. Lv, Q. F. Wei, Ceram. Int. **43**, 15911 (2017).

[5] X. P. Ni, Z. Cui, H. X. Luo, H. F. Chen, C. L. Liu, Q. L. Wu, A. Q. Ju. Chem. Eng. J. **404**, 126249 (2020).

[6] N. Lv, Z. G. Wang, W. Z. Bi, G. M. Li, J. L. Zhang, J. Z. Ni, J. Mater. Chem. B **4**, 4402 (2016).

[7] A. Seongpil, S. J. Hong, D. Y. Kim, H. J. Lee, B. K. Ju, S. S. Al-Deyab, J. H. Ahn, Y. L. Qin, M. T. Swihart, A. L. Yarin, S. S. Yoo, Adv. Mater. **28**, 7149 (2016).

[8] F. Bi, X. T. Dong, J. X. Wang, G. X. Liu, J. Mater. Sci. **49**, 7244 (2014).

[9] L. Wang, Y. Yu, P. C. Chen, D. W. Zhang, C. H. Chen, J. Power Sources **183**, 717 (2008).

[10] J. Tian, Q. L. Ma, W. S. Yu, X. T. Dong, Y. Yang, B. Zhao, J. X. Wang, G. X. Liu, New J. Chem. **41**, 13983 (2017).

[11] Z. Y. Zhang, C. L. Shao, Y. Y. Sun, J. B. Mu, M. Y. Zhang, P. Zhang, Z. C. Guo, P. P. Liang, C. H. Wang, Y. C. Liu, J. Mater. Chem. **22**, 1387 (2012).

[12] J. Zhou, J. S. Yu, D. Y. Bai, H. L. Liu, L. Li, Nanomaterials **11**, 3041 (2021).

[13] H. Y. Bai, Y. Song, D. Li, Q. L. Ma, X. T. Dong, W. S. Yu, Y. Yang, J. X. Wang, G. X. Liu, T. T. Wang, Ceram. Int. **44**, 6754 (2018).

[14] M. Gao, X. F. Lu, M. Q. Chi, S. H. Chen, C. Wang, Inorg. Chem. Front. **4**, 1862 (2017).

[15] L. Fan, Q. L. Ma, J. Tian, D. Li, X. Xi, X. T. Dong, W. S. Yu, J. X. Wang, G. X. Liu, RSC Adv. **7**, 48702 (2017).

[16] X. Xi, Q. L. Ma, X. T. Dong, D. L, W. H. Yu, J. X. Wang, G. X. Liu, Journal of Materials Science: Materials in Electronics **10**, 1007 (2018).

[17] M. Q. Chi, S. H. Chen, M. X. Zhong, C. Wang, X. F. Lu, Chem. Commun **54**, 5827 (2018).

[18] X. B. Li, Q. L. Ma, J. Tian, X. Xi, D. Li, X. T. Dong, W. S. Yu, X. L. Wang, J. X. Wang, G. X. Liu, Nanoscale **9**, 18918 (2017).

[19] A. Cebers, K. Erglis, Adv. Funct. Mater. **26**, 3783 (2016).

[20] Damien Faivre, Nature Nanotech. **5**, 562 (2010).

[21] A. Cēbers, Curr. Opin. Colloid Interface Sci. **10**, 167 (2005).

[22] L. P. Guo, J. Bai, C. P. Li, Q. R. Meng, H. O. Liang, W. Y. Sun, H. Q. Li, H. Liu, Appl. Surf. Sci. **283**, 107 (2014).

[23] T. F. Li, Y. J. Lv, J. H. Su, Y. Wang, Q. Yang, Y. W. Zhang, J. C. Zhou, L. Xu, D. M. Sun, Y. W. Tang, Adv. Sci. **4**, 1700226 (2017).

[24] Q. M. He, K. Rui, C. H. Chen, J. H. Yang, Z. Y. Wen, ACS Appl. Mater. Interfaces **9**, 36927 (2017).

[25] W. Z. Yin, S. Hao, H. Q. Cao, RSC Adv. **7**, 50420 (2017).

[26] Y. Zhang, L. K. Shen, M. Liu, X. Li, X. L. Lu, L. Lu, C. R. Ma, C. Y. You, A. P. Chen, C. W. Huang, L. Chen, M. Alexe, C. L. Jia, ACS Nano **11**, 8002 (2017).

_____
*Corresponding author: bifei1224@163.com;
                    dongxiangting888@163.com