

The effect of calcination temperature on the surface evolution and photocatalysis activity of co-doped PVAc/TiO₂ composite nanofibers

Ning Wu^{1,a}, Yanan Jiao^{1,b}, Zhiqing Yuan^{2,c}, Yunxing Liang^{1,d} and Li Chen^{1,f}

¹Tianjin and Ministry of Education Key Laboratory of Advanced Textile Composite Materials, Institute of Textile Composite, Tianjin Polytechnic University, Tianjin 300160

² Hebei entry-exit inspection and quarantine bureau, Shijiazhuang 050051

^awuning@tjpu.edu.cn, ^bjiaoyan@tjpu.edu.cn, ^cyuanzhiqing@126.com, ^dchaoyueziwo569@126.com, ^echenli@tjpu.edu.cn

Keywords: calcination temperature, Fe³⁺, La³⁺ co-doped, PVAc/TiO₂ nanofiber, surface evolution, photocatalysis activity.

Abstract. The Fe³⁺, La³⁺ co-doped polyvinyl acetate (PVAc)/titanium dioxide (TiO₂) composite nanofibers were firstly prepared by combining sol-gel method and electrospinning process, and then calcined under 300°C and 600°C separately. The effect of calcination temperature on structures, surface morphologies, crystalline state, elemental composition and photocatalysis activity were characterized by scanning electron microscope (SEM), atomic force microscope (AFM), X-ray Diffraction (XRD), energy dispersive X-ray spectroscopy (EDX) and ultraviolet-visible spectrophotometer (UV-Vis) respectively. The SEM and AFM images showed that the nanofibers were randomly distributed to form the fibrous web, the diameters and surface roughness of nanofibers were obviously changed as the calcination temperature increasing. The EDX analysis and XRD spectra indicated the percentage of C, O, Ti elements varied as the increase of temperature and the formation of anatase crystal form TiO₂ nanofibers under 600°C. The UV-Vis curves revealed strong adsorption to methylene blue under 600°C calcination.

Introduction

Titanium dioxide (TiO₂) has been recognized as a promising photocatalysis material due to its low cost, low energy consumption, stability and unique photoelectric performance. But the wide forbidden band (3.2 eV), light produced electronic and cavities easily compound result in the low photocatalytic and light quantum efficiency. In order to improve the utilization efficiency of the visible light, researchers are trying to use the precious metal deposition, metal ion doping, nonmetal ion doping, semiconductor compound, surface photosensitive change wait for method to modified TiO₂ light catalyst [1-5]. It uses transition metal ions and rare metal ions in expanding the light of doping can also reduce response range of electronic and cavities compound, thus it can effectively improve the TiO₂ photocatalytic activity [6]. Because of the porous structure of TiO₂ light catalyst has more reactive spot, which favor the surface adsorption of the reactants in optical catalyst and the desorption of degradation products [7], in recent years, researchers investigated various doping modified methods for improving the photocatalysis of TiO₂ nanofibers [8,9]. Comparing to the evolution process from doped composite nanofiber to inorganic nanofiber in different calcination temperature, these research works focused on discussing the surface and photocatalysis properties of ultimate doping TiO₂ nanofiber products.

In this work, Fe³⁺, La³⁺ co-doped PVAc/TiO₂ nanofibers are prepared by combining sol-gel method and electrospinning. The porous structure co-doped nanofibers are prepared after 300°C and 600°C calcination respectively. The effect of calcination temperature on the surface morphology, crystal, elements and catalysis activities of co-doped nanofiber in the evolution process of organic/inorganic composite nanofibers, carbonization nanofibers and inorganic nanofibers are investigated and discussed.

Experimental

PVAc solution with a concentration of 15wt % (Solution A) was prepared by dissolving the PVAc particles in acetone. The ratio of acetylacetone:Ti(OC₄H₉)₄:anhydrous ethanol in 1:1:2 with stirring (Solution B). The preparation of Solution C is by adding a given amount of Fe(NO₃)₃•9H₂O and La(NO₃)₃•6(H₂O) into the mixture solution of deionized water and ethanol. Then, Solution C was added dropwise into Solution B with vigorous stirring for 5h at room temperature, solution D prepared. Solution D was mixed with Solution A in a 1:1 ratio by stirring for 8 h, to obtain the composite solution.

The composite solution is placed in a syringe for electrospinning. A high voltage (20KV) was applied to the spinning solution via an alligator clip attached to the syringe needle. The solution was delivered to a blunt needle (the nozzle diameter was about 0.7mm) via a microinfusion pump (WZ-50C2, Zhejiang, China) to control the solution flow rate at 1.0ml/h. The electrospun fibers were collected on a sheet glass. The as-prepared composite fibers were subjected to 300°C and 600°C calcination for 2h respectively, to obtain carbonized and inorganic Fe³⁺, La³⁺ co-doped TiO₂ nanofibers.

The fibrous structures and element variation of the nanofibers were investigated by SEM (HITACHI S-4800). XRD patterns were employed to analyze the crystal form of nanofibers, which were obtained at room temperature with a BRUKER D8 diffractometer (Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$) with the scanning rate of 5°/min. The surface morphologies of single nanofiber were characterized by AFM(CSPM4000, Benyuan, China). Irradiation was provided by a 150W tungsten halogen lamp and an 8W UV lamp, located in the center of the quartz jacket. The amount of nanofibers chosen was 0.3g/L methylene blue solution was used for each photocatalytic degradation study. A certain amount of reactive solution was withdrawn at 30min intervals. The degradation ration can be calculated using the formula: $w = (c_0 - c_t) / c_0 \times 100 \%$, c_0 is the initial concentration of methylene blue; c_t is the t moment concentration of methylene blue.

Results and discussion

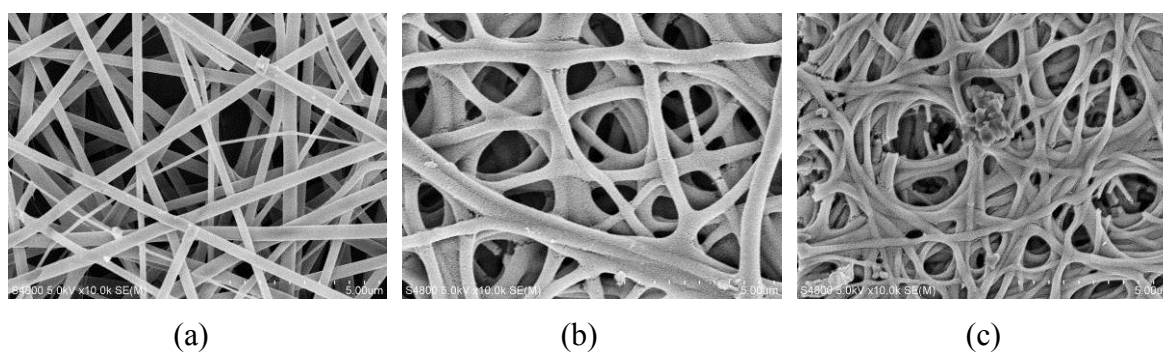


Fig. 1 The SEM images of Fe³⁺, La³⁺ co-doped TiO₂ nanofibers calcined at different temperatures,

(a) 0°C, (b) 300°C, (c) 600°C

The fibrous structure of Fe³⁺, La³⁺ co-doped TiO₂ nanofibers at different calcinate temperatures are illustrated in Fig. 1. As shown in Fig. 1, the fibrous structure is clear and straight, some threadlet structure and punctiform protuberance are appeared on the surface, this characteristic have not been found in our previous research for un-doped PVAc/TiO₂ nanofibers[10]. The doping of Fe³⁺ and La³⁺ induced the electron uneven distributed in the jet, some intensive parts produced branch, the punctiform protuberance may caused by the oxidation of metal ion. When the calcination temperature up to 300°C, the threadlet structure is disappeared, fibers become curved and thicker, some fibers adhered together. After 600°C calcined, the porous structure is obvious and the diameters of fibers become thinner.

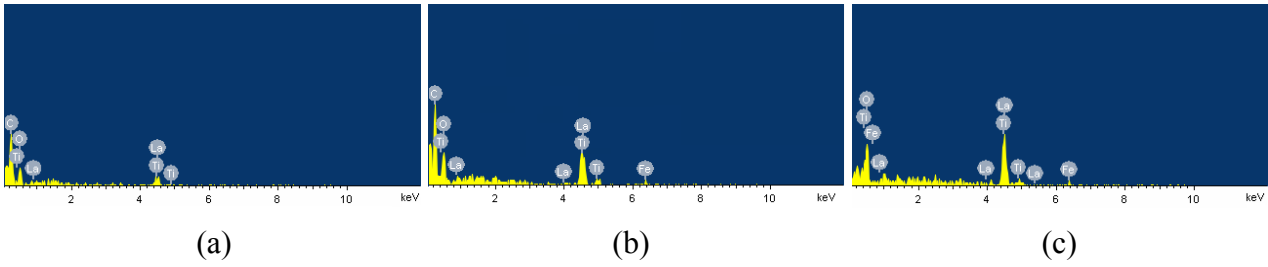


Fig. 2 The EDX spectra of Fe^{3+} , La^{3+} co-doped TiO_2 nanofibers calcined at different temperatures.

(a) 0°C , (b) 300°C , (c) 600°C

Table 1 The elements atom percentage of Fe^{3+} , La^{3+} co-doped TiO_2 nanofibers with different calcination temperature

Ratio (%) T ($^\circ\text{C}$)	C	O	Ti	Fe	La
0	49.90	46.04	3.75	—	0.31
300	52.17	32.66	13.56	0.47	1.14
600	—	67.45	27.68	2.24	2.63

The EDX spectrogram and chemical element contents are revealed in Fig.2 and Table 1. Before calcination, C, O, Ti, La elements are detected, the atomic percentage content of C is close to O, occupy 49.90% and 46.04% respectively. After 300°C calcined, the atomic percentage content of C element is increased, while the O element is obvious decreased. It is due in the thermal high temperature condition, the active sidegroup in PVAc molecular chains appear elimination reaction, which caused some molecular chains carbonized and exhibited some linear chain and crosslinking structures. The atomic percentage content of Ti, La are also increased compare with the nanofibers before calcination. When the calcination temperature up to 600°C , C element is oxidized totally, the nanofibers are constituted by O, Ti, Fe, La elements.

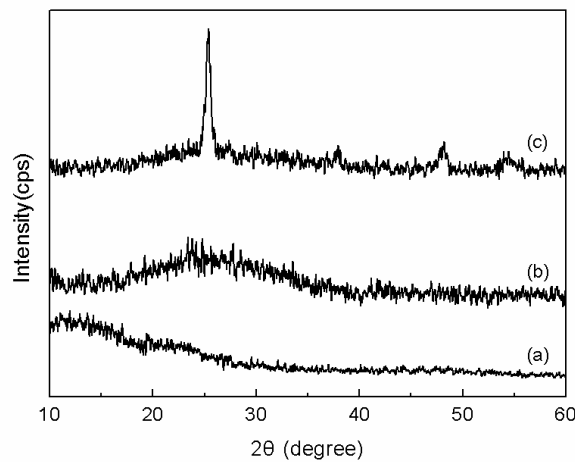


Fig. 3 The XRD pattern of Fe^{3+} , La^{3+} co-doped TiO_2 nanofibers calcined at different temperatures (a) 0°C , (b) 300°C , (c) 600°C

The XRD pattern of $\text{Fe}^{3+}, \text{La}^{3+}$ co-doped TiO_2 nanofibers calcined at 300°C and 600°C are illustrated in Fig. 3. As can be seen from Fig. 3(b), the broad peak is appeared after 300°C calcination, the TiO_2 are existed in amorphous state. Some features diffraction peak have initial formed, which corresponding to the $2\theta = 25.3^\circ, 37.8^\circ, 48.0^\circ$ and 55.1° , the product is $\text{Fe}^{3+}, \text{La}^{3+}$ co-doped TiO_2 nanofiber with anatase crystal form.

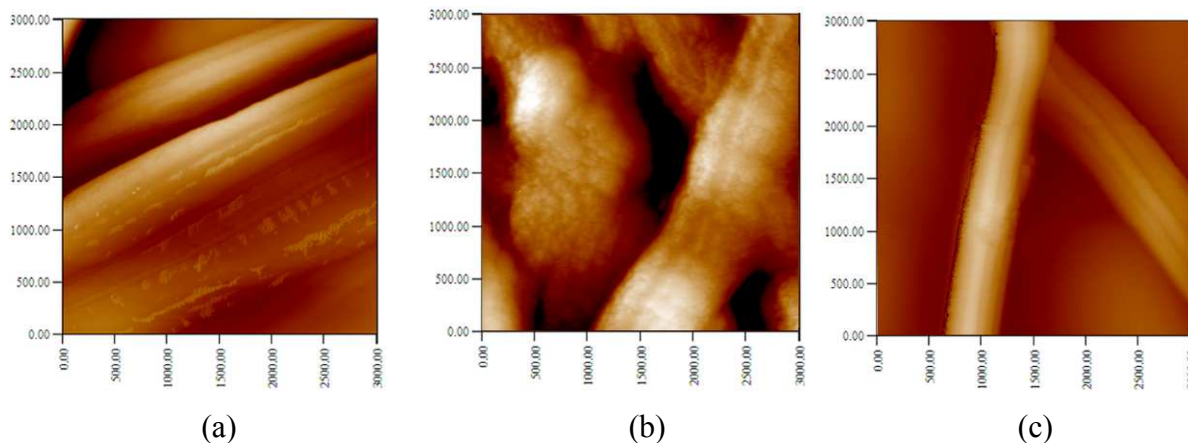


Fig. 4 The AFM images of $\text{Fe}^{3+}, \text{La}^{3+}$ co-doped TiO_2 nanofibers calcined at different temperatures (a) 0°C , (b) 300°C , (c) 600°C

Fig. 4 reveals the surface morphology of $\text{Fe}^{3+}, \text{La}^{3+}$ co-doped TiO_2 nanofiber in AFM image. Fig. 4(a) shows some intermittently particle aggregate, which corresponding to the observed punctiform protuberance structure in Fig. 1(a). After 300°C calcination, the nanofiber is undergone the carbonized process, the surface appears very coarse, which may caused by the elimination reaction products on the nanofiber surface. The coarse structures are disappeared, the $\text{Fe}^{3+}, \text{La}^{3+}$ co-doped TiO_2 nanofibers reveal the evenly stripe structure.

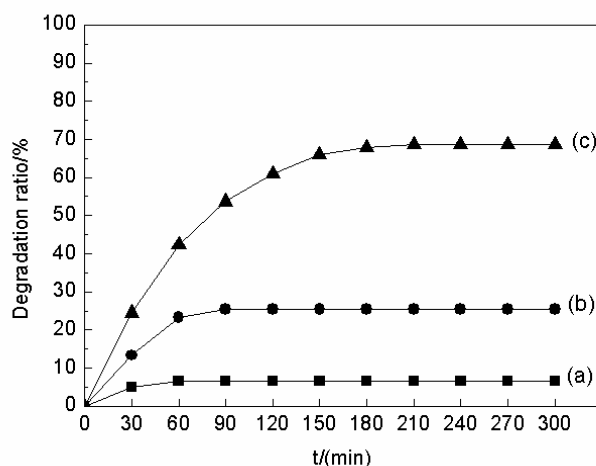


Fig.5 The photocatalysis activity of $\text{Fe}^{3+}, \text{La}^{3+}$ co-doped TiO_2 nanofibers calcined at different temperatures (a) 0°C , (b) 300°C , (c) 600°C

The photocatalysis curve of $\text{Fe}^{3+}, \text{La}^{3+}$ co-doped TiO_2 nanofibers are illustrated in Fig. 5. The curve (a) presented weak absorption of methylene blue in the first hour, which may caused by the interfacial adsorption between porous nanofiber structure and solution. It can be observed from curve (b) that after 300°C calcination, the co-doped TiO_2 nanofiber reveals better degradation ratio, which may give rise to the big amount of C element created and enlarged specific surface of nanofibers. These two factors are accelerated the adsorption and catalysis degradation process. As shown in curve c, the

degradation ration of anatase $\text{Fe}^{3+}, \text{La}^{3+}$ co-doped TiO_2 nanofiber up to 68.64%, the atom radii of $\text{Fe}^{3+}, \text{Ti}^{4+}$ and La^{3+} are 69, 74.5 and 115 pm, respectively. So the Fe^{3+} are readily to enter into the TiO_2 lattice and replace the lattice point, then some electrons and holes be caught by Fe^{3+} , which restrained the combination of electrons and holes. The doping of La^{3+} induced the lattice distortion and expansion in the crystal matrix, which enforced the unbalance of the electron system, further declined the combination of electrons and holes, leading to the improve of photocatalysis activity [11].

Conclusions

The $\text{Fe}^{3+}, \text{La}^{3+}$ co-doped TiO_2 nanofibers are prepared by combining electrospinning and high temperature calcination. The porous fibrous structure is formed by calcinating the $\text{Fe}^{3+}, \text{La}^{3+}$ co-doped PVAc/ TiO_2 nanofiber. In 300°C calcination, $\text{Fe}^{3+}, \text{La}^{3+}$ co-doped TiO_2 nanofibers in amorphous state, the content of C element reach to peak value, the surface of fibers are very coarse. Up to 600°C calcination, the $\text{Fe}^{3+}, \text{La}^{3+}$ co-doped TiO_2 nanofibers reveal anatase crystal form, the surface of single fiber appears stripe shape. In the process of photocatalyzed reaction, the $\text{Fe}^{3+}, \text{La}^{3+}$ co-doping exhibited legible promoting actions in the crystalline system. In the evolution process from organic/inorganic composite, amorous to crystalline, the increasing calcination temperature resulted in a significant variation on structure and photocatalysis property of $\text{Fe}^{3+}, \text{La}^{3+}$ co-doped TiO_2 nanofibers.

Acknowledgement

The research work was financial supported by the National Natural Science Foundation of China (NO.11072175)

References

- [1] C. H. He and J. Gong : Polym. Degrad. Stab. Vol. 81(2003), p. 117
- [2] J. Xu, Y. Ao and D. Fu: Appl. Surf. Sci. Vol. 254(2008), p. 3033
- [3] Z. H. Yuan, J. H. Jia and L. D. Zhang: Mater. Chem. Phys. Vol. 73 (2002), p. 323
- [4] W. W. So, K. J. Kim and S. J. Moon: Int. J. Hydrogen Energy Vol. 29(2004), p. 229
- [5] A. Fujishima, X. Zhang and D. A. Tryk: Surf. Sci. Rep. Vol. 63(2008), p. 515
- [6] J. W. Shi, J. T. Zheng and Y. Hub: Mater. Chem. Phys. Vol. 106(2007), p. 247
- [7] X. Wang, J. C. Yu and C. Ho: Langmuir Vol. 21(2005), p. 2552
- [8] Y. Ding, P. Zhang, Z. Long, Y. Jiang, F. Xu and J. Lei: J. Sol-Gel Sci. Technol. Vol. 46(2008), p. 176
- [9] H. Tang, F. Yan, Q. Tai and H. L. W. Chana: Biosens. Bioelectron. Vol. 25(2010), p. 1646
- [10] N. Wu, A. Wei and Q. Wei: J. Ind. Texti. Vol. 39(2010), p. 293
- [11] H. Xia, H. Zhuang and D. Xiao: J. Alloys Compd. Vol. 465(2008), p. 328