

# Preparation of Novel Nano/Submicrofiber Catalyst Containing Nano-TiO<sub>2</sub> Particles

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**ABSTRACT:** A novel Nano/submicrofiber catalyst was prepared *via* electrospinning technology from poly (vinyl pyrrolidone) (PVP) and nano-TiO<sub>2</sub>. First, nano-TiO<sub>2</sub> particles were added into the mixture of ethanol and deionized water, the mass ratio of ethanol and deionized water was 1 : 1, the TiO<sub>2</sub> suspension was obtained after 1 h with ultrasonic treatment and centrifugal effect, Then PVP was added into the above-mentioned suspension and the content of PVP in the sol was 28%. The TiO<sub>2</sub>/PVP solution was electrospun with different voltage. The effects of the content of TiO<sub>2</sub> and electrospinning voltage on diameter of nano/submicrofiber were studied. The nano/submicrofiber catalyst was characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and Fourier transform infrared. The results show that the diameter of nano/submicrofiber increases with an increase of the content of nano-

TiO<sub>2</sub> and decreases with the increase of electrospinning voltage. The analytical result showed that the nano-TiO<sub>2</sub> particles were well dispersed in the matrix of PVP, moreover, the crystal type of nano-TiO<sub>2</sub> was a mixture of anatase and rutile and the diameter of nano-TiO<sub>2</sub> particles in the nano/submicrofiber is in the range of 20–60 nm and the nano-TiO<sub>2</sub> particle was monodisperse, and the nano-TiO<sub>2</sub> particle and PVP molecule was connected by a hydrogen bonding. This nano/submicrofiber catalyst has a high efficiency on degradation on CH<sub>2</sub>O. 56.8 percent of CH<sub>2</sub>O was degraded under ultraviolet radiation in 80 min when the content of nano-TiO<sub>2</sub> is 20% in nano/submicrofibers. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** nano-TiO<sub>2</sub>; PVP; nano/submicrofiber catalyst; electrospinning; photocatalysis

## INTRODUCTION

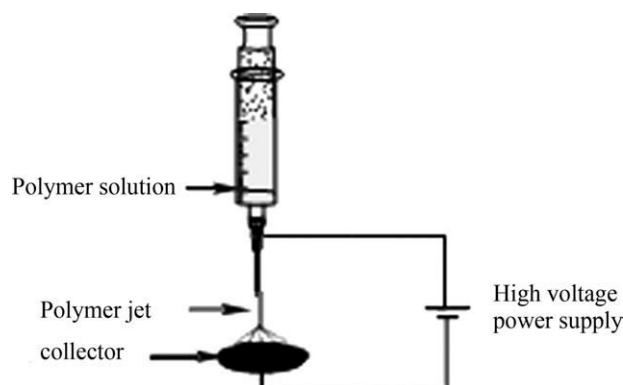
In recent years, photocatalytic degradable material has attracted increasing attention as a promising method for the removal of toxic organic contaminants from water and air, and the photocatalytic degradable material has broad applications, however, many problems, such as how to immobilize nano-TiO<sub>2</sub> on appropriate carrier to be used repeatedly and how to improve nano-TiO<sub>2</sub> utilization ratio are still left. For improving nano-TiO<sub>2</sub> utilization ratio, scientist tried to solve the problems by making more surface of nano-TiO<sub>2</sub> outside.<sup>1,2</sup> Commonly sol-gel method is used to immobilize nano-TiO<sub>2</sub>, on other hand, immobilization of nano-TiO<sub>2</sub> on glass,<sup>3</sup> metal,<sup>4</sup> nano-TiO<sub>2</sub> thin film, and nano-TiO<sub>2</sub> fiber are also tried by Sol-Gel method. For example, with a use of this method, a nano-TiO<sub>2</sub> thin film was prepared by Yu et al.,<sup>5</sup> and Zhang et al.,<sup>6</sup> Li et al. prepared nano-TiO<sub>2</sub> fiber,<sup>7</sup> Madhugiri et al. prepared mesoporous nano-TiO<sub>2</sub> fiber.<sup>8</sup> Although nanometer thin film and nanometer fiber has a high specific surface area, immobilization process needs heat

treatment at a high temperature and limits its application.

A process which does not need a high temperature for treatment can be available if nano-TiO<sub>2</sub> can be immobilized on carrier directly, and in the wide choices of carrier, polymer can be used as a good carrier of nano-TiO<sub>2</sub>. Dhannanjeyan et al. immobilized nano-TiO<sub>2</sub> on modified polyethylene film,<sup>9</sup> Naskar et al. immobilized nano-TiO<sub>2</sub> on foam polyethylene film by hot-press method for degradation of organic dyes in aqueous solution.<sup>10</sup> Above-mentioned approaches do not need annealing at high temperatures, however, nano-TiO<sub>2</sub> exposed outside is still limited.

Electrospinning can prepare nano/submicrofiber, and the diameter of electrospun fibers is 1–2 orders of magnitude lower than the diameter of tradition spinning fiber, and the electrospinning fibers have very high specific surface area.<sup>11,12</sup> Taking water and alcohol (mass ratio 1 : 1) as solvent, Yang et al. prepared poly (vinyl pyrrolidone) (PVP) ( $M_w = 1,300,000$ ) nanofibers is about 20 nm in diameter.<sup>13</sup> Adding nanometer catalyst particles into the polymer, many nanometer catalyst particles are unmasked and situated on the surface of the electrospinning fiber. In this article, TiO<sub>2</sub>/PVP nano/submicrofiber catalyst can be prepared by directly adding nano-TiO<sub>2</sub> particles into PVP solution *via*

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**Figure 1** Schematic representation of electrospinning.

electrospinning technique. This article studied the dispersivity of nano-TiO<sub>2</sub> into polymer matrix, formation of nanofibrous catalyst *via* electrospun technique. Photocatalysis performance of the TiO<sub>2</sub>/PVP nano/submicrofiber catalyst was also studied.

## EXPERIMENTAL

### Preparation of nano-TiO<sub>2</sub>/PVP suspension system

In our experiment, the certain quantity of nano-TiO<sub>2</sub> with a particles in the diameter from 20 to 60 nm, was mixed together with solvents of ethanol and water (w/w = 1 : 1). The lower layer precipitate was removed and the upper layer suspension was dried after a treatment with ultrasonic for 1 h. The maximum concentration of nano-TiO<sub>2</sub> suspension is 5.6 wt %, then the PVP (K30) was added into the diluted upper layer suspension. The nano-TiO<sub>2</sub>/PVP suspension system (28% weight of PVP) can be prepared by an ultrasonic treatment for 30 min.

### Preparation of nano/submicrofibers

The basic experimental setup used is shown in Figure 1. The above-mentioned nano-TiO<sub>2</sub>/PVP suspension system was electrospun at 10, 15, 20, 25, and 30 kV with a tip-to-collector distance of 20 cm. The PVP nano/submicrofiber and TiO<sub>2</sub>/PVP nano/submicrofiber with different content of nano-TiO<sub>2</sub> were prepared. The PVP solution (the concentration of PVP in alcohol-water mixed solvents is 28 wt %) was used as the blank control.

### Characterization of nano/submicrofibers

The structure of nano/submicrofibers was characterized by Fourier transform infrared (FTIR). Infrared spectrum was obtained by KBr method. The phase structure analyses had been performed by using an X-ray diffractometer. Through images of field emission scanning electron microscope (SEM), we

obtained the surface morphology of fiber and the diameter of fibers. Because of the ununiformity of the diameter of nano/submicrofibers, the average diameters of 50-fibers were used as measurement value of the diameter of fiber. The dispersion of nano-TiO<sub>2</sub> in fibers was obtained by transmission electron microscopy (TEM).

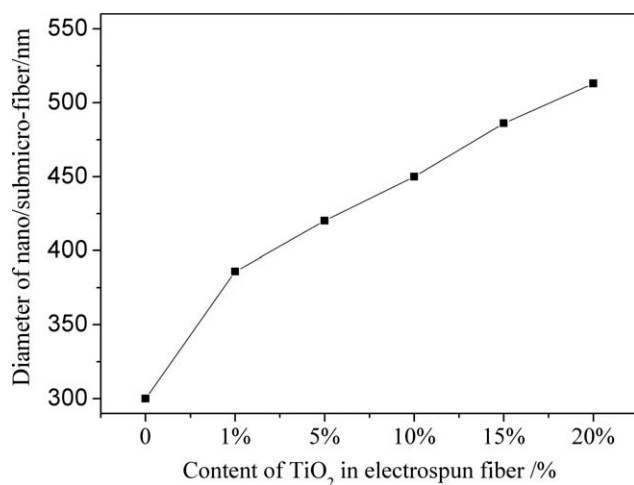
### Photocatalysis experiment of the nano/submicrofiber catalyst

Photocatalysis experiment was conducted in self-making glass tube reactor with a power of 15W of the ultraviolet lamp which is parallel with and above the glass tube. The strength of UV is 385 μW/cm<sup>2</sup> when operating ultraviolet lamp. The nano/submicrofibers were electrospun on glass fibers the area of which is 3.8 × 19 cm<sup>2</sup>. First, the samples were get into the reactor before the experiment, and the reactor was exposed to air and formaldehyde, the rates of which were controlled by gas flow controller. Stopping ventilating after 15 min, then we got 1 mL gas sample from one side of the reactor using syringe. We got gas sample five times. The ultraviolet lamp was turned on when there was no significant difference in the concentration of formaldehyde which was detected by gas chromatography, and then the experiment began. The concentration of formaldehyde was detected every 4 min.

## RESULTS AND DISCUSSION

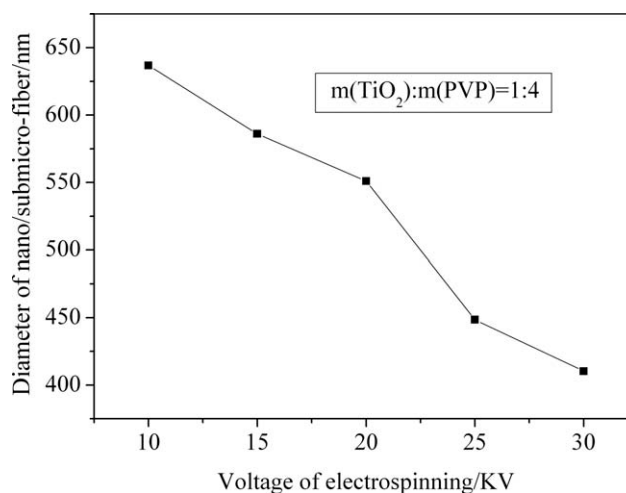
### Discussion on the electrospinning with suspension system of nano-TiO<sub>2</sub>/PVP

Some properties of solution (such as viscosity, conductivity, surface tension), fluid pressure, electrospinning voltage, deposition distance, and temperature have effect on the diameter of electrospinning fiber.<sup>14</sup> The effects of the content of nano-TiO<sub>2</sub> and electrospinning voltage on the diameter of fiber were mainly investigated. A series of suspension were electrospun with the concentration of PVP suspension of 28 wt % and nano-TiO<sub>2</sub> at different contents. Figure 2 shows the relationship of the diameter of fibers and the content of nano-TiO<sub>2</sub>. The diameter of fibers increase with an increase of the content of nano-TiO<sub>2</sub>. In the suspension system of TiO<sub>2</sub>/PVP in ethanol and water, PVP molecular adsorb at the surface of TiO<sub>2</sub>, and PVP molecular and nano-TiO<sub>2</sub> particle tangle together *via* interaction. Tangled PVP molecular increases with an increase of the content of nano-TiO<sub>2</sub>, and PVP molecular motion was hindered, and the diameter of fiber increases. Figure 3 shows the relationship of electrospinning voltage and diameter of fiber when fixing the content of TiO<sub>2</sub> and PVP. The diameter of



**Figure 2** The relationship between diameter of nano/submicrofibers and the content of TiO<sub>2</sub>.

fiber decreases with an increase of electrospinning voltage, this is because jet of polymer solution has more surface charge density and thus have larger electrostatic repulsive force. Higher electric field intensity makes the jet acquiring larger acceleration simultaneously. The two factors could all cause jet, and make fibers acquiring stronger tensile stress

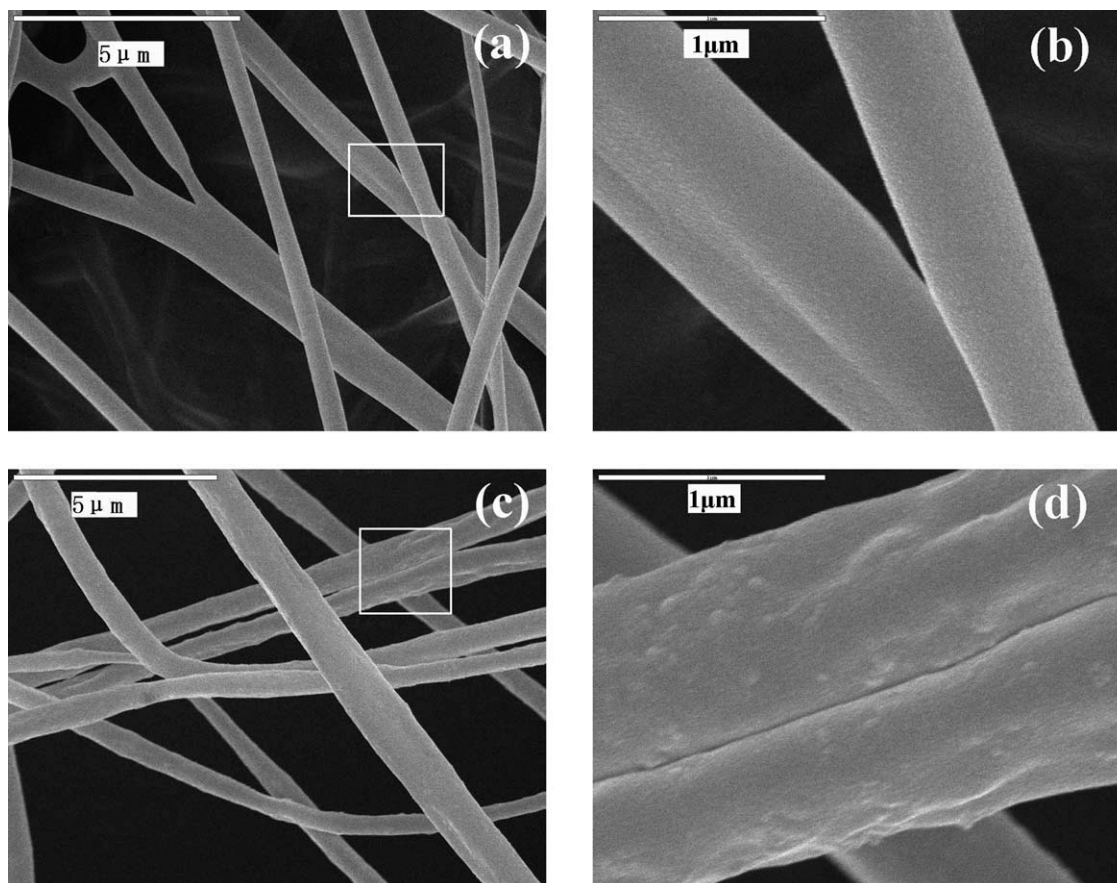


**Figure 3** The relationship between nano/diameter of submicrofiber and electrospinning voltage.

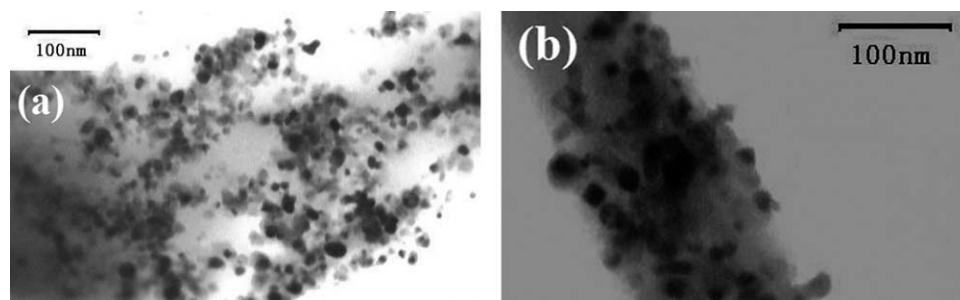
which cause higher tensile strain rate, and thus facilitate preparing ultrafine fiber.<sup>15</sup>

#### The analysis of SEM

Figure 4 shows SEM images of fiber electrospinning from PVP solution or suspension. Figure 4(a) is SEM



**Figure 4** (a) and (b) SEM images of nano/submicrofibers of PVP (c) and (d) SEM images of nano/submicrofibers of TiO<sub>2</sub>/PVP.



**Figure 5** (a) TEM image of  $\text{TiO}_2/\text{PVP}$  suspension (b) TEM image of  $\text{TiO}_2/\text{PVP}$  nano/submicrofiber.

image of PVP nano/submicrofiber, and Figure 4(b) is a local enlarged drawing of white block in Figure 4(a). It was noticed that PVP nano/submicrofiber had a uniform smooth surface, but the diameter of fiber was non-uniform extremely, and it was in the range of 80–1000 nm; Figure 4(c) shows SEM image of  $\text{TiO}_2/\text{PVP}$  nano/submicrofiber, and Figure 4(d) is a local enlarged drawing of white block in Figure 4(c). It can be observed that fibers surface is rough with gibbosity which is possible as a result of nano- $\text{TiO}_2$  particles in PVP matrix.

#### The analysis of TEM

Figure 5(a) shows TEM image of  $\text{TiO}_2/\text{PVP}$  suspension system. It can be observed that nano- $\text{TiO}_2$  particulates which are in the range of 20–60 nm and are almost monodisperse are almost homogeneously distributed in PVP matrix. Figure 5(b) shows TEM image of  $\text{TiO}_2/\text{PVP}$  nano/submicrofiber which is electrospun from  $\text{TiO}_2/\text{PVP}$  suspension on the copper net and is the finest fiber we select under TEM. It was noticed that nano- $\text{TiO}_2$  was dispersed in  $\text{TiO}_2/\text{PVP}$  nano/submicrofiber the diameter of which is about 30 nm. It can be also observed that fibers surface has gibbosity. Combination of the gibbosity we saw in the TEM image, we can determine that the gibbosity of fibers surface is nano- $\text{TiO}_2$  particle.

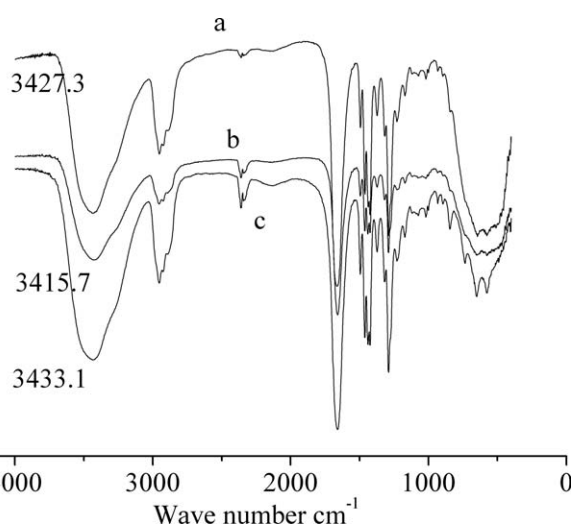
#### The analysis of FTIR spectroscopy

Figure 6 shows FTIR spectra of PVP nano/submicrofiber and  $\text{TiO}_2/\text{PVP}$  nano/submicrofiber before and after high temperature treatment. Except hydroxyl group absorption peak, the others did not change a lot. Figure 6(a) shows FTIR spectra of  $\text{TiO}_2/\text{PVP}$  nano/submicrofiber with  $\text{TiO}_2$  content 20% after high temperature treatment at 200°C for 1 h. Figure 6(b) shows FTIR spectra of  $\text{TiO}_2/\text{PVP}$  nano/submicrofiber with  $\text{TiO}_2$  content 20%. Figure 6(c) shows FTIR spectra of PVP nano/submicrofiber. It was discovered that the 3433.1  $\text{cm}^{-1}$  is the stretch vibration absorption peak of hydroxyl groups, as shown in Figure 6(c). Addition of  $\text{TiO}_2$ , the absorption peak of

hydroxyl groups of composite fiber is at 3415.7  $\text{cm}^{-1}$ , and the absorption peak shifted 17.4  $\text{cm}^{-1}$  to lower waves, while its width increases. This is because of the formation of hydrogen bands between  $\text{TiO}_2$  and PVP.<sup>15</sup> The absorption peak of hydroxyl groups of high temperature treated  $\text{TiO}_2/\text{PVP}$  nano/submicrofiber is at 3427.3  $\text{cm}^{-1}$  in Figure 6(c). This is because of breakage of hydrogen bands after high temperature treatment.<sup>16,17</sup>

#### The analysis of XRD

Figure 7(a) shows a X-ray diffraction (XRD) pattern of nano- $\text{TiO}_2$  powders. The result shows that there are two crystal types of anatase and rutile; Figure 7(b) shows a XRD pattern of  $\text{TiO}_2/\text{PVP}$  nano/submicrofiber. Compared with Figure 7(a), the base line of Figure 7(b) was higher obviously which was caused by PVP of composite fiber, but the station of diffraction peak remained invariable, so the crystal type of nano- $\text{TiO}_2$  was a mixture of anatase and rutile. Nano- $\text{TiO}_2$  we used in our experiment was a mixture of anatase and rutile. Rutile and anatase were



**Figure 6** IR spectra of different nano/submicrofibers (a)  $\text{TiO}_2/\text{PVP}$  nano/submicrofibers after high temperature treatment (b)  $\text{TiO}_2/\text{PVP}$  nano/submicrofibers without high temperature treatment (c) PVP nano/submicrofibers.

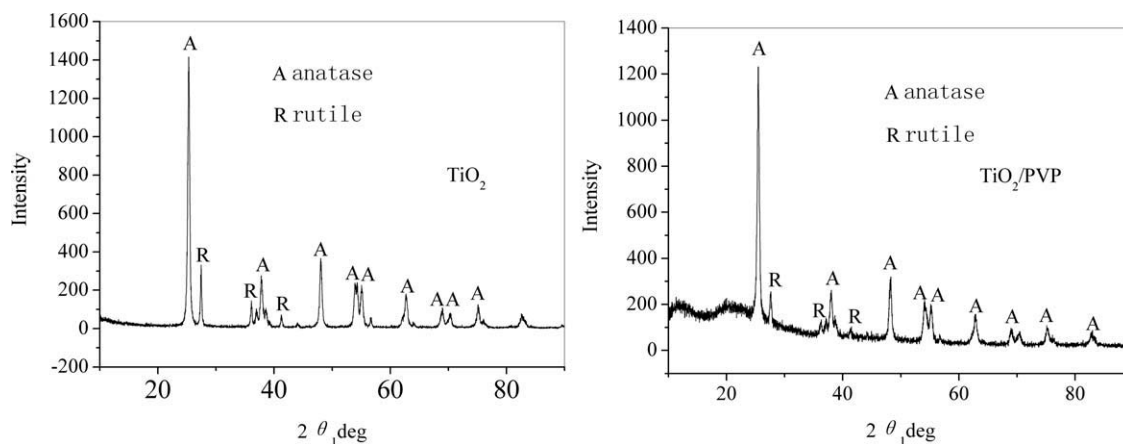


Figure 7 XRD patterns of nano-TiO<sub>2</sub> and TiO<sub>2</sub>/PVP nanocomposite fiber.

still found in the TiO<sub>2</sub>/PVP nano/submicrofiber after dispersion and electrospinning. Accordingly, nano/submicrofiber catalyst can be prepared using whether rutile TiO<sub>2</sub> or anatase TiO<sub>2</sub> in the experiment.

#### Testing of photocatalysis performance

TiO<sub>2</sub>/PVP nano/submicrofiber with TiO<sub>2</sub> content 20% and 10% and PVP nano/submicrofiber with no nano-TiO<sub>2</sub> were tested in our test experiment of photocatalysis performance. The curves of the concentration of formaldehyde-time had been drawn in Figure 8. When the content of TiO<sub>2</sub> was 20% in nano/submicrofibers, the concentration of formaldehyde declined from 1653 to 714 ppm after light exposure for 80 min, and 56.8 percent of CH<sub>2</sub>O was degraded. When the content of TiO<sub>2</sub> was 10% in nano/submicrofibers, the concentration of formaldehyde declined from 1515 to 802 ppm, and only 47 percent of CH<sub>2</sub>O was degraded. The reason was that only TiO<sub>2</sub> exposed to fiber surface can play a role in

photocatalysis. Compared with nano/submicrofiber with TiO<sub>2</sub> content 10%, nano/submicrofiber with TiO<sub>2</sub> content 20% had more TiO<sub>2</sub> exposed to fiber surface and had greater efficiency of photocatalysis degradation for formaldehyde. Testing photocatalysis performance of TiO<sub>2</sub>/PVP nano/submicrofiber, the concentration of formaldehyde increased at first and then decreased after UV light irradiation. The reason was that the specific surface area of nano/submicrofiber was large, and a little formaldehyde gas was adsorbed on the surface of nano/submicrofiber when the gas was injected into the reactor, then temperature of reactor increased and desorption of formaldehyde on the surface of nano/submicrofiber made the concentration of formaldehyde increasing under UV light irradiation. Testing photocatalysis performance of PVP nano/submicrofiber, the concentration of formaldehyde was increasing from 989 to 2090 ppm. So the adsorption quantity of fiber for formaldehyde was greater. Degradation rate of formaldehyde is much larger than 56.8% considering desorption of formaldehyde in our experiment. The maximum concentration of distributed nano-TiO<sub>2</sub> suspension was 5.6 wt %, and the electrospinning was comparatively easy from concentration of PVP 28%, so the maximum content of TiO<sub>2</sub> was 20% in electrospun fiber. For further improving the efficiency of nano/submicrofiber catalyst, experiment technology must be improved for the smaller diameter of fiber.

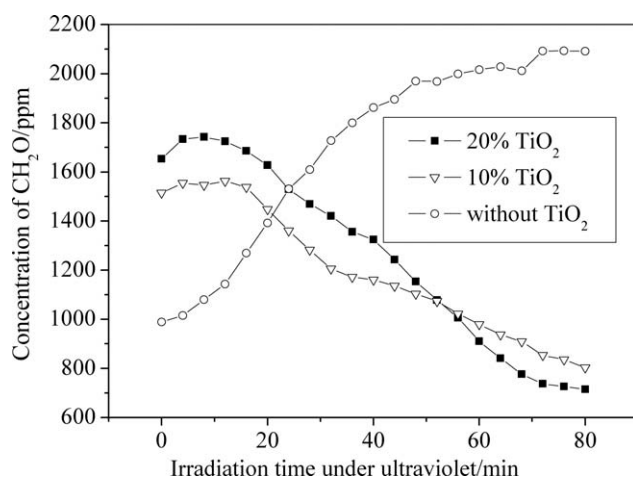


Figure 8 Effect of the time under ultraviolet on the concentration of CH<sub>2</sub>O.

#### CONCLUSIONS

TiO<sub>2</sub>/PVP nano/submicrofiber catalyst was prepared by electrospinning. The diameter of nano/submicrofiber increased with adding nano-TiO<sub>2</sub> or decreasing voltage. Nano-TiO<sub>2</sub> particle and PVP molecule was connected by a hydrogen bonding and the crystal type of nano-TiO<sub>2</sub> did not change in TiO<sub>2</sub>/PVP nano/submicrofiber. The TEM result

showed that the nano-TiO<sub>2</sub> particles the diameter of which was in the range of 20–60 nm were well dispersed in the matrix of PVP; testing of photocatalysis performance indicated that nano/submicrofiber catalyst had good photocatalysis performance. Nano/submicrofiber catalyst with photocatalysis activity had been prepared successfully. Nano/submicrofiber photocatalysis catalyst with visible light photocatalysis activity is underway.

## References

1. Lu, C.; Yang, P.; Du, Y. K.; Hua, N. P.; Song, H. Y. *Chin J Catal* 2003, 24, 248.
2. Cai, N. C.; Wang, Y. P.; Cao, Y. L. *Chin J Catal* 1999, 20, 177.
3. Chen, S. F.; Cao, G. Y. *J Environ Sci* 2003, 15, 83.
4. Zhang, L.; Zhu, Y. F.; He, Y. *Appl Catal B Environ* 2003, 40, 287.
5. Yu, G.; Chen, Z. Y.; Zhang, Z. L. *Catal Today* 2004, 90, 305.
6. Zhang, P. Y.; Jiang, Z. P. *Catal Today* 2004, 90, 305.
7. Li, D.; Xia, Y. *Nano Lett* 2003, 3, 555.
8. Madhugiri, S.; Sun, B.; Smirniotis, P. G. *Microporous Mesoporous Mater* 2004, 69, 77.
9. Dhananjeyan, M. R.; Mielczarski, E.; Thampi, K. R.; Buffat, P.; Bensimon, M.; Kulik, A.; Mielczarski, J.; Kiwi, J. *J Phys Chem B* 2001, 105, 12046.
10. Naskar, S.; Pillay, S. A.; Chanda, M. *J Photochem Photobiol A Chem* 1998, 113, 257.
11. Yang, Q. B.; Li, Z. Y.; Hong, Y. L.; Zhao, Y. Y.; Qiu, S. L.; Wang, C.; Wei, Y. Y. *Polym Sci Part B: Polym Phys* 2004, 42, 3721.
12. Liu, T. Q. *Nanotechnology for Air Purification*; Chemical Industry Press: Beijing 2004.
13. Zhang, S. M.; Liu, T. Q. *Polym Mater Sci Eng* 2005, 21, 292.
14. Reneker, D. H.; Doshi, J. *J Electrostat* 1995, 35, 151.
15. Sato, T.; Sato, A.; Arai, T. *Colloid Surf A: Physicochem Eng Aspects* 1998, 142, 117.
16. Wu, D. C.; Du, Z. L.; Gao, X. S. *Nanofiber*; Chemical Industry Press: Beijing, 2003, p 60.
17. He, X. X.; Sun, D. Q.; Wang, Z. M. *Practical Infrared Spectroscopy*, 2nd ed.; Petroleum Industry Press; Beijing, 1990; Vol.10, p 335.