

ACTIVATION OF ELECTROSPUN TITANATE / POLYACRYLONITRILE NANOFIBERS WITH H₃PO₄

Donghua TENG¹, Yunhua YU¹, Xiaoping YANG^{1}, Seungkon RYU²*

¹ *The Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer, Beijing University of Chemical Technology, Beijing 100029, China*

² *Department of Chemical Engineering, Chungnam National University, 220, Gung-dong, Yuseong-gu, Daejeon 305-764, Korea*

Abstract

Tetrabutyl titanate [Ti(OC₄H₉)₄] / polyacrylonitrile (PAN) nanofibers were electrospun and activated with H₃PO₄ treatment. The morphologies of the nanofibers and their changes in structures and composition were then investigated using SEM, FT-IR and XRD analyses. SEM images showed that the average diameters of the as-spun and preoxidated titanate / PAN nanofibers were 252 nm ± 22 nm and 270 nm ± 25 nm, respectively. XRD analysis indicated that crystal titanium phosphate and TiO₂ nanoparticles yielded on the nanofibers which had been immersed in H₃PO₄ solution and then calcined at 600 °C in N₂.

Keywords: polyacrylonitrile; nanofiber; electrospinning; activation; photocatalyst

1. Introduction

Anatase titanium dioxide (TiO₂), a typical n-type semiconductor with the band gap of 3.2 eV, has attracted great attentions due to its excellent photocatalytic decomposition of organic materials and high chemical stability^[1-4]. As a simple technique, sol-gel method is the most way to prepare anatase TiO₂ nanoparticles, because the control of stable particle size and crystalline phase can be obtained^[5-6]. However, the suspended TiO₂ nanoparticles have tendencies to coagulate with corresponding decreases in their activities and increases in their difficulties of recovery^[7]. Hence the immobilization of TiO₂ has been widely investigated, involving various supporters and immobilizing methods^[8-12].

Due to its abundant microporous structures, high specific surface area and strong adsorption capacity, activated carbon fiber (ACF) has been increasingly used to load TiO₂ photocatalyst^[13-16]. However, TiO₂, in the form of ultra-thin films, just adhere to the surfaces of ACF unfirmly by sol-gel and dip-drawing methods in most previous researches, which leads to weaken the adsorption capacity of ACF sharply and shorten the life-spans of TiO₂/ACF photocatalysts greatly^[17]. Fortunately, electrospinning technique is well suited to solve these drawbacks, thus it has attracted increasing attentions in preparing TiO₂/ACF photocatalysts.

Since its first patent issued in 1934^[18], electrospinning technique has been used to prepare polymer and inorganic nanofibers increasingly, such as polyacrylonitrile (PAN)^[19-23], TiO₂/PAN^[24-25], and TiO₂/MWNTs/PAN^[26]. In electrospun TiO₂/PAN nanofibers, the TiO₂ particles embed on the surfaces of PAN dispersedly instead of forming integrated films^[24]. Up to now, although the preparations of PAN and TiO₂/PAN nanofibers by electrospinning have been investigated continuously, the activation of as-spun nanofibers is still not reported. Moreover, phosphoric acid (H₃PO₄) is a frequently applied activating agent for preparing microporous activated carbon, because that the activation temperature

can be felled from above 850 °C (physical activation) to 400~500 °C [27].

Therefore, in the present study, we expect to prepare anatase TiO₂-containing activated carbon nanofibers. In the paper, titanate / polyacrylonitrile nanofibers were electrospun and subsequently stabilized and activated with H₃PO₄ solution. Moreover, the morphologies of all nanofibers and their changes in structures and composition were then investigated.

2. Experiment

2.1 Materials

PAN fibril with an average molecular weight of $M_w = 100,000$ g/mol was purchased from UK courteds Co. Its composition includes acrylonitrile (93 wt%), methylacrylate (5.3 wt%), and itaconic acid (1.7 wt%). Dimethyl sulfoxide (DMSO) (solvent for PAN) was purchased from Beijing Yi Li Fine Chemicals Co., Ltd. All other reagents were purchased from Beijing Chemical Reagents Company. All reagents were used directly without further purification.

2.2 Preparation and activation of titanate / PAN nanofibers

2.0 g PAN was added into 25 ml DMSO with ultrasonic stirring, and then 10 ml mixed solution (the volume ratio of Ti(OC₄H₉)₄ to CH₃COOH was maintained at 3 : 2 [24]) was added into the PAN solution after the PAN was dissolved completely into the DMSO. Subsequently, the incorporated mixture was stirred further to homogeneous before electrospinning. The solution was electrospun from a hypodermic needle with an inner diameter of 1.1 mm fixed on a 20 ml syringe. The electrostatic potential was maintained at 10 kV, and the distance between the spinneret and an aluminium roller (the diameter is 50 mm) collector was kept at 20 cm. The feed rate of the solution was fixed at 0.3~0.5 ml/h and the rotate speed of the roller was regulated at 3000~3500 r/min. All the above experiments were performed at room temperature in air. For preoxidation, the as-spun fibers were stabilized at 250 °C for 1 h in air [20-21], and then immersed into H₃PO₄ solution (10 v%) for 2 h and dried at room temperature for 24 h. Subsequently, the immersed nanofibers were calcined at 600 °C for 2 h with a heating rate of 3 °C/min in highly pure nitrogen atmosphere.

2.3 Characterization

The morphologies of the nanofibers were observed by a field emission scanning electron microscope (SEM, HITACHI S-4700) at an acceleration voltage of 20 kV using Pt coated samples. The average diameters of the nanofibers were calculated by measurements of 100 single nanofibers with the SEM images. The Fourier transfer infrared (FT-IR) spectra of the nanofibers were measured with a NEXUS 670 FT-IR in a transmission mode at room temperature. The samples were loaded on KBr disks (0.5 mg sample with 200 mg KBr). A Rigaku D/max 2500 VB2+/PC X-ray diffractometer (XRD), operated at 40 kV and 200 mA to produce Cu K α ($\lambda = 1.54$ Å), was utilized to study the changes in the crystallization of titanate and PAN.

3. Results and discussion

3.1 Morphological characterization

The SEM images of electrospun nanofibers under different treatments were shown in Figure 1. In comparison with as-spun PAN nanofibers (Figure 1a), titanate / PAN nanofibers (Figure 1b) still retained high uniformity and orientation degree. However, the average diameter of the as-spun titanate / PAN nanofibers was $252 \text{ nm} \pm 22 \text{ nm}$, while the average diameter of the as-spun PAN nanofibers was $293 \text{ nm} \pm 22 \text{ nm}$. It because that the concentration of PAN was lowered when $\text{Ti}(\text{OC}_4\text{H}_9)_4$ and CH_3COOH mixed solution were added in. After preoxidation, the titanate / PAN nanofibers still maintained their incipient morphologies (Figure 1c), though their average diameter increased to $270 \text{ nm} \pm 25 \text{ nm}$. The increase of the average diameter was due to the longitudinal shrinkage of the nanofibers. After activation, the titanate / PAN nanofibers which had already been immersed in H_3PO_4 solution also kept the fibriform morphology and their average diameter was $257 \text{ nm} \pm 17 \text{ nm}$ (Figure 1d). The image clearly indicated that lots of crystal particles yielded on the nanofibers. Through latter XRD analytic results, it testified that these crystals were titanium phosphate and TiO_2 .

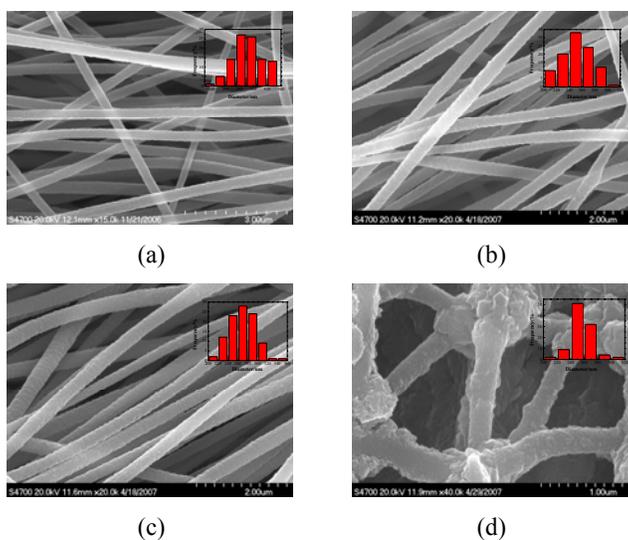


Figure 1. SEM images of: (a) as-spun PAN nanofibers; (b) as-spun titanate / PAN nanofibers; (c) preoxidated titanate / PAN nanofibers; and (d) titanate / PAN nanofibers activated at 600°C with H_3PO_4 treatment

3.2 Compositional characterization

Figure 2 presented the FT-IR spectrums of the electrospun nanofibers under different treatments. The addition of titanate and CH_3COOH resulted in the appearances of peak $\gamma_s(-\text{COO}^-)$ (1590.29 cm^{-1}) and out-of-plane deviational vibration of $-\text{COO}^-$ (659.23 cm^{-1}), which attributed to the formation of $\text{TiO}(\text{OAc})_2$ [24]. At the same time, the absorptions due to asymmetrical and symmetrical bending vibrations of $-\text{CH}_2-$ (2926.45 cm^{-1} and 1448.89 cm^{-1}) were still clearly observed. However, after preoxidation, both the strong peak at 1448.89 cm^{-1} and the absorption due to $-\text{C}\equiv\text{N}$ stretching vibration

(2241.96 cm^{-1}) decreased, which was owing to the cyclization reaction. Subsequently, after activation, characteristic peak of $\text{C}=\text{N}$ stretching vibration (1237.54 cm^{-1}) appeared, while the absorptions due to $\text{C}\equiv\text{N}$ stretching vibration and $\text{C}=\text{C}$ stretching vibration (1590.29 cm^{-1}) were disappearing. The results further indicated the cyclization of $\text{C}\equiv\text{N}$ and $\text{C}=\text{C}$ [28]. Most importantly, the peaks at 505.15 cm^{-1} ($\text{Ti}-\text{O}$ stretching vibration) and 1080.86 cm^{-1} ($\text{Ti}=\text{O}$ characteristic peak) were detected, which suggested the formation of TiO_2 from the precursor $\text{Ti}(\text{OC}_4\text{H}_9)_4$ [29].

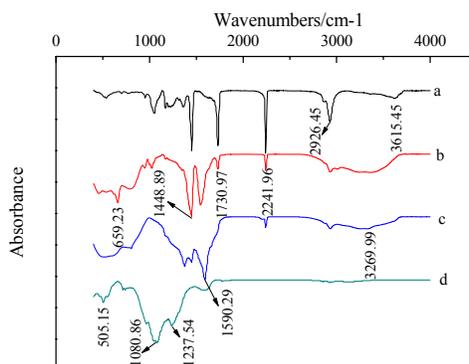


Figure 2. FT-IR spectra of: (a) as-spun PAN nanofibers; (b) as-spun titanate / PAN nanofibers; (c) preoxidated titanate / PAN nanofibers; and (d) titanate / PAN nanofibers activated at 600°C with H_3PO_4 treatment

3.3 Crystallographic characterization

The X-ray diffraction patterns of the electrospun nanofibers under different treatments were shown in Figure 3. After preoxidation, the sharp peak at $2\theta = 9.438^\circ$ disappeared, which was attributable to the transformation of the substituent groups ($\text{C}\equiv\text{N}$) arranged in a partially inerratic manner to annularly structural groups. Moreover, the broad peak at $2\theta = 16.482^\circ$ also disappeared, which indicated the rod-like PAN chains turn into hexagonal structure [21]. After activated at 600 °C in N_2 with H_3PO_4 treatment, the amorphous titanate were crystallized into titanium phosphate and TiO_2 , as testified by the sharp peak at $2\theta = 22.398^\circ$ (corresponding to titanium phosphate with interplanar spacing $d = 0.397$ nm [30]), 24.983° [corresponding to the crystal plane (101) of anatase TiO_2 with interplanar spacing $d = 0.356$ nm], and 27.402° [corresponding to the crystal plane (110) of rutile TiO_2 with interplanar spacing $d = 0.325$ nm].

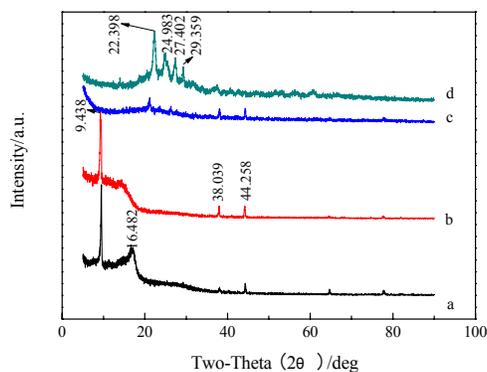


Figure 3. X-ray diffraction patterns of: (a) as-spun PAN nanofibers; (b) as-spun titanate / PAN nanofibers; (c) preoxidated titanate / PAN nanofibers; and (d) titanate / PAN nanofibers activated at 600 °C with H₃PO₄ treatment

4. Conclusions

Titanate / polyacrylonitrile hybrid nanofibers were electrospun, and the succedent preoxidation and activation with H₃PO₄ treatment were investigated. The average diameter of the as-spun titanate / PAN nanofibers was 252 nm ± 22 nm, and increased to 270 nm ± 25 nm after preoxidation. SEM, XRD, and FT-IR results indicated that titanium phosphate and TiO₂ nanoparticles yielded on the activated nanofibers. The average diameter of the activated nanofibers was 257 nm ± 17 nm.

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