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Titanium Dioxide Nanofibers Prepared by Using Electrospinning Method

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Abstract: The synthesis of titanium dioxide nanofibers with 200-300 nm diameter was presented. The new inorganic-organic hybrid nanofibers were prepared by sol-gel processing and electrospinning technique using a viscous solution of titanium isopropoxide (TiP)/poly(vinyl acetate) (PVAc). Pure titanium dioxide nanofibers were obtained by high temperature calcination of the inorganic-organic composite fibers. SEM, FT-IR, and WAXD techniques were employed to characterize these nanofibers. The titanium dioxide nanostructured fibers have rougher surface and smaller diameter compare with PVAc/TiP composite nanofibers. The anatase to rutile phase transformation occurred when the calcination temperature was increased from 600 °C to 1000 °C.

Keywords: Hybrid nanofibers, Titanium isopropoxide/Poly(vinyl acetate), Titanium dioxide, Calcination

Introduction

Recently, nanosized titanium dioxide materials have attracted much interest due to their wide application in many fields such as, ceramic microporous membranes [1], dye-sensitized solar cells [2,3], catalysis [4-6], humidity and fiber-optic cable sensors [7] and photocatalysis by TiO_2 for the treatment of water and air pollutants [8]. In the earlier studies, TiO_2 nanomaterials were prepared by many techniques including sol-gel process [9,10], pyrolysis [11], reactive sputtering [12,13], electron beam evaporation [14], plasma-enhanced chemical vapor deposition [15], atomic-layer deposition [16,17], molecular beam epitaxy [18], hydrothermal technique [19]. All the above methods yielded only titanium dioxide nanocrystalline powders or films. Electrospinning is a novel and direct way to make polymer nanofibers from polymer solution or melt [20,21]. The diameter of electrospun nanofibers generally ranged from 50 to 500 nm. To date, over 30 natural or synthetic polymers have been electrospun. Recently, we have found a novel way to make high valence metal oxide nanofibers by electrospinning technique followed by high temperature calcinations [22]. The preparation of inorganic nanofibers involved the following steps: (1) Preparation of a sol with suitable inorganic precursor. (2) Mixing the inorganic sol with a polymer template to get the solution for electrospinning with appropriate viscosity. (3) Electrospinning of the solution to obtain inorganic/organic composite fibers. (4) Calcination of the as-prepared composite fibers to yield pure metal oxide fibers.

In present work, we describe the preparation of titanium dioxide nanofibers according to the above method. Titanium (IV) isopropoxide is well known as a feasible parent material for the synthesis of pure titanium dioxide [23]. PVAc, was choosen as template because of its cheap availability, hydrophobicity and no designed crosslinks [24]. A new hybrid organic-inorganic solution was obtained by the chemical crosslinking reaction between TiP and PVAc. This process was carried out in a *N,N*-dimethylformamide solution, via a controlled crosslinking process that yield macroscopically homogeneous and transparent solution [24]. Some strong interactions existed between PVAc and TiP phase, avoiding a macroscopic phase separation. After calcinations of the hybrid nanofibers, all organic groups were eliminated and titanium dioxide was formed as nanofibers [25].

There have been few reports in the literature on the preparation of titanium dioxide with nanofiber dimensions. This work was undertaken with an aim to prepare titanium dioxide nanofibers using electrospinning technique.

Experimental

Poly(vinyl acetate) (PVAc) (Mn 500,000) was obtained from Celanese Ltd. Titanium isopropoxide (TiP), *N,N*-dimethylformamide (DMF) and acetic acid (99 wt%) were purchased from Aldrich and used without further purification.

PVAc (11.5 wt%) solution was prepared in *N,N*-dimethyformamide (DMF) with vigorous stirring. A solution of TiP and PVAc (11.5 wt%) with the metal contents of 63.5, 72.3, 77.7, 81.3 wt% were prepared by stirring and few drops of acetic acid was added to the solution under stirring to get a transparent solution.

This transparent solution was placed in a plastic capillary. The plastic capillary was then clamped to a ring-stand, which was above a grounded tubular layer. The tubular layer was covered by a piece of aluminum foil. The power supply was connected to the metal capillary tip. The voltage was 19 kV, and the tip-to-collector distance (TCD) was 15 cm. The droplet instantly disintegrated into fibers, which were drawn to the tubular layer. Non-woven mats were collected

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on the surface of aluminum foil that was covered on the grounded tubular layer. The fabrics were dried at 80 °C for 12 hrs under high vacuum to remove the solvent.

The dried hybrid nanofibers were calcined at 600 °C, 800°C, and 1000 °C at the rate of 10 °C/min in air for 2 hrs to get the pure titanium dioxide nanofibers. The morphology and diameter of the hybrid and inorganic nanofibers were determined using scanning electron microscopy (SEM). FT-IR spectra of the samples were recorded in KBr pellets in the range 400-1400 cm^{-1} using FTIR-8101 Shimadzu spectrophotometer. WXAD patterns were obtained using a Philips diffractometer in the range of 20 to 60 °.

Results and Discussion

In hybrid solution system, transesterification of PVAc occurs and interchain links are formed. Titanium isopropoxide has been used as catalyst for transesterification reaction of PVAc [26]. Furthermore, titanium is one of the most active metals for catalysis of ester polycondensation [27,28]. Crosslinking of PVAc through transesterification reactions has been illustrated in different experimental conditions [29,30]. But, it is difficult to get nanofibers by electrospinning highly crosslinked solution because of their high viscosity and surface tension. Therefore, acetic acid was used as a chelating agent of titanium isopropoxide, to decrease the crosslinking degree of TiP and PVAc [31,32]. As a result of this, the crosslinking of PVAc through transesterification reactions with TiP were controlled to get a solution with suitable viscosity for electrospinnig.

A series of nanofiber samples were prepared by electrospinning the hybrid PVAc/TiP solution with different titanium contents and calcined at various temperatures to get the respective nanofibers.

SEM images of nanofibers with 63.5 wt% of TiP calcined at different temperature were shown in Figure 1. The as-prepared composite nanofibers were straight with smooth surface (Figure 1(a)). After calcinations at different temperatures also the nanofibers retained their fibrous structure. The SEM images of the samples after calcinations at 600 °C

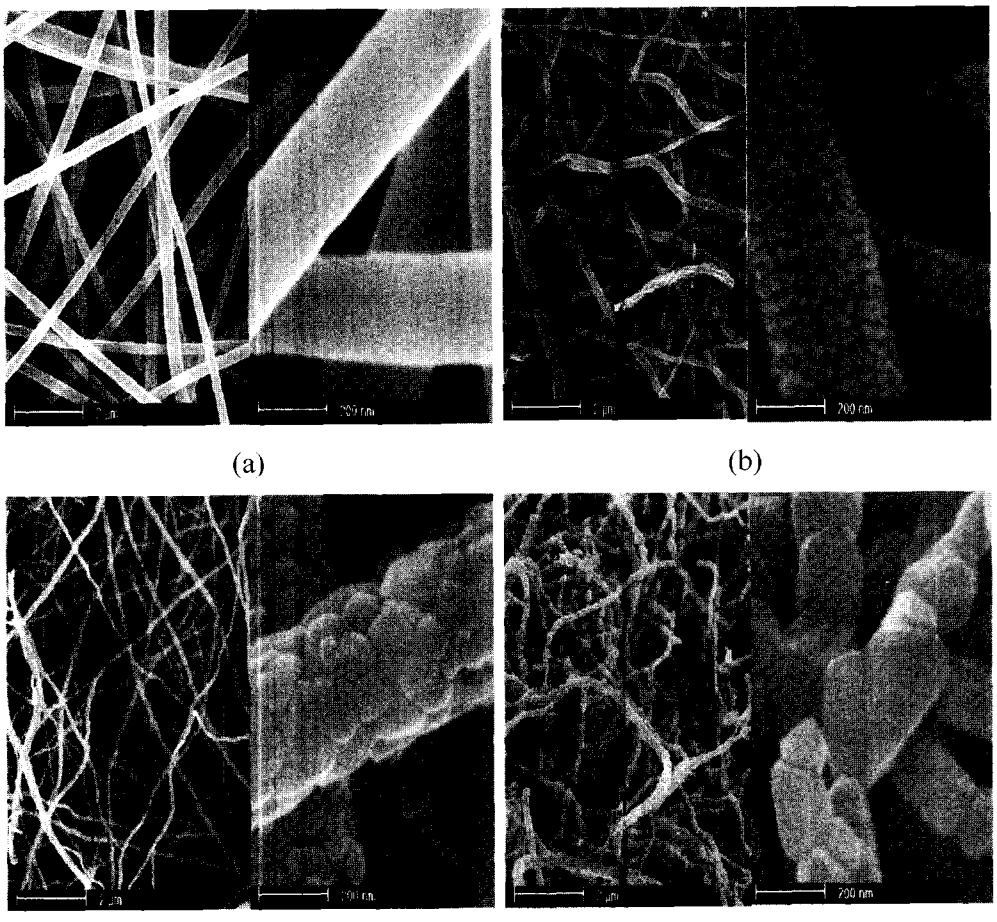

Figure 1. SEM images of nanofibers with 63.5 wt% of TiP calcined at different temperatures. (a) as prepared hybrid fibers; (b) 600 °C; (c) 800 °C; (d) 1000 °C.

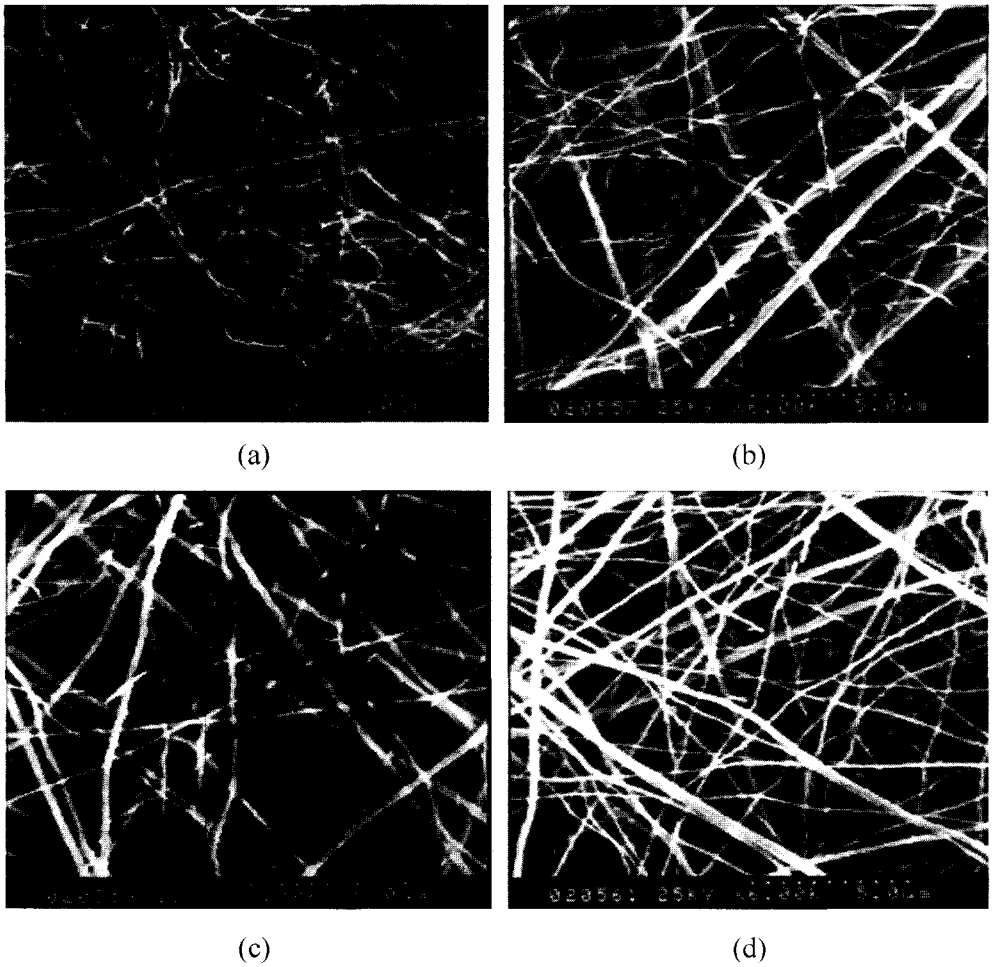

Figure 2. SEM images of nanofibers with different content of TiP calcined at 800 °C. (a) 63.5 wt%; (b) 72.3 wt%; (c) 77.7 wt%; (d) 81.3 wt%.

were found to have curved appearance and the surface became little rough due to crystallization of titanium dioxide (Figure 1(b)). When calcined at 800 °C, the fibers showed some burls on their surface (Figure 1(c)). Nanofibers calcined at 1000 °C showed that they consisted of linked polycrystalline nature (Figure 1(d)). The reason may be due to the better crystalline growth with increasing the calcination temperature.

Figure 2 illustrated the SEM images of nanofibers calcined at 800 °C with different content of TiP. The average diameter and size distribution of calcined nanofibers was found to increase from 170 to 290 nm with increasing the content of TiP from 63.5 to 81.3 wt% in the hybrid fibers. From the above SEM images, we observed that the titanium dioxide nanofibers with small diameter were formed from the hybrid nanofibers with low TiP content.

Figure 3 gave the WAXD patterns of nanofibers with 63.5 wt% of TiP calcined at different temperature. There were no peaks appeared in the case of as-prepared composite fibers due its amorphous nature [33]. Sample calcined at 600 °C (Figure 3(a)) showed only anatase phase of titanium dioxide. When calcined at 800 °C, the fibers (Figure 3(b)) showed the

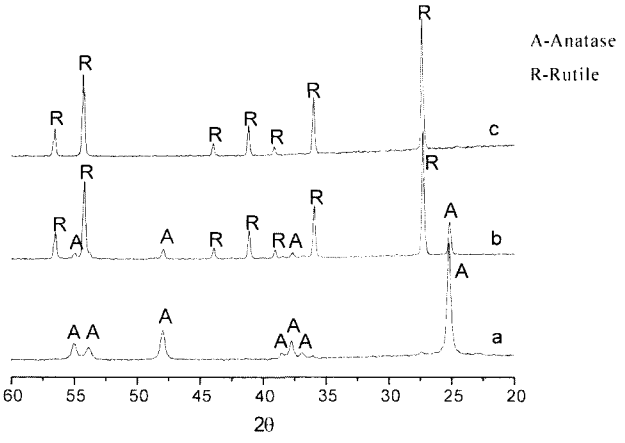

Figure 3. WAXD patterns of nanofibers with 63.5 wt% of TiP calcined at different temperature. (a) 600 °C; (b) 800 °C; (c) 1000 °C.

peaks corresponding to both rutile and anatase phases. For the sample calcined at 1000 °C (Figure 3(c)), only diffraction peaks due to rutile phase of titanium dioxide was observed. These results indicated the formation of anatase phase began

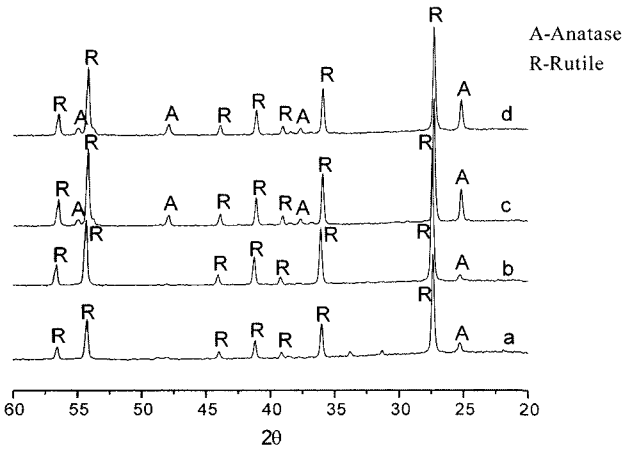

Figure 4. WAXD patterns of nanofibers with different content of TiP calcined at 800 °C. (a) 63.5 wt%; (b) 72.3 wt%; (c) 77.7 wt%; (d) 81.3 wt%.

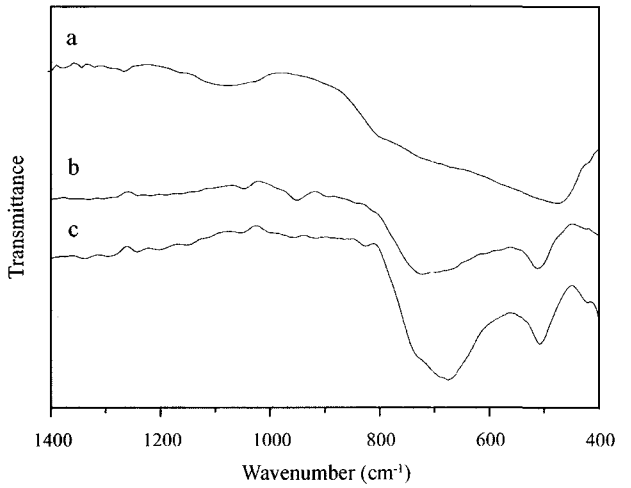

Figure 5. FT-IR spectra of nanofibers with 63.5 wt% of TiP calcined at different temperature. (a) 600 °C; (b) 800 °C; (c) 1000 °C.

at 600 °C and the anatase to rutile phase transformation was completed by increasing the calcination temperature from 600 to 1000 °C.

WAXD patterns of nanofibers calcined at 800 °C with different content of TiP were shown in Figure 4. All the samples displayed the peaks due to both anatase and rutile phase. But, the intensity of anatase phase in Figure 4c and 4d is higher than that of Figure 4(a) and 4(b). As described in Figure 2, the average nanofibers diameter was increased with increasing the content of TiP. It was observed that the anatase-rutile transformation was also affected by the fiber diameter.

Figure 5 showed the FT-IR spectra of nanofibers with 63.5 wt% of TiP in the range 400-1400 cm^{-1}calcined at different temperature. In the spectra of the samples calcinated at 600 °C, the bands associated with the vibration mode of the skeletal O-Ti-O bonds of anatase phase appeared at 474 cm^{-1} (Figure 5(a)), and several components not well resolved in the range of 500 to 900 cm^{-1} [34]. After calcination at 800 °C for 2 hrs (Figure 5(b)), there was a shift of the main anatase band from 474 to 510 cm^{-1} and a new band appeared at around 700 cm^{-1}. The shift of the main adsorption at 474 cm^{-1} has been generally attributed to variations in particle size and morphology. On increasing the calcination temperature to 1000 °C, the appearance of the band near 700 cm^{-1} with higher intensity (Figure 5(c)) was associated with the TiO_2 rutile phase [34]. These results also showed the anatase-rutile transformation occurred at this temperature.

Conclusion

In this paper, we presented the preparation of hybrid PVAc/TiP nanofibers by electrospinning technique. After calcination of the hybrid nanofibers, titanium dioxide nanofibers with diameter of 200-300 nm were obtained. WAXD studies showed the anatase to rutile transformation was complete when calcination temperature was increased from 600 °C to 1000 °C. FT-IR results also showed the formation of anatase titanium dioxide at 600 °C and its transformation into rutile phase at 1000 °C.

Acknowledgment

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References

1. Q. Xu, M. A. Anderson, and J. Am, *Avartsm. Adaov.*, **77**, 1939 (1994).
2. C. T. Kresge, M. E. Leonowicz, W. J. Roth, C. Vartuli, and J. S. Beck, *Nature*, **359**, 710 (1992).
3. J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. Mccullen, J. B. Higgins, and J. L. Schlenker, *J. Am. Chem. Soc.*, **114**, 10834 (1992).
4. P. Ball, *Nature*, **377**, 290 (1995).
5. K. N. P. Kumar, K. Keizer, and A. J. Burggraf, *J. Mat. Sci. Lett.*, **13**, 59 (1994).
6. F. F. Fan, H. Y. Liu, and A. J. Bard, *J. Phys. Chem.*, **89**, 4418 (1985).
7. G. E. Badini, K. T. V. Grattan, A. C. C. Tseung, and A. W. Palmer, *Optical Fiber Technol.*, **2**, 378 (1996).
8. E. Stathatos, D. Tsiourvas, and P. Lianos, *Colloids and Surfaces A*, **149**, 49 (1999).
9. H. Lin, H. Kozuka, and T. Yoko, *Thin Solid Films*, **315**, 111 (1998).
10. P. Christopolou, D. Davazoglou, C. Trapalis, and G. Kordas, *Thin Solid Films*, **323**, 188 (1998).

11. P. Murugavel, M. Kalaiselvam, A. R. Raju, and C. N. R. Rao, *J. Mater. Chem.*, **7**, 1433 (1997).
12. D. Guerin and S. I. Shah, *J. Vac. Sci. Technol. A*, **15**, 712 (1997).
13. M. Georgson, A. Roos, and C. G. Ribbing, *J. Vac. Sci. Technol. A*, **9**, 2191 (1991).
14. K. N. Rao and S. Mohan, *J. Vac. Sci. Technol. A*, **8**, 3260 (1990).
15. Y. H. Lee, K. K. Chan, and M. J. Brady, *J. Vac. Sci. Technol. A*, **13**, 596 (1995).
16. J. Aarik, A. Aidla, and T. Vustare, *Phil. Mat. Lett.*, **73**, 115 (1996).
17. J. Aarik, A. Aidla, V. Sammelseg, and T. Uustare, *J. Cryst. Growth*, **181**, 259 (1997).
18. Y. Gao, Y. Liang, and S. A. Chambers, *Surf. Sci.*, **365**, 638 (1996).
19. M. Tan, G. Wang, and L. Zhang, *J. Appl. Phys.*, **80**, 1186 (1996).
20. D. H. Reneker and I. Chun, *Nanotechnology*, **7**, 216 (1996).
21. B. Ding, H. Y. Kim, S. C. Lee, D. R. Lee, and K. J. Choi, *Fiber Polym.*, **3**, 73 (2002).
22. C. Shao, H. Y. Kim, J. Gong, B. Ding, D. R. Lee, and S. J. Park, *Mater. Lett.*, **57**, 1579 (2003).
23. K. M. S. Khalil and M. I. Zaki, *Powder Technology*, **92**, 233 (1997).
24. B. Lantelme, M. Dumon, C. Mai, and J. P. Pascault, *J. Non-Crystalline Solids*, **194**, 63 (1996).
25. S. R. Kumar, C. Suresh, A. K. Vasudevan, N. R. Suja, P. Mukundan, and K. G. K. Warrier, *Mater. Lett.*, **38**, 161 (1999).
26. G. L. Brown, D. F. Warner, and J. H. Byon, *European Patent*, 0004966 (1979).
27. A. Fradet and E. Marechal, *Eur. Polym. J.*, **14**, 761 (1978).
28. T. H. Shah, J. I. Bhatty, G. A. Ganulen, and D. Dollimore, *Polymer*, **25**, 1333 (1984).
29. M. Lambla, J. Druz, and A. Bouilloux, *Polym. Eng. Sci.*, **27**, 1221 (1987).
30. P. Cassagnau, M. Bert, V. Verney, and A. Michel, *Polym. Eng. Sci.*, **32**, 998 (1992).
31. J. Livage, M. Henry, and C. Sanchez, *Progr. Solid State Chem.*, **18**, 259 (1988).
32. G. L. Wilkes, *Mater. Res. Soc. Symp. Proc. U.S.A.*, **171**, 15 (1990).
33. G. Busca, G. Ramis, J. M. Gallardo Amores, B. S. Escribano, and P. Piaggio, *Chem. Soc. Faraday Trans.*, **90**, 3181 (1994).
34. M. Ocana, V. Fornes, J. V. Garcia Ramos, and C. J. Serna, *J. Solid State Chem.*, **75**, 364 (1988).