

Article

Synthesis and Characterization of Novel PVA/SiO₂-TiO₂ Hybrid Fibers

Haihong Ma *, Tiejun Shi and Qiusheng Song

School of Chemistry and Chemical Engineering, Hefei University of Technology, Hefei 230009, Anhui, China; E-Mails: shitiejunbs@hfut.edu.cn (T.S.); qssong@hfut.edu.cn (Q.S.)

* Author to whom correspondence should be addressed; E-Mail: mahaihong@hfut.edu.cn.

External Editor: Stephen C. Bondy

Received: 4 September 2014; in revised form: 14 October 2014 / Accepted: 15 October 2014 /

Published: 21 October 2014

Abstract: Hybrid sols of poly (vinyl alcohol) (PVA)/Silicon oxide-titanium oxide (SiO₂-TiO₂) were prepared with tetraethoxysilane and tetrabutyl titanate as precursor using Sol-Gel method. PVA/SiO₂-TiO₂ hybrid fibers were prepared by drawing from the hybrid sols using dip-coating method and aging treatment. The spinnability of hybrid sols was investigated. Spinnable time (*t*) and spinnable length (*l*) of hybrid sols increased with either the PVA content or the molar ratio of SiO₂ and TiO₂. The hybrid fibers were characterized by Fourier transform infrared (FT-IR), Scanning electron microscopy (SEM), X-ray diffraction (XRD), Ultraviolet Visible Spectrometry (UV-Vis) and (Thermo-gravimetric Analysis) TGA. FT-IR results suggested that PVA was linked with (SiO₂-TiO₂) network by chemical bonds. SEM measurements indicated that when the fibers arrives the maximum spinning length, the diameter of the fibers was about 50 μm, and the whole system was homogeneous. XRD results revealed that the crystallinity of hybrid fibers was decreased distinctly. UV-Vis measurements confirmed that the shielding properties to Ultraviolet (UV) were greatly improved with titania filled in the hybrid fibers. TG measurements suggested that the hybrid fibers show better resistance to heat than pure PVA fibers.

Keyword: sol-gel method; PVA; Silicon oxide-titanium oxide; hybrid fibers

1. Introduction

The sol-gel method has been widely used as an alternative technology in preparing monoliths, powders, coatings and fibers [1–4]. In recent years, there has been significant interest in preparing continuous inorganic and organic-inorganic hybrid fibers using sol-gel method [5,6]. And functional inorganic fibers containing Si, Ti, Zr, V and Al [7–11], as well as Organic-inorganic hybrid fibers containing SiO₂ have been reported [12]. Titania-Silica binary inorganic materials have been attracted a lot of interests from the researchers [13,14], they have been widely used as anti-reflecting coating, optical-chemical sensors, glasses, supporting materials and catalysts because of their superior optical and thermal properties. Kim and coworkers studied the photocatalytic property of SiO₂/TiO₂ nanoparticles by sol-hydrothermal process [15]. Xavier Orignac *et al.* [16] investigated SiO₂/TiO₂ films via sol-gel method from solutions containing different concentrations of ethanol and found that the porosity volume fraction can reach a minimum when the ethanol volume ratio is around four. Tang *et al.* [17] developed a process for preparing SiO₂/TiO₂ fibers by means of precursor transformation method from titanium-modified polycarbosilane.

Poly (vinyl alcohol) (PVA) is a polymer that has been studied intensively because of its good film forming and physical properties, high hydrophilicity, processability, biocompatibility, and good chemical resistance [18,19]. The properties of PVA can be improved or modified by the introduction of other functional materials. PVA/ZnO-nanorods fibers that exhibit higher anisotropic photonic properties, were synthesized through co-axial flux extrusion by Kinadjian *et al.* [20]. Some PVA/silica nanocomposite materials have also been reported [21,22]. However, only the gels or films properties of PVA/silica nanocomposite materials or nanofibers were investigated until now. To our knowledge, there are few reports on the spinnability of hybrid sols and the preparation of hybrid fiber of PVA/SiO₂-TiO₂ composite. In this paper, hybrid fibers of PVA/SiO₂-TiO₂ were prepared by a sol-gel dip-coating technique, the spinnability of hybrid sols and the structures and properties of as-prepared hybrid fibers were investigated simultaneously. The hybrid fibers shield UV radiation effectively and decreases the aging of the hybrid material of PVA/SiO₂ with the introducing of titanium dioxide. At the same time, the fibers are expected to be used for a certain optical fiber materials.

2. Experimental Section

2.1. Materials

PVA, supplied by Chaohu Wanwei Co. (Anhui, China), is Dp. 1788. Tetraethoxysilane (TEOS), tetrabutyl titanate (TBT), acetylacetone (AcAc) and HCl were purchased from Xilong Pure Chemical Co. (Shanghai, China). Distilled water was made by us.

2.2. Preparation of PVA/SiO₂-TiO₂ Hybrid Sols

PVA was dissolved in H₂O in a weight ratio of 6%. TEOS, distilled water and 0.1 mol/L HCl was added successively into a 250-mL three-neck glass-flask equipped with a condenser, and the mixture was mixed by vigorous stirring for about 2 h at 25 °C, thus reactive silica sol was made. Then, the silica/titania composite sol was obtained after the addition of TBT and AcAc (n(TBT/AcAc) = 1:2)

into the silica sol with another 4 h of stirring. At the end, stoichiometric aqueous PVA solution with weight ratio of 6% (see Table 1) was dropped slowly into the above silica/titania composite sol with stirring, and then reacted in a water bath at 60 °C for another 2 h. Thus, the PVA/ SiO₂-TiO₂ hybrid sols were prepared.

2.3. Spinnability of the Hybrid Sols and Preparation of the Hybrid Fibers

The hybrid sols were kept still for aging at room temperature with 24 h. A glass rod with a diameter of 8 mm was immersed into the above hybrid sol repeatedly, and then drawn up slowly, according to the reported process [23]. If a hybrid fiber could be drawn from them, the drawing-ability of the hybrid sols was called “yes”; otherwise, the drawing-ability of the hybrid sols was called “no”. The spinnable time (t) is defined as the period between the hybrid sols started to become viscous enough to be drawn out and become cured gradually and unable to be drawn out. The spinnable length (l) is defined as the longest length of the fibers that can be drawn up from the hybrid sol (see Table 2).

2.4. Characterizations

FTIR (Nicolet-IR, Madison, WI, USA) and SEM (SIRION200, Hitachi, Tokyo, Japan) were used to confirm the chemical structures and determine the morphologies of silica/titania hybrid fibers, respectively. The UV-Vis spectra were recorded on a Scan UV-Vis spectrophotometer (UV-2550, Shimadzu, Kyoto, Japan). Thermal property was measured using TGA at 25–800 °C with 10 °C/min of the heating rate under nitrogen atmosphere.

3. Results and Discussion

3.1. Spinnability of the Hybrid Sols

The preparation conditions for the hybrid sols and the effect parameters of spinnability are listed in Tables 1 and 2, respectively. The contents of PVA and the molar ratio of TEOS and TBT inside the hybrid sols are varied.

Table 1. Recipe for the hybrid sols preparation.

Order	n(TEOS) (mol)	n(H ₂ O) (mol)	n(HCl) (mol)	n(SiO ₂):n (TiO ₂)	w(PVA in the hybrid fibers) (%)
1	0.5	1	0.05	10	17
2	0.5	1	0.05	10	20
3	0.5	1	0.05	10	25
4	0.5	1	0.05	10	33
5	0.5	1	0.05	20	17
6	0.5	1	0.05	5	17
7	0.5	1	0.05	2.5	17
8	0.5	1	0.05	1.25	17
9	0	0	0	0	100

Table 2. Spinnability of the hybrid sols.

Sample order	Spinnability	Spinning time (min)	Spinning length (m)
1	yes	50	1.4
2	yes	148	1.5
3	yes	193	1.7
4	yes	205	2.5
5	yes	292	3.0
6	yes	35	1.0
7	yes	14	0.5
8	no	0	0
9	yes	–	2.1

In sol-gel transition of PVA/SiO₂-TiO₂ hybrid materials, the main chemical reaction was hydrolysis and condensation of TEOS and TBT. According to the reported mechanism [5,20], the reaction included three stages. The first step is the hydrolysis of TEOS and TBT for forming the Si–OH or Ti–OH groups. Subsequently, condensation between Si–OH or Ti–OH and Si–OH groups, and low molecular polymers were formed. Finally, condensation between low molecular polymers formed the cross-linked silica-titania network. Generally, spinnable hybrid sols can be produced in the final stage because a suitable molecular structure for drawing can be formed [6,24]. According to Ref. [6,24], the molecules of the spinnable hybrid sols should be large enough with lower cured degree.

3.2. Structure and Morphology of the Hybrid Fibers

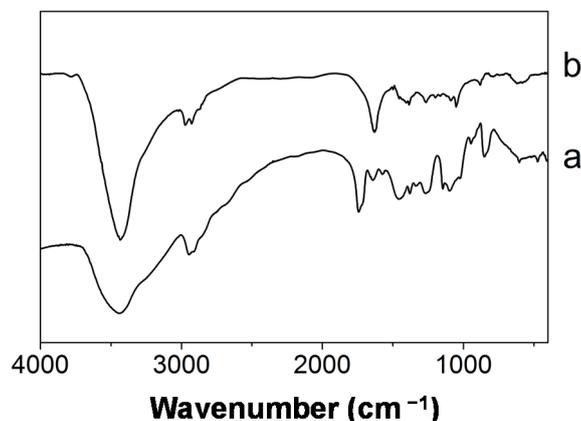
In Table 2, the spinnable time (t) and spinnable length (l) increased gradually with PVA content. The spinnability is based on the intensity of the sol, namely, the sol should have certain molecular weight and appropriate cured degree. The increasing of t means that the elongation of the time needed to produce the macromolecules that are suitable for drawing. The reason is that PVA is a linear macromolecule with hydroxyl group, and it can react with the product, which produced from the hydrolysis and condensation of TEOS and TBT. This hybrid reaction slows down the increasing speed of molecular weight and cured degree of the sol, and this effect become more and more obviously with the increasing content of PVA.

We can also see from Table 2 that the spinnable time (t) and spinnable length (l) decreased gradually with the molar ratio of SiO₂ and TiO₂. Long Si–O–Si chain can be formed by condensation reaction when the content of TBT is low and lineal structure is the major part in the structure of sol. At the same time, due to its high stability, the sol has a very good spinnability.

The FT-IR spectra of the pure SiO₂-TiO₂ gel fibers and the hybrid fibers were shown in Figure 1a,b, respectively. From Figure 1, we can see that there is a broad band near 3440 cm⁻¹ resulted from the stretching vibrations of Si–OH or Ti–OH groups, and this may be due to the incompleteness of the condensation of the inorganic network. Meanwhile, the SiO₂-TiO₂ dual inorganic phase in the hybrid fiber was proved to be linked via Si–O–Si and Si–O–Ti bonds because the peaks at 1052 cm⁻¹ and 940 cm⁻¹ belong to the Si–O–Si and Si–O–Ti stretching vibration, respectively [25]. In Figure 1b, the peak at 1085 cm⁻¹ assigning to the Si–O–C stretching vibrations demonstrated that the organic phase was linked with inorganic phase through covalent bond. Compare with the IR spectra of pure

SiO₂-TiO₂ gel fiber (Figure 1a), the peak of the stretching vibrations of –OH group shifts to the lower wave number. This phenomenon indicated that a large amount of hydroxyl in the PVA reacted with the product of hydrolysis of TEOS and TBT, and formed hydrogen bond association.

Figure 1. FT-IR spectra of samples. (a) SiO₂-TiO₂ gel fiber; (b) PVA/SiO₂-TiO₂ hybrid fiber.



The SEM images of hybrid fibers were displayed in Figure 2. Figure 2a,b showed the smooth surface and uniform dimension of the fibers, with diameters of around 50 μm. Figure 2c,d, indicated that the fibers were oblate and the linear section was uniform. The whole hybrid material was a macroscopical homogeneous system.

Figure 2. SEM photographs of PVA/SiO₂-TiO₂ hybrid fiber. (a) and (b) of fiber appearance; (c) and (d) of the cross-section of fiber.

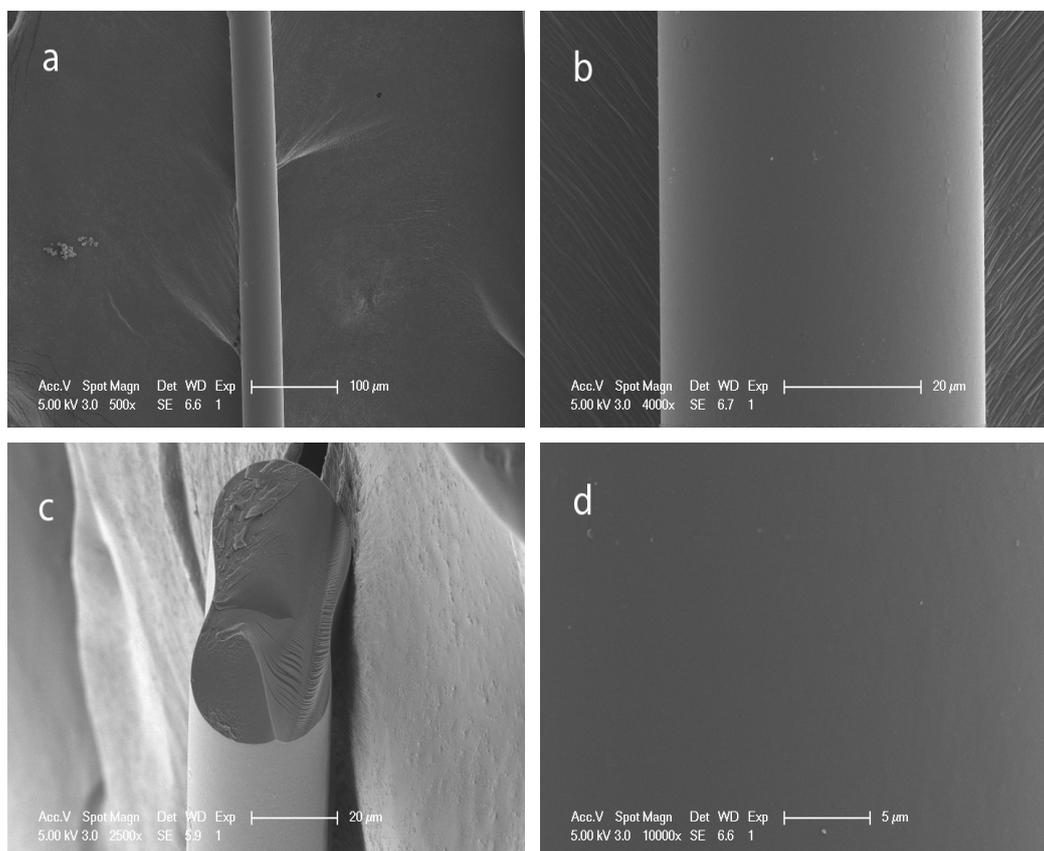
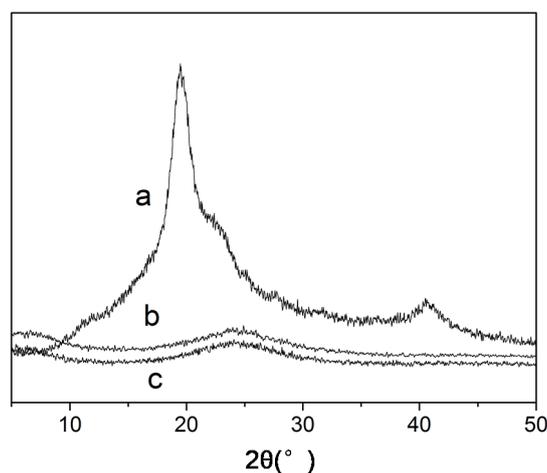


Figure 3 gave the XRD curve for various fibers samples. As shown in Figure 3a, one peak around 2θ equals to 20° appeared, corresponding to the (101) plane of PVA semi-crystalline in pure PVA fiber [26]. However, the peak is much broader and shifts in the samples containing silica-titania; and with the increasing of the content of $(\text{SiO}_2\text{-TiO}_2)$, the diffraction peaks became more and more flat. The broader peak in the hybrid fibers indicates that the hybrid fibers are amorphous and there are no any sign of Anatase or Rutile or Brookite. These results revealed that the crystallinity of PVA was largely influenced by the content of $(\text{SiO}_2\text{-TiO}_2)$ in the hybrid fibers. For pure PVA fiber, the crystallinity was high due to the hydroxyl groups in its side-chain. However, for PVA/ $\text{SiO}_2\text{-TiO}_2$ hybrid fibers, the hydroxyl groups of PVA molecules would react with silica or titania species; thus, the amounts of hydroxyl groups could be decreased, resulting in the decreasing of crystallinity.

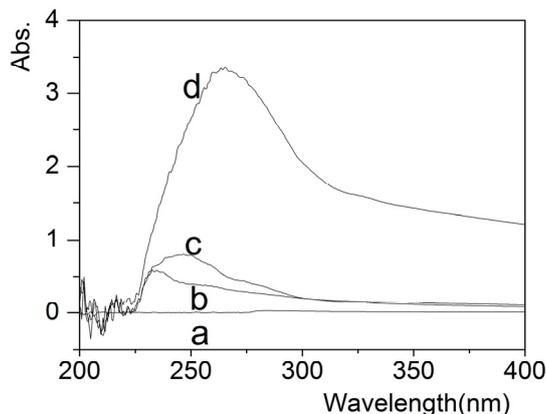
Figure 3. X-ray diffraction patterns of PVA/ $\text{SiO}_2\text{-TiO}_2$ hybrid fibers with different mass ratio. (a) is pure PVA fiber; (b) and (c) are the mass ratio of 1:5 and 1:3 between PVA and $\text{SiO}_2\text{-TiO}_2$, respectively.



3.3. UV-shielding Properties of the Hybrid Fibers

UV-Vis spectra of the hybrid fibers with different molar ratio of $(\text{SiO}_2\text{-TiO}_2)$ were illustrated in Figure 4. The appearance of absorption peaks around 250 nm for all three samples indicate the existence of titanium component in the hybrid fibers, while the absorption peaks was absent for non-titanium fibers. With the increasing amount of TiO_2 in the fibers, the UV permeating intensity decreased and the red shift appeared, which result from the competing effect between the UV scattering and absorption in the shielding process of the nano-sized TiO_2 . By the measuring of UV Spectrophotometer, the shielding efficiency of nano-sized TiO_2 to UV ray of above 200 nm is high to 99.99% [27]. According to the existed optical theory that the particles would possess high scattering capacity when the size of particles were only half of the light wavelength, UV light with wavelength ranging from 200 nm to 400 nm should be scattered by the nano-sized TiO_2 [27]. The ultraviolet light with wavelength of 200–400 nm can cleave the molecular bond inside the polymers and sequentially age the materials. The aging of the PVA/ SiO_2 hybrid material may become slowly due to the effective shielding to UV light of nano- TiO_2 .

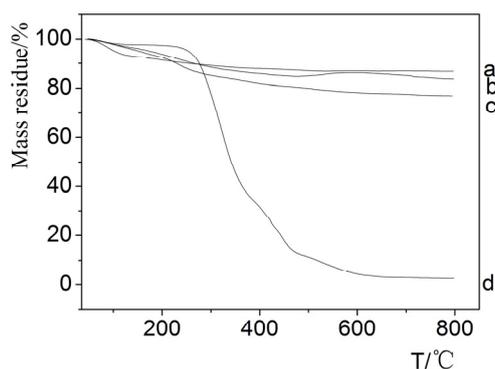
Figure 4. UV-Vis spectra of PVA/SiO₂-TiO₂ hybrid fibers. The molar ratio of TiO₂ and SiO₂: (a) 0; (b) 1:10; (c) 1:5; (d) 2:5.



3.4. Thermal Properties of Hybrid Fibers

TGA curves for fibers with different inorganic component content were illustrated in Figure 5 (molar ratio of TiO₂ and SiO₂ was constantly at 1:5). It is obvious that the heat resistance of pure PVA fiber is very poor (Figure 5a, 2.60% residual weight), and that of pure SiO₂-TiO₂ gel fiber is very good (Figure 5c, around 86.72% residual weight). However, four degradation steps were observed for PVA/SiO₂-TiO₂ hybrid fiber (Figure 5b). The first step at 100–200 °C resulted from the loss of the small molecules, such as residual water and ethanol inside the fibers. The following step at 200–330 °C corresponds to the continuing reaction between PVA and Si–OH, Ti–OH, Si–O–Et, or Ti–O–Bu. The third step at 330–595 °C results from the rupture of the C–O and C–H bond in the hybrid fibers. The fourth step was above 595 °C, which correspond to the decomposition of C–C, Si–C, and Ti–C bond. The final residual weight occupies 76.9%–83.6% of the whole weight. The ratio of weightlessness in every step of the hybrid fibers increase with the content of PVA, and the thermal decomposition temperature (T_d) decrease with PVA content. The T_d of fiber b and c is 342 °C and 320 °C, respectively, while the T_d of pure PVA is 230 °C. This result confirmed the existence of strong interaction between the organic and the inorganic phase in hybrid fibers, which enhanced the rupture energy of the polymers and improved the thermal stability of the PVA/SiO₂-TiO₂ hybrid fiber.

Figure 5. TGA curves of PVA/SiO₂-TiO₂ hybrids. (a) SiO₂-TiO₂ gel fiber; (b) PVA/SiO₂-TiO₂ hybrid fiber (w(SiO₂:TiO₂)% = 85); (c) PVA/SiO₂-TiO₂ hybrid fiber (w(SiO₂:TiO₂)% = 70); (d) PVA fiber.



4. Conclusions

PVA/SiO₂-TiO₂ hybrid fibers were prepared by sol-gel dip-coating method. PVA and SiO₂-TiO₂ were linked through chemical bond in the hybrid fiber, and forms a homogeneous system. Comparing with pure PVA fiber, the crystallinity of hybrid fibers decreased dramatically. The hybrid fibers shield the ultraviolet rays effectively by adding TiO₂, and this can slow the aging process of the PVA/SiO₂ hybrid materials. And also the thermal resistance of hybrid fiber is better than pure PVA fiber. The resulting PVA/SiO₂-TiO₂ hybrid materials may be very promising for use in ultraviolet radiation shield fibers due to the ultraviolet radiation shield effect of TiO₂. This work is currently underway.

Acknowledgments

The authors gratefully acknowledge the support from National Natural Science Foundation of Peoples Republic of China (grant No. 50373010).

Author Contributions

Haihong Ma conceived the research, organized the experiments, interpreted the results, wrote and edited the manuscript. Tiejun Shi conceived the research and helped to interpret the results. Qiusheng Song edited the manuscript and was responsible for the spinnability of the fibers. All authors read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Pan, Z.W.; Dai, Z.R.; Wang, Z.L. Nanobelts of semiconducting oxides. *Science* **2001**, *291*, 1947–1949.
2. Liu, H.Y.; Zhou, X.J.; Chen, Y. Titanium dioxide fibers prepared by sol-gel process and centrifugal spinning. *J. Sol-Gel Sci. Technol.* **2014**, *71*, 102–108.
3. Hosgor, Z.; Kayaman-Apohan, N.; Karatas, S. Nonisocyanate polyurethane/silica hybrid coatings via a sol-gel route. *Adv. Polym. Technol.* **2012**, *31*, 390–400.
4. You, Y.; Zhang, S.Y.; Wan, L. Preparation of continuous TiO₂ fibers by sol-gel method and its photocatalytic degradation on formaldehyde. *Appl. Surf. Sci.* **2012**, *258*, 3469–3474.
5. Yu, L.Y.; Xu, Z.L.; Shen, H.M.; Yang, H. Preparation and characterization of PVDF-SiO₂ composite hollow fiber UF membrane by sol-gel method. *J. Membr. Sci.* **2009**, *337*, 257–265.
6. Dong, H.; Xiao, K.J.; Li, X.L. Preparation of PVDF/Al₂O₃ hybrid membrane via the sol-gel process and characterization of the hybrid membrane. *Desalin. Water Treat.* **2013**, *51*, 3685–3690.
7. Hasegawa, I.; Fukuda, Y.; Kajiwara, M. Inorganic–organic hybrid route to synthesis of ZrC and Si–Zr–C fibres. *Ceram. Int.* **1999**, *25*, 523–527.

8. Leroy, C.M.; Achard, M.F.; Babot, O.; Steunou, N.; Massé, P.; Binet, L.; Brun, N.; Livage, J.; Backov, R. Designing nanotextured vanadium oxide based microscopic fibers: Applications as alcohol sensors. *Chem. Mater.* **2007**, *19*, 3988–3999.
9. Serier, H.; Achard, M.-F.; Steunou, N.; Maquet, J.; Livage, J.; Leroy, C.; Babot, O.; Backov, R. Designing width and texture of vanadium oxide macroscopic fibers toward controlling their mechanical and alcohol-sensing properties. *Adv. Funct. Mater.* **2006**, *16*, 1745–1753.
10. Kinadjian, N.; le Behec, M.; Prouzet, E.; Henrist, C.; Lacombe, S.; Backov, R. Varying TiO₂ macroscopic fiber morphologies toward tuning their photocatalytic properties. *ACS Appl. Mater. Inter.* **2014**, *6*, 11211–11218.
11. Kinadjian, N.; le Behec, M.; Pigot, T.; Dufour, F.; Bentaleb, A.; Prouzet, E.; Lacombe, S.; Backov, R. Photocatalytic TiO₂ macroscopic fibers obtained through integrative chemistry. *Eur. J. Inorg. Chem.* **2012**, *2012*, 5350–5359.
12. Cao, J.Y.; Shi, T.J.; Wang, H.L. Study on spinnable PMMA/SiO₂ hybrid solution. *Polym. Mater. Sci. Eng.* **2007**, *23*, 204–207.
13. Li, D.; Mathew, B.; Mao, C. Biotemplated synthesis of hollow double-layered core/shell titania/silica nanotubes under ambient conditions. *Small* **2012**, *8*, 3691–3697.
14. Siwinska-Stefanska, K.; Ciesielczyk, F.; Kolodziejczak-Radzimska, A. TiO₂-SiO₂ inorganic barrier composites: from synthesis to application. *Pigment. Resin Technol.* **2012**, *41*, 139–148.
15. Kim, E.Y.; Whang, C.M.; Lee, W.I. Photocatalytic property of SiO₂/TiO₂ nanoparticles prepared by sol-hydrothermal process. *J. Electroceram.* **2006**, *17*, 899–902.
16. Xavier Orignac, H.C.; Vasconcelos, H.C.; Du, X.M.; Almeida, R.M. Influence of solvent concentration on the microstructure of SiO₂-TiO₂ sol-gel films. *J. Sol-Gel Sci. Technol.* **1997**, *8*, 243–248.
17. Tang, X.Y.; Yu, Y.X.; Yang, D.X. SiO₂/TiO₂ fibers from titanium-modified polycarbosilane. *J. Membr. Sci.* **2010**, *45*, 2670–2674.
18. Gimenez, V.; Mantecon, A.; Cadiz, V. Modification of poly(vinyl alcohol) with acid chlorides and crosslinking with difunctional hardeners. *J. Polym. Sci. Part A Polym. Chem.* **1996**, *34*, 925–934.
19. Krumova, M.; Lopez, D.; Benavente, R.; Perena, J.M. Effect of crosslinking on the mechanical and thermal properties of poly(vinyl alcohol). *Polymer* **2000**, *41*, 9265–9272.
20. Kinadjian, N.; Achard, M.-F.; Julián-López, B.; Maugey, M.; Poulin, P.; Prouzet, E.; Backov, R. ZnO/PVA macroscopic fibers bearing anisotropic photonic properties. *Adv. Funct. Mater.* **2012**, *22*, 3994–4003.
21. Tamaki, R.; Chujo, Y. Synthesis of poly(vinyl alcohol)/silica gel polymer hybrids by *in-situ* hydrolysis method. *Appl. Organomet. Chem.* **1998**, *12*, 755–762.
22. Liu, Y.; Ren, W.; Zhang, L.Y.; Yao, X. New method for making porous SiO₂ thin films. *Thin Solid Films* **1999**, *353*, 124–128.
23. Xu, Y.D.; Zhou, W.C.; Zhang, L.T.; Cheng, L.F. Spinnability and crystallizability of silica glass fiber by the sol-gel method. *J. Mater. Process Technol.* **2000**, *101*, 44–46.
24. Song, Q.S.; Shi, T.J.; Wang, H.L.; Hang, G.P. Preparation and characterization of continuous fibres of PVA/SiO₂ hybrid by sol-gel method. *Chin. Polym. Mater. Sci. Eng.* **2007**, *23*, 216–219.
25. Sheng, D.Y. *The Application of IR in Polymer Research*; Science Press: Beijing, China, 1988; pp. 83–88. (in Chinese)

26. Koji, N.; Tomonori, Y.; Kenji, I.; Fumio, S. Properties and structure of poly (vinyl alcohol)/silica composites. *J. Appl. Polym. Sci.* **1999**, *74*, 133–138.
27. Zhang, L.D.; Mou, J.M. *Nano-Materials Science*; Liaoning Science and Technology Press: Shenyang, Liaoning, China, 1994; pp. 38–44. (in Chinese)

© 2014 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).