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Preparation of TiO_2/SiO_2 composite fiber by thermal decomposition of polycarbosilane–tetrabutyl titanate hybrid precursor

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Received 24th March 2009, Accepted 14th May 2009
First published as an Advance Article on the web 22nd June 2009
DOI: 10.1039/b905860e

A hybrid polymer as the precursor for TiO_2/SiO_2 composite fibers was prepared by blending polycarbosilane (PCS) and tetrabutyl titanate, named as PCST, which contains unreacted organic tetrabutyl titanate compound. The PCST was characterized by FT-IR, TGA and NMR (^1H, ^{13}C and ^{29}Si). The results showed that the PCST could be described as a part dispersion of $Ti(OC_4H_9)_4$ groups in the PCS chain matrix. The TiO_2/SiO_2 composite fibers were manufactured by melt-spinning PCST, maturing and curing the resulting fibers in air, followed by a final pyrolysis at 1200 °C in air. Based on the XRD, EPMA, EDS, SEM and HRTEM measurements, the TiO_2/SiO_2 fibers were made up of anatase-TiO_2 nanocrystallites with a mean size of ~10 nm and in the amorphous silica phase.

Introduction

Polycarbosilane (PCS) is a silicon containing polymer and a well known precursor for SiC ceramic products, with the use of PCS in SiC fiber production being the earliest and most typical example.[1–8] In the production of SiC fibers, polymeric fibers are melt-spun from PCS, cured in air or by an electron beam, and converted to SiC fibers through thermal decomposition in an inert atmosphere.[2–9] The PCS produced from polydimethylsilane (PDMS) by Kumada rearrangement has a complex structure involving Si–C–Si linkage and pendant Si–R (R = H, Me) groups. The presence of Si–H bonds in PCS chain can considerably enhance reaction activity. Moreover, the PCS can be easily modified by chemical reactions with a metallic alkoxide to obtain new systems.[10–21] For example, polytitanocarbosilane, which is produced by a condensation reaction of PCS with titanium (IV) tetraalkoxide, transformed into a SiC/TiC ceramic during thermal decomposition in nitrogen atmosphere.[22–25] Polyzirconocarbosilane obtained by a condensation reaction of PCS with zirconium (IV) acetylacetonate was used as a precursor of commercial Tyranno ZM SiC ceramic fiber.[21] Polyaluminocarbosilane as a precursor of Tyranno SA SiC ceramic fiber was prepared by thermolysis of a mixture of PCS and aluminium acetylacetonate.[14–17]

Recent work has shown that SiO_2 fibers, which have generally been produced from sol–gel processes,[26] could be obtained using PCS precursor method. A new type of TiO_2/SiO_2 functional fibers have been prepared by Ishikawa[27,28] through polytitanocarbosilane. The strength of TiO_2/SiO_2 fibers prepared from PCS precursor was markedly higher (>2.5 GPa) than that of ordinary sol–gel TiO_2/SiO_2 fibers prepared from sol–gel (<1 GPa). Up to now, only a few papers have appeared in the literature concerning the preparation of SiO_2 fibers from polymer precursor pyrolysis. The detailed information of SiO_2 fiber from polymer precursors has not been disclosed.

In the present work, we prepared the TiO_2/SiO_2 composite fibers by thermal decomposition of polycarbosilane–tetrabutyl titanate hybrid polymer, named as PCST, which was formed by the reaction of PCS with an excess amount of tetrabutyl titanate. The objectives of this study are (1) characterization of the synthesized precursor and (2) analysis of microstructure of TiO_2/SiO_2 composite fibers.

Experimental

Materials

The PCS which has a main chain structure represented by the formula, $[SiHCH_3CH_2]_n$, was prepared according to the Yajima[1–3] process. The PCS obtained has a softening point of 200 °C and a molecular weight of 1500 Da with a dispersion coefficient of 1.8. Tetrabutyl titanate ($Ti(OC_4H_9)_4$) with a reagent grade of 99% was purchased from Aldrich. Solvent xylene was purified by distillation with sodium. All samples described in this investigation were manipulated in a purified nitrogen or argon atmosphere.

Synthesis of PCST hybrid precursor

The PCST hybrid polymer as the precursor of TiO_2/SiO_2 composite fibers was synthesized from PCS and $Ti(OC_4H_9)_4$. It was preferred to select the amount of the two reagents under which an unreacted organic $Ti(OC_4H_9)_4$ compound was intentionally left. The weight fraction of $Ti(OC_4H_9)_4$ in the precursor was fixed at 50% since the excellent spinnality of the precursor can be obtained at this composition. On the other hand, in order to produce the fiber having a homogeneous constitution, it is required to select slow reaction conditions under which only part of the organic titanium compound forms a bond with the PCS. In a typical experiment, 10g of PCS and 10g of $Ti(OC_4H_9)_4$ were dissolved in 250 mL of xylene in a 1 litre, three-neck round-bottom flask under nitrogen gas with vigorous stirring at 100 °C.

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The mixture temperature was maintained at 100 °C for 1 h, a clear solution was obtained, and then increased to 150 °C to remove the xylene. The solution turned from orange to dark blue. Finally, the temperature was increased to 200 °C, and the reaction was carried out for 5 more hours. The PCST hybrid precursors with dark blue color were obtained.

Preparation of TiO_2/SiO_2 fibers

A melt spinning apparatus with a single spinneret was used in order to get a fiber from PCST hybrid precursor produced by the present method. The PCST melt was extruded by a piston in a stream of nitrogen through a 300 μm spinneret. The spinning conditions were optimized with respect to the melting temperature of PCST since the degree of viscosity critically affected the spinnability. Normally, the spinning temperature of PCST was 165 °C, which is markedly lower than that of raw material PCS (260 °C). The green fibers were stretched by winding them up on a rotating spool at velocities between 200 and 600 m min^{-1}. The as-spun fibers were then matured in air at 100 °C for 100 h. After the maturation, the fiber materials were thermally cured under air atmosphere with a ramp rate of 20 °C h^{-1} to 200 °C and a dwell time of 5 h. Finally, the cured fibers were thermally decomposed at 1200 °C for 1 h in air to obtain the TiO_2/SiO_2 fibers. The heating rate to 1200 °C was 10 °C min^{-1}. The fibers obtained in this experiment were colorless, transparent and flexible. The tensile strength and average diameter of the TiO_2/SiO_2 fibers are about 2.0 GPa and 13 μm, respectively.

Characterizations

The Fourier transform-infrared (FT-IR) spectra of precursors were recorded between 4000 and 400 cm^{-1} on a Nicolet-360 spectrometer by the KBr pellet method. The ^{1}H, ^{29}Si and ^{13}C NMR spectra were measured with a Bruker AV 300 spectrometer at 300 MHz for ^{1}H, 59.6 MHz for ^{29}Si and 75.5 MHz for ^{13}C in $CDCl_3$ solution. The chemical shift reference was TMS for ^{1}H, ^{29}Si and ^{13}C. The thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA 7 at a heating rate of 10 °C/min under air. The elemental analyses of the TiO_2/SiO_2 fibers were performed on the polished cross section by electron probe microanalysis (EPMA) using a Camebax 75 (Cameca) in the wavelength dispersion mode (thallium acid phthalate (TAP) crystal for Si$K\alpha$, pentaerytritole (PET) for Ti$K\alpha$ and a multilayer pseudo crystal multilayer (PCII) for C$K\alpha$ and O$K\alpha$) with standard (SiC, Ti and SiO_2) whose compositions were assumed to be stoichiometric. The phase compositions of the fibers were analyzed with an X-ray diffractometer (XRD, CuK_α radiation, X'Pert PRO, PANalytical, Almelo, Netherlands) and scanning electron microscope (SEM, JEOL JSM-6300) equipped with an energy dispersive spectrometer (EDS, Rontec SDD quad detector, XFLASH Quad4040, Bruker AXS Microanalysis, Berlin, Germany). The microstructure of the monofilaments was studied at the nanometer scale by high resolution transmission electron microscopy (HRTEM) using CM200-FEG. The samples were embedded in an epoxy resin and cut into thin foils with an ultramicrotome. The foils were then set on copper microgrids. The HRTEM analyses were performed in lattice fringes (LF) and selected area electron diffraction (SAED) modes.

Results and discussion

Nature of PCST

To identify the functional units presented, the FT-IR spectra of the PCS and PCST are shown in Fig.1. The peaks were assigned with reference to literature on known organic compounds and PCS.[13–18] In the FT-IR spectra of the PCS and PCST, the absorption peaks at 2950 and 2900 cm^{-1} (C–H stretching), 2100 cm^{-1} (Si–H stretching), 1400 cm^{-1} (C–H deformation in Si–CH_3), 1355 cm^{-1} (CH_2 deformation in Si–CH_2–Si), 1250 cm^{-1} (Si–CH_3 deformation), 1020 cm^{-1} (CH_2 deformation in Si–CH_2–Si) and in the vicinity of 800 cm^{-1} (Si–CH_3 deformation and Si–C stretching) were seen, and this suggests that PCST is composed of nearly the same Si–C skeleton as PCS. In order to estimate the reaction degree of Si–H bonds, the Si–H bond content was calculated from the absorbency ratio of characteristic absorption peaks at 2100 and 1250 cm^{-1} (A_{Si-H}/A_{Si-CH3}). The values of A_{Si-H}/A_{Si-CH3} ratio were 0.696 for PCS and 0.297 for PCST. Decrease in the absorption peak at A_{Si-H}/A_{Si-CH3} ratio and appearance of absorption peak at 1090 cm^{-1} (Ti–O–C)[22–24] in the spectrum of PCST show the obvious difference in its structure from PCS. The above results imply that chemical reactions occur between PCS and $Ti(OC_4H_9)_4$ during the preparation of PCST precursors, resulting in the appearance of a new absorption peak at 1090 cm^{-1}, causing a change in the ligands of $Ti(OC_4H_9)_4$ and structural alterations in PCS.

The ^{1}H-NMR spectra of the PCS and PCST are presented in Fig.2. A large peak centered at 0.5 ppm and a small peak

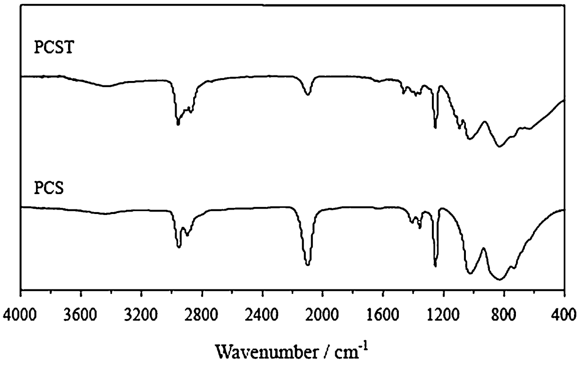


Fig. 1 The FT-IR spectra of PCS and PCST.

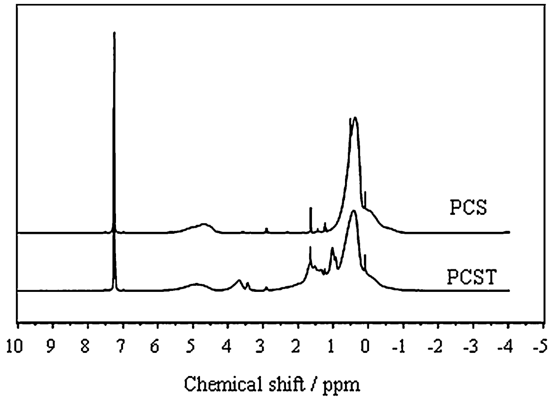


Fig. 2 The ^{1}H NMR spectra of PCS and PCST.

appeared in the range of 4.0∼5.5 ppm were observed; the former is due to hydrogen atoms in Si–CH_3, Si–CH_2– *etc.*, (C–**H**), and the latter to a hydrogen atom in Si–H (Si–**H**). The integrated ratios of the C–H and Si–H signals for the PCS and PCST were 11.4 and 13.7, respectively. The decrease in Si–H content in the PCST is consistent with the FT-IR result. Consequently, the consumption of the Si–H bond indicates the existence of hydrosilylation crosslinking between the PCS and $Ti(OC_4H_9)_4$. The variations in the ^{1}H-NMR spectra of the PCS and PCST confirm the different structure between the PCS and PCST.

In Fig.3, the ^{29}Si-NMR spectrum of the PCST is compared with that of the PCS. The assignments given were based on spectra of known organic compounds and earlier work on PCS.[13–20] The signal at the chemical shift of around +0.4 ppm was assigned to the resonance of silicon bonded to four carbons (**Si**C_4). The signal at −16 ppm was assigned to silicon bonded to one hydrogen and three carbons (**Si**C_3H). The relative intensity of the signal at around +0.4 ppm due to **Si**C_4 units remained almost constant, while the relative intensity of the signal at −16 ppm due to **Si**C_3H groups was reduced for the PCST. The reduction in the SiC_3H signal correlated with the reduction of the Si–H and Si–CH_3 contents in the FT-IR spectra. In the PCST, a signal at around +15 ppm due to Si–O units appeared. This may be due mainly to the oxidation/hydrolysis of the Si–H bonds in PCS, although a clear reaction mechanism is still not fully established. Here, the ^{29}Si-NMR data has confirmed the presence and relative amounts of Si–O bonds in the PCST which was not clearly resolved by FT-IR spectroscopy.

The ^{13}C-NMR spectra of the PCS and PCST are shown in Fig.4. The main peak at +2 ppm indicated carbon atoms bonded to silicon. This peak was probably due to superimposed Si–**C**H_3 and Si–CH_2 groups because the difference of chemical shifts between these two carbon environments is very small. In the PCST, the characteristic peaks of Ti(O**C**$_4H_9)_4$ were observed at +77, +35, +19 and +14 ppm. These indicate that some $Ti(OC_4H_9)_4$ groups remained in the structure of PCST, which is beneficial to reduce the melt-spun temperature and improve the spinnability of PCST.

In experiment observations, it was found that the $Ti(OC_4H_9)_4$/PCS molar ratio has a profound influence in the structure of PCST. When the $Ti(OC_4H_9)_4$/PCS molar ratio is in the range of 0.25 to 1, PCST with cross-linked structure is obtained, resulting in the deterioration of spinnability of PCST. As this ratio increases from 1 to 3, the PCST formed with more and more $Ti(OC_4H_9)_4$ groups remain in the PCS, resulting in an appearance of excellent spinnality of PCST. As a suitable precursor of fiber, polymer should have good spinnability and high pyrolysis yield. The TGA curve of PCST in air is given in Fig.5. The conversion of PCST into inorganic compound was completed at about 700 °C, and the residue weight was 87 *wt* % at 1200 °C. The PCST showed a very high ceramic yield, and it is worth pointing out that a high ceramic yield is very beneficial in the production of dense ceramic fibers. The high ceramic yield of PCST was attributed to the oxidation of PCS and $Ti(OC_4H_9)_4$.

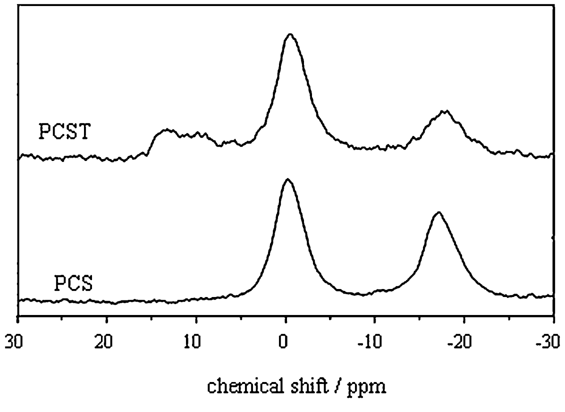


Fig. 3 The ^{29}Si NMR spectra of PCS and PCST.

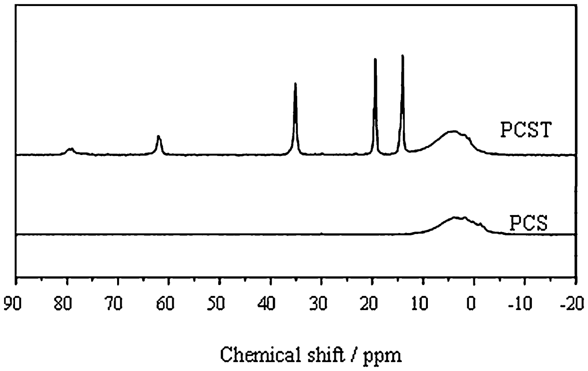


Fig. 4 The ^{13}C NMR spectra of PCS and PCST.

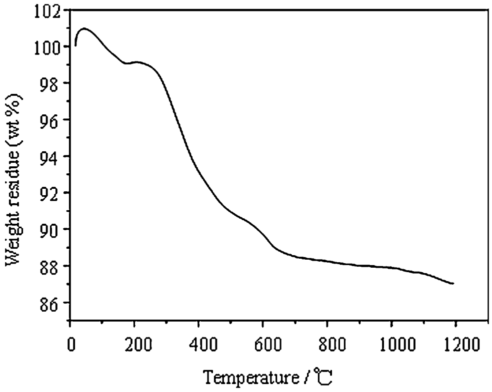


Fig. 5 The TG curve of PCST in air.

Composition and microstructure of the TiO_2/SiO_2 fibers

The PCST precursor was continuously melt-spun and then matured and cured in air. By thermal decomposition at 1200 °C in air of the cured PCST fiber, the TiO_2/SiO_2 composite fibers can be obtained. The EDS elemental analysis of the TiO_2/SiO_2 fibers is shown in Fig.6. The EDS spectrum of the TiO_2/SiO_2 fibers exhibits characteristic peaks of silicon, titanium and oxygen confirming that the TiO_2/SiO_2 fibers only contain silicon, titanium and oxygen elements. The carbon content of the fibers was not detected by EDS. The carbon element could have been oxidized completely. The chemical composition of the TiO_2/SiO_2 fibers, as locally assessed by EDS, is presented in Table 1. The TiO_2/SiO_2 fibers contained 11.8 *wt*% titanium, 39.5 *wt*% silicon, and 48.6 *wt*% oxygen. It is noteworthy that carbon was absent in the fibers. To better show any radial gradient in composition, the

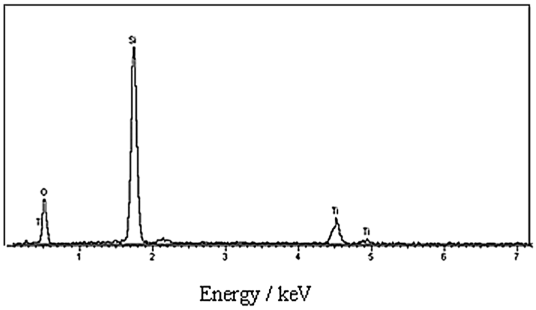


Fig. 6 The EDS elemental analysis of the TiO_2/SiO_2 fibers.

Table 1 Chemical composition of the TiO_2/SiO_2 fibers from EDS

Element	*wt*%	*at*%
O *K*	48.6	64.8
Si *K*	39.5	29.9
Ti *K*	11.9	5.3
Totals	100.00	

EPMA linescan measurements along the diameter of the TiO_2/SiO_2 fiber were made. An example of composition profiles for the TiO_2/SiO_2 fiber is presented in Fig. 7. The diameter of the fiber was 13 μm. The EPMA results revealed homogeneous elemental compositions (Si, Ti and O) along the fiber diameter. And in the case of carbon element, the content was nil. The skeleton of the precursor PCST is Si–C bonds, and consequently, carbon atoms exist in the main chain and the side chain. During the thermal decomposition of PCST green fiber in air, these carbon atoms are oxidized and are completely evolved from the fiber. The amounts of carbon evolved and oxygen introduced are very large, because the carbon content in the PCST was about 40 *wt*%. Finally, it was estimated that exchange between carbon and oxygen occurs at the atomic ratio $C/O \approx 1$. The exact mechanism of exchange between carbon and oxygen will be studied in detail in the near future.

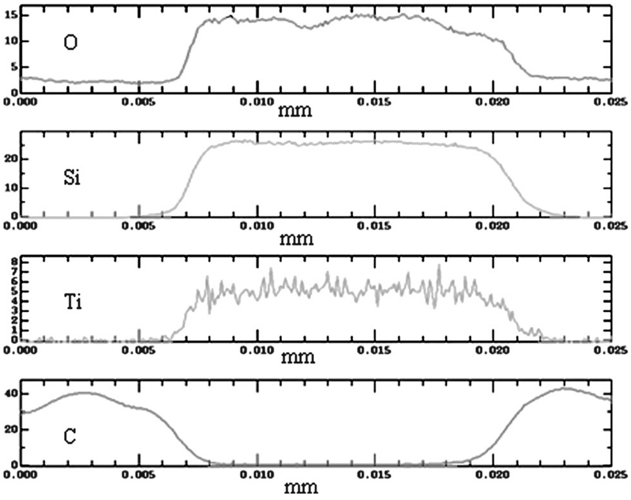


Fig. 7 The atomic concentrations of Si, O, Ti and C along the diameter of a TiO_2/SiO_2 fiber cross-section measured by EPMA.

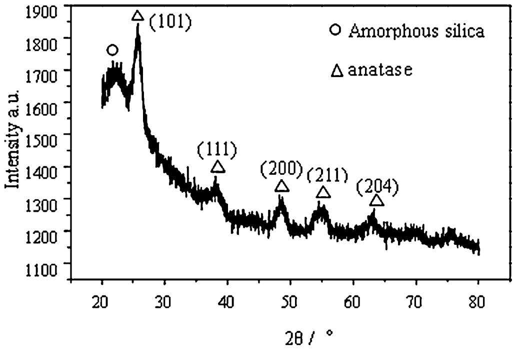
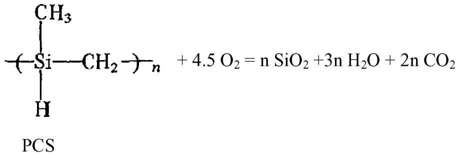


Fig. 8 The X-ray diffraction pattern of the TiO_2/SiO_2 fibers.

The microstructures of the TiO_2/SiO_2 fibers were characterized by XRD. Fig.8 shows the XRD patterns of fibers. The broad diffraction pattern at $2\theta = 22°$ is assigned to amorphous silica, while a sharp peak and four small peaks are attributed to the (101), (111), (200), (211) and (204) planes of anatase-TiO_2 crystal.[28] The XRD results suggest that the TiO_2/SiO_2 fibers are mainly composed of anatase-TiO_2 along with amorphous silica. In other words, the TiO_2/SiO_2 fibers contained 11.9 *wt*% titanium, 39.5 *wt*% silicon and 48.6 *wt*% oxygen, were made up of anatase-TiO_2 and amorphous silica. During the pyrolysis process, the precursor PCST fibers were converted into a titania-dispersed, silica-based fiber (confirmed by HRTEM) according to the following reactions[28]:



$$\left(\underset{H}{\overset{CH_3}{Si}} - CH_2 \right)_n + 4.5\,O_2 = n\,SiO_2 + 3n\,H_2O + 2n\,CO_2 \qquad (1)$$

PCS

$$Ti(OC_4H_9)_4 + 24\,O_2 = TiO_2 + 18\,H_2O + 16\,CO_2 \qquad (2)$$

The oxidation of the PCS transforms into amorphous silica with a concomitant generation of H_2O and CO_2 gases by Reaction (1), and the oxidation of the $Ti(OC_4H_9)_4$ crystallizes into TiO_2 with the generation of H_2O and CO_2 gases by Reaction (2). The escaping of H_2O and CO_2 gases causes significant mass loss, however, the formation of SiO_2 and TiO_2 resulting in a mass gain. The carbon in the precursor PCST fibers is completely removed through these reactions. Ideally, the oxygen picked up in these oxidation reactions is just enough to react with carbon to form CO_2 gas.

It is well known that, when pure PCS fiber is pyrolysed at high temperature in air, it transforms to silica amorphous phase, with a concomitant growth of grain size, and further changes to the α-quartz, eventually can not retain fiber shape. However, it is expected from this investigation that the TiO_2/SiO_2 fibers obtained from the PCST green fibers may retain the fiber shape and strength during thermal decomposition in air due to the retardation in the growth of the crystalline phase. Fig.9 shows typical surface micrograph of the TiO_2/SiO_2 fiber. The fibers have a very smooth surface without any observable flaws. It is worth noting that the degradation of ceramic strength at high temperature was partly caused by a fast rate of crystallization,

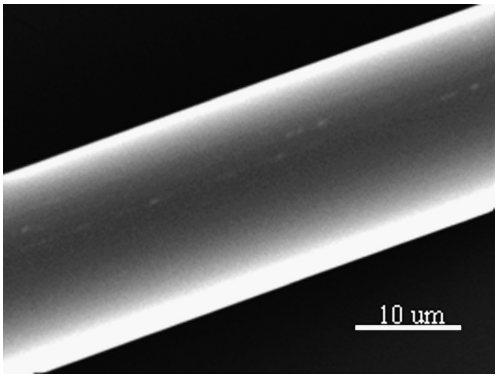


Fig. 9 The surface micrograph of the TiO_2/SiO_2 fiber.

and there have been attempts to slow down the crystallization by introduction of hetero-elements, *e.g.* titanium, in commercial Tyranno fibers.[25] Therefore, an excess amount of $Ti(OC_4H_9)_4$ in the PCST played important roles during the formation of the TiO_2/SiO_2 fibers, and carbon could be eliminated in thermal decomposition at high temperature. In the pyrolysis process, the evolution of H_2O and CO_2 gases occurred, this means that a densification process must be produced. Furthermore, after the thermal decomposition in air at 1200 °C, the PCST fibers shrank by a remarkable 27% from 18 to 13 μm in an average diameter. The high shrinkage of fibers indicates a high level of densification, and suggests that pores and defects formed by the removal of carbon might be efficiently healed by calcination in the presence of titanium element.

The HRTEM images of the TiO_2/SiO_2 fiber are provided in Fig. 10(a) and (b) (where (b) is a higher magnification of (a)). The corresponding selected area electron diffraction (SAED) image is inserted in Fig. 9(b). The HRTEM images and corresponding SAED image show that the TiO_2/SiO_2 fibers consist of TiO_2 crystal and silica amorphous continuous phase. It also indicates the nanoparticles with the mean size of ~10 nm were bound with the amorphous silica phase. The distance between these planes is 0.353nm, which is the same as the distance between {101} planes in an anatase-TiO_2 crystal. Therefore, this amorphous phase is concluded to be silica from the thermal decomposition of PCST in air. It is reported that in the pure TiO_2 fibers obtained by sol–gel method, anatase-TiO_2 was converted to rutile at above 700 °C.[27,28] In the present investigation, although the TiO_2/SiO_2 fibers were fired at 1200 °C, no obvious rutile phase could be observed. It seems that the surrounding silica phase maintained the stabilization of the anatase phase.

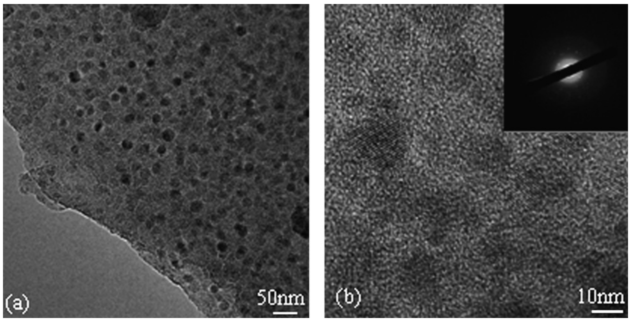


Fig. 10 (a) and (b) The HRTEM images with the insertion of SAED image in (b) for the TiO_2/SiO_2 fiber.

Conclusion

In summary, in this study, we developed a convenient method of preparing the TiO_2/SiO_2 composite fibers from the thermal decomposition of PCS-$Ti(OC_4H_9)_4$ hybrid precursor, named as PCST. The TiO_2/SiO_2 fibers were manufactured by melt-spinning PCST, maturing and curing the resulting fibers in air, followed by a final pyrolysis at 1200 °C in air. It was clearly demonstrated from this investigation that during the pyrolysis process the PCST green fibers could be transformed *in situ* into TiO_2/SiO_2 fibers under an air atmosphere, and the carbon atoms could be substituted by oxygen atoms. The TiO_2/SiO_2 fibers were mainly composed of anatase-TiO_2 nanocrystallites with the mean size of ~10 nm and amorphous silica phase.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 50532010) and Fujian Key Laboratory of Advanced Materials, China (Grant No. 2006L2003).

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