

## Research Article

# Synthesis and Characterization of Structure-Controlled Micro-/Nanocomposite TiO<sub>2</sub> Fibers with Enhanced Photocatalytic Activity

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A series of structure-controlled composite TiO<sub>2</sub> fibers combining micro- and nanostructures (hereafter, micro-/nanocomposite) were fabricated using a combination of electrospinning and calcination methods, and their photocatalytic activities were investigated. Smooth microscale fibers were obtained by electrospinning a precursor solution containing tetrabutyl titanate and TiF<sub>4</sub>. TiO<sub>2</sub> nanocrystals formed on the microfibers with the help of HF which was produced from the decomposition of TiF<sub>4</sub> in calcination. The size and quantity of TiO<sub>2</sub> nanocrystals can be controlled by tuning the mass ratio of TiF<sub>4</sub> in the sol-gel precursor solutions and the calcination time. The obtained micro-/nanocomposite TiO<sub>2</sub> fibers were found to exhibit enhanced photocatalytic properties when compared with the bare microfibers. These micro-/nanocomposite structures exhibit the advantages of both the nanocrystals and microfibers, which will lead to new developments in photocatalysis.

## 1. Introduction

Since 1972, when Fujishima and Honda found that titanium dioxide could work as photocatalyst for the decomposition of H<sub>2</sub>O [1], many efforts have been devoted to developing heterogeneous photocatalysts for environmental applications such as air purification, water disinfection, and hazardous waste remediation [2–7]. Up to now, titanium dioxide has been proved to be one of the most suitable materials for widespread environmental applications because of its biological and chemical inertness, strong oxidizing power, cost effectiveness, and long stability against photocorrosion and chemical corrosion [8]. For example, a variety of TiO<sub>2</sub> materials with different morphologies such as spheres, fibers, and particles [9–16] have been fabricated to provide better photocatalytic performance in both industrial applications and chemical research. Compared with nanoparticles or nanospheres, microscale fibers can be reclaimed easily because they are more stable than nanosized structures in terms of aggregation [8]. However, microfibers are limited by their relatively smaller surface area [17] and lower photocatalytic efficiency. Therefore, fabrication of TiO<sub>2</sub> materials with

both large surface areas and easy reclamation has become an imperative research area for many researchers.

Electrospinning has been proven to be one of the most simple and versatile methods of producing complex structures such as fibers, tubes, and films [18–23]. In this paper, composites of microscale fibers and nanoscale particles (hereafter, such structures are called micro-/nanocomposite) were prepared through two steps. First, microfibers were produced by electrospinning a precursor solution containing titanium tetrafluoride (TiF<sub>4</sub>) and tetrabutyl titanate (Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>). Then the as-prepared fibers were calcined at high temperature and nanocrystals formed on the surfaces of the fibers. In order to evaluate the formation mechanism of the micro-/nanocomposite fibers, a series of different mass ratios of TiF<sub>4</sub> in the precursor solution were used and the calcination time was changed. After further analysis of the morphology, elemental composition, and phase composition of the micro-/nanocomposite fibers obtained from the precursor solutions with different TiF<sub>4</sub> mass ratios, we found that the crucial factor in the fabrication was the crystallization of the TiO<sub>2</sub> in HF atmosphere created by the decomposition of TiF<sub>4</sub> during calcination. The photocatalytic activity of

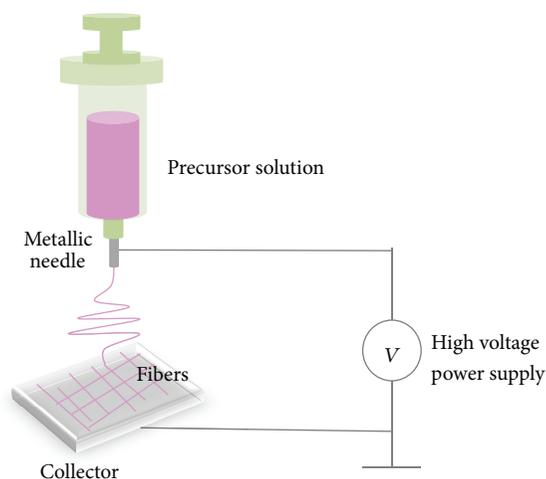


FIGURE 1: Illustration of electrospinning instrument.

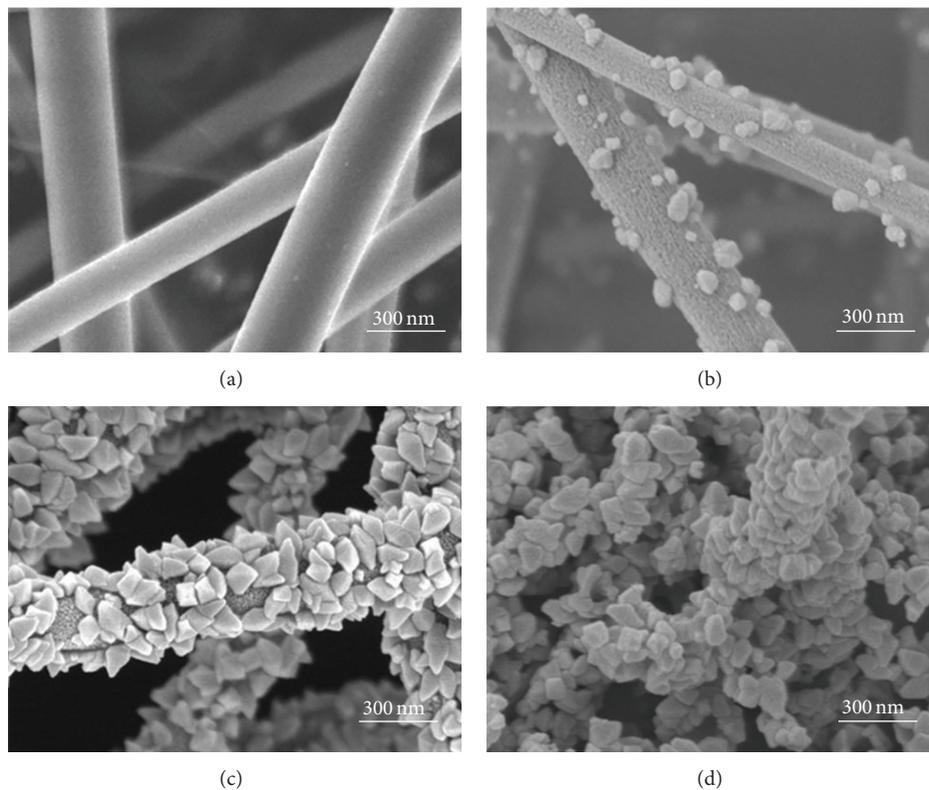


FIGURE 2: SEM images of micro-/nanocomposite  $\text{TiO}_2$  fibers obtained from samples (a) F0, (b) F2, (c) F4, and (d) F6 after calcination at  $500^\circ\text{C}$  for 5 hours in a crucible covered with a cap.

the  $\text{TiO}_2$  fibers was also analyzed, and it was found that such micro-/nanocomposite fibers can provide enhanced photocatalytic activity compared with smooth microscale fibers. The high surface area and the multiphase composition were responsible for the enhanced photocatalytic activity of the fibers. These micro-/nanocomposite fibers have the advantages of both the  $\text{TiO}_2$  particles and the fibers, and they

will exhibit excellent photocatalytic performance in various areas.

## 2. Materials and Method

**2.1. Materials.** Polyvinylpyrrolidone (PVP) ( $M_w \approx 100000$ , Aldrich Chemical Co.), tetrabutyl titanate ( $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ,

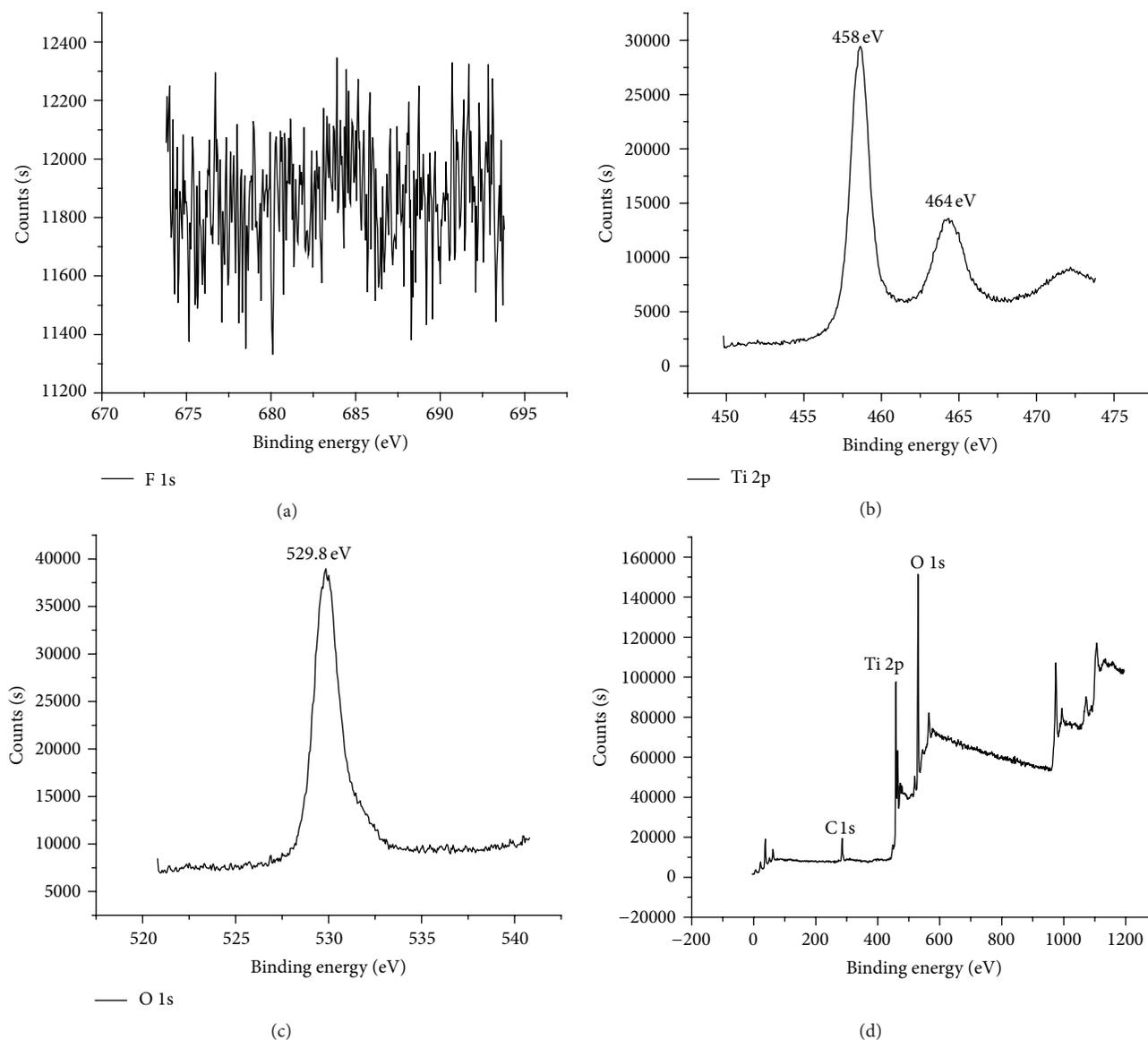


FIGURE 3: XPS spectra of the micro-/nanostructured  $\text{TiO}_2$  fibers obtained from sample F4 after calcination at  $500^\circ\text{C}$  for 5 hours in a crucible covered with a cap: (a) F 1s, (b) Ti 2p, (c) O 1s spectra, and (d) spectrum of all elements in the fibers.

Sinopharm Chemical Reagent Co., Ltd.), titanium tetrafluoride ( $\text{TiF}_4$ , Aldrich Chemical Co.), absolute ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ , Beijing Chemical Works), acetic acid ( $\text{CH}_3\text{COOH}$ , Beijing Chemical Works), and hexadecyl trimethyl ammonium bromide ( $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NBr}$  (CTAB), Fine Chemical Research Institute of Tianjin Jinke) were used as received without further purification.

**2.2. Preparation of Precursor Sol-Gel Solutions.** First, 12 g ethanol, 1.5 g acetic acid, 1.1 g PVP, 6 g tetrabutyl titanate, and 0.03 g CTAB were added in a capped bottle, and the solution was stirred for 0.5 hours until it became transparent. Then 0 g, 0.2 g, 0.4 g, or 0.6 g  $\text{TiF}_4$  was added to the solution, and this mixture was continuously stirred for 0.5 hours to generate a

homogeneous solution. The obtained solutions were named S0, S2, S4, and S6 according to the  $\text{TiF}_4$  mass ratios (0 wt%, 0.96 wt%, 1.85 wt%, and 2.83 wt%) in the solution.

**2.3. Microfiber Fabrication by Electrospinning.** The designation of the electrospinning instrument was mainly consulted the previous work [24], which is illustrated in Figure 1. The precursor solution was loaded using an external syringe with a metallic needle, and a grounded metallic plate covered with a piece of tin foil was used as a collecting substrate. The voltage was controlled at 10–30 kV, and the work distance was 10–20 cm, depending on the conditions for each individual experiment. The obtained fibers were named F0, F2, F4, and F6 according to the  $\text{TiF}_4$  mass ratios (0 wt%, 0.96 wt%, 1.85 wt%, and 2.83 wt%) in the precursor solution.

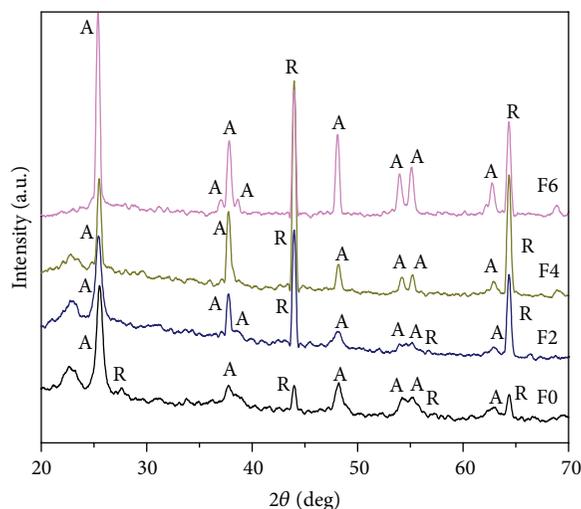


FIGURE 4: Powder X-ray diffraction patterns of micro-/nanostructured  $\text{TiO}_2$  fibers obtained from samples F0, F2, F4, and F6 after calcination for 5 hours in a crucible covered with a cap.

#### 2.4. Formation of Nanoparticles on Microfibers by Calcination.

The electrospun products were calcined at  $500^\circ\text{C}$  in a crucible with a cap for 4, 5, or 6 hours. Afterwards, the micro  $\text{TiO}_2$  fibers with nanoparticles grow on the surface were obtained. As a control experiment, the electrospun products were calcined at  $500^\circ\text{C}$  in air and smooth microfibers were got.

**2.5. Characterization.** The morphology of the  $\text{TiO}_2$  fibers was characterized by scanning electron microscopy (SEM; JSM-6700F, JEOL, Japan). Powder X-ray diffraction (XRD) measurements were performed on a Rigaku D/Max-2500 diffractometer (Rigaku Co., Japan) with  $\text{Cu K}\alpha$  radiation. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Escalab 220i XL XPS System (Thermo VG Scientific Ltd., UK). The UV-vis spectrum was obtained using a UV-vis 3100 instrument (Hitachi Co., Japan).

**2.6. Photocatalytic Activity of the Micro-/Nanocomposite Fibers.** The photocatalytic activity of the micro-/nanostructured fibers was evaluated by using them to catalyze the degradation of rhodamine 6G ( $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$ , Sigma Chemical Co.) in a 150 mL reactor. In each photocatalytic experiment, 0.05 g of  $\text{TiO}_2$  fibers was used as the photocatalyst. Samples prepared from F0, F2, and F4 after calcination were selected as the photocatalysts because they could maintain their fiber morphology during the experiment and can be easily reclaimed. The initial concentration of rhodamine 6G was  $1.5 \times 10^{-5}$  mol/L. The changes in the concentration of rhodamine 6G during photocatalytic decomposition were monitored by in situ UV-vis spectroscopy. The system was kept in the dark for 0.5 h for adsorption equilibration and then was irradiated with UV lamps with a peak wavelength of 365 nm. The UV-vis spectrum with a 526 nm absorption peak was recorded every 30 minutes.

### 3. Results and Discussion

**3.1. Characterization of Micro-/Nanocomposite Structured  $\text{TiO}_2$  Fibers.** Figure 2 shows the micro-/nanocomposite  $\text{TiO}_2$  fibers obtained from samples F0, F2, F4, and F6 after calcination at  $500^\circ\text{C}$  for 5 hours in a crucible covered with a cap. No nanoparticle formed on the surfaces of the fibers obtained from the solution without  $\text{TiF}_4$  after calcination (Figure 2(a)), but fibers obtained from the precursor solution containing  $\text{TiF}_4$  had nanoparticles formed on their surfaces (Figures 2(b)–2(d)). The size and quantity of the nanoparticles increase with increasing mass ratio of  $\text{TiF}_4$  in the precursor solution. When the  $\text{TiF}_4$  concentration in the precursor solution was sufficient (e.g., 2.83 wt%), the fibers completely transformed into nanoparticles after calcination (Figure 2(d)).

To determine the elemental composition of the micro-/nanostructured fibers, XPS spectra for the fibers obtained from sample F4 were analyzed (Figure 3). There are nearly no peaks at 684 eV and 691 eV, which means that there is no F element in the fiber (Figure 3(a)). Ti 2p region is located at 458 eV and 464 eV, indicating that the Ti element exists in the  $\text{Ti}^{4+}$  form [25]. The O 1s region is located at 530 eV, which results from the  $\text{O}^{2-}$  in the  $\text{TiO}_2$  and hydroxyl groups on the surface of the sample [26].

As shown in Table 1, the atomic ratio of Ti and O in the fibers obtained from sample F4 is about 1 : 2, which confirms the existence of  $\text{TiO}_2$ . Therefore, we can conclude that the micro-/nanostructured fiber is mainly composed of  $\text{TiO}_2$ . In addition, as shown in Figure 3(d) and Table 1, the C 1s peak is located at 284.8 eV, which reveals that the C element exists in the micro-/nanostructured fibers. The existence of C element is probably due to the contaminant C introduced during calcination and contamination of the XPS instrument [26].

Figure 4 shows the phase composition of the different micro-/nanostructured  $\text{TiO}_2$  fibers obtained from samples

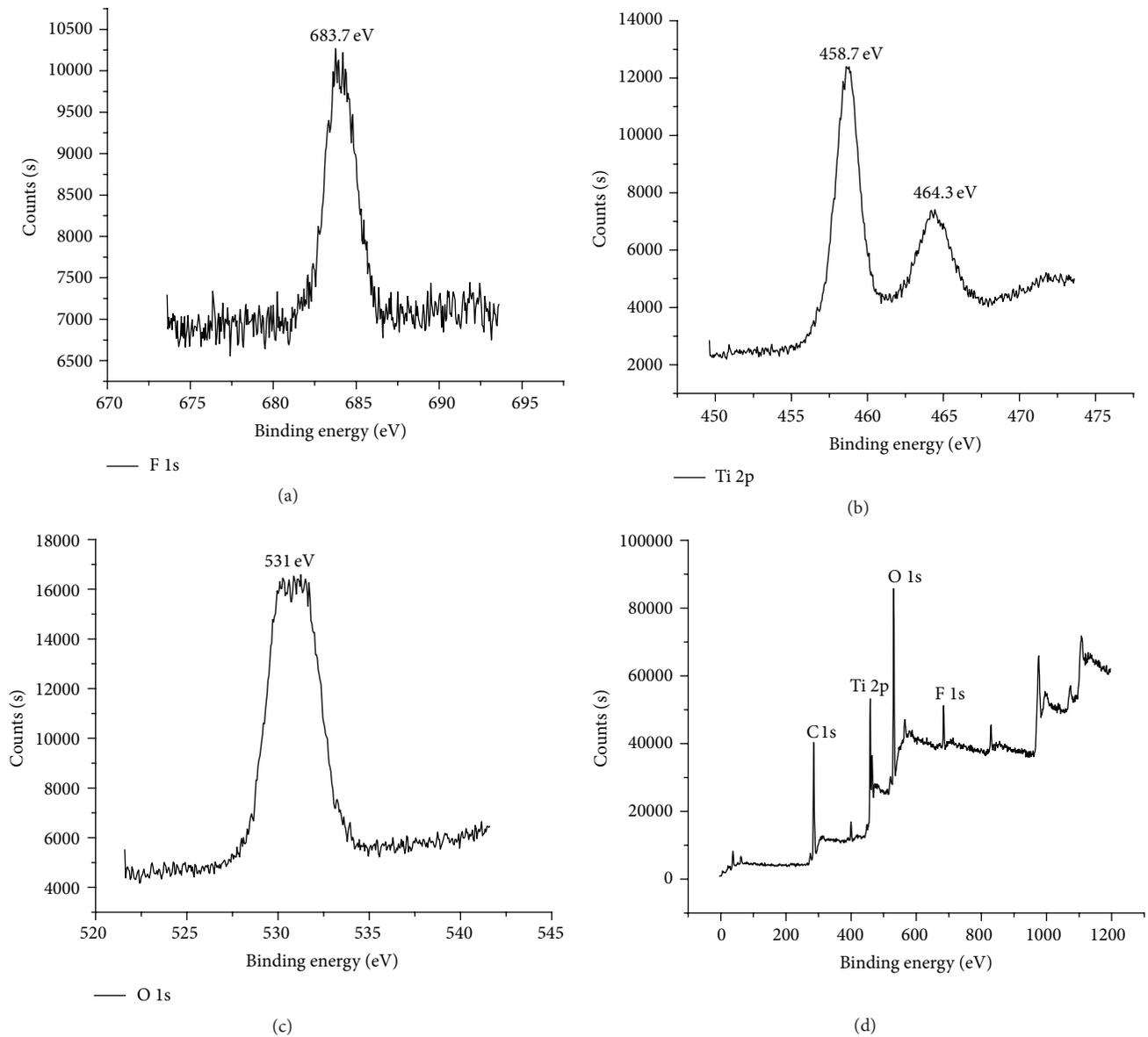


FIGURE 5: XPS spectra of fibers of sample F4 before calcination: (a) F 1s, (b) Ti 2p, (c) O 1s spectra, and (d) spectrum for all the elements in the fiber.

TABLE 1: Elements and atomic ratios of the micro-/nanostructured fibers obtained from sample F4 after calcination at 500°C for 5 hours in a crucible covered with a cap.

Elements	Atomic ratio (%)
C 1s, 284.8 eV	18.91
O 1s, 529.7 eV	57.39
Ti 2p, 458.4 eV	23.7

F0, F2, F4, and F6. From Figure 4, we can see that different samples of TiO<sub>2</sub> fibers exhibited similar mixed anatase and rutile phases (PDF cards 75–1537 and 75–1755, JCPDS). The peaks attributed to the TiO<sub>2</sub> anatase and rutile phases become

stronger with increasing TiF<sub>4</sub> mass ratio in the precursor solution.

**3.2. Mechanism of the Formation of Micro-/Nanocomposite TiO<sub>2</sub> Fibers.** Before calcination but after electrospinning, XPS results of the obtained fibers show that there is an F 1s peak located at 683.7 eV (Figure 5(a)), which could be attributed to F<sup>-</sup> ions physically adsorbed on the surfaces of the fibers [27, 28]. The Ti 2p peaks are located at 458.7 eV and 464.3 eV, which shows that the Ti element is in the Ti<sup>4+</sup> form. The O 1s region is located at 531 eV, which results from the O<sup>2-</sup> in the TiO<sub>2</sub> and hydroxyl groups on the surface of the sample. Therefore, before calcination, TiF<sub>4</sub>, HF, and TiO<sub>2</sub> are probably present in the fibers. After calcination in air, we only obtained

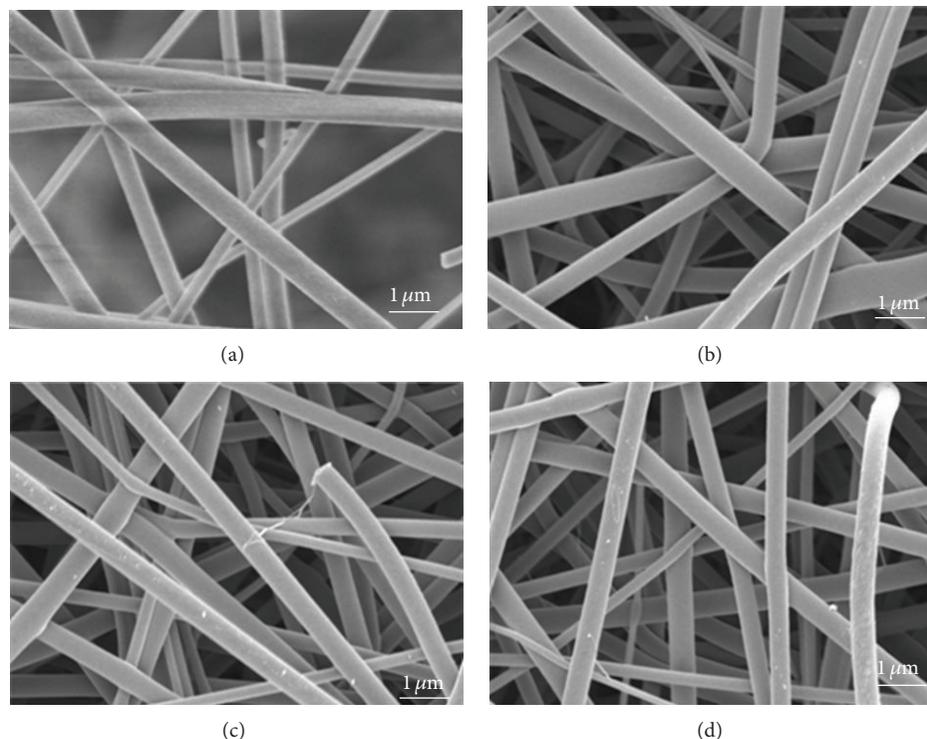


FIGURE 6: SEM images of fibers obtained from samples (a) F0, (b) F2, (c) F4, and (d) F6 after calcination at 500°C for 5 hours in air.

smooth fibers (Figure 6). The XPS results showed that there was no F in the smooth fibers, because there is no peak at 684 eV or 691 eV (Figure 7(a)). The smooth fibers were mainly composed of TiO<sub>2</sub> because Ti element is mainly in the Ti<sup>4+</sup> form and O is mainly in the O<sup>2-</sup> form (Figures 7(b)–7(d)). When calcination was carried out in a crucible covered with a cap, micro-/nanostructured TiO<sub>2</sub> fibers formed, in which there was also no F element.

From all of these facts, we deduce that, during the electrospinning and calcination, the TiF<sub>4</sub> in the fibers obtained from the precursor solution hydrolyzes by moisture in the air and HF is produced:



In air, the density of HF is low and it has little influence on the fibers. However, when the fiber is calcined in a crucible covered with a cap, the density of HF can be kept relatively high. Absorption of HF is known to be beneficial for the formation of TiO<sub>2</sub> crystals [29–31], so micro-/nanostructured TiO<sub>2</sub> fibers are obtained after calcination in a crucible covered with a cap. The more TiF<sub>4</sub> there is in the precursor solution, the higher the HF density is in the calcination process. Therefore fibers obtained from precursor solutions containing more TiF<sub>4</sub> will have more nanocrystals formed on the surface. In our experiment, sample F6 has a high TiF<sub>4</sub> mass ratio and, in the calcination process, the majority of TiO<sub>2</sub> once in the fiber morphology will gradually be transformed into nanocrystals with the assistance of the high HF density atmosphere. Therefore the samples obtained from fibers F6 are mainly composed of nanocrystals and cannot

maintain the nanoparticle-on-fiber morphology any more (Figure 2(d)).

We further investigated the effect of calcination time on the formation of micro-/nanostructured fibers. Figure 8 shows SEM images of the micro-/nanostructured fibers obtained from samples F4 after calcination for 4, 5, and 6 hours. All of these samples exhibited the micro-/nanostructure, and the quantity of nanoparticles increased with increasing calcination time. When the calcination time was 6 hours, the TiO<sub>2</sub> once constructed for the fibers has grown into nanoparticles; therefore the surfaces of the samples were entirely composed of nanoparticles.

The powder X-ray diffraction (XRD) patterns (Figure 9) show that the anatase and rutile phase peaks of the micro-/nanostructured fibers increase in intensity with the increasing of calcination time, which means that a longer calcination time is beneficial for the crystallization of TiO<sub>2</sub> fibers. The reason for this can be explained as follows: as for fibers calcined for a long time, the HF produced from the decomposition of TiF<sub>4</sub> will have a long time to react with the TiO<sub>2</sub> fibers, so there will be more TiO<sub>2</sub> crystals formed on the fiber surfaces.

**3.3. Enhanced Photocatalytic Ability of the Micro-/Nanostructured TiO<sub>2</sub> Fibers.** Figure 10 shows the UV-vis absorption spectra of the micro-/nanocomposite TiO<sub>2</sub> fibers obtained from precursor solutions with different mass ratios of TiF<sub>4</sub>. Compared with the smooth TiO<sub>2</sub> fibers (fibers obtained from sample F0 after calcination), there is no obvious shift in the fundamental absorption edge of the

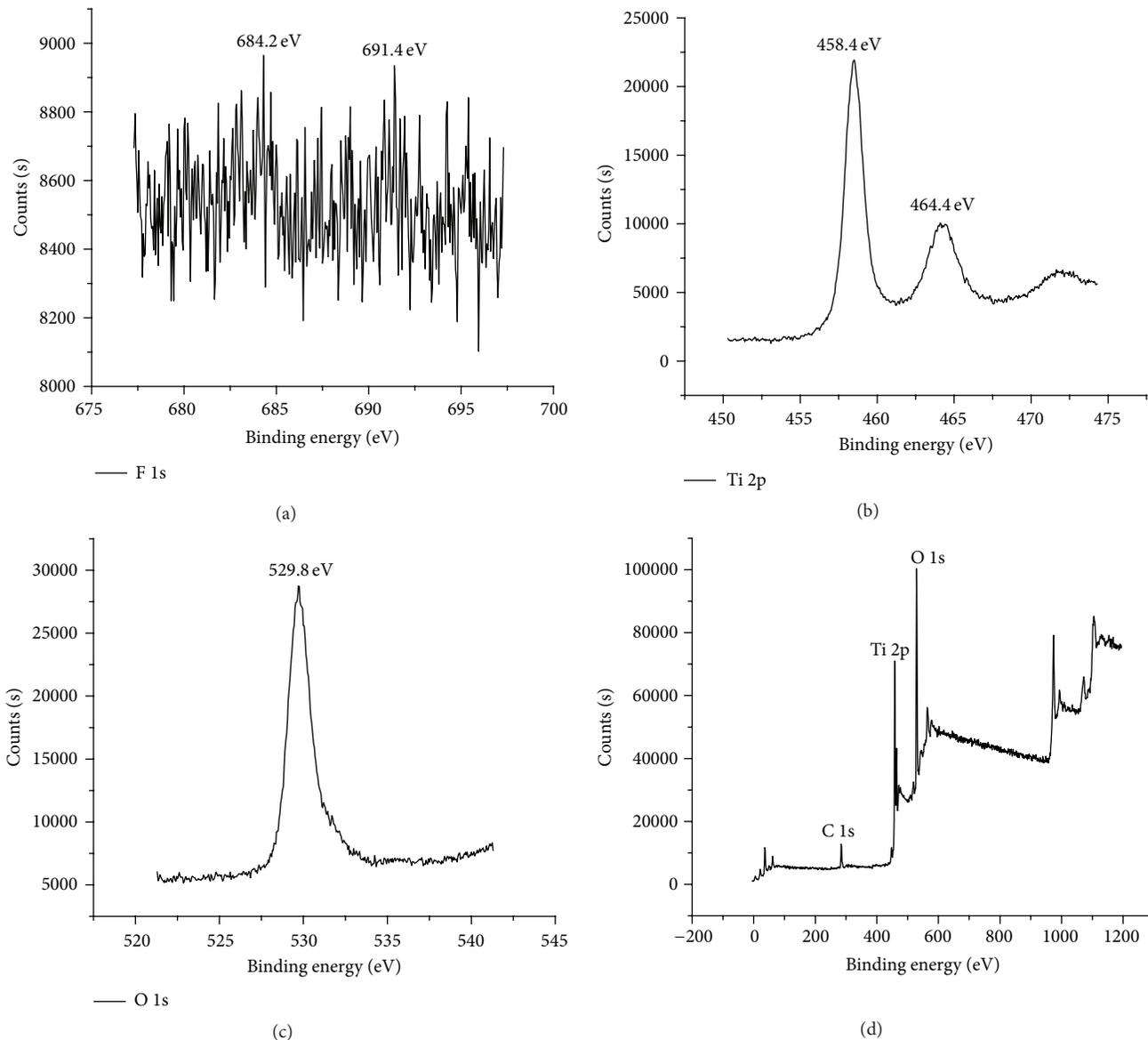


FIGURE 7: XPS spectra of sample F4 after calcination at 500°C for 5 hours in air: (a) F 1s, (b) Ti 2p, (c) O 1s spectra, and (d) spectrum for all the elements in the fiber.

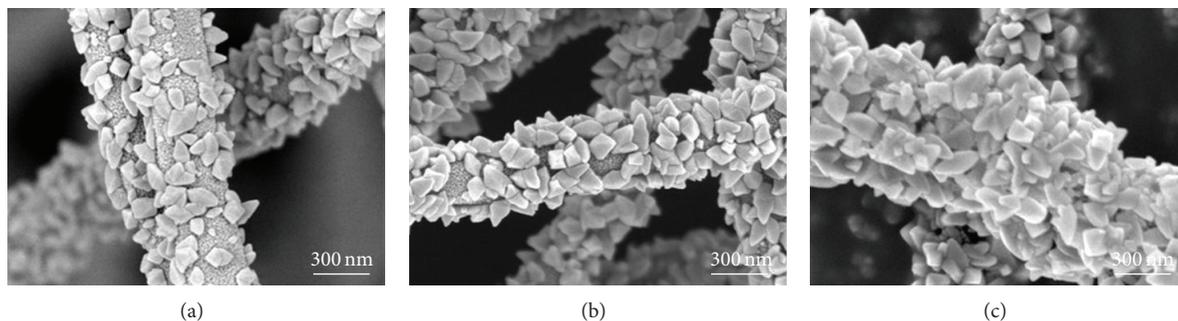


FIGURE 8: SEM images of micro-/nanostructured fibers obtained from sample F4 after calcination in a crucible covered with a cap at 500°C for different times: (a) 4 hours, (b) 5 hours, and (c) 6 hours.

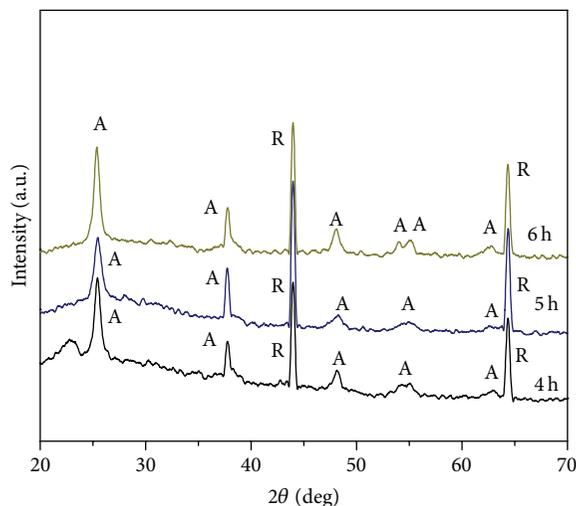


FIGURE 9: Powder X-ray diffraction patterns of micro-/nanostructured fibers obtained from sample F4 after calcination in a crucible covered with a cap at 500°C for 4, 5, and 6 hours.

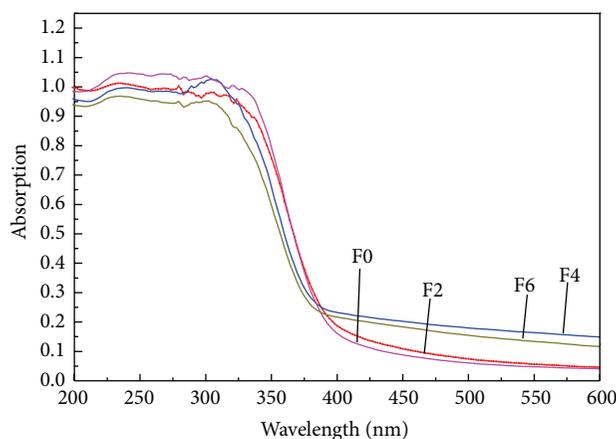


FIGURE 10: UV-vis absorption spectrum of the micro-/nanostructured fibers obtained from samples F0, F2, F4, and F6 after calcination for 5 hours in a sealed crucible.

micro-/nanostructured  $\text{TiO}_2$  fibers (fibers obtained from F2, F4, and F6 after calcination). The micro-/nanostructured  $\text{TiO}_2$  fibers obtained from samples of F2, F4, and F6 showed enhanced light absorption at wavelengths larger than 350 nm, which is probably due to the C elements in the micro-/nanostructured fibers (Figure 3(d)).

The photocatalytic activity of the micro-/nanostructured  $\text{TiO}_2$  fibers was evaluated by using them to catalyze the degradation of rhodamine 6G. For each fiber sample, we calculated the initial rate constant ( $k$ ) of rhodamine 6G degradation. The photocatalytic degradation of rhodamine 6G by  $\text{TiO}_2$  is found to follow first-order kinetics, because the plot of  $\ln(C_0/C_t)$  versus photocatalytic reaction time in our experiment is linear (Figure 11). Here  $C_t$  is the concentration of rhodamine 6G after a photocatalytic reaction time  $t$  in minutes, and  $C_0$  is the initial concentration of rhodamine 6G. According to Figure 11, we obtained  $k(\text{F0})$ ,  $k(\text{F2})$ , and  $k(\text{F4})$  as  $-0.003$ ,  $-0.00493$ , and  $-0.008$ , respectively. The absolute

value of  $k(\text{F4})$  is larger than that of  $k(\text{F2})$ , and the absolute value of  $k(\text{F2})$  is larger than that of  $k(\text{F0})$ , so we can conclude that the initial rate constant for rhodamine 6G degradation increases with increasing number of nanocrystals on the fibers. This means that the photocatalytic activity of the micro-/nanostructured fibers increases with the quantity of nanocrystals on the fibers.

**3.4. Mechanism for the Enhanced Photocatalysis of the Micro-/Nanostructured Fibers.** We analyzed the difference between the smooth  $\text{TiO}_2$  microfibers and the micro-/nanostructured  $\text{TiO}_2$  fibers and arrived at the following reasons for the enhanced photocatalytic ability of the micro-/nanostructured fibers. First, the  $\text{TiO}_2$  nanocrystals on the surface of the fiber lead to a high surface area, which is beneficial to the photocatalytic activities because it provides a large reactive area and facilitates the absorption of the target species, which is rhodamine 6G in our case [32]. Therefore, the larger

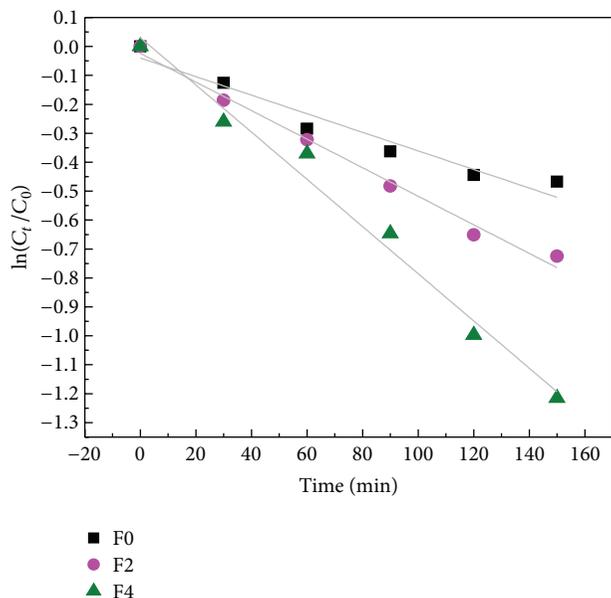


FIGURE 11: Kinetics data for the degradation of rhodamine 6G over micro-/nanostructured TiO<sub>2</sub> fibers obtained from samples F0, F2, and F4.

the surface area is, the higher catalytic efficiency the photocatalyst shows. Second, the micro-/nanocomposite fibers are composed of TiO<sub>2</sub> in anatase and rutile phases. The different band edges of these two phases help facilitate the charge separation and electron transfer in the photocatalytic process [33] and the multiphase composition in our sample could enhance the catalytic efficiency of the photocatalysts [34]. Therefore, the augment of the photocatalytic activity of the micro-/nanostructured fibers can be attributed to both the enlargement of surface area and the multiphase composition of TiO<sub>2</sub>.

#### 4. Conclusions

In summary, we successfully fabricated micro-/nanocomposite TiO<sub>2</sub> fibers using the electrospinning method and calcination. The nanoparticles resulted from the decomposition of the TiF<sub>4</sub> in the fibers left over from the precursor solutions. By changing the TiF<sub>4</sub> mass ratio in the precursor solution and the calcination time, we can control the quantity and size of the nanoparticles. The micro-/nanostructured TiO<sub>2</sub> fibers exhibited enhanced photocatalytic activity compared with smooth TiO<sub>2</sub> fibers because of the high surface area provided by the nanoparticles and the complex anatase and rutile phase composition. Since the micro-/nanostructured TiO<sub>2</sub> fibers exhibit enhanced photocatalytic activity and can be reclaimed easily, they will exhibit excellent photocatalytic performance for various applications.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

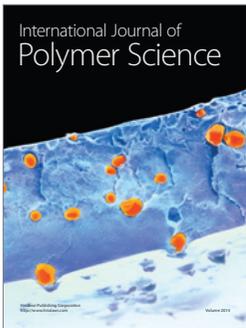
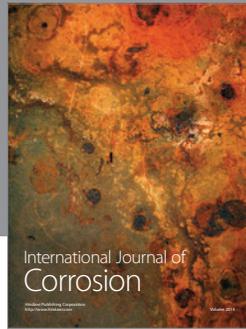
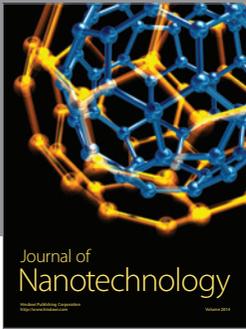
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