

SnO₂ Nanostructures-TiO₂ Nanofibers Heterostructures: Controlled Fabrication and High Photocatalytic Properties

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Combining the versatility of the electrospinning technique and hydrothermal growth of nanostructures enabled the fabrication of hierarchical SnO₂/TiO₂ composite nanostructures. The results revealed that not only were secondary SnO₂ nanostructures successfully grown on primary TiO₂ nanofiber substrates but also the SnO₂ nanostructures were uniformly distributed without aggregation on TiO₂ nanofibers. By adjusting fabrication parameters, the morphology as well as coverage density of secondary SnO₂ nanostructures could be further controlled, and then SnO₂/TiO₂ heterostructures with SnO₂ nanoparticles or nanorods were facilely fabricated. The photocatalytic studies suggested that the SnO₂/TiO₂ heterostructures showed enhanced photocatalytic efficiency of photodegradation of Rhodamine B (RB) compared with the bare TiO₂ nanofibers under UV light irradiation.

1. Introduction

TiO₂ has been well-known as an excellent photocatalytic material which can find applications in various fields including water splitting, environmental purification, self-cleaning and superhydrophilic surfaces, sensors, and disinfection.^{1–6} However, enhancing the photocatalytic efficiency of TiO₂ to meet the practical application requirements is still a challenge because of the bottleneck of poor quantum yield caused by the rapid recombination of photogenerated electrons and holes. Much effort has been made to increase the electron–hole pair separation efficiency. Therein, TiO₂ based homostructure and heterostructure such as anatase/rutile homo-

structure,⁷ noble metal (Ag,⁸ Au,⁹ Pt,¹⁰ Pd,¹¹ etc.)/TiO₂, carbon (nanotube,¹² nanowall,¹³ nanofiber,¹⁴ graphene,¹⁵ etc.)/TiO₂, M_xO_y (ZnO,¹⁶ SnO₂,¹⁷ etc.)/TiO₂ and M_xS_y (CdS,¹⁸ PbS,¹⁹ etc.)/TiO₂ heterostructures have received the most attention recently because of their excellent catalytic activity. Among the semiconductor/TiO₂ systems, SnO₂/TiO₂ heterostructure attracts much interest in particular because of their structural analogy. That is, both oxides TiO₂ and SnO₂ belong to the same crystal symmetry (tetragonal) and have two molecular units per primitive unit cell (*Z* = 2).²⁰ Additionally, the band gap of SnO₂ (*E*_g = 3.5–3.6 eV) is higher than that of TiO₂ (*E*_g = 3.0 eV for rutile, *E*_g = 3.2 eV for anatase), but the conduction band (CB) of SnO₂ (*E*_{CB} for SnO₂ = 0 V versus NHE at pH 7) is lower than that of TiO₂ (*E*_{CB} for TiO₂ = –0.5 V versus NHE at pH 7). As a consequence, in the SnO₂/TiO₂ heterostructure, the interface between SnO₂ and TiO₂ is a “type II heterojunction”, meaning that the valence band (VB) of TiO₂ is positioned (energetically) between the VB and CB of SnO₂, and the CB of TiO₂ is positioned above the VB and CB of SnO₂.

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Table 1. Experimental Conditions, SnO₂ Nanostructure Characteristics, and Chemical Component of the Prepared Composite Samples

sample	[SnCl ₄] (mM)	temperature (°C)	morphology	crystal size (nm)	Sn/Ti ratio
					starting (actual ^a)
TS1	0.6	150	nanoparticles	50	1:10 (1:9.90)
TS2	1.2	150	nanoparticles	70	1:5 (1:5.00)
TS3	0.6	200	nanorods	30–60 × 150–250	1:10 (1:9.78)

^aThe value is determined by EDX.

When both SnO₂ and TiO₂ are activated simultaneously, the practical implication of this “staggered” configuration of energy levels is that the CB of SnO₂ acts as a sink of photogenerated electrons. Since the photogenerated holes move in the opposite direction, they accumulate in the VB of TiO₂, and thereby hinder charge recombination and improve photocatalytic efficiency.

Besides, very recently, electrospun TiO₂ nanofibers have been the focus of research.^{21–24} TiO₂ nanofibers have opened a wide spectrum of new possibilities for high photocatalytic activity and easy recovery. Moreover, the electrospun nanofibers with both high porosity and large surface area being available for reaction are promising materials for surface modification and functionalization. Motivated by the above concerns, in this work we fabricate SnO₂/TiO₂ heterostructured photocatalysts based on TiO₂ nanofibers by combining the electrospinning technique with the hydrothermal method. The adopted synthesis route ensures not only the successful growth of SnO₂ nanostructures on TiO₂ nanofibers substrate but also the high dispersion of SnO₂ nanostructures on TiO₂ nanofibers without aggregation. By simply tuning the precursor concentration or reaction temperature, we can vary the coverage density as well as the morphology of nanostructured SnO₂ (nanoparticles or nanorods), aiming at assessing the photocatalytic application potential of SnO₂/TiO₂ heterostructure. Furthermore, owing to its simple, cost-effective, and environmental-friendly process, the synthetic strategy may be fairly applicable for the synthesis of other TiO₂ nanofibers based heterostructures. Last, the photocatalytic characteristics of the as-obtained SnO₂/TiO₂ heterostructures are investigated by measuring the degradation of dye RB and compared with those of the pure electrospun TiO₂ nanofibers.

2. Experimental Section

2.1. Preparation of TiO₂ Nanofibers. One milliliter of titanium butyloxide was mixed with 1.5 mL of acetic acid and 5 mL of ethanol. Then the homogeneous solution was added to poly(vinyl pyrrolidone) (PVP) solution of about 8 wt %, followed by vigorous stirring at room temperature for 4 h. Composite PVP/titanium butyloxide nanofiber film was fabricated by electrospinning from a syringe at an applied electric voltage of 10 kV. TiO₂ nanofibers were obtained after annealing of the obtained composite nanofibers in the air at 500 °C for 12 h.

2.2. Fabrication of SnO₂/TiO₂ Heterostructures. In a typical procedure, 10 mg of the electrospun TiO₂ nanofibers were put into an autoclave containing 20 mL of SnCl₄–H₂O–C₂H₅OH

solution. The concentration of the SnCl₄ solution was fixed at 0.6 mmol L⁻¹. The pH value of the solution was adjusted to 10 by a 0.1 M NaOH aqueous solution. The autoclave was maintained at 150 °C for 12 h and then allowed to cool to room temperature. The as-fabricated products were collected out, washed with ethanol and deionized water, respectively, and then dried in an oven at 60 °C for 12 h. By this method, three samples of SnO₂/TiO₂ heterostructures were fabricated, and then were denoted as TS1, TS2, and TS3, respectively. The detailed experimental conditions were listed in Table 1. In addition, for simplicity, pure TiO₂ nanofibers were denoted as TS0.

2.3. Characterization. X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku, D/max-2500 X-ray diffractometer. Field emission scanning electron microscope (FESEM, Hitachi S-4800) was used to observe morphology of samples. Energy dispersive X-ray (EDX) spectroscopy being attached to scanning electron microscopy (SEM) was used to analyze the composition of samples. The high-resolution transmission electron microscopy (HRTEM) images were acquired using a JEOL JEM-2100 (acceleration voltage of 200 kV). X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALAB LKII instrument with Mg K α -ADES ($h\nu = 1253.6$ eV) source at a residual gas pressure of below 10⁻⁸ Pa. FT-IR spectra were obtained on Magna 560 FT-IR spectrometer. The photoluminescence (PL) spectra of photocatalysts were detected with a Jobin Yvon HR800 micro-Raman spectrometer using a 325 nm line from a He–Cd laser.

2.4. Photocatalytic Test. The photoreactor was designed with an internal light source (50 W high pressure mercury lamp with main emission wavelength 313 nm and an average light intensity of 2.85 mW cm⁻²) surrounded by a water-cooling quartz jacket to cool the lamp, where a 100 mL of the RB solution with an initial concentration of 10 mg L⁻¹ in the presence of solid catalyst (0.01 g). The solution was stirred in the dark for 30 min to obtain a good dispersion and reach adsorption–desorption equilibrium between the organic molecules and the catalyst surface. Decreases in the concentrations of dyes were analyzed by a Cary 500 UV–vis–NIR spectrophotometer at $\lambda = 554$ nm. At given intervals of illumination, the samples of the reaction solution were taken out and analyzed.

3. Results and Discussion

Figure 1a presents the SEM image of sample TS0. It can be clearly seen that the TiO₂ non-woven nanofibers are of relatively smooth surface without secondary nanostructures. The diameter of the fibers ranges from 200 to 400 nm. SEM image of the sample TS1 shown in Figure 1b indicates that there is essentially no change to the non-woven nanofibers' morphology during the growth of the SnO₂ nanoparticles. Moreover, the nanoparticles are uniformly distributed across the surface of each fiber without aggregation, offering high level exposure of the nanoparticle surface. It is worth pointing out that the high porosity and large surface area of TiO₂ non-woven nanofibers are advantageous for uniform growth and distribution of SnO₂ nanoparticles on the surface of TiO₂ nanofibers. The diameter of SnO₂ nanoparticles is about 50 nm. The EDX spectrum in Figure 1c demonstrates the

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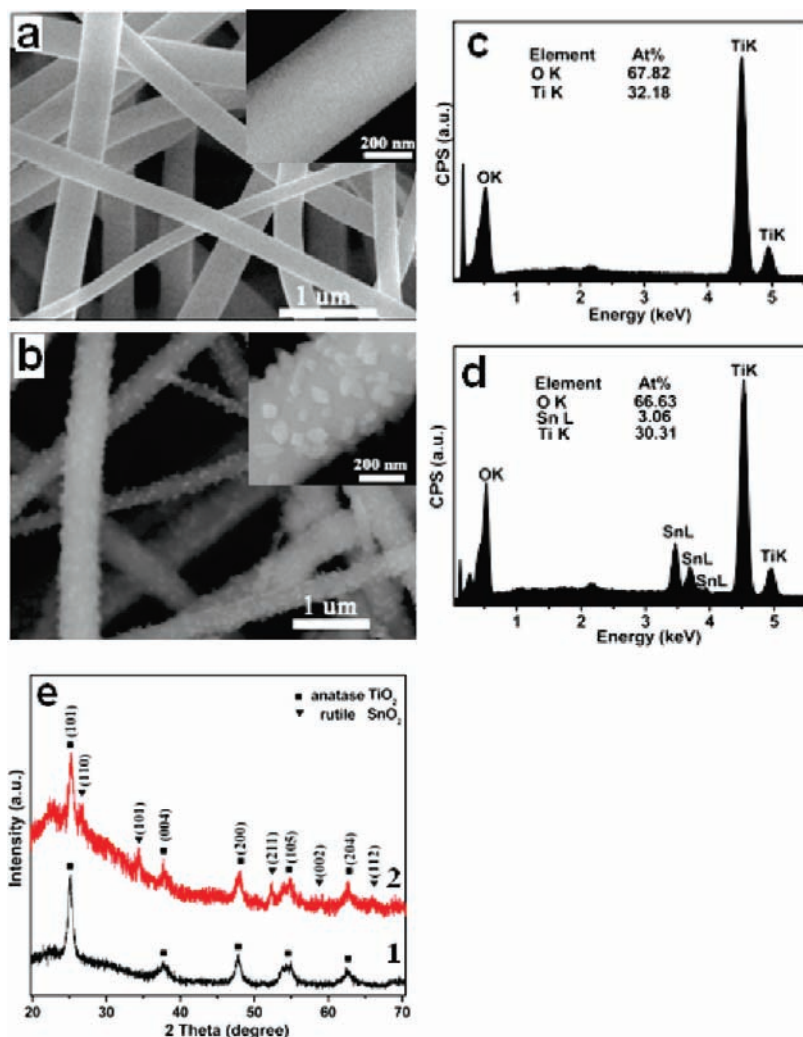


Figure 1. SEM images of sample (a) TS0 and (b) TS1; EDX spectra of sample (c) TS0 and (d) TS1; (e) XRD patterns of (1) sample TS0 and (2) TS1.

high purity of TiO₂ nanofibers. As expected, the atomic ratio of Ti to O is close to 1:2. In Figure 1d, the existence of the tin element is detected in the SnO₂/TiO₂ composite. Five different places of the SnO₂/TiO₂ heterostructures surface are analyzed by EDX, and the atomic ratio of Sn to Ti is about 1:10, confirming the uniformity of the SnO₂ nanoparticles grown on the TiO₂ nanofibers. XRD patterns of TS0 and TS1 are shown in Figure 1e. The curve 1 reveals that the crystal phase of TiO₂ nanofibers is anatase (JCPDS No. 21-1272). The curve 2 indicates that all the diffraction peaks of the SnO₂/TiO₂ heterostructures can be well indexed as rutile SnO₂ (JCPDS No. 41-1445) and the anatase TiO₂. No other impurity peaks are detected, indicating the non-existence of other impurities such as SnO, orthorhombic SnO₂, or rutile TiO₂. It is obvious that the synthesis route adopted successfully achieves SnO₂/TiO₂ heterostructure integrating the rutile phase SnO₂ with the anatase TiO₂.

TEM was used to investigate the microstructure of the sample TS1 composite in more detail. Figure 2a shows that SnO₂ nanoparticles are uniformly attached on the TiO₂ nanofibers surface, and the selected circular area is enlarged (Figure 2b). It can be observed that the diameter of SnO₂ nanoparticles is about 50 nm, which is in agreement with the SEM analysis above. A high-resolution image of the SnO₂/TiO₂ heterostructure (Figure 2c) reveals the simultaneous

presence of crystalline TiO₂ and SnO₂ crystal lattices in the region of the junction. The fringes observed correspond to the interplanar distances of 0.35 and 0.26 nm, which agree well with the lattice spacing of the (101) and (101) low-index facets of the anatase TiO₂ and rutile SnO₂ crystal, respectively. Figure 2d shows the further magnified HRTEM image of the SnO₂ crystal; the measured lattice spacing of 0.26 nm can be clearly observed. These results confirm that the heterostructures are well formed between SnO₂ nanoparticles and TiO₂ nanofibers.

The chemical composition and purity of the sample TS1 composite was studied and compared with that of the sample TS0 by XPS analysis. The fully scanned spectra (Figure 3a) demonstrate that Ti, O, and C elements exist in bare TiO₂ nanofibers, while Ti, Sn, O, and C exist in SnO₂/TiO₂ heterostructures, respectively. The C element can be ascribed to the adventitious carbon-based contaminant, and the binding energy for the C1s peak at 284.6 eV is used as the reference for calibration. The high resolution XPS spectra with scanning over the following areas are analyzed: the binding energies for the Ti 2p region around 460 eV, the Sn 3d region around 490 eV, and the O 1s region around 530 eV. As shown in Figure 3b, there are two peaks in the Ti 2p region. The peak located at 464.2 eV corresponds to the Ti 2p_{1/2} and another one located at 458.5 eV is assigned to Ti 2p_{3/2}. The

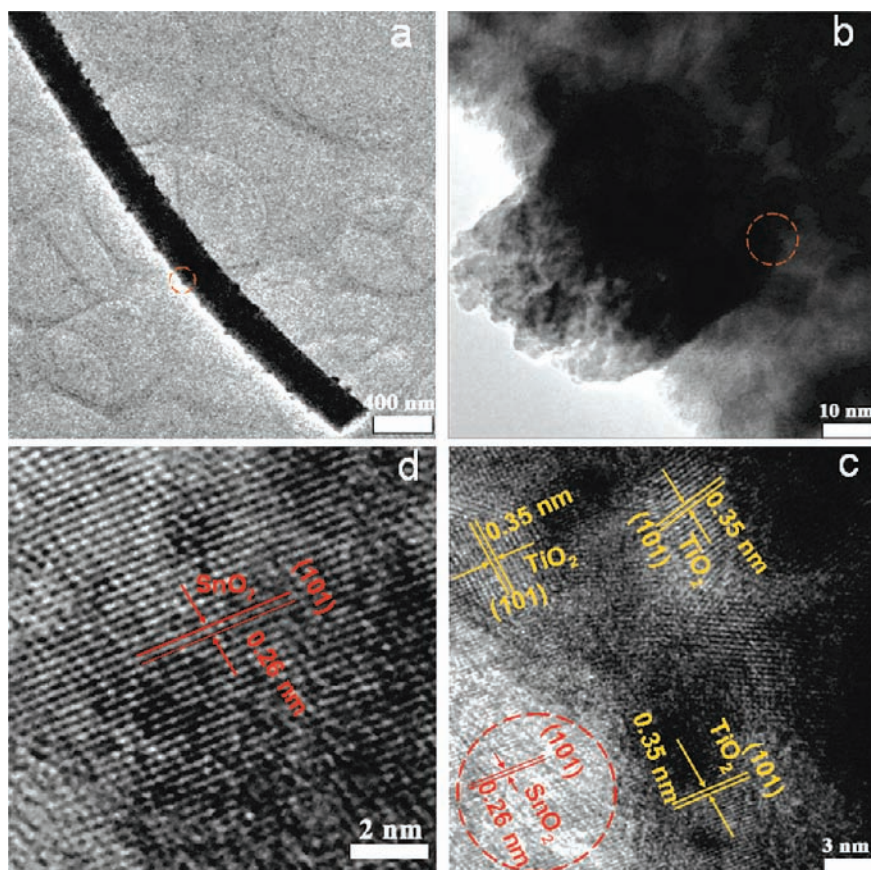


Figure 2. (a,b) TEM image of sample TS1 at different magnification. (c) HRTEM of the SnO₂/TiO₂ heterojunction region. (d) HRTEM of SnO₂ nanoparticles.

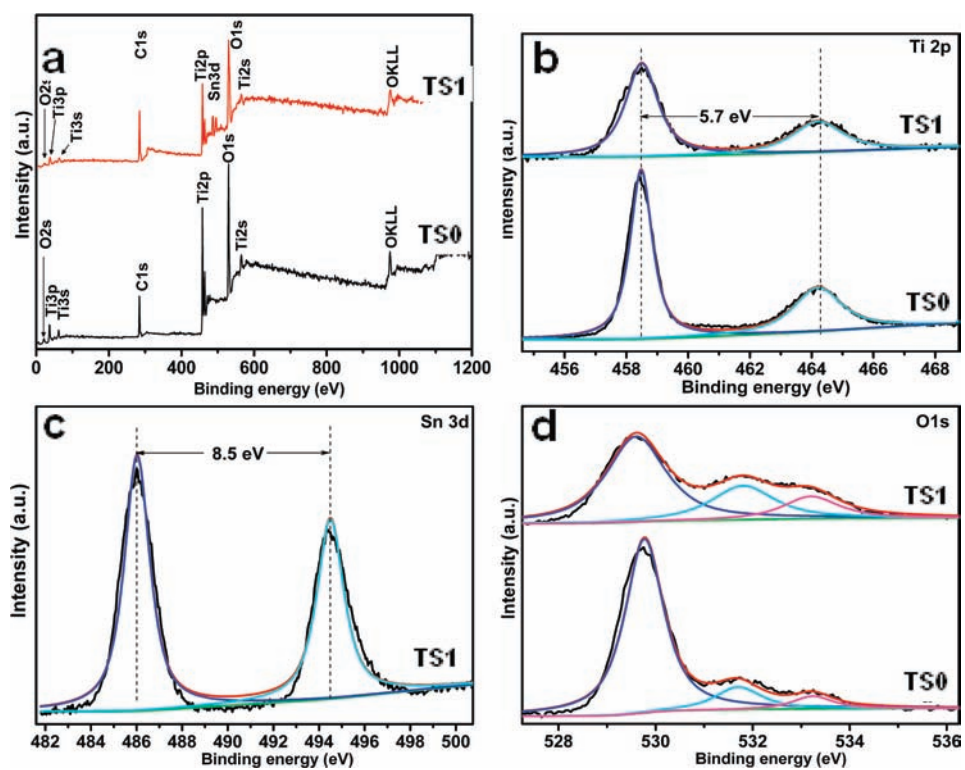


Figure 3. (a) XPS fully scanned spectra of the sample TS0 and TS1. (b) XPS spectra of Ti 2p for the sample TS0 and TS1. (c) XPS spectra of Sn 3d for the sample TS1. (d) XPS spectra of O 1s for the sample TS0 and TS1.

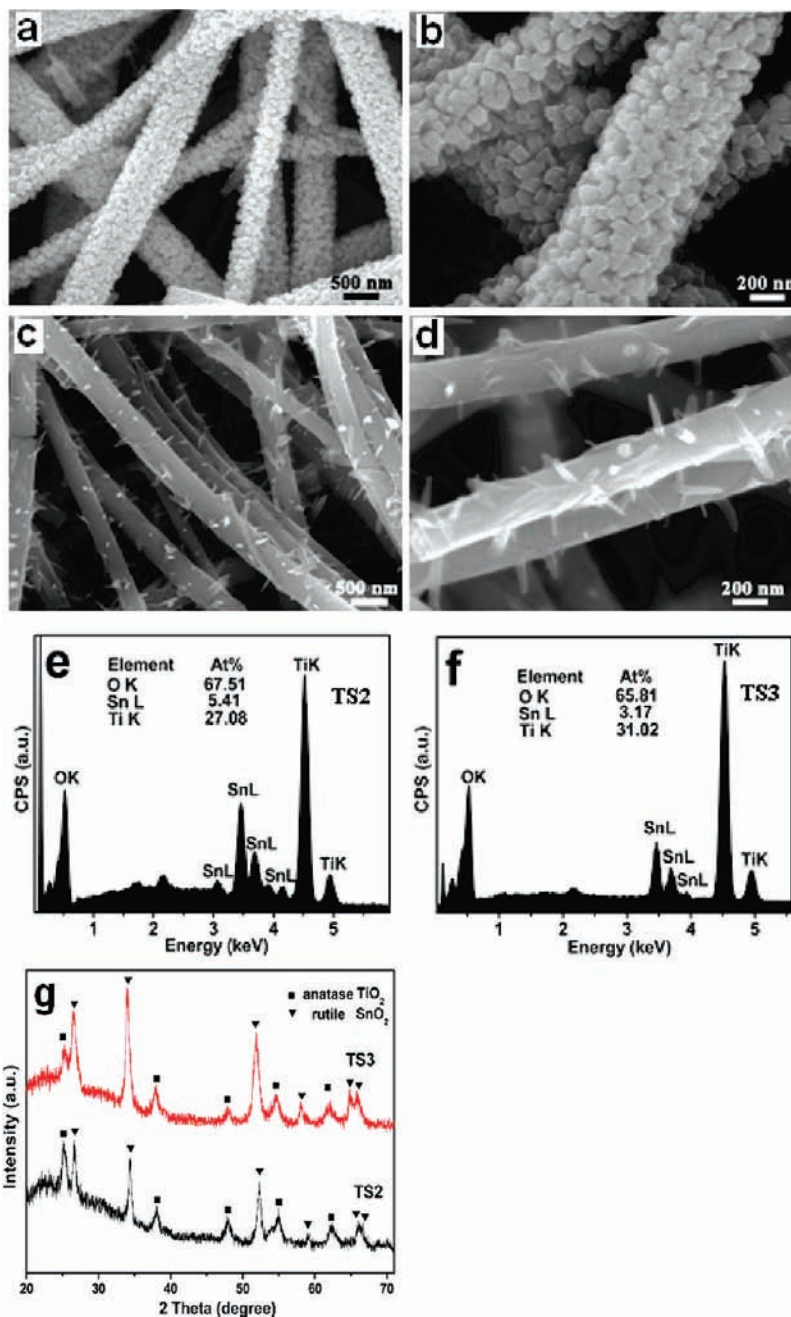


Figure 4. (a,b) SEM images of the sample TS2; (c,d) SEM images of the sample TS3; (e,f) EDX spectra of the sample TS2 and TS3; (g) XRD patterns of sample TS2 and TS3.

splitting between Ti 2p_{1/2} and Ti 2p_{3/2} is 5.7 eV, indicating a normal state of Ti⁴⁺ in the as-prepared SnO₂/TiO₂ heterostructures. Besides, the peaks for Ti 2p in the composite show no shift compared with that in bare TiO₂, confirming that the structure of TiO₂ remains intact after synthesis of SnO₂ nanoparticles. In Figure 3c, the Sn 3d_{5/2} peak is located at 486.0 eV and the Sn 3d_{3/2} peak is found at 494.5 eV. Moreover, the splitting of the 3d doublet of Sn is 8.5 eV, indicating that the valence state of Sn is +4. The atomic number ratio of Sn to Ti is about 0.1, as determined from our experimental XPS peak areas and their relative sensitivity factors, which is in good agreement with the EDX results above. Figure 3d presents the O 1s photoelectron peaks. The shape of a wide and asymmetric peak of O 1s spectrum indicates that there can be more than one chemical state according to the binding

energy. It includes crystal lattice oxygen (O_{Ti-O} or O_{Sn-O}), surface hydroxyl groups (O_{OH}), and adsorbed water with increasing binding energy. Using the XPS Peak fitting program, version 4.1, each O 1s XPS spectrum is fitted to three kinds of chemical states. After calculation, the apparent O_{OH}/O_{Ti-O} ratio is determined to be 0.44 for the TS1 composite, which is three-times higher than that of TS0. FT-IR spectra were also further utilized to detect the surface OH groups and water adsorption on the surface of the sample (not shown). For the SnO₂/TiO₂ composite, an overlapped broad peak of high intensity at 3375 cm⁻¹ is observed, which is characterized as surface Ti-OH and hydrogen-bonded molecular H₂O species. On the other hand, for the pure TiO₂ nanofibers, the intensity of the surface hydroxyl group band at 3375 cm⁻¹ is significantly decreased compared with that of

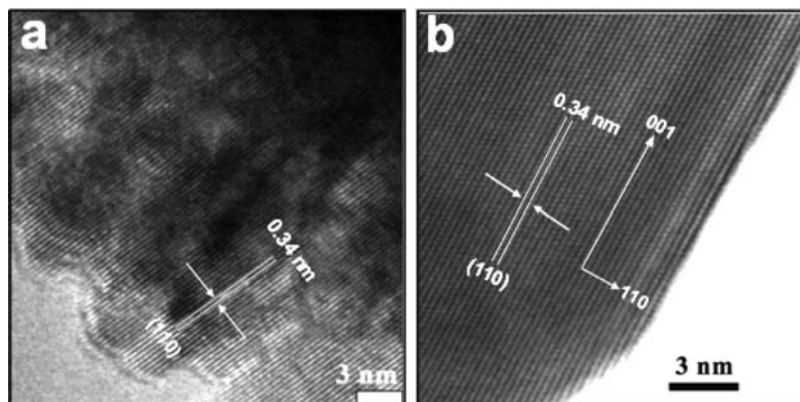


Figure 5. HRTEM images of (a) SnO₂ nanoparticles of the sample TS2 and (b) SnO₂ nanorods of the sample TS3.

the SnO₂/TiO₂ composite. Thus, it can be deduced that the amounts of surface OH groups on the surface of the composite are significantly increased by the modification of SnO₂ based on the analyses of XPS and IR. The increasing amount of surface hydroxyl group in the SnO₂/TiO₂ composite may originate from the high dispersion and hygroscopic nature of the SnO₂ nanostructure. In other words, the adsorption affinity of SnO₂ to water is much stronger than that of TiO₂. In comparison with TiO₂, SnO₂ is very sensitive to water. SnO₂ has been extensively used as a moisture sensor for this very reason.

By tuning the experimental parameters including precursor concentration and temperature, the secondary SnO₂ nanostructures grown on TiO₂ nanofibers with different density and shapes can be further controlled. Panels a and b of Figure 4 show the SEM images of the sample TS2. It can be observed that the density of the nanoparticles is dramatically increased when the precursor concentration [SnCl₄] is increased to 1.2 mmol L⁻¹. At the same time, the diameters of the grown nanoparticles also change from 50 to 70 nm. On the other hand, when the precursor concentration is 0.6 mmol L⁻¹ and the growth temperature is increased to 200 °C, the morphology of secondary SnO₂ nanostructures grown on TiO₂ nanofibers changes significantly. Panels c and d of Figure 4 show the SEM images of the as-fabricated sample TS3. It can be observed that SnO₂ nanorods instead of nanoparticles are grown on the nanofiber substrates. The nanorods have diameters of 30–60 nm and lengths of 150–250 nm. In addition, for the as-fabricated sample TS2 and TS3, the atomic ratio of Sn to Ti is about 1:5 and 1:10, respectively, as determined by the EDX analysis (Figure 4e,f). As expected, it is in agreement with the stoichiometric composition. Figure 4g shows the XRD patterns of TS2 and TS3. The diffraction peaks indicate the SnO₂/TiO₂ composites to be a mixture of rutile SnO₂ and anatase TiO₂ phases with no other impurity phases, suggesting that neither appreciable chemical reaction between TiO₂ and SnO₂ nor anatase-to-rutile phase transition occurs during the synthesis of the SnO₂ nanostructures.

To further study the fine structures of the as-grown SnO₂ nanoparticles and nanorods, HRTEM was analyzed. The typical HRTEM images of an individual nanoparticle and nanorod are shown in Figure 5, panels a and b, respectively. Both the images reveal that the lattice spacings are 0.34 nm, which are related to the (110) plane of tetragonal rutile SnO₂. Meanwhile, Figure 5b clearly indicates that the SnO₂ nano-

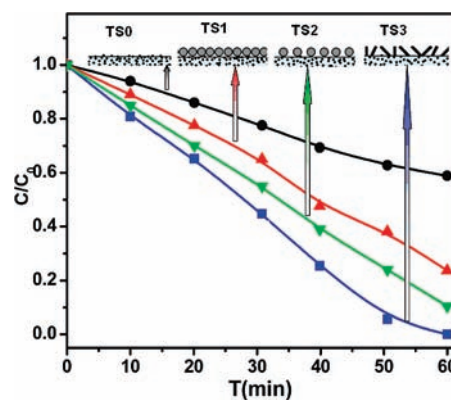


Figure 6. Curves of photocatalytic degradation of RB over different catalysts.

rods are highly crystallized with few defects and grow along [001] direction. Since there is neither a template nor a surfactant in the synthesis system, it is reasonable to hypothesize that the driving forces for the growth of 1D SnO₂ nanorods come from the inherent crystal structure of SnO₂. For the rutile structure of SnO₂, the sequence of surface energy per crystal face can be described as (110) < (100) < (101) < (001) according to the calculated data.²⁵ Accordingly, the surfaces of (110) and (001) have the lowest and the highest surface energy, respectively, thereby the low-index (110) face is the thermodynamically most-stable bulk termination. It can properly explain the preferential growth of SnO₂ along the [001] direction in thermodynamic aspects.

The photocatalytic degradation of rhodamine B has been chosen as a model reaction to evaluate the photocatalytic activities of the present SnO₂/TiO₂ heterostructures, and they are compared with that of the bare TiO₂ nanofibers. Figure 6 shows the degradation curves of RB on the SnO₂/TiO₂ heterostructures and bare TiO₂ nanofibers. In general, the SnO₂/TiO₂ heterostructures show enhanced photocatalytic activities in comparison with the bare TiO₂ nanofibers. The order of photocatalytic activities is TS3 > TS1 > TS2 > TS0.

Several reasons may account for the enhancement of the photocatalytic activity of the SnO₂/TiO₂ heterostructured photocatalyst. First, the high activity of the composite is related to the role of SnO₂ nanostructures on the surface of

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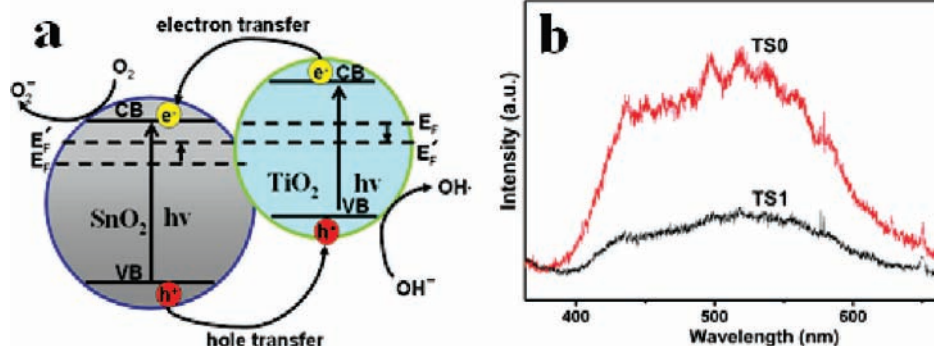
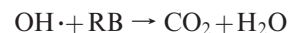
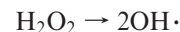
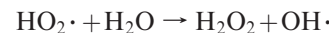
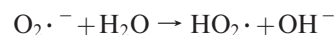
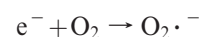


Figure 7. (a) Schematic diagram showing the energy band structure and electron–hole pair separation in the SnO₂/TiO₂ heterostructure. (b) PL emission spectra of TS0 and TS1.

TiO₂ nanofibers. A proposed mechanism for the enhanced photocatalysis of the SnO₂/TiO₂ composite is shown schematically in Figure 7a. To understand the charge transfer at the SnO₂/TiO₂ heterojunction, three relevant material properties of TiO₂ and SnO₂ including band gap, electron affinity, and work function are given. The band gap of anatase TiO₂ and rutile SnO₂ is 3.2 and 3.5 eV, respectively; the work function of TiO₂ is around 4.2 eV, its electron affinity is about 4.2 eV; the work function of SnO₂ is around 4.4 eV, its electron affinity is about 0.5 eV larger than that of TiO₂. Accordingly, a type II heterojunction is formed in the staggered arrangement at the SnO₂/TiO₂ interface. The Fermi energy level of TiO₂ is higher than that of SnO₂ because of its smaller work function, so that electron transfer occurs from the conduction band of light activated TiO₂ to the conduction band of light activated SnO₂ and, conversely, hole transfer can take place from the valence band of SnO₂ to the valence band of TiO₂. Because the Fermi level (E_F) of the semiconductor is directly related to the number of accumulated electrons, as illustrated by following: $E_F = E_{CB} + kT \ln nc/Nc$,²⁶ where E_{CB} is the conduction band energy, nc is the density of accumulated electrons, and Nc is the charge carrier density of the semiconductor, a negative shift in the Fermi level of the SnO₂ and a positive shift in the Fermi level of the TiO₂ would be expected. The efficient charge separation increases the lifetime of the charge carriers and enhances the efficiency of the interfacial charge transfer to adsorbed substrates, and then, account for the higher activity of the composite SnO₂/TiO₂ photocatalyst. On the contrary, in the absence of the SnO₂ nanostructures attached to the surface of the TiO₂ nanofibers, most of charges quickly recombine without doing any chemistry. Typically, only a small number of electrons (1%) and holes are trapped and participate in photocatalytic reactions, resulting in low reactivity. The better separation of electrons and holes in the SnO₂/TiO₂ heterostructures is confirmed by PL emission spectra of TS1 and TS0. (Figure 7b). It is found that TS1 exhibits much lower emission intensity than TS0, indicating that the recombination of photogenerated charge carrier is inhibited greatly in the SnO₂/TiO₂ heterostructures.

Second, the hypothetical mechanism is proposed for the photocatalytic degradation of RB as follows:



RB is initiated by the photoexcitation of the semiconductor system followed by the formation of the electron/hole pairs on the surface of the catalyst. Subsequent to various steps, the holes (h^+) are ultimately trapped by surface hydroxyl groups (or H₂O) at the catalyst surface to yield OH· radicals. Dissolved oxygen molecules react with conduction band electrons (e^-) to yield superoxide radical anions, O₂^{·-}, which on protonation generate the hydroperoxy, HO₂·, radicals, producing hydroxyl radical OH·, which is a strong oxidizing agent to decompose the organic dye.^{27,28} An important factor for the efficient photooxidation of organic substrates will depend on the concentration of OH· radicals by photooxidation of surface hydroxyl groups and/or chemisorbed H₂O.²⁹ As demonstrated by XPS and IR analysis above, the amount of surface hydroxyl groups for the SnO₂/TiO₂ heterostructure is larger than that of the bare TiO₂, and thereby leads to the enhancement of the photocatalytic activity of the heterostructured SnO₂/TiO₂ nanofibers.

Then why does TS2 show considerably lower activity than TS1? Although the heterojunction favors electron flow from TiO₂ to SnO₂ nanoparticles, higher surface coverage of SnO₂ nanoparticles decreases the accessibility of the active sites of the TiO₂ nanofibers surface, and thus in turn reduces the photoactivity. Moreover, SnO₂ itself is not effective as photocatalyst, which is in agreement with the previous report

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that TiO_2 showed high photocatalytic property while pure SnO_2 showed very low photocatalytic activity. Therefore, the photocatalytic activity of $\text{SnO}_2/\text{TiO}_2$ composites will decrease with the increase of SnO_2 contents when the SnO_2 content is loaded up to a certain level. Comparing the results for TS1 and TS3, which have the same composition, we suggest that the higher photocatalytic activity of the latter results from the higher crystallinity of SnO_2 nanocrystals. The higher crystallinity means fewer defects in the as-synthesized sample. It is well-known that lattice defects may act as recombination centers for photoinduced electrons and holes, thus significantly reducing the net photocatalytic activity.

4. Conclusion

The $\text{SnO}_2/\text{TiO}_2$ heterostructured photocatalyst have been fabricated via the electrospinning and hydrothermal methods. SEM and TEM reveal a uniform distribution of SnO_2 nanoparticles or nanorods on the TiO_2 nanofibers' surface and intimate contact between them. XPS demonstrates that there is a larger amount of surface hydroxyl groups for the

$\text{SnO}_2/\text{TiO}_2$ composite in comparison with the bare TiO_2 . The investigation of photocatalytic ability show that the $\text{SnO}_2/\text{TiO}_2$ composite possesses a higher photocatalytic activity than the bare TiO_2 for the degradation of RB dye under UV light irradiation because of the improvement of the separation of photogenerated electrons and holes, as well as the change of amount of surface hydroxyl groups of the catalyst. Moreover, the simple experimental procedure for the novel $\text{TiO}_2/\text{SnO}_2$ heterostructures is quite simple, environmentally benign, and cost-effective, permitting it to be used for the synthesis of future heterostructured photocatalysts.

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