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1. Introduction

In the past few decades, with the development of technology and the progress of society, various advanced technologies have been developed for environmental remediation. Among these strategies, photocatalytic reaction based on heterostructures has attracted extensive attention, and is regarded as a potential solution to the recent severe problems of environmental crises.^{1–3} Heterostructured nanomaterials based on engineered oxide–oxide or metal–oxide multimaterial junctions offer to enhance the functional performance by combining individual material characteristics, which had shown significant advantages when compared with their singlecomponent counterparts.⁴ Hence, it is timely and necessary to search for novel heterostructured nanomaterials with low cost and high performance.

Since Fujishima and Honda's first reports of UV-lightinduced redox chemistry on TiO_2 , the study of photocatalysts with the fascinating properties of nontoxicity and high chemical stability has drawn significant attention from the research and development communities.^{5–7} Extraordinarily, photocatalytic

The preparation of tubular heterostructures based on titanium dioxide and silica nanotubes and their photocatalytic activity[†]

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Tubular heterostructures based on titanium dioxide (TiO₂) and silica nanotubes (SNTs) with high photocatalytic activity have been successfully obtained by a simple combination of an electrospinning technique and a solvothermal process. The as-prepared products were characterized by field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and N₂ absorption–desorption experiments. The results confirmed that SNTs with high specific surface area were obtained by efficiently controlling the phase separation and solvent evaporation during the process of electrospinning and calcination, and TiO₂ was successfully grown on the SNT substrates. The obtained titanium dioxide/silica nanotubes (TiO₂/SNTs) heterostructures showed high photocatalytic activities to degrade Rhodamine 6G because of the formation of heterostructures, which might improve the separation of photogenerated electrons and holes. Furthermore, the TiO₂/SNTs heterostructures could be easily recycled without an evident decrease in photocatalytic activity.

> reactions on TiO₂ nanoparticles have been attracting much interest from the viewpoint of their possible applications for dealing with environmental problems, that is, purification of air as well as polluted wastewater with dilute organic compounds.^{8,9} However, TiO₂ nanoparticles are prone to aggregate and become consumed quickly, resulting in a remarkable reduction in their photocatalytic activity and enormous waste. To overcome the disadvantages, a great deal of effort has been made, for instance, putting TiO₂ nanoparticles into colloidal solutions containing surfactants or complexes with polymer ligands (coating method), the introduction of TiO₂ nanoparticles on/into catalysis carriers (supported technology), and so on.¹⁰⁻¹⁴

> In recent years, the preparation of catalysis carriers has attracted tremendous attention, considering that the strategy could efficiently avoid the aggregation of TiO₂ nanoparticles without a decrease of their catalytic activity. It is well known that a large amount of solid supports (such as carbon, organic composite, polymer, metal oxide and so forth) with different nanostructures (including nanotubes, spheres, microporous metal-organic framework (MMOF), fibers, and so on) are of great importance for broad applications in catalyst carriers.^{15–17} Among the material family, SNTs have always attracted interest because of their easy processing, facile surface modification, large specific surface area, and excellent mechanical performance and stability.^{18,19} As a novel class of inorganic structures, SNTs are particularly significant for fundamental



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science and potential applications such as catalysis carriers, bioseparation, drug delivery, and controlled release.^{20,21}

Up to now, various synthesis strategies for SNTs have been reported. As the most common and conventional routes, template methods have been extensively studied as an alternative route to prepare SNTs. Various templates, such as polycarbonate (PC) membrane, polyvinylpyrrolidone (PVP) fibers, surfactants, and gel systems,^{22,23} have been used. However, template strategies will not only bring many impurities into the resulting SNTs, but also show low efficiencies and high cost. Therefore, it remains a challenge to fabricate SNTs by template methods, and it is also necessary and important to develop a simple and direct method to obtain highly purified silica nanotubes.

During the past decade, electrospinning has emerged as a convenient, versatile and cost-effective technique for generating extremely long continuous fibers with diameters ranging from several micrometers down to a few nanometers by applying a high voltage to a polymer solution or melt.²⁴ By employing this method, one-dimensional tubular nanostructures could be fabricated, usually through a spinneret with two coaxial capillaries to produce core/shell nanofibers, followed by selective removal of the core section.²⁵ Herein, based on solvent evaporation and phase separation, we present an effective and facile route to fabricate polyvinylpyrrolidone/tetraethyl orthosilicate (PVP/TEOS) microtubes (MTs) via the traditional single-nozzle electrospinning technique. Further investigations found that SNTs could be acquired through heat treatment of the above NTs. The as-prepared SNTs might be one of the most promising supports for the fabrication of TiO₂-based tubular heterostructures due to their high specific surface area, availability, and chemical stability.^{10,26,27}

In this report, we highlight our work on the facile preparation of SNTs and TiO₂/SNTs. The SNTs were obtained by combining the sol–gel method, the electrospinning technique and the process of calcination. Then, a one-step solvothermal method was applied to prepare TiO₂/SNTs heterostructures. As-prepared TiO₂/SNTs tubular heterostructures with high specific surface area exhibited excellent photocatalytic activity and recyclability in the degradation of organic pollutants. The processes might provide a new insight into the fabrication of tubular materials and various heterostructures.

2. Experiment section

2.1 Materials

Tetraethyl orthosilicate (Si $(OC_2H_5)_4$, TEOS, 98%), polyvinylpyrrolidone ((C₆H₉NO)_n, PVP, $M_n = 1\,300\,000$), titanium butoxide (Ti $(OC_4H_9)_4$, 99%) and dimethylpyridine N-oxide (DMPO) were purchased from Aladdin Chemical Reagent Co., Ltd (Shanghai, China). Absolute ethanol (C₂H₅OH) was acquired from Hangzhou Gaojing Fine Chemical Industry Co., Ltd (Hangzhou, China). Isopropyl alcohol ((CH₃)₂CHOH, reagent grade) was supplied by Tianjin Yongda Chemical Reagent Co., Ltd (Tianjin, China). Hydrochloric acid (HCl, 36–38%) was obtained from Zhejiang Three Eagle Chemical Reagent Co., Ltd (Jinhua, China). Rhodamine 6G ($C_{28}H_{31}ClN_2O_3$, 99%) was bought from ACROS Organics (New Jersey, USA). Deionized water was prepared using a Barnstead from Thermo Scientific (Shanghai, China). All chemicals were of analytical grade and used as received without further purification.

2.2 The preparation of SNTs

In a typical preparation, PVP powder with the mass of 1.5 g was completely dissolved in 16 mL of absolute ethanol. Then, 3.2 mL of TEOS was slowly added into the above PVP solution. After being stirred for 3 h, the precursor was transferred into a plastic syringe for electrospinning under the voltage of 10 kV and the flow rate of 1.2 mL h⁻¹. The resulting products were collected at a distance of about 14 cm to the syringe tip. Afterwards, the acquired PVP/TEOS microfibers were calcined at the rate of 8 °C min⁻¹ until a temperature of 600 °C was reached and held for 3 h. Accordingly, SNTs were obtained, and kept for further characterizations and experiments.

2.3 The synthesis of TiO₂/SNTs heterostructures

 TiO_2 /SNTs hetereostructures were synthesized by a facile solvothermal method. In a typical synthesis, 0.3 mL of butyl titanate was dissolved in 6 mL of isopropanol to obtain the precursor solution. Then SNTs with the mass of 150 mg were added into the above solution under vigorous magnetic stirring, and the pH of the mixture was adjusted to 4 using hydrochloric acid (0.3 M) at room temperature. The mixture solution was then transferred into a Teflon-lined tube reactor and was kept at 160 °C for 24 h. Once cooled to room temperature, the resultant was centrifuged, washed with distilled water, and dried at 60 °C under vacuum for 24 h.

2.4 Photocatalytic activity measurements

The photocatalytic activity of the samples was evaluated by degradation of Rhodamine 6G under irradiation with a 500 W high-pressure mercury lamp with a characteristic wavelength of 365 nm in an XPA-7 Photoreaction Spectrometer (NanJing xujiang). The temperature of the reactant solution was maintained below 283 K by the flow of cold water during the reaction. In each experiment, 30 mg of the photocatalyst was added into 60 mL of Rhodamine 6G aqueous solution with a concentration of 10 mg L^{-1} in a reaction cell with a Pyrex jacket. Prior to irradiation, the suspension was magnetically stirred in the dark for 1 h to reach adsorption-desorption equilibrium of Rhodamine 6G on the surface of the photocatalyst. After given time intervals, 2 mL of the suspension solution was taken out and then centrifuged (11 000 rpm, 5 min) to remove the photocatalyst particles for UV-Vis absorption measurements. As a control, another sample was evaluated without irradiation (in order to test the adsorption ability of the catalyst), and then investigated by the aforementioned method. The percentage of degradation is reported as C/C_0 , where C is the maximum peak of the absorption spectra of Rhodamine 6G for each irradiated time interval at a wavelength of 525 nm, and C_0 is the absorption of the starting concentration.

2.5 Characterizations

2.5.1 Field emission scanning electron microscopy (FE-SEM). The morphologies of the PVP/TEOS microfibers and SNTs were characterized by a field emission scanning electron microscope (FE-SEM, JEOL ULTRA-55) operated at an accelerating voltage of 1 kV.

2.5.2 Transmission electron microscopy (TEM). The samples for transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were evaluated using a JEOL JSM-2010 (acceleration voltage of 200 kV).

2.5.3 X-ray diffraction (XRD). The compositions of the powders (SNTs and TiO₂/SNTs) were analyzed with an X-ray diffractometer (XRD, Thermo ARL X'TRA) using a Cu K α radiation source at 35 kV with a scan rate of 0.02° 2θ s⁻¹ in the 2θ range of 10–80°.

2.5.4 Fourier transform infrared spectroscopy (FT-IR). SNTs powder and as-prepared $TiO_2/SNTs$ heterostructures were spread on KBr pellets and then dried under an infrared lamp. FT-IR measurements were recorded on a Thermo Scientific Nicolet 5700 FT-IR spectrometer in the wavenumber range of 500–4000 cm⁻¹.

2.5.5 Ultraviolet-visible spectroscopy (UV-Vis). UV-Vis spectra of the as-synthesized $TiO_2/SNTs$ heterostructures were collected using a Perkin Elmer Lambda 900 UV-Vis spectrophotometer over a wavelength range of 200–800 nm.

2.5.6 Electron spin resonance (ESR). ESR spectra were acquired with a Bruker A3000 electron paramagnetic resonance spectrometer. The settings were as follows: center field, 3478.00 G; microwave frequency, 9.88 GHz; and power, 20 μ W.

2.5.7 Energy dispersive spectrometer (EDS). The elementary compositions of the $TiO_2/SNTs$ heterostructures were obtained on an Oxford Inca-6587 spectrometer.

2.5.8 N₂ absorption-desorption experiments. The process was carried out at -193 °C using a BeiShiDe Instruments S&T 3H-2000 PS1 specific surface and pore size analysis instrument. The samples were subjected to outgassing for 3 h at 200 °C before the experiment. The surface area was evaluated using the BET (Brunauer-Emmett-Teller) method.

3. Results and discussion

Fig. 1 shows the FE-SEM and TEM images of PVP/TEOS microfibers prepared by electrospinning the PVP/C₂H₅OH/TEOS precursor. It was obviously seen that large quantities of microfibers with a smooth outer surface and homogeneous diameters were synthesized *via* the electrospinning technique. The typical average diameter of the fibers was about 1 μ m and the standard deviation was 99.6 nm. TEM images indicated that the hollow structures had already formed within the samples after electrospinning. The hollow PVP/TEOS microfibers were 250–300 nm in wall thickness and 300–350 nm in inner diameter, which was consistent with the corresponding FE-SEM images.



Fig. 1 FE-SEM (a and b) and TEM (d, e and f) images of PVP/TEOS microfibers; (c) the corresponding diameter distribution of PVP/TEOS microfibers.



Fig. 2 FE-SEM (a and b) and TEM (d, e and f) images of SNTs; (c) the corresponding diameter distribution of SNTs.

In order to obtain pure SNTs, electrospun hollow PVP/TEOS microfibers were calcined so as to remove the PVP and promote the formation of silica. The morphologies and the diameter distribution of the obtained samples were investigated with FE-SEM, as shown in Fig. 2(a)-(c). It was clearly seen that these consistent tubular products have the average diameter of 335 nm. Meanwhile, it could be observed that

pure SNTs aligned in a random orientation because of the bending instability associated with the spinning jet.²⁸ In the meantime, TEM images of the SNTs further confirmed the hollow structure, as can be seen in Fig. 2(d)-(f). Fig. 2(f) exhibits a cross-section of the nanotubes, and the result reveals that our obtained products are comprised of tubular microfibers with the wall thickness of 40-60 nm and the mean diameter of 300 nm, which is in accordance with the FE-SEM observations. Evidently, the diameter of the hollow fibers decreases to less than half that of the PVP/TEOS microfibers shown in Fig. 1. The distinct contrast might be assigned to two reasons. First, PVP was completely decomposed during the high temperature annealing treatments, leaving many vacancies in the tube walls, accordingly resulting in shrinkage of the nanotubes during the calcination process.^{26,27} On the other hand, silica molecules could be reconstructed in the tube walls at high temperature, which might also lead to the diameter decrease of the nanotubes.

As is known, organic-inorganic composite fibers can be acquired by combining the sol-gel method and the electrospinning technique. Also, inorganic fibers could be obtained through calcination of the above composite fibers so as to remove the polymer binder. In our experiments, once the electrospinning process began, fibers (in Scheme 1(a)) were spun out from the nozzle, and the ethanol solvent in the precursor will evaporate rapidly from the fibers. Then, a concentration gradient of ethanol would form along the radial direction of the fibers. Obviously, the ethanol concentration at the center of the fibers is higher compared to that at the edge of the fibers, and the concentration gradient would eventually push the system into unstable phase states and a phase separation happens. As a result, TEOS would inevitably diffuse along the concentration gradient of ethanol. Meanwhile, it is well known that TEOS shows a high solubility in ethanol but is incompatible with PVP; therefore, TEOS would concentrate at the center of microfibers and PVP would be forced to migrate from the core of the fibers to the outer surface. The PVP/TEOS microtubes are filled with TEOS at this moment, as illustrated in Scheme 1(b). Moreover, as a volatile liquid, TEOS might evaporate through the wall of the microtubes



easily. Therefore, based on the above results and discussions, it is considered that the morphologies of the fibers in a way depend on the competition between the evaporation rate and the process of phase separation; when the former plays a leading role, hollow PVP/TEOS fibers are formed, as shown in Scheme 1(c).^{33–35} As the calcination process proceeds, PVP molecules would become decomposed gradually and removed completely from the composite fibers. In the meantime, pure SNTs (as can be seen in Scheme 1(d)) were obtained through the interaction of TEOS and oxygen in the air. It is evident that the nanotubes show rough walls with porous structures, which is also evidence of a rapid phase separation during the electrospinning process and drastic chemical reactions.

Successful preparation of TiO₂/SNTs heterostructures was confirmed by their corresponding TEM images and the EDS spectrum. TEM images of the samples shown in Fig. 3 indicated that there was essentially no change of the nanofibers' external morphology during the growth of TiO₂ nanoparticles. It is evident that a large amount of nanoparticles deposited on the SNTs can be found in Fig. 3. Compared with the TEM images of pure TiO₂ (Fig. S1†), TiO₂ nanoparticles loaded on the SNTs were significantly smaller in particle size. Furthermore, in Fig. 3(f), the latter fringe spacing of TiO₂ nanoparticles was 0.24 and 0.35 nm, which correspond to the (004) and (101) planes, respectively.^{35–38} The chemical elemental component of the resulting samples was characterized by the EDS spectrum, which indicates that TiO₂/ SNTs are composed of the elements Si, Ti, and O.

To evaluate the pore structure and specific surface area, N_2 adsorption-desorption isotherms of the heterostructures were performed before and after the deposition of TiO₂ nanoparticles. Typical isotherms of the SNTs and TiO₂/SNTs



Fig. 3 The TEM images of TiO_/SNTs heterostructures (a, b, d and e); (c) the EDS spectrum of TiO_/SNTs; (f) the HRTEM image of TiO_ nanoparticles.



Fig. 4 Adsorption–desorption isotherms of SNTs (a) and $\rm TiO_2/SNTs$ heterostructures (b).

samples is shown in Fig. 4. Evidently, with the loading of TiO_2 nanoparticles, the hysteresis loop became shorter, indicating a reduction of the pore volume. This seems to be logical as the loading of TiO_2 nanoparticles was dispersed and deposited on the surface of SNTs, decreasing the diameter of SNTs and thus diminishing the surface area. The BET surface areas of SNTs and TiO_2 /SNTs were determined to be around 411.58 and 279.31 m² g⁻¹, respectively. The reduction of the BET surface area of TiO_2 /SNTs can be attributed to the deposition of TiO_2 nanoparticles.

The FT-IR spectra of the SNTs and TiO₂/SNTs heterostructures were used to investigate the compositions and structures of the resulting samples. As shown in Fig. 5, the absorption peak at 3481 cm⁻¹ belongs to the asymmetrical stretching vibration of –OH groups, which are related to the bound water and free water that may absorb on the surface of the SNTs. The peak at 1633 cm⁻¹ is attributed to the bending vibration absorption peak of H–O–H which is derived from the pore water and surface absorbed water. The characteristic peaks of silica at 1090 cm⁻¹ and 802 cm⁻¹ are assigned to the asymmetrical stretching and symmetric stretching of Si–O–Si bonds, respectively.^{29–31} Compared to SNTs, no other characteristic signals are detected in TiO₂/SNTs, but the intensity of the peaks shows distinct changes, which may be attributed to the fact that the SNTs were coated by the acquired TiO₂ nanoparticles;



Fig. 5 $\,$ FT-IR spectra of SNTs (curve a) and TiO_2/SNTs heterostructures (curve b).

accordingly, the characteristic absorption peaks of SNTs are becoming much weaker.

To further verify the formation of TiO_2/SNTs heterostructures and the presence of TiO_2 nanoparticles, the SNTs and TiO_2/SNTs powder were characterized by XRD. As shown in Fig. 6, according to the literature, the strong and broad diffractions in curve a in the 2θ range between 23 and 25 degrees are assigned to amorphous silica.^{32–34} On the basis of JCPDS 21-1272, as observed in curve b, all the characteristic signals of TiO₂ can be ascribed to the (101), (004), (200), (105), (211), and (204) planes of anatase structure TiO₂,^{35–38} which is in good accordance with pure TiO₂ (Fig. S2†). From the above results, it can be further confirmed that the TiO₂/SNTs were successfully synthesized. However, the peak of amorphous silica appeared to be narrower and weaker in curve b compared to that of the pure SNTs, probably because of coating of TiO₂ nanoparticles, which might weaken the diffraction of amorphous silica.



Fig. 6 The XRD patterns of SNTs (curve a) and $\rm TiO_2/SNTs$ heterostructures (curve b).

To demonstrate the photocatalytic activity of the asobtained TiO₂/SNTs heterostructures for the degradation of organic pollutants, we carried out experiments on the photocatalytic degradation of Rhodamine 6G as a test reaction. Furthermore, in the comparative experiments, pure TiO₂ (Fig. S1 and S2[†]) was used as a photocatalytic reference to understand the photocatalytic activity of the TiO2/SNTs heterostructures. As is well known, the band gap of pure TiO_2 is 3.2 eV, which greatly limits its photoresponse to the solar energy. In order to investigate the degradation ability of the heterostructures based on TiO2 and SNTs, UV irradiation was selected as the light source. In Fig. 7, control experiments were performed under different conditions: (a) with UV irradiation but in the absence of the photocatalyst; (b) in the presence of photocatalysts but in the dark. After UV light irradiation for 90 min, the degradation efficiency of Rhodamine 6G was about 90% and 55% for the $TiO_2/SNTs$ heterostructures and pure TiO_2 , respectively. Obviously, the TiO₂/SNTs heterostructures showed much higher photocatalytic activities than pure TiO₂. Also, there was no appreciable degradation of Rhodamine 6G in the absence of photocatalysts and in the presence of photocatalysts but in the dark. Therefore, Rhodamine 6G could be degraded efficiently when UV light was used as the light source in the presence of TiO₂/SNTs heterostructure photocatalysts. More importantly, it was indicated that these heterostructures could be easily separated and recovered by sedimentation without decreasing their photocatalytic activities distinctly and would greatly promote their practical application to eliminate organic pollutants



Fig. 7 Photocatalytic activity of TiO₂/SNTs heterostructures to Rhodamine 6G: (a) no catalyst; (b) TiO₂/SNTs under dark conditions; (c) TiO₂/ SNTs; (d) TiO₂/SNTs for the second time; (e) pure TiO₂; (f) photocatalytic decomposition curves of Rhodamine 6G.

from waste water. In order to probe the effect of absorbance and identify whether there is Rhodamine 6G over the surface of the obtained heterostructure, FT-IR measurement (Fig. S3[†]) was employed to illustrate them. It could be seen clearly that the characteristic peaks of Rhodamine 6G almost disappeared after the degradation process. Zhang *et al.* have already studied the photocatalytic capability of silica/titania nanotubes composite membrane.⁴⁴ Compared with their work, we emphasized the facile preparation process of TiO₂/SNTs by electrospinning and put forward the heterostructures to explain why TiO₂/SNTs exhibited higher photocatalytic activity than pure TiO₂, which would be demonstrated by our later analysis.

The generation of a large amount of O_2 ⁻ and OH[•] radicals from the tubular TiO₂/SNTs heterostructures during the degradation of Rhodamine 6G was demonstrated by ESR with dimethylpyridine N-oxide (DMPO) as a spin-trapping reagent. As described in Fig. 8(a), four characteristic peaks for DMPO– OH[•] with an intensity ratio of 1:2:2:1 were obviously observed when the TiO₂/SNTs heterostructures were illuminated with UV irradiation. On the other hand, pure TiO₂ exhibits no characteristic peaks under the same conditions,



Fig. 8 The ESR spectra for (A) TiO₂/SNTs heterostructures, (B) pure TiO₂, (C) no catalyst at ambient temperature: (a) in aqueous dispersion for DMPO–OH'; (b) in methanol dispersion for DMPO–O₂⁻⁻.



Scheme 2 Proposed mechanisms for the photocatalysis of $TiO_2/SNTs$ heterostructures.

suggesting that there are almost no OH[•] radicals during the degradation process. In addition, it could be seen clearly in Fig. 8(b) that six characteristic peaks for DMPO-O₂^{•–} were detected in methanol. The above experimental results further verify the reason why our obtained TiO₂/SNTs heterostructures display higher photocatalytic activity than the pure TiO₂.⁴⁵⁻⁴⁷

In order to explain the difference between the TiO₂/SNTs heterostructures and pure TiO₂ in photocatalytic degradation of Rhodamine 6G, on the basis of earlier reports on the photocatalytic degradation of pollutants, a proposed mechanism of photodegradation of Rhodamine 6G with TiO₂/SNTs heterostructures is illustrated schematically in Scheme 2. The mechanism was that SNTs supported catalysts were believed to exhibit cooperative effects between SNTs and TiO₂ nanoparticles. Here, a high-energy photon excites an electron from the valence band to the conduction band of TiO₂, photogenerated electrons in TiO₂ may move freely toward the surface of the SNTs and excess of valence band holes were left in the TiO₂ to migrate to the surface and react with H₂O or OH- to produce active species such as OH',1,28,39 suggesting that the photogenerated electrons and holes were efficiently separated. Because SNTs exhibit the characteristic properties of a p-type semiconductor⁴⁰ while TiO₂ is an n-type semiconductor,⁴¹ we can conclude that the p-n junction is formed between SNTs and TiO2 and then reduces the recombination of electron-hole pairs, leading to enhanced photocatalytic activity. The mechanism of the photocatalytic degradation of Rhodamine 6G in our experiment was proposed to be the following:

$$\begin{split} \mathrm{TiO}_2/\mathrm{SNTs} + h\nu &\rightarrow \mathrm{e}^-(\mathrm{SNTs}) + \mathrm{h}^+(\mathrm{TiO}_2 \\ &\mathrm{h}^+ + \mathrm{OH}^- \rightarrow \mathrm{OH}^* \\ &\mathrm{e}^- + \mathrm{O}_2 \rightarrow \mathrm{O_2}^{*-} \\ &\mathrm{O_2}^{*-} + \mathrm{H_2O} \rightarrow \mathrm{HO_2}^* + \mathrm{OH}^- \\ &\mathrm{HO_2}^* + \mathrm{H_2O} \rightarrow \mathrm{H_2O_2} + \mathrm{OH}^* \\ &\mathrm{H_2O_2} \rightarrow \mathrm{2OH}^* \end{split}$$

Upon UV light irradiation, photogenerated electrons in TiO_2 moved freely to the surface of the SNTs; meanwhile, the photogenerated holes were left in the valence band of TiO_2 . Subsequent to the above process, the holes (h⁺) were ultimately trapped by surface hydroxyl groups (or H₂O) at the catalyst surface to yield OH[•] radicals; at the same time, the dissolved oxygen molecules react with the surface of the SNTs electrons (e⁻) to yield superoxide radical anions (O₂^{•-}), which generate hydroperoxy (HO₂[•]) and hydroxyl ions. Then the hydroxyl radical (OH[•]) was produced, which is a strong oxidizing agent to decompose the organic dye.^{42,43}

4. Conclusions

In summary, SNTs with high specific area surface were acquired through calcination of hollow PVP/TEOS microfibers, which could be generated by effectively controlling the phase separation and solvent evaporation in the process of electrospinning. Further research showed that SNTs were excellent carriers for TiO_2 nanoparticles, and as-prepared $TiO_2/SNTs$ heterostructures exhibited higher photocatalytic activities than pure TiO_2 for the degradation of Rhodamine 6G under UV light irradiation. Moreover, $TiO_2/SNTs$ heterostructures could be easily recycled without a distinct decrease of the photocatalytic activity. The study also suggests that tubular $TiO_2/SNTs$ heterostructures are an outstanding type of UV-light-driven photocatalysts for environmental remediation applications.

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