available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue on Photocatalytic H₂ Production and CO₂ Reduction)

Fabrication of TiO₂ nanofiber assembly from nanosheets (TiO₂-NFs-NSs) by electrospinning-hydrothermal method for improved photoreactivity

Yachao Lu ^a, Xiaoyu Ou ^a, Wenguang Wang ^{b,#}, Jiajie Fan ^c, Kangle Lv ^{a,*}^a Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education, College of Resources and Environmental Science, South-Central University for Nationalities, Wuhan 430074, Hubei, China^b School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, Guangdong, China^c School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, Henan, China

ARTICLE INFO

Article history:

Received 23 June 2019

Accepted 9 August 2019

Published 5 January 2020

Keywords:

TiO₂ nanofiber

Electrospinning

Photocatalytic oxidation

Acetone

Dye-sensitized solar cell

ABSTRACT

Hierarchically structured nanomaterials have attracted much attention owing to their unique properties. In this study, TiO₂ nanofibers assembled from nanosheets (TiO₂-NFs-NSs) were fabricated through electrospinning technique, which was followed by hydrothermal treatment in NaOH solution. The effect of hydrothermal reaction time (0–3 h) on the structure and properties of TiO₂ nanofibers (TiO₂-NFs) was systematically studied, and TiO₂-NFs was evaluated in terms of the photocatalytic activity toward photocatalytic oxidation of acetone and the photoelectric conversion efficiency of dye-sensitized solar cells. It was found that (1) hydrothermal treatment of TiO₂-NFs in NaOH solution followed by acid washing and calcination results in the formation of TiO₂-NFs-NSs; (2) upon extending the hydrothermal reaction time from 0 h to 3 h, the BET surface area of TiO₂-NFs-NSs (T3.0 sample) increases 3.8 times (from 28 to 106 m² g⁻¹), while the pore volume increases 6.0 times (from 0.09 to 0.54 cm³ g⁻¹); (3) when compared with those of pristine TiO₂-NFs (T0 sample), the photoreactivity of the optimized TiO₂-NFs-NSs toward acetone oxidation increases 3.1 times and the photoelectric conversion efficiency increases 2.3 times. The enhanced photoreactivity of TiO₂-NFs-NSs is attributed to the enlarged BET surface area and increased pore volume, which facilitate the adsorption of substrate and penetration of gas, and the unique hollow structure of TiO₂-NFs-NSs, which facilitates light harvesting through multiple optical reflections between the TiO₂ nanosheets.

© 2020, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Semiconductor photocatalysis is a sustainable technology for solving the problems related to environmental pollution and energy crisis, as it can be used to oxidize organic pollutants

[1–6], reduce CO₂ into hydrocarbon fuels [7–10], produce H₂ by splitting water [11–15], and convert solar energy to electricity [16–19]. Among all the semiconductor photocatalysts, TiO₂ is the most widely studied owing to its strong oxidation power, excellent photoelectrochemical stability, and good biocompati-

* Corresponding author. Tel: +86-27-67841369; Fax: +86-27-67843918; E-mail: lvkangle@mail.scuec.edu.cn

Corresponding author. Tel/Fax: +86-20-39322570; E-mail: wenguangwang2005@163.com

This work was supported by the National Natural Science Foundation of China (51672312, 21373275) and the Fundamental Research Funds for the Central Universities, South-Central University for Nationalities (CZT19006).

DOI: S1872-2067(19)63470-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 1, January 2020

bility [20–22]. However, the photoreactivity of TiO₂ is not high enough to satisfy the requirements for practical applications, which is attributed to its low quantum efficiency [23–25]. It is generally accepted that the photoreactivity of TiO₂ is a function of many parameters such as Brunauer-Emmett-Teller (BET) surface area, crystallinity, crystalline phases, morphology, and pore structure [26]. As these parameters are usually in conflict of each other, optimizing the photoreactivity of TiO₂ is very complex. For example, reducing the particle size of TiO₂ can facilitate the adsorption of photosensitizers, which improves the photoelectric conversion efficiency of a dye-sensitized solar cell (DSSC). However, if the TiO₂ particle size is too small, the photoanode film will become transparent with little light scattering, which is not good for the light absorption properties of TiO₂ photoanode film [27,28].

Although zero-dimensional (0D) TiO₂ nanoparticles usually exhibit a high photoreactivity owing to the large BET surface area, they are very hard to collect and reuse [29]. Therefore, much attention has been paid to the synthesis of one-dimensional (1D) TiO₂ nanowires [17] or nanotubes [30,31], two-dimensional (2D) TiO₂ nanosheets [32,33] or arrays [18], and even three-dimensional (3D) TiO₂ hollow microspheres [28,34] and hollow nanoboxes [3,35].

Electrospinning provides a technique to fabricate 1D structured semiconductors such as nanofibers from discrete 0D nanoparticles, which can improve the photoreactivity of the photocatalyst by retarding the recombination of carriers as the photogenerated electrons and holes are supposed to migrate along different directions [29,36–38]. In addition, the gas permeability of the nonwoven materials obtained from electrospinning facilitates photocatalytic purification of air owing to the high porosity.

To further increase the BET surface area and porosity of the TiO₂ nanofibers (TiO₂-NFs) synthesized by electrospinning, they were treated in NaOH solution. In the form of anatase, TiO₂ nanoparticles (TiO₂-NPs) can react with NaOH to produce sodium titanate nanosheets (Reaction (1)), which can then transform into anatase nanosheets (TiO₂-NSs) after acid washing and calcination (Reactions (2) and (3)) [28,39]. Using this strategy, TiO₂-NF assembly can be obtained from TiO₂-NSs (TiO₂-NFs-NSs).

The study by Lin *et al.* [40] showed that, when applied in a DSSC, TiO₂-NFs-NSs exhibited a higher photoelectric conversion efficiency than pristine TiO₂-NFs. However, the dependence of the photoelectric efficiency of TiO₂-NFs-NSs on hydrothermal reaction time was not systematically studied. In addition, the performance of a DSSC is based on a photosensitization mechanism, whereby only the surface adsorbed photosensitizer (dye) in TiO₂ photoanode film is excited under visible light irradiation to produce high-energy electrons, which then transfer to the conduction band of TiO₂. However, in photo-

catalytic oxidation, reactive oxygen species (ROS) such as hydroxyl radicals ($\bullet\text{OH}$) and super oxygen radicals ($\bullet\text{O}_2^-$) form on the surface of UV-illuminated TiO₂ photocatalyst, and these ROS can be used to oxidize organic pollutants. Therefore, in this research, we systematically studied the effect of hydrothermal reaction time on the photocatalytic performance and photoelectric conversion efficiency of TiO₂-NFs-NSs.

2. Experimental

2.1. Synthesis of TiO₂-NFs

TiO₂-NFs was fabricated by electrospinning technique [29]. Briefly, 3.4 g of tetrabutyl titanate was added dropwise into a beaker containing 15.0 g of absolute ethanol and 4.0 g of glacial acetic acid under vigorous magnetic stirring. Then, 1.0 g of polyvinylpyrrolidone (Mw = 1,300,000) was added into the mixed solution. After further stirring for 6 h, the produced viscous solution was spun using an electrospinning device (QZNT-E01, Foshan Lepton, China) with a flow rate of 0.1 ml min⁻¹ and an applied voltage of 22 kV. The distance between the needle tip and the Al foil board used for collecting fibers was kept at about 4.0 cm. The collected nanofibrous membrane was further calcined at 500 °C for 2 h to obtain TiO₂-NFs (T0 sample).

2.2. Fabrication of TiO₂-NFs-NSs

Roller brush-like TiO₂-NF assembly was synthesized from nanosheets by hydrothermal treatment of pristine TiO₂-NF (T0 sample) nanofibrous membranes in an alkaline solution, which was followed by acid washing and calcination. Typically, 2.5 g of the as-spun nanofibrous membrane was immersed in 160 ml of NaOH solution (10 M), which was then transferred into a 200 ml Teflon-lined autoclave and kept in an oven at 120 °C for 3 h. After cooling to room temperature, the supernate was removed, while the collected white powders were re-dispersed in 900 ml of diluted HCl solution (0.1 M). After magnetic stirring for 12 h, the suspensions were filtrated, and the resulted cake was washed with distilled water until the pH became neutral. Finally, the cake was calcined at 400 °C for 1 h to obtain TiO₂-NFs-NSs (T3.0 sample).

For comparison, a series of TiO₂-NFs-NS samples were prepared under identical conditions, except for the change in hydrothermal reaction time. The prepared TiO₂-NFs-NS samples were denoted as “Tx”, where “x” represents the hydrothermal reaction time (h) in NaOH solution (Table 1).

2.3. Characterization

The morphology of TiO₂ nanofibers was observed by field emission scanning electron microscopy (SEM, Hitach, Japan) at 10 kV acceleration voltage and by transmission electron microscopy (TEM; Tecnai G20, USA) at 200 kV acceleration voltage. The phase structure of the photocatalyst was identified by X-ray powder diffraction (XRD; Bruker) at 15 kV acceleration voltage and 20 mA applied current. The light-harvesting ability

Table 1Physical properties of the TiO₂ nanofibers.

Sample	Reaction time (h)	Crystalline size (nm) ^a	Nitrogen sorption results ^b			Photovoltaic parameters ^c			
			<i>S</i> _{BET} (m ² g ⁻¹)	PV (cm ³ g ⁻¹)	APS (nm)	<i>I</i> _{sc} (mA cm ⁻²)	<i>V</i> _{oc} (V)	<i>FF</i>	<i>H</i> (%)
T0	0	17.1	28	0.09	13.6	2.25	0.780	0.649	1.14
T0.5	0.5	17.1	34	0.13	15.4	2.52	0.778	0.678	1.33
T1.0	1.0	16.1	62	0.31	19.8	3.01	0.764	0.630	1.45
T1.5	1.5	14.4	84	0.40	18.8	4.22	0.760	0.717	2.30
T2.0	2.0	14.7	91	0.41	17.7	4.62	0.765	0.724	2.56
T2.5	2.5	14.4	104	0.53	20.1	4.87	0.746	0.729	2.65
T3.0	3.0	13.4	106	0.54	20.0	2.75	0.747	0.735	1.51

^a Crystalline size of TiO₂ sample was calculated based on Scherrer equation.^b *S*_{BET}, PV and APS mean BET surface area, pore volume and average pore size of the photocatalyst, respectively.^c *V*_{oc}, *I*_{sc}, *FF* are open circuit voltage, short circuit current density and fill factor, respectively. *η* represents photoelectric conversion efficiency of the photoanode film.

of the photocatalyst was measured by UV-visible diffuse reflectance spectroscopy (UV-2550, Shimadzu) by using BaSO₄ as the reference. The BET specific surface area and pore structure of the photocatalyst were analyzed with a nitrogen adsorption apparatus (ASAP2020, Micromeritics, USA). The calculation of the BET surface area was based on the adsorption data obtained by multipoint BET method in the relative pressure range 0.05–0.3, whereas Barret-Joyner-Halender method was used to determine the pore size distribution of the photocatalyst from the data of the adsorption isotherm. To obtain information on the separation and migration of photogenerated carriers in the photocatalyst, the photoluminescence (PL) spectrum was recorded by a fluorescence spectrophotometer (F-7000, Hitachi, Japan) at the excitation wavelength of 315 nm.

2.4. Photocurrent measurement

The photocurrent response of the photocatalyst was measured by an electrochemical workstation (CHI760e, Shanghai, China) with the help of the standard three-electrode photoelectrochemical cell, where a Pt-wire electrode, Ag/AgCl electrode, and the prepared samples were used as the counter electrode, reference electrode, and working electrodes, respectively. A 365 nm LED (3 W; Shenzhen Lamplic, China) was used as the light source, and Na₂SO₄ solution (0.4 M) was employed

as the electrolyte. Before measurement of the photocurrent, the working electrode was prepared by coating TiO₂ slurry onto the surface of indium tin oxide conductive glasses. First, 30 mg of TiO₂ nanofibers was dispersed in 0.75 mL of ethanol solution (50 v/v%), which was followed by sonication for 30 min. Secondly, 20 μL of Nafion, which was used as the agglomerant, was added into the above dispersion, which was followed by ultrasonication for 30 min to obtain a homogeneous slurry.

2.5. Photocatalytic oxidation of acetone

The photocatalytic activity of TiO₂ nanofibers was evaluated for photocatalytic oxidation of acetone [33]. The volume of the reactor was 15 L and an UV lamp that mainly emitted 365 nm radiation was used as the light source [41]. 0.3 g of the photocatalyst well-dispersed in 30 mL distilled water was distributed evenly in three watch glasses. Those watch glasses coated with burr-like TiO₂ nanofibers were dried overnight at 60 °C and then placed under the UV lamp. After that, 10 μL of acetone was injected into the reactor, in which the system was sealed. After about 30 min, the adsorption of acetone reached equilibrium and its concentration reached about 300 ppm. The concentrations of acetone and carbon dioxide in the reactor could be detected on-line through a photoacoustic IR multigas monitor (INNOVA Air Tech Instruments, Model 1412).

Scheme 1. Schematic diagram illustrating the fabrication of TiO₂ nanofibers assembly from nanosheets (TiO₂-NFs-NSs).

2.6. Measurement of the photoelectric conversion efficiency

The photoelectric conversion efficiency of TiO_2 -NFs was measured based on the photovoltaic current density-voltage (I - V) curve. First, we prepared a TiO_2 -NF film-based photoanode by pasting TiO_2 -NF slurry onto the surface of FTO glass by screen printing [28,42]. In order to evaporate the organic solvent, the air-dried FTO glass coated with a layer of TiO_2 -NF film was placed inside an oven and heated at 80 °C for 10 min. After cooling to room temperature, the film was placed in a tubular muffle furnace to completely remove the organics from the substrate by calcination at 450 °C for 30 min. Secondly, the calcined FTO glass coated with 10-layered TiO_2 -NF film was immersed in N719 dye anhydrous ethanol solution (0.5 mM) for 24 h to adsorb the sensitizer. Finally, the photoanode film was rinsed with ethanol to remove the physically adsorbed sensitizer, which was then heated in an oven at 80 °C for 2 h to evaporate the solvent.

To assemble DSSCs, the sensitized TiO_2 -NF film-based photoanode was clamped together with the Pt counter electrode. After injection of the electrolyte, the photoelectric conversion efficiency was immediately determined.

3. Results and discussion

3.1. Morphology and phase structure

Fig. 1 shows the SEM images of T0 sample, which was not treated with NaOH solution. It can be seen that T0 sample contains aggregates of nanofibers with diameters of about 80–100 nm (Fig. 1(a)). From the enlarged SEM image (Fig. 1(b)), we can see that these TiO_2 -NFs are assembled from nanoparticles. After treatment in NaOH solution for 0.5 h, it appears that the morphology of the TiO_2 nanofibers (T0.5 sample) almost remains unchanged (Fig. 2(a)). However, careful inspection reveals that the surface of T0.5 sample is coarse. Some nanosheets are attached to the surface of TiO_2 -NFs (Fig. 2(b)); they should have originated from the transformation of TiO_2 nanoparticles (Eq. (1)–(3)) [28].

The surface of the obtained TiO_2 -NFs becomes much coarser when the reaction time is extended to 1.0 h (Fig. 2(c)), which is ascribed to the growth of TiO_2 -NSs (Fig. 2(d)). These TiO_2 -NFs become curly brush-like upon further increasing the reaction time to 1.5 h (Fig. 2(e)), 2.0 h (Fig. 2(f)), and 2.5 h (Fig. 2(g)). The fibrous structure of TiO_2 -NFs can hardly be observed for T3.0 sample owing to the overgrowth of TiO_2 -NSs (Fig. 2(h)).

Fig. 1. SEM images of TiO_2 -NFs (T0 sample) before treated in NaOH solution.

Fig. 2. SEM images TiO_2 nanofibers for T0.5 (a, b), T1.0 (c, d), T1.5 (e), T2.0 (f), T2.5 (g) and T3.0 (h) samples. Arrows indicating the presence of TiO_2 nanoparticles.

The transformation of TiO_2 nanoparticles to TiO_2 nanosheets after the treatment in NaOH solution can also be more clearly observed in the corresponding TEM images of T0 sample (Fig. 3(a) and Fig. 3(b)) and T3.0 sample (Fig. 3(c) and Fig. 3(d)). Elemental mapping was also used to record the transformation processes from anatase (Fig. 4(a)) to Na_2TiO_3 (Fig. 4(b)), H_2TiO_3 (Fig. 4(c)), and anatase TiO_2 (Fig. 4(d)). From Fig. 4, we can see that the NaOH-treated TiO_2 sample contains a high concentration of Na element, which is due to the formation of Na_2TiO_3 (Eq. (1)). After acid washing, the concentration of Na sharply decreases because of the production of H_2TiO_3 (Eq. (2)). Therefore, by using this strategy, we successfully transformed primary TiO_2 -NFs into TiO_2 -NFs-NSs. This transformation can not only sharply increase the BET surface area of TiO_2 -NFs to provide more active sites for adsorption and photoreaction, but also facilitate the light absorption owing to the multi-reflection of light between nanosheets [43], which will be shown below.

The XRD characterization results show that all the nanofibers are mainly anatase, with a small amount of rutile phase (Fig. 5). Generally speaking, anatase exhibits a higher photoreactivity than rutile phase, and the presence of a small amount of rutile is believed to be beneficial to the photocatalytic activity

Fig. 3. TEM (a, c) and high resolution TEM images (b, d) of TiO_2 -NFs before (a, b) and after treated in NaOH solution (c, d).

Fig. 4. Elemental maps of the samples for TiO_2 -NFs before (a) and after treated in NaOH solution (b), washed in HCl solution (c), and followed by calcination (d).

of anatase owing to the formation of a TiO_2 homojunction [44].

From Fig. 5, we can also see that the XRD diffraction peaks, particularly the (101) facet of anatase, become wider and wider with the increase in the hydrothermal reaction time, which indicate reduced crystallization. By using Scherrer equation, we calculated the average crystalline sizes of the TiO_2 samples, and the results are shown in Table 1. It can be seen that the crystallite size of TiO_2 steady decreases from 17.1 nm (T0 sample) to 13.4 nm (T3.0 sample) with the increase in the hydrothermal

Fig. 5. XRD patterns of the TiO_2 nanofibers photocatalysts, together with the expected peaks for anatase TiO_2 .

time from 0 to 3.0 h. Poor crystallization means more defects, which is detrimental to the photoreactivity of photocatalytic TiO_2 materials.

3.2. Nitrogen sorption and UV-visible absorption spectrum

Specific surface area and pore structure are important factors affecting the photoreactivity of a photocatalyst. Therefore, nitrogen sorption-desorption isotherms are obtained and compared. In this research, from Fig. 6, we can see that the adsorption isotherm steadily shifts upward with an increase in the hydrothermal reaction time, which indicates an increase in the BET surface area of TiO_2 -NFs-NSs [28]. The BET surface area of TiO_2 -NFs (T0 sample) is only $28 \text{ m}^2 \text{ g}^{-1}$, which increases to 62, 91, and $106 \text{ m}^2 \text{ g}^{-1}$ after treatment in NaOH solution for 1.0, 2.0, and 3.0 h, respectively (Table 1). Therefore, the increase in the BET surface area of TiO_2 -NFs was achieved by treating TiO_2 -NFs in NaOH solution, which was followed by acid washing and calcination.

Careful inspection suggests that the hysteresis loop of the adsorption-desorption isotherm in the relative pressure range

Fig. 6. Comparison of the nitrogen sorption-desorption isotherms and corresponding pore size distribution curves (inset) of the photocatalysts.

0.6–0.9 evolves from type H2, which originates from bottle-like pores, to type H3, which is ascribed to the formation of narrow slit-shaped pores. This is consistent with the shape evolution of the building blocks of TiO₂-NFs from nanoparticles (T0) to nanosheets (T3.0) [45,46]. The inset of Fig. 6 compares the pore size distribution curves of the photocatalyst. It can be seen that the pore volume of the sample steady increases with the increase in the hydrothermal reaction time (Table 1), which is ascribed to the growth of TiO₂-NSs. The pore volume of T3.0 sample is as high as 0.54 cm³ g⁻¹, which is 6.0 times that of T0 sample (0.09 m³g⁻¹). The increased pore volume can facilitate the penetration of gas during the photocatalytic reaction, which is beneficial to the photoreactivity [47].

3.3. Photocatalytic oxidation of acetone

Acetone is a widely used organic solvent in industry that is also a typical hazardous volatile organic compound (VOC) that can cause nervous disorders [48,49]. Here, photocatalytic oxidation of acetone under UV irradiation was carried out to evaluate the photocatalytic activity of TiO₂-NFs. The oxidation of acetone is based on the following equation (Eq. (4)).

Fig. 7(A) displays the photocatalytic oxidation curves of acetone over different TiO₂-NFs. It can be seen, by using T0 sample as an example, that 32 ppm of acetone is decomposed within 30 min, and simultaneously, 77 ppm of CO₂ is produced, which indicate that the reduced acetone is mineralized instead of being adsorbed on the surface of the photocatalyst upon irradiation.

The oxidation curve of acetone can be fitted with the pseudo-zero-order kinetic equation (Eq. (5)).

$$\frac{dC}{dt} = K \quad (5)$$

where C (ppm) is the concentration of acetone at irradiation time t (min), and K (ppm min⁻¹) is the rate constant.

Then, the relative photocatalytic activity of TiO₂-NFs can be compared with the corresponding rate constant. From Fig. 7(B), we can clearly see that the photoreactivity of TiO₂-NFs steady increases with the increase in the hydrothermal reac-

tion time from 0 to 2.5 h. The photoreactivity of T2.5 sample reaches 3.41 ppm min⁻¹, which is 3.1 times that of T0 sample (1.11 ppm min⁻¹). However, upon further increasing the hydrothermal reaction time to 3.0 h, the reactivity of TiO₂-NFs reduces to 3.32 ppm min⁻¹. The drop in the photoreactivity for T3.0 sample is possibly a result of its reduced TiO₂ crystallite size (Table 1).

3.4. UV-visible absorption spectrum, PL, and photocurrent

To account for the improved photoreactivity of TiO₂-NFs-NSs, we compared the light-harvesting abilities of the photocatalyst. From the UV-visible absorption spectra shown in Fig. 8(A), we can see that the absorption of TiO₂-NFs in the UV region steadily increases with increasing hydrothermal reaction time, which is possibly due to the multi-reflection of light between the nanosheets. Further observation shows that all the samples exhibit weak absorptions at wavelengths above 410 nm. This is possibly caused by the impurities present in TiO₂, as the precursor of TiO₂-NFs contains some organics such as polyvinylpyrrolidone that may not have been completely removed during calcination. The absorption of TiO₂-NFs in the visible region is found to steadily decrease as the hydrothermal reaction time increases, which indicates that the hydrothermal reaction between TiO₂-NFs and NaOH facilitates the removal of impurities from the TiO₂-NFs.

From the corresponding PL spectra shown in Fig. 8(B), we can see that the PL intensity of TiO₂-NFs also steadily increases with the increase in the hydrothermal reaction time. These PL peaks in the visible region, ranging from 400 to 500 nm, originate from surface O vacancies and defects [50]. The increased PL intensity of TiO₂-NFs-NSs can also be attributed to the improved light-harvesting ability in the UV region.

Fig. 9 compares the transient PL spectra of pristine TiO₂-NFs (T0 sample) and TiO₂-NFs-NSs (T3.0 sample). The average lifetime of the carriers for TiO₂-NFs-NSs is calculated to be 4.3 ns, which is slightly shorter than that of pristine TiO₂-NFs (6.7 ns). Because only those pairs that are charged very fast can recombine, the shorter average carrier lifetime of TiO₂-NFs-NSs im-

Fig. 7. Photocatalytic oxidation curves of acetone (A) and comparison of the photoreactivity between different photocatalysts (B).

Fig. 8. UV-visible diffuse reflectance spectra (A) and PL spectra (B) of the photocatalysts.

plies enhanced exciton dissociation [11]. Therefore, the transformation of TiO_2 nanoparticles to TiO_2 nanosheets is beneficial to the charge dissociation and migration.

Considering that the separation/migration rate of photo-generated carriers is of great importance to the photoreactivity of semiconductor photocatalysts, we further compared the photocurrents of the photocatalyst. It is well accepted that, the larger the photocurrent, the more efficient is the separation and migration of photogenerated carriers [51]. The photocurrent of T2.0 sample reaches $0.156 \mu\text{A cm}^{-2}$, which is almost 2 times that of T0 sample ($0.085 \mu\text{A cm}^{-2}$). Therefore, it is not strange to observe a higher photoreactivity for TiO_2 -NFs-NSs, compared with that of pristine TiO_2 -NFs (Fig. 10).

3.5. Photoelectric conversion

The photoreactivity of TiO_2 -NFs was also evaluated in terms of the photoelectric conversion efficiency of DSSCs.

The photoelectric conversion efficiency (η) was calculated according to Eq. (6) [22,27]:

$$\eta(\%) = \frac{V_{oc} I_{sc} FF}{P_{in}} \times 100 \quad (6)$$

where V_{oc} , I_{sc} , FF , and P_{in} are the open circuit voltage, short circuit current density, fill factor of the film, and energy of incident light, respectively.

Fig. 11 compares the photovoltaic current density-voltage

Fig. 10. Photocurrents of the photocatalysts.

Fig. 9. Comparison of the transient photoluminescence spectra between pristine TiO_2 -NFs (T0 sample) and hierarchical TiO_2 -NFs-NSs (T3.0 sample). Conditions: $\lambda_{ex} = 310 \text{ nm}$ and $\lambda_{em} = 410 \text{ nm}$.

Fig. 11. Current-voltage curves of TiO_2 nanofibers-based photoanode DSSCs.

Fig. 12. UV-visible diffuse reflectance spectra of the TiO_2 -NFs film electrodes after adsorption of sensitizer.

(I - V) curves of TiO_2 -NF film-based DSSCs, and Table 1 summarizes the corresponding photovoltaic parameters. We can see that all the samples reveal similar open circuit voltages (of about 0.75–0.78 V), whereas the short circuit current densities of the TiO_2 -NF-based film cells steadily increase from 2.25 to 4.87 mA cm^{-2} with the increase in the hydrothermal reaction time from 0 to 2.5 h. Upon further increasing the hydrothermal reaction time to 3.0 h, the short circuit current density of T3.0 sample reduces to 2.75 mA cm^{-2} . Therefore, the photoelectric conversion efficiency of T2.5 sample-based film DSSC is the highest (2.65%), which is 2.3 times that of pristine TiO_2 -NF-based DSSC (1.14%). This trend is consistent with the photoreactivity of the photocatalyst toward acetone oxidation (Fig. 7).

Further study shows that the absorption of sensitized TiO_2 -NF film in the visible region steadily increases with the increase in the hydrothermal reaction time of the photocatalyst (Fig. 12), which can be ascribed to the improved adsorption of the dye (sensitizer) over TiO_2 -NFs-NSs. Since the BET surface area of TiO_2 -NFs is positively related to the hydrothermal reaction time (Table 1), TiO_2 -NFs-NSs (such as T3.0 sample) can provided more sites for adsorption of the dye, compared with pristine TiO_2 -NFs (T0 sample), which facilitates the harvesting of visible light [52], thus improving the photoelectric conversion efficiency (Fig. 11).

4. Conclusions

Highly photoreactive TiO_2 -NFs-NSs were prepared by simple hydrothermal treatment of electrospun TiO_2 -NFs in NaOH solution followed by acid washing and calcination. By using this strategy, TiO_2 nanoparticles can be transformed into TiO_2 nanosheets, which sharply increases the BET surface area and pore volume of TiO_2 -NFs. Compared with those of pristine TiO_2 -NFs, the photocatalytic activity of the hierarchical TiO_2 -NFs-NSs (T2.5 sample) toward acetone oxidation increases 3.1 times and the photoelectric conversion efficiency of the film-based DSSC improves 2.3 times. The enhanced photoreactivity of hierarchical TiO_2 -NFs-NSs is ascribed to the combined

effects of an enlarged BET surface that provides more active sites for substrate adsorption and photoreaction, increased pore volume that is beneficial to the diffusion/penetration of gas, improved light-harvesting ability owing to multi-reflection of light between the nanosheets, and a more efficient separation of the photogenerated carriers of TiO_2 nanosheets, compared to the case of TiO_2 nanoparticles.

References

- [1] J. Y. Li, X. A. Dong, G. Zhang, W. Cui, W. L. Cen, Z. B. Wu, S. C. Lee, F. Dong, *J. Mater. Chem. A*, **2019**, 7, 3366–3374.
- [2] B. Yuan, B. Zhang, Z. L. Wang, S. M. Lu, J. Li, Y. Liu, C. Li, *Chin. J. Catal.*, **2018**, 38, 440–446.
- [3] X. Zhao, Y. T. Du, C. J. Zhang, L. J. Tian, X. F. Li, K. J. Deng, L. Q. Chen, Y. Y. Duan, K. L. Lv, *Chin. J. Catal.*, **2018**, 39, 736–746.
- [4] Z. L. Wang, J. L. Lv, J. F. Zhang, K. Dai, C. H. Liang, *Appl. Surf. Sci.*, **2018**, 430, 595–602.
- [5] Z. L. Wang, T. P. Hu, K. Dai, J. F. Zhang, C. H. Liang, *Chin. J. Catal.*, **2017**, 38, 2021–2029.
- [6] Z. Li, X. Wang, J. F. Zhang, C. H. Liang, L. H. Lu, K. Dai, *Chin. J. Catal.*, **2019**, 40, 326–334.
- [7] S. L. Wang, M. Xu, T. Y. Peng, C. X. Zhang, T. Li, I. Hussain, J. Y. Wang, B. Tan, *Nat. Commun.*, **2019**, 10, 676.
- [8] J. B. Chen, S. K. Iyemperumal, T. Fenton, A. Carl, R. Grimm, G. H. Li, N. A. Deskins, *ACS Catal.*, **2018**, 8, 10464–10478.
- [9] T. M. Di, J. F. Zhang, B. Cheng, J. G. Yu, J. S. Xu, *Sci. China Chem.*, **2018**, 61, 344–350.
- [10] Y. Huo, J. F. Zhang, K. Dai, Q. Li, J. L. Lv, G. P. Zhu, C. H. Liang, *Appl. Catal. B*, **2019**, 241, 528–538.
- [11] J. S. Cheng, Z. Hu, K. L. Lv, X. F. Wu, Q. Li, Y. H. Li, X. F. Li, J. Sun, *Appl. Catal. B*, **2018**, 232, 330–339.
- [12] F. Chen, H. Yang, W. Luo, P. Wang, H. G. Yu, *Chin. J. Catal.*, **2017**, 38, 1990–1998.
- [13] S. U. M. Khan, M. Al-Shahry, W. B. Ingler, *Science*, **2002**, 297, 2243–2245.
- [14] T. P. Hu, P. F. Li, J. F. Zhang, C. H. Liang, K. Dai, *Appl. Surf. Sci.*, **2018**, 442, 20–29.
- [15] K. Dai, J. L. Lv, J. F. Zhang, G. P. Zhu, L. Geng, C. H. Liang, *ACS Sustainable Chem. Eng.*, **2018**, 6, 12817–12826.
- [16] A. Hegazy, N. Kinadjian, B. Sadeghimakki, S. Sivorthaman, N. K. Allam, E. Prouzet, *Solar Energy Mater. Solar Cells*, **2016**, 153, 108–116.
- [17] T. Marimuthu, N. Anandhan, R. Thangamuthu, S. Surya, *J. Alloys Compd.*, **2017**, 693, 1011–1019.
- [18] J. H. Hu, S. W. Hu, Y. P. Yang, S. Q. Tong, J. J. Cheng, M. W. Chen, L. Zhao, J. X. Duan, *Int. J. Photoenergy*, **2016**, 2016, 4651654.
- [19] H. M. Zhang, Y. H. Han, X. L. Liu, P. R. Liu, H. Yu, S. Q. Zhang, X. D. Yao, H. J. Zhao, *Chem. Commun.*, **2010**, 46, 8395–8397.
- [20] J. Schneider, M. Matsuoka, M. Takeuchi, J. L. Zhang, Y. Horiuchi, M. Anpo, D. W. Bahnemann, *Chem. Rev.*, **2014**, 114, 9919–9986.
- [21] Z. Hu, K. N. Li, X. F. Wu, N. Wang, X. F. Li, Q. Li, L. Li, K. L. Lv, *Appl. Catal. B*, **2019**, 256, 117860.
- [22] X. J. Yang, L. Zhao, K. L. Lv, B. H. Dong, S. M. Wang, *Appl. Surf. Sci.*, **2019**, 469, 821–828.
- [23] Y. H. Li, K. L. Lv, W. K. Ho, F. Dong, X. F. Wu, Y. Xia, *Appl. Catal. B*, **2017**, 202, 611–619.
- [24] Y. T. Ma, Z. H. Li, *Appl. Surf. Sci.*, **2018**, 452, 279–285.
- [25] J. W. Wan, W. X. Chen, C. Y. Jia, L. R. Zheng, J. C. Dong, X. S. Zheng, Y. Wang, W. S. Yan, C. Chen, Q. Peng, D. S. Wang, Y. D. Li, *Adv. Mater.*, **2018**, 30, 1705369.

- [26] Y. M. Xu, K. L. Lv, Z. G. Xiong, W. H. Leng, W. P. Du, D. Liu, X. J. Xue, *J. Phys. Chem. C*, **2007**, 111, 19024–19032.
- [27] J. G. Yu, J. J. Fan, K. L. Lv, *Nanoscale*, **2010**, 2, 2144–2149.
- [28] R. W. Yang, J. H. Cai, K. L. Lv, X. F. Wu, W. G. Wang, Z. H. Xu, M. Li, Q. Li, W. Q. Xu, *Appl. Catal. B*, **2017**, 210, 184–193.
- [29] Y. Y. Duan, L. Liang, K. L. Lv, Q. Li, M. Li, *Appl. Surf. Sci.*, **2018**, 456, 817–826.
- [30] X. Ning, F. X. Wei, H. Y. Fu, X. L. Qu, Z. Y. Xu, S. R. Zheng, *Appl. Surf. Sci.*, **2018**, 445, 535–541.
- [31] J. X. Low, S. Q. Qiu, D. F. Xu, C. J. Jiang, B. Cheng, *Appl. Surf. Sci.*, **2018**, 434, 423–432.
- [32] X. Y. Ma, Q. J. Xiang, Y. L. Liao, T. L. Wen, H. W. Zhang, *Appl. Surf. Sci.*, **2018**, 457, 846–855.
- [33] T. Shi, Y. Y. Duan, K. L. Lv, Z. Hu, Q. Li, M. Li, X. F. Li, *Front. Chem.*, **2018**, 6, 175/1–175/10.
- [34] Q. Li, Y. Xia, C. Yang, K. L. Lv, M. Lei, M. Li, *Chem. Eng. J.*, **2018**, 349, 287–296.
- [35] C. J. Zhang, L. J. Tian, L. Q. Chen, X. F. Li, K. L. Lv, K. J. Deng, *Chin. J. Catal.*, **2018**, 39, 1373–1383.
- [36] Q. Tang, X. F. Meng, Z. Y. Wang, J. W. Zhou, H. Tang, *Appl. Surf. Sci.*, **2018**, 430, 253–262.
- [37] Z. Y. Zhang, B. Dong, M. Y. Zhang, J. D. Huang, F. Lin, C. L. Shao, *Int. J. Hydrogen Energy*, **2014**, 39, 19434–19443.
- [38] E. Formo, E. Lee, D. Campbell, Y. Xia, *Nano Lett.*, **2008**, 8, 668–672.
- [39] Z. K. Zheng, B. B. Huang, X. Y. Qin, X. Y. Zhang, Y. Dai, *Chem. Eur. J.*, **2010**, 16, 11266–11270.
- [40] Y. P. Lin, S. Y. Lin, Y. C. Lee, Y. W. Chen-Yang, *J. Mater. Chem. A*, **2013**, 1, 9875–9884.
- [41] Y. H. Li, X. F. Wu, W. K. Ho, K. L. Lv, Q. Li, M. Li, S. C. Lee, *Chem. Eng. J.*, **2018**, 336, 200–210.
- [42] W. G. Wang, H. Y. Zhang, R. Wang, M. Feng, Y. M. Chen, *Nanoscale*, **2014**, 6, 2390–2396.
- [43] X. Li, J. Xie, C. J. Jiang, J. G. Yu, P. Y. Zhang, *Front. Environ. Sci. Eng.*, **2018**, 12, 14-1–14-32.
- [44] M. C. Yan, F. Chen, J. L. Zhang, M. Anpo, *J. Phys. Chem. B*, **2005**, 109, 8673–8678.
- [45] Z. A. Huang, Z. Y. Wang, K. L. Lv, Y. Zheng, K. J. Deng, *ACS Appl. Mater. Interfaces*, **2013**, 5, 8663–8669.
- [46] Z. Y. Wang, K. L. Lv, G. H. Wang, K. J. Deng, D. G. Tang, *Appl. Catal. B*, **2010**, 100, 378–385.
- [47] X. Li, J. G. Yu, M. Jaroniec, *Chem. Soc. Rev.*, **2016**, 45, 2603–2636.
- [48] X. B. Zhu, X. Tu, D. H. Mei, C. H. Zheng, J. S. Zhou, X. Gao, Z. Y. Luo, M. J. Ni, K. F. Cen, *Chemosphere*, **2016**, 155, 9–17.
- [49] L. Liang, K. N. Li, K. L. Lv, W. K. Ho, Y. Y. Duan, *Chin. J. Catal.*, **2017**, 38, 2085–2093.
- [50] K. L. Lv, J. C. Hu, X. H. Li, M. Li, *J. Mol. Catal. A*, **2012**, 356, 78–84.

Graphical Abstract

Chin. J. Catal., 2020, 41: 209–218 doi: S1872-2067(19)63470-4

Fabrication of TiO₂ nanofiber assembly from nanosheets (TiO₂-NFs-NSs) by electrospinning-hydrothermal method for improved photoreactivity

Yachao Lu, Xiaoyu Ou, Wenguang Wang*, Jiajie Fan, Kangle Lv*

South-Central University for Nationalities; Guangdong University of Technology; Zhengzhou University

A TiO₂ nanofiber assembly was prepared from nanosheets (TiO₂-NFs-NSs) by hydrothermal reaction of TiO₂ nanofibers in NaOH solution followed by acid washing and calcination. The unique structures enable TiO₂-NFs-NSs to exhibit improved photoelectric conversion efficiency and enhanced photoreactivity toward acetone oxidation.

[51] L. Zhang, C. Yang, K. L. Lv, Y. C. Lu, Q. Li, X. F. Wu, Y. H. Li, X. F. Li, J. J. Fan, M. Li, *Chin. J. Catal.*, **2019**, 40, 755–764.

[52] H. X. Li, Z. F. Bian, J. Zhu, D. Q. Zhang, G. S. Li, Y. N. Huo, H. Li, Y. F. Lu, *J. Am. Chem. Soc.*, **2007**, 129, 8406–8407.

静电纺丝-碱热法制备高活性由纳米片组装的TiO₂纳米纤维

陆亚超^a, 欧小雨^a, 王文广^{b, #}, 范佳杰^c, 吕康乐^{a, *}

^a中南民族大学资源与环境学院, 催化转化与能源材料化学教育部重点实验室, 湖北武汉 430074

^b广东工业大学材料与能源学院, 广东广州 510006

^c郑州大学材料科学与工程学院, 河南郑州 450001

摘要: 半导体光催化有望解决日益严峻的环境污染与能源危机, 因而得到广泛重视. 纳米TiO₂因为其强的氧化能力和良好的(光)化学稳定性与生物相容性, 成为了最受欢迎的半导体光催化材料. 到目前为止, 材料科学家们制备了多种形貌的TiO₂光催化材料, 如纳米棒(线)、纳米片和空心微球等.

作为染料太阳能电池的光阳极材料, 小颗粒尺寸的纳米TiO₂具有大的比表面积, 有利于敏化剂的吸附, 从而增强太阳能电池的光电转换性能. 但是尺寸太小的TiO₂颗粒不利于光散射, 导致入射的太阳光直接穿透光阳极薄膜而不利于吸收和利用太阳光. 为了解决敏化剂吸附和增强光散射这对矛盾, 本文设计制备了由纳米片组装的TiO₂纳米纤维: (1)首先通过静电纺丝法制备TiO₂纳米纤维前驱体; (2)将TiO₂纳米纤维前驱体在500 °C焙烧, 去除有机物, 得到晶化度良好的由纳米颗粒组装的TiO₂纳米纤维; (3)将TiO₂纳米纤维进行NaOH碱热处理, 使TiO₂纳米颗粒转化成钛酸盐纳米片, 然后经历酸洗和焙烧, 得到由纳米片组装的TiO₂纳米纤维. 染料敏化太阳能电池的性能测试结果显示, 碱热2.5 h所得TiO₂样品的光阳极薄膜的光电转化效率提升了2.3倍; 同时, 利用丙酮光催化分解的活性来评价纳米纤维的光催化活性, 发现碱热2.5 h所得纳米纤维上光催化降解丙酮的活性提升了3.1倍.

结构表征结果显示, 随着碱热时间的延长, 从纤维表面生长出来的纳米片逐渐变长, 催化剂的比表面积和孔容不断增加. 大的比表面积有利于底物的吸附, 纳米片结构有利于增强光散射, 通过延长光程增强对光的利用效率, 从而提升纳米纤维的光活性. 光电流测试的结果显示, 与碱热前的TiO₂纳米纤维相比, 碱热后的TiO₂纳米纤维光电流显著增强, 这是由于纳米片结构减小了扩散距离, 有利于光生载流子快速转移到催化剂表面, 引发丙酮的光催化氧化.

关键词: TiO₂纳米纤维; 静电纺丝; 光催化氧化; 丙酮; 染料敏化太阳能电池

收稿日期: 2019-06-23. 接受日期: 2019-08-09. 出版日期: 2020-01-05.

*通讯联系人. 电话: (027)67841369; 传真: (027)67843918; 电子信箱: lvkangle@mail.scuec.edu.cn

#通讯联系人. 电话/传真: (020)39322570; 电子信箱: wenguangwang2005@163.com

基金来源: 国家自然科学基金(51672312和21373275); 中南民族大学中央高校基本科研业务费专项资金(CZT19006).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).