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Hydrogen producing water treatment through mesoporous TiO₂ nanofibers with oriented nanocrystals

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ABSTRACT

The development of well-defined TiO₂ nanoarchitectures is a versatile strategy to achieve high-efficiency photocatalytic performance. In this study, mesoporous TiO₂ nanofibers consisting of oriented nanocrystals were fabricated by a facile vapothermal-assisted topochemical transformation of preformed H-titanate nanobelts. The vapothermal temperature is crucial in tuning the microstructures and photocatalytic redox properties of the resulting mesoporous TiO₂ nanofibers. The microstructures were characterized with XRD, TEM, XPS and nitrogen adsorption-desorption isotherms, etc. The photocatalytic activities were evaluated by photocatalytic oxidation of organic pollutant (Rhodamine B as an example) as well as photocatalytic reduction of water to generate hydrogen (H₂). The nanofibers vapothermally treated at 150 °C showed the highest photocatalytic activity in both oxidation and reduction reactions, 2 times higher than that of P25. The oriented alignment and suitable mesoporosity in the resulting nanofiber architecture were crucial for enhancing photocatalytic performances. The oriented alignment of anisotropic anatase nanocrystals shall facilitate faster vectorial charge transportation along the nanofibers architecture. And, the suitable mesoporosity and high surface area would also effectively enhance the mass exchange during photocatalytic reactions. We also demonstrate that efficient energy-recovering photocatalytic water treatments could be accomplished by a cascading oxic-anoxic process where the dye is degraded in the oxic phase and hydrogen is generated in the successive anoxic phase. This study showcases a novel and facile method to fabricate mesoporous TiO₂ nanofibers with high photocatalytic activity for both clean energy production and environmental purification.

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1. Introduction

Semiconductor photocatalysis has been widely applied for

the high-level air and water purification in terms of persistent organic pollutants mineralization [1], heavy metal ions detoxification [2] and microorganism inactivation [3,4], as well as

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sustainable solar fuels production by water splitting [5] and/or carbon dioxide reforming [6]. Titania (TiO_2) is one of the most promising photocatalysts due to its outstanding photocatalytic performance, long-term stability against photochemical and chemical corrosion, acceptable cost-efficiency and environmental sustainability in production and service [7].

The properties of TiO_2 are significantly determined by their structure, for instance, by their dimensions, crystallinity, and geometry [8–10]. Therefore, the design of nanostructures offers further opportunities to exploit advanced TiO_2 photocatalysts with commercial and industrial potential [11]. Recently, one-dimensional (1-D) TiO_2 nanostructures, such as tubes, wires and fibers, etc., have been proved to have extraordinary charge separation and transport ability, giving rise to longer lifetimes and diffusion lengths of the photo-generated charge carriers and thus leading to higher photocatalytic quantum efficiency [12–15]. In this regard, flexible design and controllable preparation of 1-D nanostructured TiO_2 photocatalyst have attracted enormous research attention and represents a basis for realization of enhanced photocatalytic performance [15–17].

Various methods, such as sol-gel [18], hydrothermal [19], solvothermal [20] and electrospinning [21,22] methods have been well developed to synthesize tailor 1-D TiO_2 nanostructures, whereas the hydrothermal-assisted method is the most widely employed one due to its simplicity and effectiveness. Typically, the hydrothermal-assisted method involves two main steps [14]. Firstly, a facile hydrothermal treatment in concentrated NaOH aqueous solutions converts random irregular TiO_2 particles into uniform 1-D nanostructured sodium titanate intermediates. Subsequently, the as-obtained titanate nanostructure is transformed into well-defined TiO_2 counterparts via hydrogen-ion exchange and following thermal transformation. Significantly, the above-mentioned titanate intermediate mediated two-step synthesis procedures allow great potentials in creating structural variety and optimizing photocatalytic performances [23]. It has been demonstrated that both the titanate intermediate formation and transformation processes regulate the structural features of the resulting TiO_2 products, including phase, size, shape and composition [24,25]. In particular, controlling thermal transformation process of H-titanate to TiO_2 products is effective in tuning the fine structures and the photocatalytic performance [9,14]. To date, two typical thermal treatment methods, calcination and hydrothermal, have been intensively studied for transformation of 1-D H-titanate nanostructures to highly active nanostructured TiO_2 photocatalysts [24–26]. However, the reaction condition of these methods are drastic and often led to the rupture of the 1-D nanofiber structure and random arrangement of grains. Previously, vapothermal method has been demonstrated as an effective method to control the nanostructure growth [24]. For example, Liu et al., [27] demonstrated that the direct growth of TiO_2 nanosheets with single-crystalline anatase structure can be obtained via vapor phase hydrothermal condition. The superiority of vapothermal method can be ascribed to the mild reaction occur within a thin-liquid layer reaction zone formed on the surface of the substrate. Nevertheless, no vapothermal

method has been reported for the fabrication of mesoporous TiO_2 nanofiber.

In this study, a novel vapothermal method was developed to transform H-titanate nanobelts to mesoporous TiO_2 nanofibers. A systematic investigation was carried out to reflect the multi-levelled structure of the resultant nanofibers. The photocatalytic activity of the mesoporous TiO_2 nanofibers were evaluated via the photocatalytic decomposition of an organic dye and water splitting to generate hydrogen. Interestingly, it is demonstrated that the oriented alignment and suitable mesoporosity in the resulting nanofiber architecture were crucial in guaranteeing the superior photocatalytic performances.

2. Experimental

2.1. Synthesis

The mesoporous TiO_2 nanofibers were synthesized via two distinctive steps. First, H-titanate were prepared using a chemical process similar to that described by Yu and coworkers [24,25]. In brief, 1.5 g of commercial-grade TiO_2 powder (P25, Degussa AG, Germany) was mixed with 100 mL NaOH solution (10 mol L^{-1}), then the mixture was subjected to hydrothermal treatment at 200°C in a 150 mL Teflon-lined stainless steel autoclave for 48 h. Subsequently, the precipitate was dispersed by sonication to obtain homogeneous reaction product. Afterwards, the reaction product was filtered, rinsed with HCl solution (0.1 mol L^{-1}) to induce hydrogen-sodium ion exchange. Thereafter, the product was washed with ultrapure water for 3 times (100 mL each time). The washed samples were vacuum-dried at 80°C for 8 h. Second, 1 g of the product was further treated in a water vapor environment in a sealed Teflon-lined autoclave at temperatures of 120, 150, 180 and 200°C , respectively, for 12 h. Thirty-milliliter ultrapure water was initially added to the Teflon to generate water vapor. A porous stainless steel holder (15 mm $\times$ 20 mm $\times$ 50 mm) with filter paper was placed into the Teflon and used to hold the products (Fig. 1) above the liquid water. After vapothermal treatment, the as-prepared products were dried in a vacuum oven at 80°C for 8 h and ready for further characterization or photocatalytic experiments.

2.2. Characterization

X-ray diffraction (XRD) patterns of the samples were ob-

Fig. 1. Schematic illustration of synthesis of mesoporous TiO_2 nanofibers by vapothermal transformation.

tained using a D/MAX-RB X-ray diffractometer (Rigaku, Japan) using Cu $K\alpha$ irradiation at a scan rate (2θ) of 0.05° per second. The applied current and accelerating voltage were 20 mA and 15 kV, respectively. Scanning electron microscopy (SEM) analyses were performed using a Sigma-500 electron microscope (ZEISS, Germany). Transmission electron microscopy (TEM) analyses were carried out using a JEM-2010FEF electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250 X-ray photoelectron spectrometer. All the binding energies were calibrated using the C 1s peak at 284.6 eV. Nitrogen adsorption-desorption isotherms of the samples were determined using an ASAP 2020 (Micromeritics Instruments, USA) nitrogen adsorption apparatus. All samples were degassed at 100°C before BET measurements. The Brunauer-Emmett-Teller (BET) specific surface area (A_{BET}) was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.25. Desorption isotherm was used to determine the pore size distribution using the Barret-Joyner-Halender (BJH) method [28]. The nitrogen adsorption volume at the relative pressure (P/P_0) of 0.970 was used to determine the pore volume and the average pore size. Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were obtained on a UV-Visible spectrophotometer (UV-2550, SHIMADZU, Japan) in the range of 200–600 nm, using BaSO_4 as a blank reference. The transient photocurrent responses of typical samples was conducted on a CHI760E electrochemical workstation with three-electrode system. In particular, a Pt wire electrode and Ag/AgCl/saturated KCl electrode were used as the counter electrode and reference electrode, respectively, and the film electrode consisting of each as-prepared sample on FTO conductive glass with an active area of ca. 1.5 cm^2 was used as the working electrode. The photoluminescence (PL) spectra of the typical samples were recorded with a fluorescence spectrophotometer (F-4500, Hitachi, Japan) using excitation at 325 nm. The PL time resolved spectra was recorded with a FLS 1000 spectrofluorometer (Edinburgh Instruments, UK) with a picosecond pulsed diode laser as the excitation light source (365 nm).

2.3. Photocatalytic activity measurements

The photocatalytic activities of the samples were evaluated by the oxidation of a typical organic dye pollutant, rhodamine B (RhB), and reduction of protons to generate hydrogen (H_2), respectively. The photocatalytic oxidation of RhB was conducted in Pyrex flask, containing the as-prepared samples under UV-light irradiation at ambient temperature and atmospheric pressure. A 15-W 365 nm UV lamp (Cole-Parmer Instrument Co.) was used as a light source. The focused UV intensity on the flask was about 3 mW cm^{-2} . The initial concentration of RhB was 10 mg L^{-1} . The concentration of photocatalyst used was 100 mg L^{-1} in a 100-mL aqueous solution of RhB. Prior to each experiment, the solutions were continuously stirred in dark for 1.0 h to achieve adsorption-desorption equilibrium between RhB and photocatalyst. At given time inter-

vals, four-milliliter of the reaction solutions was sampled and centrifuged for 10 min at a speed of 6000 rpm. The obtained dye filtrates were analyzed by a UV-2550 UV-visible spectrophotometer (Shimadzu, Japan) to estimate the dye concentrations.

The photocatalytic H_2 production experiments were carried out in a cylindrical quartz reaction cell connected to a closed gas circulation and evacuation system (Beijing Perfect Light Technology Co., Ltd China). In the photo-reaction system, 50 mg of the as-prepared samples loaded with co-catalysts Pt nanoparticles (1 wt%, using the *in-situ* photodeposition method), were dispersed in 50 mL of DI water. Unless otherwise stated 10 vol% methanol was employed as a sacrificial agent in the photocatalytic hydrogen evolution test. The solution was purged with nitrogen gas to remove dissolved air before irradiation. The solution was irradiated by a 300W Xenon lamp (Beijing Perfect Light Co. Ltd., Beijing), which was positioned 3 cm above the reactor, to trigger the photocatalytic reaction. The focused UV intensity on the reactor was about 3 mW/cm^2 . To identify and quantify the hydrogen gas produced, a volume of 1.5 mL of gas sampled and measured by a gas chromatography (GC 7806, Beijing Shiweipx analysis instrument Co., Ltd. China) equipped with a thermal conductivity detector (TCD) and a $5\text{ \AA}$ molecular sieve column, where high purity nitrogen gas was used as the carrier gas.

2.4. Scavenger study

In order to distinguish the role of the reactive species corresponding to the photocatalytic degradation of RhB, we perform the scavenger study, which employs different scavengers individually to remove the corresponding reactive species, so that we can understand the function of different reactive species in the photocatalytic RhB degradation process based on the change of dye decolorization efficiency. Isopropanol (IPA) was used to removed $\cdot\text{OH}$ diffusing into the solution bulk, sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) to remove the h^+ , 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL) was used to remove the $\cdot\text{O}_2^-$, Cr(VI) to remove the e^- , and Fe(II) to remove the H_2O_2 . The concentration of the scavenger applied was optimized according to our previous studies [29,30].

3. Results and discussion

3.1. Characterization

The SEM image of the as-prepared H-titanate is shown in the Fig. 2. It could be clearly observed that H-titanate formed a belt-like structure with a length ranging from several to several tens of μm and a width varying from 30 to 300 nm. This morphology was assumed to arise from the post-hydrothermal acid washing process, where the lamellar titanate is scrolled and transformed into nanobelts driven by the imbalanced surface energy with the gradual substitution of Na^+ with H^+ by being washed with HCl [9]. The XRD pattern of as-prepared H-titanates (Fig. 3(a)) showed a prominent diffraction peak at $2\theta = 10.9^\circ$, which corresponded to the layer structure titanates

Fig. 2. SEM image of the as-prepared H-titanate nanobelts.

family [24,31,32]. After vapothermal transformation at 120 °C for 12 h, both titanate and anatase (JCPDS, No. 21-1272) were presented in the reaction products based on its XRD pattern (Fig. 3(b)), suggesting a partial phase transition of the titanate to anatase [33,34]. When vapothermal temperature was equal to or higher than 150 °C (Fig. 3(c)–3(e)), the diffraction peak for titanates disappeared and only anatase phase was detected, indicating the high purity of anatase phase in the as-prepared samples. The average crystallite sizes of the vapothermal transformed samples at 120, 150, 180 and 200 °C were calculated as 8.22, 17.34, 20.12 and 22.84 nm, respectively, according to Debye-Scherrer formula on the diffraction peaks of anatase (101) crystallite plane. These results revealed that the vapothermal treatment induced a topochemical reaction process, which transformed the H-titanates into TiO₂ of anatase phase, and complete transition could be achieved by adjusting the reaction temperature (≥ 150 °C). Additionally, the grain size of the obtained TiO₂ anatase increased with an increase of the reaction temperature.

The typical SEM images (Fig. 4) shows that the as-prepared sample indeed mainly consist of high-yield and fiber-like nanostructures with the sizes similar to that of the untreated H-titanate. Fig. 5 shows the representative TEM images of the as-prepared samples. Likewise, it could be seen that vapothermal transformed H-titanate samples remained a 1-D fibrous structure as presented in Fig. 5(a) and (c). Higher magnification of the TEM images (Fig. 5(b) and (d)) revealed that the nanofibers were piled compactly with nanoparticles that had a primary particle size of ~ 20 nm. Moreover, these nanoparticles

Fig. 3. XRD patterns of the as-prepared H-titanate nanobelts (a), and nanofibers obtained at vapothermal temperature of 120 °C (b), 150 °C (c), 180 °C (d), 200 °C (e).

Fig. 4. Low (a) and high (b) magnification SEM images of the as-prepared mesoporous TiO₂ nanofibers prepared by vapothermal treatment of H-titanate at 150 °C.

were directionally arranged as a bundle along the fiber orientation. A HRTEM image (Fig. 5(e)) revealed that the as-prepared TiO₂ nanofibers are mainly a single crystalline structure in anatase phase, which is consistent with the XRD results. The inter-planar spacing of the nanofiber was measured as 0.35 nm, corresponding to the (101) crystal plane of anatase. These suggested that further vapothermal post-treatment for the H-titanate nanobelts enables them with well crystallized and closely packed grains in a well-ordered one-dimensional structure. Such a directional alignment of TiO₂ nanoparticles was expected to promise a rapid and efficient charge transfer between the interconnected nanoparticles, resulting in a more

Fig. 5. TEM images of the as-prepared mesoporous TiO₂ nanofibers prepared by vapothermal treatment of H-titanate at 150 °C (a, b), 180 °C (c, d), and a representative HRTEM image (e) of the TiO₂ nanofiber obtained at 150 °C.

efficient photocatalytic activity. Ordered assembly of primary nanostructures is a feasible method to create highly active photocatalysts. For instance, Bian et al. [35] revealed that the well-aligned TiO_2 mesocrystal superstructures can directionally migrate the electron generate from surface plasmon resonance (SPR) excitation of Au nanoparticles, thus retarding the charge recombination process and resulting in enhanced photocatalytic activity, as compared with the conventional aggregated nanoparticle system of P25. In this study, the H-titanate were crystallized and turned into uniform and closely contacted anatase grains during the vapothermal process while maintaining the morphology and topotaxy of 1-D nanofibers (Fig. 4). This can be attributed to the unique mild vapothermal environment created by the water vapor. Conversely, the conventional hydrothermal post-treatment often led to the rupture of the 1-D nanofiber structure and random arrangement of grains, owing to the drastic disturbance caused by the boiling water in liquid phase [24,26,36]. For example, Yu et al. [24] observed many scattered grains and ruptured nanoribbons after liquid-phase hydrothermal post-treatment of titanate at 150 °C for 24 h. This suggested that unique vapor thermal reaction environment differs remarkably from that of liquid-phase hydrothermal process, and the vapor thermal conditions can be readily used to effectively control the nanostructure through a relatively mild pathway [37,38].

The XPS was applied to probe the surface chemical compositions and chemical states of the representative mesoporous TiO_2 nanofibers obtained at vapothermal treatment of 150 °C

(Fig. 6). As shown in Fig. 6(a), the XPS survey spectrum indicated that Ti and O, and C elements were detected with the characteristic XPS peaks appearing at binding energies of 458.78 eV (Ti 2p), 529.94 eV (O 1s) and 284.6 eV (C 1s) [39], respectively. The peak for C 1s with a binding energy of 284.6 eV was attributed to the adventitious hydrocarbon from the XPS instrument. Fig. 6(b) presented the typical high-resolution XPS spectrum of Ti 2p. The two highly symmetric Ti 2p peaks were centered at around 458.78 eV (Ti 2p_{3/2}) and 464.48 eV (Ti 2p_{1/2}), and the peak-to-peak separation due to the spin-orbit coupling effect was measured as 5.7 eV, which was in excellent accordance with the reported value of the Ti⁴⁺ state in TiO_2 [40]. The two fitted peaks located at 529.94 and 531.46 eV of the O 1s (Fig. 6(c)) were ascribed to the lattice oxygen (Ti–O–Ti) and surface hydroxyl groups (Ti–OH), respectively. In addition, no Na was detected (Fig. 6(d)), which indicated the Na is eliminated in the washing process with HCl.

The specific surface area and pore size distributions of the as-prepared nanofibers were examined by nitrogen adsorption-desorption isotherms at 77 K (Fig. 7). It was observed that all the samples exhibited a type H3 hysteresis loop according to IUPAC classification, implying the presence of mesopores (2–50 nm), which was well in accordance with their porous morphology (Fig. 5). Additionally, the measured hysteresis loop approaches $P/P_0 = 1$, indicating the presence of macropores (>50 nm). The presence of pores in wide size distribution could be ascribed to either the intra- and inter-aggregation of single crystals during the formation of 1-D nanofiber structure [41].

Fig. 6. XPS survey spectrum (a) and high-resolution XPS spectra of Ti 2p (b), O 1s (c) and Na 1s (d) of the mesoporous TiO_2 nanofibers obtained at 150 °C.

Fig. 7. The nitrogen adsorption-desorption isotherms (a) of the as-prepared H-titanate and mesoporous TiO₂ nanofibers, and their corresponding pore size distributions (b).

The pore size of all the obtained samples showed a wide distribution ranging from 2 to 100 nm (Fig. 7(b)). Further analysis of the adsorption data in the relative pressure (P/P_0) range of 0.05–0.25 yielded information regarding the BET specific surface area (A_{BET}) and results indicated that the mesoporous TiO₂ nanofibers obtained at 150 °C possessed the highest A_{BET} (68 m²/g) among all the synthesized samples (Table 1). Meanwhile, mesoporous TiO₂ nanofibers obtained at 150 °C had the highest value of pore volume (0.15 cm³/g) calculated with a BJH method. As for the average pore size, they followed a rough increasing trend along with the increasing vapothermal temperature, ranging from ca. 7.5 to 11.8 nm. These results collectively indicated that the mesoporous TiO₂ nanofibers could be successfully synthesized by vapothermal transformation and the reaction temperature obviously affected the purity, A_{BET} , pore volume and average pore size of the resultant products.

3.2. Photocatalytic performance

Fig. 8 shows the light absorption characteristics of the mesoporous TiO₂ nanofibers obtained at different vapothermal temperature. It was found that a slight enhancement in the absorption band at wavelength less than 400 nm after vapothermal transformation compared with the H-titanates, and the absorption edge of the as-synthesized samples showed a

Table 1

The specific surface area and porous features of the H-titanate and mesoporous TiO₂ nanofibers obtained under different temperature.

Sample	A_{BET}^a (m ² /g)	Pore volume ^b (cm ³ /g)	Average pore size ^c (nm)
H-Titanate	43	0.09	8.3
120 °C	67	0.12	7.5
150 °C	68	0.15	8.9
180 °C	31	0.09	11.5
200 °C	22	0.06	11.8

^a BET surface areas determined from the N₂ adsorption-isotherms.

^b BJH desorption cumulative volume of pores between 2.0 nm and 100 nm.

^c BJH pore diameters determined from the nitrogen desorption branches.

red-shift in parallel with increasing temperature. This could be reasoned by the changes in both compositions and phase structures of the samples after vapothermal treatment. Further elucidation of the impact of the vapothermal temperature on the red shift could be obtained from estimation of the band gap energies. The intercept of the tangent to the plot of $(h\nu\alpha)^{1/2}$ versus photon energy ($h\nu$) (Fig. 8(b)) would enable a good approximation of the indirect band gap energies of the photocatalysts. The band gap energy for the H-titanate was estimated to be 3.21 eV, which was higher than the reported value of 3.1 eV for titanate nanotubes [42]. This could be attributed to the

Fig. 8. UV-vis spectra of the of the as-prepared of the as-prepared H-titanate and mesoporous TiO₂ nanofibers (a), and their plots of $(h\nu\alpha)^{1/2}$ versus photon energy ($h\nu$) (b).

Fig. 9. Comparison of the photocatalytic degradation of rhodamine B (a) and H_2 evolution rates (b) over various temperature mesoporous TiO_2 nanofibers and P25. Pt (1 wt%) was loaded on the photocatalysts and 10 v% methanol was incorporated as sacrificing reagents in the hydrogen production tests.

surface modification by hydrogen ion on the H-titanates. After vapothermal post-treatment, the band gap energies of the samples underwent slightly decrease, but were very close to the value of anatase phase TiO_2 (3.2 eV) [43]. The different band gap energies could be related to the synthesized method or the surface microstructures of the mesoporous TiO_2 fibers.

The photocatalytic oxidation activities of the mesoporous TiO_2 nanofibers after vapothermal treatment at various temperature were evaluated by photocatalytic oxidation of RhB as illustrated in Fig. 9(a). For comparison, the photocatalytic activity of commercial photocatalyst of TiO_2 P25 (Degussa, German) was also tested under identical conditions. The oxidation activities of the mesoporous TiO_2 nanofibers obtained at 120, 150 and 180 °C were higher than that of the P25, which is generally regarded as a model photocatalyst with good photocatalytic activity. The sample obtained at 150 °C shown the highest oxidation activities followed by 180 °C and then 120 °C. In contrast, the sample obtained at 200 °C and H-titanate exhibited relatively poor photocatalytic oxidation performance. The measurement of photocatalytic reduction properties was carried out in PLS-SXE300 reactor (PerfectLight, China) coupled with an online detection system for H_2 [44]. As shown in Fig. 9(b), the photocatalytic activity of the sample obtained at 150 °C showed the most excellent photocatalytic H_2 production activity ($3200 \mu\text{mol h}^{-1} \text{g}^{-1}$) and exceeded that of P25 TiO_2 ($1790 \mu\text{mol h}^{-1} \text{g}^{-1}$) by a factor of about 2 times. Meanwhile, the

samples prepared under other temperature exhibited H_2 production rates comparable to (180 °C) or lower than (120 and 200 °C) that of P25 TiO_2 . These results suggested that 150 °C was the best vapothermal temperature to achieve the greatest photocatalytic performance.

In order to obtain further insights into the transfer dynamics of photogenerated charge carriers, the transient photocurrent analyses was performed. Fig. 10(a) compares the transient photocurrent responses of samples P25 and mesoporous TiO_2 nanofibers with the best photocatalytic activities (150 °C), which were recorded for three on-off cycles of light irradiation. Obviously, compared with P25, the mesoporous TiO_2 nanofibers showed a significant enhancement (approximately 1.8 times) in the photocurrent response under UV-visible light irradiation. A higher photocurrent often corresponded to a higher separation efficiency of charge carriers [45]. This conclusion was further corroborated by PL results (Fig. 10(b)). The PL results clearly showed that, the characteristic PL peak of the TiO_2 (~475 nm) in the mesoporous TiO_2 nanofibers was obviously lower than that of P25, indicating that the recombination of the photogenerated charge carrier was greatly inhibited in the mesoporous TiO_2 nanofibers. The surviving time of the charge carriers were probed the by the time resolved photoluminescence spectra (Fig. 10(c)). The time resolved spectra profile shows that the TiO_2 nanofiber exhibited slower decay traces and a longer PL lifetime (~2.4 ns), compared to the P25

Fig. 10. The transient photocurrent responses (a), photoluminescence (PL) spectra (b) and time resolved PL spectra of the mesoporous TiO_2 obtained at 150 °C and P25.

(~1.1 ns). This phenomenon demonstrated that the as-prepared TiO₂ nanofiber can indeed decrease recombination chance of electron and hole [46]. The resulting efficient charge separation would increase the lifetime of the charge carriers, enhance the interfacial charge transfer efficiency and finally leading to boosting photocatalytic activities.

As a matter of fact, the overall photocatalytic activity of TiO₂ could be determined collectively by several aspects such as (1) charge separation (2) charge transport to the surface (3) charge recombination (4) crystallization and (5) specific surface area, as reported in previous literature [12,47]. In the present study, the relatively high photocatalytic activity of the as-prepared mesoporous nanofibers could be attributed to two possible reasons. Firstly, the well-ordered and aligned TiO₂ particle assembly in as-prepared mesoporous TiO₂ nanofibers provides a superior structure to enhance the separation of electron-hole charge pairs and facilitate interparticle charge transfer along the nanofiber framework [48]. Because the TiO₂ nanoparticles are directionally interconnected and arranged, a rapid and vectorial transport of photo-generated charge carriers (electrons and holes) is likely to occur between the grain boundaries [36,49], as illustrated in Fig. 11. This would possibly lead to the consequences that the oxidation and reduction sites are away from the initial photo-excitation sites, thereby lowering the radiative recombination of self-trapped excitons and enabling an effective electron-hole separation [50]. Secondly, the relatively high specific surface area and pore volume in the mesoporous structure created via the TiO₂ particle-particle interconnection is very advantageous in enhancing the adsorption of reactants and desorption of products [51]. For example, a larger specific surface area could enable more reactants to be absorbed onto the surface of the photocatalysts and a higher pore volume could lead to a faster diffusion of various gaseous products during the photocatalytic reaction. It was evident that all the mesoporous TiO₂ nanofibers obtained at temperature ≥ 150 °C exhibited the same crystal phase (anatase) with high crystallinity based on their XRD patterns (Fig. 3), but the properties in the photocatalytic performance (both oxidation and reduction) were significantly different. This suggested that the crystal phase herein had minor effect on their

Fig. 11. Schematic illustration for the mesoporous TiO₂ nanofibers and its photocatalytic reaction mechanisms.

photocatalytic performance. The superior activities of the nanofiber samples obtained at vapothermal treatment of 150 °C could be partially attributable to its mesoporosity with relatively high values of A_{BET} (68 m² g⁻¹) and pore volume (0.15 cm³ g⁻¹) (Table 1). The abovementioned two factors could work synergistically and contribute to the enhancement of photocatalytic activities.

As the above results demonstrate, the as-prepared mesoporous TiO₂ nanofibers exhibited excellent photocatalytic dye degradation (under oxic environment) and hydrogen production activities (under anoxic environment and using electron donor). It is worth noting that the many of the electron donors (e.g., methanol and ethanol) are energy resource themselves, which increases the costs of the photocatalytic process and inhibits its practical application. With the aim to address this limitation, we integrated the photocatalytic hydrogen evolution and degradation of organic dye using the mesoporous TiO₂ nanofibers (150 °C) in a single process under anoxic environment where electron donor was replaced by the RhB. As shown in Fig. 12, there was no notable hydrogen evolution and dye degradation in the first 3 h. From 3 h onward, the dye concentration decreased slightly along with an increasing H₂ generation. Nevertheless, the dye degradation efficiency were substantially lower than that of the single dye degradation test (Fig. 9(a)). These results indicated that the RhB cannot efficiently react with the photoexcited holes under anoxic environment, leading to the inferior performance of these photocatalytic system. Considering the result that hydrogen was evolved after 3 h reaction, it is reasonable to infer that the dye degradation intermediates possibly play the role of sacrificing substrates, other than the pristine dye.

To further elucidate the photocatalytic mechanism and the role RhB of in the system, scavenger experiments of reactive species (RSs) were carried out using IPA (1 mL), TEMPOL (20 mM), Na₂C₂O₄ (2 mM), Kr₂Cr₂O₇ (1 mM), FeSO₄-EDTA (0.2 mM) for hydroxyl radicals ($\bullet$ OH), superoxide radicals ($\bullet$ O₂⁻), holes (h⁺), electron (e⁻), hydrogen peroxide (H₂O₂), respectively. As displayed in Fig. 13, the addition of IPA, TEMPOL and Fe-EDTA led to 21.3%, 13.6% and 38.2% decrease in RhB concentration,

Fig. 12. Concurrent photocatalytic dye degradation and hydrogen evolution over mesoporous TiO₂ nanofibers (150 °C) without standard sacrificing reagent (10 vol% methanol).

Fig. 13. The impact of the incorporations of various scavengers for typical reactive species on the RhB degradation rate after 3 h photocatalytic test after mesoporous TiO₂ nanofibers (150 °C).

respectively, after 3 h irradiation, implying $\bullet\text{O}_2^-$ were predominantly involved in the degradation of RhB, followed by $\bullet\text{OH}$ and then H_2O_2 . However, in the presence of $\text{Na}_2\text{C}_2\text{O}_4$ and $\text{Kr}_2\text{Cr}_2\text{O}_7$, the decolorization efficiencies of RhB only declined to about 62.4% and 68.7%, respectively, indicating the contribution from h^+ and e^- were relatively minor. The relatively non-effective participation of e^- and h^+ could be possibly ascribed to the fact that their function need direct contact between the photocatalyst and RhB molecules. The generation of $\bullet\text{OH}$, $\bullet\text{O}_2^-$ and H_2O_2 in the TiO₂-UV system is well documented. For the $\bullet\text{OH}$, it is reported to be involved in the degradation of various organic compounds due to its strong oxidizing ability [52–57]. H_2O_2 can be derived from either two-hole oxidation of $\text{H}_2\text{O}/\text{OH}^-$ or two-electron reduction of O_2 . The moderate importance of H_2O_2 could be reasoned by its relatively high stability and can generate more reactive $\bullet\text{OH}$ through reaction with the e^- [43]. The generation of $\bullet\text{O}_2^-$ requires the reduction of O_2 by the photo-excited e^- . Despite the relatively low reactivity of $\bullet\text{O}_2^-$, it is the precursor of other RSs such as $\bullet\text{OH}$ and H_2O_2 [43]. As such, the primary contributive role of $\bullet\text{O}_2^-$ in the decolorization of RhB could be attributed to its direct function or the generation of other RSs derived from it. Nevertheless, the importance of $\bullet\text{O}_2^-$ highlights the role of dissolved oxygen in the degradation of RhB. This is consistent with previous reports where oxygen was required for efficient photocatalytic degradation of organic compound.

With the attempt to achieve efficient pollutant degradation as well as hydrogen evolution, we then carried out the experiment in two steps: (1) pre-phase of oxidic degradation where RhB is degraded, and (2) the post-phase of anoxic reduction where hydrogen evolution is achieved using the organic intermediates as sacrificing reagents. The impact of the pre-oxidation time on the subsequent hydrogen evolution rates was investigated. As can be seen in Fig. 14, the H_2 evolution rates improved with increased pre-oxidation time and reached a maximum value of $18.7 \mu\text{mol h}^{-1} \text{g}^{-1}$ at 3 h, followed by a gradual decrease to $8.2 \mu\text{mol h}^{-1} \text{g}^{-1}$ at 5 h. The decrease in hydrogen evolution rates after 3 h can be ascribed to the degradation of the intermediates after 3 h, corresponding to when the

Fig. 14. The impact of RhB pre-oxidation time on the subsequent hydrogen evolution rates of mesoporous TiO₂ nanofibers (150 °C) under anoxic environment where the intermediates were used as sacrificing reagents other than methanol.

decolorization was achieved in the pre-oxidation phase. This phenomena further support the hypothesis that the dye degradation intermediates play the role of sacrificing substrates. Moreover, the hydrogen evolution rates in the anoxic phase with preoxidized RhB were one order of magnitude higher than those in the hydrogen evolution tests with pristine RhB (Fig. 12) under single anoxic environment. This could be explained by the superior degradation efficiency in the pre-phase of oxidic environment, and therefore the amount of the intermediates were sufficient to support an efficient hydrogen evolution. Besides, the degradation of the light-absorbing RhB could also contribute to the enhanced hydrogen evolution in the cascading oxidic-anoxic process. As displayed in Fig. 15, untreated RhB can absorb UV light in the region from 320 to 380 nm and the absorbance decrease substantially after 3 h oxidic pretreatment. The band gap of the mesoporous TiO₂ nanofibers (150 °C) was measured as 3.14 eV, which indicated the photocatalysts can be activated by light with wavelength lower than $\sim 390 \text{ nm}$.

Fig. 15. The variation of UV-vis spectrum of the RhB over mesoporous TiO₂ nanofibers (150 °C) under oxidic environment for 3 h.

Therefore, the degradation of RhB could enable more active light available for the photocatalysts and the subsequent hydrogen evolution. In fact, many of the organic pollutants in water (e.g. dyes and antibiotics) are chromophoric, and thus would compete light source with the photocatalysts during their photocatalytic degradation process. This highlights the importance of the pre-phase of oxidic photocatalytic treatment process as photocatalysis is well-documented to be a decolorization technology in the presence of oxygen. Previously, numerous studies had attempted to achieve simultaneous water remediation and hydrogen generation under single anoxic condition, but generally inferior efficiencies of both dye degradation and hydrogen were obtained [58]. Our results herein showcases the suitable alignment of oxidic and anoxic photocatalytic processes could accomplish efficient water remediation and hydrogen generation successively.

4. Conclusions

In summary, we present a novel and simple method, vapo-thermal transformation, to synthesize mesoporous TiO₂ nanofibers using H-titanate as precursor. The vapo-thermal temperature had an impact on the microstructures and photocatalytic activity of the resultant mesoporous TiO₂ nanofibers. Among the samples obtained at various vapo-thermal temperature, the resulted anatase mesoporous TiO₂ nanofibers at 150 °C for 12 h exhibited the most remarkable photocatalytic activity both in oxidation of organic dyes (RhB) and reduction of protons to generate H₂. This could be attributed to a synergistic effect of (1) the improved structural ordering for effectively separating charge pairs and facilitating charge transfer along the nanofiber framework, and (2) the mesoporosity with relatively high specific surface area and pore volume that allowing enhanced interactions between the photocatalysts and reactants. This work can provide a simple yet effective way to synthesize highly active mesoporous TiO₂ nanofibers for both energy production and environmental application.

Drawing from these insights, we replaced the electron donor (methanol) in the photocatalytic hydrogen evolution test in an attempt to integrate the photocatalytic H₂ generation with the degradation of RhB in a single process. However, both the hydrogen evolution rates and dye degradation efficiencies were not satisfactory in this system, and the evolved hydrogen could be produced from using the dye degradation intermediates as sacrificing reagents. We then demonstrated that the energy-recovering photocatalytic water treatment could be achieved by a cascading oxidic-anoxic process where the dye is degraded in the oxidic phase and hydrogen is generated in the post-anoxic phase.

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Graphical Abstract

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Hydrogen producing water treatment through mesoporous TiO₂ nanofibers with oriented nanocrystals

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Hydrogen recovering photocatalytic water treatment process was achieved by a cascading oxidic-anoxic process where the dye is degraded in the oxidic phase and hydrogen is generated in the successive anoxic phase.

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有序介孔TiO₂纳米纤维及其串联光催化水处理-产氢性能

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摘要: 光催化技术在环境净化及新能源开发方面具有巨大的研究潜力, 特别在有机污染物降解去除和分解水制氢展示出了广泛的应用前景。二氧化钛(TiO₂)具有出色的光催化活性和稳定性、低成本和无毒性等性质, 是最有前景的光催化剂之一, 但离广泛实用还有一定距离。TiO₂光催化活性很大程度上取决于其尺寸、结晶度和形状等结构特征, 因此, TiO₂的纳米结构优化设计, 为开发高活性TiO₂光催化材料, 推动其商业和工业应用提供了新的可能。最近大量研究表明, 一维(1D)纳米结构, 如纳米管、纳米线和纳米纤维等, 具有卓越的光生电荷分离和传输能力, 可提高光催化活性。鉴于此, 1D TiO₂纳米光催化剂的设计和可控制备引起了广泛的研究关注。一般而言, 1D TiO₂制备方法包括溶胶凝胶法、水热法、溶剂热法和静电纺丝法。其中, 水热法由于简单高效, 是最广泛使用的一种制备方法。通常, 水热法制备1D TiO₂包括两个主要步骤。首先,

在浓NaOH水溶液中的水热处理,将不规则的TiO₂颗粒转化为均匀的1D纳米钛酸盐中间体。随后,通过氢离子交换和热转化,将所获得的钛酸盐转化为1D TiO₂。钛酸盐中间体的形成和转化过程,对调控所得1D TiO₂产物的结构特征,包括相、尺寸、形状和组成等,具有至关重要的作用。然而,传统水热法的反应条件非常苛刻,经常导致1D纳米结构的破坏及纳米颗粒的无序排列,降低了获得材料的光催化活性。因此,发展温和的钛酸盐转化方法,将为制备高活性光催化材料提供新思路。

本文通过新颖的蒸汽热方法,成功将钛酸盐纳米带转化为由纳米晶定向组装而成的介孔TiO₂纳米纤维。结合XRD, BET, TEM, XPS, UV-Vis和PL等分析手段详细表征了催化剂的组成与结构,基于有机污染物(以罗丹明B为例)降解以及光催化分解水制氢考察了催化剂的光催化活性。结果表明,在150 °C蒸汽热处理得到的1D TiO₂纳米纤维具有最高的光催化氧化活性与还原活性,均优于商业TiO₂(P25)。1D TiO₂纳米纤维具有介孔结构,其纳米晶排列有序,从而对增强光催化性能至关重要。各向异性锐钛矿纳米晶的有序排列,促进了光生电子与空穴沿纳米纤维结构定向传递,降低电子-空穴复合几率。介孔结构和高表面积有利于光催化反应过程中的质量交换。鉴于1D TiO₂纳米纤维同时具有最高的光催化氧化活性与还原活性,我们发展了光催化水处理-产氢集成新技术,通过光催化“有氧氧化-缺氧还原”串联工艺来实现。有机染料在有氧氧化过程中部分氧化,并在后续的缺氧还原阶段充当高效牺牲试剂以促进光催化分解水制氢。该研究为制备高活性有序介孔TiO₂纳米纤维及其应用提供了新思路。

关键词: 二氧化钛纳米纤维; 光催化; 污染物降解; 产氢

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