

# Article Solar Energy Storage in an All-Vanadium Photoelectrochemical Cell: Structural Effect of Titania Nanocatalyst in Photoanode

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Abstract: Solar energy storage in the form of chemical energy is considered a promising alternative for solar energy utilization. High-performance solar energy conversion and storage significantly rely on the sufficient active surface area and the efficient transport of both reactants and charge carriers. Herein, the structure evolution of titania nanotube photocatalyst during the photoanode fabrication and its effect on photoelectrochemical activity in a microfluidic all-vanadium photoelectrochemical cell was investigated. Experimental results have shown that there exist opposite variation trends for the pore structure and crystallinity of the photocatalyst. With the increase in calcination temperature, the active surface area and pore volume were gradually declined while the crystallinity was significantly improved. The trade-off between the gradually deteriorated sintering and optimized crystallinity of the photocatalyst then determined the photoelectrochemical reaction efficiency. The optimal average photocurrent density and vanadium ions conversion rate emerged at an appropriate calcination temperature, where both the plentiful pores and large active surface area, as well as good crystallinity, could be ensured to promote the photoelectrochemical activity. This work reveals the structure evolution of the nanostructured photocatalyst in influencing the solar energy conversion and storage, which is useful for the structural design of the photoelectroches in real applications.

**Keywords:** all-vanadium photoelectrochemical cell; photoelectrochemical activity; structure evolution; physicochemical characteristics; solar energy storage

## 1. Introduction

The inherent drawback of intermittence for solar energy significantly inhibits its efficient and large-scale utilization in reality [1,2]. Conversion of solar energy to the forms of chemical fuel (e.g., hydrogen, hydrocarbon fuel), electricity, and thermal energy are the most feasible approaches to utilizing the inexhaustible solar energy, which can alleviate not only the energy crisis but also the serious environmental issues, thus attracting widespread attention [3–5]. Among the above-mentioned energy carriers, conversion of solar energy to hydrogen through PV electricity or direct photoelectrochemical water splitting has been regarded as one of the most promising candidates for storing solar energy and subsequently using it as an alternative to fossil fuel [6,7]. However, limited by the intrinsic low-density of hydrogen, hydrogen storage and transport technology are still lacking [8]. In addition, the practical application of solar to hydrogen technology still faces some bottlenecks, in particular low conversion efficiency [8,9]. Under this circumstance, researchers have also focused their attention on constructing some new systems, which can allow the merits of large storage capacity, low costs, ease of storage and transport, etc.

In comparison with the solar to hydrogen conversion, the use of a photoelectrochemical cell (PEC) to convert solar energy to electrochemical energy in the redox couples also allows efficient storage of solar energy because of the unique potentials for both the oxidation and reduction reactions [10–12]. Among those reversible redox pairs in the PECs, the



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).  $VO_2^+/VO^{2+}$  and  $V^{3+}/V^{2+}$  pairs have been considered as competitive candidates for solar energy storage due to the following merits, including the large storage capacity, the avoidance of electrolyte cross-contamination, the fast electrochemical reaction kinetics [13–16]. In the all-vanadium photoelectrochemical cell (VPEC), the oxidation reaction of  $VO^{2+}$  +  $H_2O \rightarrow VO_2^+ + e^- + 2H^+$  ( $E_0 = 1.0$  V vs. NHE) and the reduction reaction of  $V^{3+} + e^- \rightarrow V^{2+}$  ( $E_0 = -0.26$  V vs. NHE) occur at the photoanode and cathode, respectively.

In general, photosensitive semiconductors utilized at the photoanode of VPECs are usually used as photocatalysts to capture and convert solar energy. Once the light is shed on the semiconductor, the photo-induced free charge carriers of electrons migrate to the cathode through the external circuit to participate in the reduction reaction, whereas the residual photo-excited holes at the photoanode oxidize vanadium ions [8]. To better utilize the photo-excited charge carriers and facilitate the solar energy conversion, the striking feature of the photocatalyst should allow the large specific surface area and good accommodation for the electron transport, which, on the one hand, could furnish sufficient active sites and promote the transport of both reactants and photons, resulting in efficiently scavenging the hole and promoting the anodic oxidation reaction at the photoanode, on the other hand, could effectively inhibit the charge recombination within the photoanode [17]. To date, one of the most utilized photocatalysts was the semiconductor  $TiO_2$  because of the intrinsic merits of its chemical stability, large reserves in nature, and low cost. However, the commonly-used photoanode in the VPECs was still the TiO<sub>2</sub> nanoparticles stacked film on the conductive glass. The inherent defects of low surface area and absent pore structure, as well as terrible transport efficiency of electron, photon, and reactants of such compact structure, significantly inhibit the photoelectrochemical conversion of the solar energy [18-20]. Because of this, the synthesis of TiO<sub>2</sub> nanostructures with sufficiently high surface area, the construction of the spatial photoanode structure for furnishing adequate active sites, and promoting the transport of both the reactants and photons as well as charger carriers become valid strategies for the photocatalytic performance improvement [21,22]. Therefore, it would be of great benefit to exploit and integrate the nanostructured  $TiO_2$ photocatalysts in VPECs to realize efficient solar energy conversion and storage.

Whereas regarding the cell structure, it is well known that transfer performance in those cells with microfluidic design is facilitated compared to conventional cell design typically includes the single-compartment [23] and double-compartment [24] as a result of the tremendous specific surface area [25–28]. It can be foreseen that the synergy between the microfluidic design and the nanostructured TiO<sub>2</sub> photocatalyst can facilitate solar energy conversion. Hence, in this study, a microfluidic all-vanadium photoelectrochemical cell ( $\mu$ VPEC) integrated with the nanostructured TiO<sub>2</sub> photocatalyst was proposed for solar energy storage. Considering that the calcination process in the photoanode preparation is essential and can play a significant role in affecting the physicochemical properties of nanostructured photocatalyst, it can thus influence the active surface area, reactants and ions transfer, and charge carrier transport, etc. By using a titania nanotube as a reference, particular attention was focused on the structure evolution of the  $TiO_2$  nanotube photocatalyst in the photoanode. Both the morphology and the pore structure, as well as the crystalline feature, were analyzed. The subsequent implication of structural evolution of the nanostructured  $TiO_2$  photocatalyst in influencing the photoelectrochemical activity and solar storage performance was also discussed.

## 2. Materials and Methods

### 2.1. Titania Nanotube Synthesis and Photoanode Preparation

In this work, the commercially available P25  $\text{TiO}_2$  powder was used as the precursor material for the synthesis of the nanostructured photocatalyst through an alkaline hydrothermal process [29]. The preparation procedure could be divided into the following two steps. Firstly, the alkaline hydrothermal treatment; in this step, a 70 mL alkaline solution with the NaOH concentration of 10 M was first prepared. The obtained NaOH solution was then transferred to a 100 mL Teflon-lined autoclave, in which was pre-added

2 g P25 TiO<sub>2</sub> powder. After vigorous stirring for about 24 h, the obtained suspension solution was placed in an oven at 130 °C for 48 h. Secondly, the acid-washing; during this process, 1 L diluted hydrochloric acid with a concentration of 0.1 M was prepared to wash the product obtained from the previous step. After repeating the washing step five times, the suspension solution was centrifuged to obtain the precipitate. Following this, the precipitate was placed in a vacuum oven with subsequent drying for 8 h at 100 °C to obtain the TiO<sub>2</sub> nanotube photocatalysts, which were denoted as TNT-100.

For the preparation of the photoanode, transparent FTO conductive glass was used as the substrate to ensure the transmission of sunlight. To intensify the conductivity and promote the electron transfer, a densely packed nanocrystalline TiO<sub>2</sub> layer realizing the efficient contact between the synthesized photocatalyst and the FTO conductive glass was pre-prepared on the conductive glass by the spin-coating method [30]. After that, the patterned glass was placed in a tubular furnace and calcined at 550 °C for 30 min. Subsequently, the synthesized photocatalyst was coated on the patterned FTO glass by the wet spray coating method [31]. To prepare the photocatalyst suspension, 1.2 g  $TiO_2$ photocatalysts were dispersed in an aqueous solution mixed with 12 mL deionized water, 0.04 mL acetylacetone, 0.02 mL Triton X-100, 0.24 g polyethylene glycol under vigorous stirring for 12 h. The obtained suspension was then sprayed on the FTO glass using a spray gun and finally calcined in a tube furnace. In this wet-spray coating process, the coated area was controlled at about 1.0 cm  $\times$  1.0 cm, and the final loading of the titania nanotube photocatalyst was about  $1 \text{ mg/cm}^2$ . Furthermore, considering that the calcination is essential to ensure the adhesive strength of the coated photocatalyst, both the morphology and crystalline structures can then present distinct transformations during the calcination process, thus directly influencing not only the surface area and pore structure but also the transfer of electrons, mass, and photons. Hence, the calcination process was operated under various temperatures ranging from 350 °C to 650 °C, and the prepared photoanodes were then denoted as TNT-*x*, in which the *x* represents the calcination temperature.

#### 2.2. Material Characterization

The surface morphologies of the photocatalysts were characterized using a transmission electron microscope (TEM, Tecnai G2 F20, FEI, Waltham, MA, USA). The crystalline phase composition was conducted by an X-ray diffractometer (XRD, D8 Advance, Bruker, Germany) with Cu K $\alpha$  radiation. Pore structure variation of the photocatalysts calcined at different temperature were characterized by N<sub>2</sub> adsorption-desorption isotherm at 77.35 K using a surface area and porosity analyzer (ASAP 2460, Micromeritics, Norcross, GA, USA). The Brunauer–Emmett–Teller (BET) model was utilized to calculate the specific surface area and the Barrett–Joyner–Halenda (BJH) method was chosen to evaluate the pore size distribution.

### 2.3. Experimental Setup and Data Analysis

The photoelectrochemical cell assembly is schematically illustrated in Figure 1a, where a  $TiO_2$  photoanode and a Pt-coated carbon paper cathode were used for the anodic oxidation reaction and cathodic reduction reaction, respectively. Two microchambers with a depth of 0.5 mm were used as the flow channels for the anolyte and catholyte. A Nafion-115 proton exchange membrane was used to separate the microchambers and provide a proton transport path. The experimental system is shown in Figure 1b. The system consisted of five parts: (1) The anolyte and catholyte supply unit, including two syringe pumps; (2) the Xenon light source to simulate sunlight irradiation; and (3) the photoelectrochemical cell, where the inlets of anodic and cathodic chambers were connected to the supply unit; (4) the data acquisition instrument to record the variation of photocurrent; and (5) the collecting bottles, where the outlets of microchambers were connected to the collecting bottles.



**Figure 1.** Schematic illustration of (**a**) the microfluidic all-vanadium photoelectrochemical cell and (**b**) the experimental system.

In this work, the conversion rate of vanadium ions, i.e.,  $VO^{2+}$  to  $VO_2^+$ , was used to estimate the solar energy storage performance of the photoelectrochemical cell. The conversion rate was calculated using the following equation,

$$\Delta N = \frac{Q}{T \cdot F} \tag{1}$$

where  $\Delta N$  is the conversion rate of vanadium ions,  $\mu$ mol/h; Q represents the total charge, C; T means the total reaction time, s; F denotes Faraday's constant, 96,485 C/mol. The total charge, Q, can be written as;

$$Q = \sum_{j=1}^{n} I_j \times \Delta t \tag{2}$$

where  $\Delta t$  is the recorded time interval, s;  $I_j$  (A) denotes the average photocurrent in one recorded time interval.

## 3. Results and Discussion

## 3.1. Structural Evolution of Photocatalysts

The text continues here. To bond the nanostructured photocatalyst to the FTO glass, the calcination process is essential to ensure strong adhesion. However, it should be pointed out that the sintering during calcination may result in the structural evolution of nanostructured photocatalyst and thus influence the photoelectrochemical activity [22]. Hence, in this section, the structure variation with the increase of calcination temperature was discussed and the morphology, the pore structure, and the crystalline feature were characterized and analyzed.

The morphologies of the samples that were calcined at different temperatures are shown in Figure 2. As can be seen, the pristine TNT-100 sample prepared from the hydrothermal treatment emerged from the evident nanotube structure (see Figure 2a). Benefitting from the plentiful pore structure, the pristine titania nanotube presented an extremely large BET surface area of about  $303.82 \text{ m}^2/\text{g}$  (see Figure 3a,b). However, with increasing the calcination temperature, the single nanotube structured photocatalyst gradually changed to the multi nanostructured photocatalyst. Firstly, as shown in Figure 2b,c, for the low calcination temperatures of 350 °C and 450 °C, the nanotube structure can be retained while contributing to sintering during calcination, and the BET surface area gradually decreased to 259.12 m<sup>2</sup>/g at 350 °C and 201.32 m<sup>2</sup>/g at 450 °C, respectively (see Figure 3b). Besides, when the temperature increased to 550 °C, the sintering of nanotubes became severe. Under this circumstance, the multi-nanostructured photocatalysts, including both the nanotubes and nanorods as well as nanoparticles, were observed in the high-resolution TEM images (see Figure 2d). Ascribing to such severe sintering, the photocatalytic active surface area further declined. Furthermore, because of the more severe sintering at high temperatures, no obvious nanotube structured photocatalyst was identified after being calcined under

650 °C, while distinct nanorods and nanoparticles were observed (see Figure 2e). The BET surface area further reduced from 123.80 m<sup>2</sup>/g at 550 °C to 54.20 m<sup>2</sup>/g at 650 °C, indicating a more significant decrease in the photocatalytic active area. It is worth noting that the photoelectrochemistry activity is inherently related to the pore structure since the plentiful pore structure not only allows the adequate transport path for the mass and ions transfer but also sufficient active surface area for the photoelectrochemical reaction.





**Figure 2.** TEM images of the (**a**) TNT-100, (**b**) TNT-350, (**c**) TNT-450, (**d**) TNT-550, and (**e**) TNT-650 photocatalysts.



**Figure 3.** Variations of (a)  $N_2$  adsorption-desorption isotherm, (b) BET surface area, and (c) pore size distribution of the nanostructured photocatalysts calcined under different temperatures.

To further depict the pore structure, the N<sub>2</sub> adsorption–desorption isotherms of the above-mentioned samples were also characterized. As shown in Figure 3a, for each sample, the distinct hysteresis loop can be observed, revealing that each sample emerged with the mesoporous structure. However, with the increase in calcination temperature, the hysteresis loop gradually shifted from the low relative pressure to the high relative pressure ( $P/P_0$ ). Based on the N<sub>2</sub> adsorption-desorption isotherms, the calculated pore size distributions were summarized and analyzed. As can be seen in Figure 3c, although the dominating pore size for all of these samples ranged from 1.8 nm to 5.2 nm, the pore volume corresponding to both microporous and mesoporous structures gradually decreased with increasing the calcination temperature (see inset in Figure 3c). Meanwhile, it can also be found that

mesoporous with the pore size in the range of 5 nm to 50 nm were also identified for the calcination temperature lower than 550 °C, whereas it was not distinguished when the temperature increased to 650 °C. These phenomena can be attributed to severe sintering, where the increased calcination temperature leads to more severe sintering of nanotubes to form nanorods and nanoparticles. At low temperatures, the weak sintering can preserve the nanostructure, thus, the obvious nanotube structured photocatalysts were obtained (see Figure 2b,c). While the further increase in temperature results in increasingly serious sintering, indicating that more nanotubes disappeared while more nanorods and nanoparticles and nanoparticles were found at 550 °C, while only nanorods and nanoparticles existed with further increasing the calcination temperature (see Figure 2d,e). These results also indicated that the nanostructured photocatalysts present remarkable superiority in improving the active surface area and the pore volume, but the increased calcination temperature resulted in the inevitable sintering and the decrease in both BET surface area and pore volume (see Figure 3b,c).

Moreover, the crystalline phase evolution of titania nanotubes with the increase in calcination temperature was also measured and the results are presented in Figure 4. For the low calcination temperature of 350 °C, only two characteristic peaks with larger FWHM (i.e., weak crystallinity) at  $25.3^{\circ}$  and  $48.5^{\circ}$ , corresponding to anatase-TiO<sub>2</sub>, were observed, whereas, with the increase of calcination temperature, first, the crystallinity of the characteristic peaks was improved. Besides, additional characteristic peaks denoting  $TiO_2$ crystal were also identified, especially, when the calcination increased to 650 °C, and extra rutile-TiO<sub>2</sub> with the obscure peak at  $27.4^{\circ}$  appeared. It should be pointed out that the photo-excited charge carrier transport significantly relies on the crystallinity of the photocatalysts. Good crystallinity allows the efficient charge carrier transport, thus, inhibiting the recombination of photo-excited electron-hole pairs, while poor crystallinity will play an adverse role in the charge carrier transport, resulting in the limited photoelectrochemical redox reactions at both anode and cathode. Meanwhile, it is worth noting that the pore structure and the crystallinity showed the opposite variation trends with an increase of calcination, where the BET surface area and pore volume were gradually declined while the crystallinity was significantly improved. Considering that both the superior pore structure and the good crystallinity are conducive to boosting the photocatalytic activity, it can be expected that the photoelectrochemical reaction efficiency will be determined by the trade-off between the gradually deteriorated pore structure and optimized crystallinity with the increase of calcination temperature.



Figure 4. XRD spectra of the nanostructured photocatalysts.

#### 3.2. Solar Energy Storage Performance Evaluation

In this section, both the photoelectrochemical activity and the microfluidic all-vanadium photoelectrochemical cell performance were evaluated. A  $2 \text{ M H}_2\text{SO}_4$  solution dissolving

with VO<sup>2+</sup> and V<sup>3+</sup> were used as the anolyte and catholyte, respectively. The concentrations of the vanadium ions in both anolyte and catholyte were 0.1 M. The flow rates of both anolyte and catholyte were set at 50  $\mu$ L/min. The light intensity was kept at 130 mW/cm<sup>2</sup>.

Herein, to evaluate the photoelectrochemical activity, the photoresponse behavior under intermittent illumination and the photocurrent variation during long-term operation under continuous illumination were characterized. Figure 5a presents the photo-response behaviors of those photoanodes that are calcined at different temperatures ranging from 350 °C to 650 °C. Firstly, it can be seen that all of these photoanodes emerged the excellent photoresponse behavior, where, once the light is shed on the photoanode, a stable photocurrent density and rapid response to the illumination could be allowed. The steady values of photocurrent density could be guaranteed during the periodic illumination. Meanwhile, the photocurrent densities for the above-mentioned photoanodes show remarkable disparities. For the TNT-350 photoanode, the value of average photocurrent density was only about 25.1  $\mu$ A/cm<sup>2</sup>, whereas the average photocurrent density achieved about 44.2  $\mu$ A/cm<sup>2</sup> for the TNT-450 photoanode, realizing an appreciable improvement of about 76.1%. However, when the calcination temperature further increased to 550 °C and 650 °C, the photocurrent densities gradually decreased from 36.5  $\mu$ A/cm<sup>2</sup> for TNT-550 and 33.2  $\mu$ A/cm<sup>2</sup> for TNT-650, respectively.



**Figure 5.** Comparisons of the (**a**) photoresponse behavior, (**b**) photocurrent density during long-term operation and (**c**) vanadium ion conversion rate. (Light intensity:  $130 \text{ mW/cm}^2$ , flow rate:  $50 \mu \text{L/min}$ , vanadium ion concentration: 0.1 M).

The photocurrent density variations for each photoanode during the long-term operation are presented in Figure 5b. As shown, all of the above-mentioned photoanodes presented a relatively stable photocurrent density during the long-term operation, but similar to the photoresponse behavior, with increasing the calcination temperature for the photoanode preparation, the average photocurrent densities were also firstly increased and then declined. The average photocurrent densities of about 46.4  $\mu$ A/cm<sup>2</sup> for the TNT-450 photoanode were superior to that of about 26.5  $\mu$ A/cm<sup>2</sup> for the TNT-350 photoanode. This intensification could be ascribed to the synergetic effect between the plentiful pore structure and the improved crystallinity of the TNT-450 photoanode. As shown in Figure 2b,c, for both TNT-350 and TNT-450 photoanodes, the nanotube structure was maintained in the photoanodes. These nanotube structures could allow not only plentiful pores for enhancing the reactants and ions transfer and availing the light scattering but also sufficient active sites for generating more photo-excited holes; both of these two merits then play significant roles in facilitating the vanadium oxidation reaction. However, it should be pointed out that the photoelectrochemical reaction efficiency is also inherently related to the charge carrier transport. Although the TNT-350 photoanode can also offer abundant paths for both VO<sup>2+</sup> and proton transfer and a more specific active surface area, limited by the poor crystallinity (see Figure 4), the photo-excited electron transport was inhibited. The inhibited electron transfer also indicated the aggravated recombination of the electron-hole pairs, resulting in the restrained photoelectrochemical reaction. But for the TNT-450 photoanode, during the calcination process, the nanotube structure was retained and the crystallinity was improved (see Figures 2c and 4). First of all, the vanadium ions and proton transfer were promoted. Afterward, sufficient active sites could be allowed. In the next part, electron transport was facilitated. Last but not least, the light scattering to deplete the photons was intensified. Such a synergistic effect then significantly boosted the VO<sup>2+</sup> oxidation reaction at the photoanode. Thus, compared with the TNT-350 photoanode, the prominent intensification of about 75.1% for TNT-450 photoanode in the average photocurrent density was achieved.

With further increases the temperature, as shown in Figure 5b, the average photocurrent density gradually decreased from 46.4  $\mu$ A/cm<sup>2</sup> for the TNT-450 photoanode to 35.5  $\mu$ A/cm<sup>2</sup> for the TNT-550 photoanode and 32.5  $\mu$ A/cm<sup>2</sup> for TNT-650 photoanode, respectively. This decrease could be attributed to the trade-off between the pore structure and the crystallinity of the nanostructured photocatalysts. As discussed above, on the one hand, the TNT-550 photoanode emerges not only the multi-nanostructure ascribing to the formation of both nanotube and nanorods as well as nanoparticles but also the reduced active surface area because of the increasingly severe sintering (see Figures 2d and 3). On the other hand, benefitting from the high-temperature calcination, the crystallinity of the photoanode was been optimized. It is worth noting that, firstly, the multi-nanostructured photocatalysts are able to construct the spatial photoanode structure and thus provide enough transfer paths for the reactants including vanadium ions and protons. Meanwhile, the good crystallinity can promote electron transfer and inhibit the recombination of photo-excited electron-hole pairs, thus facilitating the vanadium ions oxidation reaction. However, since the active surface area was significantly declined, the supply of active sites then dominated the photoelectrochemical reaction, resulting in the decrease of the average photocurrent density for TNT-550 photoanode. When the calcination further increased to 650 °C, the sintering became more server, leading to only a few mesopores in the range from 1.83 nm to 5 nm existing and the BET surface area remarkably decreasing to  $54.2 \text{ m}^2/\text{g}$ (see Figure 3b,c). Although the TNT-650 photoanode shows the optimum crystallinity among these photoanodes, the deteriorated reactants transferred and the limited active sites make the average photocurrent density further decreased, even though the photoelectrochemical activity of TNT-650 photoanode was better than that of TNT-350 photoanode. This is because the poor crystallinity results in the extremely low utilization efficiency of the photo-excited holes and most of them were recombined with the electrons that have not been transmitted from the photoanode to the cathode. Here, we have also made a brief summary of recently reported studies on all-vanadium photoelectrochemical cells and compared the photoelectrochemical performance between the photoanodes proposed in the literature and in the present work; the results are shown in Table 1. It can be found that, although this work did not achieve state-of-the-art photoelectrochemical activity, it did show excellent photoelectrochemical performance in solar energy conversion and storage, where the photocurrent density,  $I_d$ , of TNT-450 photoanode emerged a remarkable intensification in comparison with those photoanodes even with wide spectral response, e.g., N-doped TiO<sub>2</sub> photoanode, black TiO<sub>2</sub> photoanode. These results further reveal the significance concerning the structural evolution of photocatalyst in photoanode for the photoelectrochemical activity.

Moreover, the variation of the vanadium ion conversion rate was also summarized and the results are shown in Figure 5c. Clearly, the TNT-450 photoanode presented the optimum conversion rate of the vanadium ions. As discussed above, the plentiful pores ensured the reactant's transfer, the large active surface area allowed sufficient active sites, and the improved crystallinity promoted the transport of the photo-excited electrons. Once the light is shed on the photoanode, the synergistic effect could guarantee the adequate vanadium ions oxidation reaction, thus the larger conversion rate of the vanadium ions. For TNT-350 photoanode, the poor crystallinity inhibited the electron transfer, resulting in serious recombination and thus the extremely low conversion rate. Whereas for those photoanodes calcined under high temperatures, the gradually vanished pore structure and decreased active surface area then dominate the anodic oxidation reaction. Thus, the decrease in the conversion rate of vanadium ions with the further increase of the temperature from 450 °C to 650 °C. Consequently, it is worthwhile to pay more attention to the pore structure and crystalline feature of the nanostructured photocatalyst photoanode, because both of them can play a crucial role in influencing the photoelectrochemical reaction efficiency.

PEC Design	Photoanode	m <sub>pc</sub> (mg/cm <sup>2</sup> )	I <sub>A</sub> (mA/cm <sup>2</sup> )	I <sub>d</sub> (A/g·cm²)	Ref.
H-type	TiO <sub>2</sub> nanobelts	_	~0.029	_	[17]
μVPEC	P25	3	0.071	0.024	[30]
μVPEC	multi-nanostructured TiO <sub>2</sub>	1	0.035	0.035	[22]
μVPEC	black TiO <sub>2</sub>	1	0.040	0.040	[32]
μVPEC	N-doped TiO <sub>2</sub>	3	0.103	0.034	[31]
μVPEC	TiO <sub>2</sub> nanotube array	0.78 *	0.051	0.065	[33]
μVPEC	TNT-450	1	0.044	0.044	This work

 Table 1. Comparison of the photoelectrochemical performance.

Abbreviations:  $m_{pc}$ —photocatalyst loading;  $I_A$ —photocurrent per unit surface area;  $I_d$ —photocurrent per unit photocatalyst loading and surface area. \* Estimated from the top and cross-section views of the photoanode in FESEM images.

## 4. Conclusions

In this work, a microfluidic all-vanadium photoelectrochemical cell integrated with the nanostructured titania photoanode was proposed for solar energy storage. By using the titania nanotube as a reference photocatalyst, the effect of calcination temperature in the structural evolution of the photocatalyst during the photoanode preparation was investigated. Both the morphology and the pore structure, as well as the crystalline feature of the photocatalysts calcining at different temperatures, were analyzed.

The obtained results showed that, with the increased calcination temperature, there existed opposite variation trends for the pore structure and crystallinity of the photocatalyst. Under low temperatures, although the initial nanostructure can be well preserved to allow plentiful pores and large active surface area, the poor crystallinity significantly inhibited the charge carrier transport, and thus, the low photoelectrochemical activity. With the increase in calcination temperature, the active surface area and pore volume gradually declined while the crystallinity was significantly improved. The trade-off between the gradually deteriorated sintering and optimized crystallinity of the photocatalyst then determined the photoelectrochemical reaction efficiency. The optimal average photocurrent density and vanadium ions conversion rate emerged at an appropriate calcination temperature of about 450 °C. Benefitting from the well-preserved nanotube structure and the improved crystallinity, both the plentiful pores and large active surface area, as well as the facilitated electron transfer, could be ensured to promote the vanadium ions conversion. As a result, the average photocurrent density of about 46.4  $\mu$ A/cm<sup>2</sup> for TNT-450 photoanode was much higher than that of both low temperature treated photoanode of TNT-350 (26.5  $\mu$ A/cm<sup>2</sup>) and high temperature treated ones of TNT-550 (35.5  $\mu$ A/cm<sup>2</sup>) and TNT-650 (32.5  $\mu$ A/cm<sup>2</sup>), presenting 75.1%, 30.7%, and 42.8% improvement, respectively. This work reveals the structure evolution of the nanostructured photocatalyst in influencing the solar energy conversion and storage, which is useful for the structural design of the photoelectrodes in real applications. Meanwhile, it is worth noting that the extremely low value in both photocurrent density and vanadium conversion rate is still a serious problem faced by the large-scale deployment of VPEC. It is expected that this issue can be solved by improving the photoanode structure and further extending the absorption spectrum of the photocatalyst, which can not only improves the photoelectrocehmical activity but also broadens the spectrum utilization range.

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