Geometry-Enhanced Ultra-long TiO₂ Nanobelts in an All-Vanadium Photoelectrochemical Cell for Efficient Storage of Solar Energy

Zi Wei,^a Yi Shen,^a Dong Liu,^a Chiajen Hsu,^a Syed D. Sajjad,^a Krishnan Rajeshwar,^b and
Fuqiang Liu^{a*}

*^aElectrochemical Energy Laboratory, Department of Materials Science and Engineering,
University of Texas at Arlington, Arlington, TX 76019*

*^bDepartment of Chemistry and Biochemistry,
University of Texas at Arlington, Arlington, TX 76019*

*Email: fuqiang@uta.edu

Abstract

Direct capture and storage of abundant but intermittent solar energy using storage devices are of paramount importance in development of sustainable energy, yet the daunting challenge is to enhance the conversion efficiency. Here we report an all-vanadium (all-V) photoelectrochemical storage cell (PESC) using geometry-enhanced ultra-long TiO₂ nanobelts (TNBs) to significantly improve solar energy storage efficiency. The TNBs are synthesized using a simple stirring-assisted hydrothermal method, where the stirring speed is adopted to effectively tune the geometry and structure of the TNBs. We demonstrate that highly efficient solar energy storage is realized by ultra-quick oxidization and reduction reaction of vanadium ions with, respectively, holes and electrons produced on the TNB surface. The obtained incident photon-to-current efficiency (IPCE) is ~22% at 350 nm without any external bias, double that of commercial P25 TiO₂ (~11%). The observed improved efficiency results from enhanced photoactivity and charge separation in the semiconductor, and mass transport of vanadium ions in the photoelectrode.

KEYWORDS: Vanadium redox, Photoelectrochemical storage cell, TiO₂, Solar energy

Introduction

Photoelectrochemical (PEC) conversion of sunlight to the form of chemical fuel (e.g., H₂) [1] and electricity (in supercapacitors [2, 3], redox flow battery [4, 5], and lithium batteries [6-9]) is a most viable approach to solar energy storage. Among different systems, solar-driven chargeable batteries using electrochemical redox couples such as Sn/S²⁻ [10], Cu²⁺/Cu [11], metal/metal-chalcogenide [12], and polysulphide species [13] emerge as a promising scheme because of low cost, continuous operation, abundance of materials, and compactness of the system. However, these systems are inadequate for large-scale solar energy storage and long-term operation because PEC reaction products are normally deposited on the storage electrode as a solid in an enclosed device during photocharging. Consequently, none of these PEC storage systems have been particularly successful in terms of practical implementation.

To circumvent the above-mentioned limitation, we have developed an all-vanadium (all-V) photoelectrochemical storage cell (PESC) [14-19] for practical, efficient and scalable solar energy storage. The all-V PESC utilizes two pairs of vanadium redox couples, i.e., VO₂⁺/VO²⁺ and V³⁺/V²⁺, as in an all-vanadium redox-flow battery (VRB), and has been demonstrated to achieve a Faradaic efficiency as high as 95% [18] and incident photon-to-current efficiency (IPCE) of 45% at 350 nm [17] without any externally applied bias even using pristine TiO₂ photocatalysts. The solar energy drives the redox reactions of vanadium species energetically uphill and generates the energy-rich products: the photogenerated holes oxidize VO²⁺ to VO₂⁺, and electrons reduce V³⁺ to V²⁺. Under dark conditions these products follow kinetically fast, energetically downhill reactions such that the stored solar energy can be tapped on demand. Besides, when employing a TiO₂/WO₃ hybrid photoelectrode, the

system could store and release electrons under light and dark conditions, respectively, potentially enabling continuous solar energy conversion despite the intermittent sunlight [15].

The striking features of the system noted above originate from the extremely fast kinetics of vanadium redox (at least six orders of magnitude higher than oxygen evolution [16]), which, on one hand, could significantly minimize charge recombination at the TiO_2 /electrolyte interface [14-16, 18, 19], but, on the other hand, might also demand more stringent requirements on charge transport within the photoelectrode to accommodate the high photocurrent. However, it is well known that diffusion in nanocrystalline photoelectrodes is slow compared to single crystals. Grain boundaries between particles, in addition to surface trap states, contribute to poor diffusion in conventional TiO_2 nanocrystalline films. Eliminating or minimizing grain boundaries using oriented arrays of TiO_2 , nanowires [20], nanorods [21], and nanobelts [22] could suppress charge recombination, and exhibit a higher diffusion coefficient than the nanocrystalline counterpart (e.g., ~200 times higher reported by Feng et al. [23]). Therefore, it would be of great interests to exploit and integrate 1D geometry-enhanced TiO_2 in the newly developed all-V PESC.

In this study we demonstrate how stirring-assisted hydrothermally synthesized geometry-enhanced ultra-long TiO_2 nanobelts (TNBs) can effectively double the photocurrent and IPCE for solar energy storage in an all-V PESC. For the first time, geometry and facet control of TNBs are simply realized by tuning the stirring speed, and their elongation as well photocatalytic activity are found to be proportional to the applied speed. This is considerably advantageous compared to conventional methods using shape-control agents, such as HF [24], surfactant [25] or diethanolamine [26], which require additional steps to remove these agents

after formation of the TiO_2 nanostructure. This promising approach will be a critical step toward efficient solar energy storage and conversion in a PEC storage cell.

Experimental

Synthesis of TNBs

A stirring-assisted hydrothermal synthesis method, developed in our previous study [27], was employed to synthesize the TNBs. Typically, 1.2 g anatase TiO_2 powder (Alfa Aesar) was added to 80 ml of 10 M NaOH solution with stirring for 30 min. Then 25 ml of the solution was transferred to a 50 ml Teflon-lined stainless steel autoclave with a reaction temperature at 200°C under constant stirring at 0, 100, 250, 500, and 700 rpm for 48 h. After the system was cooled to room temperature, the product was first washed by 0.1 M HCl and then deionized water several times. After drying in the oven at 80°C for 4 h, the product was annealed in a tube furnace at 700°C for 1 h to convert the hydrogen titanate into TiO_2 TNBs.

Fabrication of Photoelectrodes

The above-synthesized oxide (0.5 g) was mixed with 2.15 g α -terpineol (Fisher Scientific, USA), and then sonicated for 20 min. Fluorine-doped tin oxide (FTO) glass substrates (2 in $\times$ 2 in) were prepared and cleaned by sonication in acetone (99.7%, Fisher Scientific, USA) for 20 min followed by methanol (99.8%, Fisher Scientific, USA) for 20 min, and then DI water. Degussa P25 (Evonik) and different TNB slurries were coated on the FTO glass substrates using a doctor blade to form uniform films and then dried in an oven at 80°C for 2 h. The as-prepared photoanodes were sintered with air flow in a tube furnace at 500°C for 1 h. The TiCl_4 -treated photoanodes were prepared using 0.5M TiCl_4 solution in ethanol. One ml of the TiCl_4 solution was used to soak the active surface of the photoanodes, and then followed by heat treatment.

Materials Characterization

Powder XRD patterns were obtained using a diffractometer (Siemens, 810-M340-32-C3000). Scanning electron microscopy (Hitachi S-3000N variable pressure SEM and Hitachi S-4800 Field emission SEM) was used to examine the morphology of the photoanodes. Nanostructure of TNBs was studied using a high resolution transmission electron microscope (HR-TEM, Hitachi H-9500). UV-Vis spectra of the photoanodes were obtained using a JASCO Corp V-570 spectrophotometer. Brunauer–Emmett–Teller (BET) surface areas were determined from N₂ adsorption using a Gemini VII 2390 surface area analyzer.

Photoelectrochemical Studies

The photodegradation test of methylene blue was conducted according to our previous study [27]. A portable UV lamp (4 W) at 360 nm wavelength was used as an irradiation source. 3 mg TiO₂ samples were dispersed in 10 ml MB solution under constant stirring in a quartz container, and then were irradiated by the UV lamp in a dark room. The MB solution was extracted and analyzed by a UV-Vis spectrometer every 10 min. The overall MB photodegradation rate constants and specific degradation rate constants for different TNB samples were calculated based on the following equations:

$$\ln\left(\frac{C_0}{C}\right) = kt \quad (1)$$

$$k' = \frac{k}{S_A} \quad (2)$$

where C_0 is the initial MB concentration, C is the concentration at time t (min), k (min⁻¹) is the first-order rate constant, and k' (g m⁻² min⁻¹) is the specific degradation rate constant.

The PEC experiments on different photoanodes in the all-V PESC [14-17, 28] were performed using a PARSTAT 2273 potentiostat. In the all-V PESC, a Nafion 117 membrane

was used to separate two different vanadium redox electrolytes, i.e., 0.01 M VO^{2+} and 0.01 M V^{3+} (balanced with 3 M H_2SO_4). The photoanode served as the working electrode (WE) in one chamber filled with VO^{2+} . A platinum mesh and an Ag/AgCl reference electrode served as the counter electrode and reference electrode (RE), respectively, in the other chamber filled with V^{3+} . Zero-resistance ammetry (ZRA) was conducted, without any external bias, to measure the photocurrent. Solar irradiance was provided by an ozone-free solar simulator system (Newport USA, calibrated using a standard photodiode) paired with an AM 1.5 global filter (Newport, USA). Electrochemical impedance spectroscopy (EIS) study was performed by applying an AC voltage of 10 mV to the cell in a frequency range from 10 mHz to 2 MHz. IPCE was recorded using a monochromator from Optometrics. The IPCE value was calculated using the following equation:

$$\text{IPCE}\% = 1240 \cdot I / (\lambda \cdot J_{\text{light}}) \cdot 100 \quad (3)$$

where I (A/cm^2) is the measured photocurrent density at a specific wavelength λ (nm), and J_{light} (W/cm^2) is the measured irradiance using a photodetector (Newport, USA).

Results and Discussion

TiO_2 nanobelts have attracted particular attention against conventional nanospheres due to multiple advantages [29], including enhanced light scattering and absorption due to high length-to-diameter ratio, rapid electron transport in the longitudinal direction, and minimized charge recombination rate realized by reduced grain boundaries and less defects. In our companion study [27], we synthesized high-aspect-ratio TNBs using a stirring-assisted hydrothermal method. These TNBs were found to be 80-110 nm wide, ~ 10 nm thick, and up to 20 μm long. Particularly, aspect ratio of the TNBs is tailored by the stirring speed as demonstrated for its nanotube counterpart [28]. In this study, we further study the stirring

effect and its vital implication to TNB length as well as photocatalytic activity, and explore the potential of TNBs as promising photocatalysts in an all-V PESC for efficient solar energy storage.

To further investigate the effect of stirring on nanostructure and morphology, TNBs were synthesized in a range of stirring speeds from 0 to 700 rpm. The stirring assisted hydrothermal reactor is illustrated in **Figure 1a**. The obtained samples are labeled as TNB-0, TNB-100, TNB-250, TNB-500, and TNB-700, where the numbers denote the applied stirring speed (in rpm) during the synthesis. As the SEM image in **Figure 1b** shows, under no stirring, bundled spherical-shaped structures were formed in the TNB-0 sample. It is believed that the original Ti-O-Ti bonds in the starting material, i.e., anatase TiO₂ powder, have not yet been completely disrupted, and therefore anisotropic growth is delayed due to slow dissolution-recrystallization process at the static condition. In contrast, higher stirring speed entirely disentangled the TiO₂ bundles and created structurally well-defined TNBs, as seen in **Figures 1c to 1f**. In TNB-100, short (ca. 1 μm) nanobelts were obtained but with small random branches, while 700 rpm resulted in much longer ($\sim 16 \mu\text{m}$) nanobelts (**Figure 1f**). Besides, BET surface area analyses (**Figure S1**) of the synthesized TNBs suggest that the specific surface area (S_A , $\text{m}^2\cdot\text{g}^{-1}$, shown in **Figure 1g** and also tabulated in **Table S1**) continuously declines with increasing stirring speed. This, in conjunction with the averaged TNB lengths in **Figure 1g**, reveals that increase of stirring speed helps create more elongated TNBs, which, however, results in shrinkage of the specific surface area. In addition, powder XRD measurements were conducted to assess crystallographic information of all TNB samples. **Figure 1h** shows that the characteristic anatase peaks, especially those corresponding to (101),

(004) and (200) planes, become gradually intensified with increasing stirring speed, implying improved crystallinity.

Figure 1. TNBs as a function of stirring speed during the hydrothermal synthesis. a) Illustration of the stirring assisted hydrothermal method, b) - f) SEM images of TNB-0, TNB-100, TNB-250, TNB-500, and TNB-700, respectively. g) Length (in μm) in the elongated direction and specific surface area (m²/g) of TNBs synthesized at different stirring speeds. h) XRD patterns of the synthesized TNBs. Letter A denotes anatase phase of TiO₂ (JCPDS # 21-1272).

To understand the role of mechanical stirring, we simulated growth of a 6-μm long TNB with a 1st-order surface reaction (see the supporting information). Formation of TNBs is assumed to be controlled by both diffusion-limited and surface reaction limited growth known as the DLSLOR model [30], which involves dissolution of solid TiO₂ precursor after breaking

of original Ti-O-Ti bonds by highly concentrated NaOH, and subsequent transfer to the growth zone. We observed a monotonic decrease of surface reaction rate along the elongated direction of the TNB when the fluid flows parallel to the elongated direction of the TNB (**Figure S3**). Besides, the front surface facing the fluid grows at a $\sim 20\%$ higher rate than the rear surface, in sharp contrast to the perpendicular case. Further study indicates that the TNBs grow at an even relatively higher rate from the front surface for the ones with higher aspect ratios, implying that the forced convective flow helps not only orientate but also grow elongated TNBs to the direction of fluid flow.

For further examination on microstructure of the TNBs, HRTEM images were taken on the TNB-700 sample. **Figure 2a** shows the TEM image of a single nanobelt with a lattice spacing of 0.357 nm corresponding to the thermodynamically stable anatase (101) facets. This is consistent with our previous finding [27] and is further confirmed by the selected area electron diffraction (SAED) pattern (inset in **Figure 2a**) that the main exposed plane is (101) and the growth direction is [010] (**Figure 2b**, denoted hereafter as Type I TNB). Additionally, considerable amounts of TNBs with a V-shape terminus (**Figure 2c**) are also observed and the opening angle of the V-shape terminus is determined to be 136.6° using a model anatase structure in **Figure S4** created by Diamond 4.0.3. Further inspection with clear lattice fringes (inset of **Figure 2c**) confirms that the V-shape terminus is formed between (011) and $(0\bar{1}0)$ planes (each with lattice spacing of 0.35 nm). According to the above analysis, the crystal structure is depicted in **Figure 2d** (designated as type II TNB hereafter) with exposed (100) and (001) facets along the long axis and on the side surface of the TNBs, respectively, which are known to possess higher surface energy than (101). These exposed high-energy facets in the TNBs, i.e., (001) and (100), are more catalytically active [31, 32] than those in the

thermodynamically stable geometry of nanosized TiO_2 , which consists of $\sim 94\%$ of low-energy (101) facets [33].

Figure 2. The TNBs synthesized at 700 rpm. a) HRTEM image of a single type I TNB where the inset figure shows the SAED pattern taken along the [100] direction of the belt. b) Crystal structure of Type I TNB. c) Type II TNB with V-shape terminus and exposed (001) facets. The inset of c) shows the crystalline orientation in the interior of the TNB. d) Crystal structure of Type II TNB.

The exposed facets of the TNBs and their implication to photoactivity are further studied using Raman spectroscopy. **Figure 3** reveals that all samples display similar characteristic peaks of anatase TiO_2 at 144 (E_g), 394 (B_{1g}), 514 (A_{1g}), and 636 cm^{-1} (E_g) [34]. Here we adopted a semi-empirical approach [35] of using the intensity ratio between A_{1g} and E_g (144 cm^{-1}) to quantify the percentage of exposed (001) facets. The inset of **Figure 3** shows a

distinct trend that the percentage of exposed (001) facets in the TNBs increases monotonically with increased stirring speed in the hydrothermal synthesis, e.g., from 8.4 % at 0 rpm to 35.4 % at 700 rpm. According to reference [35], the surface structural difference between (001) and (101) facets may be the reason why the relative intensity changes in the Raman spectra when the stirring speed increases. When the exposed (001) facets exist, the extent of symmetrical stretching vibration (unsaturated 5c-Ti and 2c-O bonding modes, shown in **Figure S4**) decreases, while the number of asymmetrical bending vibration increases, therefore leading to an increased relative intensity ratio between A_{1g} and E_g modes. Since there is no experimental condition change except for the stirring speed, the results undoubtedly prove that increasing stirring speed during the hydrothermal synthesis created higher fractions of exposed (001) facets (estimated to be 4.2 times more from 0 to 700 rpm), which resides primarily in type II TNBs. This simple yet effective *additive-free* process thus surpasses traditional facet-controlling strategies that rely on capping agents, as mentioned earlier, such as HF [24] or surfactant [25], which have to be removed in a tedious high-temperature process.

Figure 3. Raman spectra of TNBs synthesized at different stirring speeds. The inset shows percentage of exposed {001} facets calculated from relative intensity ratio between A_{1g} mode at 514 cm^{-1} and E_g mode at 144 cm^{-1} , as a function of the stirring speed.

Mindful of the discovered relationship between stirring speed and exposed crystal facets, we performed MB photodegradation test using the TNBs under 360 nm irradiation to evaluate their photoactivity. In **Figure 4a**, the TNBs synthesized at higher stirring speeds, especially at 700 rpm, display enhanced photocatalytic activity, as evidenced by faster reduction of MB concentration under illumination (e.g., 52% drop of MB concentration for TNB-700 in 30 min). The effect of the band structural change on the photocatalytic activity was insignificant as there is no apparent change in light absorption (UV-vis spectra in **Figure S5**). On the other hand, the enhanced specific photoactivity (**Table S1**) can be ascribed to more exposed highly-active (001)/(100) facets and enhanced electron mobility. Similar results were reported by Roy et al [26] for cuboid TiO_2 single crystals but with relatively smaller surface area.

To further access the performance of TNBs in our newly-developed all-V PESC, we examined TNB-700 and P25 as photocatalysts in a cell setup schematically illustrated in **Figure 4b**. The initial photocurrent (**Figure 4c**) of the TNB-700 electrode under AM1.5 illumination is almost identical to that of P25, in sharp contrast to the MB photodegradation results, but with less deterioration □ after 4 h it remains $50\text{ }\mu\text{A}$ higher than that of P25. Furthermore, stable operation for TNB-700 could be quickly established after light was temporally switched off for 1 min at 60 min compared to that using P25 TiO_2 . It is important to note here that no external bias was applied to the cell; therefore, the observed photocurrents are generated solely from the AM1.5 illumination.

Figure 4. Photoelectrochemical characterization. a) Photodegradation curves of MB under UV light for different TiO_2 samples. b) Schematic illustration of an all-V PESC. Two different vanadium redox electrolytes, i.e., 0.01 M VO^{2+} and 0.01 M V^{3+} (balanced with 3 M H_2SO_4 and separated by a Nafion 117 membrane) were used as the anolyte (in contact with the photoanode) and catholyte (in contact with a Pt mesh), respectively. Electrode reactions at the photoanode and Pt cathode follow: $\text{VO}^{2+} + \text{H}_2\text{O} \rightarrow \text{VO}_2^+ + e^- + 2\text{H}^+$ and $\text{V}^{3+} + e^- \rightarrow \text{V}^{2+}$, respectively. c) Photocurrents in an all-V PESC using TNBs and P25 TiO_2 . d) Photocurrents in an all-V PESC using photoelectrodes with and without TiCl_4 pretreatment.

As for the faster decay of photocurrent observed in the P25-based cell, photocatalyst degradation due to either chemical or photoelectrochemical corrosion can be ruled out as no evident change in the surface chemistry of both electrodes before and after the test was found. In fact, the inserted SEM images in **Figure 4c** give clues as to the relationship between electrode microstructure and the photocurrent. The electrode with P25 appears very dense though some discrete voids are sparsely spotted. The TNB-700 electrode, however, appears uniformly porous through the entire thickness of the electrode, and therefore may facilitate transport of vanadium redox species (i.e., VO^{2+}). Indeed, based on TiO_2 loading and the electrode thickness, calculated porosity values for two electrodes are 0.86 (TNB) and 0.66 (P25), respectively, which could account for a 1.7-fold improvement in effective diffusion coefficient of VO^{2+} , estimated via the Bruggman correlation [36], for the TNB-700 photoelectrode.

In addition, we employed TiCl_4 pre-treatment to the TNB-based photoelectrode in an attempt to possibly enhance the bonding and therefore charge transport between TNBs. The photoelectrode is denoted as TNB-TL hereafter. Both SEM and UV-vis spectroscopy were used to gain further insight into the structural/morphological and optical properties of the TNB-TL electrode. **Figures S6a** and **c** indicate that the TNB-TL still maintains its porous structure but with a well-connected 3D network. Both high-magnification top-view SEM image (**Figure S6b**) and microscopic images (**Figure S6d**, where a focused ion beam was used to reveal interior of the electrode) show that a thin layer of TiO_2 (from TiCl_4) film possibly form uniformly on the surface of TNBs. Further inspection using UV-vis spectroscopy (**Figure S7**) and more specifically from the red-shift of the absorption edge after

TiCl₄ treatment, allows us to speculate that this TiO₂ thin layer formed from TiCl₄ might be composed of rutile phase because of its narrower bandgap (3.03 eV).

To assess performance of TNBs in the all-V PESC, we conducted two sets of photocharging experiments (**Figure 4c**) using TiCl₄-treated (designated as P25-TL) and untreated P25, as well as treated (TNB-TL) and untreated TNBs. During the initial 1 min when the cells were kept in dark, no photocurrent was observed. Upon illumination, the photocurrents spike initially and then gradually level off. The TiCl₄ treatment to P25 only slightly improves the photocurrent (stabilized between 6 and 17 min) from 0.16 mA to 0.23 mA. In comparison, the TNB, after TiCl₄ treatment (i.e., TNB-TL), achieves a stabilized photocurrent double that of P25-TL, representing a 2.3-fold increase in photocurrent. This significant photocurrent enhancement for the TNB samples is attributed to improved charge transfer through a 3-D network of semiconductor due to TiCl₄ treatment, fast kinetics of the vanadium redox, and intrinsic properties of high-aspect ratio TNBs, including high crystallinity (**Figure 1g**), high surface specific activity (**Table S1**), 1-D elongation of the belts, long electron diffusion length, and almost two-fold higher effective donor concentration comparing to nanoparticles. Particularly, anatase TiO₂ nanobelts have been demonstrated to have electrical conductivity of about $10^{-7} \Omega^{-1} \text{ cm}^{-1}$, 100 times higher than that the nanoparticle counterpart [37].

To shed light on the implication of TiCl₄ pre-treatment to enhanced photocatalytic activity in the TNB-TL based photoelectrode, we conducted EIS measurements at open circuit in the all-V PESC. In **Figure 5**, Nyquist plots of both TNB and TNB-TL electrodes were composed of similar arcs/partial arcs. The small arc and an even bigger arc (only a portion) at low frequency, according to references [38, 39], correspond to electron transport resistance and

interfacial capacitance at the Pt/electrolyte and TiO_2 /electrolyte interfaces, respectively. Upon illumination, diameter of the high-frequency arc for the TNB electrode shrinks considerably indicating that charge transfer resistance at the Pt/electrolyte interface was reduced. And the low frequency arc corresponding to charge transfer at the TiO_2 /electrolyte interface was also reduced under illumination, indicated reduced charge transfer resistance. On the other hand, smaller diameter of the high frequency arc for the TNB-TL electrode, which was only one quarter of that of the bare TNB electrode, remains almost unchanged upon light illumination, suggesting enhanced charges injection into Pt/electrolyte interface enabled by the TiCl_4 -treated TNB photoanode. Moreover, the lower frequency arc for TNB-TL smaller than bare TNB regardless of illumination or dark condition, indicate that the charge transfer resistance and interfacial capacitance at TiO_2 /vanadium (IV) interface was reduced by the TiCl_4 treatment.

Figure 5. EIS spectra in Nyquist plots obtained from all-V PESC using a) TNB-700 and b) TNB-TL as the photoelectrode.

IPCE measurements were also conducted to assess the overall photocharging efficiency of the all-V PESC using TNB-TL as the photoanode. The results were benchmarked against P25

which has been extensively used as a reference in our previous efforts [14-19] and treated with TiCl_4 in this study (P25-TL). In **Figure 6**, the IPCE remains almost zero at wavelength above 450 nm owing to the wide bandgap of TiO_2 . In the range from 350 to 400 nm, the IPCE increases with decreasing wavelength of the irradiating light. At 350 nm the IPCE of the cell with TNB-TL reaches a maximum (~22 %), double that of commercial P25-TL (~11 %). This is strongly indicative of three efficient processes in the TNB-TL based cell: light harvesting (LH), charge separation (CS), and charge collection (CC), which correspond, respectively, to three process efficiencies, i.e., η_{LH} , η_{CS} , and η_{CC} , since the IPCE can be expressed in the following equation: $\text{IPCE} = \eta_{\text{LH}} \cdot \eta_{\text{CS}} \cdot \eta_{\text{CC}}$.

Figure 6. IPCE spectra of all-V PESCs assembled using TNB-TL as the photoelectrode, collected at the incident wavelength range from 350 to 550 nm, in comparison to P25.

Because of comparable light absorbing characteristics (**Figure S7**) of the TNB-TL and P25 electrodes, the enhancement of IPCE for the former may solely originate from the following

three factors, as illustrated in the inserted schematic in **Figure 6**. First, the more exposed high-energy (001)/(100) (in type II TNB) TiO_2 facets, as the reaction sites for photoelectrochemical oxidation of VO^{2+} , could yield high η_{LH} . Second, the longitudinal dimension of the highly crystalline TNB-TL improves electron diffusion with depressed scattering at particle-particle interfaces. It also provides a large scale in the elongated direction to minimize electron-hole recombination. As a result, both η_{CS} and η_{CC} improve. Third, the largely populated low-energy (101) facets (in type I TNB) and high-energy (001) facets (in type II TNB) could preferentially collect electrons and holes, respectively, according to Ref. [26], therefore further enhancing e^-/h^+ separation. Most important, the above phenomena benefit from TiCl_4 pre-treatment that essentially bonds the geometry-enhanced ultra-long TiO_2 nanobelts. Fast charge transport is enabled within the established interconnected network of TNBs, which were found to be laid down along the in-plane direction of the photoelectrode in **Figure S8** (therefore poor adhesion between TNBs). Research is currently underway to align the TNBs along the through-plane direction of the photoelectrode to fully assess their fast electron diffusion in the longitudinal dimension.

Conclusions

In conclusion, we have built on our companion studies and demonstrated in this study [14-19, 27], a facile stirring-assisted hydrothermal method to prepare geometry-enhanced TNBs for highly efficient all-vanadium photoelectrochemical storage cells. We have presented evidence that increasing the stirring speed in the hydrothermal synthesis from 0 to 700 rpm creates 4.2 times more exposed high-energy (001) facets. The all-V PESC demonstrated a peak IPCE of ~22% without any external bias, double that of commercial P25 TiO_2 (~11%) benchmark. The enhanced photocatalytic performance is largely attributed to (i) the improved

charge separation efficiency because of the enhanced geometry of TNBs, (ii) more exposed high-energy (001)/(100) facets, and (iii) facilitated charge transfer enabled by high electron mobility. The capability of enhancing semiconductor geometry using mechanical stirring during synthesis could open up exciting new avenues for design and fabrication of future functional materials in various areas, such as photoelectrochemical water splitting, dye sensitized solar cells, photocatalysis, and particularly in the all-V PESC.

Acknowledgements

The authors acknowledge support of this work from National Science Foundation ECCS #1254915 (F.L). We also acknowledge Drs. Feng Wang and Leszek Nikiel from Fort Worth Research Center, Sid Richardson Carbon & Energy Co. for assistance with BET measurement. TEM characterization and sample preparation were carried out in part at the Characterization Center for Materials and Biology (C²MB), University of Texas at Arlington.

References

- [1] A. Fujishima, K. Honda, *Nature* 238 (1972) 37-38.
- [2] T. Chen, L. Qiu, Z. Yang, Z. Cai, J. Ren, H. Li, H. Lin, X. Sun, H. Peng, *Angew. Chem. Int. Ed.* 51 (2012) 11977-11980.
- [3] G. Wee, T. Salim, Y.M. Lam, S.G. Mhaisalkar, M. Srinivasan, *Energy Environ Sci* 4 (2011) 413-416.
- [4] P. Liu, Y.I. Cao, G.R. Li, X.P. Gao, X.P. Ai, H.X. Yang, *ChemSusChem* 6 (2013) 802-806.
- [5] N. Yan, G. Li, X. Gao, *J. Mater. Chem. A* 1 (2013) 7012-7015.
- [6] M. Yu, W.D. McCulloch, D.R. Beauchamp, Z. Huang, X. Ren, Y. Wu, *JACS* 137 (2015) 8332-8335.
- [7] W. Guo, X. Xue, S. Wang, C. Lin, Z.L. Wang, *Nano Lett.* 12 (2012) 2520-2523.
- [8] M. Yu, X. Ren, L. Ma, Y. Wu, *Nat Commun* 5 (2014).

- [9] N. Li, Y. Wang, D. Tang, H. Zhou, *Angew. Chem. Int. Ed.* 54 (2015) 9271-9274.
- [10] S. Licht, J. Manassen, *J. Electrochem. Soc.* 134 (1987) 1064-1070.
- [11] A.K. Jana, S. Roy, B.B. Bhowmik, *Energy* 13 (1988) 161-166.
- [12] G. Hodes, J. Manassen, D. Cahen, *Nature* 261 (1976) 403-404.
- [13] S. Licht, G. Hodes, R. Tenne, J. Manassen, *Nature* 326 (1987) 863-864.
- [14] D. Liu, Z. Wei, C.-j. Hsu, Y. Shen, F. Liu, *Electrochim. Acta* 136 (2014) 435-441.
- [15] D. Liu, W. Zi, S.D. Sajjad, C. Hsu, Y. Shen, M. Wei, F. Liu, *ACS Catal.* 5 (2015) 2632-2639.
- [16] D. Liu, F. Liu, J. Liu, *J. Power Sources* 213 (2012) 78-82.
- [17] D. Liu, Z. Wei, Y. Shen, S.D. Sajjad, Y. Hao, F. Liu, *J. Mater. Chem. A* (2015).
- [18] Z. Wei, D. Liu, C. Hsu, F. Liu, *Electrochem. Commun.* 45 (2014) 4.
- [19] Z. Wei, D. Liu, Y. Shen, H. Chia-jen, F. Liu, *ECS Trans* 66 (2015) 213-221.
- [20] Y.-C. Pu, G. Wang, K.-D. Chang, Y. Ling, Y.-K. Lin, B.C. Fitzmorris, C.-M. Liu, X. Lu, Y. Tong, J.Z. Zhang, Y.-J. Hsu, Y. Li, *Nano Lett.* 13 (2013) 3817-3823.
- [21] J. Yan, G. Wu, N. Guan, L. Li, Z. Li, X. Cao, *Physical Chemistry Chemical Physics* 15 (2013) 10978-10988.
- [22] W. Zhou, Z. Yin, Y. Du, X. Huang, Z. Zeng, Z. Fan, H. Liu, J. Wang, H. Zhang, *Small* 9 (2013) 140-147.
- [23] X. Feng, K. Zhu, A.J. Frank, C.A. Grimes, T.E. Mallouk, *Angew. Chem.* 124 (2012) 2781-2784.
- [24] H.G. Yang, C.H. Sun, S.Z. Qiao, J. Zou, G. Liu, S.C. Smith, H.M. Cheng, G.Q. Lu, *Nature* 453 (2008) 638-641.
- [25] D.L. Liao, B.Q. Liao, *J. Photochem. Photobiol. A* 187 (2007) 363-369.
- [26] N. Roy, Y. Sohn, D. Pradhan, *ACS Nano* 7 (2013) 2532-2540.
- [27] C. Hsu, Y. Shen, Z. Wei, D. Liu, F. Liu, *J. Alloys Compd.* 613 (2014) 117-121.
- [28] Y. Tang, Y. Zhang, J. Deng, J. Wei, H.L. Tam, B.K. Chandran, Z. Dong, Z. Chen, X. Chen, *Adv. Mater.* 26 (2014) 6111-6118.
- [29] J. Wang, D.N. Tafen, J.P. Lewis, Z. Hong, A. Manivannan, M. Zhi, M. Li, N. Wu, *JACS* 131 (2009) 12290-12297.
- [30] K. Biswas, B. Das, C.N.R. Rao, *J Phys Chem C* 112 (2008) 2404-2411.
- [31] J. Pan, G. Liu, G.Q. Lu, H.-M. Cheng, *Angew. Chem. Int. Ed.* 50 (2011) 2133-2137.

- [32] B. Wu, C. Guo, N. Zheng, Z. Xie, G.D. Stucky, JACS 130 (2008) 17563-17567.
- [33] A.S. Barnard, L.A. Curtiss, Nano Lett. 5 (2005) 1261-1266.
- [34] R. Baddour-Hadjean, J.-P. Pereira-Ramos, Chem. Rev. 110 (2010) 1278-1319.
- [35] F. Tian, Y. Zhang, J. Zhang, C. Pan, J Phys Chem C 116 (2012) 7515-7519.
- [36] C. Ding-Wen, E. Martin, R.E. David, W. Vanessa, R.E. García, Modell. Simul. Mater. Sci. Eng. 21 (2013) 074009.
- [37] Z. Zhao, J. Tian, Y. Sang, A. Cabot, H. Liu, Adv. Mater. 27 (2015) 2557-2582.
- [38] I. Abayev, A. Zaban, F. Fabregat-Santiago, J. Bisquert, Phys Status Solidi A 196 (2003) R4-R6.
- [39] Y.R. Ahn, C.R. Park, S.M. Jo, D.Y. Kim, Appl. Phys. Lett. 90 (2007) 122106.

energy conversion, solar fuel production, photoelectrochemistry, photocatalysis, and advanced material design and fabrication.

Chiajen Hsu received his B.S. degree from the Department of Materials Science and Engineering, National Cheng Kung University (NCKU), Taiwan in 2004, and then obtained his Ph.D. from University of Texas at Arlington, United States in 2013. His research interests focus on synthesis of catalysts, electrochemical mechanism analysis for high efficient fuel cells and photoelectrochemical cells.

Syed Dawar Sajjad is a polymer scientist at Dioxide Materials. He received his Bachelor Degree in Materials Science & Engineering from Ghulam Ishaq Khan Institute (GIKI), Pakistan in 2009 and then obtained his Ph.D. Degree from University of Texas at Arlington in 2015. His current research interests focus on electrochemical processes for energy storage and conversion as well as polymer ion exchange membranes for applications including Li-ion batteries, photocatalysis, fuel cells and water electrolyzers.

Krishnan Rajeshwar specialized in solid-state chemistry for his Ph.D. degree at the Indian Institute of Science in Bangalore, India. After a post-doctoral stint in Colorado State University, Fort Collins, CO, he joined the faculty of the Department of Chemistry & Biochemistry at the University of Texas at Arlington. He is now a Distinguished University

Professor there. He is also Senior Vice President and President-elect of the Electrochemical Society. His research interests span a broad spectrum in solid-state chemistry, materials chemistry, and energy R&D.

Fuqiang Liu is currently an associate professor in Department of Materials Science and Engineering at University of Texas at Arlington. He received his Ph.D. from Pennsylvania State University in 2006. His research group is currently focusing on Li-ion battery materials, advanced rechargeable batteries, fuel cells, and photoelectrochemical storage devices and materials. Dr. Liu and his group have made significant contributions in the area of all-vanadium photoelectrochemical solar cell for potentially efficient and large-capacity solar energy storage.

Graphical Abstract