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Effect of Ti foil size on the micro sizes of anodic TiO$_2$ nanotube array and photoelectrochemical water splitting performance

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Anodic TiO$_2$ nanotube (NT) array is promising for the flexible and efficient photoanode in photoelectrochemical water splitting (PECWS) cell. However, the photocurrent response of pristine anodic TiO$_2$ NT photoanode in literature has a ca 50 times difference, viz. from 0.05 to 1 mA/cm$^2$. Improvement of the pristine TiO$_2$ NT is the base for achieving a high efficient anode. Here, we examine the size effect in different scale on the PECWS performance with manipulating the macro size of the Ti foil. With decrease of the Ti foil size from 6 to 1 cm$^2$, corresponding to the anodic TiO$_2$ NT growth active area of 3.45 to 0.65 cm$^2$, the photocurrent response increased by 50.6%, achieving 1.13 mA/cm$^2$ at 1.23 V$_{RHE}$ (V versus reversible hydrogen electrode). The Ti foil size also significantly influences the micro sizes of the nanotubes including crystallite size, double wall thickness, inner diameter and tube length, which have profound effects on WS efficiency. The relationships between involved length scales, a span of six orders of magnitude from ten nanometers (10$^{-8}$ m) to centimeter (10$^{-2}$ m), and the PECWS efficiency is analyzed and discussed. Transient i-t curves are used to represent the chemical kinetics during the growth of anodic TiO$_2$ NT array. Finally, photon capture scheme is proposed to explain the physics behind the multi length scale effect of the TiO$_2$ NT photoanode. The need of quantitative models during the scale-up of the PECWS process is stressed.

1. Introduction

As the firstly and mostly reported semiconductor in sunlight-driven water splitting (WS), TiO$_2$ has been intensively employed as the powder photocatalyst in photocatalytic WS and as the anode semiconductor in photoelectrochemical (PEC) cells. [1] However, the solar to hydrogen efficiency of TiO$_2$ is limited by its wide bandgap nature. To improve the TiO$_2$ catalytic efficiency in WS towards practical use of the process, great effort has been devoted to the approaches such as bandgap narrowing, surface step accelerating, and morphology controlling etc. Among them, TiO$_2$ morphology has been shown have strong influences on the performances both as powder and anode catalysts. Nanorods, [2] nanowires, [3] nanotubes, [4] and nanofibers [5] of TiO$_2$ have been successfully prepared and applied either as the only or component of the powder photocatalyst and photoanode in PECWS.

One-dimensional (1D) TiO$_2$ nanotube (NT) array prepared with anodic oxidation method have been an attractive catalyst for photoanode as it exhibits fast electron transfer, high specific surface area and low charge carrier recombination rate [6–7]. Moreover, TiO$_2$ NT array intrinsically takes the advantage of the metallic substrate, which is much more flexible and conformable in fabrication and compatible to the other components of the cell than the glass substrates [7]. It is also appealing towards a zero bias PECWS cell in academic research and future application due to an inherent advantage, an onset potential lower than Fe$_2$O$_3$ and its composites as photoanode semiconductors (0.4–0.8 V$_{RHE}$) [8–9]. The first report of anodic grown TiO$_2$ NT application as anode in PECWS cell was illustrated with 1 M KOH electrolyte under UV light source as a function of anodization bath temperature by...
Mor et al. [10] in 2005, which was stimulated by the milestone works of Assefpoor-Dezfuly et al. [11] and Zwilling et al. [12] for the anodic growth of TiO₂ NT arrays. Afterwards, many works [13–17] have examined the controlling of the dimensions of the anodic TiO₂ NT, e.g., the tube length, the inner diameter and the wall thickness etc. and their effect on the performance in PECWS. The reported photocurrent response of the pristine anodic TiO₂ NT, viz. without modifications with loading cocatalysts of metallic nature and forming junctions with other semiconductors, as anode in PECWS cell has been in the range of ca 50 μA/cm² to 1.0 mA/cm². A vast difference, ca 50 times, exists due to the inconsistency of the conditions used in different labs for preparation and utilization! For instance, under AM 1.5 G simulated sunlight at 1.6 V_RHE, a pristine TiO₂ NT array with an average tube length ~8 μm and diameter of 100 nm gave a 0.1 mA/cm² photo response in 1 M KOH solution, [18] while another, with a tube length of around 3.6 μm, showed a photocurrent of 0.52 mA/cm² in 1 M NaOH solution. [19] One of the highest photocurrent responses, ca. 0.71 mA/cm² in 1 M NaOH solution, reported with pristine TiO₂ NT was obtained with a tube length of 14.1 μm and a diameter of 115 nm on a Ti foil with 1.0 cm² active area [4].

Recent efforts on enhancing the anode performance of TiO₂ NT array are intensive. Improvement of the pristine TiO₂ NT is the base for achieve high efficient anode, thus the input of effort has been always active and important [20–27]. Nevertheless, the approaches on element doping and cocatalyst loading on the TiO₂ NT to widen the solar energy absorption spectrum and accelerate the surface steps for oxygen evolution reaction are also vital [28–33]. Very recently, Lucas et al. [34] coated a SrTiO₃ layer on the anodic TiO₂ NT surface and further doped the layer with La³⁺ to form a La:STO/TiO₂ NT junction and obtained a photocurrent response of 0.1442 mA/cm² at 1.23 V_RHE in a Na₃SO₄ electrolyte buffered with phosphate at pH = 7.1 under AM 1.5G. A carbon bridged BiO₂/ TiO₂ NT gave 0.1915 mA/cm² output at 0.81 V_RHE in a 0.05 M phosphate buffer solution (pH = 7) under visible light [26]. Xiao et al. [37] reported a 0D/1D g-C₃N₄ and TiO₂ NT heterostructure with showing a 0.72 mA/cm² at 1.23 V_RHE in a 0.1 M Na₂SO₄ electrolyte under visible light.

Very recently in 2021, Wang et al. [35] specified the needs to standardize the testing and accreditation of efficiency, procedure and protocol of solar-to-chemical devices. To understand and optimize the photoelectrode preparation parameters and to correlate the effects and responses in different scale level would be important steps towards the commercial application of the PECWS converters.

Herein, with the in-lab optimized electrolyte and cell configuration in anodic growth of the TiO₂ NT array, we illustrate the effects of the Ti foil size in the TiO₂ NT array growth on the micro-sizes of the nanotubes and on the photocurrent response of the TiO₂ NT anode in PECWS cell. Moreover, the relevance of the sizes in different length scale to the scale up of the anodic TiO₂ NT as anode of the PECWS cell is discussed.

2. Experimental

2.1. Chemicals and materials

Titanium foil (Ti, purity 99.5%, thickness: 0.02 cm, Beijing Zhong-nuo Advanced Material Technology Co., Ltd), ethylene glycol (C₂H₄O₂, EG, anhydrous 99.8%, Sigma Aldrich and Merck), ammonium fluoride (NH₄F, ACS reagent, ≥98.0%, Sigma-Aldrich) and sodium hydroxide (NaOH, Merck KGaA, 64271 Darmstadt Germany, EMD Millipore Co.,) were used as received without further treatment. The aqueous solutions were prepared with deionized (DI) water. And DI water for 30 min sequentially and dried in an oven (UF 75, Memmert GmbH Co. KG) at 70 °C. The anodic oxidation was carried out in a two-electrode configuration with Ti foil as the anode and a Pt sheet (1.00 cm²) as the counter electrode in the growth electrolyte under a constant voltage of 60 V powered with a DC power supply (E3647A, Keysight) for 3 h at room temperature. The electrolyte is a solution of a mixture of 0.3 wt% NH₄F, DI H₂O and EG (V_F : V_EG = 3:47) [4]. The as formed TiO₂ NT samples were annealed at 450 °C for 30 min with a heating rate of 4 °C/min in a muffle oven (Nabertherm, Germany) in air. The samples are referred to as a, b, c and d corresponding to the four different Ti foil sizes.

2.3. Characterization

The morphology was observed with a field-emission scanning electron microscope (SEM, Tescan MIRA 3, Brno, Czech Republic) and a transmission electron microscope (TEM; JEOL, JEOL JEM-2200FS, existed at 200 kV). The structure was characterized with X-ray diffraction (XRD) (PANalytical X’PertPro) using Cu-Kα (λ = 1.540598 Å) radiation.

2.4. Photoelectrochemical measurements

The PEC performance measurements were carried out with the TiO₂ NT sample as the work electrode, a Pt sheet as the counter electrode, and Ag/AgCl as the reference electrode in 1.0 M NaOH (pH = 13.6) as electrolyte under AM 1.5 G simulated sunlight from a Xenon lamp (94011A-ES, LCS-100, Newport). The active areas, i.e., the immersed area in the 1 M NaOH aqueous solution of the sample are listed in Table 1. The photocurrent was measured with an electrochemical work station (ZENNIUM pro, Zahner-Elektrik, Germany). It should be noted that TiO₂ NT arrays always grow symmetrically on both sides of the Ti foil. However, in the condition range with interest for WS reaction, the photocurrent under dark is always negligible. Therefore, in the context of the photocurrent response description with respect to WS research, the irradiation is from one side and the response of the dark side is neglected.

The measured potential vs. Ag/AgCl electrode was converted to that versus reversible hydrogen electrode (RHE) with the Nernst equation [36]:

\[ E_{RHE} = E_{Ag/AgCl} + 0.059 \text{pH} + 0.196 \]  

where J is the photocurrent density (mA/cm²) at the potential, and P is the incident light intensity of 100 mW/cm².

3. Results

3.1. Photoelectrochemical performance

In Fig. 1 (A), the dashed line under the bottom is the response of sample a under dark condition. The photocurrent responses of the four TiO₂ NT samples in PEC cell are measured with a three-electrode configuration in 1 M NaOH electrolyte under AM 1.5 G simulated sunlight (100 mW/cm²) irradiation from one side. Under the same condition, the four samples exhibit LSV curves well in the order of a > b > c > d. The four samples all already give rather high photocurrent at 0.2 V_RHE, the starting point of the LSV measurements. The photocurrent response of the four samples become almost stable after the inflexion points, with the inflexion point of curve a locates at the lowest 0.446 V_RHE. At 1.23 V_RHE, the photocurrent densities of the samples are all well
stabilized and take the values from a to d as 1.13, 1.06, 0.91 and 0.75 mA/cm$^2$, respectively. Compared to that of the sample d, samples a, b and c achieved 50.6%, 41.3% and 21.3% enhancement, respectively. As compared with literatures, for example: Wang et al. [37] reported a TiO$_2$ NT with a sample size of 1*1 cm$^2$, showing a photocurrent density of less than 0.4 mA/cm$^2$ at 1.23 V$_{RHE}$. A nitrogen-doped carbon quantum dots anchored TiO$_2$ NT gave the highest performance of ca 1.1 mA/cm$^2$ [37]. Lucas et al. [34] reported a sample with the exposed area of 1.3 cm$^2$. The pristine TiO$_2$ NT produced a photocurrent density of 0.0589 mA/cm$^2$ at the applied bias of 1.23 V$_{RHE}$. A pristine TiO$_2$ NT fabricated on 2*1 cm$^2$ Ti foil showed a photocurrent density less than 0.5 mA/cm$^2$ at 1.23 V$_{RHE}$. [38] Koiki et al. [39] reported a TiO$_2$ NT with a photocurrent density ca 0.05 mA/cm$^2$ at 1.23 V$_{RHE}$, which was fabricated on 5*3 cm$^2$ Ti foil. The ABPE% of the four samples under light conditions are derived from the J-V curves and are illustrated in Fig. 1 (B). The curves show a sequence of a > b > c > d in the whole bias range. The four samples give different maxima values at different bias. The ABPE value of a is 0.957% at 0.324 V$_{RHE}$, b 0.760% at 0.417 V$_{RHE}$, c 0.635% at 0.475 V$_{RHE}$, and d 0.572% at 0.386 V$_{RHE}$, respectively. Among the TiO$_2$ NT samples, sample a has the largest cathodic shift of the bias at the highest

| No | Ti foil (cm$^2$) | $\sqrt[3]{\text{Ti(cm)}}$ | Active area TiO$_2$ NT (cm$^2$) | $\sqrt{\text{active area (cm)}}$ | Crystallite size (nm) | TiO$_2$ NT Tube length (μm) | Inner diameter (nm) | Double wall thickness (nm) |
|----|-----------------|-----------------------------|---------------------------------|-----------------------------|-------------------------|----------------------------|------------------------|------------------------|
| A  | 1.00            | 1.00                        | 0.65                            | 0.806                       | 20.1                    | 13.8                       | 121                    | 26.6                   |
| B  | 2.00            | 1.41                        | 1.08                            | 1.04                        | 27.2                    | 11.0                       | 99.3                   | 31.8                   |
| C  | 4.00            | 2.00                        | 2.30                            | 1.52                        | 50.6                    | 9.78                       | 93.8                   | 39.3                   |
| D  | 6.00            | 2.45                        | 3.45                            | 1.86                        | 55.2                    | 9.96                       | 97.1                   | 39.0                   |

Fig. 1. (A). LSV curves of the a, b, c and d samples at a scan rate of 10 mV/s in 1 M NaOH under the dark and AM 1.5 G simulated light (100 mW/cm$^2$) conditions, (B) ABPE curves of a the a, b, c and d samples under AM 1.5 G simulated light (100 mW/cm$^2$).

Fig. 2. SEM micrographs of the top surface view of 4 TiO$_2$ NT samples (A) a, (B) b, (C) c, (D) d; cross-sectional view of TiO$_2$ NT samples (E) a, (F) b, (G) c, (H) d.
3.2. Characterization

Fig. 2 gives the SEM micrographs of the TiO₂ NT samples. All the tubes have open-tops and are vertically aligned. The three parameters, average value of tube length, tube inner diameter and double wall thickness (note, two walls are combined) were estimated with the Nano Measurer software and are listed in Table 1. The average tube lengths of the 4 samples, a to d, are 13.8, 11.0, 9.78 and 9.96 μm, their average inner-wall diameters are 121, 99.3, 93.8 and 97.1 nm, and their double wall-thicknesses are 26.6, 31.8, 39.3 and 39.0 nm, respectively. Both the average tube length and the average inner diameters are decreased, while the average double wall thickness increased with the increase of the active TiO₂ NT growth area.

The crystallinity and phase composition of the TiO₂ NT samples were measured with XRD and the patterns are illustrated in Fig. 3. All the samples exhibit similar XRD patterns (Fig. 3(A)) composing the typical peaks of anatase phase (JCPDS no. 21-1272), and the peaks of hexagonal closely packed Ti metal α phase (JCPDS no. 44-1294). As the samples are anodic grown anatase phase, the preferential oriented growth of the crystal is obvious with specially strengthening of the peaks at 2θ = 25.28°, 48.05°, 62.69° and 70.31° show some differences among the 4 samples. Furthermore, the estimated crystallite sizes derived from XRD patterns are plotted in Fig. 3 (B). The crystallite sizes of the a to d samples are 20.1, 27.2, 50.6 and 55.2 nm (Table 1), respectively. With the increase of the Ti foil and active area of TiO₂ NT, the crystallite size of the TiO₂ NT is increased.

3.3. Signals during the anodic growth of nanotube array

Fig. 4 shows the transient current–time (i-t) curves during the anodic oxidation growth of TiO₂ NT on the surface of the different sized Ti foils in 50 ml EG/NH₄F electrolyte under the same cell condition with DC voltage 60 V. In Fig. 4 (A), the recorded initial current increased from 37.0 mA with sample a to 49.0 mA with sample d, with the increase of the active growth areas. During the whole anodic oxidation TiO₂ NT growth process, the i-t curve for a specific sample gives a horizontal S-shape, but the sequence of the overall current of the four samples remains the same, i.e. d > c > b > a. In Fig. 4 (B) the current densities, i.e., the normalized current per cm² are plotted. The sequence of the initial values of the TiO₂ NT samples are reversed. The TiO₂ NT samples from a to d exhibit initial values as 54.8, 31.8, 19.6 and 14.2 mA/cm², respectively, indicating a substantial decrease of the current density along with the increase of the size of the TiO₂ NT growth area of the Ti foil.

4. Discussion

4.1. Size effects in micro scale

The photocurrent density response at bias 1.23 VRHE is often discussed and one of the most important output of the photoanode in the PECWS cell. Here, we take the response values at bias 1.23 VRHE for comparison. Fig. 5 (A) plots the six size factors measured in this work as the Y-axis and the photocurrent density response values of the four samples at 1.23 VRHE as the X-axis. For visual aid, the sizes are the numbers read on the Y-axis multiplied by the scale in the parentheses after the term of the factor.

Both the crystallite size and the double wall thickness have a scale of 10⁻³ m level. With the increase of the two sizes in 10⁻³ m scale, the photocurrent density at 1.23 VRHE in PECWS cell is decreased. The double wall thickness has a stronger effect on the output of the anode than the crystallite size. The inner-wall diameter is of sub-micron scale (ca 0.1 μm, viz. 10⁻⁶ m) and tube length is set in micron-scale (ca 10 μm, viz. 10⁻⁶ m). With both the increase of inner diameter and tube length, the photocurrent density increased, while increase the tube length (10⁻⁵ m) seems a little bit more powerful than widening the wall thickness (10⁻⁷ m).

The effects of semiconductor component sizes in the micro-scale on the solar-to-energy efficiency in PECWS have been intensively investigated [29,40]. Tuning the size of quantum dots [41], the size of plasmonic metal nanodots [42], semiconductor particle size [43], semiconductor layer thickness [44] etc. have been shown effective in monitoring and enhancing PECWS efficiency. Here, the micro sizes of anodic grown TiO₂ NT including the tube length, inner wall diameter and wall thickness all affect the efficiency of the solar to energy device [7,29,45–46].

Here, we also observed the periodically regular decoration of the nanoparticles and photonic crystals on the outer surface, illustrated as in Fig. 5 (B). These photonics structures in different scale, may contribute enhancement of the photon to electron transformation. These facts indicate that we are in need quantitative models to correlate such observations.

4.2. The growth of the nanotubes and the effect of macro size

The micro sizes of TiO₂ NT in anodic growth are known controllable with the reaction temperature, reaction time, the composition of organic solvent, the concentration of F⁻ element and the applied voltage etc. [13,28] The morphology of the anodic grown TiO₂ NT has also been sensitive to the supplier of Ti metal with which the purity, thickness and other parameters are given as equivalent [47]. Here, we demonstrated that tailoring the macro size of Ti foil shows a remarkable effect on the
mentioned micro sizes of TiO$_2$ NT. In turn, the micro-size factors measured all effectively influence the photocurrent response of the TiO$_2$ NT photoanode. The anodic growth of the TiO$_2$ NT array is complex and the mechanism and kinetics are still unclear [48]. However, some general outlines on these factors and the macro size effects can be provided. A dense oxide layer with high-resistance to oxidation always exists on the surface of a Ti foil. The growth of anodic TiO$_2$ NT has three steps. The primary stage: The fluoride (F$^-$) ions in the electrolyte etch the dense TiO$_2$ layer with the driving of the potential and pores form. The second stage: The continuous dissolution of Ti metal results in small cavities, which are gradually deepened and the continuous pores are developed to form an orderly independent nanotube structure. The competition between the formation and dissolution of TiO$_2$ is a crucial factor to determine the morphology of TiO$_2$. The final stage: The length of the tube does not increase, when the rate of formation of the oxide and the dissolution rate are equal [49–50].

The macro size of the Ti foil in the TiO$_2$ NT growth reaction limits the space, and thus exerts a strong influence on the examined micro sizes: crystallite size, tube length, tube diameter and wall thickness. The transient $i$-$t$ curves in Fig. 4 show clearly that the TiO$_2$ NT growth rate reflected by the current density becomes larger when the active area of the growth is reduced. The difference in the micro sizes between the samples can be explained with the space competition and the difference in growth rates.

As anodic grown TiO$_2$ NT arrays are gaining interest as a versatile photoanode catalyst in PECWS and scaling-up efforts of the process are underway [51], increasing the macro size of the photoelectrodes is of a lot of interest. This work clearly shows that the process parameters in anodic TiO$_2$ NT array growth strongly affect the TiO$_2$ NT anode efficiency in PECWS cell and a properly prepared sample gives an outstanding performance. The multi-scale modelling of the PEC water splitting electrodes will definitely facilitate the approach to practical use of the process [52].

4.3. Photon capture scheme of the anode

We propose the photon capture, charge carrier flow and water splitting mechanism (Fig. 6) to explain the outstanding performance of the anodic grown TiO$_2$ NT array. When light irradiated on the TiO$_2$ NT film, the open top of the tubes allows the photon directly running into the inside space of the tube and interacting with the inner wall. When photon excites the electrons (e$^-$) in the valence band (VB) of TiO$_2$ to the conduction band, stimulating an enrichment of VB holes (h$^+$) for O$_2$ evolution reaction on the tube tops. The excited e$^-$ drives to the tube bottom towards the Ti foil substrate and then flows in the circuit to the Pt electrode for the reduction of water to H$_2$. The separated e$^-$ and h$^+$ transfer pathways in the tube wall but in opposite directions reduce the probability of recombination of the charge carries. The excellent conductivities of the TiO$_2$ NT semiconductor and the metallic Ti foil facilitate the charge flow in high rates.
5. Conclusion

The effects of the Ti foil macro size on both the anode performance of the TiO$_2$ NT array in PECWS and the micro sizes of the nanotubes in the array are examined in this work under exactly the same condition, i.e. same DC voltage and electrolyte during the growth. Four Ti foil sizes, with areas of 1, 2, 4 and 6 cm$^2$, provided 4 active areas 0.65, 1.08, 2.30 and 3.45 cm$^2$ of the photoanode in the PECWS cell. With the increase of the Ti foil size, the photocurrent density of the TiO$_2$ NT anode decreased from 1.13 (sample a) to 0.75 mA/cm$^2$ (sample d). Compared to that of the sample d, sample a, b and c achieved 50.6%, 41.3% and 21.3% enhancement of the photocurrent just because of the decrease of the TiO$_2$ NT growth area. The highest ABPE value achieved with sample a was 0.957% at 0.324 V RHE. The characteristic micro sizes: crystallite size, double wall thickness, inner-wall diameter and tube length, measured with SEM and XRD techniques are found all influenced by the Ti foil size and in turn they decide the photocurrent output of the photoanode in PECWS reaction. The current density plotted in the transient $i$-$t$ curve is a measure of the rate of anodic TiO$_2$ NT growth. The largest Ti foil (6 cm$^2$) with the largest active area (3.45 cm$^2$) gave the highest current 49.0 mA, but the lowest current density. The normalized transient $i$-$t$ curves indicated that the sample grown on the smallest active area of 0.65 cm$^2$ on the 1 cm$^2$ Ti foil exhibited the highest current density of 54.8 mA/cm$^2$, indicating the highest growth rate. Decrease the sizes set in the 10$^{-8}$ m scale, the double tube wall thickness and crystallite size facilitate achieving the enhancement of the photocurrent density at 1.23 V RHE. Increase the sizes in the scale of 10$^{-7}$ ~ 10$^{-5}$ m, i.e. the tube length and inner-wall thickness will achieve PEC performance enhancement. In 10$^{-2}$ m scale, decreasing the TiO$_2$ NT active area and the Ti foil size will improve the photocurrent density. The multi length scale effects and interactions can be explained with the chemical kinetics and physical forces during the TiO$_2$ phase nucleation and growth. The proposed mechanism shows that the separated $e^-$ and $h^+$ transfer pathway in the tube wall but in opposite direction reducing the probability of recombination of the charge carries. The results of this work will be useful to scaling-up of PECWS through helping construction multi length scale quantitative models to explain the multi scale effects both in the preparation and application of the photoelectrodes.

Author contributions

Xuelan Hou proposed the topic and contributed to experiment, analysis of the data and writing of the manuscript. Zheng Li contributed to the experiments. Lijun Fan contributed to SEM characterization, Jiashu Yuan contributed to XRD characterization, and both of them joined the discussion of experimental details. Peter D. Lund proof-read and commented the manuscript. Yongdan Li secured funding, lab facility, and discussed and improved the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, Nature 238 (5358) (1972) 37-38.
[2] H. Huang, X. Hou, J. Xiao, L. Zhao, Q. Huang, H. Chen, Y. Li, Effect of annealing atmosphere on the performance of TiO$_2$ nanorod arrays in photoelectrochemical water splitting, Catal. Today 330 (2019) 189-194.
[3] S. Hoang, S.P. Berglund, N.T. Hahn, A.J. Bard, C.B. Mullins, Enhancing visible light photo-oxidation of water with TiO$_2$ nanowire arrays via cotreatment with H$_2$ and NH$_3$ synergistic effects between Ti$^{3+}$ and N, J. Am. Chem. Soc. 134 (8) (2012) 3659-3662.
