available at www.sciencedirect.com

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

Article (Special Issue of Photocatalysis for Solar Fuels)

Efficient development of *Type-II* TiO₂ heterojunction using electrochemical approach for an enhanced photoelectrochemical water splitting performance

Yuanxing Fang, Yiwen Ma, Xinchun Wang *

State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350002, Fujian, China

ARTICLE INFO

Article history:

Received 26 December 2017

Accepted 12 January 2018

Published 5 March 2018

Keywords:

Type II heterojunction structure

Photoelectrochemical water splitting

TiO₂

Electrochemical reduction

Modification

ABSTRACT

Type-II-heterojunction TiO₂ nanorod arrays (NAs) are achieved by a combination of reduced and pristine TiO₂ NAs through a simple electrochemical reduction. The heterojunction-structured TiO₂ NAs exhibit an enhanced photo-efficiency, with respect to those of pristine TiO₂ NAs and completely reduced black TiO₂. The improved efficiency can be attributed to a synergistic effect of two contributions of the partially reduced TiO₂ NAs. The light absorption is significantly increased, from the UV to the visible spectrum. Moreover, the *type II* structure leads to enhanced separation and transport of the electrons and charges. The proposed electrochemical approach could be applied to various semiconductors for a control of the band structure and improved photoelectrochemical performance.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Water splitting using photoelectrochemical (PEC) cells with metal oxides attracts a significant research interest, owing to the potentials to overcome energy and environmental issues [1]. Over the past four decades, various oxides have been investigated, including TiO₂ [2], ZnO [3,4], Fe₂O₃ [5,6], BiVO₄ [7,8], WO₃ [9,10], etc. [11–13], whose band structures are suitable with respect to the water redox potentials. However, the photoefficiency is still very low for photoanodes based on a bare material, mainly owing to the narrow absorption range in the visible spectrum and high probability of electron-charge recombination [14]. Therefore, the development of efficient methods to overcome the above challenges is required for the improvement of the photoefficiency for water splitting.

Several strategies were proposed to enhance the overall

photoefficiency [13], including an introduction of foreign elements and formation of heterojunction structure [15]. As a typical example, a sub-stoichiometric TiO₂ was extensively studied for an enhanced performance in photocatalysis. This structure can be formed by annealing pristine TiO₂ under an oxygen-deficient/-reducing environment; it exhibits black-color characteristics [16]. In addition, it exhibits significantly improved optical properties, with a narrower band gap for an enhanced visible-light absorption. Furthermore, oxygen vacancies can form, which increase the charge carrier density. The abundant charge carriers could increase the efficiency of charge separation by enhancing the band bending at the interface between TiO₂ and electrolyte [5]. However, this method is time-consuming and complex [17]. Recently, a rapid electrochemical method was developed to facilitate the formation of a sub-stoichiometric metal oxide

* Corresponding author. Tel/Fax: +86-591-83920097; E-mail: xcwang@fzu.edu.cn

This work was supported from the National Natural Science Foundation of China (21425309, 21761132002, 21703040), China Postdoctoral Science Foundation (2017M622051), and the 111 Project.

DOI: 10.1016/S1872-2067(18)63037-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 3, March 2018

photoelectrode [18]. This method was widely employed, as it is simple and cost-effective [19–22]. It was also employed in other metal oxides; for example, reduced WO_3 , ZnO , and BiVO_4 were successfully obtained in different environments to enhance the PEC water splitting efficiency [20]. In the electrochemical approach, the deposition of elements is driven by the formed electrostatic field between the anode and cathode. Therefore, for a determined electrostatic field strength, the deposition of elements can be easily controlled by the duration of the applied potential. In the transient state, before the completion of the formation of black TiO_2 , Ti(III) oxide is induced at the bottom, near the substrate, while the Ti(IV) oxide is preserved at the top, far away from the substrate, which exhibit distinct electronic and optical properties, and form a heterostructure.

In general, three types of heterojunction structure are employed in the design of a photoanode, as illustrated in Fig. 1. For an efficient use of the electrons and charges in the redox reaction, the *type II* band alignment is the most suitable alignment, as it provides an efficient extraction of the photo-generated electrons and charges for the interfacial reactions of hydrogen and oxygen evolutions. It reduces the possibility for recombinations, and improves the overall water splitting efficiency. $\text{TiO}_2/\text{BiVO}_4$ [23], ZnO/BiVO_4 [24], and $\text{TiO}_2/\text{Fe}_2\text{O}_3$ [25], exhibited significantly improved PEC water splitting efficiencies. However, in these systems, at least two materials are needed for the formation of the heterojunction; therefore, the synthesis normally required sophisticated procedures with limited candidates of suitable materials, and the performances were not easily reproducible.

In this study, a *type-II*-heterojunction TiO_2 nanorod arrays (NAs) are obtained by a combination of reduced and pristine TiO_2 , through a conventional electrochemical reduction. The obtained TiO_2 heterojunction structure is characterized by electrochemical and spectroscopic measurements. It exhibited an increased photoefficiency by more than three times and by approximately 20%, with respect to those of the pristine TiO_2 NAs and completely reduced black TiO_2 , respectively. Two factors contribute to the enhanced water splitting efficiency. For the partially reduced TiO_2 , the light absorption is significantly increased, from the ultraviolet (UV) to the visible spectrum. Moreover, the *type II* heterostructure provides efficient charge separation and transport, which leads to an improved PEC water splitting efficiency [26]. This highly controllable approach

can be easily employed for various semiconductors for the control of the band structure [27], with applications in energy harvesting, conversion, and storage [28–30], as well as sensor and biology applications [31,32].

2. Experimental

2.1. Preparation

TiO_2 NAs were synthesized through hydrothermal methods. First, 0.1 mol/L TiCl_3 was dissolved in a solution that consists of a mixture of 13 ml hydrochloric acid and 15 ml water. The as-prepared solution was transferred into a 50-ml teflon-line stainless-steel autoclave, and several clean fluorine-doped tin oxide (FTO) glasses were submerged into the solution. The sealed autoclave was heated in an oven at 150 °C for 5 h, and cooled down to room temperature. TiO_2 NAs were homogeneously deposited on the FTO glass, and the samples were thoroughly washed with deionized (DI) water. The as-prepared TiO_2 NAs were further annealed at 550 °C for 1 h to obtain a ratio between anatase and rutile of approximately 3:1. The electrochemical reduction was performed using a VSP-300 electrochemical station (Bio-Logic), with a typical three-electrode system. TiO_2 NAs, Pt foil, and Ag/AgCl were used as the anode, cathode, and reference electrode, respectively. The TiO_2 NAs underwent an electrochemical reduction under a negative potential (−0.5 V vs reversible hydrogen electrode (RHE)) in 0.05 M H_2SO_4 solution for different time periods. The reduced electrode was dried at ambient conditions for 1 h.

2.2. Characterization

The morphology and elemental composition of the photoanode were studied using field-emission scanning electron microscopy (FE-SEM, Jsm-6700F). Ultraviolet-visible diffuse reflectance spectroscopy (UV-VIS DRS, Varian Cary 500 Scan UV-VIS system) was employed to study the optical properties of the photoanode. The crystallinity of the samples was investigated using X-ray powder diffraction (XRD, Bruker D8 Advance with $\text{Cu } K_{\alpha 1}$ radiation, $\lambda = 1.5406 \text{ \AA}$). In addition, electrochemical impedance spectroscopy (EIS) was employed, and Mott-Schottky and Nyquist plots were obtained.

2.3. Measurement

The as-prepared TiO_2 NAs photoanode was used in the same electrochemical station with a typical three-electrode system. The edge of the modified TiO_2 electrode was sealed using insulating epoxy resin, except for an active surface area of $1 \times 1 \text{ cm}^2$; it was functionalized as a photoanode, while a Pt foil and Ag/AgCl were used as the cathode and reference electrode, respectively. Linear sweeps and electrochemical impedance spectra were obtained in 1 mol/L NaOH (pH = 13.6) using an AM 1.5 solar simulator (Newport 94023A). The incident-photon conversion efficiency (IPCE) was measured using the same electrochemical setup with an IPCE station (Newport,

Fig. 1. Illustration of the three types of heterojunction structure of a photoanode

QEPV-B), coupled with an infrared filter and aligned monochromator. Cyclic voltammetry (CV) scans of the TiO_2 electrodes were performed in a solution of tetrabutylammonium hexafluorophosphate (TBAPF6) in anhydrous acetonitrile, using TiO_2 , Pt, and Ag/AgNO_3 as the anode, cathode, and reference electrode, respectively.

The carrier density is estimated using the Mott-Schottky relation [33]:

$$\frac{1}{C_{sc}^2} = \frac{2}{\epsilon \epsilon_0 A^2 e N_d} (V - V_{fb} - \frac{k_b T}{e}) \quad (1)$$

where C_{sc}^2 is the capacitance of the space-charge region, e is the elementary charge of the electron (1.602×10^{-19} C), ϵ_0 is the permittivity of vacuum ($\epsilon_0 = 8.854 \times 10^{-12}$ F/m), ϵ is the dielectric constant of TiO_2 ($\epsilon \sim 55$) [34], A is the electrochemically active surface area (1 cm^2 in the employed system), V is the applied voltage, V_{fb} is the flat-band potential, and N_d is the donor density. The IPCE is obtained using the quantum-based equation:

$$\text{IPCE}(\%) = 1240 \times I/(\lambda P_{\text{input}}) \quad (2)$$

where λ and P_{input} are the wavelength and power (mW/cm^2) of the incident light (Xenon lamp), respectively, I is the photocurrent density; the IPCE is a relative value expressed in percentages. The band gaps of the samples are obtained through Tauc plots, using the relation:

$$(\alpha h\nu)^n = A_0(h\nu - E_{bg}) \quad (3)$$

where A_0 is a constant that depends on the electron and hole mobilities of the material, h denotes the Planck's constant, ν is the frequency of the incident photon, and $h\nu$ is the light intensity; n can be either $1/2$ or 2 , for an indirect- or direct-band-gap semiconductor, respectively; TiO_2 was considered to exhibit a direct band gap.

3. Results and discussion

The electrochemical treatment is an efficient approach for a precise control of the deposition of elements onto the electrode [35]. As illustrated in Fig. 2(a), when an electrostatic field is applied between the TiO_2 NAs anode and Pt cathode with a proton-abundant environment, the protons are driven towards the TiO_2 electrode owing to the negative charge. As the electrostatic force at the bottom side of the NA is larger than that at the top side, the reduction gradually occurs from the bottom to the top of the NAs, as illustrated in Fig. 2(b). The pristine, heterojunction, and black TiO_2 are denoted as N0, N1, and N2, respectively. N3 is a state that corresponds to an excessive reduction, when the TiO_2 NAs are peeled off. The dependence of the current as a function of the time (I - t plot) is shown in Fig. 2(e). The negative current gradually decreases, reaching a steady state. The corresponding images of the samples are shown as insets in Fig. 2(e). The behavior of the curve is highly dependent on the morphology and thickness of the film. In this study, the thickness of the TiO_2 film is approximately $2 \mu\text{m}$, while the average diameter of the rods is approximately 150 nm (Fig. 2(c) and (d)). In the reduction curve, the decrease indicates the reduced resistance of the anode owing to the insertion of protons, which implies that the black TiO_2 exhibits a larger number of charge/donor carriers than the white TiO_2 , owing to the formation of $\text{TiO}_{3-x}(\text{OH})_x$ [35]. Therefore, the conductivity of the black TiO_2 is significantly improved, compared with that of the pristine white TiO_2 . The electron transport and migration at the bottom part of the TiO_2 NAs are increased, with respect to those of the pristine TiO_2 . The reduction cycle is complete for approximately 52 min,

Fig. 2. Illustrations of the insertion of protons in the metal oxide (a) and time dependence of the reduction of TiO_2 (b). Typical morphology (top (c) and cross-sectional (d) views) of the partially reduced TiO_2 NAs (sample N1). (e) Current as a function of the time, at a voltage of -0.5 V . The insets in (e) are images of the samples at the corresponding time moments.

longer than in previous studies, as the values of the proton concentration (0.05 mol/L H_2SO_4) and applied bias (−0.5 V) are relatively low [20,36], in order to achieve a controlled electrochemical process. In contrast, the pristine FTO does not exhibit reduction under the employed conditions, as shown in Fig. S1. Fig. 2(c) and (d) shows a top and cross-sectional views of N2, respectively. There are no considerable differences in morphology compared with N0 (Fig. S2). A bottom view of the peeled film at the state N3 is also obtained (Fig. S3), and it shows that the rectangular shape of the rods is well preserved. The aggregates observed around them could be attributed to the irregular initial nucleation owing to the hydrothermal approach. This phenomenon indicates that the peeling of the film is mainly caused by the proton attack at the fragile section between the rods and FTO substrate.

The optical properties of the samples are studied using UV DRS, as shown in Fig. 3(a). The corresponding band gaps are calculated using the Tauc plots (Fig. S4). The pristine TiO_2 NAs exhibit absorption up to 394 nm, which confirms that the band gap is approximately 3.15 eV. The absorption of N1 is extended up to 431 nm; therefore, its band gap is narrower, with a value of approximately 2.88 eV. At complete reduction, the band gap of N2 is approximately 2.85 eV, corresponding to a wavelength of approximately 435 nm, very similar to those of N1. The bandgap is mainly determined by the dominant absorption peak. The black color is mainly attributed to the band bending owing to the reduction [37]. Both valence and conduction bands are tailed from the original positions, which decreases the band gap [16]. The absorption wavelength extends up to 700 nm, as shown in Fig. 3(a). However, the absorption of N2 in the UV spectrum is slightly lower than those of N0 and N1.

The crystalline structures of the samples are studied using powder XRD, as shown in Fig. 3(b). The as-prepared NAs are annealed at 550 °C for 1 h to form a combined TiO_2 phase of anatase (JCPDS No. 21-1272) and rutile (JCPDS No. 21-01276). The relatively high peak at approximately 37° originates from both anatase and FTO substrate (SnO_2 : JCPDS No. 46-1088). Two small peaks at 20.78° and 22.87° can be observed for N2, which can be attributed to the formation of reduced TiO_2 , such as Ti_4O_7 and Ti_6O_{11} [26]. At these positions, in the XRD spectrum of N1, only a relatively high noise level can be

observed.

The band edges of the samples are obtained by electrochemical measurements using CV scans, as shown in Fig. 4; the experiments are conducted with TBAPF6 in anhydrous acetonitrile. As the reduced TiO_2 exhibits an activity for a reaction with TBAPF6 in the organic environment, the scan was performed in the range of −1.5 to 1.5 eV, in order to avoid a redox reaction with Ti(III) in the organic environment. The pristine TiO_2 is scanned from −2 to 2 eV, and exhibits a high chemical stability. Fig. 4(a) reveals that the conduction band edges of the pristine and completely reduced TiO_2 are located at −3.74 and −4.14 eV, respectively, with respect to the vacuum level. These values correspond to approximately 0.1 and −0.3 eV vs. RHE, at pH = 7, which is consistent with the values reported in the literature [35,38]. The CV scan of N1 is performed (Fig. 4(b)) in a smaller scan range of 0 to −1.5 eV, in order to minimize the effects of trivial redox reactions. Peaks are observed at −3.74 and −4.14 eV, which indicate the formation of the TiO_2 heterojunction. Three additional peaks can be observed, which emerge most likely owing to the high reactivity between the semi-reduced TiO_2 (interfacial region between the reduced and pristine TiO_2) and TBAPF6. Both phases of TiO_2 and reduced black phase are very stable, as shown in Fig. 4(a). However, in the crystal structure of the dual-phase TiO_2 , the interfacial layer could be a transient state from TiO_2 to black TiO_2 . In addition, this layer is likely to be highly unstable, and cannot be maintained owing to the highly reactive TBAPF6; this could be attributed to the appearance of the three additional peaks in Fig. 4(b).

The PEC performances of the samples are investigated, and the results are shown in Fig. 5. The light-off current density is negligible for N1, which indicates that the TiO_2 NAs heterojunction is inactive under ambient conditions, as the other samples. The pristine TiO_2 exhibits a photocurrent density of approximately 0.8 mA/cm^2 at 1.23 V (vs. RHE) under the irradiation of AM 1.5, using 1 mol/L NaOH solution as an electrolyte. The photocurrent density of N1 (2.5 mA/cm^2) is higher than that of N2 (2.1 mA/cm^2). The stability of the photoanode is similar to the reported performance with a moderate value [16]. N1 preserves approximately 70% of its efficiency after 35 min, as shown in Fig. S5.

Fig. 3. UV DRS spectra (a) and XRD patterns (b) of the electrochemically reduced TiO_2 photoanodes.

Fig. 4. CV scans of the photoelectrodes in a solution of TBAPF6 in anhydrous acetonitrile. (a) Results for N0 and N2, whose conduction band edges are located at -0.9 and -0.5 eV (vs. AgNO_3), respectively. (b) Results for N1, which exhibits peaks at -0.9 and -0.5 eV (vs. AgNO_3).

Fig. 5. PEC and electrochemical measurements of N0, N1, and N2. (a) PEC performances with and without light irradiation. (b) Dependence of the IPCE as a function of the wavelength. EIS measurements with a Nyquist plot, with (c) and without (d) light irradiation.

Furthermore, EIS is performed to characterize the interfacial reaction between the electrolyte and semiconductor surface. Nyquist plots of the three samples at 1.23 V (vs. RHE) with and without light irradiation are obtained, as shown in Fig. 5(c) and (d), respectively. The curve with a semicircle shape reveals the charge transfer between the solid semiconductor and liquid electrolyte, as the diameter of the semicircle is equal to the charge transfer resistance of the sample [39]. Among the samples, N1 exhibits the largest diameter of the semicircle under both light-on and -off conditions. It is worth noting that without the light irradiation, the semicircle's diameter of N1 is slightly larger than that of N2, which implies that the small

portion of the unreduced TiO_2 acts as a resistance for the interfacial charge transfer. In contrast, when the photoanodes are irradiated under the AM 1.5 irradiation, the semicircle's diameter of N1 is slightly smaller than that of N2, owing to the enhanced charge transport and separation by the formed heterojunction structure. The IPCE is also investigated to provide insights into the relation between the wavelength of the incident photons and capability for a catalytic redox reaction; the details of the calculations are presented in the experimental section. The obtained performances, shown in Fig. 5(b), are consistent with those reported in a previous study [40]. N0 exhibited a low absorption in the UV range and

Fig. 6. (a) Schematic of the *type II* heterojunction-structured TiO₂. (b) Illustration of the TiO₂ NAs during light absorption, where the UV and visible light are effectively absorbed at the top and bottom parts of the NAs for PEC water splitting, respectively.

relatively low conversion efficiency, compared with those of the other two samples. N1 and N2 exhibited very similar absorptions in the visible range. In the UV spectrum, at wavelengths in the range of approximately 330–360 nm, N1 exhibited a higher conversion efficiency than that of N2, which confirms that the white TiO₂ portion at the top of the rods enhances the absorption of UV light, leading to an enhanced PEC water splitting performance.

The band structure of N1 is illustrated in Fig. 6(a). The conduction band edge of the reduced TiO₂ is located at 0.4 eV (vs. RHE, pH = 0), while that of the pristine TiO₂ is located at 0.1 eV. The flat-band potentials of the samples are obtained from the EIS measurements through the Mott-Schottky plots at a frequency of 1 Hz (Fig. S6). The flat-band potentials of N0 and N2 are approximately 0.13 and 0.75 eV (vs. RHE). N1 exhibits almost the same curve as that of N2, which indicates that the TiO₂ heterojunction exhibits electrochemical properties as those of the reduced TiO₂ without irradiation. This demonstrates the formation of the *type II* heterojunction structure, which increases the PEC performance for water splitting. In addition, the donor densities of the pristine and reduced TiO₂ can be estimated from the results; it significantly increased from ~10¹⁵ to ~10¹⁷ [34] upon the reduction of TiO₂. Therefore, in this case, as shown in Fig. 6(b), high-energy charges and electrons emerge in the pristine TiO₂ upon the absorption of the incident UV light. The reduced TiO₂ could effectively harvest visible light. In addition to the formation of the *type II* heterojunction structure, the highly concentrated donor carriers facilitate the migration of the electrons, and reduce the probability for recombination. The high-energy electrons and charges injected from the pristine portion further facilitate the photocatalytic reaction towards the desired direction, promoting the oxygen and hydrogen evolutions.

4. Conclusions

Heterojunction-structured TiO₂ NAs were synthesized through a simple electrochemical approach. The obtained sample exhibited an increased PEC performance, with respect to those of pristine and reduced TiO₂, owing to a synergistic effect of light absorption, from the UV to the visible spectrum, and formation of the *type II* heterojunction structure for an effective

electron/charge separation and transport. This simple and highly controllable approach can be employed for various semiconductors, and exhibits large potentials for energy, environmental, sensor, and biology applications [41–47].

References

- [1] A. Fujishima, K. Honda, *Nature*, **1972**, 238, 37–38.
- [2] A. Wolcott, W. A. Smith, T. R. Kuykendall, Y. P. Zhao, J. Z. Zhang, *Small*, **2009**, 5, 104–111.
- [3] W. C. Lee, G. E. Canciani, B. O. S. Alwhshe, Q. Chen, *Int. J. Hydrogen Energy*, **2016**, 41, 123–131.
- [4] W. C. Lee, Y. X. Fang, D. Commandeur, R. Qian, Z. T. Y. Al-Abdullah, Q. Chen, *Nanotechnology*, **2017**, 28, 355402.
- [5] M. Forster, R. J. Potter, Y. C. Ling, Y. Yang, D. R. Klug, Y. Li, A. J. Cowan, *Chem. Sci.*, **2015**, 6, 4009–4016.
- [6] J. Yang, C. X. Bao, T. Yu, Y. F. Hu, W. J. Luo, W. D. Zhu, G. Fu, Z. S. Li, H. Gao, F. M. Li, Z. G. Zou, *ACS Appl. Mater. Interfaces*, **2015**, 7, 26482–26490.
- [7] T. W. Kim, K. Choi, *Science*, **2014**, 343, 990–994.
- [8] Y. Pihosh, I. Turkevych, K. Mawatari, T. Asai, T. Hisatomi, J. Uemura, M. Tosa, K. Shimamura, J. Kubota, K. Domen, T. Kitamori, *Small*, **2014**, 10, 3692–3699.
- [9] H. F. Zhang, W. W. Zhou, Y. P. Yang, C. W. Cheng, *Small*, **2017**, 13, 201603840.
- [10] Y. X. Fang, W. C. Lee, G. E. Canciani, T. C. Draper, Z. F. Al-Bawi, J. S. Bedi, C. C. Perry, Q. Chen, *Mater. Sci. Eng. B*, **2015**, 202, 39–45.
- [11] Z. A. Lan, Y. X. Fang, Y. F. Zhang, X. C. Wang, *Angew. Chem. Int. Ed.*, **2018**, 57, 470–474.
- [12] Y. X. Fang, X. C. Wang, *Angew. Chem. Int. Ed.*, **2017**, 56, 15506–15518.
- [13] Y. X. Fang, Y. W. Ma, M. F. Zheng, P. J. Yang, A. M. Asiri, X. C. Wang, *Coord. Chem. Rev.*, DOI: 10.1016/j.ccr.2017.09.013 (2017).
- [14] M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.*, **1995**, 95, 69–96.
- [15] X. F. Chen, X. C. Wang, X. Z. Fu, *Energy Environ. Sci.*, **2009**, 2, 872–877.
- [16] X. B. Chen, L. Liu, F. Q. Huang, *Chem. Soc. Rev.*, **2015**, 44, 1861–1885.
- [17] Z. Wang, C. Y. Yang, T. Q. Lin, H. Yin, P. Chen, D. Y. Wan, F. F. Xu, F. Q. Huang, J. H. Lin, X. M. Xie, M. H. Jiang, *Adv. Funct. Mater.*, **2013**, 23, 5444–5450.
- [18] F. Fabregat-Santiago, E. M. Barea, J. Bisquert, G. K. Mor, K. Shankar, C. A. Grimes, *J. Am. Chem. Soc.*, **2008**, 130, 11312–11316.
- [19] H. Li, Z. H. Chen, C. K. Tsang, Z. Li, X. Ran, C. K. Lee, B. Nie, L. X.

Graphical Abstract

Chin. J. Catal., 2018, 39: 438–445 doi: 10.1016/S1872-2067(18)63037-2

Efficient development of Type-II TiO₂ heterojunction using electrochemical approach for an enhanced photoelectrochemical water splitting performance

Yuanxing Fang, Yiwen Ma, Xinchun Wang *
Fuzhou University

Type II heterojunction structure

Type-II-heterojunction TiO₂ nanorod arrays exhibit an enhanced photoelectrochemical water splitting performance, achieved through a simple electrochemical reduction. The prepared photoanode presents enhanced photo efficiency with respect to the pristine and completely reduced TiO₂.

- Zheng, T. Hung, J. Lu, B. C. Pan, Y. Y. Li, *J. Mater. Chem. A*, **2013**, 2, 229–236.
- [20] G. M. Wang, Y. Yang, Y. C. Ling, H. Y. Wang, X. H. Lu, Y. C. Pu, J. Z. Zhang, Y. X. Tong, Y. Li, *J. Mater. Chem. A*, **2016**, 4, 2849–2855.
- [21] Z. H. Zhang, M. N. Hedhili, H. B. Zhu, P. Wang, *Phys. Chem. Chem. Phys.*, **2013**, 15, 15637–15644.
- [22] J. W. Yun, K. Y. Ryu, T. K. Nguyen, F. Ullah, Y. C. Park, Y. S. Kim, *RSC Adv.*, **2017**, 7, 6202–6208.
- [23] X. Q. An, T. Li, B. Wen, J. W. Tang, Z. Y. Hu, L. M. Liu, J. H. Qu, C. P. Huang, H. J. Liu, *Adv. Energy Mater.*, **2016**, 6, 201502268.
- [24] L. Yan, W. Zhao, Z. F. Liu, *Dalton Trans.*, **2016**, 45, 11346–11352.
- [25] M. Wang, M. Pyeon, Y. Gonullu, A. Kaouk, S. H. Shen, L. J. Guo, S. Mathur, *Nanoscale*, **2015**, 7, 10094–10100.
- [26] S. Choudhary, S. Upadhyay, P. Kumar, N. Singh, V. R. Satsangi, R. Shrivastav, S. Dass, *Int. J. Hydrogen Energy*, **2012**, 37, 18713–18730.
- [27] X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.*, **2009**, 8, 76–80.
- [28] M. W. Zhang, Z. S. Luo, M. Zhou, G. G. Zhang, K. A. Alamry, L. A. Taib, A. M. Asiri, X. C. Wang, *Appl. Catal. B*, **2017**, 210, 454–461.
- [29] M. W. Zhang, X. C. Wang, *Energy Environ. Sci.*, **2014**, 7, 1902–1906.
- [30] P. J. Yang, J. H. Zhao, W. Qiao, L. Li, Z. P. Zhu, *Nanoscale*, **2015**, 7, 18887–18890.
- [31] R. Asahi, T. Morikawa, H. Irie, T. Ohwaki, *Chem. Rev.*, **2014**, 114, 9824–9852.
- [32] H. Meixner, U. Lampe, *Sens. Actuators B*, **1996**, 33, 198–202.
- [33] X. Y. Yang, A. Wolcott, G. M. Wang, A. Sobo, R. C. Fitzmorris, F. Qian, J. Z. Zhang, Y. Li, *Nano Lett.*, **2009**, 9, 2331–2336.
- [34] M. C. K. Sellers, E. G. Seebauer, *Thin Solid Films*, **2011**, 519, 2103–2110.
- [35] J. M. Jimenez, G. R. Bourret, T. Berger, K. P. McKenna, *J. Am. Chem. Soc.*, **2016**, 138, 15956.
- [36] T. Berger, T. Lana-Villarreal, D. Monllor-Satoca, R. Gómez, *Electrochem. Commun.*, **2006**, 8, 1713–1718.
- [37] J. W. Yun, K. Y. Ryu, T. K. Nguyen, F. Ullah, Y. C. Park, Y. S. Kim, *RSC Adv.*, **2017**, 7, 6202–6208.
- [38] Y. Zhou, M. Y. Leng, Z. Xia, J. Zhong, H. B. Song, X. S. Liu, B. Yang, J. P. Zhang, J. Chen, K. H. Zhou, J. B. Han, Y. B. Chen, J. Tang, *Adv. Energy Mater.*, **2014**, 4, 1301846.
- [39] T. Lopes, L. Andrade, H. Ribeiro, A. Mendes, *Int. J. Hydrogen Energy*, **2010**, 35, 11601–11608.
- [40] Q. Kang, J. Y. Cao, Y. J. Zhang, L. Q. Liu, H. Xu, J. H. Ye, *J. Mater. Chem. A*, **2013**, 1, 5766–5774.
- [41] H. H. Ou, L. H. Lin, Y. Zheng, P. J. Yang, Y. X. Fang, X. C. Wang, *Adv. Mater.*, **2017**, 56, 10905–10910.
- [42] J. N. Qin, S. B. Wang, H. Ren, Y. D. Hou, X. C. Wang, *Appl. Catal. B*, **2015**, 179, 1–8.
- [43] W. C. Lee, Y. X. Fang, J. F. C. Turner, J. S. Bedi, C. C. Perry, H. Y. He, R. Qian, Q. Chen, *Sens. Actuators B*, **2016**, 237, 724–732.
- [44] M. I. Setyawati, C. Y. Tay, D. T. Leong, *Small*, **2015**, 11, 3458–3468.
- [45] Y. Lei, H. M. Jia, W. W. He, Y. C. Zhang, L. W. Mi, H. W. Hou, G. S. Zhu, Z. Zheng, *J. Am. Chem. Soc.*, **2012**, 134, 17392–17395.
- [46] T. Wang, W. W. Li, D. D. Xu, X. M. Wu, L. W. Cao, J. X. Meng, *Chin. J. Catal.*, **2017**, 38, 1184–1195.
- [47] S. Toston, R. Camarillo, F. Martinez, C. Jimenez, J. Rincon, *Chin. J. Catal.*, **2017**, 38, 636–650.

电化学制备异质二氧化钛结构增强其在光电分解水中转化效率

方元行, 马一文, 王心晨*

福州大学化学学院能源与环境光催化国家重点实验室, 福建福州350002

摘要: 本文描述了一种利用电化学方法合成第二型异质二氧化钛纳米棒结构的方法, 这种纳米棒由部分还原的黑色二氧化钛和原始的白色二氧化钛组成. 这种异质结构的半还原的二氧化钛纳米棒与原始的白色二氧化钛和完全还原的黑色二氧化钛纳米棒相比, 展现出更好的光电催化性能. 这可归结于这种条件下合成的纳米棒具备的协同作用. 一方面, 这类结构增强了整个太阳光光谱的利用率. 底层的黑色二氧化钛能够大量吸收可见光, 而上层的白色二氧化钛能够较好的利用太阳光中紫外光的部分. 另一方面, 因为形成了第二型异质结构, 电荷的激发分离和传输得到了有效的控制. 这种简单的制备方法可进一步拓展合成其他金属氧化物, 来进一步研究光电分解水的性能.

本文利用传统的三电极系统: 0.05 mol/L的硫酸作为电解液, 在加-0.5 V的偏压下进行. 相比与已报道的还原手段, 该电解液中质子的浓度相对较低, 可以保证这个还原过程逐步发生. 电化学还原曲线可以明显反映二氧化钛还原的过程, 尽管从扫描电子显微镜中很难观察到响应的区别, 但是在该过程中, 电极片的颜色发生了明显的变化. 相应的, 我们将这个系列的电极进行了光学和晶体学的研究, 发现其在还原过程中, 能带能够逐步减小. 而在X射线衍射测试当中, 仅最终完全还原的得到的样品在20度左右出现两个额外的峰, 可归结为还原状态的二氧化钛. 电化学扫描进一步测试其能带的相应位置, 证明了黑色被还原的二氧化钛和白色的原始二氧化钛是同时存在的.

最后将这个系列光电催化分解水的性能进行了比较, 发现在同等的测试条件下, 形成异质结构的二氧化钛具有最高的光催化效率, 其值大约是白色二氧化钛的三倍, 同时也比纯黑的二氧化钛增长了20%左右. 另外, 异质结构的二氧化钛与黑色的相比, 在可见光区域有相同的效率的同时具备更好的紫外光转化效率. 最后, 我们分析了异质结形成以后的相对应的能带结构, 该结构能够更好的促进光吸收和转化.

关键词: 第二型异质结构; 光电催化水分解; 二氧化钛; 电化学还原; 改性

收稿日期: 2017-12-26. 接受日期: 2018-01-12. 出版日期: 2018-03-05.

*通讯联系人. 电话/传真: (0591)83920097; 电子信箱: xcwang@fzu.edu.cn

基金来源: 国家自然科学基金(21425309, 21761132002, 21703040); 中国博士后科学基金(2017M622051); 高等学校学科创新引智计划.

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