Journal of Electrochemistry

Volume 15 | Issue 4

2009-11-28

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Xiao-jun LV

Yue-ming LI

Hao ZHANG

Da CHEN

Hensel Jennifer

Z Zhang Jin

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Recommended Citation

Xiao-jun LV, Yue-ming LI, Hao ZHANG, Da CHEN, Hensel Jennifer, Z Zhang Jin, Jing-hong LI. Enhanced Visible Light Photoelectrochemical Performances with Nitrogen Doped TiO_2 Nanowire Arrays[J]. *Journal of Electrochemistry*, 2009 , 15(4): 432-440. DOI: 10.61558/2993-074X.2020 Available at: https://jelectrochem.xmu.edu.cn/journal/vol15/iss4/12

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Artical D: 1006-3471 (2009) 04-0432-09

Enhanced Visible L ight Photoelectrochem ical Performances with Nitrogen Doped TiO₂ Nanowire Arrays

LV Xiao-jun¹, LI Yue-ming¹, ZHANG Hao¹, CHEN Da¹,

Jennifer Hensel², Jin Z Zhang^{2*}, L I Jing-hong^{1*}

(1. Department of Chenistry, Tsinghua University, Beijing 100084, China;

2 Department of Chenistry and Biochenistry, University of California, Santa Cruz, California 95064, USA)

Abstract: Self-organized anodic anatase TD₂ nanow ire arrays doped with nitrogen have been successfully fabricated and their photoelectrochemical (PEC) properties have been characterized and found to be substantially improved compared to undoped nanow ires or commercial P25 nanoparticles Photocurrent measured with monochromatic incident light showed that the incident photon-to-current efficiency (IPCE, %) values of nanow ire array electrodes with or without N-doping were obviously higher than that of commercial P25 nanoparticle electrodes, and nitrogen-doped TD₂ nanow ire arrays (NTNA) had noticeable absorption in the visible region. The NTNA electrodes showed the highest photocurrent density and power conversion efficiency under 100 mW/cm² visible light illumination. A maximumolphotoconversion efficiency of 0.52% was achieved for the NTNA sample at an applied potential of 0.09 V versus Ag/AgC1 (saturated KC1) electrode under visible illumination, much higher than that of the undoped nanow ire and commercial P25 nanoparticle electrodes. These results demonstrate that NTNA thin films are promising for enhancing the photoresponse and effectively improving PEC performances of nanostructured TD₂ in the visible region for different applications including solar hydrogen generation.

Key words: nitrogen doped; TO_2 nanowire arrays; visible light; photoelectrochemical performances; photocatalysis

CLC Number: TB383

Document Code: A

 TO_2 as a wide bandgap n-type metal oxide sem iconductor has been extensively investigated for water splitting due to its good stability, nontoxicity, low cost, and high catalytic activity ^[1-3]. Recently, there have been extensive studies on nanostructured TO_2 , such as noanotubes, nanowires and nanorods, as the electron transport materials due to their unique physical properties and wide range of applications ^[4-6]. Compared to nanoparticles, one dimensional (1D) nanostructures such as nanowires and nanorods have better charge transport properties while, in the meantime, they have larger surface area in comparison to bulk or two dimensional (2D) nanostructures Thus, TD₂ nanowires and nanorods are considered as highly desired structures for both photovoltaic and photoelectrochemical applications Different strategies have

Received date: 2009-06-17, Accepted date: 2009-06-17 * Corresponding author, Tel: (86-10) 62795290, E-mail: jhli@mail tsinghua edu cn Supported by the National Natural Science Foundation of China (No 20628303) and 863 Project (2006AA05Z123)

been developed for synthesizing TO_2 nanowires and nanorods, including sol-gel^[7], chemical vapor deposition (CVD)^[8], solvothermal method^[9], anodization^[10] and glancing angle deposition (GLAD)^[11]. Among these strategies, electrochemical anodization is relatively simple and provides a facile and direct approach for producing TO_2 nanowires with high surface area and long wire length^[10].

Despite the promising properties of TiO_2 nanowires mentioned above, the wide bandgap of TO_2 (3. 0 eV for rutile and 3. 2 eV for anatase) limits its photoresponse mainly to the UV region, which accounts for only $\sim 5\%$ of solar spectrum lenergy. Much effort has been made to narrow the effective bandgap of TD_2 while maintaining its superior charge transfer and transport properties and photocorrosion stability. It has been shown that nitroge-doping (Ndoping) is an effective method to narrow the bandgap of anatase TO_2 and thereby increase the visible light absorption ^[12-14]. For example, N-doping of TO_2 nanotubes has been demonstrated using pure $NH_3^{[15]}$. TO_2 nanowire arrays (TNA), especially when doped with N, are considered as promising for photoelectrochemical applications because of the combination of expected enhanced visible absorption and better charge transport along long nano wire. However, to date the study of TNA or N-doped TO₂ nanowire arrays (NTNA) has been very limited.

In the present work, N-doped self-organized anodic TiO_2 nanow ire arrays (NTNA) have been fabricated using a simple electrochemical approach Optical and photoelectrochemical studies have shown that the NTNA electrodes had substantially enhanced visible light photoresponse and improved photoconversion efficiency compared to TNA and nanoparticle electrodes These improved properties are expected to be useful in applications including solar energy conversion, water splitting for hydrogen generation, as well as photoelectrochemical degradation of pollutants

1 Experimental Section

1. 1 Preparation of TO_2 N anowire A rrays

 TO_2 nanowire arrays (TNA) were prepared by a

modified method developed by Choi et al ¹¹⁰¹. Typically, the polished Ti foil (0. 25 mmolthick, 99. 38% purity, fromol Beijing General Research Institute for Nonferrous Metals) was pretreated by rinsing in an ultrasonic bath of acetone, alcohol and deionized water for 5 min in turn, then chemically etched by immersing in a mixture solution of HF, HNO₃ and H₂O acids in the ratio of 1 4 5 (by Vol) for 30 s, rinsed in an ultrasonic bath of acetone, isopropanol and methyl alcohol for 5 min in turn, and finally rinsed in deionized water At the end, the obtained substrate was dried with N₂ at roomoltemperature.

The anodization process was carried out at roomoltemperature using a direct current power supply (Dahua Wireless Instrument Co., Beijing) in a twoelectrode electrolytic cell, with the pretreated Ti foil serving as the anode and Pt foil serving as the cathode The anodizing voltage increased gradually fromol 0 to 50 V with an increasing rate of 100 mV/s and was then kept at 50 V for 10 h The electrolyte was 15 mL of ethylene glycol (EG) solution containing $NH_4 F$ (0. 25%, by mass) and 500 µL deionized water Generally, a small amount of water in the EG solution is essential for the formation of anodic TO_2 nanowires at a high potential After the anodization, the obtained substrate was immediately rinsed with deionized water and dried with a N₂ stream. Then, the anodized substrate was annealed at 450 in oxy- $\cdot \min^{-1}$ to gen for 3 h with the cooling rate of 2 convert the amorphous phase to the anatase crystalline phase

The process of introducing the nitrogen dopant was carried out in a tube furnace The obtained TiO_2 nanowires were immersed in 0. 5 mol $\cdot L^{-1}$ hexamethylenete tramine (HMT) solution for two days Subsequently, the specimens were put in quartz tube, and the dopant was carried out by tube furnace at 400 for 1 h where N₂ acted as the carrier gas After heating, the sample remained in the furnace until naturally cooling down to roomoltemperature.

1. 2 Characterization

Powder X-ray diffraction (XRD) was performed

on a Bruker D8-Advance X-ray powder diffractometer with monochromatized K radiation (= 0. 15406 nm). The 2 range used in the measurements was from 20° to 80°. X-ray photoelectron spectroscopy (XPS) studies of the films were carried out on an Xray photoelectron spectrometer (PHIOuantera SXM) using a non-monochromatized A1 K X-ray source (1486. 6 eV). The energy resolution of the spectrometer was set at 0. 5 eV, and the binding energy was calibrated using a C 1s (284. 6 eV) spectrum of a hydrocarbon that remained in the XPS analysis chamber as a contaminant SEM images were acquired on a field emission (FE) scanning electron microscope (JEOL JSM-7401F) operated at 3. 0 kV. Mott-Schottky (MS) spectra were measured with a three-electrode cell, using the TO₂ -based samples as the working electrode, a platinumolwire as the counter electrode, and a standard Ag/AgCl in saturated KCl as the reference electrode. The electrolyte was 0. 1 mol $\cdot L^{-1}$ KNO₃ aqueous solution Mott-Schottky (MS) spectra were obtained with a PARSTAT-2273 Advanced Electrochemical Systemol (Princeton Applied Research) controlled by a computer

1. 3 Photoelectrochemical Measurements

Photocurrent action spectra were measured in a two-electrode configuration, home-built experimental system, where the sintered TO_2 photoanode served as the working electrode with an active area of about 1 cm^2 defined using Teflon tape and a platinum like was used as the counter electrode. The generated photocurrent signal was collected by using a lock-in amplifier (Stanford Instrument SR830 DSP) synchronized with a light chopper (Stanford Instrument SR540). Photocurrent density vs bias potential characteristic was conducted with a three-electrode cell, using the sintered photoanode as the working electrode, a platinum lwire as the counter electrode, and a standard Ag/AgCl in saturated KCl as the reference electrode Photocurrent density vs bias potential characteristic spectra was obtained with a PARSTAT-2273 Advanced Electrochemical Systemol (Princeton Applied Research) controlled by a computer A 500 W Xe lamp with a monochromator and equipped with

AMOL 1. 5 filter (filter off lights with wavelength shorter than 400 nm for 100 mW/cm² visible light measurements) respectively, was used as the light source. The electrolyte was 0. 1 mol \cdot L⁻¹ KNO₃ aqueous solution All measurements were carried out after bubbling N₂ for 20 m in and controlled automatically by a computer

2 Results and Discussion

2 1 Structural Properties of N itrogen Doped TiO₂ N anow ire A rrays

Figure 1 shows typical FESEM images of the morphologies of TNA and NTNA. As shown in Figure 1a, the TO_2 nanowires were more than 10 μ m in length and 60 nm in diameter, and there remained the TO₂ nanotubes with a diameter of about 100 nm undemeath the nanowires Figures 1b and c show different magnifications of TNA. Figure 1d shows that, after nitrogen doping, the morphologies of TNA did not indicating that the N-doping obviously change, process had little effect on the nanostructures of the as-prepared TNA. The morphologies of the TNA at low magnification were just like blooming flowers (Figures 1b and 1c), which seemed to follow the bamboo-splitting nanowire formation model^[10], i.e., highly organized TO₂ nanotubes firstly formed in Ti foil at the beginning of the anodization, and the nanotubes were then vertically split off into several parts by the electric-field-directed etching The splitting led to the formation of NTNA on the entire TiO_2 nanotube arrays

Figure 2 shows the XRD patterns of fabricated TNA, NTNA and Ti foil According to the XRD results, the diffraction peaks of Ti foil could be indexed into hexagonal phase (**CDD-JCPDS** No. 44-1294). The diffraction peaks of TNA shown in curve b in Figure 2 could be indexed into anatase phase (**CDD-JCPDS** No. 21-1272). As shown in curve c in Figure 2, the peaks of N-doped TNA showed no obvious change compared with those of TNA, which means the N-doping process did not change the phase of TNA.

The N - bonding information and the effect of

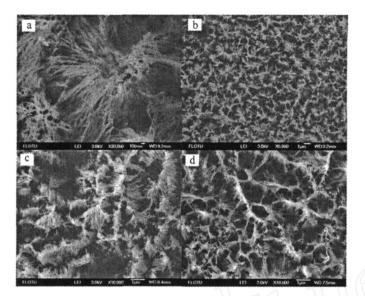


Fig 1 FE-SEM images of (a), (b) and (c) different magnified TO₂ nanowire arrays, (d) N-doped TO₂ nanowire arrays

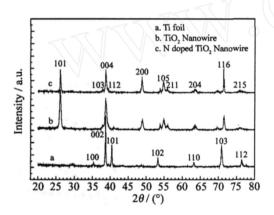


Fig 2 XRD patterns of (a) Ti foil, (b) TO_2 nanowires and (c) N doped TO_2 nanowires

nitrogen doping on the optical properties of NTNA were identified by the XPS technique From Figure 3a, it can be seen that the NTNA contained Ti, O, N and C, and the binding energies of Ti 2p, O 1s, C 1s, and N 1s were 459. 7 eV, 530. 2 eV, 400. 2 eV and 284. 9 eV, respectively. Figure 3b shows the XPS spectra of only the nitrogen binding energies from 396 eV to 412 eV with three peaks at 398. 7 eV, 400. 2 eV and 405 eV, respectively. The XPS spectra of Ti $2p_{3/2}$ and O 1s peaks are shown in Figure 3c, which verified the substitution of N for O in TiO₂ crystals^[16].

As Figure 3b shows, the peak at 400. 2 eV corresponds to molecularly chemisorbed nitrogen $(-N_2)$

at the surface^[14,17] or N atoms from N—N, N—H, O—N or N-containing organic compound absorbed on the surface ^[13]. It has been reported that the N 1s features appearing above 400 eV is due to Ti—O—N linkage ^[18], suggesting that some nitrogen atoms were doped in the interstitial sites of TNA lattices In addition, the intense peak at 405. 3 eV could be originated from nitrite ions ^[19], and the peak at 398. 7 eV was assigned to nitrogen atoms which substituted for O and doped into the crystal lattices of nanowires to form the Ti-N bonds ^[20-21].

As for the Ti $2p_{3/2}$, a peak is located at 458. 9 eV for NTNA (Figure 3c), which was significantly bwer than that of P25 TD_2 powders (459. 7 eV)^[22] and T O_2 nanowires (459. 3 eV) ^[17], also indicating the nitrogen incorporation into the TNA. And the Ti $2p_{1/2}$ at 463. 5 eV peak was characteristic of the Ti^N oxidation state^[17]. The lower binding energy of Ti $2p_{3/2}$ in the NTNA showed that the electronic interaction of Ti with anions was significantly different from that of TO_2 nanoparticles and nanowires, where the interaction was between Ti and O rather than N. It is known that the lower electron negativity of nitrogen compared with that of oxygen resulted in a decrease in percent ionicity and electron density around the N anion, causing the increase of the Ti electron density^[22].

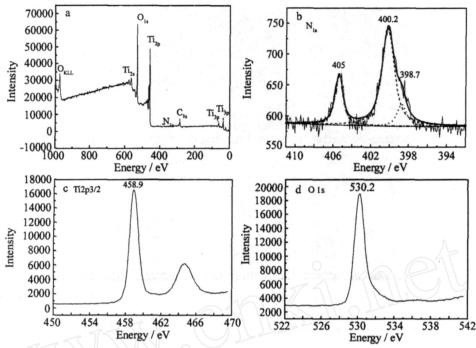


Fig 3 XPS spectra of N-doped TO₂ nanowires a elemental survey, b N 1s, c Ti 2p_{3/2}, d O 1s

The O 1s peak appeared at around 530 2 eV corresponding to Ti—O in Figure 3d, which was similar to that for the TO₂ nanowires^[17], indicating that there was no discernible change in the chemical environment for oxygen In addition, broadening on the higher bonding energy band for N-TO₂ at 531. 4 eV could be found The appearance of this additional peak was attributed to the nitridation process This feature was previously assigned to the presence of another kind of oxygen in N-TO₂^[22]. On the basis of the above results and analysis, XPS results indicate that N doping into the crystal mainly results in Ti—N or N—Ti—O bonding

2. 2 Mott-Schottky (MS) Studies

Figure 4 shows Mott-Schottky (MS) measurement results, which were used to determ ine the difference in electronic properties of the TNA electrodes with or without N-dop ing^[23-24]. As is clear from Figure 4, reversed signoidal plots were observed with an overall shape consistent with that typical for n-type semiconductors; And the reproducible flat-band potentials could be obtained from the intercepts of the linear region^[25]. TNA electrodes showed a large

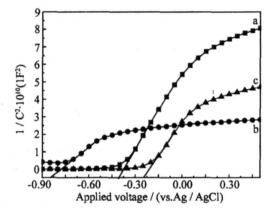


Fig 4 Mott-Schottky plots of for P25 nanoparticle films (a), TO₂ nanowires (b) and N-doped nanowires (c) electrodes Mott-Schottky measurements were done at the frequency of 1 kHz in the aqueous solution of 0 1 mol
L⁻¹ KNO₃, pH 7. 5

positive shift of the conduction band as compared with the P25 nanoparticle electrodes, and NTNA had more positive flat-band potential than TNA electrodes

It is well known that the presence of a large number of surface states can lead to a considerable change of the band position^[26]. In most cases, a large number of surface states or oxygen vacancies are present in the P25 TO₂ nanoparticles, whereas TO₂

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nanowire structures have a lower density of surface states or oxygen vacancies that can lead to a change of the band position Furthermore, in the case of NT-NA, N atoms could substitute for some oxygen vacancies and reduce the recombination centers of charge carriers, leading to the much higher photocurrent density observed in comparison to the P25 nanoparticles Mott-Schottky results show that the NTNA electrodes have lower density of surface states and thereby improve charge transport properties, which are useful for enhancing photocurrent density.

2. 3 Photoelectrochemical

Characterization

Photocurrent measurements with monochromatic incident light of P25 TO_2 nanoparticles and TNA with and without N-doping were performed without bias in a two-electrode configuration The illumination area of the photoanode was about 0. 12 cm². The incident photon-to-current efficiency (IPCE) was calculated using the following equation ^[3]:

 $\mathbb{P}CE/\% =$

$$\frac{(1240 \text{eV} \cdot \text{nm}) (\text{photocurrent density } \mu\text{A/cm}^2)}{(\text{ nm}) (\text{irradiance } \mu\text{W/cm}^2)}$$
×100 (1)

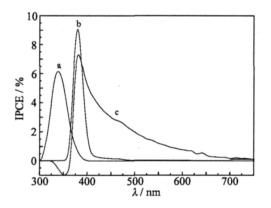


Fig 5 Incident photon-to-current efficiency (IPCE) spectra with monochromatic light at different wavelengths of P25 nanoparticles (a), TD₂ nanowires (b) and N-doped TD₂ nanowires (c) as photoanodes in 0. 1 mol
 ·L⁻¹ KNO₃ solution under Xe lamp irradiation

As shown in Figure 5, the maximum IPCE (%) values of NTNA and TNA electrodes reached 7. 2%

and 9% at 380 nm, respectively, obviously higher than 4% measured for P25 TO₂ thin film electrodes at 340 nm. The NTNA electrodes also showed noticeably higher photocurrent in the visible region, extending all the way to about 675 nm. In contrast, the undoped TNA and TO₂ nanoparticles exhibited little or no photoresponse in the visible region NTNA and TNA electrodes showed an apparent photocurrent maximumolat about 380 nm, while the P25 TiO₂ layer electrodes showed a photocurrent maximum at about 340 nm. The positions of the photocurrent maximum are likely related to bandgap as well as the effective light absorption and scattering of the nanostructure films The bandgap of anatase TiO₂ is at 387 nm or 3. 2 eV^[14].

The higher IPCE (%) values of NTNA and TNA than P25 TiO₂ nanoparticle electrodes could be attributed to the different space charge layer within the wire wall^[27]. Compared to random structures, the ordered nanowire array structures could also allow for reduced scattering and enhanced photoabsorption^[28], similar to photonic crystals or gratings In addition, the higher crystallinity of TD₂ nanowires could also enable more efficient electron injection and transport within the array electrodes, leading to longer electron lifetime and diffusion length in TD₂ nanowires compared to nanoparticles^[29]. It is clear that N doping is an ef-</sup> fective way to improve the visible absorption of anatase TD_2 by decreasing the effective TD_2 bandgap with N-T iO_2 as a result of either mixing O2p states with its 2p states^[3] or creating isolated N2p states above the valence band maximumolof $TO_2^{[30-31]}$. And nitrogen doping into TD₂ substituted oxygen and decreased the surface oxygen concentration in TO₂ crystalline structure leading to lower maximum peak of **IPCE** of NTNA than that of TNA.

Figure 6 shows that the photocurrent density as a function of applied potentials for the NTNA, TNA and P25 electrodes in 0. 1 mol \cdot L⁻¹ KNO₃ solution under 100 mW/cm² visible light irradiation. The dark current density was found to be negligible, and the photocurrent density of nanoparticle electrodes was very low in the visible. However, the photocurrent densit

ties of the NTNA and TNA electrodes were much higher in the visible; and, furthermore, the photocurrent density of the NTNA electrodes was about three times as much as that of the TNA electrodes Considering the results in Figure 4, this result is consistent with the expectation of enhanced photocurrent density for the NTNA electrodes

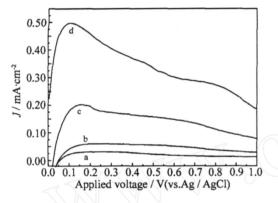


Fig 6 Variation of photocurrent density vs bias potential for P25 nanoparticle films(b), TO₂ nanowires(c) and N-doped TO₂ nanowires(d) in 0. 1 mol · L⁻¹ KNO₃ solution under visible light illum ination

The photoconversion efficiency of light energy to chemical energy in the presence of an external applied potential could be calculated according to the following equation^[32]:

(%) =

(total power output - electrical power output) light power input

$$\times 100 = j_{p} \frac{(E_{rev}^{p} - |E_{app}|)}{l_{0}} \times 100$$
 (2)

where i_{b} is the photocurrent density (mA/cm^2) , i_{b} (E_{rev}^0) is the total power output, $i_{b} | E_{app} |$ is the electrical power input, and I_{b} is the power density of the incident light (mW/cm^2) . E_{rev}^0 is the standard reversible potential (which is 1. 23 V for the water-splitting reaction), and $|E_{app}|$ is the absolute value of the applied potential E_{app} , which is obtained as

$$E_{\rm app} = (E_{\rm meas} - E_{\rm ocp}) \tag{3}$$

where E_{meas} is the electrode potential of the working electrode at which j_i is measured under 100 mW /cm² visible light illumination, and E_{ocp} is the applied potential at open circuit under the same illumination at which j_i is measured in the same electrolyte solution E_{meas} and E_{ocp} are with respect to the same Ag/AgCl (saturated KCl) reference electrode.

Figure 7 shows that the photoconversion efficiency as a function of applied potential for the different photoanodes studied According to Eq. 2, a maximumolphotoconversion efficiency of 0. 52% was obtained for the NTNA electrodes at an applied potential of 0. 09 V versus Ag/AgC1 (saturated KC1) electrode under $100 \text{ mW} / \text{cm}^2$ visible light illumination However, under the same condition, a maximum photoconversion efficiency of 0. 2% was observed for the TNA electrodes at an applied potential of 0. 15 V, and a maximum photoconversion efficiency of 0. 05% was achieved for the P25 nanoparticles at an applied potential of 0. 17 V. The results clearly indicate that the NTNA electrodes could harvest visible light more effectively than the TNA electrodes and P25 nanoparticle electrodes under the same irradiation The efficiency for NTNA in the visible compares favorably well with obviously reported efficiency of 0. 27% for TiO_2 nanotubes doped with boron^[4].

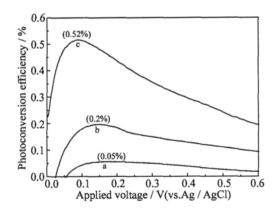


Fig 7 Photoconversion efficiency as a function of applied potential in 0.1 mol·L⁻¹ KNO₃ solution for P25 nanoparticle (a), TD₂ nanowire (b) and N-doped TD₂ nanowire (c) electrodes under visible light illumination

3 Conclusions

In summary, self-organized anodic anatase TD₂ nanowire arrays doped with nitrogen have been successfully fabricated and systematically investigated

using a combination of FESEM, XRD, XPS, Mott-Schottky and photoelectrochemistry techniques The structure of NTNA has been found to be in anatase phase. Nitrogen doping into the TiO₂ lattice results in a red-shift of absorption and enhanced photocurrent response in visible region relative to undoped TiO_2 films Photocurrent measured with monochromatic incident light showed the IPCE (%) values of NTNA electrodes were obviously higher than that of commercial P25 nanoparticle electrodes Furthermore, NTNA electrodes displayed a clear increase in its saturated photocurrent density under 100 mW /cm² visible light illumination than the undoped electrodes A maximum photoconversion efficiency of 0. 52% for NTNA electrodes was obtained, which was much higher than that on TNA and commercial P25 nanoparticle electrodes The results suggest that N-doped TO_2 nanowire arrays have good prospect for solar energy and other applications due to their inproved optical and photoelectrochemical performances

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氮掺杂 TiO₂纳米线阵列优越的可见光光电性能

吕小军¹, 李悦明¹, 张 吴¹, 陈 达¹, Jennifer Hensel², 张金中^{2*}, 李景虹^{1*}

(1.清华大学化学系,北京 100084; 2.美国加利福尼亚大学 Santa Cruz分校化学与生物化学系,美国 加利福尼亚)

摘要: 成功制备了氮掺杂锐钛矿 TD₂纳米线,并研究了它的光电化学性质.结果表明,与商用 P25 TD₂纳 米粒子和未掺杂 TD₂纳米线相比,氮掺杂 TD₂纳米线作为光阳极明显地提高了光电转换效率(IPCE%),在 可见光区有明显光吸收;在 100 mW /cm²可见光光照下,氮掺杂 TD₂纳米线具有最大的光电流密度和能量转 换效率.例如,当电压为 0 09 V (vs Ag/AgCl)时最大能量转换效率为 0 52%,均高于未掺杂 TD₂纳米线和 商用 P25 TD₂纳米粒子的,充分表现出它优越的光响应和光电化学性能,在光电化学池、太阳能制氢等方面 具有广泛的应用前景.

关键词: 氮掺杂; TD_2 纳米线阵列; 可见光吸收; 光电化学; 光催化