available at www.sciencedirect.com

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

Article (Special Issue on Photocatalysis)

Design and construction of a film of mesoporous single-crystal rutile TiO₂ rod arrays for photoelectrochemical water oxidation

Chao Zhen ^a, Tingting Wu ^a, Mohammad W. Kadi ^{b,#}, Iqbal Ismail ^b, Gang Liu ^{a,*}, Hui-Ming Cheng ^{a,b}^a Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, Liaoning, China^b Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

ARTICLE INFO

Article history:

Received 29 August 2015

Accepted 20 September 2015

Published 20 December 2015

Keywords:

Titania

Photoanode

Mesopore

Single crystal

Rod array

ABSTRACT

A film of mesoporous single-crystal rutile TiO₂ rod arrays supported on a transparent conductive glass substrate was synthesized with the assistance of a template layer of closely packed silica nanospheres. This film was used as a photoanode and showed significant improvement for photoelectrochemical water oxidation compared with a reference film of nonporous single-crystal rutile TiO₂ rod arrays.

© 2015, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Constructing highly efficient semiconductor photoelectrodes for desirable photoelectrochemical (PEC) conversion systems, such as PEC water-splitting cells and dye (or quantum dots) sensitized solar cells, has attracted tremendous attention owing to their great potential for using the abundance of solar energy [1–4]. The mesoporous structure, with the advantages of a short charge carrier diffusion length and large surface area, has been actively pursued in the development of photoelectrodes [5–19]. A typical example is the mesoporous polycrystalline films of TiO₂ nanoparticles, which show the improved performance as photoanodes in both PEC water-splitting cells and sensitized solar cells [14–20]. However, the boundaries between TiO₂ nanoparticles in the films, where photo-generated charge carriers suffer from strong scattering and recombination processes induced by lattice distortions, may impair the efficiency of collecting charge carriers [21]. Mesoporous single crystals of anatase TiO₂ with a large percentage of (001) facets synthesized by a seeded-silica-template hydrothermal route have been demonstrated to exhibit an improved electric conductivity. The electrodes of these crystals used in nonporous-state dye-sensitized solar cells correspondingly showed an improvement in collecting charge carriers [22]. Inspired by this pioneering work, several studies have synthesized mesoporous TiO₂ single crystals with different morphologies as photocatalysts for water splitting or photoanodes for PEC water splitting [23–25]. Although charge carrier transport within each particle of these photoanodes is favored, the transport is still greatly limited by the boundaries between the mesoporous single-crystal particles in the photoanode film.

To completely remove the particle boundaries in an elec-

* Corresponding author. Tel: +86-24-23971088; Fax: +86-24-23971682; E-mail: gangliu@imr.ac.cn

Corresponding author. Tel: +966-2-6952293; Fax: +966-2-6952292; E-mail: mkadi@kau.edu.sa

This work was supported by the National Basic Research Program of China (2014CB239401), the National Natural Science Foundation of China (51402306, 51422210, 21090343), and the Deanship of Scientific Research (50-130-35-HiCi), King Abdulaziz University, Saudi Arabia.

DOI: 10.1016/S1872-2067(15)60981-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 12, December 2015

trode film, all single-crystal particles need to directly grow on the substrate and penetrate the whole film. One-dimensional single-crystal rod arrays of rutile TiO_2 have emerged as a promising structure in improving the carrier collection efficiency of electrode films [26–28]. However, the number of surface-reactive sites of these rod array films is usually much less than that of mesoporous nanoparticle films owing to their relatively small specific surface area [26], which limits the performance of PEC cells. The integration of high carrier collection efficiency and abundant reactive sites in electrodes remains a desirable challenge. Some attempts to realize this purpose have been made to increase the specific surface area of rod arrays. One simple method is tuning the length and diameter of rods [29]. Further attempts have included growing TiO_2 nanodendrite arrays through two hydrothermal steps [30] and decorating the nanodendrite arrays with nanoparticles to further increase the specific surface area [31]. Besides these attempts, a promising alternative solution is to develop mesoporous single-crystal rod array films, which provide both a large specific surface area and high carrier collection efficiency. Here, we report a template-assisted hydrothermal method for the synthesis of mesoporous single-crystal rod array films of rutile TiO_2 . To the best of our knowledge, this is the first report of mesoporous single-crystal rod array films on conductive substrates. This method could be generalized for the fabrication of other metal oxide films with the features of mesoporous structure and single crystals. The obtained film as the photoanode in a PEC water-splitting cell has an improved performance of 2.6 times that of the reference nonporous rod array film without mesopores.

2. Experimental

2.1. Synthesis of SiO_2 spheres

H_2O (32 mL), ammonium hydroxide (18 mL), and tetraethyl orthosilicate (TEOS, Sigma Aldrich, 99 mL) were added to 750 mL ethanol to form the mixture. The mixture was stirred at 700 rpm for 24 h and then centrifuged at 5000 rpm for 5 h to collect SiO_2 spheres with a diameter of around 50 nm. The recovered spheres were heated at 500 °C in air for 30 min (ramping time 250 min) to remove surface-adsorbed organic reagents.

2.2. Preparation of mesoporous TiO_2 single-crystal rod arrays

Titanium *n*-butoxide (1 mL) was added to 60 mL of an aqueous solution of hydrochloric acid (6 mol/L) in a 100-mL glass beaker to form a clear solution. The SiO_2 spheres powder (600 mg), prepared as above, was added to the clean solution. The mixture solution was sonicated for 1 h to form the solution with well-dispersed SiO_2 spheres. Such solution (40 mL) together with fluorine-doped tin oxide (FTO) glass substrates was transferred to a Teflon container with a volume of 80 mL, where the FTO substrates were placed at the bottom with their conductive surface facing upwards. The SiO_2 spheres were coated on the FTO substrates by centrifuging the Teflon container at 5000 rpm for 1 h. The Teflon container was then filled

in a stainless steel autoclave and heated at 150 °C in an oven for 12 h. After heating, the autoclave was naturally cooled to room temperature. A white SiO_2 sphere/ TiO_2 nanorod film was uniformly coated on the FTO glass substrate. The sample was thoroughly washed with deionized water and dried in air. Prior to removing SiO_2 spheres from the film by immersing the sample in 2 mol/L NaOH solution at 80 °C for 2 h, the sample was heated at 550 °C in air for 2 h to improve both the crystallinity of TiO_2 rods and their adherence to the substrate.

2.3. Preparation of nonporous rod arrays of TiO_2 single crystals

Titanium *n*-butoxide (1 mL) was added to 60 mL of an aqueous solution of hydrochloric acid (6 mol/L) in a 100-mL glass beaker to form a clear solution. The clear solution (40 mL) together with FTO glass substrates was transferred to a Teflon-lined stainless steel autoclave with a volume of 80 mL. The sealed autoclave was heated at 150 °C in an oven for 12 h, and then naturally cooled to room temperature. A white film of TiO_2 rods was uniformly coated on the FTO glass substrate. The sample was thoroughly washed with deionized water and dried in air. The sample was heated at 550 °C in air for 2 h to improve both the crystallinity of TiO_2 nanorods and their adherence to the substrate.

2.4. Characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku diffractometer using $\text{Cu } K\alpha$ irradiation. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained on a Nova NanoSEM 430 and JEOL 2100, respectively. Diffuse reflectance absorption spectra were recorded using a UV-visible spectrophotometer (JASCO-550). The chemical states were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250, a monochromatic Al $K\alpha$ X-ray source). Binding energy was referenced to the C 1s peak (284.6 eV) from adventitious carbon.

2.5. Photoelectrochemical water oxidation measurements

The photoelectrochemical water splitting was carried out in a three-electrode system, where the rod array film, Ag/AgCl electrode, and Pt foil act as working electrode, reference electrode, and counter electrode, respectively, in the electrolyte of aqueous solution (1 mol/L NaOH) under AM 1.5G illumination with light density of 100 mW/cm² (Newport). According to the Nernst equation ($E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + 0.196$), the measured potentials versus the RHE scale can be obtained from the potentials versus Ag/AgCl.

3. Results and discussion

The nonporous single-crystal TiO_2 array film grown on an FTO transparent conductive substrate was fabricated by directly treating the FTO substrate in a hydrochloric acid aqueous solution containing the titanium precursor under hydrothermal conditions according to the literature [27]. The FTO

film itself can act as a seed layer to induce the growth of rutile TiO_2 rods owing to their identical crystal structures and the similar lattice parameters between rutile TiO_2 and SnO_2 . The FTO film on the substrate consists of SnO_2 particles with a preferential aligning along the $\langle 002 \rangle$ direction. Each particle acts as a seed for the growth of single-crystal rutile TiO_2 . Rutile TiO_2 crystals prefer to grow along the $\langle 001 \rangle$ direction, which leads to the formation of a rod-like morphology, because of the much higher surface energy of (001) facets than the thermodynamically stable (110) facets. This is the basis of the rutile TiO_2 film growing epitaxially on the FTO film usually showing a rod array morphology and growing along the $\langle 001 \rangle$ direction. To introduce mesopores into the single-crystal TiO_2 rods, a film of closely packed SiO_2 nanospheres as the template was deposited on the FTO substrate to regulate the shape of single-crystal TiO_2 rods grown up from the FTO layer during the subsequent hydrothermal process. Removing the template from the obtained SiO_2 - TiO_2 composite film leads to the formation of the desired mesoporous single-crystal array film of rutile TiO_2 . The key synthesis steps are summarized in Fig. 1.

The challenge for the fabrication of the mesoporous single-crystal array film is how to cast a robust template film of closely packed SiO_2 nanospheres that can firmly attach to the FTO film under the hydrothermal process. A high-speed centrifugation-assisted method was developed for the deposition of the SiO_2 nanosphere film. In brief, SiO_2 nanospheres with a diameter of approximately 50 nm were fabricated by a modified Stöber method [22], and the SiO_2 nanospheres synthesized were then fully dispersed in the titanium precursor aqueous solution by ultrasonic treatment. Finally, these SiO_2 spheres were deposited on a FTO substrate located at the bottom of a Teflon-lined autoclave by centrifugation.

XRD patterns (Fig. 2) of the as-prepared mesoporous and nonporous rod array films on the FTO substrates suggest the formation of phase-pure rutile TiO_2 crystals (space group $P4_2/mnm$). The sharp diffraction peaks indicate the high crystallinity of the TiO_2 rods in both samples. The close full widths at half maximum of the two major diffraction peaks of rutile (110) and (101) suggest that the mesoporous rods have a similar crystal grain size to the nonporous rods. In contrast to the XRD pattern with the (110) peak being the most prominent for rutile TiO_2 powder, the XRD pattern of the rod array films exhibits the (101) peak as the most prominent. This feature is

Fig. 1. Schematic of the synthesis procedures of the films of nonporous single-crystal rod arrays (the top panel) and mesoporous single-crystal rod arrays (the bottom panel) of rutile TiO_2 supported on fluorine-doped tin oxide (FTO) glass substrates.

Fig. 2. XRD patterns of (1) solid and (2) mesoporous single-crystal nanorod array films of rutile TiO_2 supported on FTO glass substrates. The solid squares indicate the diffraction peaks from the substrate.

attributed to the oriented arrangement of the rutile rods in the films, as shown in the SEM images in Fig. 3(a) and (b). The top ends of nearly all rods are exposed to air. These rods have a width from 300 to 500 nm and length of approximately 2 μm . Both SEM and TEM images (Fig. 3(c) and (d)) show the presence of abundant mesopores in the rods synthesized with the silica template. The pore size in the rods is around 50 nm, which is consistent with the diameter size of the silica nanospheres used as the template. Compared with the uniform width of the nonporous rods, the top part of the mesoporous rods is narrower than the other parts. This is proposed to arise from the steric effect of the top silica nanospheres of the template layer in restraining the growth of the TiO_2 rods.

Each single nonporous or mesoporous rod is a single crystal, as indicated by the selected area electron diffraction (SAED) patterns and high-resolution transmission electron microscopy (HRTEM) images (Fig. 3(e) and (f)). The set of periodic diffraction spots (insets of Fig. 3(e) and (f)) indicates the single-crystal nature for both nonporous and mesoporous rods. The different arrangements of the diffraction spots between nonporous and porous rods are explained as a result of the different zones of TiO_2 detected. For the nonporous rods, the rectangular diffraction patterns belong to the $\langle 1-10 \rangle$ zone axis of rutile TiO_2 . The distances between the lattice fringes along two perpendicular directions are 0.325 and 0.296 nm, as shown in the HRTEM image (Fig. 3(e)), which are assigned to the (110) and (001) facets of rutile TiO_2 , respectively. The parallelogram diffraction patterns recorded from the mesoporous rod belong to the $\langle 010 \rangle$ zone axis of rutile TiO_2 . The lattice fringe spaces along two directions with an angle of 114.4° are 0.249 nm, as displayed in Fig. 3(f), which is assigned to the (101) facets of rutile TiO_2 . The growth direction of the rods is in the $\langle 001 \rangle$ orientation according to the SAED patterns and HRTEM images (Fig. 3(e) and (f)).

The chemical state of Ti and O in both samples was studied by XPS. The oxidation state of Ti and O in the high-resolution Ti 2p and O 1s XPS spectra of both samples (Fig. (4)) is clearly assigned to the full oxidation state of Ti^{4+} (binding energy: Ti 2p_{1/2} 463.8 eV, Ti 2p_{3/2} 458.1 eV) and O^{2-} (binding energy:

Fig. 3. Top-view SEM images of (a) nonporous and (b) mesoporous rutile TiO_2 rod array films supported on FTO substrates; low-magnification TEM images of a single (c) nonporous and (d) mesoporous rutile TiO_2 rod scratched from the corresponding films; HRTEM images recorded from the (e) nonporous and (f) mesoporous rutile TiO_2 rods; the insets are SAED patterns.

0 1s 529.2 eV). Raman spectra (Fig. (5)) of the rods show the typical active modes of rutile TiO_2 and no obvious difference is observed between the samples. These results suggest that the mesoporous structure itself does not affect the chemical state and surface atomic structures of TiO_2 rods.

UV-visible absorption spectra and XPS valence band spectra of the nonporous and mesoporous single-crystal rod array films were recorded to compare their optical and electronic structure properties. A gradually increased absorption from 500 to 900 nm observed in both mesoporous and nonporous

Fig. 5. Raman spectra of the (1) solid and (2) mesoporous single-crystal nanorod array films of rutile TiO_2 supported on FTO glass substrates.

samples results from the presence of oxygen vacancies in the samples. More oxygen vacancies are expected in the mesoporous sample owing to its larger specific surface area, which leads to a higher absorbance in this range for the mesoporous sample. The mesoporous rods show a higher absorbance in the UV region. This absorbance improvement could be attributed to light trapping and multiple reflecting effects arising from the mesopores in the rods. Moreover, the absorption edge of the mesoporous rods is blue-shifted by approximately 10 nm compared with that of the nonporous rods (Fig. 6). The bandgap of the mesoporous rods is larger than that of the nonporous rods by approximately 0.1 eV, as shown in their corresponding plots of transformed Kubelka-Munk function versus the energy of light (inset of Fig. 6). The blue-shift of the bandgap of mesoporous TiO_2 rods can be attributed to the incorporation of Si dopants from SiO_2 template into TiO_2 crystal lattices during the fabrication process. This is clearly confirmed by the high-resolution Si 2p XPS spectrum of the mesoporous rods (Fig. 7). The binding energy (101.6 eV) of Si 2p is much smaller than that of the reference SiO_2 (103.4 eV) as a result of the formation of Si–O–Ti bonds, which reduces the oxidation state of Si atoms. The blue-shift of absorption edge for Si-doped TiO_2 compared with pure TiO_2 was also observed in the porous TiO_2 nanotube array and compact TiO_2 films [32,33]. The positions of valence band edges of the two samples at 1.8 eV are the same, as indicated by the valence band spectra (Fig. 8). The

Fig. 4. High-resolution XPS spectra of Ti 2p and O 1s of the (1) solid and (2) mesoporous single-crystal nanorod array films of rutile TiO_2 supported on FTO glass substrates.

Fig. 6. UV-visible absorption spectra of the (1) solid and (2) mesoporous single-crystal nanorod array films of rutile TiO_2 supported on FTO glass substrates. The inset is the plots of transformed Kubelka-Munk function versus the energy of light.

Fig. 7. High-resolution XPS spectrum of Si 2p of the mesoporous single-crystal nanorod array films of rutile TiO_2 supported on FTO glass substrates.

band alignments between the two samples are given in Fig. 9. The mesoporous rods have a higher conduction band edge by approximately 0.1 eV than the nonporous rods.

TiO_2 -based materials are capable of playing versatile roles in photocatalytic H_2 generation [34–36]. PEC water splitting is

Fig. 8. XPS valence band spectra of the (1) solid and (2) mesoporous single-crystal nanorod array films of rutile TiO_2 supported on FTO glass substrates.

Fig. 9. The electronic energy band alignments of the solid and mesoporous single-crystal nanorods of rutile TiO_2 .

considered a promising strategy in solar energy conversion and storage. The activity of the nonporous and mesoporous rod array films as photoanodes for PEC water oxidation was investigated and the results are shown in Fig. 10. The photocurrent density generated by the mesoporous rod photoanode is 0.74 mA/cm^2 at 1.23 V (versus a reversible hydrogen electrode) under AM 1.5 G simulator irradiation with a power density of 100 mW/cm^2 , which is 2.6 times higher than that of the nonporous rod photoanode. The photoelectrochemical or photocatalytic activities of TiO_2 photocatalysts are known to be sensitive to the crystal phase, electronic structure, optical absorption, surface area, crystallinity, surface facets, and structural and chemical defects [37,38]. The much-improved photocurrent density of the mesoporous rod photoanode in comparison with the nonporous rod photoanode can be attributed to the synergistic effect of four favorable factors as follows.

(1) The mesoporous structure endows a larger specific surface area of the mesoporous rods than that of the nonporous rods, which decorates the mesoporous rods with abundant surface-reactive sites for water oxidation. (2) The diffusion distance of the photo-generated holes from the bulk of the mesoporous rods to the interface between the rods and electrolyte is greatly shortened by the introduced mesopores. This can decrease the bulk recombination probability of the pho-

Fig. 10. Applied potential bias-dependent photocurrent density of the (1) nonporous and (2) mesoporous rutile TiO_2 rod array photoanodes in the dark and under AM 1.5 G simulator irradiation with a power density of 100 mW/cm^2 . Measurement conditions: 1 mol/L aqueous NaOH electrolyte, scanning rate of 50 mV/s , Ag/AgCl reference electrode.

to-generated charge carriers. (3) The increased absorbance favors the use of solar light to excite valence band electrons for the generation of more charge carriers for surface redox reactions. (4) Finally, but also importantly, the higher conduction band edge by around 100 meV facilitates the transport of photo-generated electrons from the mesoporous rods to the current collector (FTO layer) by providing a larger driving force. This is indicated by the negatively shifted photocurrent onset potential (approximately 100 mV) of the mesoporous rods relative to the nonporous rods.

4. Conclusions

The films of mesoporous single-crystal rod arrays of rutile TiO_2 directly growing on FTO conductive substrates were synthesized by a silica template-assisted hydrothermal method. The resultant films as photoelectrodes integrate several merits including abundant surface reactive sites, shortened diffusion distance of photoexcited charge carriers, and improved both light absorbance and driving force for the charge separation. As a demonstration, the mesoporous rod based photoanode for PEC water oxidation gives a much higher activity than the nonporous rod based photoanode. The developed films are anticipated to also act as an attractive electrode in other solar energy conversion systems including dye/quantum dot sensitized solar cells.

References

- [1] Walter M G, Warren E L, McKone J R, Boettcher S W, Mi Q X, Santori E A, Lewis N S. *Chem Rev*, 2010, 110: 6446
- [2] Rühle S, Shalom M, Zaban A. *ChemPhysChem*, 2010, 11: 2290
- [3] Kouhnavard M, Ikeda S, Ludin N A, AhmadKhairudin N B, Ghaffari B V, Mat-Teridi M A, Ibrahim M A, Sepeai S, Sopian K. *Renew Sustain Energy Rev*, 2014, 37: 397
- [4] Grätzel M. *Nature*, 2011, 414: 338
- [5] Sivula K, Zboril R, Formal F L, Robert R, Weidenkaff A, Tucek J, Frydrych J, Grätzel M. *J Am Chem Soc*, 2010, 132: 7436
- [6] Brillet J, Grätzel M, Sivula K. *Nano Lett*, 2010, 10: 4155
- [7] Stefik M, Cornuz M, Mathews N, Hisatomi T, Mhaisalkar S, Grätzel M. *Nano Lett*, 2012, 12: 5431
- [8] Kim T W, Choi K S. *Science*, 2014, 343: 990
- [9] McDonald K J, Choi K S. *Energy Environ Sci*, 2012, 5: 8553
- [10] Luo W J, Yang Z S, Li Z S, Zhang J Y, Liu J G, Zhao Z Y, Wang Z Q, Yan S C, Yu T, Zou Z G. *Energy Environ Sci*, 2011, 4: 4046
- [11] Saito M, Fujihara S. *Energy Environ Sci*, 2008, 1: 280
- [12] Tan B, Toman E, Li Y G, Wu Y Y. *J Am Chem Soc*, 2007, 129: 4162
- [13] Guo P, Aegerter M A. *Thin Solid Films*, 1999, 351: 290
- [14] O'Regan B, Grätzel M. *Nature*, 1991, 353: 737
- [15] Nazeeruddin M K, Kay A, Rodicio I, Humphry-Baker R, Müller E, Liska P, Vlachopoulos N, Grätzel M. *J Am Chem Soc*, 1993, 115: 6382
- [16] Wang J, Mora-Seró I, Pan Z X, Zhao K, Zhang H, Feng Y Y, Yang G, Zhong X H, Bisquert J. *J Am Chem Soc*, 2013, 135: 15913
- [17] Robel I, Subramanian V, Kuno M, Kamat P V. *J Am Chem Soc*, 2006, 128: 2385
- [18] Youngblood W J, Lee S H A, Kobayashi Y, Hernandez-Pagan E A, Hoertz P G, Moore T A, Moore A L, Gust D, Mallouk T E. *J Am Chem Soc*, 2009, 131: 926
- [19] Cheng C W, Karuturi S K, Liu L J, Liu J P, Li H X, Su L T, Tok A I Y, Fan H J. *Small*, 2012, 8: 37
- [20] Chen X B. *Chin J Catal* (陈晓波. 催化学报), 2009, 30: 839
- [21] Turner G M, Beard M C, Schmittenmaier C A. *J Phys Chem B*, 2002, 106: 11716
- [22] Crossland E J W, Noel N, Sivaram V, Leijtens T, Alexander-Webber J A, Snaith H J. *Nature*, 2013, 495: 215
- [23] Zheng X L, Kuang Q, Yan K Y, Qiu Y C, Qiu J H, Yang S H. *ACS Appl Mater Interf*, 2013, 5: 11249
- [24] Jiao W, Xie Y P, Chen R Z, Zhen C, Liu G, Ma X L, Cheng H M. *Chem Commun*, 2013, 49: 11770
- [25] Fang W Q, Huo Z Y, Liu P R, Wang X L, Zhang M, Jia Y, Zhang H M, Zhao H J, Yang H G, Yao X D. *Chem Eur J*, 2014, 20: 11439
- [26] Feng X J, Shankar K, Varghese O K, Paulose M, Latempa T J, Grimes C A. *Nano Lett*, 2008, 8: 3781
- [27] Liu B, Aydil E S. *J Am Chem Soc*, 2009, 131: 3985
- [28] Wang H, Bai Y S, Zhang H, Zhang Z H, Li J H, Guo L. *J Phys Chem C*, 2010, 114: 16451

Graphical Abstract

Chin. J. Catal., 2015, 36: 2171–2177 doi: 10.1016/S1872-2067(15)60981-0

Design and construction of a film of mesoporous single-crystal rutile TiO_2 rod arrays for photoelectrochemical water oxidation

Chao Zhen, Tingting Wu, Mohammad W. Kadi *, Iqbal Ismail, Gang Liu *, Hui-Ming Cheng
Institute of Metal Research, Chinese Academy of Sciences, China; King Abdulaziz University, Saudi Arabia

A film of mesoporous single-crystal rutile TiO_2 rod arrays supported on a conductive substrate as the photoanode shows significant improvement in photoelectrochemical water oxidation compared with the reference film of nonporous single-crystal rutile TiO_2 rod arrays.

- [29] Hwang Y J, Hahn C, Liu B, Yang P D. *ACS Nano*, 2012, 6: 5060
- [30] Cho I S, Chen Z B, Forman A J, Kim D R, Rao P M, Jaramillo T F, Zheng X L. *Nano Lett*, 2011, 11: 4978
- [31] Yang J S, Liao W P, Wu J J. *ACS Appl Mater Interfaces*, 2013, 5: 7425
- [32] Su Y, Chen S, Quan X, Zhao H M, Zhang Y B. *Appl Surf Sci*, 2008, 255: 2167
- [33] Su Y, Wu J S, Quan X, Chen S. *Desalination*, 2010, 252: 143
- [34] Liu J, Liu Z Y, Zhang T R, Zhai J, Jiang L. *Nanoscale*, 2013, 5: 6139
- [35] Yu H J, Zhao Y F, Zhou C, Shang L, Peng Y, Cao Y H, Wu L Z, Tang C H, Zhang T R. *J Mater Chem A*, 2014, 2: 3344
- [36] Meng C H, Liu Z Y, Zhang T R, Zhai J. *Green Chem*, 2015, 17: 2764
- [37] Xia T, Zhang Y L, Murowchick J, Chen X B. *Catal Today*, 2014, 225: 2
- [38] Liu L, Chen X B. *Chem Rev*, 2014, 114: 9890

光电化学水氧化用多孔单晶金红石TiO₂纳米棒阵列光阳极的设计和构建

甄超^a, 吴亭亭^a, Mohammad W. Kadi^{b, #}, Iqbal Ismail^b, 刘岗^{a, *}, 成会明^{a, b}

^a中国科学院金属研究所沈阳材料科学国家(联合)实验室, 辽宁沈阳110016

^b阿卜杜勒阿齐兹国王大学理学院化学系, 吉达21589, 沙特阿拉伯

摘要: 光电化学电池(如染料敏化太阳能电池、量子点敏化太阳能电池以及光电化学水分解电池)是实现太阳能转化及存储的有效手段之一。其中, 光电极是光电化学电池的核心组成部分, 它集光吸收、光生电荷输运及转移等决定光转化效率的关键过程于一身, 因此构筑高活性半导体光电极以实现高效太阳能转化利用引起研究者广泛关注。

多孔TiO₂纳米颗粒堆垛薄膜光阳极因具有大的比表面积, 可提供更多的染料(量子点)负载和反应活性位点, 在光电化学电池中表现出优异活性而被广泛研究。然而, TiO₂纳米颗粒间大量存在的晶界对光生电荷有较强的散射作用, 降低了光生电荷的收集效率。英国牛津大学Snaith研究小组利用模板辅助水热过程首次获得了(001)晶面占优的多孔单晶锐钛矿TiO₂微米颗粒, 这种多孔单晶TiO₂微米颗粒在具有大比表面积的同时, 其单晶结构还能有效去除晶界对电荷的散射作用, 因而具有优异的电荷输运特性。利用这种多孔单晶TiO₂微米颗粒组建的光阳极用于染料敏化太阳能电池中, 展现出优异的太阳能光电转化性能。受该工作启发, 各种形貌的多孔单晶TiO₂微米颗粒作为光催化剂和光电化学分解水用光阳极材料被广泛研究, 并表现出优异活性。

在单晶微米颗粒堆垛成的薄膜光电极中, 虽然单个单晶微米颗粒中晶界对电荷的散射作用被有效抑制, 但是单晶颗粒间的晶界仍然存在并影响光生电荷的收集效率。为了彻底抑制晶界对光生电荷的散射作用, 每个单晶颗粒都应该贯穿整个薄膜, 例如一维TiO₂纳米棒单晶阵列薄膜。虽然一维单晶阵列薄膜能够有效提高光生电荷的收集效率, 但相对于多孔薄膜具有较小的比表面积, 限制了负载染料(量子点)和反应位点的数量。为了增大TiO₂单晶纳米棒阵列薄膜的比表面积, 目前主要的手段包括调控纳米棒长径比、表面修饰TiO₂纳米颗粒以及二次生长构建TiO₂枝晶阵列。

本文首次提出通过制备多孔单晶TiO₂纳米棒单晶阵列薄膜来获得高比表面积和高光生电荷收集效率的光阳极, 提高光电化学电池的效率。

在透明导电薄膜(FTO)表面利用水热生长TiO₂纳米棒阵列薄膜之前, 预先在FTO基体上沉积一层SiO₂球密堆模板, TiO₂纳米棒单晶阵列在从FTO表面上生长过程中, 会将SiO₂球模板包裹进TiO₂纳米棒中, 再通过碱溶液将SiO₂球模板溶解, 首次在FTO基体上原位生长出多孔单晶TiO₂纳米棒阵列薄膜。将所得多孔单晶金红石TiO₂纳米棒阵列薄膜作为光电化学分解水电池光阳极, 其光电化学分解水活性相对于实心单晶金红石TiO₂纳米棒阵列提高了2.6倍。

多孔单晶金红石TiO₂纳米棒阵列光阳极性能的提升可归因于: (1)多孔结构赋予多孔单晶金红石TiO₂纳米棒阵列薄膜更大的比表面积, 可提供更多的反应活性位点; (2)多孔结构能够有效缩短单晶金红石TiO₂纳米棒中光生电荷体相输运距离, 提高光生电荷的收集效率; (3)多孔结构通过对光多次反射吸收可有效增强光吸收, 产生更多光生电荷参与水分解反应; (4)在制备过程中引入Si掺杂, 导致多孔单晶金红石TiO₂纳米棒带隙扩大了0.1 eV, 带隙增大归因于导带位置负移0.1 eV, 光生电子具有更强的还原能力, 光电流起始电位相应负移约0.1 V。

关键词: 氧化钛; 光阳极; 多孔; 单晶; 纳米棒阵列

收稿日期: 2015-08-29. 接受日期: 2015-09-20. 出版日期: 2015-12-20.

*通讯联系人. 电话: (024)23971088; 传真: (024)23971682; 电子信箱: gangliu@imr.ac.cn

#通讯联系人. 电话: +966-2-6952293; 传真: +966-2-6952292; 电子信箱: mkadi@kau.edu.sa

基金来源: 国家重点基础研究发展计划(973计划, 2014CB239401); 国家自然科学基金(51402306, 51422210, 21090343); 阿卜杜勒阿齐兹国王大学院长科研基金(50-130-35-HiCi).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).