Sputtered Highly Ordered TiO₂ Nanorod Arrays and Their Applications as the Electrode in Dye-Sensitized Solar Cells

Lijian Meng^{1,2,3,*}, Aifeng Ma¹, Pinliang Ying¹, Zhaochi Feng¹, and Can Li^{1,*}

¹State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

²Departamento de Física, Instituto Superior de Engenharia do Porto, Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Portugal

³Centro de Física, Universidade do Minho, 4800-058 Guimarães, Portugal

For the first time, the TiO₂ nanorod arrays have been prepared on ITO substrates at room temperature by dc reactive magnetron sputtering technique. These TiO₂ nanorods have a preferred orientation along the (220) direction and are perpendicular to the ITO substrate. Both the X-ray diffraction and Raman scattering measurements show that the highly ordered TiO₂ nanorod arrays have an anatase crystal structure. The diameter of the nanorod varies from 30 nm to 100 nm and the nanorod length can be varied from several hundred nanometers to several micrometers depending on the deposition time. The TiO₂ nanorod arrays with about 3 micrometers length have been used as an electrode for dye-sensitized solar cell (DSSC). Short-circuit photocurrent density, open-circuit voltage, fill factor and light-to-electricity conversion efficiency at 100 mW/cm² light intensity are estimated to be 12.76 mA/cm², 0.65 V, 0.63 and 5.25%, respectively, for the DSSC made of the TiO₂ nanorods.

Keywords: TiO₂, DSSC, Nanorod, Sputtering.

1. INTRODUCTION

One-dimensional inorganic nanostructures (nanotubes, nanorods and nanowires) are very interesting as they exhibit a wide range of electrical and optical properties that depend on both size and shape.¹ As an *n*-type wide band-gap semiconductor material, nanocrystalline TiO₂ has attracted much interest in recent years due to its applications in dye-sensitized solar cells (DSSC) and photocatalysts. DSSC is a promising alternative to the conventional *p-n* junction solar cell as they are candidates for low-cost and high energy conversion efficiency photovoltaic devices.^{2–3} This kind of the solar cells consist of a dye adsorbed on a nanoporous TiO₂ film, an electrolyte as a hole transport layer containing redox couples and opposite electrode. The dyes on the surface of the film absorb light and inject electrons into the conduction band of the TiO₂. The original state of the dye is subsequently restored by electrolyte. It is well known that DSSC devices are a very complicated system including the

processes in such as light absorption, charge separation, charge transport, charge collection, and electrolyte diffusion. Therefore, there are many factors which can influence the light to electricity conversion efficiency. TiO₂ nanorod, nanowire, and nanotube arrays have been used in DSSC devices as they can increase the surface area which is favorable for the dye adsorption.^{4–9} In addition, the highly crystalline nanorod is one of the most promising routes to high conversion efficiency as the barrier effect of inter-crystalline titania is greatly decreased by using long highly crystalline nanorods instead of a porous TiO₂ film.⁴ Both the nanorods and nanotubes mentioned in these works are prepared by chemical methods. Colloidal chemistry is almost a routine method for preparing nanostructured TiO₂ films for photovoltaic applications.^{10–11} However, the randomly porous structure of TiO₂ electrode prepared by this technique also causes several problems, such as low conductivity and charge density. Moreover, in such conventional wet processes, it is difficult to produce uniform TiO₂ films with a large area.

Reactive magnetron sputtering is a promising technique for the large scale uniform coatings to produce high quality

* Authors to whom correspondence should be addressed.

film with strong adhesion to substrate. Another attractive point is that reactive magnetron sputtering does not need a stage of heat treatment at high temperatures as that for colloidal chemistry method, therefore the use of conducting polymer substrates is possible. In addition, the TiO₂ films prepared by reactive magnetron sputtering have a better electronic transport than that prepared by colloidal method.¹² In the beginning of this century, Gomez et al. published several papers on DSSC devices based on TiO₂ electrode prepared by dc reactive magnetron sputtering method.^{12–16} They obtained a conversion efficiency about 4% for 10 μ m TiO₂ film.¹⁴ In recent two years, there are some works published for TiO₂ films prepared by magnetron sputtering technique as electrode for DSSC devices, but the efficiency is not over 4% which has been obtained by Gomez et al. before.^{17–19} All the works reported in the literature focused on the (101) oriented anatase phase. In this work, we firstly prepared the (220) oriented TiO₂ nanorod arrays by dc reactive magnetron sputtering technique. The prepared TiO₂ nanorod arrays have been used as the electrode for DSSC devices and a conversion efficiency of 5.25% has been achieved for a 3 μ m thickness TiO₂ nanorod arrays without any extra treatment.

2. EXPERIMENTAL DETAILS

The TiO₂ nanorod arrays were prepared on commercial ITO (sheet resistance of 20 Ω per square and 100 nm thickness) substrates by dc reactive magnetron sputtering technique using a commercial sputtering system equipped with a turbo molecular pumping system. A titanium metal disk (60 mm in diameter and 3 mm in thickness) with a purity of 99.99% was used as the target. After pumping down to 1×10^{-3} Pa, the oxygen and argon gases (99.99% purities) were introduced into the chamber through the mass flow controllers. The oxygen partial pressure and the total sputtering pressure were 0.25 Pa and 2.0 Pa, respectively. The flat TiO₂ film was prepared at 0.5 Pa sputtering pressure. The sputtering was carried out using a constant current mode. The sputtering current was kept at 0.56 A and the sputtering power was about 235 W. In order to remove surface contaminants of the target, pre-sputtering was done for 20 minutes with a shutter covering the substrate. The deposited TiO₂ films were sensitized with N719 (Ru(II)L2(NCS)2:2TBA, where L = 2,2'-bipyridyl-4,4'-dicarboxylic acid) dye by soaking the films in an ethanolic solution of N719 dye (0.5 mM) of for 24 hours at room temperature. The counter-electrode was made by sputtering Pt on an FTO glass and the electrolyte is composed of 0.1 M I₂, 0.1 M LiI, 0.6 M 1-hexyl-3-methylimidazolium iodide, and 0.5 M 4-tert-butylpyridine in 3-methoxypropionitrile. The photocurrent–voltage measurements were carried out with a Princeton 2273 applied research electrochemical system, a 500 W Xenon lamp under AM 1.5 G illumination with a water filter was used.

The light intensity was adjusted to 100 mW/cm². Cells with an active area of 0.15 cm² were tested.

3. RESULTS AND DISCUSSION

The field emission scanning electron microscopy (FE-SEM) images of a prepared TiO₂ film indicate that the nanorod arrays are formed on the ITO substrate as shown in Figure 1. For comparing, a surface image of the flat TiO₂ film is also given in Figure 1(e). The dimension of the nanorods varies from 30 to the 100 nm and the average dimension is about 65 nm. It also can be seen that the big dimension is formed with some small nanorods which are bunched together. From Figures 1(b and c), it can be seen clearly that the nanorods are very well-aligned and perpendicular to the substrate surface. In addition, these well-aligned nanorods grow throughout whole film without any rupture. Figure 1(d) shows some separate nanorods which are about 50 nm in diameters and 1000 nm in length. Figure 1(e) shows the flat TiO₂ film has

Fig. 1. FE-SEM images of TiO₂ nanorod arrays. (a): top view; (b): view from a special angle; (c): cross-section view; (d): some spread nanorods; (e): top view of a flat TiO₂ film.

a dense structure. Figure 2 shows the transmission electron microscopy (TEM) images of some spread nanorods and the surface structure of a nanorod. Figure 2(b) shows clearly that the surface of these nanorods is quite rough which is favorable for the dye adsorption. Generally, the sputtered films are quite dense as the energy of the sputtered atoms arriving at the substrate is relatively high comparing to the other kind of deposition techniques as shown in Figure 1(e). However, as the nanorod arrays are prepared at a high sputtering pressure (about 2 Pa) and a large substrate-target distance (about 80 mm), the sputtered atoms will be scattered several times before they arrive at the substrate, so the sputtered atoms arrive at the substrate with a quite low energy. With this low energy, the formed adatoms on the substrate surface are difficult to migrate and results in this 1-D growth. The formation of the 1-D nanorods can be explained qualitatively by the Thornton structure zone model.²⁷ According to this model, at high sputtering pressures, owing to low adatom mobility (slow surface diffusion), a columnar microcrystals with voids structure are formed. Nanorods may be formed as the

adatom mobility decreases further. It is quite clear that the deposition parameters need to be optimized carefully in order to get the 1-D nanorods. The flat TiO₂ film prepared at low sputtering pressure has a dense structure as shown in Figure 1(e). It agrees well with this growth model.

The XRD patterns (Fig. 3) of the TiO₂ nanorods and a flat TiO₂ film show that both the as-deposited TiO₂ nanorods and flat TiO₂ film have a polycrystalline anatase structure. (PDF card 21-1272) and It shows clearly that the flat TiO₂ film and TiO₂ nanorods have different growth directions. The flat TiO₂ film has a strong (101) diffraction peak and TiO₂ nanorods have a very strong (220) diffraction peak. This suggests that the TiO₂ nanorods are formed along the [110] direction. Column structures which develop during low-temperature film growth often have a common crystallographic axis oriented perpendicular to the plane of the substrate. For example, fcc, bcc and hcp films are frequently formed with their most densely populated planes, (111), (110) and (001), respectively, parallel to the substrate surface. The minimization of surface energies and the variation in condensation coefficients on different crystal faces have been used to explain the observed textures.²⁰ In the latter case, the fast-growing crystal surfaces will grow out of existence if the adatom mobility is insufficient to overcome the difference in condensation coefficients.²⁰⁻²¹ In addition, the growth behavior of the crystal is mainly determined by the structure of a given crystal and is affected by growth conditions too.²² Wu et al. have prepared TiO₂ nanorods on Si and fused silica substrates by MOCVD method at high temperatures. They have proposed the fast deposition rate along the [110] crystal faces and then a preferred orientation along the (220) direction.⁸ By analyzing the results of XRD and SEM measurements, it can be concluded that, for the sputtered TiO₂ nanorods in this work, the fast growth rate is along the [110] crystal plane. The average crystalline dimension along the [110] crystal plane has been estimated from the

Fig. 2. TEM images of TiO₂ nanorods. (a): spread nanorods; (b): detailed surface view of one nanorod.

Fig. 3. X-ray diffraction patterns of a flat TiO₂ film (a) and a TiO₂ nanorod arrays (b).

Fig. 4. Raman spectra of a flat TiO₂ film (a) and a TiO₂ nanorod arrays (b).

half-width of the (220) diffraction peak using Scherrer's equation. The calculated grain size along the (220) direction of the TiO₂ nanorod arrays is about 10 nm.

The Raman spectra of the sputtered TiO₂ nanorods and the flat TiO₂ film are shown in Figure 4. Raman bands at 144, 195, 396, 513 and 637 cm⁻¹ are assigned to anatase phase of TiO₂.²³ Both the TiO₂ nanorod and flat TiO₂ film show a similar Raman spectra. However, considering the thicknesses of the flat TiO₂ film (650 nm) and the TiO₂ nanorod (2850 nm), the Raman peak intensity of the flat TiO₂ film is much stronger than that of the nanorod. It means that the porous [110] direction oriented TiO₂ nanorod structure will result in the decrease of the lattice vibration intensity.

Figure 5 gives the transmittance of the sputtered TiO₂ nanorod arrays and the flat TiO₂ film. Although the transmittance of the TiO₂ nanorod is lower comparing to the flat TiO₂ film, this transmittance (about 65% in the visible region) for the 3 μm thickness TiO₂ nanorod is a relative high transmittance comparing to the TiO₂ films prepared

Fig. 5. Transmittance of a flat TiO₂ film (a) and a TiO₂ nanorod arrays (b).

by chemical methods. This is an advantage of the sputtering technique over other techniques, specially chemical methods in the preparation of TiO₂ films. For example, Kao et al., got less than 60% transmittance for the 2 μm thickness TiO₂ films prepared by a chemical method.²⁴ The refractive index of the nanorod TiO₂ and Flat TiO₂ have been obtained by fitting the transmittance as shown in Figure 6. The flat TiO₂ film has a dense structure and then a high refractive index. The porosity of the flat TiO₂ film and TiO₂ nanorod can be estimated using the Eq. (28)

$$n_f = n_s(1 - q) + n_v q \quad (1)$$

where q is the porosity, n_v is the refractive index of the TiO₂ void filling material and n_s is the refractive index of bulk TiO₂ material. If we assumed that all the voids are filled with air, then $n_v = 1$. For anatase TiO₂ bulk material, $n_s = 2.57$. Using these data, the porosities of the flat TiO₂ film and the TiO₂ nanorod have been calculated. The porosities are 1% and 11% for the flat TiO₂ film and TiO₂ nanorod using data at 500 nm, respectively. Later it will be seen that these differences of the porosity will influence greatly the conversion efficiency of the DSSC.

The optical band gap energy can be estimated from the transmittance by using the following equation for a semiconductor:

$$\alpha h\nu = A * (h\nu - E_g)^m \quad (2)$$

where α is the absorption coefficient, h is the Plank's constant, A is a constant, E_g is the band gap, and m is equal to 0.5 or 2 for a direct or a indirect transition.²⁵ The band gap can be estimated from a plot of $(\alpha h\nu)^2$ or $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$). The intercept of the tangent to the plot can give a good approximation of the band gap energy for the direct or indirect band gap materials. As TiO₂ is an indirect transition band gap material, we have plotted $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) for the

Fig. 6. The refractive index n for a flat TiO₂ film (a) and a TiO₂ nanorod arrays (b).

Fig. 7. The determination of the band gap energy for a flat TiO₂ film (a) and a TiO₂ nanorod arrays (b), from the plot of $(\alpha h\nu)^{1/2}$ versus the excitation energy, $h\nu$.

nanorod TiO₂ and the flat TiO₂ film as shown in Figure 7. The optical bandgaps are about 3.15 eV and 3.35 eV for the nanorod TiO₂ and the flat TiO₂ film, respectively. The reported band gap value of anatase phase in bulk material is 3.2 eV.²⁶ The difference of the structure may result in the difference of the bandgap.

The photocurrents (I) and photovoltages (V) of the DSSCs made from the sputtered TiO₂ nanorod arrays with different thickness were measured and the conversion efficiencies were calculated based on these measurements. A relative high current density has been obtained for a

Fig. 8. The J - V curves for DSSC prepared using a flat TiO₂ film (a) and a TiO₂ nanorod arrays (b).

3 μm thickness TiO₂ nanorod arrays, as shown in Figure 8, comparing to the results obtained by sputtering technique in the literature.^{12–19} A short-circuit photocurrent density (J_{sc}) of 12.76 mA/cm², an open-circuit voltage (V_{oc}) of 0.65 V, a fill factor (FF) of 0.63 and a photoelectron conversion efficiency (η) of 5.25% are obtained for the DSSC using this nanorod arrays as an electrode material. It is the highest conversion efficiency until now has been obtained for TiO₂ films prepared by sputtering technique without any post-deposition treatments. For comparing, the efficiency of the DSSC using the flat TiO₂ film as electrode is also given in Figure 8. As the flat TiO₂ film is quite dense, it is difficult to absorb the dye molecules, so the efficiency is very low as shown in the figure. Many parameters can influence the conversion efficiency of the DSSC. Two of them have been improved by our TiO₂ nanorod arrays. Firstly, the TEM images (Fig. 2(b)) shows that the TiO₂ nanorod made by dc reactive magnetron sputtering has a very rough surface. More dye molecules can be adsorbed on the TiO₂ surface and results in an increase of the amount of the electrons generated by photon, and then an increase of the current density; Secondly, 1-D nanorod may improve the electron transport through the photoelectrode which is controlled by diffusion coefficient of electron and phonon relaxation in which, electrons usually lose their energy through electron–phonon interaction. These improvements result in the high light-to-electron conversion efficiency. The amount of the anchored dye molecules on the TiO₂ nanorod arrays has been determined qualitatively by measuring the transmittance after soaking it in dye solution as shown in Figure 9. The evident band due to the adsorbed dye at 500 nm indicates that large amount of dye has been anchored on the TiO₂ nanorod surface. The inset of the Figure 9 is the photograph of the flat TiO₂ film and nanorod TiO₂ after soaking them in the N719 dye solution for 24 hours. It can be seen that for flat TiO₂ film, it is almost no color, it means the absorbed dye molecules

Fig. 9. Transmittance of TiO₂ nanorod arrays before and after dye-sensitized (Inset is the photograph of a flat TiO₂ film and a TiO₂ nanorod arrays after dye sensitized).

are very small. That is the reason why the efficiency is lower for the DSSC using this film as electrode.

4. CONCLUSIONS

In summary, the TiO₂ thin films mainly composed by nanorod arrays have been prepared onto ITO substrates by dc reactive magnetron sputtering technique at room temperature. These TiO₂ nanorod arrays are in anatase phase and show an excellent orientation along the (220) direction. The nanorod arrays are well-aligned and are perpendicular to the substrate. The nanorods have a very rough surface which is favorable for the dye adsorption. The DSSC has been made using the TiO₂ nanorod arrays as photoelectrode material and a conversion efficiency as high as 5.25% has been achieved. This is the highest efficiency until now has been reported for TiO₂ electrode prepared by sputtering technique without any post-deposition treatment. Further work is going on for increasing the efficiency.

Acknowledgment: This work was done during Lijian Meng's sabbatical stay in DICP (SFRH/BSAB/862/2008, FCT, Portugal) and was supported by the Solar Energy Action Project of the Chinese Academy of Sciences. The authors thank Mr. Xuming Wei, Mr. Shishan Sheng and Miss Jingying Jiang from the State Key Laboratory of Catalysis, DICP for their assistances in SEM, XRD and TEM characterizations.

References and Notes

1. B. O'Regan and M. Gratzel, *Nature* 353, 737 (1991).
2. A. Kay and M. Gratzel, *Sol Energy Mater. Sol. Cells* 44, 99 (1996).
3. C. M. Lieber, *Solid State Comm.* 107, 607 (1998).
4. J. Jiu, S. Isoda, F. Wang, and M. Adachi, *J. Phys. Chem. B* 110, 2087 (2006).
5. G. K. Mol, K. Shankar, M. Paulose, O. K. Varghese, and C. A. Grimes, *Nano Lett.* 6, 215 (2006).
6. L. Miao, S. Tanemura, S. Toh, K. Kaneko, and M. Tanemura, *J. Cryst. Growth* 264, 246 (2004).
7. B. Liu and E. S. Aydil, *J. Am. Chem. Soc.* 131, 3985 (2009).
8. J. Wu and C. Yu, *J. Phys. Chem. B* 108, 3377 (2004).
9. S. H. Kang, S. H. Choi, M. S. Kang, J. Y. Kim, H. S. Kim, T. Hyeon, and Y. E. Sung, *Adv. Mater.* 20, 54 (2008).
10. A. Hagfeldt and M. Gratzel, *Chem. Rev.* 95, 49 (1995).
11. M. Gratzel, *Inorg. Chem.* 44, 6841 (2005).
12. M. M. Gomez, N. Beermann, J. Lu, E. Olsson, A. Hagfeldt, G. A. Niklasson, and C. G. Granqvist, *Sol Energy Mater. Sol. Cells* 76, 37 (2003).
13. M. Gomez, J. Rodriguez, S. E. Lindquist, and C. G. Granqvist, *Thin Solid Films* 342, 148 (1999).
14. M. Gomez, E. Magnusson, E. Olsson, A. Hagfeldt, S. E. Lindquist, and C. G. Granqvist, *Sol Energy Mater. Sol. Cells* 62, 259 (2000).
15. M. Gomez, J. Lu, E. Olsson, A. Hagfeldt, and C. G. Granqvist, *Sol Energy Mater. Sol. Cells* 64, 385 (2000).
16. M. Gomez, J. Lu, J. L. Solis, E. Olsson, A. Hagfeldt, and C. G. Granqvist, *J. Phys. Chem. B* 104, 8712 (2000).
17. Y. M. Sung and H. J. Kim, *Thin Solid Films* 515, 4996 (2007).
18. M. F. Hossain, S. Biswas, T. Takahashi, Y. Kubota, and A. Fujishima, *Thin Solid Films* 516, 7149 (2007).
19. S. H. Kang, J. W. Lim, H. S. Kim, J. Y. Kim, Y. H. Chung, and Y. E. Sung, *Chem. Mater.* 21, 2777 (2009).
20. B. Lewis and J. C. Andersson, *Nucleation and Growth of Thin Films*, Academic Press, London, UK (1978).
21. A. van de Drift, *Philips Res. Repts.* 22, 267 (1967).
22. R. A. Laudise and A. A. Ballman, *J. Phys. Chem.* 64, 688 (1960).
23. T. Ohsaka, F. Izumi, and Y. Fujiki, *J. Raman Spectroscopy* 7, 321 (1978).
24. M. C. Kao, H. Z. Chen, S. L. Young, C. Y. Kung, and C. C. Lin, *Thin Solid Films* 517, 5096 (2009).
25. J. I. Pankove, *Optical Processes in Semiconductor*, Prentice Hall, New York (1971).
26. J. Tauc, *Mater. Res. Bull.* 5, 721 (1970).
27. J. A. Thornton, *J. Vac. Sci. Technol. A* 4, 3059 (1986).
28. Y. Tachibana, H. Y. Akiyama, and S. Kuwabata, *Sol Energy Mater. Sol. Cells* 91, 201 (2007).

Received: 23 December 2009. Accepted: 26 March 2010.